Photochemical and Photothermal Reduction of Carbon Dioxide for Solar Fuels Production

by

Abdinoor Abdullahi Jelle

A thesis submitted in conformity with the requirements for the degree of doctor of philosophy

Department of Materials Science and Engineering
University of Toronto

© Copyright by Abdinoor Abdullahi Jelle 2017
Abstract

Catalytic conversion of greenhouse gas carbon dioxide to value-added chemicals and fuels powered by solar energy is envisioned to be a promising strategy to realize both energy security and environmental protection. This work demonstrates that earth abundant, low cost nanomaterials based on silicon and iron can be used to harvest both light and heat energy from the sun to reduce CO$_2$ and generate solar fuels. Herein, we have demonstrated that ruthenium supported ultra-black silicon nanowires can drive the Sabatier reaction both photochemically and photothermally where both incident photons absorbed by and heat generated in the black silicon nanowires accelerate the photomethanation reaction. This allows the reaction to be activated at ambient temperatures removing the need for external heating that could cause sintering, mechanical degradation and eventual catalyst deactivation and therefore improves the overall energy efficiency of the process. Additionally, we have shown that the rate of photomethanation is greatly enhanced when highly dispersed nanocrystalline RuO$_2$ is chemically deposited onto the black silicon nanowires support. Furthermore, we have
demonstrated that other silicon structures such as three-dimensional silicon photonic crystals can be used as an efficient support for CO$_2$ hydrogenation. Unlike other insulating supports, these silicon nanostructured supports are particularly attractive for solar-powered catalysis because, with a band-gap of 1.1 eV, they can potentially absorb 80% of the solar irradiance. Moreover, they exhibit excellent absorption strengths and low reflective losses across the entire solar spectral wavelength range of the ultraviolet, visible and near-infrared portion of the solar spectrum. Finally, we demonstrated a comprehensive comparative study of the physical, electronic, and photocatalytic properties of ironoxyhydroxide (FeOOH) polymorphs by studying the extent of methylene blue photodegradation. This work led to the transformation of these FeOOH polymorphs into magnetite (Fe$_3$O$_4$) which effectively reduced CO$_2$ to CO via the reverse water gas shift (RWGS) reaction.
Acknowledgments

First and foremost, I thank the Almighty God for giving me the strength to complete my doctoral work and produce this thesis. I would like to thank my supervisors, Prof. Geoffrey Ozin and Prof. Doug Perovic for their constant support, guidance and extraordinary patience throughout the course of my graduate work. I am extremely grateful to the rest of my committee members, Prof. Jun Nogami and Prof. Charles Mims, for their advice and invaluable suggestions throughout my Ph.D. program. I would like to thank all the academic collaborators I had the pleasure of working with throughout my graduate degree – Dr. Paul O’Brien and Dr. Mohamad Hmadeh for their constant mentoring and helpful discussions that shaped my thesis work, Dr. Thomas Wood and Amit Sandhel for their help with sample testing and helpful discussions on gas-phase heterogeneous catalysis, Dr. Kulbir Ghuman for the many hours she spent doing computational measurements and extremely vital discussions. I thank members of Ozin Research Group, the rest of the Solar Fuels Team and the Department of Materials Science and Engineering. I would like to thank our lab manager Sue Mamiche Afara who is the glue that keeps the research team together. I am grateful to World University Service of Canada (WUSC) for giving me the opportunity to study in one of the best Universities around the globe. I thank my parents, siblings and my friends who were always there for me throughout my graduate studies. Finally, I would like to thank my beautiful wife for her constant support throughout my Ph.D. studies.
# Table of Contents

List of Tables .............................................................................................................. x
List of Figures ............................................................................................................. xi
List of Abbreviation ................................................................................................... xix

## Chapter 1 – Background and Introduction to Solar Fuels .................................. 1
1.1 Research Motivation ................................................................................. 1
1.2 Solar fuels generation through artificial photosynthesis ................. 3
1.3 Nanostructured Silicon supports for CO₂ reduction catalysts ........... 12

1.3.1 Silicon nanowires ............................................................................. 12
1.3.2 Inverse silicon opal photonic crystals ........................................ 15
1.4 Iron-based photocatalytic materials .................................................. 17

1.4.1 Iron oxyhydroxides (FeOOH) ...................................................... 17
1.4.2 Magnetite (Fe₃O₄) ....................................................................... 21
1.5 Focus of this thesis ............................................................................... 21

1.6 References .............................................................................................. 22

## Chapter 2 - Photomethanation of CO₂ over Sputtered Ru/Silicon Nanowire Catalysts with Visible and Near-Infrared Photons ........................................ 32
2.1 Statement of Contributions ................................................................. 32
2.2 Abstract ................................................................................................. 32
2.3 Introduction to Black silicon nanowires ........................................... 33
2.4 Experimental Procedure ...................................................................... 37
4.2 Abstract.........................................................................................................................81
4.3 Introduction...................................................................................................................82
4.4 Experimental Procedure.................................................................................................85
  4.4.1 Fabrication of inverse silicon opal photonic crystal support......................................85
  4.4.2 Deposition of nanocrystalline RuO$_2$ on inverse silicon opal photonic crystal support.................................................................................................................................86
  4.4.3 Gas Phase Sabatier reaction rate measurements.........................................................86
  4.4.4 Characterization of the photocatalysts.........................................................................87
  4.4.5 Computational details................................................................................................87
4.5 Results and Discussion....................................................................................................88
4.6 Conclusion.......................................................................................................................109
4.7 References.....................................................................................................................110

Chapter 5 - Photocatalytic Properties of All Four Polymorphs of Nanostructured Iron Oxyhydroxides.........................................................................................................................118

5.1 Statement of Contributions.............................................................................................118
5.2 Abstract........................................................................................................................118
5.3 Introduction.....................................................................................................................119
5.4 Experimental Procedure.................................................................................................123
  5.4.1 Synthesis of goethite ..................................................................................................123
  5.4.2 Synthesis of akaganeite ............................................................................................123
  5.4.3 Synthesis of lepidocrocite........................................................................................123
  5.4.4 Synthesis of feroxyhyte............................................................................................124
5.5 Characterization.............................................................................................................124
5.6 Photocatalytic measurements........................................................................................125
Chapter 6 - Transformation of FeOOH Polymorphs to Fe₃O₄ and Their Photocatalytic Activity towards RWGS Reaction

6.1 Statement of Contributions

6.2 Abstract

6.3 Introduction

6.4 Experimental Procedure

6.4.1 Synthesis of FeOOH nanomaterials

6.4.2 Transformation of FeOOH nanomaterials to Fe₃O₄

6.4.3 Photocatalytic gas-phase measurements

6.4.4 Analytical methods for the characterization of the photocatalysts

6.5 Comprehensive study of the transformation of FeOOH polymorphs into Fe₃O₄

6.6 Activation of RWGS reaction over Fe₃O₄ transformed from FeOOH polymorphs

6.7 Gas-phase flow experiment

6.8 Conclusions

6.9 References

Chapter 7 - Conclusions and Future Work

7.1 Conclusions
7.2 Future Work..................................................................................................................191

7.3 References.....................................................................................................................192

Appendix A: Photomethanation of CO$_2$ over Ni/Silicon Nanowires.......................194

References..........................................................................................................................198
List of Tables

Table 2.1. Total number of photons for each of the tests from A to E.........................47

Table 4.1. Bond length and Bader charge analysis for H₂ adsorption on neutral and charged RuO₂ surfaces.[75] ..............................................................................................................107

Table 5.1. Fe 2p and O 1s core level binding energies of FeOOH polymorphs........134

Table 5.2. Summary of first order rate constants, surface areas and normalized rate constants of the four FeOOH polymorphs.................................................................149

Table 6.1. Electron diffraction planes and the corresponding inter-planar d-spacing of different planes of Fe₃O₄ transformed from FeOOH polymorphs..............................168
List of Figures

Figure 1.1. Illustration of a solar fuels machine in which captured carbon dioxide, water and sunlight are converted by a heterogeneous photocatalyst into an energy rich fuel such as methane or methanol.........................................................................................................................3

Figure 1.2. Illustration of semiconductor-metal junction where the metal acts as an electron sink facilitating charge transfer and suppressing charge recombination........10

Figure 1.3. (a) Chemically etched silicon wafer showing the formation of black silicon nanowires (b) Cross-sectional SEM image of silicon nanowires fabricated through metal-assisted chemical etching of silicon (c) Absorption spectrum of the silicon nanowires........................................................................................................................................14

Figure 1.4. SEM image of photonic crystals (a) SiO$_2$ opaline structure (b) inverse silicon opal structure..............................................................................................................................................16

Figure 1.5. Structures of the FeOOH polymorphs. (a) Goethite (b) Akaganeite (c) Lepidocrocite and (d) Feroxyhyte........................................................................................................................................18

Figure 2.1. SEM image of 10 nm of Ru sputtered onto (a) a polished silicon wafer, (b) a glass substrate, and (c, d) silicon nanowires. Images (a, b, d) were acquired at 250,000 magnification while the cross-sectional SEM image shown in (c) was acquired at a magnification of 10,000. (e) The absorption spectra for the polished Si, glass and SiNW supports are plotted as a function of wavelength.......................................................................................................................................41

Figure 2.2. Reflectance spectra for catalysts comprised of ~10 nm of Ru sputtered onto glass (blue line) polished silicon (orange) and silicon nanowire (black line) supports. The reflectance spectrum from a bare polished Si wafer is also shown for comparison........................................................................................................................................43

Figure 2.3. Methanation rates over Ru-based catalysts on the SiNW, glass and polished Si supports at (a) 150 °C and 45 psi. (b) Temperature profiles recorded for batch reactions performed at 15, 30 and 45 psi and (c) corresponding methanation rates. All tests were performed at a H$_2$:CO$_2$ gas ratio of 4:1. Note that the methanation rates are normalized to the weight of the Ru catalyst.......................................................................................................................................45

Figure 2.4. The Sabatier reaction rate is plotted as a function of the number of absorbed photons with energy greater than the bandgap of silicon for the seven batch reaction tests. The Sabatier reaction rates for the dark test as well as the test carried out under sub-bandgap irradiation (Test F) are both = 0.2 molecules s$^{-1}$cm$^{-2}$.................49
Figure 2.5. Photomethanation rates for the Ru/Glass catalyst under filtered irradiance from a 300W Xe lamp at a temperature of ~90°C. For Test 1 (left) the wavelength of the incident photons is 300nm or greater while for Test 2 (right) the wavelength of the incident photons is longer than 615nm.

Figure 3.1. (a) Cross-sectional scanning electron microscope (SEM) images of ncRuO$_2$/SiNW, (b) TEM image of a single silicon nanowire coated with RuO$_2$ nanoparticles (c) Energy dispersive X-ray (EDX) horizontal line scan of ncRuO$_2$/SiNW hybrid films (d) Corresponding EDX spectrum of Fig 3.1c (e) Energy dispersive X-ray (EDX) vertical line scan of ncRuO$_2$/SiNW hybrid films and (f) Corresponding spectrum of Fig. 3.1e.

Figure 3.2. (a) Top view SEM image of ncRuO$_2$/SiW sample at magnification of 30X (b) Top view SEM image of ncRuO$_2$/SiW sample at magnification of 150X.

Figure 3.3. High-resolution TEM image of an individual SiNW coated with RuO$_2$ nanoparticles from ncRuO$_2$/SiNW sample with different magnifications (a) 30,000X (b) 150,000X (c) 600,000X (d) FFT of figure 3.1(c) showing diffracting lattice planes of RuO$_2$.

Figure 3.4. (a) $^{13}$CH$_4$ production rate of ncRuO$_2$/SiNW and ncRuO$_2$/SiW hybrid photocatalysts. The green bars correspond to samples under high intensity Xe lamp illumination (~ 24 suns) without external heating while the black bars correspond to experiments done in the dark at 150 °C, (b) the ion mass 17 peak corresponding to $^{13}$CH$_4$ for the methanation tests of ncRuO$_2$/SiNW (black) and ncRuO$_2$/SiW (red) under illumination from Xe lamp at 24 suns intensity, (c) Temperature profile for ncRuO$_2$/SiW under 24 suns intensity, (d) Temperature profile recorded for ncRuO$_2$/SiNW under 24 suns light intensity.

Figure 3.5. (a) Photomethanation rates of RuO$_2$NP/SiNW sample under different light intensities, (b) the ion mass 17 peak corresponding to $^{13}$CH$_4$ for the methanation tests of RuO$_2$NP/SiNW under different light intensities, (c) temperature profiles obtained during the methanation tests of the RuO$_2$NP/SiNW sample under different light intensities.

Figure 3.6. XPS survey spectrum of RuO$_2$/SiNW showing (a) survey spectrum, (b) Ru3d peak, (c) Si2p and (d) O1s.

Figure 4.1. SEM secondary electron images of ncRuO$_2$/i-Si-o sample under different magnifications (a) 20X, (b) 70X, (c) 150X and (d) 500X.

Figure 4.2. (a) Cross-sectional SEM image of the ncRuO$_2$/i-Si-o sample, which was used to determine the average diameter of the RuO$_2$ nanocrystals and to estimate the weight of RuO$_2$, loaded onto the i-Si-o support, (b) SEM image of ncRuO$_2$/SiW sample.
where similar amount (weight) of RuO$_2$ nanocrystals, as that of the ncRuO$_2$/i-Si-o sample, were deposited, (c, d) SEM image of ncRuO$_2$/SiW sample where similar sizes of RuO$_2$ nanocrystals, as that of the ncRuO$_2$/i-Si-o sample, were deposited.

**Figure 4.3.** Comparison of XPS spectra of the ncRuO$_2$/i-Si-o sample measured before (black) and after (red) performing the photomethanation rate tests (a) survey spectrum (b) Ru3d core-levels (c) Ru3p core-levels (d) Si2p core-levels.[74]

**Figure 4.4.** XPS core-level spectra of ncRuO$_2$/SiW sample (a) Ru3d core-levels (b) Ru3p core-levels.[74]

**Figure 4.5.** $^{13}$CH$_4$ production rate of ncRuO$_2$/i-Si-o and ncRuO$_2$/SiW hybrid samples. The samples that are tested under high intensity Xe lamp illumination (22 kW/m$^2$) without external heating are shown in purple color while the black bars correspond to experiments done in the dark at 150 °C.

**Figure 4.6.** The ion mass 17 peak for the first and final photomethanation tests carried out over the ncRuO$_2$/i-Si-o sample had been subjected to testing for over 30 h. The peaks, which were acquired using an Agilent 7890A gas chromatographic mass spectrometer, confirm that the $^{13}$CH$_4$ product originated from $^{13}$CO$_2$ rather than adventitious carbon sources.

**Figure 4.7.** Diffuse reflectance (a) and absorption (b) of ncRuO$_2$/i-Si-o (in red) and ncRuO$_2$/SiW samples (in black).

**Figure 4.8.** Temperature profiles recorded for the two samples during the photomethanation testing. (a) ncRuO$_2$/SiW sample, (b) ncRuO$_2$/i-Si-o sample.

**Figure 4.9.** (a) Photomethanation rate over the ncRuO$_2$/i-Si-o catalyst tested under different illumination conditions; for Test 1 the incident light spectra from the Xe lamp was passed through a 625 nm high-pass cut-off filter, for Test 2 a 495 nm high-pass cut-off filter was used, and no filter was used for Test 3. The relative intensity of the incident light spectra for Tests 1, 2 and 3 are 1.8, 5.0 and 22 kW/m$^2$, respectively, (b) GC-MS spectrum ion mass 17 peak for the three photomethanation tests carried out over the ncRuO$_2$/i-Si-o sample, (c) Temperature profiles recorded for the three batch reaction tests.

**Figure 4.10.** The incident light spectra for Test 1 with a 625nm high-pass cut-off filter, Test 2 with a 495nm high-pass cut-off filter, and Test 3 without using a filter.

**Figure 4.11.** XPS measurement of O1s spectrum ncRuO$_2$/i-Si-o sample after the photomethanation test. The peak with binding energy of 530 eV (in red) is associated with lattice oxygen of the RuO$_2$ while the peak around 531 eV (in blue) is assigned to oxygen vacancy or hydroxyl groups. The green peak at 532.3 eV (in green) is from the
SiO$_2$, the peak around 533 eV (in purple) is associated with C/O species adsorbed on the catalyst and the peak at 534 eV (in dark blue) is associated with adsorbed water.

**Figure 4.12.** Top view (left) and side view (right) of RuO$_2$(110) surface. A, B and C represent the various absorption sites considered for the calculation. A: top of 5-fold coordinated Ru, B: bridge site and C: on top of 2-fold coordinated O. Color code: Ru, Gray and O, red.

**Figure 4.13.** H$_2$ adsorption on various sites on neutral and charged (110) RuO$_2$ surfaces. A: top of 5-fold coordinated Ru, B: bridge site and C: on top of 2-fold coordinated O. Color code: H, blue; Ru, gray and O, red.

**Figure 4.14.** CO$_2$ adsorption on site A (left) of all the surfaces, on site B (middle) of [RuO$_2$(110)]$^{+1}$ surface and on site C (right) of all the surface.

**Figure 4.15.** CO$_2$ adsorption on (a) site A, (b) site B, and (c) site C of H$_2$ adsorbed [Ru(110)]$^{-1}$ surface.

**Figure 5.1.** Synthesized FeOOH polymorphs: (a) goethite (brown), (b) akaganeite (yellowish-brown), (c) feroxyhyte (reddish-brown) and (d) lepidocrocite (orange-brown).

**Figure 5.2.** Powder X-ray diffraction of goethite. The average crystal size was about 6 - 7 nm and the unit cell dimensions are: a = 4.621 Å, b= 9.981 Å and c=3.032 Å. The blue pattern represents the as synthesized goethite and the black pattern is the simulated goethite.

**Figure 5.3.** (a) SEM image, (b, c) HR-TEM images, and (d) FFT of goethite nanostructures. The scale bars are 5 mm, 20 nm, and 5 nm for Figure 2a, b, and c, respectively.

**Figure 5.4.** Powder X-ray diffraction of akaganeite. The unit cell dimensions are: a = 10.54 Å and c = 3.03 Å, with an average crystal size of 45 nm.

**Figure 5.5.** (a) SEM image, (b) TEM image, (c) HR-TEM image, and (d) FFT analysis of akaganeite nanostructures. The scale bars are 100 nm, 500 nm, and 5 nm for Figure 2a, b, and c, respectively.

**Figure 5.6.** Powder X-ray diffraction of lepidocrocite. The unit cell dimensions are: a = 3.07 Å, b = 12.53 Å, and c = 3.87 Å.
Figure 5.7. (a) SEM image, (b) TEM image, (c) HR-TEM image, and (d) FFT analysis of lepidocrocite nanostructures. The scale bars are 1 mm, 500 nm, and 10 nm for Figure 3a, b, and c, respectively.

Figure 5.8. Powder X-ray diffraction of feroxyhyte. The unit cell dimensions are: a = 2.947 Å and c = 4.520 Å, with an average crystal size of 14 nm.

Figure 5.9. (a) SEM image, (b) TEM image, (c) HR-TEM image, and (d) FFT analysis of feroxyhyte nanostructures. The scale bars are 4 mm, 500 nm, and 10 nm for Figure 4a, b, and c, respectively.

Figure 5.10. Comparison of the survey spectra of the FeOOH polymorphs obtained using a Thermo Scientific K-Alpha XPS spectrometer, with an Al Kα X-ray source operating at 12 kV, 6 Å and X-ray wavelengths of 1486.7 eV. Some of the spectra were vertically shifted for clarity.

Figure 5.11. XPS spectra of FeOOH: (a) Fe 2p, (b) O1s of α-FeOOH, (c) O1s of β-FeOOH, (d) O1s of γ-FeOOH, (e) O1s of δ-FeOOH.

Figure 5.12. UV-Vis spectra of MB after being treated with each of the FeOOH polymorphs for five hours: (a) goethite (b) akaganeite (c) lepidocrocite and (d) feroxyhyte.

Figure 5.13. Extent of methylene blue degradation under visible-light irradiation in the presence of FeOOH polymorphs.

Figure 5.14. Extent of methylene degradation under visible irradiation by α-FeOOH and δ-FeOOH in the presence of ethanol as hole scavenger.

Figure 5.15. Diffuse reflectance spectra of the FeOOH polymorphs.

Figure 5.16. The plots of (ahv)² versus hv calculated from the UV-Vis diffuse reflectance spectrum of (a) goethite, (b) akaganeite, (c) lepidocrocite and (d) feroxyhyte.

Figure 5.17. Valence band minimums (VBM) obtained by extrapolating the two fitted linear lines shown in red. The point where the two red lines cross is an estimate of the VBM of the FeOOH polymorphs. These measurements together with the band gap obtained from UV-Vis diffuse reflectance are used to plot the energy band diagram of the FeOOH polymorphs in Figure 5.18.

Figure 5.18. Energy band diagrams of the FeOOH polymorphs. Photogenerated electrons in the conduction band reduce oxygen to form superoxide while the holes...
react with dissolved oxygen in water to form reactive hydroxyl radicals that photodegrade MB...146

Figure 5.19. N2 isotherms showing the BET surface area values of FeOOH polymorphs: (a) goethite, (b) akaganeite, (c) lepidocrocite, and (d) feroxyhyte...147

Figure 5.20. Kinetic analysis of MB degradation showing a plot of ln(C0/Ct) vs. time for the FeOOH polymorphs...148

Figure 6.1. Custom built batch reactor used to perform photocatalytic measurements...161

Figure 6.2. PXRD of (a) α-Fe3O4, (b) β-Fe3O4, (c) δ-Fe3O4, (d) γ-Fe3O4 and (e) commercial Fe3O4 sample for comparison. Here α-Fe3O4, β-Fe3O4, γ-Fe3O4 and δ-Fe3O4, are Fe3O4 nanomaterials transformed from α-FeOOH, β-FeOOH, γ-FeOOH and δ-FeOOH respectively...164

Figure 6.3. TEM images of FeOOH and Fe3O4 samples. (a) α-FeOOH (b, c) α-Fe3O4 (d) β-FeOOH (e, f) β-Fe3O4 (g) γ-FeOOH (h, i) γ-Fe3O4 (j) δ-FeOOH (k, l) δ-Fe3O4...166

Figure 6.4. SAED of (a) α-Fe3O4 (b) β-Fe3O4 (c) γ-Fe3O4 and (d) δ-Fe3O4. Here α-Fe3O4, β-Fe3O4, γ-Fe3O4 and δ-Fe3O4 represent Fe3O4 nanomaterials transformed from α-FeOOH, β-FeOOH, γ-FeOOH and δ-FeOOH respectively...167

Figure 6.5. XPS spectra of Fe2p and O1s photoemission peaks of Fe3O4 transformed from FeOOH showing Fe2p of (a) α-Fe3O4 (b) β-Fe3O4 (c) γ-Fe3O4 and (d) δ-Fe3O4 and the O1s (e) α-Fe3O4 (f) β-Fe3O4 (g) γ-Fe3O4 and (h) δ-Fe3O4...170

Figure 6.6. XPS spectra of Fe2p and O1s photoemission peaks of FeOOH showing Fe2p of (a) α-FeOOH (b) β-FeOOH (c) γ-FeOOH (d) δ-FeOOH and the O1s (e) α-FeOOH (f) β-FeOOH (g) γ-FeOOH (h) δ-FeOOH...171

Figure 6.7. The valence band spectra of (a) α-Fe3O4 (b) β-Fe3O4 (c) γ-Fe3O4 and (d) δ-Fe3O4 (e) α-FeOOH (f) β-FeOOH (g) γ-FeOOH (h) δ-FeOOH...172

Figure 6.8. (a) Comparison of CO production rates of Fe3O4 photocatalysts under solar simulated irradiation of ~15 kW/cm2. Here α-Fe3O4, β-Fe3O4, γ-Fe3O4 and δ-Fe3O4 represent Fe3O4 nanomaterials transformed from α-FeOOH, β-FeOOH, γ-FeOOH and δ-FeOOH respectively...174

Figure 6.9. Temperature profiles of the four Fe3O4 photocatalysts recorded during the testing under high solar simulated illumination of ~15 kW/cm2...175
Figure 6.10. (a) Batch reactor used to test the RWGS reaction. The top corner of the reactor, circled in green, shows the water condensate observed during the testing of the $\delta$-Fe$_3$O$_4$ sample. (b) Higher magnification picture of the batch reactor

Figure 6.11. GC-MS spectra at 29 amu of (a) $\alpha$-Fe$_3$O$_4$ (b) $\beta$-Fe$_3$O$_4$ (c) $\gamma$-Fe$_3$O$_4$ and (d) $\delta$-Fe$_3$O$_4$ under $\sim$15 kW/cm$^2$ of illumination

Figure 6.12. (a) Pictures of the Fe$_3$O$_4$-$\beta$ sample (outer grey spots) and a-β-Fe$_3$O$_4$ sample (inner ultra-black spot), (b) PXRD of a-β-Fe$_3$O$_4$ sample, (c) TEM image of a-β-Fe$_3$O$_4$ sample, and (d) SAED of a-β-Fe$_3$O$_4$ sample

Figure 6.13. (a) Comparison of survey spectrum of (a) a-β-Fe$_3$O$_4$ sample and (b) β-Fe$_3$O$_4$ sample. (c) Fe2p of a-β-Fe$_3$O$_4$ sample (d) O1s of a-β-Fe$_3$O$_4$ sample

Figure 6.14. Flow reactor set up used for measuring RWGS reaction rates

Figure A.1. SEM micrograph of nickel nanoparticles deposition on black silicon nanowires support at different loading conditions (a) 15 minutes (b) 30 minutes (c) 120 minutes and (d) 120 minutes at X5 the concentration of the regular deposition concentration

Figure A.2. Rate of photomethanation under alternating light and dark tests performed on nickel deposited on black silicon nanowires from the sample shown in Figure A.1b

Figure A.3. (a) SEM image of nickel film deposited on black silicon nanowires (b) STEM image of nickel film deposited on black silicon nanowires (c) PXRD showing the presence of both nickel and silicon. The two very sharp peaks at 33° and 62° 2θ originate from the [100] face of the silicon wafer, which was etched to make the silicon nanowires. (d) EDX elemental mapping of the sample shown in Figure A.3a
List of Appendices

Appendix A: Photomethanation of $\text{CO}_2$ over Ni/Silicon Nanowires
List of Abbreviations

AMU – Atomic Mass Unit
BET – Brunauer-Emmett-Teller
CB – Conduction Band
CVD – Chemical Vapor Deposition
DFT – Density Functional Theory
EDX – Energy Dispersive X-Ray Spectroscopy
E\textsubscript{g} – Energy Gap
EISA – Evaporation-Induced Self-Assembly
FFT – First Fourier Transform
FID - Flame Ionization Detector
FTIR – Fourier Transform Infrared
GC – Gas Chromatography
GC-MS – Gas Chromatography Mass Spectrometry
HRTEM – High Resolution Transmission Electron Microscopy
MACE - Metal-assisted chemical etching of silicon
MB – Methylene Blue
Nps - Nanoparticles
PXRD – Powder X-ray Diffraction
RF – Radio Frequency
**RWGS** – Reverse Water Gas Shift

**SEM** – Scanning Electron Microscopy

**SiNWs** - Silicon nanowires

**STEM** – Scanning Transmission Electron Microscopy

**TEM** – Transmission Electron Microscopy

**TCD** - Thermal Conductivity Detector

**UV** – Ultraviolet

**VB** – Valence Band

**VLS** - Vapor Liquid Solid

**XPS** – X-ray Photoelectron Spectroscopy
Chapter 1 – Background and Introduction to Solar Fuels

1.1 Research Motivation

Two major challenges facing humanity today are climate change and developing and sustaining a clean energy supply. The vast majority of the global energy we consume today comes from burning fossil fuels such as oil, coal and natural gas. The consumption of these fossil fuels results in the emission of the greenhouse gas CO$_2$ into the atmosphere, which increases global temperatures by means of the radiative forcing effect, namely the difference between the amount of sunlight absorbed by the earth and the energy radiated back to space. The increased emission of CO$_2$ to the atmosphere has raised serious concerns about climate change. To address this problem, intensive research efforts are devoted towards finding alternative sources of clean renewable energy that can meet the demands of the growing world population.

Solar energy is by far the largest exploitable natural resource, providing more energy in one hour to the earth than all of the energy consumed by humans in an entire year. If a small portion of this abundant energy can be utilized, it will go a long way towards attaining sustainable energy for a growing world population. In principle, solar power can be utilized to produce energy such as electricity, by using photovoltaic devices for example. However, due to the intermittent nature of the sun, it is more desirable to store the sun's energy in the form of solar fuels. This not only solves the solar intermittency problem but also provides a way to easily store solar energy in the form of energy rich fuels. Hydrogen was the first fuel produced from solar energy, which was achieved through electrochemical photolysis of water using a TiO$_2$ electrode. Although
hydrogen can be used as a fuel for a variety of applications such as transport and feedstock in industrial applications, it requires a proper transportation and storage system so that it can be used on demand whenever and wherever it is needed. Currently, only 10% of the gases transported through natural gas pipelines can be hydrogen, and it is costly to build dedicated distribution pipelines for hydrogen transportation.[9] On the other hand, carbon-based solar fuels such as methane and methanol are fully compatible with existing transportation and storage systems already in place and therefore can be easily transported and stored using these systems, relieving the need to build and establish new transportation and storage systems.[1, 10, 11]

Moreover, carbon-based solar fuels generally have high energy density compared to hydrogen fuel. Due to the ease of transportation and storage of these carbon-based fuels, they can be released on demand and transported to wherever they are required. Such synthetic fuels can be obtained from the photocatalytic conversion of cheap raw materials such as CO₂ and H₂O, allowing solar energy to be stored in the form of chemical bonds (Figure 1.1).[10-15] This concept is sometimes referred to as the “artificial photosynthesis” and the man-made materials that use solar energy to convert H₂ or CO₂ into fuels are referred to as an “artificial leaf”. While solar-powered chemical conversion of CO₂ is possible, there are significant challenges involved with finding robust and inexpensive materials that are capable of efficiently capturing and converting CO₂ into value-added products. Herein, we have designed a material that can absorb efficiently the solar spectrum and drive chemical conversion of CO₂ to chemical fuels. Moreover, our approach allows us to take full advantage of both light and heat energy from the sun to power the photocatalytic conversion of CO₂ into value-added chemical products.
Figure 1.1. Illustration of a solar fuels machine in which captured carbon dioxide, water and sunlight are converted by a heterogeneous photocatalyst into an energy rich fuel such as methane or methanol.

We hope this combined photothermal/photochemical approach of using both light and heat energy from the sun to generate solar fuels from abundant raw materials such as CO$_2$ and H$_2$O can encourage the scientific community to develop more efficient photocatalysts for solar fuels generation.

1.2 Solar fuels generation through artificial photosynthesis

As an alternative to fossil fuels, photocatalytic solar fuels production was first discovered by Fujishima and Honda using the TiO$_2$ photocatalyst as a photoanode.$^8$ TiO$_2$ was identified as a bench mark photocatalyst with an enormous technological
significance due to its numerous applications. A Variety of photocatalytic reactions such as dye degradation, water splitting and CO$_2$ reduction could be activated using TiO$_2$. Unlike most other semiconductors, TiO$_2$ is a cheap, nontoxic and a very stable compound and has therefore been applied extensively in the photocatalytic reduction of CO$_2$.\cite{17-22} However, TiO$_2$ has a large electronic band gap energy of 3.2 eV, which limits its light absorption to the ultraviolet portion of the solar spectrum.\cite{17, 21} Various methods have been employed to engineer the band gap of TiO$_2$ including doping,\cite{23, 24} and surface sensitization,\cite{25, 26} in order to reduce the electronic gap and enhance visible light absorption. As a result, the photocatalytic reduction of CO$_2$ in the visible region of the solar spectrum was realized. Following the discovery of TiO$_2$ as an efficient photocatalyst, numerous other photocatalysts have been developed towards the photocatalytic reduction of CO$_2$ to generate solar fuels.\cite{27, 28} Metal oxides, nitrides, sulphides, and phosphides are the main compounds used for the photocatalytic reduction of carbon dioxide.\cite{29-41} These photocatalytic CO$_2$ reduction reactions discussed above are mainly done in homogeneous aqueous-phase medium and the reaction rates are generally very low on the order of $\mu$molg$_{\text{cat}}^{-1}$h$^{-1}$ or less.

Despite the many advantages of homogeneous aqueous-phase catalysis, it is more desirable to generate solar fuels through gas-phase heterogeneous catalysis, mainly for the easy separation of products from the reactants. Therefore, the scientific community has extensively investigated the heterogeneous gas-phase hydrogenation of CO$_2$ over the last couple of decades. Hydrogen is obtained from solar-powered water splitting or generated using excess electricity. The hydrogenation of CO$_2$, which is presently a thermally driven process, could be activated using a variety of photocatalysts, thereby
generating solar fuels. Although conversion efficiencies and selectivities of photocatalytic hydrogenation of CO$_2$ are presently very low, they continue to improve with the discovery of new nanomaterial architectures and superior reactor designs. Numerous photocatalysts consisting of metal oxide nanoparticles or metal oxide supported metals have been studied for the hydrogenation of CO$_2$ to produce solar fuels.$^{[42-47]}$ The three major products obtained from the catalytic hydrogenation of CO$_2$ are methane, carbon monoxide and methanol (see Eqs. 1 - 3).

Methanation: CO$_2$ (g) + 4H$_2$ (g) $\rightarrow$ CH$_4$ (g) + 2H$_2$O (g)  

Reverse water gas shift reaction: CO$_2$ (g) + H$_2$ (g) $\rightarrow$ CO (g) + H$_2$O (g)  

Methanol synthesis: CO$_2$ (g) + 3H$_2$ (g) $\rightarrow$ CH$_3$OH (g) + 2H$_2$O (g). 

The products obtained from CO$_2$ hydrogenation depend on the materials used and the operating conditions employed. These three products of CO$_2$ hydrogenation are extremely important fuels and are used in a variety of industrial and domestic applications. For example, carbon monoxide is used as a reactant for Fischer Tropsch synthesis, a very important industrial process for producing liquid fuels. Methane is obtained through the Sabatier reaction (methanation) while carbon monoxide is produced in the reverse water gas-shift reaction. The reverse water-gas shift reaction is an endothermic reaction that is highly favoured at high temperature whereas both methanol synthesis and methanation reactions are exothermic and are favoured at relatively low temperatures (below 300 °C). Ruthenium, nickel and rhodium are the three most effective Sabatier reaction catalysts used to drive methanation of CO$_2$. While there are plenty of ruthenium-based thermal methanation catalysts in the literature, the first
light promoted ruthenium based methanation catalyst was reported by Graetzel and co-workers.\[^{48}\] The catalyst was made up of Ru/RuO\(_x\)/TiO\(_2\) and could convert CO\(_2\) into CH\(_4\) under solar-simulated irradiation. Although the enhanced reaction rate was first attributed towards the photo-excitation of the TiO\(_2\) support, it later became clear that this enhancement was associated with localized photoactive species on the ruthenium surface, an effect modified by the nature of the TiO\(_2\) support.\[^{49}\] Thereafter, several other Sabatier reaction catalysts were found to be very active towards the methanation of CO\(_2\).\[^{50-52}\] It should be mentioned that the reaction rates reported in the literature for the light promoted methanation of CO\(_2\) are by and large very low. Moreover, most of these reports don’t include isotope labelling experiments which calls into question whether the reaction products are obtained from the reactants or from adventitious carbon sources.\[^{53}\] However, very recent reports by Sastre et al described the complete photocatalytic reduction of CO\(_2\) to methane in a hydrogen environment using a catalyst comprised of Ni on a silica-alumina support producing methane at a rate well over 10 mmolg\(_{cat}\)^{-1}h\(^{-1}\).\[^{54}\] It was proposed that the reaction mechanism involves the formation of Ni-H which accelerates the overall reduction of the CO\(_2\). Furthermore, optical measurement experiments performed showed that 76% of CO\(_2\) photoreduction was due to UV, which is consistent with the bandgap excitation of NiO.\[^{55}\] Similar photomethanation mechanism was proposed by Ogura et al using NiO/Kieselguhr catalyst that was pretreated in H\(_2\) atmosphere under UV-light.\[^{56}\]

Moreover, several catalysts have been reported to be very active in the synthesis of methanol.\[^{57-60}\] For example, there are several copper and zinc-based double hydroxide layered compounds that are active towards the hydrogenation of CO\(_2\) to produce
methanol at a rate of 490 nanomol\textsubscript{cat}^{-1} h^{-1}.\cite{61, 62} Additionally, reverse water gas shift reaction is known to be activated by numerous metal oxides. The most common ones are based on ZrO\textsubscript{2} although alkaline earth metal oxides have also been reported to be active towards the reverse water gas shift reaction.\cite{41, 43, 45, 63}

A careful examination of the literature reveals that most of the photoactive materials used in the photocatalytic reduction of CO\textsubscript{2} are in the form of heteronanostructures or employ some kind of support material.\cite{27, 30, 31, 36, 40, 48, 54, 56} This support material may be innocent or photoactive itself. Even if the support material is inert and doesn’t participate in the activation and charge transfer process, it provides a medium for efficient dispersion increasing the surface area of the catalyst leading to enhanced reaction rates. For example, an increased methanol production was observed when NiO catalyst was used as a cocatalyst with InTaO\textsubscript{4}.\cite{33} Moreover, an enhanced photomethanation rate was observed when Ru was loaded onto NaTaO\textsubscript{3} catalyst producing methane at a rate of 51.8 \textmu mol\textsubscript{cat}^{-1} h^{-1}.\cite{47} Additionally, carbon monoxide was produced at a rate of 139.1 \textmu mol\textsubscript{cat}^{-1} h^{-1} when Pt was loaded onto the NaTaO\textsubscript{3} catalyst. Charge transfer from the NaTaO\textsubscript{3} catalyst support was the driving force for the increased photoreduction of CO\textsubscript{2}. Furthermore, Ru catalysts supported on TiO\textsubscript{2} is very active towards photomethanation of CO\textsubscript{2}.\cite{48-50} CO photomethanation using TiO\textsubscript{2} supported Ni catalyst under UV light produced methane in hydrogen environment.\cite{52} It is proposed that photogenerated electron transferred from the TiO\textsubscript{2} to the adjacent Ni metal increased the surface electron density which in turn enhanced the adsorption and activation of CO. In addition, NiO deposited on inert supports was able to produce methane at very
high rates. All these cases show the significance of the support material and the role it plays in the reaction rate enhancement.

The above is a brief summary of some of the research dedicated towards the production of solar fuel through artificial photosynthesis utilizing CO$_2$ and H$_2$/H$_2$O as a raw material to generate hydrocarbon fuels. There is no doubt that as the field of solar fuels grows, the development of more efficient photocatalysts will continue to develop in the future and the performance of the current photocatalysts will continue to improve significantly as well. With the tremendous research going on in the field of solar fuels, it is only a matter of time before the current state of the art reaction rates are exceeded.

While the literature presents several interesting approaches and strategies to CO$_2$ utilization such as homogeneous and heterogeneous catalysis, biocatalysis, solar thermal catalysis etc., we focus on heterogeneous gas-phase reduction of CO$_2$ mainly because it is the most practical and economically viable approach for large scale solar fuels production. Besides, the majority of the industrial catalytic processes are heterogeneously catalyzed due to the flexibility in operating reaction conditions and easiness of reaction products separation. Over the last couple of decades, significant advancements have been attained in the field of light-driven heterogeneous gas-phase CO$_2$ reduction and numerous photocatalysts have been discovered to activate the gaseous reduction of CO$_2$. Despite the enormous progress, the development of efficient and ideal heterogeneous gas-phase photocatalysts still remain a challenge today. The goal is to design and engineer novel photocatalytic materials that are capable of producing solar fuels from CO$_2$ at an industrial large scale. Such an ideal photocatalyst
should be cheap and easily scalable otherwise the commercialization of such technology will be extremely difficult. Furthermore, an ideal gas-phase photocatalyst would be capable of absorbing the broad solar irradiance, separating photogenerated charges, and allowing surface chemical reactions to occur efficiently. In addition, an ideal photocatalyst will be stable under optimal reaction conditions. Semiconductors are preferred for photocatalysis mainly because they have a band gap that allows the separation of photogenerated charges once they absorb photons with energy greater than their band gap. Ideally, a small band gap semiconductor is necessary in order to absorb the majority of the solar spectrum. However, the band gap should be sufficiently big to allow the redox potential of the desired reaction to straddle the band gap of the material. Once these charges are generated, they must be separated and moved to the surface for catalytic reaction to take place, otherwise the photogenerated charges will be quenched through various recombination pathways. For this to happen, the distance travelled by these photogenerated charges before reaching the surface has to be reduced by choosing materials that have nanoscale features instead of using bulk materials. This will allow the charges to move a short distances to get to the surface where the reaction takes place. Additionally, because the Fermi energy levels of metals such as Pt, Rh, Pd, Ru, Cu, Ag and Au are typically lower than the conduction band of the semiconductors, these metal nanoparticles can act as electron sinks, facilitating interfacial electron transfer and ultimately decrease the electron‒hole recombination rate as well as creating a new catalytic site for CO₂ reduction (Figure 1.2). It has been demonstrated that different co-catalysts have different selectivities towards certain reaction products. It is therefore critical to choose the right co-catalyst to drive the
desired reaction. For example, nickel metal is known to be an active thermal catalyst for the Sabatier reaction. It is therefore conceivable to use nickel as a co-catalyst if the desired reaction is the methanation of CO$_2$.

This thesis investigates novel photocatalytic materials for solar-powered CO$_2$ reduction reactions. Firstly, nanostructured silicon-based catalyst supports with different catalysts loadings are tested for gas-phase photomethanation of CO$_2$. Secondly, a set of four iron oxyhydroxide polymorphs are synthesized and tested for aqueous phase photocatalytic degradation of methylene blue dye and gas-phase photocatalytic reduction of CO$_2$ via reverse water gas shift.

Figure 1.2: Illustration of semiconductor-metal junction where the metal acts as an electron sink facilitating charge transfer and suppressing charge recombination.
In the remainder of this chapter we present a brief introduction concerning our approach towards the design of an ideal and efficient solar fuel photocatalyst. In order to satisfy most of the criteria of an ideal photocatalyst, the performance of nanostructured silicon nanostructures functioning as catalyst supports for solar-driven CO$_2$ reduction reactions was extensively investigated. Because silicon is a small band gap material (1.1 eV), it can potentially absorb 80% of the solar spectrum across the UV, visible and near infrared portion of the solar spectrum. One type of silicon-based nanostructured support investigated are silicon nanowires. Silicon nanowires have the advantage of minimal reflectivity and a relatively large surface area, which increases the likelihood that photogenerated charges will reach the surface of the catalyst where the carbon dioxide reduction reaction takes place. Additionally, silicon-based inverse opal photonic crystals were also tested as a catalyst support. These inverted silicon photonic crystals supports offer the advantages of low reflectivity, and furthermore, their open-porous structure may allow for rapid diffusion of gaseous reactants and products to and from the reaction site, respectively. The use of these silicon supports gave several orders of magnitude enhancement in the rate of CO$_2$ reduction and is seen as an ideal photocatalyst support as described in this thesis.

Furthermore, we explored iron-based photoactive materials for a variety of photocatalytic applications including dye photodegradation and the reverse water gas shift reaction. In particular, the use of iron oxyhydroxide (FeOOH) polymorphs as an active photocatalyst for the photodegradation of dyes is discussed. Furthermore, we discuss their photoactivity for solar fuels production through their in situ transformation
to magnetite (Fe₃O₄) and applying it towards the reduction of CO₂ to produce CO via reverse water gas shift.

1.3 Nanostructured Silicon supports for CO₂ reduction catalysts

1.3.1 Silicon nanowires

Owing to their unique structural, optical and electronic properties, silicon nanowires (SiNWs) have recently been used for energy conversion and storage applications including photovoltaics, thermoelectrics and photocatalysis.[64-66] Silicon is an ideal material because it is low cost, scalable and with a small band gap of 1.1eV, it is capable of absorbing 80% of the solar spectrum. Therefore, silicon nanowires are used as a substrate for a variety of photocatalysts.[67-69] Several methods have been developed to fabricate silicon nanowires using bottom-up or top-down approaches. These include; vapour liquid solid (VLS) growth, reactive ion etching, template-assisted growth, laser ablation and metal assisted chemical etching (MACE).

Among all the methods used to fabricate SiNWs, MACE has gained the most interest over the past couple of decades for a number of reasons. The fabrication of SiNWs via MACE is very simple, and cost-effective, because it doesn’t require ultra-high vacuum conditions that are necessary for many other silicon nanowire fabrication techniques.[70] Furthermore, vertically-aligned, well-oriented, high aspect ratio, large-scale forests of silicon nanowires can be grown on silicon substrates and wafers using the MACE technique.[71] The fabrication of SiNWs by MACE is a solution-based etching technique where hydrofluoric acid is mainly used as the etchant solution, although other etchants such as ammonium fluoride are sometimes employed.[72] The process requires the use
of a metal catalyst, preferably a noble metal, to speed up the etching process. The noble metal helps in the reduction of oxidants such as H$_2$O$_2$, which generates holes that are then injected into the valence band of the silicon to accelerate the etching process. Several noble metals such as Ag, Au, Pt and Pd have been used as a catalyst to speed up the chemical etching of silicon. These noble metals are deposited on the silicon substrate through various methods ranging from sputtering,\cite{73, 74} electrode deposition,\cite{75} thermal evaporation,\cite{76, 77} spin coating\cite{78} and electroless deposition.\cite{79} Electroless deposition was shown to be the simplest and preferred method. Typically, AgNO$_3$ is used as the source of Ag for the fabrication of SiNWs in the MACE technique.

During the fabrication of SiNWs by the MACE technique, a silicon wafer (intrinsic or extrinsic) is etched in a solution consisting of HF, AgNO$_3$ and H$_2$O$_2$. Figure 1.3a shows a picture of the etched silicon wafer to produce SiNWs, which appears to be ultra-black. Figure 1.3b shows a typical cross-sectional SEM image of the fabricated silicon nanowires. The length of the nanowires is greatly influenced by a variety of factors such as the etching time, the etching temperature and the concentration of the solution.\cite{80} Typically, one hour etching at room temperature produces nanowires that are 5-10 µm in length. The unique advantage of this silicon nanowire fabrication process is that the process is scalable in that large area vertically-aligned nanowire arrays can be grown on silicon wafers. In this context, black silicon is considered an ideal catalyst support material due to its small band gap of 1.1 eV, which can be tailored to absorb more than 80% of the solar irradiance in the UV-Visible and near infrared portion of the solar spectrum as can be seen from the absorption spectrum in Figure 1.3c.
Figure 1.3: (a) Chemically etched silicon wafer showing the formation of black silicon nanowires  
(b) Cross-sectional SEM image of silicon nanowires fabricated through metal-assisted chemical etching of silicon  
(c) Absorption spectrum of the silicon nanowires.
The enhanced absorption strengths of the SiNWs is due to the very low reflective losses of the vertically-aligned SiNW arrays throughout the UV-Visible and near infrared solar spectral wavelength range. On the other hand, the red curve in Figure 1.3c shows that planar silicon wafers exhibit lower absorption strengths due to its high reflective losses compared to the SiNWs.

### 1.3.2 Inverse silicon opal photonic crystals

In addition to the SiNWs, other silicon structures have been used as support for photocatalysts to drive various solar fuels reactions. In particular, inverse silicon opal (i-Si-o) photonic crystals have become a popular photocatalytic support due to their optical and electronic properties. Inverse silicon opal structures are three dimensional photonic crystals fabricated by infiltrating silicon into the interstices of closely-packed array of silica spheres and then etching the silica away with hydrofluoric acid. Typically, silica opaline films are deposited onto substrates such as a silicon wafers as shown in Figure 1.4a. This is followed by infiltration of the silica interstitial voids with silicon by chemical vapour deposition. The SiO$_2$ is then etched with HF to produce a silicon inverse opal architecture as shown in Figure 1.4b. Polystyrene beads can also be used instead of the silica opaline spheres. Inverse silicon opal photonic crystals have excellent light harvesting properties which helps in increasing the photoactivity of catalysts deposited on these structures. This photocatalytic enhancement is due to slow photons that have energies close to the band gap of the semiconductor which increases the path length of light allowing it to be absorbed more efficiently. Scattering of light by inverse silicon photonic crystals additionally contributes to light absorption which results in a great enhancement in the photoactivity of the catalyst.
In addition to silicon, other inverse opal photonic crystals have gained huge interest in photocatalytic applications due to their superior light harvesting properties by controlling the way light propagates inside these materials. For example, Chen et al showed enhanced photoactivity of inverse opal TiO$_2$ in the photo-oxidation of methylene blue.$^{[81]}$ This enhanced photoactivity was due to slow photons with energies close to the electronic bandgap band gap of TiO$_2$, which increased the path length of light allowing it to be absorbed more efficiently. Moreover, Ramiro-Monzano et al have shown that dye-sensitized photoelectrochemical solar cells comprising of a photonic sponge architecture could be used to efficiently trap light and harvest photons in the near UV and visible region of the solar spectrum.$^{[82]}$ In addition, Li et al have demonstrated enhanced photocatalytic activity of inverse opal photonic crystal TiO$_2$ whereby the stop band and multiple scattering effects both contributed to greatly improve the light harvesting properties of the material leading to its superior photocatalytic activities.$^{[83]}$
Several other studies have also reported an enhancement in the photocatalytic properties by inverse opal photonic crystals enabled by the slow photon effect.[84-89]

1.4 Iron-based photocatalytic materials

Iron is one of the most abundant elements in nature.[90] Iron-based materials are therefore an important class of materials to employ as photocatalysts due to their low cost, stability and abundance. Additionally, photoactive iron-based nanomaterials are easily scalable. Although there are several iron-based photoactive materials, iron oxides and hydroxides are the most commonly reported iron-based photocatalysts in the literature.[91-95] Hematite is a prime example of an iron oxide used for variety of light driven catalytic reactions including photocatalysis, photoelectrochemistry and thermocatalysis.[92, 96] Several other iron oxides and oxyhydroxides have also been reported to perform water splitting and carbon dioxide reduction.[94, 97, 98] In Chapter 5 we explore the photocatalytic activity of iron oxyhydroxide (FeOOH) polymorphs for photodegradation of dyes. Additionally, in chapter 6, these FeOOH polymorphs are converted into magnetite (Fe₃O₄) and applied in the reverse water gas shift reaction.

1.4.1 Iron oxyhydroxides (FeOOH)

Iron oxyhydroxides have attracted the attention of the scientific community mainly due to their outstanding properties including environmental compatibility, high photostability and excellent visible light absorption. There are four common polymorphs of iron oxyhydroxides: goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and feroxyhyte (δ-FeOOH). They consist of arrays of Fe³⁺ and OH⁻ in different geometrical arrangements. As the anions are larger than the cations, the arrangement
of the anions governs the crystal structure and the topological interconversion between the different polymorphs. These iron oxyhydroxides can be dehydroxylated to form other iron oxide compounds. The basic structures of these iron oxyhydroxide compounds are based on double strands of FeO$_3$(OH)$_3$ octahedra. These octahedra share corners, edges, or faces and through various combinations of these linkages form different structural arrays, which are shown in Figure 1.5 and are described below.\cite{90}

![Figure 1.5: Structures of the FeOOH polymorphs. (a) Goethite (b) Akaganeite (c) Lepidocrocite and (d) Feroxyhyte.](image-url)
In goethite, the double strands are linked by corner sharing in such a way as to form 2×1 octahedral “tunnels” connected by hydrogen bridges. This arrangement leads to orthorhombic symmetry. For akaganeite, the structure is formed by square channels bounded by four double rows of octahedra. These channels are stabilized by space-filling anions (chloride, fluoride, or other anions smaller than 0.35 nm) to form a body-centered cubic array. Unlike α- and β-FeOOH, which have tunnel structures, lepidocrocite is a layered compound with orthorhombic symmetry. The structure consists of double strands of octahedra that share edges to form zigzag layers. The layers are connected to each other by hydrogen bonds. Finally, the structure of feroxyhyte is based on layers of edge-sharing octahedra in hexagonal symmetry. The FeOOH polymorphs offer interesting opportunities in photocatalysis because their electronic band gap energies (2.0 ≤ E_g ≤ 2.5 eV) fall in the visible wavelength range. Moreover, nanoscale FeOOH with large surface areas can be synthesized with different sizes, shapes, and exposed facets and are colloidally stable in water.

Several synthetic techniques have been developed to synthesize iron oxyhydroxides. These vary from hydrothermal synthesis to colloidal synthesis to thermal transformation of one iron oxyhydroxide polymorph to another. For example, goethite can be synthesized through hydrothermal synthesis.\[^{[99]}\] This is done by dissolving Fe_2(SO_4)_3 in water and heating it in a Teflon-lined stainless steel autoclave at temperatures of ~120 °C for 8 hours. This yields brown precipitate of goethite nanoparticles. Moreover, goethite can also be synthesized through the addition of Fe(NO_3)_3 in a basic solution such as KOH and heating the resulting solution in a flask at ~70 °C for 60 hours.\[^{[100]}\] Additionally, room temperature synthesis of goethite involves air oxidation of a FeCl_2
solution until a yellow precipitate of goethite nanoparticles is formed from the green solution. This procedure involves the use of a buffer solution of NaHCO$_3$ and yields poorly crystalized nanoparticles.$^{[100]}$ The conversion of lepidocrocite and ferrihydrite in basic solution at relatively low temperatures also yields goethite nanoparticles.$^{[101]}$ The synthesis of akaganeite involves hydrothermal techniques where FeCl$_3$ solution is heated in an autoclave at 120 °C for 2 hours.$^{[99]}$ Rice-like yellowish-brown akaganeite precipitates are formed. It should be noted that the presence of chloride is necessary for the formation of akaganeite nanoparticles. Another synthetic route towards the formation of akaganeite is the hydrolysis of FeCl$_2$ solution both in water in and in urea.$^{[102]}$ Lepidocrocite is synthesized at room temperature through the slow oxidation of Fe$^{2+}$ at a pH close to neutral.$^{[99]}$ Typically, FeCl$_2$·4H$_2$O is dissolved in water and the pH is adjusted to 6.7 with NaOH after which air is bubbled through the solution until the greenish-blue solution turns yellowish orange. The solution must be constantly stirred throughout the oxidation process. The reaction should be complete in 3 hours. This yields well-defined lepidocrocite nanocrystals with lath-like shapes. Another common synthesis technique for lepidocrocite involves the addition of Fe(NO$_3$)$_3$·9H$_2$O solution to ethylene glycol followed by the addition of urea.$^{[103]}$ The synthesis of feroxyhyte involves the rapid oxidation of Fe$^{2+}$ with H$_2$O$_2$. FeSO$_4$(NH$_4$)$_2$SO$_4$.6H$_2$O is dissolved with NaOH forming a green precipitate.$^{[99]}$ H$_2$O$_2$ is then rapidly added to the solution. This leads to the immediate formation of reddish-brown feroxyhyte nano-sized precipitates. A relatively new synthetic routes to feroxyhyte is the γ-irradiation of a deoxygenated iron (III) chloride alkaline aqueous colloidal solution in the presence of 2-propanol and diethylaminoethyl-dextran hydrochloride.$^{[104]}$
1.4.2 Magnetite (Fe₃O₄)

Magnetite is a mixed valence metal oxide composed of both Fe²⁺ and Fe³⁺. The Fe³⁺ occupy all the tetrahedral sites in the structure and the octahedral sites are occupied by both Fe²⁺ and Fe³⁺. It is black in colour and ferromagnetic in nature. It has a cubic inverse spinel crystal structure with a unit cell lattice parameter of 0.836 nm. Magnetite is usually non-stoichiometric with cation deficiency. There are a number of ways to synthesize Fe₃O₄ nanoparticles. Alkaline hydrolysis of iron (II) sulphate followed by heating the resulting products to 100 °C produces magnetite nanoparticles.\textsuperscript{[105]} The reaction should be carried out in a N₂ atmosphere. The reduction of hematite under hydrogen atmosphere at elevated temperatures can also produce magnetite nanoparticles.\textsuperscript{[105]} Thermal decomposition of iron (II) sulphide is known to produce magnetite as well.\textsuperscript{[106]}

1.5 Focus of this thesis

This introductory Chapter has provided a brief overview of solar fuels generation through artificial photosynthesis. We have discussed our approach towards the design of an efficient solar fuel catalyst using cheap, earth-abundant photoactive nanomaterials made from some of the most naturally occurring elements on earth; silicon and iron. Our approach is based on the use silicon-based supports that consist of black silicon nanowires and inverse silicon opal photonic crystals to generate solar fuels. Additionally, the photocatalytic properties of iron-based catalysts are investigated.

This section summarizes the main work contained in this thesis. Chapter 2 of this thesis discusses photomethanation of gaseous CO₂ over ruthenium sputtered onto black
silicon nanowires using visible and near infrared photons. Chapter 3 summarizes the main results of use of the liquid phase deposition of RuO$_2$ nanoparticles on black silicon nanowires and its application towards driving the Sabatier reaction. Chapter 4 discusses highly efficient ambient temperature CO$_2$ photomethanation catalyzed by nanostructured RuO$_2$ nanoparticles deposited on silicon photonic crystal supports. In chapter 5 the photocatalytic properties of all four polymorphs of nanostructured iron oxyhydroxides are discussed and a comparative study of the physical and electronic properties of these FeOOH polymorphs is presented. Chapter 6 describes the transformation of FeOOH polymorphs to magnetite and their application towards reverse water gas shift reaction at ambient temperatures under high intensity solar simulated light. Chapter 7 concludes the main results contained in this thesis and provides suggestions for future work to develop efficient photocatalyst for the conversion of CO$_2$ to value-added solar fuels.

1.6 References


76. H. Fang, Y. Wu, J. H. Zhao, J. Zhu, Silver Catalysis in the Fabrication of Silicon Nanowire Arrays *Nanotechnology* 2006, 17, 3768.


100. U. Schwertmann, R. M. Cornell, Iron Oxides in the Laboraroty. 2nd ed. Weinheim, 2000, pp.188.


Chapter 2 - Photomethanation of CO$_2$ over Sputtered Ru/Silicon Nanowire Catalysts with Visible and Near-Infrared Photons

(Reproduced in part with permission from *Adv. Sci.* **2014**, *1*, 1400001)

2.1 Statement of Contributions

Dr. Thomas Wood, Dr. Laura Hoch and Amit Sandhel performed the gas-phase testing of the catalysts. Dr. Paul O’Brien sputter-deposited the ruthenium on the silicon nanowires and drafted the manuscript which was edited by Professors Doug Perovic, Charles Mims and Geoffrey Ozin. I carried out the fabrication of the silicon nanowire supports and characterization of the samples. Portions of this chapter are currently published in Advanced Science Journal.


2.2 Abstract

Herein, we report the photomethanation of gas-phase CO$_2$ over Ru nanoparticles sputtered onto black silicon nanowire (SiNW) supports in a hydrogen environment. Photomethanation rates over the Ru/SiNW catalyst are on the order of 1 mmol gcat$^{-1}$ h$^{-1}$ when normalized to the weight of the Ru, and are expected to be greatly increased by optimizing the Ru nanoparticle dispersion over the SiNWs and using solar
concentration. Moreover, regarding the chemical reaction mechanism, experimental results provided herein show that these Ru/SiNW catalysts photoactivate the Sabatier reaction both thermochemically and photochemically. That is, from a thermochemical standpoint, the Ru/SiNW catalyst heats up when irradiated with solar-simulated light and methanation rates are enhanced due to increased temperatures. Additionally, regarding photochemical activation, we show that at a set temperature, the rate of the Sabatier reaction increases proportionally to the number of incident photons with energy greater than the band-gap of Si. Based on this strong experimental evidence we propose that a small fraction of photogenerated electrons and/or holes in the Si support facilitate the formation of active hydrogen atoms that participate in the overall photomethanation reaction. The use of black silicon nanowire supports to activate gaseous CO\textsubscript{2} both thermochemically and photochemically to produce fuels such as methane represents a general advancement in the field of solar fuels.

### 2.3 Introduction to Black silicon nanowires

As discussed in Chapter 1, black silicon nanowires have exceptional optical properties where they are able to absorb over 90% of the solar irradiance in the UV-Vis and near infrared solar spectrum making them a perfect candidate for solar fuels applications. Black silicon nanowires are produced through metal-assisted chemical etching (MACE) of silicon which is a solution-based wet chemical etching fabrication technique that employs hydrofluoric acid as an etchant solution.\textsuperscript{[1]} The process uses noble metal catalyst such as silver to accelerate the etching process. The work of the noble metal is mainly to speed up the reduction of oxidants such as H\textsubscript{2}O\textsubscript{2} used in the etching
process.\textsuperscript{[2]} The mechanistic details of the formation of black silicon nanowires by MACE was thoroughly investigated over the last two decades.\textsuperscript{[3-6]} The etching process is a nano-electrochemical process where both reduction and oxidation take place simultaneously. Once the silicon wafer is placed in the etching solution, silver ions from AgNO\textsubscript{3} in the solution are reduced to metallic silver nanoparticles which accelerate the etching process while at the same time silicon is oxidized to silica and then etched by the HF in the solution. Generally, the silicon in contact with the Ag nanoparticles etches faster than the silicon surface that is not in contact with Ag nanoparticles (off-metal areas) allowing the Ag nanoparticles to sink into the silicon substrate leading to the formation of silicon pillars (nanowires) in the off-metal areas. The cathodic reaction is the preferential reduction of H\textsubscript{2}O\textsubscript{2} (H\textsubscript{2}O\textsubscript{2} + 2H\textsuperscript{+} → 2H\textsubscript{2}O + 2h\textsuperscript{+}) on the metal surface producing holes that are injected into the valence band of the silicon facilitating the oxidation of the silicon at the Si/metal interface and the eventual etching by the HF.\textsuperscript{[6]} On top of the H\textsubscript{2}O\textsubscript{2} reduction, proton reduction into hydrogen which generates holes (2H\textsuperscript{+} → H\textsubscript{2} + 2h\textsuperscript{+}) for the oxidation of the silicon is proposed to be another cathodic reduction reaction.\textsuperscript{[1, 7]} Both of the above cathodic reactions generate holes which are essential for the dissolution of silicon. The concentration of these holes are maximum at the Si/metal interface, which is why the “on-metal areas” are etched much faster than the “off-metal areas”. The anodic reaction involves the oxidation and dissolution of silicon. Although the dissolution process of the silicon is not completely understood due to the complexity of the process, the overall reaction equation is understood to be: Si + 2H\textsubscript{2}O\textsubscript{2} + 6HF → H\textsubscript{2}SiF\textsubscript{6} + 4H\textsubscript{2}O.
Silicon nanowires fabricated through metal-assisted chemical etching of silicon have become prime candidates for energy conversion and storage due to their unique optical, electrical and thermal properties.\textsuperscript{[8-10]} They have been applied in photovoltaics, photocatalysis and solid state lithium ion battery applications.\textsuperscript{[11-16]} Density functional theory (DFT) has also been used to calculate the band structure and predict that silicon nanowires are good photocatalysts for water splitting.\textsuperscript{[17]} These silicon nanowires are mainly used as a support for catalysts to drive variety of reactions. For example, Peng \textit{et al} have reported very high power conversion of PtNPs decorated silicon nanowires fabricated through MACE.\textsuperscript{[18]} Similarly, Ilwhan \textit{et al} reported enhanced photovoltage using Pt/SiNW compared to planar silicon structures.\textsuperscript{[19]} Liu \textit{et al} reported the improved performance of silicon nanowire photocathode for carbon dioxide photofixation.\textsuperscript{[20]} Photogenerated charges in the silicon nanowires are transferred to a nickel complex which allows the CO$_2$ fixation. Mayer \textit{et al} on the other hand showed that atomic layer deposition of hematite on silicon nanowires allows for production of an efficient dual-absorber photoelectrode system for electrochemical water splitting where the silicon nanowires absorb the majority of the visible and infrared solar spectrum.\textsuperscript{[21]} Moreover, LaTempa \textit{et al} reported the production of hydrocarbon fuels, mainly methane and ethylene, when light-driven, electrically biased photoelectrochemical pn-junction cells was immersed in CO$_2$ saturated with 1.0 M NaHCO$_3$ solution.\textsuperscript{[22]} The photocathode consisted of p-type silicon nanowires coated with copper and the photoanode consisted of n-type TiO$_2$.

Additionally, silicon nanowires fabricated through MACE was reported to be an efficient photocatalyst for solar hydrogen production.\textsuperscript{[23]} Moreover, Wang \textit{et al} have reported a
core-shell structure made of silicon nanowires coated with TiO$_2$ as an efficient heteronanostructure for water splitting.$^{[24]}$ Higher photocurrent density was observed when silicon nanowires were used compared to planar silicon due to low reflective losses and higher surface area of the silicon nanowires. Photogenerated charges could also be efficiently separated by the heteronanostructure leading to decreased charge recombination. Enhanced external quantum efficiency and photoconductivity was also reported when hybrid nanostructures composed of silicon nanowires and TiO$_2$ coating were used.$^{[10]}$ A heterostructure consisting of silicon nanowire arrays coated with nanocrystalline Cu$_2$O was reported to be very active towards photocatalytic water splitting.$^{[25]}$ The high surface area coupled with the low reflective losses and the efficient charge separation exhibited by the heterostructure was said to be responsible for the enhanced photocatalytic activity. Furthermore, Yang et al reported iodine-doped-PEDOT coated on top of silicon nanowires as an efficient photocatalyst for solar hydrogen generation producing solar-to-chemical energy-conversion efficiency of 3.0%, and a H$_2$ evolution rate of 112.39 cm$^2$ h$^{-1}$. $^{[23]}$

Following the successful application of black silicon nanowires for energy conversion and storage exemplified by the aforementioned research work, we began to explore the photomethanation of gas-phase CO$_2$ over ruthenium nanoparticles sputtered onto black silicon nanowire support in a hydrogen environment. While the thermal methanation of CO$_2$ over Ru catalyst is very well known in the literature, the photomethanation of CO$_2$ over Ru nanoparticles was first reported using a catalyst made of Ru-RuO$_2$ dispersed on TiO$_2$. $^{[26]}$ Subsequently, several other catalysts were found to be photoactive towards the reduction of CO$_2$. $^{[27, 28]}$ In general, when testing catalysts for the photoactive
reduction of CO₂ it is important to ensure that the products do not originate from adventitious carbon sources.[29] In this context, isotope tracing experiments using Fourier transform infrared (FTIR) spectroscopy and mass spectroscopy are particularly effective.[30] Using C-13 labelled CO₂ we verified that the methane was obtained from the reduction of CO₂ and not from adventitious carbon sources.

2.4 Experimental Procedure

2.4.1 Catalyst Fabrication:

Silicon nanowires were fabricated using a metal-assisted chemical etching (MACE) technique. P-type silicon wafers were cut into 1 inch squares and then cleaned with ethanol, acetone and de-ionized water. The wafers were further cleaned with piranha solution (H₂SO₄:H₂O₂ = 3:1 by volume) for 3 hours and then rinsed with de-ionized water. Subsequently, the wafers were immersed in an etching solution consisting of 5 M HF, 0.02 M AgNO₃, and 3 mL of 10% HF solution in order to remove surface oxides. The solution was then placed in an autoclave and allowed to etch for 1 hour at room temperature. After the etching process, silver dendrites covering the silicon nanowires were washed off with deionized water. To ensure all the silver nanoparticles and dendrites were removed the etched wafers were placed in concentrated nitric acid (18 M HNO₃) for 30 minutes. The etched wafers were then washed and dried before being cut into 1cm² pieces. Eagle XG and P-type polished silicon wafers were cleaned in a solution of sulfuric acid/hydrogen peroxide (3:1 v/v) and then rinsed with distilled water. Ru was sputtered onto these samples which were subsequently cut into 1 cm². The deposition was carried out in a custom-built sputtering system (Kurt J. Lesker Co.) by
radio frequency (RF) magnetron sputtering using a 99.95% pure Ru sputtering target purchased from Angstrom Sciences, Inc. The base pressure of the sputtering chamber was pumped down to $1 \times 10^{-7}$ Torr before argon was introduced into the chamber at a flow rate of 20 sccm. The chamber pressure was set to 3 mTorr during the deposition, which was carried out at room temperature. The forward power was 100 W and the substrate-to-target distance was 14 cm. The sputtering process was terminated when 10 nm of Ru, as measured from an in situ thickness monitor (SQM-242 from Sigma), had been deposited.

2.4.2 Characterization:

Absorption and reflection measurements were performed using a Lambda 1050 UV/VIS/NIR spectrometer from Perkin Elmer equipped with an integrating sphere with a diameter of 150 mm and a center mount holder. SEM images were taken using a Hitachi S-5200 scanning electron microscope.

2.4.3 Sabatier Reaction Rate Measurements:

Gas-phase photocatalytic rate measurements were conducted in a custom-built 1.5 mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings. All samples were cleaned using the ZONE-SEM cleaning system from Hitachi for 10 minutes prior to being loaded into the reactor. For heated tests the reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller combined with a thermocouple placed in contact with the sample. The pressure inside the reactor was monitored using an Omega PX309 pressure transducer. Product gases were analyzed
with a flame ionization detector (FID) and thermal conductivity detector (TCD) installed in a SRI-8610 Gas Chromatograph (GC) with a 3’ Mole Sieve 13a and 6’ Haysep D column. The thermocouple was placed at the front face of the sample and shielded from incident light unless otherwise specified. Isotope tracing experiments were performed using $^{13}\text{CO}_2$ (99.9 atomic% Sigma Aldrich). The reactor was heated to 150 °C and purged with H$_2$ for 10 min prior to being infiltrated with CO$_2$ and H$_2$ at a H$_2$:CO$_2$ ratio of 4:1. Isotope product gases were separated using a 60 m GS-Carbonplot column and measured using an Agilent 7890A gas chromatographic mass spectrometer (GC-MS).

To measure the activation energy the reactor was purged with H$_2$ for 10 min prior to being infiltrated to a pressure of 45 psi with H$_2$ and CO$_2$ gas at a H$_2$:CO$_2$ ratio of 4:1. For tests carried out in the dark the reaction chamber was heated before purging with H$_2$ gas. For tests wherein the sample was irradiated with light the lamp was turned on once the reactor valves were closed and the temperature of the sample was recorded over the duration of the test. A typical temperature profile shows the sample heating quickly at the beginning of the test when the light is turned on. Extra precautions were taken to ensure accuracy in measuring CO$_2$ methanation rates as a function of the number of incident photons. The thermocouple was pressed firmly against the center of the back-side of the SiNW sample. The sample was pre-irradiated for 1 hour in a pure H$_2$ atmosphere at 45 psi prior to each test. The reactors were then infiltrated with CO$_2$ and H$_2$ gas. Manual valves were closed to seal the reactor from the infiltrating gases when the CO$_2$ and H$_2$ pressures had reached 3 psi and 12 psi, respectively. To be precise, the final partial pressure of CO$_2$ and H$_2$ in the reactor ranged from 3.0 to 3.2 psi and from 12.0 to 12.2 psi, respectively. This small variance in partial pressures may have
produced some deviation from the linear trend for batch reactions A through F (for example the reaction rate for batch reaction D is 6.9% less than that of E despite there being a greater incident photon flux for D). Nevertheless, despite this small variation in reactant partial pressures, the data shows a strong linear correlation with a measure of goodness-of-fit of linear regression of $r^2 = 0.90$. The incident light spectra was varied between runs using high-pass cut of filters. For each test using a different filter the intensity of the lamp was adjusted until the stabilized temperature of the sample was 93 °C. However, when the $\lambda = 715$ nm, $\lambda = 850$ nm, and $\lambda = 1110$ nm cut-off filters were used the stabilized temperature of the sample was 65 °C, 54 °C, and 39 °C, respectively; for these cases supplementary heat was supplied using the OMEGA CN16 6-Zone temperature controller until the sample reached 93 °C. The spectral output was measured using a StellarNet Inc spectrophotometer and the power of the incident irradiation was measured using a Newport 91150V calibrated reference cell and meter.

### 2.5 Results and Discussion

Black SiNWs were prepared using the metal-assisted chemical etching (MACE) technique.$^{[31]}$ Control samples were prepared on Corning Eagle XG glass and polished Si wafers, which were first cleaned in piranha solution. Subsequently, approximately 10 nm of Ru was sputtered onto the SiNW, glass and polished Si substrates to form the Ru/SiNW, Ru/Glass and Ru/Si catalysts, respectively. Scanning electron microscopy (SEM) images of the polished Si, Eagle XG glass, and cross-sectional SEM images of the SiNW with Ru sputtered onto their surfaces are shown in Figure 2.1.
Figure 2.1. SEM image of 10 nm of Ru sputtered onto (a) a polished silicon wafer, (b) a glass substrate, and (c, d) silicon nanowires. Images (a, b, d) were acquired at 250,000 magnification while the cross-sectional SEM image shown in (c) was acquired at a magnification of 10,000. (e) The absorption spectra for the polished Si, glass and SiNW supports are plotted as a function of wavelength.
The SiNWs are about 100 nm in diameter and approximately 6 µm in length. The sputtered Ru resides primarily at the top of the SiNWs and no Ru is present at the base of the SiNWs next to the Si wafer. The absorption spectra for these Ru/SiNW, Ru/glass and Ru/silicon catalysts are shown in Figure 2.1e. The absorption of the Ru/glass sample increases gradually from about 20% at λ = 300 nm to 40% at λ = 2500 nm. The absorption occurs almost entirely in the Ru as the absorption of the glass sample is low over this spectral region. The absorption of the Ru/Si sample is a bit higher than that of the Ru/glass sample, but follows a similar trend. There is also a dip in the absorption spectrum of the Ru/Si sample at the absorption edge of the Si wafer around 1100 nm. The Ru/SiNW catalysts absorbs 97% or more over the spectral region λ < 1000 nm and then drastically decreases to less than 70% at λ = 1200 nm. Beyond λ = 1200 nm the absorption of the Ru/SiNW catalyst decreases steadily to a value of ≈40% at λ = 2500 nm. The Ru/SiNW catalyst is highly absorbing compared to the Ru/glass and Ru/Si samples because, as shown in Figure 2.2, it exhibits low reflection losses over the entire solar spectrum. This minimal reflective loses originating from the black silicon nanowire is responsible for the high photomethanation rates observed. We initially tested the photoactivity of the Ru/SiNW, Ru/glass and Ru/Si catalysts at a temperature of 150 °C under solar simulated light from a Xe lamp over a duration of 6 hours. The lamp intensity was 3.2 suns and the irradiated area of each sample was 1 cm². The H₂:CO₂ gas ratio was 4:1 at a pressure of 45 psi and the results are plotted in Figure 2.3. The Sabatier reaction proceeded at a rate of 6.18×10⁻² mmolg⁻¹h⁻¹ over the Ru/glass sample in the dark and 7.52×10⁻² mmolg⁻¹h⁻¹ when irradiated with the Xe lamp. CO₂ methanation rates over the Ru/Si sample increased by 84% from 7.44 × 10⁻²
mmolg$^{-1}$h$^{-1}$ in the dark to 0.14 mmolg$^{-1}$h$^{-1}$ in the light. However, CO$_2$ methanation rates were the highest over the Ru/SiNW catalyst, proceeding at a rate of 0.51 mmolg$^{-1}$h$^{-1}$ in the dark and increasing by 94% to 0.99 mmolg$^{-1}$h$^{-1}$ in the light.

**Figure 2.2:** Reflectance spectra for catalysts comprised of ~10 nm of Ru sputtered onto glass (blue line) polished silicon (orange) and silicon nanowire (black line) supports. The reflectance spectrum from a bare polished Si wafer is also shown for comparison.

Furthermore, these methanation rates were confirmed using $^{13}$CO$_2$ isotope tracing experiments. Using isotope tracing experiments we also showed that bare SiNW without Ru were not active towards the Sabatier reaction. Having verified the photoactivity of the Ru/SiNW catalyst at 150 °C, a second set of experiments were carried out to
investigate the activity of this catalyst when exposed to solar simulated light without supplemental heating from an external source. That is, we disconnected the heater and monitored the temperature of the Ru/SiNW catalyst under the Xe lamp at an intensity of 14.5 suns. Moreover, to gain insight regarding the degree of conductive and convective cooling from the gaseous reactants we performed batch reaction tests using a H₂:CO₂ gas ratio of 4:1 at 15, 30 and 45 psi and the temperature profiles over the three hour duration of these tests are plotted in Figure 2.3b. For each run the temperature of the sample increases rapidly at the beginning of the test when the Xe lamp was turned on and then continues to rise gradually over the duration of the reaction until the lamp is switched off at the 3 h point. It is also noteworthy that the sample temperature of the reactions run at 15, 30, and 45 psi reach a maximum temperature of 125 °C, 117 °C, and 107 °C, respectively. As to be expected, raising the reactor pressure increases the amount of conductive and convective cooling thereby decreasing the maximum temperature attained by the Ru/SiNW catalyst. The CO₂ methanation rates corresponding to the reactions carried out at 15, 30, and 45 psi are plotted in Figure 2.3c. While the CO₂ methanation rates are comparable for the three different pressures, within about 20% of each other, a maximum methanation rate of 0.80 mmolg⁻¹h⁻¹ is measured at a pressure of 30 psi. It is known that the Sabatier reaction rate increases with increasing pressure of the reactant gases, however as shown in Figure 2.3b, in going from a pressure of 30 psi to 45 psi the catalyst temperature drops by about 10 °C causing a decrease in reaction rates. That is, higher concentrations of reactants at higher reactor pressures accelerates the reaction but also increases the amount of conductive and convective cooling which decreases the reaction rate.
Figure 2.3: Methanation rates over Ru-based catalysts on the SiNW, glass and polished Si supports at (a) 150 °C and 45 psi. (b) Temperature profiles recorded for batch reactions performed at 15, 30 and 45 psi and (c) corresponding methanation rates. All tests were performed at a H₂:CO₂ gas ratio of 4:1. Note that the methanation rates are normalized to the weight of the Ru catalyst.
As a consequence of these two opposing effects, the highest reaction rates are observed at an intermediate pressure of 30 psi. We also performed a set of experiments to measure the activation energy of the Ru/SiNW catalyst which was found to be 54.5 kJmol\(^{-1}\). This is in agreement with the activation energy of 54 kJmol\(^{-1}\) reported in the literature for the Sabatier reaction when carried out over Ru-based catalysts.\(^{[26]}\)

Furthermore, we also measured the effective activation energy under solar-simulated radiation. Specifically, we disconnected the heater and performed a set of batch reactions with varying light intensities in order to measure the Sabatier reaction rates. Using these photomethanation rates we then calculate an effective activation energy of 53.1 kJmol\(^{-1}\). Thus, while the Sabatier reaction rates are greater under solar-simulated radiation, the activation energy does not differ significantly whether heating via solar-simulated radiation or a resistive heating source. The fact that the activation energy is comparable, whether the Ru/SiNW catalyst is heated with solar simulated radiation or with a resistive heater, suggests that the reaction mechanism under irradiation is similar to that in the dark. However, since the reaction rates are higher under Xe lamp illumination, incident photons must cause some effect that accelerates the Sabatier reaction mechanism. To gain more insight into how the impinging photons accelerate the reaction rates we performed another set of experiments wherein the temperature was held constant while the incident photon flux impinging onto the Ru/SiNW catalyst was varied. This set of experiments included seven batch reactions all carried out at a temperature of 93 °C. Specifically, five of these seven tests, labelled A through E, were performed using high-pass cut-off filters such that for A: \(\lambda > 300\) nm, B: \(\lambda > 495\) nm, C: \(\lambda > 615\) nm, D: \(\lambda > 715\) nm, and E: \(\lambda > 850\) nm. For each batch reaction the intensity of
the Xe lamp was adjusted such that the temperature of the Ru/SiNW catalyst was always set to 93 °C. Moreover, the total number of photons with energy greater than 1.1 eV (the bandgap of the Si support) for each of these batch runs is also provided in Table 2.1.

**Table 2.1**: Total number of photons for each of the tests from A to E.

<table>
<thead>
<tr>
<th>Test</th>
<th>Wavelength ((\lambda))</th>
<th>Photon flux (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(\lambda &gt; 300) nm</td>
<td>1.3E+18</td>
</tr>
<tr>
<td>B</td>
<td>(\lambda &gt; 495) nm</td>
<td>1.4E+18</td>
</tr>
<tr>
<td>C</td>
<td>(\lambda &gt; 615) nm</td>
<td>1.7E+18</td>
</tr>
<tr>
<td>D</td>
<td>(\lambda &gt; 715) nm (HS)</td>
<td>1.1E+18</td>
</tr>
<tr>
<td>E</td>
<td>(\lambda &gt; 850) nm (HS)</td>
<td>8.1E+17</td>
</tr>
</tbody>
</table>

**Table 2.1 shows** that the total number of photons impinging onto the sample increases as the cut-off wavelength of the high-pass filter decreases. This is because the average thermalization energy provided to the Ru/SiNW sample is smaller for longer wavelength photons and thus more photons are required to heat the sample to 93 °C. However, for cases D: \(\lambda > 715\) nm, and E: \(\lambda > 850\) nm, when the Xe lamp was set to full intensity the sample reached a maximum temperature of 65 °C and 54 °C, respectively. Thus, for tests D and E, supplementary heating was supplied using the temperature controller such that the temperature of the Ru/SiNW catalyst was maintained at 93 °C for all
reactions. The two other tests performed in the set of seven experiments include one test carried out in the dark and Test F, wherein the Ru/SiNW catalyst was subjected only to sub-bandgap photons with \( \lambda > 1100 \) nm. For Test F the Ru/SiNW catalyst reached a temperature of 39 °C when subjected to the long wavelength radiation and supplementary heating was also provided in this case to increase its temperature to 93 °C.

The Sabatier reaction rate is plotted as a function of the number of incident photons with energy greater than the bandgap of Si for the seven batch reactions performed in this set of experiments in Figure 2.4. The methanation rate for the test carried out in the dark and for Test F: \( \lambda > 1100 \) nm is about \( 2 \times 10^9 \) molecules per second. This suggests that sub-band gap photons with energy less than the band-gap of silicon do not activate the Sabatier reaction photochemically. Alternatively, we propose that heat generated from sub-band gap photons absorbed in the Ru/SiNW sample activates the Sabatier reaction thermochemically, similarly to as if the heat was provided entirely from a thermal heating source. Figure 2.4 also shows that the Sabatier reaction proceeds five times faster when the Ru/SiNW sample is irradiated with photons in the spectral region 615 nm < \( \lambda < 1100 \) nm as compared to tests performed in the dark. Furthermore, when the Ru/SiNW catalyst is irradiated with photons in the near-infrared spectral range (850 nm < \( \lambda < 1100 \) nm), the reaction rate is more than twice that of the dark reaction rate. Moreover, the slope of the line in Figure 2.4 is \( 4 \times 10^{-9} \) CH\(_4\) molecules/photon. This suggests that only a very small fraction of incident photons induce photochemical activity in the Ru/SiNW catalyst. Thus, we can make the following two statements based on the results shown in Figure 2.4.
Figure 2.4. The Sabatier reaction rate is plotted as a function of the number of absorbed photons with energy greater than the bandgap of silicon for the seven batch reaction tests. The Sabatier reaction rates for the dark test as well as the test carried out under sub-bandgap irradiation (Test F) are both ≈ 0.2 molecules s\(^{-1}\)cm\(^{-2}\).

1. Photons with energy less than the band-gap of silicon absorbed in the Ru/SiNW catalyst provide thermal energy that activates the Sabatier reaction thermochemically.
2. Photons with energy greater than the band-gap of Si generate electron-hole pairs in
the Ru/SiNW. These excited charge carriers ultimately thermalize and recombine thereby producing heat that thermochemically accelerates the Sabatier reaction.

Furthermore, a small fraction of incident photons with sufficient energy to excite electron-hole pairs (EHPs) in the SiNW, on the order of 10 ppb, photochemically activate the Sabatier reaction. Here it is important to note that while the photomethanation rates are proportional to only a small fraction of incident photons, the photochemical contribution to the overall Sabatier reaction rate is significant under concentrated solar-simulated irradiation. In fact, in comparing batch reactions C and F in Figure 2.4, it is apparent that the photochemical contribution to the reaction rate over the Ru/SiNW catalyst can be as much as 5 times greater than the thermochemical contribution. Furthermore, it should be noted that the photochemical contribution to the overall photomethanation rate on the Ru/ SiNW catalyst is not observed for the Ru/glass catalyst as shown in Figure 2.5. As shown in Figure 2.5, the rates for the two tests are nearly identical, showing that the methanation reaction rates depend on the power of the incident radiation rather than the number of impinging photons. This suggests that photomethanation proceeds thermochemically rather than photochemically on the Ru/Glass sample. Moreover, similar experiments recently reported in the literature show that photomethanation reactions on Ru-based catalysts with Al₂O₃ supports are driven photothermally and do not exhibit photochemical activity. The photochemical activity over the Ru/SiNW catalysts reported herein may be attributed to the lower band-gap energy of silicon compared to other supports such as Al₂O₃ and may also be attributed to the quality of the interface between the Ru and the SiNW support formed during the vacuum-based sputtering deposition.
Figure 2.5: Photomethanation rates for the Ru/Glass catalyst under filtered irradiance from a 300W Xe lamp at a temperature of ~90°C. For Test 1 (left) the wavelength of the incident photons is 300nm or greater while for Test 2 (right) the wavelength of the incident photons is longer than 615nm.

There are a number of ways a small fraction of absorbed photons with energy greater than the bandgap of Si could photochemically enhance the Sabatier reaction rate over the Ru/SiNW catalyst. In this context, photochemical reaction mechanisms could involve localized heating or plasmon excitation at the surface of the Ru particles,\textsuperscript{33} or photogenerated EHPs could influence the electronic polarity of the Ru/SiNW catalyst in a favorable manner.\textsuperscript{34} However, the Sabatier reaction has been studied extensively in the literature\textsuperscript{35} and is known to proceed thermochemically over Ru-based catalysts at relatively low temperatures. In this context, and based on the comparable activation
energies observed, we do not expect that the Sabatier reaction mechanism over the Ru/SiNW catalysts under illumination from the Xe lamp differs substantially from the thermochemical reaction mechanism that occurs in the dark. Rather, as discussed subsequently, we propose that photogenerated EHPs in the SiNW support accelerate the Sabatier reaction by activating adsorbed hydrogen atoms. It is generally accepted that in the first step of the Sabatier reaction on Ru-based catalysts CO\(_2\) readily dissociates to form adsorbed CO and O on the surface of Ru. The rate limiting step then involves the reaction of CO with 6 H atoms adsorbed on the Ru metal surface to form CH\(_4\) and H\(_2\)O.[36–38] While the exact reaction mechanism between the adsorbed CO and H atoms is still under debate it is clear that a large number of active H atoms in close proximity to reaction sites will enhance the Sabatier reaction rate. We expect that photogenerated EHPs assist with the formation of Ru-H bonds that react with adsorbed CO to form CH\(_4\). The charge transfer is possible because the work function of Ru straddles the band gap of silicon.[39,40] The valence and conduction bands in the p-type SiNWs bend down towards the Ru metal. Thus, electrons excited into the conduction band of the SiNW will be accelerated towards the Ru metal while holes generated in the SiNW see a potential barrier at the SiNW-Ru interface. We expect that H atoms interact with photogenerated holes (h\(^+\)) to form H\(^+\) ions. These H\(^+\) ions can then interact with photogenerated electrons at the Ru surface to form Ru-H bonds that participate in the overall Sabatier reaction. This process may involve tunneling of electrons from H atoms at the Ru surface into holes photogenerated in the SiNW or migration of protons to the Ru metal surface or both.
2.6 Conclusions

In conclusion, we have shown that Ru/SiNW catalysts prepared by sputtering small amounts of Ru onto SiNWs activate the Sabatier reaction both thermochemically and photochemically under solar-simulated light. We have also shown that the photochemical effect can be induced using near-infrared photons. Specifically, at 93 °C the Sabatier reaction rate is roughly doubled when the Ru/SiNW catalyst is irradiated with photons in the spectral range (850 nm < λ < 1100 nm). The ability of the Ru/SiNW catalyst to activate the Sabatier reaction using infrared photons has promising implications for the design of tandem solar fuels reactors that utilize the ultraviolet and visible portion of the solar irradiance to split water and generate H₂, which can subsequently be used to reduce CO₂. The discovery that CO₂ can be reduced photochemically using a broad spectral range covering most of the solar spectrum is an important point to consider in designing solar fuels reactors. For example, rather than heating the entire reactor, solar radiation can be focused onto the catalyst in order to reduce the heating load and also to use available land-space more efficiently. Furthermore, considering the Sabatier reaction rates as shown in Figure 2.3 as an example, a given reaction rate can be attained at a lower temperature by photochemically driving the reaction. This ability to achieve higher reaction rates at lower temperatures may produce numerous advantages. For example, lower operating temperatures may reduce the deleterious effects of sintering, poisoning, mechanical degradation and eventual deactivation of the catalyst. In addition, one can expect to achieve much higher reaction rates by optimizing the dispersion of the Ru over the SiNW support. For instance, the sputtering process deposits the Ru only at the region
near the upper surface of the silicon nanowires and the Ru dispersion can be improved by using other deposition processes such as wet impregnation, electrodeposition or atomic layer deposition. Moreover, it is expected that improving the Ru dispersion will significantly enhance photochemically induced reaction rates because electron-hole pairs photogenerated along the length of the nanowires will have less distance to traverse and are less likely to recombine before reaching the active catalytic site at the Ru metal.

### 2.7 References


31. X. Li, P. W. Bohn, Metal-assisted chemical etching in HF/H$_2$O$_2$ produces porous silicon Appl. Phys. Lett. 2000, 77, 2572.


Chapter 3 – PhotoMethanation of CO₂ over Liquid Phase Deposited RuO₂ Nanoparticles on Silicon Nanowire Support

3.1 Statement of Contributions

Dr. Mohamad Hmadeh helped with the characterization of the samples. Dr. Paul O’Brien helped with the gas-phase testing of the catalysts and optical measurements. I carried out all other synthesis, characterization, and experiments presented in this chapter. Portions of this chapter are currently being prepared for publication.

3.2 Abstract

Sunlight-driven conversion of greenhouse gas CO₂ to value-added chemicals is of great technological importance and has the potential to ultimately provide a more sustainable alternative energy to fossil fuels. Of particular interest is gas-phase photomethanation of CO₂ using nanostructured Sabatier reaction catalysts. Here we show that the Sabatier reaction can be activated using high intensity solar simulated light over nanostructured catalysts composed of 2-4 nm RuO₂ nanocrystals grown on one-dimensional black silicon nanowire supports. Photomethanation rates as high as 8 mmol·g_{cat}⁻¹·hr⁻¹ have been achieved, more than an order of magnitude greater than the thermal reaction for the same catalyst in the dark. The high absorption strengths and low reflective losses of these high surface area black ncRuO₂/SiNW materials, across the UV-Visible and near-infrared solar spectrum are responsible for the high photomethanation rates. The use of nanostructured silicon supports could be applied to enhance the photoactivity of variety of materials.
3.3 Introduction

Today the world relies mainly on the burning of fossil fuels such as coal, oil and natural gas to satisfy the core energy needs of our civilization.\textsuperscript{[1-3]} These energy sources have huge impact on climate change as they produce greenhouse gas carbon dioxide that increase global temperatures by trapping heat leading to global warming.\textsuperscript{[4, 5]} Solar energy is understood to be the most viable alternative source of energy to replace fossil fuels because it is by far the largest exploitable natural resource, that provides more energy in one hour to the earth than all of the energy consumed by humans in an entire year.\textsuperscript{[6]} In principle, solar power can be utilized to produce synthetic fuels using carbon dioxide and water, allowing solar energy to be stored in the form of chemical bonds.\textsuperscript{[7-14]} Of the many ways of storing solar energy in the form of chemical bonds, one is by the production of CH$_4$ from CO$_2$ through the Sabatier reaction (CO$_2$ + 4H$_2$ $\rightarrow$ CH$_4$ + 2H$_2$O). The hydrogen used in this reaction can be obtained from a renewable source such as solar-powered water splitting.\textsuperscript{[15-19]} The ability to activate the Sabatier reaction by means of solar energy has been reported using a variety of catalysts that include nanostructured semiconductors,\textsuperscript{[20, 21]} metal supported semiconductor\textsuperscript{[22-24]} and metal supported insulator heteronanostructures.\textsuperscript{[25, 26]} Direct photolysis of CO$_2$/H$_2$ mixtures to CH$_4$ using UV light has also been described in the literature.\textsuperscript{[27]}

Although silicon nanowires (SiNWs) have been widely employed in the field of optoelectronics\textsuperscript{[28]}, electronics\textsuperscript{[29]} and solar cells\textsuperscript{[30]}, there are not many reports in the literature that use them as a catalyst support for solar fuels generation through processes such as Sabatier reaction. Variety of methods have been developed to
fabricate SiNWs including top-down fabrication and bottom-up synthesis techniques such as reactive ion etching,\[^{31}\] vapour-liquid-solid (VLS) growth,\[^{32}\] and metal-assisted chemical etching (MACE) of silicon.\[^{33, 34}\] The MACE technique makes use of silicon wafers and can produce large area arrays of vertically aligned and oriented single crystal silicon nanowires, known as black silicon.\[^{34, 35}\] These black SiNW arrays have broad-band and efficient solar spectral harvesting properties, traversing the near infrared, visible and ultraviolet wavelength range and because of the availability and low cost of silicon in the form of large-area wafers and tiles offers the benefit of economy of scale. In this context, black silicon is considered an ideal catalyst support material due to its small band gap of 1.1 eV, which can be tailored to absorb more than 90% of the solar irradiance. Moreover, the vertically aligned SiNW arrays have very low reflective losses throughout the solar spectral wavelength range.\[^{36, 37}\]

In Chapter 2, we showed that black silicon could be used as a photoactive support material on which nanostructured catalysts can be loaded and efficiently drive the Sabatier reaction.\[^{38}\] Specifically, a significant enhancement in photomethanation rate of gaseous CO\(_2\) in a H\(_2\) environment was observed over metallic Ru nanoparticles sputtered on SiNWs. In that study, we showed that the Sabatier reaction could be activated photochemically with a photochemical contribution to the reaction rate from photogenerated electron-hole pairs created in the SiNWs, and photothermal contribution, whereby thermal energy generated from non-radiative recombination of photogenerated electrons and holes in the SiNWs drives the Sabatier reaction. The Sabatier reaction proceeded at a rate of about 1 mmol·g\(_{\text{cat}}\)\(^{-1}\)·hr\(^{-1}\) when normalized to the weight of the Ru catalyst. In the work described in this chapter, we show that
photomethanation rates of gaseous CO\textsubscript{2} can be enhanced by the use of well-dispersed nanostructured RuO\textsubscript{2} supported on black silicon nanowires, denoted as ncRuO\textsubscript{2}/SiNW. The catalysts investigated in this study are tested under a high intensity solar simulated light in a CO\textsubscript{2}/H\textsubscript{2} environment without external heating. Wet chemical synthesis methods were used to uniformly deposit the RuO\textsubscript{2} nanoparticles over the entire length of the SiNWs in the array, as opposed to non-uniformly distributed Ru nanoparticles obtained by sputtering onto the SiNWs as reported in Chapter 2. This hybrid photocatalyst is able to drive the Sabatier reaction (CO\textsubscript{2} + 4H\textsubscript{2} → CH\textsubscript{4} + 2H\textsubscript{2}O) and produce methane at a rate as high as 8 mmol·g\textsubscript{cat}·hr\textsuperscript{-1} normalized to the weight of the RuO\textsubscript{2} under high solar simulated light with no external heating. These methanation rates are significantly higher compared to a reference sample composed of nanocrystalline RuO\textsubscript{2} deposited on a planar silicon wafer, denoted as ncRuO\textsubscript{2}/SiW. The results of this study indicate that broadband highly absorbing black nanostructures, exemplified by silicon nanowires are scientifically interesting and potentially technologically relevant support materials for nanostructured catalysts able to hydrogenate gas-phase CO\textsubscript{2} to value-added chemicals and fuels.

3.4 Experimental Procedure

3.4.1 Silicon nanowire fabrication:

Silicon nanowire substrates were made using a top-down fabrication technique known as metal-assisted chemical etching (MACE) as previously reported.\textsuperscript{33, 34} Briefly, p-type silicon wafers (University wafers, 1-100 Ω/cm) were cut into 1 inch squares and then cleaned with ethanol, acetone and de-ionized water. The wafers were further cleaned
by soaking in piranha solution \((\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1 \text{ by volume})\) for 3 hrs and then rinsed with de-ionized water. To fabricate the silicon nanowires, the cleaned wafers were immersed in 23 ml of an etching solution consisting of 5 M HF (48%HF, Sigma Aldrich) 0.02 M AgNO_3 (VWR redi-pak) and allowed to etch for 1 hr at room temperature. Following etching, the sample was removed from the solution. The silver dendrites covering the silicon nanowires were washed off with deionized water. To ensure all the silver nanoparticles and dendrites were removed the etched wafers were placed in concentrated nitric acid (18 M HNO\(_3\)) bath for 1 hour. The wafers were then washed and dried before being cut into 1 cm\(^2\) pieces.

### 3.4.2 Catalyst deposition:

The deposition of ncRuO\(_2\) on the silicon nanowires and silicon wafer were done using a wet chemical deposition technique. Each of these samples were first placed in 48% hydrogen fluoride solution for 1-2 minutes in order to remove any SiO\(_2\) on the surface and terminate the surface of these supports with hydrogen. The hydrogen-terminated samples were placed in a solution containing 30 mg of RuCl\(_2\)NO.H\(_2\)O dissolved in 40 mL of water. This solution was then placed in a water bath heated to 40-45°C and 3 to 5 drops of hydrazine was added to the solution to facilitate the reduction of ruthenium and formation of ncRuO\(_2\) on these supports.

### 3.4.3 Sabatier reaction rate measurements:

Gas-phase photocatalytic reaction rate measurements were conducted in a custom-built 12 mL stainless steel batch reactor with a fused silica view port sealed with Viton O-
rings. The pressure inside the reactor was monitored using an Omega PX309 pressure transducer. The duration of all runs was 2-3 hours. Product gases were analyzed with a flame ionization detector (FID) and thermal conductivity detector (TCD) installed in a SRI-8610 Gas Chromatograph (GC) with a 3’ Mole Sieve 13a and 6’ Haysep D column. For heated tests, the reactor temperature was controlled by an OMEGA temperature controller combined with a thermocouple placed in contact with the rear side of the sample. The reactor was heated to 150°C and purged with H₂ for twenty minutes prior to being infiltrated with CO₂ and H₂ at a H₂:CO₂ ratio of 4:1. For tests wherein the sample was irradiated with light, the lamp was turned on once the reactor valves were closed. The spectral output was measured using a StellarNet Inc spectrophotometer and the power of the incident irradiation was measured using a Spectra-Physics power meter (model 407A).

3.4.4 Characterization of the photocatalysts:

Both scanning and transition electron microscopy were used to study the morphology and structure of the samples. A Hitachi S-5200 SEM was used to study the surface topography of the samples while a Hitachi H-3300 TEM, working at an operating voltage of 300 KV was used to further characterize the samples. X-ray photoelectron spectroscopy (XPS) measurements were carried out to study the surface and the electronic structure of the samples. XPS was performed in an ultrahigh vacuum chamber with base pressure of 10⁻⁹ mTorr. The system used a Thermo Scientific K-Alpha XPS spectrometer, with an Al Kα X-ray source operating at 12 kV, 6 A and X-ray energy of 1486.7 eV. The spectra were obtained with analyzer pass energy of 50 eV.
with energy spacing of 0.1 eV. All data analysis was carried out using Thermo Scientific Avantage software.

3.5 Results and Discussion

RuO$_2$ nanoparticles were deposited on SiNWs using wet chemical synthesis methods (see experimental section for details). This allowed a uniform coating of RuO$_2$ nanoparticles to nucleate and grow on the SiNWs. Figure 3.1a shows a cross-section SEM image of a representative ncRuO$_2$/SiNW sample, which displays a uniform distribution of RuO$_2$ nanoparticles coated on the SiNWs. Figure 3.1b shows a higher magnification TEM image of an individual silicon nanowire coated with RuO$_2$ nanoparticles. To confirm the uniformity of the RuO$_2$ nanoparticle coverage on the silicon nanowires, an EDX horizontal line scan measurement was performed (Figure 3.1c) and the elemental mapping confirmed the presence of silicon, oxygen and ruthenium as represented by green, red and blue lines, respectively in Figure 3.1d. The yellow line in Figure 3.1c shows the area where the line scan was recorded. To ensure the ruthenium coverage was uniform throughout the SiNWs, a vertical EDX line scan on an individual silicon nanowire was performed (Figure 3.1e) and the presence of these three elements were again confirmed in the corresponding EDX spectrum (Figure 3.1f).

To investigate the importance of the SiNW support, we carried out a comparative study where a control sample was prepared, which consisted of RuO$_2$ nanoparticles deposited onto a silicon wafer (ncRuO$_2$/SiW). The ncRuO$_2$/SiW sample was prepared in exactly the same way as that of the ncRuO$_2$/SiNWs sample except a silicon wafer was used instead of SiNWs.
Figure 3.1. (a) Cross-sectional scanning electron microscope (SEM) images of ncRuO$_2$/SiNW, (b) TEM image of a single silicon nanowire coated with RuO$_2$ nanoparticles (c) Energy dispersive X-ray (EDX) horizontal line scan of ncRuO$_2$/SiNW hybrid films (d) Corresponding EDX spectrum of Fig 3.1c (e) Energy dispersive X-ray (EDX) vertical line scan of ncRuO$_2$/SiNW hybrid films and (f) Corresponding spectrum of Fig. 3.1e.
The RuO$_2$ nanoparticles deposited on the silicon wafer ranged from 10 - 50 nm although the average size was about 30 nm as shown in Figure 3.2.

**Figure 3.2.** (a) Top view SEM image of ncRuO$_2$/SiW sample at magnification of 30X (b) Top view SEM image of ncRuO$_2$/SiW sample at magnification of 150X.

Contrary to the ncRuO$_2$/SiW sample, the RuO$_2$ nanoparticles deposited onto the SiNWs were too small to be observed under SEM. Therefore, to investigate further the nature and the size of the RuO$_2$ nanoparticles deposited onto the SiNWs, we performed high resolution TEM imaging of the ncRuO$_2$/SiNW sample as shown in Figure 3.3, which reveals an individual silicon nanowire coated with RuO$_2$ nanoparticles under different magnifications. It can be clearly seen from Figure 3.3b and 3.3c that the RuO$_2$ nanoparticles are 2-4 nm is diameter and that two variants of lattice planes are observed. Fast Fourier Transform (FFT) analysis in Figure 3.3d, confirms the fringe spacing of 3.17 Å and 2.25 Å, which are consistent with the d-values of the (110) and (200) reflections of the rutile form of RuO$_2$. 
Figure 3.3. High-resolution TEM image of an individual SiNW coated with RuO$_2$ nanoparticles from ncRuO$_2$/SiNW sample with different magnifications (a) 30,000X (b) 150,000X (c) 600,000X (d) FFT of figure 3.1(c) showing diffracting lattice planes of RuO$_2$.

The photocatalytic testing experiments were conducted in a custom-designed stainless steel batch reactor with a quartz window (see experimental section for details). During the test, a 1:4 ratio of $^{13}$CO$_2$ and H$_2$ gas was used as reactant gases and the reactor
was pressurized to a total of 30 psi. The samples were then illuminated with a 300 W Xe lamp. The dimensions of the test samples used were 1 cm by 1 cm. We first measured the photocatalytic activity of the ncRuO$_2$/SiNW sample under solar simulated light concentrated to an intensity of ~24 suns (24 kW/cm$^2$), without external heating. We compared the Sabatier reaction rate obtained to that of the ncRuO$_2$/SiW sample under the same testing conditions. The results are plotted in green in Figure 3.4a, which shows the photomethanation rates of both the ncRuO$_2$/SiNW and ncRuO$_2$/SiW samples (See green bars in Figure 3.4a). While the rates under illumination for the ncRuO$_2$/SiNW sample were as high as 8 mmol·g$_{\text{cat}}$·hr$^{-1}$, the rates under the same conditions for the ncRuO$_2$/SiW sample were only 0.4 mmol·g$_{\text{cat}}$·hr$^{-1}$, about twenty times lower. Because RuO$_2$ is the active catalyst, these rates are normalized to the weight of the RuO$_2$ nanoparticles. This increased methanation rate for the ncRuO$_2$/SiNW can best be attributed to the superior light harvesting properties of the silicon nanowires compared to the silicon wafer. Moreover, the smaller RuO$_2$ nanoparticles are very well dispersion onto the silicon nanowires increasing the surface area of the photocatalyst and providing more catalytic sites for the Sabatier reaction.

It is very important to ensure that the CH$_4$ sampled from the reactor to the GC comes from the reactant gases and not from adventitious carbon sources. To this end, we performed isotope-tracing experiment where we used $^{13}$C-labeled CO$_2$ as a reactant gas. This gave $^{13}$CH$_4$ products, which confirmed that the $^{13}$CH$_4$ originated from $^{13}$CO$_2$ rather than carbonaceous contaminants. This is displayed in Figure 3.4b, which shows the ion mass 17 peak of the methane for the two samples. Moreover, we monitored the temperature of both catalysts during the testing and the temperature profiles of both
samples are plotted as shown in **Figure 3.4c** and **Figure 3.4d** for ncRuO$_2$/SiW and ncRuO$_2$/SiNW respectively.

![Graphs and figures]

**Figure 3.4.** (a) $^{13}$CH$_4$ production rate of ncRuO$_2$/SiNW and ncRuO$_2$/SiW hybrid photocatalysts. The green bars correspond to samples under high intensity Xe lamp illumination (~ 24 suns) without external heating while the black bars correspond to experiments done in the dark at 150 °C, (b) the ion mass 17 peak corresponding to $^{13}$CH$_4$ for the methanation tests of ncRuO$_2$/SiNW (black) and ncRuO$_2$/SiW (red) under illumination from Xe lamp at 24 suns intensity, (c) Temperature profile for ncRuO$_2$/SiW under 24 suns intensity, (d) Temperature profile recorded for ncRuO$_2$/SiNW under 24 suns light intensity.

It can be seen from these results that once the lamp is turned on, the temperature rapidly rises and levels off throughout the testing time until the lamp is turned off when
the reaction is complete. Under the same light intensity, the ncRuO$_2$/SiNW was able to reach temperatures as high as 200 °C while the ncRuO$_2$/SiW could only reach a temperature of 150 °C. To explore the importance of light energy impinging on the samples during the photocatalytic measurements, we measured the rate of methane formation of the two samples in the dark at 150 °C using resistive heating (see black bars in Figure 3.4a) and compared it to the results from the illumination experiments. Interestingly, while the methanation rates of the ncRuO$_2$/SiW remained almost the same both under solar simulated light and in the dark at 150 °C, the methanation rate of ncRuO$_2$/SiNW in the dark at 150 °C was only 0.3 mmol·g$_{\text{cat}}^{-1}$·hr$^{-1}$ compared to 8 mmol·g$_{\text{cat}}^{-1}$·hr$^{-1}$ under solar simulated light. This result indicates that light has a significant impact on enhancing the methanation rate of the ncRuO$_2$/SiNW sample.

To obtain an insight into the enhanced photomethanation rates by the ncRuO$_2$/SiNW sample under illumination with a Xe lamp, we performed a series of five tests with different illuminating conditions and light intensities. In particular, we subjected the test sample to a light intensity of 17, 19, 20.5, 22.5 and 24.5 suns with the corresponding photomethanation rates plotted in Figure 3.5a. The reaction rates increased with increasing photon flux from 0.6 mmol·g$_{\text{cat}}^{-1}$·hr$^{-1}$ at 17 suns to 8 mmol·g$_{\text{cat}}^{-1}$·hr$^{-1}$ when the sample was illuminated with 24.5 suns. This increasing photomethanation rate trend closely correlated with the CH$_4$ mass spectrum ion peak as shown in Figure 3.5b (colour coded with the red corresponding to 24 suns and blue corresponding to 17 suns). Figure 3.5c shows the temperature profiles of the five tests performed. The highest temperature of about 200 °C was recorded for the sample under 24.5 suns and the lowest temperature of around 135 °C was recorded for the sample under 17 suns.
Figure 3.5. (a) Photomethanation rates of RuO$_2$NP/SiNW sample under different light intensities, (b) the ion mass 17 peak corresponding to $^{13}$CH$_4$ for the methanation tests of RuO$_2$NP/SiNW under different light intensities, (c) temperature profiles obtained during the methanation tests of the RuO$_2$NP/SiNW sample under different light intensities.
Interestingly, the sample irradiated with 19 suns was able to reach a temperature of \(\sim 145 \, ^{\circ}\text{C}\). The rate of methane formation of this sample is about 1.1 mmol·g\(_{\text{cat}}\)·hr\(^{-1}\), about 4 times the rate of methane formation when the same sample is heated in the dark at 150 \(^{\circ}\text{C}\) indicating the superior methanation activity in the light compared to thermal heating in the dark. In the literature, ruthenium-based materials which are used as Sabatier reaction catalysts are mainly supported on TiO\(_2\).[22-24] Although the enhanced reaction rate was first attributed towards the photo-excitation of the TiO\(_2\) support, it later became clear that this enhancement was rather associated with localized photoactive species on the ruthenium surface, an effect modified by the nature of the TiO\(_2\) support.[23] Because TiO\(_2\) absorbs mainly in the UV portion of the solar spectrum, other photoactive supports that are capable of absorbing visible and near infrared photons have been explored. For example, we have shown in Chapter 2 the importance of photoexcitation of small band-gap supports such as black silicon towards the photomethanation of CO\(_2\). In particular, we have shown that black silicon substrates enhance the photomethanation rates by increasing the absorption of the solar spectrum through trapping light due to its small band gap of 1.1 eV and its inherent minimum reflectance losses. We have also shown that the Sabatier reaction can be enhanced both photochemically and photothermally when ruthenium nanoparticles are sputtered on these black silicon nanowire supports.[38] In this context, we believe that the Sabatier reaction is enhanced by ncRuO\(_2\)/SiNW in a similar manner, mainly by the enhanced absorption of the silicon nanowires. RuO\(_2\) is a metal oxide with metallic electronic properties arising from the partially filled Ru 4d states. It has a slightly higher effective work function of \(\sim 5.1\) eV compared to \(\sim 4.8\) eV of Ru, which is why it is used as a gate
electrode in metal oxide semiconductor field effect transistors.\textsuperscript{[39-43]} This high work function allows the Fermi energy of RuO\textsubscript{2}, to be aligned with the Fermi level of the p-type silicon nanowire support material, which is about 5 eV. This may have the effect of decreasing the band bending thereby allowing photogenerated e-h pairs to be transferred more easily from SiNW$\rightarrow$ RuO\textsubscript{2}NP, thereby facilitating the effective hydrogenation of carbon dioxide.\textsuperscript{[43, 44]} We believe that under illumination with solar simulated light, photo-generated electron-hole pairs are created in the SiNW support. These photogenerated electron-hole pairs are transferred to the surface of the RuO\textsubscript{2} nanoparticles, which interact with the adsorbed reactants on its surface. According to the literature, the first step in the hydrogenation of CO\textsubscript{2} in ruthenium-based materials is the adsorption of CO\textsubscript{2} onto the surface active ruthenium site, which is followed by the dissociation of CO\textsubscript{2} into CO and O.\textsuperscript{[45, 46]} This is followed by the hydrogenation of CO, which is believed to be the rate-limiting step in the overall Sabatier reaction. Therefore, the enhanced methanation rate is believed to have as its origin, the electron-hole pairs generated in the silicon support that are transferred to the RuO\textsubscript{2} to assist in the hydrogenation process.

Although there have been many studies reported on the hydrogenation of carbon dioxide on metallic ruthenium-supported photocatalysts, there are only a few reports that utilize supported RuO\textsubscript{2}. Even when supported RuO\textsubscript{2} is employed for hydrogenation of carbon dioxide, the nature of the RuO\textsubscript{2} under the Sabatier reaction conditions is highly debated. While some believe that the RuO\textsubscript{2} does not undergo significant change in the hydrogen environment under relatively low temperatures, others believe that the RuO\textsubscript{2} is greatly reduced under such reaction conditions. For example, Sassoye \textit{et al}
reported the methanation of carbon dioxide over RuO$_2$/TiO$_2$\cite{47}. However, it was subsequently proposed that the RuO$_2$ is reduced to metallic Ru under the Sabatier reaction conditions.\cite{48} While the reduction of RuO$_2$ is conceivable, XPS measurement of the ncRuO$_2$/SiNW sample before and after the test revealed that there was no change in the oxidation state of the RuO$_2$ as shown in Figure 3.6.

![Figure 3.6](image)

**Figure 3.6.** XPS survey spectrum of RuO$_2$/SiNW showing (a) survey spectrum, (b) Ru3d peak, (c) Si2p and (d) O1s.

By inspection of the survey XPS spectrum shown in Figure 3.6a, it can be seen that the main elements present are ruthenium, oxygen and silicon. Figure 3.6b shows the Ru 3d core level spectrum of RuO$_2$ showing Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$ spin-orbit component ionization potentials separated by the expected 4.2 eV. The binding energy of the Ru 3d$_{5/2}$ component is at 281 eV in full agreement with the literature values for RuO$_2$.\cite{49}
The O1s spectrum in Figure 3.6d has characteristic peaks due to hydroxyl and adsorbed water, indicating that the RuO₂ may be hydrated possibly by the water product of the Sabatier reaction. The Ru 3d peaks of the RuO₂ are also broader compared to Ru metal providing additional evidence that our material is RuO₂. Figure 3.6c shows the Si 2p peak consisting of both elemental silicon and silicon dioxide. This is expected because the silicon nanowires are partly oxidized. Although, the XPS measurements were not performed in situ under the Sabatier reaction conditions, the sample was immediately transferred from the reactor to the XPS machine before any significant change could occur on the sample.

### 3.6 Conclusions

This study demonstrates that a bottom-up solution phase synthetic technique can be used to nucleate and grow a uniform distribution of very small RuO₂ nanocrystals, of about 2 - 4 nm in diameter, on the surface of a vertically aligned SiNW array, to form a hybrid catalyst denoted RuO₂NP/SiNW. The photomethanation of gaseous CO₂ / H₂ under different intensity solar irradiation and ambient conditions on this catalyst is found to be significantly enhanced compared to the thermally driven reaction on the same catalyst in the dark. With this hybrid photocatalyst, we were able to achieve a photomethanation rate of 8 mmol·g_{cat}⁻¹·hr⁻¹ normalized to the weight of the RuO₂ nanoparticles. The enhanced photomethanation rate is attributed to the enhanced formation of Ru-H and Ru-CO surface bonds by photogenerated electron-hole pairs. The high absorption strength and low reflective losses across the entire near infrared to visible to ultraviolet solar spectral wavelength range, together with the large surface
area of the black silicon nanowire support significantly increase the photomethanation rate of ncRuO₂/SiNW compared to a ncRuO₂/SiW control sample. Although, nanostructured forms of silicon are not traditionally used as a support material for methanation catalysts, the ability to realize such a high methanation rate under ambient conditions that is competitive with the state-of-the-art catalysts indicates its significance as an important material to drive the Sabatier reaction.

### 3.7 References


22. K. R. Thampi, J. Kiwi, M. Graetzel, Methanation and photo-methanation of carbon

Ye, Photothermal Conversion of CO$_2$ into CH$_4$ with H$_2$ over Group VIII
2014, 126, 11662.

24. F. Sastre, A. V. Puga, L. Liu, A. Corma, H. García, Complete photocatalytic
reduction of CO$_2$ to methane by H$_2$ under solar light irradiation, *J. Am. Chem. Soc.*
2014, 136, 6798.

25. F. Sastre, A. Corma, H. García, 185 nm Photoreduction of CO$_2$ to Methane by
14137.

26. B. Tian, X. Zheng, T. J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, C. M. Lieber,
Coaxial silicon nanowires as solar cells and nanoelectronic power sources, *Nature*
2007, 449, 885.

nanowire vertical surround-gate field-effect transistor, *Small* 2006, 2, 1, 85.

28. K. Peng, J. Jie, W. Zhang, S. T. Lee, Silicon nanowires for rechargeable lithium-ion

29. Y. Q. Fu, A. Colli, A. Fasoli, J. K. Luo, A. J. Flewitt, A. C. Ferrari, W. I. Milne, Deep
reactive ion etching as a tool for nanostructure fabrication, *J. Vac. Sci. Technol. B*
2009, 27, 1520.

30. S. Christiansen, R. Schneider, R. Scholz, U. Gösele, Th. Stelzner, G. Andrä, E.
Wendler, W. Wesch, Vapor-liquid-solid growth of silicon nanowires by chemical

31. C. Chartier, C. Lévy-Clément, S. Bastide, Metal-assisted chemical etching of silicon

32. Z. Huang, N. Geyer, P. Werner, J. D. Boor, U. Gosele, Metal-Assisted Chemical


34. Yang, J. B. Li, Q. H. Gong, J. H. Teng, M. H. Hong, High aspect ratio SiNW arrays
with Ag nanoparticles decoration for strong SERS detection, *Nanotechnology* 2014,
25, 465707.


Chapter 4 - Highly Efficient Ambient Temperature CO₂ Photomethanation Catalyzed by Nanostructured RuO₂ on a Silicon Photonic Crystal Support

4.1 Statement of Contributions

Dr. Mohamad Hmadeh helped with the characterization of the samples. Dr. Paul O'Brien and Amit Sandhel helped with the gas-phase testing of the catalysts and optical measurements. Dr. Kulbir K. Ghuman carried out the DFT calculations. I carried out all other synthesis, characterization, and experiments presented in this chapter. Portions of this chapter are currently under review for publication.

4.2 Abstract

Sunlight-driven catalytic hydrogenation of CO₂ is an important reaction that generates useful chemicals and fuels and if operated at industrial scales can decrease greenhouse gas CO₂ emissions into the atmosphere. In this work, we report the photomethanation of CO₂ over highly dispersed nanostructured RuO₂ catalysts on three-dimensional silicon photonic crystal supports, achieving impressive conversion rates as high as 4.4 mmol·g⁻¹·hr⁻¹ at ambient temperatures under high intensity solar simulated irradiation. This performance is an order of magnitude greater than photomethanation rates achieved over control samples made of nanostructured RuO₂ on silicon wafers. The high absorption and unique light harvesting properties of the silicon photonic crystal across the entire solar spectral wavelength range coupled with
its large surface area are proposed to be responsible for the high methanation rates of the RuO$_2$ photocatalyst. A DFT study on the reaction of CO$_2$ with H$_2$ revealed that H$_2$ splits on the surface of the RuO$_2$ to form hydroxyl groups that participate in the overall photomethanation process.

4.3 Introduction

Carbon dioxide utilization as a chemical feedstock to produce value-added chemicals and fuels is a promising endeavour that has the potential to provide sustainable energy security and address several global challenges including climate change and environmental protection.[1-11] Among the different ways of utilizing CO$_2$, gas-phase CO$_2$ reduction has gained huge interest due to its technological and economic feasibility for large-scale fuel production.[12-14] In the literature, several catalysts have been studied for the reduction of CO$_2$ to produce various chemical feed-stocks and fuels.[15-18] One of the most desirable fuels obtained from the reduction of CO$_2$ is methane, which is obtained through the Sabatier reaction (CO$_2$ + 4H$_2$ → CH$_4$ + 2H$_2$O), an important reaction that generates CH$_4$ used both for domestic and industrial applications.[19,20] The most commonly used catalysts to drive the Sabatier reaction are based on ruthenium[21-24] and nickel,[25-28] although several other catalysts have also been investigated.[29-32] Traditionally, the Sabatier reaction had been thermally driven until Thampi et al first reported that it can also be activated photochemically with solar simulated irradiation using Ru/RuO$_x$ loaded on TiO$_2$.[33] A more thorough investigation of this reaction demonstrated that it was catalyzed photothermally.[34] Thereafter, several different photocatalysts have been reported to be active for the photomethanation of CO$_2$. For
example, complete photocatalytic reduction of CO$_2$ to CH$_4$ by H$_2$ under solar-simulated irradiation was achieved with a Ni/silica-alumina photocatalyst.$^{[35]}$ In Chapter 2, we reported gas-phase photomethanation of CO$_2$ over Ru sputtered on vertically aligned silicon nanowires (black silicon), which produced CH$_4$ at rates as high as 1 mmol·g$_{cat}^{-1}$·hr$^{-1}$ under solar simulated light using visible and near infrared photons.$^{[36]}$ These rates were further enhanced when highly dispersed RuO$_2$ nanoparticles were supported on the black silicon nanowires as reported in Chapter 3. The high photomethanation rate was ascribed to the enhanced light absorption provided by the black silicon support. Subsequently, we also developed a hybrid photocatalyst consisting of defect-engineered indium oxide nanostructures coated on the black silicon support that efficiently converts CO$_2$ into CO under simulated solar irradiation and found that superior light harvesting properties coupled with minimal light reflectance losses exhibited by the black silicon support were instrumental in enhancing the CO$_2$ reduction rates.$^{[37]}$ Additionally, we showed that the hybrid photocatalyst was able to utilize both light (photochemically) and heat (photothermally) to drive the photoreduction of CO$_2$ to CO. These studies highlight the importance of the support material, which is critical for providing better catalyst dispersion and stability to sintering, and enhanced light absorption properties. It is therefore very important for sunlight-driven CO$_2$ reduction reactions to rationally select and design a support material that is able to absorb most of the solar spectrum from the UV to the near infrared region. Silicon is the natural choice, with an electronic band gap of 1.1 eV, enabling absorption of over 80% of the solar spectrum.
In this study, we expand and enrich upon this strategy by exploring for the first time the gas-phase photomethanation of CO$_2$ using a silicon inverse opal as a photonic crystal support for nanostructured RuO$_2$ driven by high intensity simulated solar irradiation from a 300W Xe lamp. Inverse opal photonic crystals have recently gained huge interest in photocatalytic applications due to their superior light harvesting properties by controlling the way light propagates through these materials. For example, Chen et al showed enhanced photoactivity of inverse opal TiO$_2$ in the photo-oxidation of methylene blue.$^{[38]}$ This enhanced photoactivity was due to slow photons with energies close to the electronic band gap of TiO$_2$, which increased the path length of light allowing it to be absorbed more efficiently. Moreover, Ramiro-Monzano et al have shown that dye-sensitized photoelectrochemical solar cells comprising of a photonic sponge architecture could be used to efficiently trap light and harvest photons in the near UV and visible region of the solar spectrum.$^{[39]}$ In addition, Li et al have demonstrated enhanced photocatalytic activity of inverse opal photonic crystal TiO$_2$ whereby the stop band and multiple scattering effects both contributed to greatly improve the light harvesting properties of the material leading to its superior photocatalytic activities.$^{[40]}$ Several other studies have also reported enhanced photocatalysis by inverse opal materials enabled by the slow photon effect.$^{[41-46]}$

Inspired by the photocatalytic attributes of inverse opal photonic crystal supports, we employed a novel solution phase synthetic route to nucleate and grow RuO$_2$ nanocrystals on a silicon inverse opal photonic crystal, which we denote as ncRuO$_2/i$-Si-O, and examined its catalytic activity towards the photomethanation of CO$_2$. Notably we achieved an impressive photomethanation rate as high as 4.4 mmol·g$_{\text{cat}}$·hr$^{-1}$ under
solar simulated light focused to an intensity of ~22 kW/m² (~22 suns) with no external heating. This rate represents a significant improvement over the RuO₂ nanocrystals deposited on planar silicon wafers (ncRuO₂/SiW) and tested under the same reaction conditions. Furthermore, isotope tracing experiments using ¹³CO₂ were performed to confirm the CH₄ products did not originate from adventitious carbon sources. The bare silicon inverse opal photonic crystal support is not active towards the methanation of CO₂ in the light or dark. Moreover, we performed preliminary DFT calculations to understand the interaction of the reactant CO₂ and H₂ molecules with the surface of the catalyst and gain more atomistic insight into the overall methanation reaction mechanism.

4.4 Experimental Procedure

4.4.1 Fabrication of inverse silicon opal photonic crystal support

SiO₂ spheres with a diameter of ~ 460 nm were first synthesized using a modified Stöber process and subsequently crystallized as SiO₂ opaline films using the evaporation-induced self-assembly (EISA) method on a polished silicon wafer with a surface area of approximately 1cm x 1cm. The i-Si-o film was fabricated by infiltrating the interstitial voids in these SiO₂ films with amorphous silicon using a home-built dynamic chemical vapor deposition (CVD) apparatus and subsequently removing the SiO₂ template by etching in a solution containing HF. The attained i-Si-o films were then crystallized by subjecting them to an annealing treatment at a temperature of 630 °C for 5 hours.
4.4.2 Deposition of nanocrystalline RuO$_2$ on inverse silicon opal photonic crystal support

The deposition of ncRuO$_2$ onto the silicon inverse opal and the silicon wafer was done by wet chemical deposition. Each of these samples were first placed in 48% hydrogen fluoride solution for 1-2 minutes in order to remove any SiO$_2$ on the surface and to terminate the surface of these supports with hydrogen. The hydrogen-terminated silicon samples were placed in a solution containing 30mg of RuCl$_2$NO.H$_2$O dissolved in 40 mL of water. This solution was then placed in a water bath heated to 40-45°C and 3 to 5 drops of hydrazine was added to the solution to facilitate the reduction of ruthenium and formation of Ru NPs, which was later oxidized to RuO$_2$ NPs by heating it in an oven heated to 400 °C for 2 hours.

4.4.3 Gas Phase Sabatier reaction rate measurements

Gas-phase photocatalytic rate measurements were conducted in a custom-built 12 mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings. The sample dimensions used for the photocatalytic rate measurements were 1 cm by 1 cm. The pressure inside the reactor was monitored using an Omega PX309 pressure transducer. The duration of all runs was 2 hours. Product gases were analyzed with a flame ionization detector (FID) and thermal conductivity detector (TCD) installed in a SRI-8610 Gas Chromatograph (GC) with a 3' Mole Sieve 13a and 6’ Haysep D column. For heated tests, the reactor temperature was controlled by an OMEGA temperature controller combined with a thermocouple placed in contact with the rear side of the sample. The reactor was heated to 150 °C and purged with H$_2$ for twenty minutes prior
to being infiltrated with CO$_2$ and H$_2$ at a H$_2$:CO$_2$ ratio of 4:1. For tests wherein the sample was irradiated with light, the lamp was turned on once the reactor valves were closed. The spectral output was measured using a StellarNet Inc spectrophotometer and the power of the incident irradiation was measured using a Spectra-Physics power meter (model 407A).

4.4.4 Characterization of the photocatalysts

Scanning electron microscopy (SEM) was used to study the morphology and structure of the samples. A Hitachi S-5200 SEM was used to study the surface topography of the samples. X-ray photoelectron spectroscopy (XPS) measurements were carried out to study the surface and the electronic properties of the RuO$_2$ nanocrystals. XPS was performed in an ultrahigh vacuum chamber with base pressure of 10$^{-9}$ mTorr. The system used a Thermo Scientific K-Alpha XPS spectrometer, with an Al K$_\alpha$ X-ray source operating at 12 kV, 6 A and X-ray energy of 1486.7 eV. The spectra were obtained with analyzer pass energy of 50 eV with energy spacing of 0.1 eV. All data analysis was carried out using Thermo Scientific Avantage software.

4.4.5 Computational details

The plane wave DFT implemented in Quantum ESPRESSO code$^{[69]}$ is used. The plane-wave-pseudopotential approach, together with the Perdew-Burke-Ernzerhof (PBE)$^{[70,71]}$ exchange-correlation functional, and Vanderbilt ultrasoft pseudopotentials$^{[72]}$ was utilized throughout. All calculations are non-spin polarized. The kinetic energy cut-offs of 40 and 160 Ry were used for the smooth part of the electronic wave functions and
augmented electron density, respectively. The self-consistent field convergence criterion was set to $1 \times 10^{-6}$ Ry per Bohr and the structures were relaxed using a conjugate gradient minimization algorithm until the magnitude of residual Hellman–Feynman force on each atom was less than $10^{-3}$ Ry per Bohr for surfaces. Brillouin zone integrations were performed using a Monkhorst-Pack\cite{73} grid of 4X4X1 k points.

4.5 Results and Discussion

In this study, we used a 3D photonic crystal in the form of an inverted silicon opal (i-Si-o) as a substrate for RuO$_2$ nanocrystals and investigated the gas-phase photomethanation of CO$_2$ under solar simulated light. The i-Si-o sample was fabricated by infiltrating the interstitial voids of silica spheres with silicon using dynamic chemical vapor deposition. The silica spheres were later removed by etching them in a solution containing HF/H$_2$O. This procedure is described in our previous work.\cite{47} The RuO$_2$ nanocrystals were then deposited on the i–Si-o support using a wet chemical deposition technique to form ncRuO$_2$/i-Si-o (see experimental section for details). SEM images of the resulting ncRuO$_2$/i-Si-o catalysts are shown in Figure 4.1, which show the RuO$_2$ nanocrystals are well dispersed on the i-Si-o structure thus providing a large surface area and stability towards sintering. Furthermore, the porous structure of the i-Si-o facilitates a high degree of contact between the nanocrystalline catalysts and the reactant gases CO$_2$ and H$_2$. The average diameter and mass of the RuO$_2$ nanocrystals dispersed on the i-Si-o supports were determined to be 24 nm and 318 µg/cm$^2$, respectively (Figure 4.2a). As a reference sample, we deposited RuO$_2$ nanocrystals on a silicon wafer, ncRuO$_2$/SiW (c.f. Figure 4.2b). The average size of the RuO$_2$ nanocrystals on the silicon wafer is ~45 nm, almost twice the size but nearly the same.
mass as the RuO$_2$ loaded on the inverse photonic crystal. Fortunately, the reaction conditions can be adjusted and the particle sizes can be tuned. As a result, another ncRuO$_2$/SiW sample with an average particle size of ~20 nm similar to the one deposited on the photonic crystal was prepared as shown in Figure 4.2c and 4.2d but only a small amount of RuO$_2$ nanoparticles could be deposited. Hence, we used the ~20 nm RuO$_2$/SiW sample shown in Figure 4.2b as a reference.

**Figure 4.1.** SEM secondary electron images of ncRuO$_2$/i-Si-o sample under different magnifications (a) 20X, (b) 70X, (c) 150X and (d) 500X.

In addition, we used XPS measurements to determine the chemical state of the ruthenium deposited onto the i-Si-o support. This data is presented in Figure 4.3 and
shows the survey spectrum and the core-levels for Ru 3d, Ru 3p and Si 2p of the ncRuO$_2$/i-Si-o sample before and after the photomethanation reaction.

Figure 4.2. (a) Cross-sectional SEM image of the ncRuO$_2$/i-Si-o sample, which was used to determine the average diameter of the RuO$_2$ nanocrystals and to estimate the weight of RuO$_2$, loaded onto the i-Si-o support, (b) SEM image of ncRuO$_2$/SiW sample where similar amount (weight) of RuO$_2$ nanocrystals, as that of the ncRuO$_2$/i-Si-o sample, were deposited, (c, d) SEM image of ncRuO$_2$/SiW sample where similar sizes of RuO$_2$ nanocrystals, as that of the ncRuO$_2$/i-Si-o sample, were deposited.
The binding energy of the Ru 3d\textsubscript{5/2} and Ru 3d\textsubscript{3/2} spin-orbit components are at 280.7 eV and at 284.9 eV respectively, confirming the existence of Ru(IV) in RuO\textsubscript{2} nanocrystals.\cite{48} Moreover, XPS measurements performed before and after the testing revealed that the chemical state of ruthenium of the RuO\textsubscript{2} nanocrystals did not change during the Sabatier reaction (Figure 4.3).

![Image of XPS spectra](image)

**Figure 4.3.** Comparison of XPS spectra of the ncRuO\textsubscript{2}/-Si-o sample measured before (black) and after (red) performing the photomethanation rate tests (a) survey spectrum (b) Ru3d core-levels (c) Ru3p core-levels (d) Si2p core-levels.\cite{74}

Because of the interference from the C 1s peak that appears close to Ru 3d, it is generally a good idea to use other photoemission peaks to further confirm the chemical nature of the deposited RuO\textsubscript{2} nanocrystals. To this end, we have measured Ru 3p core-
levels of the ncRuO$_2$/i-Si-o sample (**Figure 4.3c**). This gives the binding energy of the 3p$_{3/2}$ peak as 463.8 eV, which is assigned to the Ru(IV) of RuO$_2$.\[^{[49]}\] **Figure 4.3d** displays the Si 2p spectrum of the ncRuO$_2$/i-Si-o sample, which shows that the surface of the silicon inverse opal is oxidized as SiO$_2$. Similarly, XPS measurements of ncRuO$_2$/SiW sample revealed the formation of the RuO$_2$ nanocrystals on the silicon wafer. **Figure 4.4** depicts Ru 3d and 3p core-levels of ncRuO$_2$/SiW sample, which are consistent with the formation of RuO$_2$.

**Figure 4.4.** XPS core-level spectra of ncRuO$_2$/SiW sample (a) Ru3d core-levels (b) Ru3p core-levels.\[^{[74]}\]

After characterization of the samples with XPS, their photocatalytic activities were measured by evaluating the gas-phase photomethanation reaction between CO$_2$ and H$_2$. The samples used in the photocatalytic testing were cut into 1x1 cm squares. The photocatalytic measurements were performed using a custom-built batch reactor made of stainless steel with a quartz window. The reactor was filled with a stoichiometric mixture of $^{13}$CO$_2$ and H$_2$ (1:4) to a pressure of 2 atm. The Sabatier reaction rate of the ncRuO$_2$/i-Si-o sample was measured and compared to that of the reference sample.
ncRuO$_2$/SiW under solar simulated light from a 300 W Xe lamp, focused to an intensity of ~22 kW/m$^{2}$ (~22 suns) without any external heating. For comparison, the Sabatier reaction rates of these two samples in the dark with external heating at 150 °C were also measured and are plotted in Figure 4.5.

![Figure 4.5](image)

**Figure 4.5.** $^{13}$CH$_4$ production rate of ncRuO$_2$/i-Si-o and ncRuO$_2$/SiW hybrid samples. The samples that are tested under high intensity Xe lamp illumination (22 kW/m$^{2}$) without external heating are shown in purple color while the black bars correspond to experiments done in the dark at 150 °C.

The purple bars represent tests performed using high intensity Xe lamp illumination whereas the black bars represent the tests performed at 150 °C in the dark. Clearly, the
methanation rate over the ncRuO$_2$/Si-o under illumination is significantly higher than that performed in the dark at 150 °C. The photomethanation rate of the ncRuO$_2$/Si-o sample under illumination is 4.4 mmol·g$_{cat}$·hr$^{-1}$ compared to 0.2 mmol·g$_{cat}$·hr$^{-1}$ in the dark, which is 22 times higher. However, the Sabatier reaction proceeds at a similar rate over the ncRuO$_2$/SiW sample both in the dark (0.2 mmol·g$_{cat}$·hr$^{-1}$) and under full illumination (0.4 mmol·g$_{cat}$·hr$^{-1}$). Moreover, comparing the methanation rates of both samples under illumination, we find that the methanation rate of the ncRuO$_2$/Si-o sample (4.4 mmol·g$_{cat}$·hr$^{-1}$) is significantly higher than that of the ncRuO$_2$/SiW sample (0.4 mmol·g$_{cat}$·hr$^{-1}$) by a factor of 11. Because RuO$_2$ is the active catalyst, the photomethanation rates are normalized to the weight of the RuO$_2$ nanocrystals. More importantly, the Sabatier reaction rates did not decrease after the ncRuO$_2$/Si-o sample had been tested for 30 h (Figure 4.6) indicating that the catalyst did not deactivate with time.

Key factors that could contribute to the enhanced photomethanation rates over the ncRuO$_2$/Si-o sample were investigated. Firstly, we considered whether the enhanced methanation rate of the ncRuO$_2$/Si-o sample is due to the relatively smaller size of the RuO$_2$ nanocrystals on the silicon photonic crystal compared to the ones deposited on the silicon wafer (Figure 4.2). To this end, the RuO$_2$ deposition technique of the ncRuO$_2$/SiW sample was tailored so that similar sizes of RuO$_2$ nanocrystals as that of ncRuO$_2$/Si-o sample were deposited on the silicon wafer. However, the photomethanation rates ncRuO$_2$/SiW sample remained very similar to that presented in Figure 4.5 indicating that the sizes of RuO$_2$ nanocrystals of the ncRuO$_2$/SiW samples
we tested (in the range of 10-50 nm) did not have significant impact on the rate of photomethanation.

![Graph showing mass 17 peak for first and final tests.](image)

**Figure 4.6.** The ion mass 17 peak for the first and final photomethanation tests carried out over the ncRuO$_2$/i-Si-o sample had been subjected to testing for over 30 h. The peaks, which were acquired using an Agilent 7890A gas chromatographic mass spectrometer, confirm that the $^{13}$CH$_4$ product originated from $^{13}$CO$_2$ rather than adventitious carbon sources.

Secondly, there is a large difference in surface area between the two samples. While the silicon wafer is flat, the inverse opal photonic crystal with large voids provides a large surface area for RuO$_2$ nanocrystal deposition and could be the key to the observed enhanced photomethanation rates in contrast to a low surface area silicon wafer. Moreover, the fact that the rate of methanation under high intensity illumination is an order of magnitude higher in the ncRuO$_2$/i-Si-o sample compared to the ncRuO$_2$/SiW
sample is an inherent optical property of the silicon inverse opal photonic crystal. It is well known in the literature that 3D silicon photonic crystals can be used to increase light absorption over certain spectral regions by scattering and increasing the path length of light that propagates through the material. The superior optical absorption properties of the i-Si-o resulting from light scattering are expected to play an important role in absorbing the majority of the incident photons in the UV-visible and near infrared region of the solar spectrum compared to the silicon wafer, which reflects most of the incident photons in these regions of the solar spectrum. To this end, the diffuse reflectance and absorption of both samples were measured and the result is shown in Figure 4.7.

![Figure 4.7](image)

**Figure 4.7.** Diffuse reflectance (a) and absorption (b) of ncRuO$_2$/i-Si-o (in red) and ncRuO$_2$/SiW samples (in black).

It can be seen from Figure 4.7a that the ncRuO$_2$/i-Si-o sample reflects less of the incident photons in the UV-visible and near infrared region of the solar spectrum compared to the ncRuO$_2$/SiW sample. This low reflectance of the ncRuO$_2$/i-Si-o sample translates to higher absorption (an average of 80%) particularly in the UV-visible region.
where the incoming photons are most energetic as can be seen in Figure 4.7b. These absorbed incident photons produce photogenerated electrons and holes, which mainly recombine and thermalize producing heat energy that drives the Sabatier reaction photothermally. It is possible that some of these photogenerated charges may interact with the reactant species and drive the Sabatier reaction photochemically but we believe the majority of them thermalize and produce heat that drives the reaction photothermally. The evidence of this comes from the temperature profile of the samples, which was monitored during the photomethanation testing. As can be seen from Figure 4.8, the temperature of both samples rapidly increased once the Xe lamp was turned on and remained fairly constant throughout the test until the Xe lamp was turned off. The ncRuO$_2$/i-Si-o sample reached ~170°C while the ncRuO$_2$/SiW sample reached only up to 150°C under the same illumination conditions. While both samples were exposed to the same number of incident photons, the ncRuO$_2$/i-Si-o sample absorbs more photons producing electrons and holes that recombine non-radiatively and produce thermal energy required to drive the Sabatier reaction.

In order to further understand the enhanced photomethanation rate of CO$_2$ by the ncRuO$_2$/i-Si-o sample, we performed a wavelength-dependent study where we used high pass cut off filters and analyzed the different temperatures reached by each test and compared the resulting photomethanation rates. The Sabatier reaction rate over the ncRuO$_2$/i-Si-o catalyst was measured under illumination from a 300W Xe lamp with a 625 nm high pass filter, a 495 nm high pass filter and without a filter and the results are plotted as Tests 1, 2, and 3 in Figure 4.9a, respectively.
Figure 4.8. Temperature profiles recorded for the two samples during the photomethanation testing. (a) ncRuO$_2$/SiW sample, (b) ncRuO$_2$/i-Si-o sample.

The measured Sabatier reaction rates for Tests 1, 2, and 3 are 0.2, 0.8 and 4.4 mmol·g$_{\text{cat}}$·hr$^{-1}$, respectively, normalized to the weight of the RuO$_2$. The relative intensity of the incident light spectra for Tests 1, 2 and 3 are 1.8, 5.0 and 22 kW/m$^2$ respectively. The spectral irradiance that is incident on the three tests is shown in Figure 4.10. This trend in photomethanation rates for the three tests is closely correlated with the $^{13}\text{CH}_4$ mass spectrum ion peak in Figure 4.9b.
Figure 4.9. (a) Photomethanation rate over the ncRuO$_2$/i-Si-o catalyst tested under different illumination conditions; for Test 1 the incident light spectra from the Xe lamp was passed through a 625 nm high-pass cut-off filter, for Test 2 a 495 nm high-pass cut-off filter was used, and no filter was used for Test 3. The relative intensity of the incident light spectra for Tests 1, 2 and 3 are 1.8, 5.0 and 22 kW/m$^2$, respectively, (b) GC-MS spectrum ion mass 17 peak for the three photomethanation tests carried out over the ncRuO$_2$/i-Si-o sample, (c) Temperature profiles recorded for the three batch reaction tests.

Test 1 had the lowest $^{13}$CH$_4$ peak and Test 3 had the highest $^{13}$CH$_4$ mass peak. We have also monitored the temperature profiles of these three tests (Figure 4.9c). The highest temperature was reached during Test 3 with an average of 170°C while the lowest temperature was reached during Test 1 with an average temperature of 122°C.
Test 2 reached an average temperature of 138°C. The photomethanation rates plotted in Figure 4.9a together with the temperature profiles in Figure 4.9c clearly show the i-Si-o support heats up under high intensity illumination.

Figure 4.9a. The incident light spectra for Test 1 with a 625nm high-pass cut-off filter, Test 2 with a 495nm high-pass cut-off filter, and Test 3 without using a filter.

The thermal energy produced is then transferred to the attached RuO$_2$ nanocrystals, which drives the reaction photothermally. For efficient photomethanation, it is necessary to remove the bi-product H$_2$O produced during the photomethanation process from the
active sites where it is produced so that these active sites are available for further reaction. The temperature required to completely remove the H$_2$O bi-product is ~147°C,[51] which to some extent explains the very low methanation rates of Test 1 and Test 2 compared to Test 3. From this wavelength-dependent study, we conclude that photomethanation rates increase with increasing relative intensity of incident photons. Additionally, it is observed that the photomethanation rate of Test 3 is the same as the sample heated to 150 °C in the dark whereas the photomethanation rate of Test 2 is 4 times higher than the sample heated to 150 °C in the dark. Yet both Tests 2 and 3 registered a lower temperatures profile during the photomethanation tests. This indicates that the incident photons impinging on the photonic crystal do not just provide thermal energy required to activate the Sabatier reaction but rather enhance the photomethanation reaction photochemically as well. The photons that enhance Sabatier reaction photochemically may only be a small fraction of the total incident photons irradiated on the sample.[36]

In the literature, the mechanistic details of CO$_2$ methanation over ruthenium-based materials is highly debated. It is not clear whether CO$_2$ is adsorbed on the catalyst first followed by the hydrogenation of the adsorbed species to produce CH$_4$[52,53] or CO$_2$ directly dissociates on the surface of the catalyst into adsorbed CO$_{ad}$ and O$_{ad}$ which is then hydrogenated to form CH$_4$.[54,55] Several factors such as temperature, reactant gas ratios and type of supports used are responsible for the different mechanisms.[56,57] In either case, the hydrogenation step is the rate-limiting step. The most reported ruthenium-based Sabatier reaction catalysts consist of metallic ruthenium supported on metal oxides such as TiO$_2$.[21,53,58-60] During the Sabatier reaction, hydrogen splits on the
ruthenium metal and methanation takes place at the interface between the metal and the support.\cite{53} Whereas metallic ruthenium can readily form surface metal hydrides, which facilitates methanation, very little is known about the methanation details of RuO$_2$. Carenco and coworkers investigated the active state of 2 nm supported RuO$_2$ on titania (RuO$_2$/TiO$_2$). Using ambient-pressure X-ray photoemission spectroscopy, they concluded that the active state is indeed metallic ruthenium, which resulted from the reduction of the RuO$_2$ in a hydrogen environment.\cite{61} While RuO$_2$ can be reduced in a hydrogen environment, we do not expect our RuO$_2$ to be greatly reduced due to the large size of the nanocrystals used and the low temperature reaction conditions employed. Furthermore, XPS measurement performed after the tests confirmed that the oxidation state of the Ru remained at +4 indicating that the RuO$_2$ was not reduced to metallic Ru (\textbf{Figure 4.3}).

Accordingly, we propose that the photomethanation reaction on the ncRuO$_2$/i-Si-\textit{o} catalyst begins with the splitting of H$_2$ on the surface of the RuO$_2$ to form hydroxyl groups as a result of the interaction of H$_2$ with the oxygen of the RuO$_2$. Subsequently, CO$_2$ interacts with hydroxyl groups to form intermediates such as, formates, carbonates and bicarbonates, which lead to the final methane product. In addition, a H$_2$ molecule may also interact with the oxygen of the RuO$_2$ to form water, which will then desorb at high temperatures to create oxygen vacancies that act as active sites for further reaction. Using XPS, we were able to identify both oxygen vacancies\cite{15,62,63} and adsorbed water\cite{64-66} on the surface of the catalyst as seen from the O1s peak of our photocatalyst after the photomethanation test (see \textbf{Figure 4.11}). In order to gain a deeper insight into the high CO$_2$ methanation rates and understand the details of the
interaction of the reactant gases with the surface of the highly dispersed nanocrystalline RuO$_2$ nanocrystals supported on the silicon inverse photonic crystal, density functional theory (DFT) analysis were conducted. In the DFT analysis, a 7-layer slab geometry of the most common orientation (110) of RuO$_2$ surface with a vacuum layer of about 20 Å was chosen, further sandwiched by the semi-infinite vacuum called the ‘effective screening medium’ (ESM).

![Image of XPS measurement of O1s spectrum](image)

**Figure 4.11.** XPS measurement of O1s spectrum ncRuO$_2$/i-Si-o sample after the photomethanation test. The peak with binding energy of 530 eV (in red) is associated with lattice oxygen of the RuO$_2$ while the peak around 531 eV (in blue) is assigned to oxygen vacancy or hydroxyl groups. The green peak at 532.3 eV (in green) is from the SiO$_2$, the peak around 533 eV (in purple) is associated with C/O species adsorbed on the catalyst and the peak at 534 eV (in dark blue) is associated with adsorbed water.
The modelled system is a continuous layer, about 10 Å in thickness, which represents a nanoscale film, and captures the behaviour of non-edge nanocrystal regions, which form the majority of the surface area. We treated the slab part that consists of substrate and adsorbate atoms microscopically within DFT and we treated the medium part within a continuum characterized by a relative permittivity with a value of unity. In order to incorporate the effect of photogenerated electrons and holes from the silicon substrate to the RuO₂ surface, we investigated the RuO₂(110) surface with extra electrons and extra holes denoted by [RuO₂(110)]⁻ and [RuO₂(110)]⁺, respectively. The neutral RuO₂(110) surface was also simulated for comparison. Further, on the RuO₂(110) surface, there are two types of Ru atoms: the six-fold coordinated (same as bulk Ru atom) and the five-fold coordinated, and two types of O atoms: the three-fold coordinated (same as bulk O atom) and the two-fold coordinated. Therefore, in order to analyze the interaction of adsorbates on RuO₂(110) surface we considered site A which is on top of 5-fold coordinated Ru, site B which is the bridge site and site C which is on the top of 2-fold coordinated O as shown in Figure 4.12. The interaction of one of the reactant gases, H₂ with neutral and charged (±1,0) RuO₂(110) surfaces was first investigated. Here, H₂ was placed sufficiently far away from each of the three surfaces before optimization. The final optimized structures for the hydrogenated surfaces are shown in Figure 4.13. Bader charge⁶⁷ and bond length analysis on these optimized geometries was then performed (see Table 4.1). This analysis showed that the H₂ molecule interacts in the same way with charged surfaces as it does with the neutral surface. On all three surfaces, H₂ is physisorbed on site A, splits and forms OH groups on site B and is chemisorbed and forms water on site C.
Figure 4.12. Top view (left) and side view (right) of RuO$_2$(110) surface. A, B and C represent the various absorption sites considered for the calculation. A: top of 5-fold coordinated Ru, B: bridge site and C: on top of 2-fold coordinated O. Color code: Ru, Gray and O, red.

Bader charge analysis shows that the negative surface forms more basic OH groups, having about -0.03 to -0.02e higher charge, as compared to the other surfaces. Formation of H$_2$O on site C leads to coordinately unsaturated Ru atoms, which can subsequently dissociate H$_2$ to form Ru-H bonds that participate in the Sabatier reaction. Further, H$_2$ interaction with adsorption site B and C leads to the formation of hydroxyl groups and adsorbed water, respectively, as seen in experimental O1s XPS spectrum in Figure 4.11. The interaction of H$_2$ with the negatively charged surface results in adsorbed H$_2$ having an oxidation state different from when it interacts with other two surfaces (Table 4.1). Further, the calculations done by placing CO$_2$ vertically as well as
horizontally on all the adsorption sites showed that none of the surfaces were able to
dissociate CO$_2$. The CO$_2$ molecule is adsorbed on site A and C of all the surfaces, and
site B of the positively charged surface (Figure 4.14) but it never dissociates. However,
a noticeable increase in bond length and decrease in bond angle of the CO$_2$ molecule
after adsorption on the aforementioned sites of different surfaces shows that CO$_2$ might
dissociate into CO at room temperature, which can subsequently be hydrogenated by
the Ru-H surface species.

**Figure 4.13.** H$_2$ adsorption on various sites on neutral and charged (110) RuO$_2$
surfaces. A: top of 5-fold coordinated Ru, B: bridge site and C: on top of 2-fold
coordinated O. Color code: H, blue; Ru, gray and O, red.
Table 4.1. Bond length and Bader charge analysis for H\textsubscript{2} adsorption on neutral and charged RuO\textsubscript{2} surfaces.\textsuperscript{[75]}

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Bond lengths (in Å)</th>
<th>(Valence electrons-Bader Charge (e))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>+: holes, -: electrons</td>
</tr>
<tr>
<td>Neutral Surface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Ru-H1=1.90, Ru-H2=1.89, H1-H2=0.81</td>
<td>H1=+0.034, H2=0.0022,Ru105=+1.7182</td>
</tr>
<tr>
<td>B</td>
<td>O-H1=O-H2=0.980</td>
<td>H1=+0.9991, H2=0.9993,O106=-1.5693,0107=-1.5384</td>
</tr>
<tr>
<td>C</td>
<td>OH1=OH2=0.980, &lt;H1-O-H2=107.99</td>
<td>H1=+0.9988,H2=+0.9989,O103=-1.9149</td>
</tr>
<tr>
<td>+1e Charged</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Ru-H1=1.91, Ru-H2=1.91, H1-H2=0.81</td>
<td>H1=+0.0415, H2=0.0115,Ru105=+1.7312</td>
</tr>
<tr>
<td>B</td>
<td>O-H1=O-H2=0.985</td>
<td>H1=+0.9992, H2=0.9994,O106=-1.5606,0107=-1.5346</td>
</tr>
<tr>
<td>C</td>
<td>OH1=OH2=0.982, &lt;H1-O-H2=106.48</td>
<td>H1=+0.9989,H2=+0.9990,O103=-1.8978</td>
</tr>
<tr>
<td>-1e Charged</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Ru-H1=1.89, Ru-H2=1.89, H1-H2=0.81</td>
<td>H1=+0.0349, H2=-0.0025,Ru105=+1.7083</td>
</tr>
<tr>
<td>B</td>
<td>O-H1=O-H2=0.982</td>
<td>H1=+1.0038, H2=1.0032,O106=-1.5781,0107=-1.5424</td>
</tr>
<tr>
<td>C</td>
<td>OH1=OH2=0.980, &lt;H1-O-H2=109.15</td>
<td>H1=+1.01, H2=+1.0089,O103=-1.9313</td>
</tr>
</tbody>
</table>
Further, we investigated the adsorption of CO$_2$ on the surfaces that have already interacted with H$_2$. Since H$_2$ interaction with all the positive, negative and neutral surfaces is more-or-less the same we considered only the negatively charged surfaces for this calculation. Multiple simulations were conducted whereby CO$_2$ was adsorbed (a) on physisorbed H$_2$ site A, (b) on surface OH formed from the splitting of H$_2$ on site B, and (c) on bare Ru formed by desorption of H$_2$O that resulted from the reaction of H$_2$ with surface O at Site C (See Figure 4.15). The most interesting case is the one where CO$_2$ interacts with the surface OH groups and forms OCOH, a possible intermediate that may lead to formation of surface CO or C that can be further hydrogenated to form the main product CH$_4$ as observed in our experiments. A similar reaction mechanism was recently proposed by Sharma et al who investigated the CO$_2$ methanation over ruthenium substituted CeO$_2$.[68] They also found that the substituted Ru was in the +4 oxidation state and the surface of the active catalyst consists of Ru and O, which is consistent with our observations. Overall, from the DFT studies, we conclude that H$_2$ splits on the surface of the RuO$_2$ to form hydroxyl groups, which then interact with the
CO₂ to form intermediates, which ultimately lead to the formation of CH₄ as observed in our experiments.

**Figure 4.15.** CO₂ adsorption on (a) site A, (b) site B, and (c) site C of H₂ adsorbed [Ru(110)]⁻¹ surface.

### 4.6 Conclusion

We have developed a solution phase technique to deposit nanostructured RuO₂ nanocrystals on three-dimensional silicon photonic crystals, ncRuO₂/i-Si-o and investigated its activity towards gas-phase photomethanation of CO₂ with H₂ at ambient temperatures under high intensity solar simulated light. The rate of CO₂ hydrogenation
was an order of magnitude higher compared to when the RuO$_2$ was supported on a planar silicon wafer, ncRuO$_2$/SiW. DFT calculations were performed in order to understand the interaction of the reactants, CO$_2$ and H$_2$ with the photocatalyst and gain a deeper insight in the overall mechanistic details of the photomethanation process. The methanation process was activated via the interaction of H$_2$ with the oxygen of RuO$_2$ to form hydroxyl groups, which interacted with CO$_2$ to ultimately produce CH$_4$. The large surface area coupled with the unique light absorption properties of the photonic crystal was found to be responsible for the enhanced photomethanation rate. The ability of these highly absorbing nanostructured catalysts to utilize light and heat energy provided by the broadband solar irradiance to drive CO$_2$ reduction reactions represents a general advancement that is applicable to a wide range of catalysts in the field of solar fuels.

4.7 References:


Chapter 5 - Photocatalytic Properties of All Four Polymorphs of Nanostructured Iron Oxyhydroxides

(Reproduced in part with permission from ChemNanoMat 2016, 2, 1047-1054)

5.1 Statement of Contributions

Dr. Hmadeh helped with the synthesis of some of the FeOOH polymorphs. Dr. Paul O’Brien performed optical measurements. I carried out all other synthesis, characterization, and experiments presented in this chapter. I drafted the manuscript, which was edited by Professors Doug Perovic and Geoffrey Ozin. Portions of this chapter are currently published in ChemNanoMat journal.


5.2 Abstract

Four different polymorphs of nanostructured iron oxyhydroxides, namely; goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and feroxyhyte (δ-FeOOH) were synthesized and fully characterized by X-ray diffraction, electron microscopy, UV/Visible spectrophotometry, Brunauer–Emmett–Teller (BET) measurements, and X-ray photoemission spectroscopy. The relationship between these iron oxyhydroxide polymorphs and their photocatalytic properties was explored by examining the extent of methylene blue (MB) degradation by each polymorph under visible light irradiation. Feroxyhyte exhibited the best photocatalytic properties and degraded 85% of the MB
dye in five hours. In comparison, goethite, akaganeite, and lepidocrocite degraded only 40%, 35%, and 30% of the MB in five hours, respectively. To understand this trend, the surface area, particle size and shape, and electronic band properties were systematically studied and discussed. It was found that the rate of MB degradation relates mainly to the surface area of the FeOOH polymorphs more than any other factor. This is the first report of a comparative study of the physical, electronic, and photocatalytic properties of all four polymorphs of nanostructured iron oxyhydroxides.

5.3 Introduction

Dyes are considered to be one of the most hazardous materials entering the environment in industrial effluents generated while manufacturing many products such as textiles, leather, paper, plastics, and cosmetics.\(^1\) Once in the environment, dyes induce carcinogenic and mutagenic effects in aquatic organisms and also restrict their availability to sunlight and dissolved oxygen. Numerous methods for removing organic dyes from wastewater have been investigated, including adsorption,\(^2,3\) precipitation,\(^4\) flocculation and filtration,\(^5\) reverse osmosis,\(^6\) sonochemical degradation,\(^7\) biochemically assisted methods,\(^5\) and photocatalytic degradation.\(^9-17\) Of these methods, photocatalytic degradation is particularly attractive because it is inexpensive, can be carried out at ambient conditions, and can be driven with solar energy.\(^18\) In this context, the development of photoactive materials that are cheap and non-toxic has been of great interest over the past few decades.\(^19-23\) Titania is the most commonly used photocatalyst to perform many solar-powered catalytic reactions such as water oxidation and dye degradation.\(^24,25\) However, TiO\(_2\) has a large electronic band gap of
3.2 eV and absorbs only the UV portion of the solar spectrum, which greatly restricts its applications.[26]

In this context, the development of abundant, non-toxic, and inexpensive small electronic band gap photoactive materials that are capable of using visible light to drive useful chemical reactions has been thoroughly investigated.[27,28] Amongst the most earth-abundant materials are the iron oxyhydroxides (FeOOH).[29] These compounds are attracting increasing interest owing to their outstanding chemical and physical properties, including environmental compatibility, high photostability, and excellent visible-light absorption.[30–32] Iron oxyhydroxide has four common polymorphs: goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and feroxyhyte (δ-FeOOH). FeOOH polymorphs offer interesting opportunities in photocatalysis because their electronic band gap energies (2.0 ≤ E_g ≤ 2.5 eV) fall in the visible wavelength range.

Additionally, only a few studies have reported the photocatalytic degradation of organic dyes by FeOOH. For example, urchin-like nanostructures of α-FeOOH were recently reported to efficiently photodegrade Rhodamine 6G (R6G) in the presence of H_2O_2. The α-FeOOH used in this study was synthesized under low-temperature water-bath conditions and had micro/nanostructural features.[33] The high photocatalytic activity was attributed to the high surface area (118 m^2g^{-1}) of the urchin-like goethite compared with goethite nanorods. In addition, a recent study reported that TiO_2 fiber-supported β-FeOOH nanostructures are effective photocatalysts for the degradation of methylene orange (MO) and have excellent gas sensing capabilities as well.[34] The enhanced photoactivity was ascribed to the high surface area and efficient charge separation.
capabilities of the photocatalyst. Another study reported visible-light photocatalytic activity towards Rhodamine B degradation in the presence of H\textsubscript{2}O\textsubscript{2} by rod-like α-FeOOH and α-Fe\textsubscript{2}O\textsubscript{3}.[35]

In this study, the photoactivities of α-FeOOH and α-Fe\textsubscript{2}O\textsubscript{3} nanorods were compared with α-FeOOH and α-Fe\textsubscript{2}O\textsubscript{3} microrods. It was observed that the nanorods were much more photoactive than the microrods displaying the importance of surface area towards the photodegradation process. Zhou et al. have investigated the visible-light photodegradation dependence of Rhodamine B dye with different facets of various hematite architectures.[36] They have also explored the origin and the underlying mechanism for the selective photodegradation of different dyes by using different hematite nanostructures.[37].

Another study reported the high photocatalytic activity of hierarchical porous α-FeOOH compared with α-Fe\textsubscript{2}O\textsubscript{3} for the degradation of Rhodamine B solution. These hierarchical porous α-FeOOH network structures were successfully constructed by using a facile polystyrene microspheres-templated method. UV light was used to irradiate the sample during photocatalytic testing. The high photoactivity was found to be related to the structural features of the hierarchically porous structure, namely high surface area and uniform distribution of the α-FeOOH nanoparticles.[38] Composites of titania and iron oxyhydroxide have also been prepared and their photocatalytic activity for dye degradation was studied. Indeed, TiO\textsubscript{2} /β-FeOOH nanocomposites showed very good performance for visible-light degradation of methyl orange. The heterostructures were said to be responsible for the effective separation of the photogenerated electrons and
holes, thereby prolonging their lifetime to activate photocatalytic reactions.\textsuperscript{[39]} Similarly, it has been reported that TiO\textsubscript{2}/β-FeOOH heterostructured nanocomposites demonstrated excellent photodegradation of methyl orange, which has been attributed to the unique matching of energy band potentials between the β-FeOOH nanorods and the anatase phase of TiO\textsubscript{2} nanoparticles, which facilitated efficient electron–hole transport and separation between the two semiconductors.\textsuperscript{[40]} Moreover, efficient separation of photogenerated charge carriers by nanocomposites\textsuperscript{[41]} and core–shell structures\textsuperscript{[42]} were reported to improve the photocatalytic degradation of various dyes including pentachlorophenol, methyl orange, and Rhodamine B. In all cases, electron–hole recombination is retarded by the heterostructures, leading to the high photocatalytic activities.

To our knowledge, no comprehensive study exists that explores the correlation between the electronic structures of FeOOH polymorphs and their photocatalytic properties. In this Chapter, we report the first side-by-side comparative study of the physical, electronic, and photocatalytic properties of all four polymorphs of iron oxyhydroxides, the latter by analyzing the rate and extent of methylene blue degradation. Methylene blue is a very important dye commonly used in coloring paper, cotton wools, and sometimes temporarily coloring hair. Although it is not considered to be very toxic, inhaling MB is known to cause nausea, vomiting, diarrhea, and difficulty in breathing.\textsuperscript{[43]} It is important to note that all dye photodegradation studies reported in the literature to-date have employed H\textsubscript{2}O\textsubscript{2} to produce ‘OH radicals that accelerate the oxidation process, whereas our tests were performed in aqueous solution in the absence of H\textsubscript{2}O\textsubscript{2}.
5.4 Experimental Procedure

5.4.1 Synthesis of goethite

Goethite was synthesized by using a hydrothermal technique. In short, Fe$_2$(SO$_4$)$_3$ (300 mg, 0.075 mol) was dissolved in water (20 mL) and heated to 120 °C for 8 h in a Teflon-lined stainless steel autoclave. A brown precipitate of goethite nanoparticles was produced. The product was washed and dried in a low-temperature oven (40 °C).

5.4.2 Synthesis of akaganeite

Similarly, the synthesis of akaganeite involved the use of a hydrothermal technique. FeCl$_3$ (300 mg, 0.093 mol) was dissolved in water (20 mL) and heated in a Teflon-lined stainless steel autoclave at 120 °C for 2 h. Rice-like yellowish brown akaganeite nanoparticles were obtained. The product was washed, centrifuged, and dried in an oven heated at 40 °C.

5.4.3 Synthesis of lepidocrocite

Lepidocrocite nanoparticles were synthesized by the oxidation of Fe$^{2+}$ at a pH close to neutral. In short, FeCl$_2$·4H$_2$O (4 g, 0.2 mol) was dissolved in water (100 mL). The pH was adjusted to around 6.7 with NaOH before the solution was slowly oxidized with air by bubbling air through an inlet tube. During the oxidation process, the color of the solution changed from dark greenish blue to grey and finally to yellowish orange. The reaction, carried out at room temperature, was complete in 2–3 h. Pure well-defined
crystalline reddish brown precipitates of lepidocrocite were formed. The products were
washed and centrifuged several times before being dried in an oven at 40 °C.

5.4.4 Synthesis of feroxyhyte

Feroxyhyte was synthesized through the rapid oxidation of Fe$^{2+}$ with H$_2$O$_2$. Briefly, a
solution containing FeSO$_4$(NH$_4$)$_2$SO$_4$.6H$_2$O (200 mL, 5.56 g, 0.071 mol) was mixed with
a 2 M NaOH solution (200 mL), forming a green precipitate. Immediately, 30% H$_2$O$_2$ (5
mL) was added. The precipitate turned reddish brown within a few seconds, indicating
the formation of feroxyhyte nanoparticles. The products were washed and dried in an
oven at 40 °C.

5.5 Characterization

Both scanning and transition electron microscopy were used to study the morphology
and structure of the FeOOH polymorphs. A Hitachi S-5200 scanning electron
microscope (SEM) was used to study the surface topography of the different
crystalline precipitates of lepidocrocite were formed. The products were polymorphs. A Hitachi H-700 transmission electron microscope (TEM), working at an
operating voltage of 100 kV, was used to further study the FeOOH polymorphs. In
addition, a high-resolution environmental TEM (Hitachi HF3300), working at an
operation voltage of 300 kV, was employed to understand the internal structure of the
polymorphs. Powder X-ray diffraction (PXRD) patterns of all the polymorphs were
recorded and identified with a Bruker D$_2$ phaser instrument, using Cu$_{K\alpha}$ radiation at 30
kV. The surface areas of the catalysts were determined from N$_2$ adsorption isotherms at
$T=77$ K by using a Quantachrome Autosorb. Multipoint Brunauer–Emmet– Teller (BET)
measurements were performed at relative pressures \( \frac{P}{P_0} \) in the range 0.1–0.3. Prior to the measurements, samples were degassed under vacuum at \( T=80 \, ^\circ\text{C} \) for 12 h. Diffuse reflectance of the samples was measured by using a PerkinElmer Lambda 1050 UV/Vis/NIR spectrometer equipped with an integrating sphere with a diameter of 150 mm. These diffuse reflectance measurements were used in plotting a modified Kubelka– Munk function, which in turn was used to determine the band gaps of the FeOOH polymorphs. X-ray photoelectron spectroscopy (XPS) measurements were carried out to study the surface and electronic band structure of the FeOOH polymorphs. XPS was performed in an ultrahigh vacuum chamber with base pressure of \( 10^{-9} \) Torr. The system used a Thermo Scientific K-Alpha XPS spectrometer, with an Al\( K_\alpha \) X-ray source operating at 12 kV, 6 A, and X-ray energy of 1486.7 eV. The spectra were obtained with an analyzer pass energy of 50 eV with energy spacing of 0.1 eV. The samples for XPS analysis were prepared by drop casting them on p-doped Si (100) substrates. All data analysis was carried out by using Thermo Scientific Avantage software.

5.6 Photocatalytic measurements

The photocatalytic activity of the different FeOOH polymorphs towards the degradation of MB was evaluated by measuring the absorbance of the irradiated solution as a function of time. At first, the UV/Vis spectrum of pure MB, which was diluted with water, was recorded. Subsequently, the FeOOH polymorph (50 mg) was dissolved in MB (40 mL) and thoroughly mixed in the dark for 30 min until a state of adsorption–desorption equilibrium was achieved. An aliquot (3 mL) of solution was extracted and passed
through a 0.2 mm filter to remove the FeOOH photocatalyst. The UV/Vis adsorption spectra of the filtered solution were then recorded. The solution was then illuminated with a 300 W Xenon arc lamp at an intensity of 100 mW cm$^{-2}$. An AM 1.5 cut-off filter was used to block the UV light. After one hour of illumination, once again 3 mL of the solution was extracted and passed through a 0.2 mm filter to remove the FeOOH photocatalyst and its absorption spectra was recorded. This measurement procedure was repeated after every hour of illumination for a period of five hours. The effective concentration of the solution was corrected after taking each aliquot. The evolution of the absorbance band centered at 666 nm was recorded and compared for all FeOOH polymorphs to establish their photodegradation activity.

5.7 Results and Discussion

We have successfully synthesized all four FeOOH polymorphs (see Experimental Section for details). Whereas goethite and akaganeite were synthesized by using a hydrothermal technique, lepidocrocite and feroxyhyte were synthesized with slow and rapid oxidation of Fe$^{2+}$, respectively. The range of colors exhibited by these FeOOH polymorphs is shown in Figure 5.1. We have characterized these polymorphs by using PXRD, electron microscopy, and X-ray photoelectron spectroscopy (XPS) as discussed below. The brown goethite nanoparticles were first characterized with PXRD, which confirmed that these nanoparticles were of the pure goethite phase (Figure 5.2).

The average crystal size was about 6–7 nm and the lattice parameters were $a$=4.621 Å, $b$=9.981 Å, and $c$=3.032 Å, which are consistent with the lattice parameters of the orthorhombic unit cell of goethite. The morphology of goethite studied by using SEM
showed that urchin-like α-FeOOH particles were formed (Figure 5.3a). Higher magnification reveals that these urchin-like structures consist of nanorods of about 30–50 nm in diameter and less than 200 nm in length with ends that are aggregated to form urchin-like shapes.

Figure 5.1: Synthesized FeOOH polymorphs: (a) goethite (brown), (b) akaganeite (yellowish-brown), (c) feroxyhyte (reddish-brown) and (d) lepidocrocite (orange-brown).

To investigate further, high-resolution (HR)-TEM imaging of an individual nanorod was performed (Figure 5.3b). As shown in Figures 5.3c and 5.3d, several lattice planes of goethite were observed. Fast Fourier transform (FFT) analysis clearly confirms the
fringe spacings of 2.68 Å, 2.19 Å, and 1.71 Å, which are consistent with the d-values of the (301), (401), and (212) reflection planes of orthorhombic goethite, respectively. Similarly, akaganeite nanoparticles were characterized by using PXRD. Rietveld refinement revealed that the PXRD pattern matches that of β-FeOOH (Figure 5.4).

![Figure 5.2](image)

**Figure 5.2:** Powder X-ray diffraction of goethite. The average crystal size was about 6 - 7 nm and the unit cell dimensions are: $a = 4.621 \, \text{Å}$, $b = 9.981 \, \text{Å}$ and $c = 3.032 \, \text{Å}$. The blue pattern represents the as synthesized goethite and the black pattern is the simulated goethite.

The lattice parameters were found to be $a = 10.54 \, \text{Å}$ and $c = 3.03 \, \text{Å}$, which are consistent with the tetragonal unit cell of β-FeOOH. The synthesized akaganeite nanostructures
precipitated in nanoscale rice-like morphology of about 20–30 nm in diameter and 200–300 nm in length as evident from the SEM and TEM images (Figures 5.5a and 5.5b).

Figure 5.3. (a) SEM image, (b, c) HR-TEM images, and (d) FFT of goethite nanostructures. The scale bars are 5 µm, 20 nm, and 5 nm for Figure 5.3a, 5.3b, and 5.3c, respectively.
HR-TEM imaging was also performed to reveal the details of the akaganeite nanostructures. As shown in Figure 5.5c, lattice planes were observed with a spacing of 6.07 Å and 2.34 Å, which could be ascribed to the (211) and (321) reflection planes, respectively. The FFT in Figure 5.5d confirmed the existence of such planes in the akaganeite structure. The PXRD pattern of lepidocrocite nanoparticles was collected and Rietveld refinement was performed (Figure 5.6).

**Figure 5.4**: Powder X-ray diffraction of akaganeite. The unit cell dimensions are: $a = 10.54$ Å and $c = 3.03$ Å, with an average crystal size of 45 nm.

The structure of lepidocrocite was confirmed, showing an orthorhombic unit cell with lattice parameters of $a=3.07$ Å, $b=12.53$ Å, and $c=3.87$ Å. The morphology of the
synthesized γ-FeOOH was lath-like as observed from the SEM and TEM images in Figures 5.7a and 5.7b.

Figure 5.5. (a) SEM image, (b) TEM image, (c) HR-TEM image, and (d) FFT analysis of akaganeite nanostructures. The scale bars are 100 nm, 500 nm, and 5 nm for Figure 5.5a, 5.5b, and 5.5c, respectively.
HR-TEM imaging (Figure 5.7c) shows that two main lattice planes are apparent, which correspond to the (200) and (101) planes of γ-FeOOH with d-values of 6.27 Å and 2.98 Å, respectively. The FFT in Figure 5.7d further confirms the existence of these reflection planes. Unlike lepidocrocite, feroxyhyte was synthesized by the rapid oxidation of Fe²⁺ with H₂O₂. PXRD analysis confirms the formation of feroxyhyte with a hexagonal crystal structure (See Figure 5.8).

Figure 5.6: Powder X-ray diffraction of lepidocrocite. The unit cell dimensions are: a = 3.07 Å, b = 12.53 Å, and c = 3.87 Å.

The unit cell parameters are found to be a = 2.947 Å and c = 4.520 Å. The reddish-brown product was imaged by using SEM and TEM and small thin plate-shaped crystals
were observed (Figures 5.9a and 5.9b). Further analysis was conducted by using HR-TEM. The obtained images and the accompanying FFT are shown in Figures 5.9c and 5.9d. The lattice fringes with interplanar spacings of 2.52 Å and 1.45 Å are consistent with the (100) and (110) planes of hexagonal δ-FeOOH, respectively.

**Figure 5.7.** (a) SEM image, (b) TEM image, (c) HR-TEM image, and (d) FFT analysis of lepidocrocite nanostructures. The scale bars are 1 μm, 500 nm, and 10 nm for Figure 5.7a, 5.7b, and 5.7c, respectively.
XPS measurements of the four FeOOH polymorphs were carried out to study their electronic properties. All four FeOOH polymorphs show very similar XPS spectra as can be seen from the survey spectra in Figure 5.10. To amplify, Figure 5.11 shows the XPS spectra of the Fe2p and O1s core levels of the FeOOH polymorphs. It is evident from Figure 5.11a that Fe⁰ is absent in the structure, the Fe2p core level binding energy of which is approximately 706.7 eV. The peak around 711–712 eV is assigned to Fe³⁺ 2p₃/₂ whereas the peak around 725 eV is assigned to Fe³⁺ 2p₁/₂. Both of these Fe³⁺ peaks have satellite peaks around 720 eV and 734 eV, respectively. The O1s peak can be deconvoluted into two major peaks around 530 eV and 531 eV, which can be respectively ascribed to oxide and hydroxide groups bound to Fe. Adsorbed hydroxide and water often exist in these FeOOH materials and are evident in the O1s peaks of Figure 5.11. Table 5.1 summarizes the peak positions of the Fe2p and O1s peaks.

Table 5.1: Fe 2p and O 1s core level binding energies of FeOOH polymorphs.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Fe³⁺ 2p₁/₂</th>
<th>Fe³⁺ 2p₃/₂</th>
<th>Fe-Oₗₐₜ</th>
<th>Fe-ΟHₗₐₜ</th>
<th>Fe-ΟHₐd</th>
<th>Fe-ΟH₂ₐd</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-FeOOH</td>
<td>711.6</td>
<td>725.1</td>
<td>529.9</td>
<td>531.5</td>
<td>532.6</td>
<td>533.1</td>
</tr>
<tr>
<td>β-FeOOH</td>
<td>711.5</td>
<td>725.1</td>
<td>529.9</td>
<td>531.1</td>
<td>-</td>
<td>533.2</td>
</tr>
<tr>
<td>γ-FeOOH</td>
<td>711.8</td>
<td>725.5</td>
<td>530.2</td>
<td>531.0</td>
<td>532.0</td>
<td>533.0</td>
</tr>
<tr>
<td>δ-FeOOH</td>
<td>711.2</td>
<td>724.7</td>
<td>530.3</td>
<td>531.4</td>
<td>532.7</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5.8: Powder X-ray diffraction of feroxyhyte. The unit cell dimensions are: \( a = 2.947 \text{ Å} \) and \( c = 4.520 \text{ Å} \), with an average crystal size of 14 nm.

With this understanding of the nanostructured FeOOH polymorphs, we performed photocatalytic testing to determine their photoactivity. The photodegradation of MB was used as a probe (see the photocatalytic measurements in the Experimental Section). The rate and extent of MB degradation were determined from the time-dependent reduction of the MB concentration, which was calculated from the change in the UV/Vis absorbance peaks of MB. It is very important in the MB photodegradation experiments for the dye to exist as monomers on the FeOOH polymorphs instead of forming aggregates. Fortunately, the nature of the adsorbed dye molecule can be judged by
analysis of the absorbance spectra, which can be controlled by the concentration of the MB dye.[44,45]. The monomeric form has a peak absorbance around 660 nm whereas the dimers and multimers have absorbance peaks that are blue-shifted to around 610 nm and 570 nm as a result of π−π interactions between adjacent molecules.[44]

Figure 5.9. (a) SEM image, (b) TEM image, (c) HR-TEM image, and (d) FFT analysis of ferroxyhyte nanostructures. The scale bars are 4 µm, 500 nm, and 10 nm for Figure 5.9a, 5.9b, and 5.9c, respectively.
We performed our experiments with a low concentration of MB ($1 \times 10^{-5}$ M) to ensure we had monomeric coverage of the dye instead of forming aggregates. As can be clearly seen in Figure 5.12, the absorbance peaks from the MB monomers are the most dominant. Hence, the changes in the intensity of the monomer peak at 667 nm with irradiation time were monitored. The UV/Visible spectra of the MB solutions exhibit a decrease in both the aromatic and chromophoric absorbance maxima of MB centered at 667 nm and 292 nm, indicating that dye is being degraded and not simply decolorized.

Figure 5.13 shows the time profile of the decrease in MB concentration in the presence of FeOOH polymorphs under solar simulated illumination. $C_0$ and $C_t$ denote the concentration of the MB solution at the beginning of the photocatalytic test and after a duration of testing time, $t$, respectively. In the case of feroxyhyte, the MB solution turned colorless after five hours of testing whereas the blue color of MB solutions was prominent for the other three FeOOH polymorphs after five hours of illumination. Out of the four FeOOH polymorphs, feroxyhyte showed the highest activity towards the photodegradation of MB. Specifically, 85% of the MB degraded in five hours when feroxyhyte was used, whereas only 40%, 35%, and 30% was degraded when goethite, akaganeite, and lepidocrocite were used, respectively. The reference, consisting of pure MB with no catalyst, showed no degradation after five hours of illumination. We also performed control experiments to identify the major species responsible for the degradation of the MB dye. In this experiment, we performed photodegradation tests with the two most active photocatalysts, $\alpha$-FeOOH and $\delta$-FeOOH, and used ethanol as a hole scavenger. This is shown in Figure 5.14 where the $\delta$-FeOOH and $\alpha$-FeOOH
could only degrade 9% and 7% of the MB dye in the presence of a hole scavenger compared with 85% and 40%, respectively, in the absence of a hole scavenger.

**Figure 5.10:** Comparison of the survey spectra of the FeOOH polymorphs obtained using a Thermo Scientific K-Alpha XPS spectrometer, with an Al Kα X-ray source operating at 12 kV, 6 Å and X-ray wavelengths of 1486.7 eV. Some of the spectra were vertically shifted for clarity.

This result is expected because it is the photogenerated holes that react with water or adsorbed hydroxyl groups to form very reactive hydroxyl radicals that are responsible for the degradation of the MB. The long-term stability of photocatalysts is very important when assessing their performance. We therefore performed PXRD and TEM characterization of the FeOOH samples after the photocatalytic measurements, which showed that the samples did not change during the photocatalytic testing.
Figure 5.11. XPS spectra of FeOOH: (a) Fe 2p, (b) O1s of α-FeOOH, (c) O1s of β-FeOOH, (d) O1s of γ-FeOOH, (e) O1s of δ-FeOOH.
Figure 5.12: UV-Vis spectra of MB after being treated with each of the FeOOH polymorphs for five hours: (a) goethite (b) akaganeite (c) lepidocrocite and (d) feroxyhyte.

This demonstrates the high chemical stability of the FeOOH polymorphs under our experimental conditions. It should be noted that photocatalytic degradation rates reported in the literature are most often based on experiments in which H$_2$O$_2$ is added to speed up the photodegradation process. It is known that H$_2$O$_2$ enhances photodegradation rates by acting as a scavenger towards photogenerated electrons thereby extending the lifetime of holes required to form the OH radicals necessary for the dye degradation process. However, in this work H$_2$O$_2$ was not added.
Figure 5.13: Extent of methylene blue degradation under visible-light irradiation in the presence of FeOOH polymorphs.

Figure 5.14: Extent of methylene degradation under visible irradiation by α-FeOOH and δ-FeOOH in the presence of ethanol as hole scavenger.
The photodegradation process begins with the absorption of incident photons with energy greater than the band gap of FeOOH, generating holes and electrons, which are powerful oxidizing and reducing agents, respectively. The photogenerated electrons react with oxygen dissolved in solution or adsorbed on the surface of the FeOOH polymorphs to produce the superoxide radical anion (O$_2^-$). On the other hand, the photogenerated holes react with water or hydroxyl groups to form reactive hydroxyl radicals. These reactive OH radicals are responsible for the degradation of MB. The presence of OH radicals is usually confirmed by using a photoluminescence (PL) technique, where terephthalic acid (TA) is reacted with the OH radicals to form a highly fluorescent 2-hydroxyterephthalic acid. The PL intensity of this compound is measured and therefore the amount of OH radicals can be determined. Several studies have reported the intimate relationship between the OH radicals and the photocatalytic degradation of organic dyes.\textsuperscript{[46–48]} The complete degradation of MB leads to the formation of CO$_2$ and H$_2$O.\textsuperscript{[49]} For ideal photodegradation of organic compounds, it is important that the redox potential of the H$_2$O/ OH couple (OH$^-$ → OH$^\cdot$ + e$^-$; $E^0 = 2.8$ V) lies within the band gap of the semiconductor.\textsuperscript{[9]} However, the conduction band energy of most of the stable photoactive semiconductors is lower than the redox potential of the H$_2$O/ OH couple. Therefore, the reactive hydroxyl radicals have to be generated in some other way. To define the electronic band structure of the four FeOOH polymorphs, we measured and analyzed their XPS and diffuse reflectance measurements (Figure 5.15). The electronic band gap of each FeOOH polymorph was calculated by using the Kubelka–Munk function as shown in Figure 5.16.
Figure 5.15: Diffuse reflectance spectra of the FeOOH polymorphs.

The band gaps of the four FeOOH polymorphs are 2.24 eV, 2.27 eV, 2.16 eV, and 2.03 eV for goethite, akaganeite, lepidocrocite, and feroxyhyte, respectively. By using these band gap energies, calculated from the reflectance measurements along with the valence band position determined from XPS measurements (Figure 5.17), the conduction band energy of each FeOOH polymorphs was determined, resulting in the band energy diagram for all four polymorphs as plotted in Figure 5.18. It is noteworthy that both goethite and akaganeite have very low conduction band energy levels in comparison with lepidocrocite and feroxyhyte, which have slightly more negative
conduction band edge positions than the O\textsubscript{2}/O\textsubscript{2}− potential, indicating that both can readily perform the photodegradation of MB dye.

![Graphs of (\(\alpha h\nu\))^2 versus \(h\nu\) for different FeOOH semiconductors](image)

**Figure 5.16**: The plots of \((\alpha h\nu)^2\) versus \(h\nu\) calculated from the UV-Vis diffuse reflectance spectrum of (a) goethite, (b) akaganeite, (c) lepidocrocite and (d) feroxyhyte.

But the fact that lepidocrocite could not effectively degrade MB meant that there was more to this photodegradation process than the conduction band edge position of the FeOOH semiconductors.
Figure 5.17: Valence band minimums (VBM) obtained by extrapolating the two fitted linear lines shown in red. The point where the two red lines cross is an estimate of the VBM of the FeOOH polymorphs. These measurements together with the band gap obtained from UV-Vis diffuse reflectance are used to plot the energy band diagram of the FeOOH polymorphs in Figure 5.18.

To understand the MB photodegradation results exhibited by the FeOOH polymorphs, other important parameters that affect their photocatalytic activity were examined. It is well documented in the literature that the crystal size and shape as well as the surface area of the photocatalysts have important implications for its photoactivity. In this regard, we measured the surface areas of the FeOOH polymorphs by using the
Brunauer–Emmett–Teller (BET) method. N\textsubscript{2} adsorption–desorption isotherms of all FeOOH samples were collected at 77 K (Figure 5.19).

\textbf{E (eV)}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.18}
\caption{Energy band diagrams of the FeOOH polymorphs. Photogenerated electrons in the conduction band reduce oxygen to form superoxide while the holes react with dissolved oxygen in water to form reactive hydroxyl radicals that photodegrade MB.}
\end{figure}
Goethite and feroxyhyte polymorphs show isotherms that are categorized as type IV, characteristic of mesoporous materials; however, akaganeite and lepidocrocite polymorphs exhibit type II isotherms according to the IUPAC convention. From the N$_2$ adsorption–desorption isotherm measurements, the BET surface areas of the polymorphs were calculated to be 150, 30, 76, and 185 m$^2$g$^{-1}$ for goethite, akaganeite, lepidocrocite, and feroxyhyte, respectively. The higher surface area values for feroxyhyte followed by goethite paralleled the trend in photocatalytic activity observed towards MB degradation by the FeOOH polymorphs.

![Figure 5.19. N$_2$ isotherms showing the BET surface area values of FeOOH polymorphs: (a) goethite, (b) akaganeite, (c) lepidocrocite, and (d) feroxyhyte.](image)

The large surface area provides more active sites for photocatalysis. To investigate whether or not the surface areas of the FeOOH polymorphs was the only factor
contributing to the enhanced photocatalytic activity, we normalized the photoactivity by the surface areas of the different polymorphs. It is known that the photodegradation rate of the dyes obeys the pseudo-first-order kinetic equation \(-dC/dt = K_{obs}C\) where \(C\) is the concentration of MB and \(K_{obs}\) is the observed first-order rate constant.\(^{[51,52]}\) Integrating this kinetic equation leads to the concentration–time equation \(\ln(C_0/C_t) = K_{obs}t\). A plot of \(\ln(C_0/C_t)\) versus time should be linear with a slope equal to the observed rate constant as shown in Figure 5.20. The normalized rate constants are all on the order of \(10^{-5}\) min\(^{-1}\) as can be seen from Table 5.2. This data supports the proposal that the photodegradation of MB by all four FeOOH polymorphs depends primarily on their surface area.

Figure 5.20: Kinetic analysis of MB degradation showing a plot of \(\ln(C_0/C_t)\) vs. time for the FeOOH polymorphs.
**Table 5.2:** Summary of first order rate constants, surface areas and normalized rate constants of the four FeOOH polymorphs.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$-FeOOH</th>
<th>$\beta$-FeOOH</th>
<th>$\gamma$-FeOOH</th>
<th>$\delta$-FeOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{obs}$ (min$^{-1}$)</td>
<td>0.0015</td>
<td>0.0008</td>
<td>0.0006</td>
<td>0.0039</td>
</tr>
<tr>
<td>Surface Area (m$^2$/g)</td>
<td>150</td>
<td>30</td>
<td>76</td>
<td>185</td>
</tr>
<tr>
<td>$K_{obs}$ normalized by SA</td>
<td>1.00000E-05</td>
<td>2.66667E-05</td>
<td>7.89474E-06</td>
<td>2.10811E-05</td>
</tr>
</tbody>
</table>

**5.8 Conclusions**

We have successfully synthesized the four known FeOOH polymorphs; goethite, akaganeite, lepidocrocite, and feroxyhyte. The structures and morphologies of these FeOOH polymorphs were defined by powder X-ray diffraction and scanning and transmission electron microscopy. A combination of XPS and diffuse reflectance optical measurements was used to analyze the electronic band properties of these polymorphs. The BET gas adsorption method was used to study their surface areas and their photocatalytic properties were tested by studying the rate and extent of methylene blue degradation. The results showed that out of the four polymorphs, the highest photocatalytic activity towards MB degradation was shown by feroxyhyte. The enhanced visible-light photocatalytic activity was mainly attributed to its larger surface area and the slightly smaller electronic band gap of feroxyhyte compared with the other three.
FeOOH polymorphs. The natural abundance of FeOOH minerals makes them interesting candidates for cleaning environmental air and water pollution.

5.9 References


Chapter 6 - Transformation of FeOOH Polymorphs to Fe$_3$O$_4$
and Their Photocatalytic Activity towards RWGS Reaction

6.1 Statement of Contributions

Dr. Mohamad Hmadeh helped with the synthesis of FeOOH polymorphs. Dr. Paul O'Brien helped with the gas-phase testing of the catalysts and optical measurements. I carried out all other synthesis, characterization, and experiments presented in this chapter. Portions of this chapter are currently being prepared for publication.

6.2 Abstract

The solar-powered chemical conversion of greenhouse gas CO$_2$ to valuable chemical fuels and feedstocks has been identified as a potential source of sustainable energy and the solution to several environmental problems. The major challenge towards making this dream a reality has always been finding very cheap, stable and non-toxic photoactive materials capable of converting CO$_2$ into chemical fuels. In this chapter, we explore the possibility of using iron-based photocatalysts to convert CO$_2$ to solar fuels. In particular, we study the \textit{in situ} transformation of four different polymorphs of iron oxyhydroxides (goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH) and feroxyhyte (δ-FeOOH)) into magnetite (Fe$_3$O$_4$). We denote α-Fe$_3$O$_4$, β-Fe$_3$O$_4$, γ-Fe$_3$O$_4$ and δ-Fe$_3$O$_4$, to represent Fe$_3$O$_4$ nanomaterials transformed from α-FeOOH, β-FeOOH, γ-FeOOH and δ-FeOOH, respectively. Several analytical techniques such as PXRD, XPS and HRTEM were employed to fully characterize and confirm the complete transformations of these FeOOH polymorphs to Fe$_3$O$_4$. The resulting Fe$_3$O$_4$ was very
active towards the reverse water gas shift (RWGS) reaction where carbon dioxide was reduced to carbon monoxide in a hydrogen environment under moderately concentrated solar-simulated irradiation (15 kW/cm²). Of the four resulting Fe₃O₄ nanoparticles, the δ-Fe₃O₄ was the most active and produced CO at a rate of 7.5 mmol·g_{cat}⁻¹·hr⁻¹. Furthermore, under a higher concentration of solar-simulated irradiation (~25 kW/cm²), the β-Fe₃O₄ underwent further transformation where it was partially reduced to metallic iron and the RWGS reaction was further enhanced to a rate of 19.2 mmol·g_{cat}⁻¹·hr⁻¹. Moreover, a small amounts of CH₄ were also produced at rates on the order of µmol·g_{cat}⁻¹·hr⁻¹ as side reaction products. The reduction of CO₂ to valuable chemicals under solar simulated light using cheap and abundant materials represents a general advancement in the field solar fuels.

6.3 Introduction

Climate change and sustainable energy sources are two of the most pressing concerns that threaten the existence of human civilization.[1] Rising global temperatures, ocean acidification and other environmental issues are a result of increased greenhouse gases, primarily, carbon dioxide emissions into the atmosphere, which will continue to rise as long as fossil fuels are the major source of energy that powers our planet.[2-4] To address these two interconnected problems, intensive research efforts are currently being devoted towards finding alternative sources of energy that can meet the demands of the growing global population without the associated environmental impacts.[5,6] It has been suggested that the conversion of CO₂ to chemical fuels and feedstocks such as methanol, carbon monoxide, methane and other hydrocarbons using solar energy not
only provides an alternative source of energy to fossil fuels but also recycles carbon sustainably.[7-12] In particular, there has been remarkable progress in the heterogeneous chemical conversion of carbon dioxide using a range of photoactive materials capable of using sunlight to drive useful chemical transformations.[13-15]

The reverse water gas shift (RWGS) reaction (CO₂ + H₂ → CO + H₂O) is an important industrial reaction. Using H₂ from a sustainable source, CO₂ can be converted into an important chemical feedstock, CO, which is an essential chemical fuel. However, this chemical reaction is mostly catalyzed by expensive rare earth metals, which renders its application unsustainable in the long run.[16,17] Moreover, less expensive catalysts developed for the RWGS reaction require high temperatures, which requires large energy input to drive the reaction.[18] Our group has demonstrated that defected In₂O₃-x(OH)y can reduce gas-phase CO₂ to CO under solar simulated light through RWGS reaction.[19,20] We were able to achieve competitive rates in the range of µmol·gcat⁻¹hr⁻¹. Despite the success in the chemical conversion of CO₂ to CO, the catalysts employed are expensive and unobtainable, which prevents the large-scale commercialization of these catalysts from providing a feasible alternative to fossil fuels. Therefore, the use of earth-abundant nanomaterials that can convert CO₂, at ambient temperatures is highly sought after and constitutes significant achievement towards a sustainable future.

One of the cheapest and most abundant materials are the iron oxides and oxyhydroxides, which have generated significant interests from different scientific disciplines ranging from geology to mineralogy to soil science and chemistry.[21] Among other applications, iron oxides and oxyhydroxides are used in catalysis. An important
industrial catalytic reaction that uses iron oxides catalysts is CO$_2$ hydrogenation via Fischer-Tropsch (FT) synthesis. FT synthesis using iron oxide catalysts usually takes place in two steps, namely the conversion of CO$_2$ to CO via RWGS and the subsequent hydrogenation of CO to form different hydrocarbons and chemicals.[22] Therefore, RWGS is an important reaction for the formation of CO which is then used in FT synthesis to produce liquid fuels. Although other catalysts such as cobalt catalysts are used for FT synthesis, iron catalysts are preferred due to the formation of olefinic hydrocarbons.[22]

CO$_2$ reduction by iron-based materials such as Fe$_3$O$_4$ nanomaterials has been hugely investigated over the years.[23, 24] Generally, Fe$_3$O$_4$ is supported on carbon nanotubes or other forms of carbon. For example, Chew et al investigated the hydrogenation of CO$_2$ using iron nanoparticles supported on oxygen-functionalized carbon nanotubes.[22] Using this catalyst, they were able to convert CO$_2$ to a number of hydrocarbons. Furthermore, Minett et al have used iron nanoparticle-carbon nanotube arrays grown on monoliths to convert CO$_2$ to different hydrocarbons.[25] The presence of magnetite and iron carbide was credited with the effective CO$_2$ hydrogenation and capability to perform Fischer Tropsch synthesis. Similarly, O'Byrne et al studied the conversion of CO$_2$ and CO conversion to hydrocarbons using bridged Fe nanoparticles on carbon nanotubes and realized very high conversion rates.[26] Likewise, Tu et al have designed carbon-encapsulated Fe$_3$O$_4$ nanocrystals capable of reducing CO$_2$ to several hydrocarbons.[27] Very recently, Gupta et al investigated the influence of composition of nanostructured iron-based carbon-coated core-shell nanocatalyst on the hydrogenation of CO$_2$.[28] In all these reports, the Fe$_3$O$_4$ catalyst is either supported or encapsulated by carbon, which
is believed to be a very important support due to its high surface area, excellent heat transfer and high thermal stability. Moreover, at high temperatures carbon coating on Fe$_3$O$_4$ forms Fe$_5$C$_2$ which is very active towards hydrogenation of carbon dioxide.

In Chapter 5, the photocatalytic activities of four different polymorphs of FeOOH towards the degradation of methylene blue (MB) dye was discussed.[29] Of the four FeOOH polymorphs, feroxyhyte exhibited the best photocatalytic properties and degraded 85% of the MB dye in five hours. In comparison, goethite, akaganeite, and lepidocrocite degraded only 40%, 35%, and 30% of the MB in five hours, respectively. Additionally, the photocatalytic activities were closely correlated to the surface area of the FeOOH polymorphs. In this chapter, we report on the transformation of FeOOH polymorphs to Fe$_3$O$_4$ and activation towards the RWGS reaction in a hydrogen environment. Interestingly, the FeOOH samples were not active towards the reduction of carbon dioxide when tested under solar-simulated irradiation at an intensity of 1 kW/cm$^2$. However, when the incident light intensity is increased to 15 kW/cm$^2$, the FeOOH polymorphs underwent a transformation to Fe$_3$O$_4$, which did exhibit very high photocatalytic activity towards the RWGS under these higher light intensities. Herein we discuss the transformation of the ironoxyhydroxide polymorphs to magnetite in detail and report on the high photocatalytic activity of the resulting magnetite towards the reduction of CO$_2$ to CO via RWGS.

The FeOOH transformation to Fe$_3$O$_4$ is performed inside a custom-built batch reactor. The FeOOH polymorphs were first deposited onto borosilicate glass microfiber filters before placing them inside the reactor, which was then pressurized with H$_2$ to 2 atm.
Concentrated solar-simulated light was then irradiated on the samples for one hour which led to the complete transformation of FeOOH polymorphs to Fe$_3$O$_4$. The resulting Fe$_3$O$_4$ was characterized with PXRD, HRTEM and XPS. These characterization techniques revealed that all four FeOOH polymorphs underwent complete transformation to magnetite inside the reactor under the concentrated solar simulated light in the presence of H$_2$. After the sample transformations to Fe$_3$O$_4$, their photocatalytic activity towards carbon dioxide reduction via RWGS reaction was investigated. All of the Fe$_3$O$_4$ samples transformed from the FeOOH polymorphs were very active catalyst towards the conversion of CO$_2$ to CO at very high rates in the range of mmol·g$_{cat}$·hr$^{-1}$.

6.4 Experimental Procedure

6.4.1 Synthesis of FeOOH nanomaterials

The synthesis of all four polymorphs of FeOOH materials are clearly described in Chapter 5 and briefly stated here. Both α-FeOOH and β-FeOOH were synthesized by a hydrothermal techniques. Fe$_2$(SO$_4$)$_3$ was used as the precursor for the α-FeOOH synthesis whereas FeCl$_3$ was used as the source of Fe for the β-FeOOH. The γ-FeOOH is synthesized through the slow oxidation of Fe$^{2+}$ at a neutral pH using FeCl$_2$.4H$_2$O as the Fe source. The synthesis of δ-FeOOH was achieved through the rapid oxidation of Fe$^{2+}$ with H$_2$O$_2$ using FeSO$_4$(NH$_4$)$_2$SO$_4$.6H$_2$O as the source of Fe.

6.4.2 Transformation of FeOOH nanomaterials to Fe$_3$O$_4$
The transformation of FeOOH into Fe₃O₄ was performed inside a custom-built batch reactor (See Figure 6.1).

![Custom built batch reactor used to perform photocatalytic measurements.](image)

**Figure 6.1:** Custom built batch reactor used to perform photocatalytic measurements.

The stainless steel batch reactor has a volume of 12 mL and a fused silica view port sealed with Viton O-rings. The FeOOH samples were first deposited on borosilicate glass microfiber filters prior to being loaded into the reactor. In short, a small portion of FeOOH powder was dissolved in water and sonicated to break up the particle clumps and generate fine nanoparticles. Vacuum filtration was used to deposit the FeOOH
nanoparticles on the borosilicate glass microfiber filters and the samples were dried in an oven heated to 40 °C. The weight of the borosilicate glass microfiber filters were recorded before and after the sample deposition to determine the exact weight of the photocatalyst. The samples were then transferred into the batch reactor. The reactor was pressurized with H₂ gas up to 2 atm. Subsequently, high intensity solar simulated light from a 300 W Xe lamp (Newport) was concentrated to 15 kW/cm² and irradiated on the samples for one hour. Under the solar simulated light, the brown/orange FeOOH polymorphs turned grey/dark at the center of the spot where light is incident onto the sample displaying the transformation of FeOOH to Fe₃O₄ at the high temperatures created by the concentrated solar simulated light. The spot size under illumination was about 1 cm in diameter. Alternatively, the FeOOH samples deposited on the borosilicate glass microfiber filters can be transformed to Fe₃O₄ by simply placing them in a tube furnace filled with H₂ gas and heated to ~250 °C. Then the samples are transferred into the batch reactor where the RWGS reaction rates were measured.

6.4.3 Photocatalytic gas-phase measurements

Custom-built batch reactor (see Figure 6.1) was used to perform the gas-phase photoreduction of CO₂. During the gas-phase photocatalytic rate measurements, the reactor was purged with H₂ for twenty minutes prior to being infiltrated with CO₂ and H₂ at a H₂:CO₂ ratio of 4:1. For the irradiated samples, the lamp was turned on once the reactor valves were closed. The pressure inside the reactor was monitored using an Omega PX309 pressure transducer. The duration of all runs was 30 minutes. Product gases were analyzed with a flame ionization detector (FID) and thermal conductivity
detector (TCD) installed in a SRI-8610 Gas Chromatograph (GC) with a 3’ Mole Sieve 13a and 6’ Haysep D column. The spectral output was measured using a StellarNet Inc spectrophotometer and the power of the incident irradiation was measured using a Spectra-Physics power meter (model 407A). The dimensions of the test samples were 1 cm x 1 cm.

6.4.4 **Analytical methods for the characterization of the photocatalysts**

Powder X-ray diffraction (PXRD) patterns of all the FeOOH polymorphs and the resulting Fe$_3$O$_4$ from the *in situ* transformation of FeOOH to Fe$_3$O$_4$ were recorded and identified with a Bruker D2 phaser instrument, using Cu-$\text{K}_\alpha$ radiation at 30 kV. High-resolution environmental transmission electron microscopy (HRTEM) was used to further study the crystalline samples. In particular, Hitachi H-3300 TEM, working at an operating voltage of 300 KV, was used to image the samples. X-ray photoelectron spectroscopy (XPS) measurements were carried out to study the surface and the electronic structure of the samples. XPS was performed in an ultrahigh vacuum chamber with base pressure of 10$^{-9}$ mTorr. Thermo Scientific K-Alpha XPS spectrometer was used with an Al K$_\alpha$ X-ray source operating at 15 kV, 27 A and X-ray energy of 1486.7 eV. The spectra were obtained with analyzer pass energy of 50 eV with energy spacing of 0.1 eV. All data analysis was carried out using Thermo Scientific Avantage software.

6.5 **Comprehensive study of the transformation of FeOOH polymorphs into Fe$_3$O$_4$**
The synthesis and characterization of all four polymorphs of FeOOH has been previously reported in Chapter 5.[29] We carefully studied the transformation of FeOOH polymorphs to Fe$_3$O$_4$ using a variety of analytic techniques such as PXRD, TEM and XPS. We first recorded the PXRD of all four the α-Fe$_3$O$_4$, β-Fe$_3$O$_4$, γ-Fe$_3$O$_4$ and δ-Fe$_3$O$_4$ samples. This data is presented in Figure 6.2a-d.

![Figure 6.2](image)

**Figure 6.2**: PXRD of (a) α-Fe$_3$O$_4$, (b) β-Fe$_3$O$_4$, (c) δ-Fe$_3$O$_4$, (d) γ-Fe$_3$O$_4$ and (e) commercial Fe$_3$O$_4$ sample for comparison. Here α-Fe$_3$O$_4$, β-Fe$_3$O$_4$, γ-Fe$_3$O$_4$ and δ-Fe$_3$O$_4$, are Fe$_3$O$_4$ nanomaterials transformed from α-FeOOH, β-FeOOH, γ-FeOOH and δ-FeOOH respectively.

**Figure 6.2e** shows the PXRD spectrum of a commercial magnetite sample for comparison. As it can be seen from Figure 6.2, the PXRD patterns of the α-Fe$_3$O$_4$, β-
Fe₃O₄, γ-Fe₃O₄ and δ-Fe₃O₄ samples are identical to the commercial Fe₃O₄ sample and to that obtained from the database (COD 1010369 Fe₃O₄). The diffraction planes that are mostly visible in the pattern include (311), (400), (511) and (440). The fact that there are no additional peaks that are present in the PXRD pattern confirms the purity of the obtained phase and therefore the complete transformation of the FeOOH polymorphs to magnetite. Furthermore, we performed high-resolution TEM imaging of the α-Fe₃O₄, β-Fe₃O₄, γ-Fe₃O₄ and δ-Fe₃O₄ samples. Figure 6.3 shows HRTEM images of all FeOOH polymorphs and the corresponding Fe₃O₄ obtained after the transformation. Figures 6.3a, 6.3d, 6.3g and 6.3j show the as synthesized goethite, akaganeite, lepidocrocite and feroxyhyte nanoparticles, respectively. Goethite has a nanorod shape, akaganeite exhibits a grainy, rice-like morphology, and lepidocrocite is lath-like while the feroxyhyte has thin plate-shaped crystal morphology. Figures 6.3b and 6.3c show α-Fe₃O₄ nanoparticles while Figures 6.3e and 6.3f show the β-Fe₃O₄ nanoparticles. Moreover, Figures 6.3h and 6.3i show γ-Fe₃O₄ nanoparticles and Figures 6.3k and 6.3l show δ-Fe₃O₄ nanoparticles. In all cases, the shape and morphology of the resulting Fe₃O₄ nanomaterial is different from the starting FeOOH material, although the general appearance has not significantly changed. The Fe₃O₄ samples look more porous than the starting FeOOH material mainly due to dehydration causing the structural rearrangement of the iron and the oxygen atoms in the lattice structure of the materials. Additionally, we performed selected area diffraction (SAED) measurements of the Fe₃O₄ samples shown in Figure 6.3 and the results are presented in Figure 6.4, which shows the SAED of Fe₃O₄ transformed from the four different FeOOH polymorphs.
Figure 6.3: TEM images of FeOOH and Fe$_3$O$_4$ samples. (a) $\alpha$-FeOOH (b, c) $\alpha$-Fe$_3$O$_4$ (d) $\beta$-FeOOH (e, f) $\beta$-Fe$_3$O$_4$ (g) $\gamma$-FeOOH (h, i) $\gamma$-Fe$_3$O$_4$ (j) $\delta$-FeOOH (k, l) $\delta$-Fe$_3$O$_4$. 
Figure 6.4: SAED of (a) α-Fe₃O₄ (b) β-Fe₃O₄ (c) γ-Fe₃O₄ and (d) δ-Fe₃O₄. Here α-Fe₃O₄, β-Fe₃O₄, γ-Fe₃O₄ and δ-Fe₃O₄ represent Fe₃O₄ nanomaterials transformed from α-FeOOH, β-FeOOH, γ-FeOOH and δ-FeOOH respectively.
Table 6.1 summarizes the inter-planar d-spacing and the corresponding diffraction planes that match the diffraction planes of Fe₃O₄ and confirm the formation of the Fe₃O₄ samples from the different FeOOH polymorphs.

**Table 6.1:** Electron diffraction planes and the corresponding inter-planar d-spacing of different planes of Fe₃O₄ transformed from FeOOH polymorphs.

<table>
<thead>
<tr>
<th>Planes</th>
<th>d-spacing of α-Fe₃O₄ (nm)</th>
<th>d-spacing of β-Fe₃O₄ (nm)</th>
<th>d-spacing of γ-Fe₃O₄ (nm)</th>
<th>d-spacing of δ-Fe₃O₄ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>-</td>
<td>0.486</td>
<td>0.487</td>
<td>-</td>
</tr>
<tr>
<td>(220)</td>
<td>0.298</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(222)</td>
<td>-</td>
<td>-</td>
<td>0.244</td>
<td>0.242</td>
</tr>
<tr>
<td>(311)</td>
<td>0.258</td>
<td>0.252</td>
<td>-</td>
<td>0.253</td>
</tr>
<tr>
<td>(422)</td>
<td>-</td>
<td>0.169</td>
<td>-</td>
<td>0.171</td>
</tr>
<tr>
<td>(511)</td>
<td>-</td>
<td>-</td>
<td>0.162</td>
<td>-</td>
</tr>
<tr>
<td>(533)</td>
<td>0.124</td>
<td>0.127</td>
<td>0.128</td>
<td>0.124</td>
</tr>
<tr>
<td>(731)</td>
<td>0.111</td>
<td>0.111</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(751)</td>
<td>-</td>
<td>-</td>
<td>0.097</td>
<td>-</td>
</tr>
<tr>
<td>(800)</td>
<td>0.106</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(951)</td>
<td>0.080</td>
<td>0.082</td>
<td>0.082</td>
<td>0.081</td>
</tr>
</tbody>
</table>
In addition to PXRD and TEM, we employed XPS to further characterize our samples and unequivocally confirm the transformation of FeOOH to Fe$_3$O$_4$. The most commonly studied photoemission peaks of iron oxides are the Fe2p and O1s peaks. **Figure 6.5** shows the Fe2p and O1s photoemission peaks from the XPS spectra for the four Fe$_3$O$_4$ samples transformed from the FeOOH polymorphs. For comparison, the Fe2p and O1s photoemission peaks of the four FeOOH polymorphs are shown in **Figure 6.6**. It is well known that one of the most distinctive features that distinguishes Fe$_3$O$_4$ from other iron oxides is the appearance of a shoulder peak at 708 – 709 eV in the Fe2p peak.$^{[30]}$ This shoulder peak, which is absent in other iron oxides, is clearly observed in our Fe$_3$O$_4$ samples and indicates the formation of Fe$^{2+}$ in Fe$_3$O$_4$ (**Figures 6.5 a-d**). Another known XPS feature confirming the structural change to Fe$_3$O$_4$ is the disappearance of the Fe2p$^{3/2}$ satellite peak at 719 - 720 eV, which is present in all FeOOH polymorphs (see Fe2p spectra **Figure 6.6**). This satellite peak becomes less resolved or completely disappears in Fe$_3$O$_4$ (**Figure 6.5**). The O1s spectra were very important in order to confirm the complete transformation process because one of the most telling signs of the formation to Fe$_3$O$_4$ is apparent in the O1s peak. Indeed, the hydroxyl peak (~531.5 eV) was the dominant peak in the FeOOH material (see O1s spectra in **Figure 6.6**). However, after the transformation, the oxygen peak (~530.5 eV) became more pronounced, indicating the formation of Fe$_3$O$_4$ (see **Figure 6.5**). In addition, the appearance of the peak at 0.83 eV in the valence spectrum demonstrates the formation of Fe$^{2+}$ due to the formation of Fe$_3$O$_4$. This peak is absent for all of the FeOOH polymorphs (See **Figure 6.7**).
Figure 6.5: XPS spectra of Fe2p and O1s photoemission peaks of Fe₃O₄ transformed from FeOOH showing Fe2p of (a) α-Fe₃O₄ (b) β-Fe₃O₄ (c) γ-Fe₃O₄ and (d) δ-Fe₃O₄ and the O1s (e) α-Fe₃O₄ (f) β-Fe₃O₄ (g) γ-Fe₃O₄ and (h) δ-Fe₃O₄.
Figure 6.6: XPS spectra of Fe2p and O1s photoemission peaks of FeOOH showing Fe2p of (a) α-FeOOH (b) β-FeOOH (c) γ-FeOOH (d) δ-FeOOH and the O1s (e) α-FeOOH (f) β-FeOOH (g) γ-FeOOH (h) δ-FeOOH.
Figure 6.7: The valence band spectra of (a) α-Fe₃O₄ (b) β-Fe₃O₄ (c) γ-Fe₃O₄ and (d) δ-Fe₃O₄ (e) α-FeOOH (f) β-FeOOH (g) γ-FeOOH (h) δ-FeOOH.

The PXRD, HRTEM and XPS data unequivocally confirm the full transformation of FeOOH polymorphs to Fe₃O₄. In addition, thermal transformation of iron oxides and oxyhydroxides are well studied in the literature.⁴¹,⁴² When heated in a hydrogen
environment, FeOOH polymorphs undergo several transformations from one iron oxide to another until it is finally reduced to metallic iron (α-Fe).\textsuperscript{[33]} Upon heating at relatively low temperatures (200-300 °C) in a hydrogen environment, FeOOH is first dehydrated by losing water molecules in its structure and transforms to α-Fe\textsubscript{2}O\textsubscript{3} which is further reduced to Fe\textsubscript{3}O\textsubscript{4}.\textsuperscript{[34]} At higher temperatures (above 350 °C) further transformation to FeO and metallic α-Fe is observed.\textsuperscript{[33]}

The amount of hydrogen exposed to the samples dictates the rate and the temperature of the transformation.\textsuperscript{[35]} For example, in pure 100% hydrogen environment, the transformation is relatively fast and takes place at lower temperatures compared to 5% hydrogen or without any hydrogen.

6.6 Activation of RWGS reaction over Fe\textsubscript{3}O\textsubscript{4} transformed from FeOOH polymorphs

Having thoroughly characterized and confirmed the complete transformation of FeOOH to Fe\textsubscript{3}O\textsubscript{4}, we measured the photocatalytic activity towards carbon dioxide reduction. This was achieved by measuring the extent of gas-phase CO\textsubscript{2} conversion in a hydrogen environment. The details of the testing is described in the experimental section. Although a very small amount of methane was produced, the major product of the reaction measured was carbon monoxide. The RWGS reaction rates of all the samples were measured as presented in Figure 6.8. Under solar simulated light of ~15 kW/cm\textsuperscript{2}, all four Fe\textsubscript{3}O\textsubscript{4} samples showed very high rates of CO production in the order of mmol·g\textsubscript{cat}\textsuperscript{-1}·hr\textsuperscript{-1}. These rates are significantly higher than the solar powered CO\textsubscript{2} reduction rates over iron oxide photocatalysts reported in the literature.\textsuperscript{[36]} Comparing
the activities of the four samples, it can be seen from Figure 6.8 that $\delta$-Fe$_3$O$_4$ is the most active catalyst towards the RWGS reaction with CO production rates of 7.5 mmol·g$_{cat}^{-1}$.hr$^{-1}$.

![Figure 6.8](image)

**Figure 6.8**: (a) Comparison of CO production rates of Fe$_3$O$_4$ photocatalysts under solar simulated irradiation of ~15 kW/cm$^2$. Here $\alpha$-Fe$_3$O$_4$, $\beta$-Fe$_3$O$_4$, $\gamma$-Fe$_3$O$_4$ and $\delta$-Fe$_3$O$_4$ represent Fe$_3$O$_4$ nanomaterials transformed from $\alpha$-FeOOH, $\beta$-FeOOH, $\gamma$-FeOOH and $\delta$-FeOOH respectively.

The $\alpha$-Fe$_3$O$_4$ produces CO at a rate of 3.1 mmol·g$_{cat}^{-1}$.hr$^{-1}$ while $\gamma$-Fe$_3$O$_4$ and $\beta$-Fe$_3$O$_4$ produced CO at a rate of 2.1 and 0.35 mmol·g$_{cat}^{-1}$.hr$^{-1}$, respectively. Interestingly, a similar photocatalytic trends were observed when the FeOOH polymorphs were employed in the degradation of methylene blue dye.$^{[29]}$ As noted in Chapter 5, the $\delta$-FeOOH was the most active catalyst and the $\beta$-FeOOH was the least active catalyst.
The major difference between the polymorphs was the surface area. Since the δ-FeOOH had the largest surface area, it was the most active but when the rates were normalized to their surface area, similar rates resulted. Since there is no major morphology change with the transformation of FeOOH to Fe₃O₄, we expect the difference in the rates is due to the difference in the surface area between the four materials.

Fe₃O₄ activates the conversion of CO₂ to CO by a photothermal process where photon energy is converted into heat energy which subsequently activates the RWGS reaction. The temperature profiles of the four samples during the testing were therefore monitored. The results are shown in Figure 6.9.

**Figure 6.9:** Temperature profiles of the four Fe₃O₄ photocatalysts recorded during the testing under high solar simulated illumination of ~15 kW/cm².
Each test was run for a period of about half an hour. As shown in Figure 6.9, once the light was turned on, the temperature rises rapidly and remains fairly constant throughout the testing time and drops off once the high intensity lamp was turned off. Other than the δ-Fe₃O₄ sample, which could only reach an average temperature of 180 °C, the three other samples could reach temperatures well over 250 °C, which activated the RWGS reaction. We expected the δ-Fe₃O₄ sample to reach very high temperatures because it was the most active photothermal catalyst but interestingly it showed the lowest temperature profile among all the four samples. A closer look inside the reactor however revealed that a dense cloud of water vapor was formed on the walls of the reactor. The water, which is a product of the RWGS reaction can be clearly seen on the quartz window of the reactor circled in green in Figure 6.10. This water condensate lowered the temperature reading of the thermocouple although the local temperature of the sample could be significantly higher. Additionally, the FeOOH transformation tests done in the tube furnace revealed that the FeOOH samples didn’t transform to Fe₃O₄ below 250 °C indicating that the temperature of the sample must be higher than 180 °C. Moreover, it should be noted that the temperature profiles of the samples recorded during the testing is only an approximation and may not represent the local temperature of the catalyst. This is partly because the borosilicate glass filter paper used to deposit the samples is not conductive and doesn’t transfer heat effectively to the thermocouple. Nevertheless, it gives a fairly rough estimate of the sample temperatures during the testing. The majority of the reported products from the photoreduction of CO₂ originate from carbon contamination from residual carbon deposited on the catalyst or even from inside the reactor.[38]
Figure 6.10: (a) Batch reactor used to test the RWGS reaction. The top corner of the reactor, circled in green, shows the water condensate observed during the testing of the δ-Fe₃O₄ sample. (b) Higher magnification picture of the batch reactor.

To ensure that the produced CO in our reactor is generated from the reactant CO₂ and not from adventitious carbon sources, which is comprised of the abundant naturally occurring C-12 isotope, we used C-13 labelled CO₂ as our reactant gas for all our tests. The products collected from the reactor confirmed the formation of ¹³CO products. Figure 6.11 shows the GC-MS spectra showing the 29 amu mass fragment for Fe₃O₄ samples, which confirm the production of ¹³CO. The N₂ peak shown in Figure 6.11 is a result of residual air in the transfer line between the photoreactor and inlet to the GC-MS. Several attempts were made to minimize it thorough evacuation of the lines with vacuum pump but this peak did not disappear from the GC-MS. The base pressure of the pump used to evacuate the lines is ~50 mTorr. The use of a better pump would reduce or eliminate the N₂ peak. Furthermore, the dependence of the RWGS reaction
rate on the incident light intensity was investigated by increasing the solar simulated light intensity from 15 kW/cm² to 25 kW/cm² and the rate of $^{13}$CO formation was measured for all samples.

![Figure 6.11](image)

**Figure 6.11**: GC-MS spectra at 29 amu of (a) α-Fe$_3$O$_4$ (b) β-Fe$_3$O$_4$ (c) γ-Fe$_3$O$_4$ and (d) δ-Fe$_3$O$_4$ under ~15 kW/cm² of illumination.

The RWGS reaction rates of the β-Fe$_3$O$_4$ increased from 0.35 mmol·g$_{cat}^{-1}$·hr$^{-1}$ to ~ 19.2 mmol·g$_{cat}^{-1}$·hr$^{-1}$, whereas there was no significant change in the reaction rates of the other three catalysts. The origin of the increased RWGS reaction rate over β-Fe$_3$O$_4$ at
higher light intensities was investigated and carefully examined. By visual inspection, the centre of $\beta$-$\text{Fe}_3\text{O}_4$ sample, where the light intensity was very high and centered, the sample was much darker, suggesting that the sample may have undergone further transformation (See Figure 6.12a). We performed PXRD on the centre spot of $\beta$-$\text{Fe}_3\text{O}_4$ sample as shown in Figure 6.12b and the diffraction planes of $\beta$-$\text{Fe}_3\text{O}_4$ shown in Figure 6.2b disappeared and the material looks amorphous (denoted as a-$\beta$-$\text{Fe}_3\text{O}_4$ to represent amorphous $\beta$-$\text{Fe}_3\text{O}_4$). Further characterization was performed using TEM. Figure 6.12c shows a TEM image of a-$\beta$-$\text{Fe}_3\text{O}_4$. The sample doesn’t show any lattice fringes compared to the crystalline $\beta$-$\text{Fe}_3\text{O}_4$ shown in Figure 6.3f. Moreover, the SAED shown in Figure 6.12d doesn’t show diffraction spots like other $\text{Fe}_3\text{O}_4$ samples but rather shows a ring, which is characteristic of non-crystalline structures. Due to the difficulty of identifying non-crystalline materials with PXRD and TEM, we performed XPS in order to further characterize the structure of the obtained phase. Figure 6.13a shows the survey spectrum of a-$\beta$-$\text{Fe}_3\text{O}_4$ and Figure 6.13b is the survey spectrum $\beta$-$\text{Fe}_3\text{O}_4$ sample. The prominent feature of the survey spectrum of a-$\beta$-$\text{Fe}_3\text{O}_4$ is the C1s peak but the $\beta$-$\text{Fe}_3\text{O}_4$ sample has several visible features including the photoemission peaks of iron, oxygen and carbon (See Figure 6.13b). High resolution scans of other photoemission peaks of a-$\beta$-$\text{Fe}_3\text{O}_4$ sample revealed the presence of a small amount of Fe2p and O1s peak as shown in Figure 6.13c and Figure 6.13d respectively. A closer look at the Fe2p peak in Figure 6.13c shows the two major peaks located at 711 eV and 725 eV are assigned to $\text{Fe}^{3+}$ 2p$_{3/2}$ and $\text{Fe}^{3+}$ 2p$_{1/2}$ of iron oxide respectively but there is an additional peak at 706.8 eV which is assigned to metallic iron.
Figure 6.12: (a) Pictures of the $\beta$-Fe$_3$O$_4$ sample (outer grey spots) and $a$-$\beta$-Fe$_3$O$_4$ sample (inner ultra-black spot), (b) PXRD of $a$-$\beta$-Fe$_3$O$_4$ sample, (c) TEM image of $a$-$\beta$-Fe$_3$O$_4$ sample, and (d) SAED of $a$-$\beta$-Fe$_3$O$_4$ sample.
Figure 6.13: (a) Comparison of survey spectrum of (a) a-β-Fe₃O₄ sample and (b) β-Fe₃O₄ sample. (c) Fe2p of a-β-Fe₃O₄ sample (d) O1s of a-β-Fe₃O₄ sample.

There is no major change with the O1s peak of a-β-Fe₃O₄ sample and appears similar to the other O1s peaks of Fe₃O₄. Therefore, under the high temperatures resulting from the high intensity light and in the presence of reductive hydrogen environment, it is conceivable that some of the Fe₃O₄ is reduced to metallic iron which is known to become a very active catalyst towards RWGS reaction as well as Fischer-Tropsch synthesis.[34] During the reaction, as the concentration of the CO products build up, it disproportionates and forms carbon which is chemisorbed on the catalytically active metallic sites. Over time, large deposits of carbon are formed which form multilayers and covers the entire catalytic surface leading to the deactivation of the catalyst.[39] This
large carbon deposit is evident from the survey spectrum in Figure 6.13a and explains why the Fe2p and O1s of the α-β-Fe₃O₄ are not prominent in the structure that it is covered by huge deposits of carbon layers.

### 6.7 Gas-phase flow experiment

In all the previous tests performed a batch reactor was used for testing the gas-phase reduction of CO₂. However, several issues related to the use of batch reactors have to be addressed. These include the accumulation of product in the reactor chamber and the carbon deposition on the surface of the catalysts leading to its deactivation. In order to overcome these problems, a flow reactor was used and some preliminary tests on the CO₂ reduction capacity of some of our samples were performed.

*Figure 6.14: Flow reactor set up used for measuring RWGS reaction rates.*
In particular, we tested the δ-Fe₃O₄ sample using gas-phase flow reactor. The reaction was carried out in the system depicted in Figure 6.14. The δ-Fe₃O₄ catalyst was placed in a quartz tube and immobilized with glass fiber plugs on both ends. The quartz tube had an inner diameter of 2 mm and a wall thickness of 1 mm. A copper block with a cartridge heater inserted inside was positioned underneath the quartz tube as the heating source. Temperature was controlled by an Omega temperature controller connected to a K-type thermocouple inserted into the quartz tube and in contact with the catalyst. The pressure on the inlet and outlet were monitored by digital pressure detectors and gas flows were controlled by Aalborg digital flow controllers. The products were analyzed by an Agilent 5977 mass spec detector. A 120 W Newport Xe arc lamp was positioned above the catalyst plug for experiments under illumination.

The flow rate employed was 2 + 2 mL/min H₂ and CO₂ and a mass of 43 mg of the sample was used. The δ-FeOOH was first reduced in the tube furnace at 250 °C in 5% H₂ gas before performing the gas-phase CO₂ reduction flow experiments. The sample was tested under different temperatures from 100 °C to 300 °C. The results showed that CO was not detected below 250 °C. The rate of CO formation increased gradually with increasing temperatures from 250 °C to 300 °C. We therefore decided to carry out the flow experiments at 300 °C. The tests were performed both in the dark and under low intensity solar simulated irradiation (1 kW/cm²). The rate of the RWGS reaction of the δ-Fe₃O₄ sample in the flow reactor was compared to that of the batch reactor. The rate in the flow tests was almost twice that of the batch reactor when normalized with the light intensity. This was expected because in the flow experiments, the products are constantly being removed and the active sites are available for further reaction.
Furthermore, there was enhancement in the rate of RWGS reaction with light compared
to the dark tests. That is, the tests carried out at 300 °C under low intensity solar
irradiation of 1 kW/cm² from the 120 W Newport Xe arc lamp was higher than that
carried out in the dark at 300 °C.

6.8 Conclusions

In this chapter, we studied the transformation of four different polymorphs of iron
oxyhydroxide nanomaterials into magnetite. Various analytical tools such as powder X-
ray diffraction (PXRD), high-resolution transmission electron microscope (HRTEM) and
X-ray photoemission spectroscopy (XPS) were used to investigate these in situ
transformations. Additionally, we investigated the photocatalytic activities of these Fe₃O₄
nanomaterials towards RWGS reaction using custom-built batch reactor. Of the four
magnetite nanomaterials, δ-Fe₃O₄ was the most active photocatalyst and produced CO
at a rate of 7.5 mmol·g_cat⁻¹·hr⁻¹. Furthermore, high intensity solar simulated irradiation
studies revealed further partial reduction of β-Fe₃O₄ to metallic iron, which was super
active towards the activation of RWGS reaction at a rate of 19.2 mmol·g_cat⁻¹·hr⁻¹. We
also performed preliminary tests using flow reactor to measure the rate of RWGS
reaction of the δ-Fe₃O₄ sample and the rates of CO production was significantly
enhanced.

6.9 References

1. G. A. Olah, G. K. S. Prakash, A. Goeppert, Anthropogenic Chemical Carbon Cycle


7. Y. Izumi, Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond, Coord. Chem. Rev. 2013, 257, 171.


Chapter 7 - Conclusions and Future Work

7.1 Conclusions

The work described in this thesis demonstrates that earth abundant, low cost nanomaterials can be used to harvest both light and heat energy from the sun to reduce carbon dioxide and generate solar fuels. These carbon based chemical fuels have the potential to one day replace fossil fuels and offer a promising solution towards solving the interrelated energy and climate change crisis.[1-4] The use of these earth abundant nanomaterials based on silicon and iron allows for large scale production of solar fuels which can be generated in an industrial scale. In chapter 2 we have shown that black silicon nanowire is an effective catalytic support for Ru nanoparticles to drive gas-phase photomethanation of CO$_2$ in hydrogen environment producing methane at a very technologically significant rate. We have also shown that the Sabatier reaction could be activated both thermochemically and photochemically where both heat and incident photons absorbed by the black silicon nanowires accelerate the photomethanation reaction. Using this black silicon nanowires we have achieved a very high photomethanation rates using visible and near infrared photons to activate Sabatier reaction. Furthermore, we have shown in chapter 3 that the Sabatier reaction can further be enhanced by an order of magnitude when highly dispersed nanocrystalline RuO$_2$ is deposited on black silicon nanowire support. The enhanced reaction rate is due to the large surface area provided by the very small RuO$_2$ nanoparticles deposited using liquid-phase deposition technique that allows the formation of an intimate contact between the RuO$_2$ nanoparticles and the black silicon nanowires. The key to this
enhanced photomethanation rates is excellent absorption strengths and low reflective losses of the high surface area black silicon nanowire supports that is able to absorb over 80% across the entire solar spectral wavelength range of the ultraviolet, visible and near-infrared portion of the solar spectrum.

Moreover, we have demonstrated in chapter 4 that the enhancement of the Sabatier reaction is not limited to silicon nanowire supports but rather can be extended to other silicon nanostructured supports. In this context we have shown that three-dimensional silicon photonic crystal can be used as a photocatalytic support for RuO₂ nanoparticles that can activate the hydrogenation of CO₂. The unique light trapping ability of silicon photonic crystals allowed the enhancement of photomethanation rates through photothermal effect and enhanced light scattering that is evident in the periodic structures of the silicon photonic crystals. In order to understand how the photogenerated charges generated in the silicon and transferred to the RuO₂ accelerated the Sabatier reaction, we conducted DFT calculations to explore the interaction of reactant gases CO₂ and H₂ with the catalyst. In this case we modelled charged RuO₂ surfaces by adding extra electron [(Ru(0001))⁻¹ and hole [(Ru(0001))⁺¹ on RuO₂ (110) surface (the most common surface). The results from the DFT studies suggest that H₂ splits on the surface of the RuO₂ to form hydroxyl groups on the RO₂ surface, which then interact with the CO₂ to form intermediates, which ultimately lead to the formation of CH₄.

In chapter 5, we synthesized four different polymorphs of nanostructured iron oxyhydroxides and characterized them extensively using PXD, XPS, BET and electron
microscopy. We then did a comprehensive comparative study of the physical, electronic, and photocatalytic properties of these FeOOH polymorphs by studying the rate and extent of methylene blue photodegradation. The results showed that out of the four polymorphs, the highest photocatalytic activity towards MB degradation was shown by feroxyhyte followed by goethite, akaganeite, and lepidocrocite in that order. We concluded that the rate of MB degradation related mainly to the surface area of the FeOOH polymorphs more than any other factor we have studied.

In chapter 6 we transformed these four nanostructured iron oxyhydroxides to magnetite and investigated the photocatalytic activities of the resulting magnetite nanostructures towards reverse water gas shift reaction. Of all the four resulting magnetite nanoparticles, those transformed from δ-FeOOH were the most active and produced CO at a rate of 7.5 mmol·g\textsubscript{cat}⁻¹·hr⁻¹ under solar simulated light intensity of 15 suns. Furthermore, when the incident solar simulated light intensity was increased to ~25 suns, the Fe\textsubscript{3}O\textsubscript{4} transformed from β-FeOOH underwent further transformation where it was partially reduced to metallic iron and the RWGS reaction rate was further enhanced to a rate of 19.2 mmol·g\textsubscript{cat}⁻¹·hr⁻¹.

### 7.2 Future Work

Despite the tremendous advances made in the field of solar fuels over the last couple of decades there is still a lot of work to be done as the field grows from laboratory scale to commercial large scale production. We have achieved remarkable success in greatly enhancing photomethanation rates of gas-phase CO\textsubscript{2} using variety of silicon supports for ruthenium based catalysts which are traditionally used as a thermal catalysts that
drive Sabatier reaction at elevated temperatures and at an inefficient reaction conditions. Despite these successes, there remain a lot of questions regarding how photoexcited charge carriers in the silicon are transferred to the ruthenium and its interaction with reactant gases CO\textsubscript{2} and H\textsubscript{2}. We employed DFT simulations to understand preliminary details of interaction between the reactant gases and catalysts but these simulations are done at absolute zero which is not the ideal representation of the status of the catalyst during the reaction. The details of the reaction mechanism including the reaction intermediates has to be sorted out in order to understand how the light driven Sabatier reaction is enhanced under these conditions.

Additionally, while metallic ruthenium is very well studied for methanation of gas-phase CO\textsubscript{2} reaction in the literature, very little is known about the methanation details of nanocrystalline RuO\textsubscript{2}.\textsuperscript{[5-7]} Using ambient-pressure X-ray photoemission spectroscopy, recent reports have suggested that in hydrogen environment, the active state of the RuO\textsubscript{2} is indeed metallic in nature and that the RuO\textsubscript{2} nanoparticles in the range of 2-5 nm are greatly reduced to metallic Ru under these reaction conditions.\textsuperscript{[8]} Because our RuO\textsubscript{2} nanoparticles have similar sizes, we would like to verify the active state of the catalyst using \textit{in situ} ambient pressure X-ray photoemission spectroscopy.

7.3 References


Appendix A: Photomethanation of CO$_2$ over Ni/Silicon Nanowires

Although a very small amount of ruthenium catalyst is used in our experiments described in chapters 2-4, nonetheless it is an expensive rare earth metal and not an ideal catalyst for large scale photomethanation of CO$_2$. In light of this, we sought to use an alternative cheaper metal that is capable of activating Sabatier reaction. Nickel and rhodium are the most commonly used catalyst besides ruthenium for thermal activation of Sabatier reaction.[1-7] Therefore, we sought to deposit nickel nanoparticles on silicon nanowires using liquid phase deposition technique similar to the one used for ncRuO$_2$ deposition as described in chapter 3 and 4. SEM images of the nickel nanoparticles deposited on the silicon nanowires are shown in Figure A.1. Different amounts of nickel nanoparticles were deposited on the black silicon nanowires support. In particular, the nickel nanoparticles were deposited on the silicon nanowires for 15, 30, and 120 minutes as shown in Figure A.1a, b and c respectively. As can be seen from Figure A.1, both the nickel coverage and the size of the nickel nanoparticles deposited on the silicon nanowires increased with deposition time. In addition, we deposited the nickel nanoparticles on the silicon nanowires for 120 minutes but increased the concentration of the nickel precursor by five times as can be seen in Figure A.1d. The rate of methane production by each of the four samples was then measured. While each sample produced methane, the highest rate was observed for the sample where nickel nanoparticles were deposited for 30 minutes (Figure A.1b). It should be mentioned that a very small amount of carbon monoxide was produced as a side product by each
sample. A series of alternating light and dark tests were performed using the 30 minute nickel deposition sample and the rate of photomethanation of this sample is measured and plotted in Figure A.2. Except for Test 1 (T1), the rates of methane produced under illumination was higher or almost the same as the ones produced in the dark.

**Figure A.1.** SEM micrograph of nickel nanoparticles deposition on black silicon nanowires support at different loading conditions (a) 15 minutes (b) 30 minutes (c) 120 minutes and (d) 120 minutes at X5 the concentration of the regular deposition concentration.
It should be noted that isotope tracing experiments performed using $^{13}\text{CO}_2$ confirmed that the products came from the photoreduction of CO$_2$ rather than adventitious carbon sources. However, there was a general trend of decrease in the rate of methane formation after several tests indicating that the sample deactivated with time. There are a variety of ways nickel-based catalysts get deactivated including carbon deposition, sulphur poisoning, nickel oxide passivation and sintering. $^{[8-10]}$

![Figure A.2: Rate of photomethanation under alternating light and dark tests performed on nickel deposited on black silicon nanowires from the sample shown in Figure A.1b.](image)

In an attempt to solve the deactivation process, the nickel deposition technique was modified and we were able to deposit a nickel film instead of nickel nanoparticles on the black silicon nanowires as shown in Figure A.3a and A.3b. Figure A.3c and A.3d show
the PXRD pattern and the elemental mapping of the sample shown in Figure A.3a. Although there was no apparent improvement in the photomethanation rates, the sample didn’t show any deactivation. That is, the rate of methane formation didn’t drop after several tests. Careful characterization of the samples before and after the photomethanation tests are currently underway to understand the deactivation process. We are also optimizing the nickel deposition to achieve the maximum photomethanation rate. Although the rate of photomethanation is not as high as in the case of the Ru or RuO$_2$ deposited on silicon nanowires, there is no doubt that with careful characterization and study, it can be significantly enhanced in the future.

![Figure A.3](image_url)

**Figure A.3.** (a) SEM image of nickel film deposited on black silicon nanowires (b) STEM image of nickel film deposited on black silicon nanowires (c) PXRD showing the
presence of both nickel and silicon. The two very sharp peaks at 33° and 62° 2θ originate from the [100] face of the silicon wafer, which was etched to make the silicon nanowires. (d) EDX elemental mapping of the sample shown in Figure A.3a.

References


