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Graphene Oxide Shells on Plasmonic Nanostructures Lead to High-Performance Photovoltaics: A Model Study Based on Dye-Sensitized Solar Cells

Yoon Hee Jang†, Adila Rani†, Li Na Quan†‡, Valerio Adinolfi†, Pongsakorn Kanjanaboos†‡, Olivier Ouellette‡, Taehwang Son§, Yu Jin Jang‡, Kyungwha Chung‡, Hannah Kwon‡, Donghyun Kim§, Dong Ha Kim*†, and Edward H. Sargent*‡

†Department of Chemistry and Nano Science, Ewha Womans University, 52, Ewhayeodae-gil, Seodaemun-gu, Seoul, 03760, South Korea

‡Department of Electrical and Computer Engineering, University of Toronto, 10 King’s College Road, Toronto, Ontario, M5S 3G4, Canada

§School of Electrical and Electronic Engineering, Yonsei University, 50, Yonsei-ro, Seodaemun-gu, Seoul, 03722, South Korea

Corresponding Author

*Dong Ha Kim: dhhkim@ewha.ac.kr

*Edward H. Sargent: ted.sargent@utoronto.ca
The incorporation of plasmonic nanoparticles (NPs) into photovoltaic devices can increase light absorption and in turn improve solar cell performance. The graphene oxide-encapsulated gold NPs (Au@GO NPs) are designed and incorporated into photoanodes to demonstrate plasmonic dye-sensitized solar cells. The coupling between GO and the Au NPs has the beneficial effect of extending solar spectral utilization in the long-wavelength portion of the visible spectrum. In addition, the GO encapsulation reduces charge recombination on the surface of the NPs and facilitates improved charge transport. As a result, champion devices with plasmonic photoanodes containing Au@GO NPs deliver a power conversion efficiency that reaches 9.1%. This corresponds to an enhancement in photocurrent and power conversion efficiency of 19% and 17%, respectively, compared control devices.

**TOC GRAPHICS**
Plasmonic effects have been widely reported as a solution to overcome the limited light absorption of thin film photovoltaic devices.\textsuperscript{1-6} To date, the development of plasmonic photovoltaics has been based on diverse enhancement mechanisms. Near-field enhancement by locally-enhanced surface-plasmon excitation of metal nanoparticles (NPs) is a representative route to increase the light absorption cross-section of photoactive materials.\textsuperscript{7-10} In addition, far-field scattering effects by relatively large NPs can increase the optical path length by effectively reflecting light into solar cells.\textsuperscript{11-14} Another possible route is plasmon-induced charge-carrier generation directly participating in photocurrent generation.\textsuperscript{15-17} These plasmonic contributions were shown to have a beneficial effect in diverse photovoltaic systems, particularly dye-sensitized solar cells (DSSCs), in which the number of photons absorbed by sensitized-dye molecules can notably increase through the incorporation of plasmonic NPs.\textsuperscript{7-8, 15, 18-26}

In a seminal investigation of the applicability of plasmon resonance effects in DSSCs, Ag NPs were deposited on TiO\textsubscript{2} films, resulting in an improvement of the optical absorption of the dye due to Ag plasmon resonance.\textsuperscript{20} In 2008, Hägglund et al. observed that the localized surface plasmon resonance of elliptical Au disks enhanced the charge-carrier generation rate in the dye.\textsuperscript{21} Since then, several studies have been conducted, and still more efforts are underway to further increase power conversion efficiencies (PCE) by introducing properly designed plasmonic structures into DSSCs. To the best of our knowledge, the plasmonic DSSCs presenting the greatest increase in PCE were augmented with small Au NPs (~2 nm in size) in a TiO\textsubscript{2} photoanode, enhancing the efficiency by 84%.\textsuperscript{22} In that study, it was shown that improving photovoltage by a negative shift of the quasi-Fermi level of Au-inlaid TiO\textsubscript{2} composite, as well as increasing dye excitation by plasmon resonance of the Au NPs, played a major role in achieving high-efficiency DSSCs. Hammond and Belcher demonstrated wide-spectrum DSSCs using multiple core–shell
plasmonic structures and achieved a PCE of 10.8%, which represents the highest value among reported plasmonic DSSCs to date.\textsuperscript{23} In this case, efficiency was maximized when light harvesting was balanced between photoabsorption within the dye and localized surface plasmon resonance (LSPR) of tailored plasmonic NPs.

Graphene-based materials have been applied to photovoltaic devices in various ways, which contributed to marked improvements in charge transport properties.\textsuperscript{27-31} Yang et al. reported two-dimensional graphene layers introduced into the TiO\textsubscript{2} electrodes of DSSCs that functioned as bridges between TiO\textsubscript{2} NPs to bring a faster electron transport and lower recombination.\textsuperscript{28} Back-transport reaction resulting from the direct contact between the electrolyte and fluorine doped tin oxide (FTO) was effectively suppressed by configuring the graphene-TiO\textsubscript{2} nanocomposite interfacial layer between FTO and TiO\textsubscript{2} electrode.\textsuperscript{27} Yang et al. demonstrated graphene oxide (GO) having a higher work function (5.2 eV) as an efficient hole transporting layer in organic solar cells.\textsuperscript{29} Most recently, nanocomposites of graphene/TiO\textsubscript{2} were applied as the electron collection layer in perovskite-based solar cells. Charge-collection in the nanocomposites was superiorly improved by virtue of the graphene nanoflakes.\textsuperscript{30}

Taking note of the above observations, optimizing the configuration of plasmonic NPs may be a crucial factor in increasing light collection in DSSCs. Thus, in this work, we designed GO-encapsulated Au NPs (Au@GO NPs) and configured a stable plasmonic photoanode to maximize the photocurrent and efficiency of a ruthenium-dye-sensitized TiO\textsubscript{2} based solar cell. Au@GO NPs showed remarkably enhanced absorption properties in the long-wavelength portion of the visible spectrum (600–800 nm), as well as surface plasmon features, allowing broadband light harvesting. Furthermore, the GO thin shell played an important role in the improvement of charge transport by suppressing charge recombination. The origin and mechanism of the plasmonic enhancements
were investigated by conductivity measurements, electrochemical impedance spectroscopy (EIS), and intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS).

Au@GO Nanoparticle Characterization

Thin layers of graphene oxide (GO) were attached to the surface of Au nanoparticles (NPs) through the electrostatic interaction between Au NPs and GO sheets. First, to cover the citrate-capped Au NPs’ surface with GO, positively-charged GO suspensions were synthesized. According to the modified Hummer method, the oxidation of graphite in an acidic medium and the following exfoliation of graphitic oxide attach a chemical functional group, e.g., carboxylic acid (COOH), onto the surface of GO sheets, resulting in negatively-charged GO (GO-COO\textsuperscript{-}).\textsuperscript{32} Subsequently, the surface functional carboxylic acids were activated by EDC and reacted with ethylenediamine (or triethylamine). Amine groups (NH\textsubscript{2}) were introduced on the surface of the graphene oxide, and positively-charged GO (GO-NH\textsubscript{3}\textsuperscript{+}) suspensions were obtained. These positively-charged GO sheets were characterized using X-ray photoelectron spectroscopy (XPS), UV–Vis absorption, and zeta (ζ)-potential analysis. As shown in the XPS survey spectra (Figure S1a and b, Supporting Information), the N1s peak at 400 eV was only observed in the case of positively charged GO, due to the presence of the surface amine groups of GO-NH\textsubscript{3}\textsuperscript{+}. To provide further evidence of formation of GO-NH\textsubscript{3}\textsuperscript{+}, C1s peak was deconvoluted using Gaussian fitting model. The high-resolution C1s spectrum of initially synthesized GO-COO\textsuperscript{-} (Figure S1c, Supporting Information) clearly showed carbon species in different functional groups, \textit{i.e.} sp\textsuperscript{2} and sp\textsuperscript{3} hybridized carbons in aromatic ring (C=\text{C}, 284.0 eV; C-C, 284.8 eV), epoxy or hydroxy (C-O, 286.8 eV), carbonyl (C=O, 288.2 eV), and carboxylate (O-C=O, 289.0 eV). Meanwhile, additional components at 286.0 and 287.5 eV corresponding to carbon in C-N and O=C-N bonds, respectively, were
observed, which confirms the successful NH$_2$ functionalization (Figure S1d, Supporting Information).

The initial negatively charged GO suspension in DI-water exhibits an absorption band at ~230 and a weak shoulder at ~300 nm, attributed to the π–π* and n–π* transitions of the C=C and C=O bonds, respectively.\textsuperscript{33} During the reaction between negatively charged GO and ethylenediamine with EDC, a hypsochromic shift in the peak of the π–π* transitions was observed as seen in the UV–Vis measurement (Figure S1e, Supporting Information), this is explained by the dissociation of oxygen-containing functional groups of GO, including carboxyl groups and aromatic hydroxyl groups.\textsuperscript{34} Additionally, ζ-potential values of GO suspensions further support the formation of surface functional groups, indicating the positive characteristic of amine functional groups on GO (Figure S1f, Supporting Information).

Electrostatic interactions caused citrate-capped Au NPs to be covered by GO-NH$_3^+$ sheets (Figure 1a). As shown in the TEM image (Figure 1b and Figure S2, Supporting Information), the obtained Au NPs are elliptical in shape with a diameter of 50~60 nm along the long-axis. In addition, rough and crinkled features associated with flexible and ultrathin graphene oxide sheets can be clearly observed on the surface of the Au NPs, indicating a GO shell thickness of 4~5 nm. During the synthesis procedure, the overall structure or morphology of Au NPs was not altered, except for the formation of a thin GO shell on the surface of Au NPs (Figure S2, Supporting Information).

The optical properties of the as-synthesized Au NPs and Au@GO NPs were then investigated. A noticeable difference in the UV–Vis absorption spectra of the Au NPs with and without a GO shell is evident in Figure 1c. The position of the LSPR band of Au NPs is sensitive to the change in the surrounding medium. Therefore, the broadening and red-shift of the LSPR
band at ~520 nm was attributed to the presence of a thin GO shell. In addition, the overall absorption in the whole spectral range was enhanced after GO coating. The characteristic absorption peak of GO is also present at ~230 nm. The total absorbed power (Figure 1d) was calculated based on three-dimensional finite-difference time-domain (FDTD) method and the result coincides with the experimental spectrum. The calculated electromagnetic intensity profiles at the resonance wavelength of Au NPs (520 nm) and Au@GO NPs (530 nm) are displayed in Figure 1e. The electric field around Au@GO is diminished compared to Au NPs, most likely because of the shielding effect of the GO shell.

The presence of the GO shell was further confirmed by Raman spectroscopy. Figure 1f shows the Raman spectra of positively charged GO sheets, Au NPs, and Au@GO NPs under 630 nm excitation. In the Raman spectrum of graphene, $D$- and $G$-bands are usually observed. The $D$-band at ~1350 cm$^{-1}$ is derived from the structural defects of graphite (the symmetry $A_{1g}$ mode). The first-order scattering of the $E_{2g}$ mode of $sp^2$ carbon atoms in graphene gives rise to a peak at ~1580 cm$^{-1}$, named $G$-band. The Raman spectrum of GO-NO$_2^-$ exhibits both the $D$- and $G$-bands at ~1337 and ~1595 cm$^{-1}$, respectively. The intensity of the $D$-band was even higher than that of the $G$-band. The 2$D$ peak (i.e., overtone of $D$-band at ~2700 cm$^{-1}$) was not revealed due to significant structural disorders or defects arising from the harsh oxidation synthesis process. After the encapsulation of GO, two characteristic peaks were still present, and the $D$- and $G$-band positions remained the same.
Figure 1. Characterization of Au@GO NPs. a) Schematic illustration of GO-wrapped Au NPs synthesis process. b) TEM image of Au@GO NPs. c) Experimental and d) calculated UV–Vis absorption spectra of Au NPs and Au@GO NPs. e) Normalized electric field intensity distribution calculated by the FDTD simulation of Au NP and Au@GO NP. f) Normalized Raman spectra of GO and Au@GO NPs.

Fabrication of Plasmonic DSSCs and Device Performance

Plasmonic photoanodes inlaid with GO-encapsulated Au NPs were fabricated following the overall procedure depicted in Figure 2a. First, a TiO$_2$ film was deposited on a FTO substrate by the doctor-blade method and crystallized by high-temperature sintering. Then, to ensure the chemical interaction between TiO$_2$ and Au@GO NPs, the TiO$_2$ film was modified with APTES. Even after the as-synthesized GO was functionalized with amine groups, surface functional OH groups
partially remained on the surface of GO, which might interact with APTES. The APTES-modified TiO\(_2\) film was finally immersed in the as-prepared Au@GO NPs colloidal solution and washed with DI water to remove the unbound NPs. The SEM images in Figure 2b show the fabricated plasmonic photoanodes where discrete Au NPs were well distributed on the surface of TiO\(_2\) without any noticeable agglomeration. However, partial agglomeration of Au@GO NPs was observed, which may result from the multiple synthetic steps to form GO shells.

![Figure 2. a) Schematic describing the fabrication of the plasmonic photoanodes. b) SEM images of plasmonic photoanodes configured with (left) FTO/TiO\(_2\)/APTES/Au NPs and (right) FTO/TiO\(_2\)/APTES/Au@GO NPs.](image)

The amount of incorporated NPs was tuned simply by controlling the immersion time of APTES-modified TiO\(_2\) films into the NPs colloidal solution. With increasing immersion time, the amount of NPs deposited was gradually increased, which was verified through a series of SEM images (Figure S3, Supporting Information). The performance of devices with varying amounts of NPs was investigated first and the results were displayed in Figure S4 and Table S1, Supporting Information. With short dipping times (less than 30 min), only a slight improvement was observed (results not shown) due to insufficient incorporation of NPs. The best performance was obtained in both types of devices (with Au and Au@GO NPs) with a dipping time of 30 min, after which
PCE gradually decreased with the increasing the amount of plasmonic NPs on TiO$_2$ films, suggesting that the presence of Au NPs in too large amounts could cause undesirable effects such as increased charge carrier recombination. The performance of the champion solar cell with the optimal amount of plasmonic nanoparticles is shown in Figure 3a and listed in Table 1 (average cell performance with variation was indicated in Figure S5 and Table S2, Supporting Information). Interestingly, while both open-circuit voltage ($V_{oc}$) and fill-factor (FF) remained unaffected, the photocurrent was greatly enhanced by the introduction of plasmonic nanoparticles, the leading cause of the enhancement in efficiency. Short-circuit current ($J_{sc}$) values are compared in Figure 3b, in which the improvement in plasmonic cells is apparent. A remarkably enhanced $J_{sc}$ of 17.19 mA·cm$^{-2}$ was obtained from the cell containing Au@GO under the optimal condition, corresponding to an increase of ~18.8% with respect to the control device (without the plasmonic nanoparticles). In contrast, plasmonic cells without GO wrapping showed a $J_{sc}$ of 15.2 mA·cm$^{-2}$, which was ~13.1% lower than the plasmonic cell with GO wrapping. Considering the overall device performance, the outer, thin GO shell plays a significant role in enhancing the optical and electrical properties of plasmonic solar cells. We further investigated the mechanism of the performance enhancement of the plasmonic solar cells with optimal Au@GO NPs by performing optical and electrical characterization.
Figure 3. a) Photocurrent density-voltage (J-V) characteristic of control and plasmonic champion DSSCs with Au NPs and Au@GO NPs. b) Corresponding enhancement ratio of current density over the control device. c) Incident photon-to-current conversion efficiency (IPCE, %) curves of control and plasmonic DSSCs with Au NPs and Au@GO NPs. d) IPCE enhancement (ΔIPCE (%)) of plasmonic DSSCs with Au NPs and Au@GO NPs over the control device.

Table 1. Photovoltaic parameters for the best performance cell of control and plasmonic DSSCs with Au and Au@GO NPs at a dipping time 30 min.

<table>
<thead>
<tr>
<th>Photoanode types</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF</th>
<th>$\eta$ [%]</th>
<th>$R_2$ [Ω]</th>
<th>$\tau_e$ [ms]</th>
</tr>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.787</td>
<td>14.47</td>
<td>0.682</td>
<td>7.77</td>
<td>99.99</td>
<td>5.04</td>
</tr>
<tr>
<td>TiO$_2$/Au NPs</td>
<td>0.788</td>
<td>15.20</td>
<td>0.664</td>
<td>7.95</td>
<td>77.41</td>
<td>5.70</td>
</tr>
<tr>
<td>TiO$_2$/Au@GO NPs</td>
<td>0.780</td>
<td>17.19</td>
<td>0.676</td>
<td>9.06</td>
<td>70.98</td>
<td>6.37</td>
</tr>
</tbody>
</table>

a) Control and plasmonic photoanodes with Au and Au@GO NPs; b) Charge transport resistance; c) electron lifetime ($\tau_e = 1/(2\pi f_{mid})$) calculated from the EIS results.

Optical and Electrical Characterization
To investigate the origin of the performance enhancement by optical effects, the incident photon-to-current conversion efficiency (IPCE) spectra was measured for devices with and without plasmonic photoanodes (Figure 3c), which was obtained from a different set of cells than those reported in Table 1. In comparison with the control device (without plasmonic NPs), the IPCE spectra of the plasmonic devices showed increased values over the entire wavelength range. Furthermore, the device with Au@GO NPs exhibits a higher IPCE value than the one with Au NPs. The enhancement in the IPCE (ΔIPCE, %) was subsequently calculated and is displayed in Figure 3d. A broadly distributed enhancement is observed from 400 to 800 nm for both plasmonic devices, and strong enhancement was achieved from 600 to 700 nm for the devices containing Au@GO. The notable enhancement in IPCE, especially in longer-wavelength regions, is attributed to broadband light absorption by GO-encapsulated Au NPs, as shown in the UV-Vis absorption profile of Au@GO NPs. However, IPCE enhancement does not follow the LSPR band at ~540 nm.

To address the contribution of plasmonic effects to the improved device performance, scanning kelvin probe microscopy (SKPM) was performed, providing information about surface potential changes of TiO$_2$ by injection of hot-electrons from plasmon decay of Au NPs to trap sites in the conduction band of TiO$_2$. The samples were excited under a Xenon light source for 380 s, and the surface potential changes were recorded. No significant differences in the work function were observed, i.e., the surface potential between TiO$_2$ and TiO$_2$/Au@GO film remained the same (Figure S6, Supporting Information). Based on the IPCE and SKPM results, we can conclude that the solar cell efficiency increased primarily through broadband light absorption by Au@GO NPs, whereas plasmonic effects, such as LSPR-induced charge injection or near-field enhancement, played a minor role in the performance enhancement. In addition to the enhancement of light-
harvesting capability by synergistic coupling of Au NPs and GO shell, the performance improvement may result from enhanced charge transport and reduced recombination effects.

To corroborate these potential impacts on the electrical properties, conductivity, EIS, and IMPS/IMVS measurements were performed. We examined the electronic transport properties of the prepared photoanodes by performing conductivity measurements on films kept in the dark. For this measurement, a symmetric film was constructed with the hole extracting contact layers (MoO$_3$/Au/Ag) on the top of photoanode films. The plasmonic photoanodes (FTO/TiO$_2$/Au or Au@GO NPs) showed higher conductivity than the photoanode without plasmonic NPs (FTO/TiO$_2$), in which the conductivity was obtained from the slope of the current density–(voltage/thickness) curves (Figure 4a) based on Ohm’s law. The FTO/TiO$_2$/Au@GO NPs film showed the highest conductivity of 0.0238 $\Omega^{-1}\cdot$cm$^{-1}$, representing a 9.9-fold and 1.6-fold increase compared to the FTO/TiO$_2$ (0.0024 $\Omega^{-1}\cdot$cm$^{-1}$) and FTO/TiO$_2$/Au NPs (0.0153 $\Omega^{-1}\cdot$cm$^{-1}$) films, respectively. Therefore, the conductivity of the pristine TiO$_2$ films can be increased by incorporating plasmonic components. In addition, it is conjectured that the electrical conductivity of the GO shell was partially recovered during the ethylenediamine-mediated functionalization process via restoration of a portion of $sp^2$ bonding networks, granting a further increase in the conductivity of TiO$_2$ film.$^{40}$

The electrical properties of the devices were further investigated by the EIS analysis. Under the one-sun illumination and at open-circuit voltage, the Nyquist plots (Figure 4b) and the corresponding Bode phase plots (Figure 4c) of the control and plasmonic devices were obtained from the EIS measurement. As shown in the Nyquist plots, the diameter of the semicircles in the middle frequency region, corresponding to the charge transfer resistance $R_2$, notably decreased in the case of plasmonic devices. The $R_2$ of the control device and plasmonic devices with Au NPs
and Au@GO NPs was measured to be 100 Ω, 77 Ω, and 71 Ω, respectively. The reduction of $R_2$ was attributed to the contribution of plasmonic Au NPs, leading to better charge separation. Furthermore, the GO shell could also effectively reduce the recombination rate by protecting the Au NPs, and as a result, the charge transfer resistance markedly decreased. The corresponding Bode phase plots to support this result are presented in Figure 4c. The electron lifetime ($\tau_e$) can be determined from the middle-frequency ($f_{\text{mid}}$) of the Bode phase plots with $\tau_e = 1/(2\pi f_{\text{mid}})$. The device with Au@GO NPs has the longest calculated electron lifetime (6.4 ms) compared to the device with Au NPs (5.70 ms) and control device (5.0 ms). Au@GO NPs in DSSCs allow for longer electron transport by inhibiting the charge recombination. To further study the behavior of photo-injected charge carriers relating to charge transport and extraction, we performed IMPS and IMVS. Figure 4d and 4e show the electron diffusion length ($L_n$) and electron collection efficiency ($\eta_{cc}$, %), respectively. Each parameter ($L_n$ and $\eta_{cc}$) of the device with Au@GO were greater than those of the others.

According to our experimental findings, the existence of a thin GO shell can improve the performance through increased charge collection in longer wavelength ranges by GO-induced broadband light absorption (minor possibility) and improved charge transport by enhanced electrical conductivity (major possibility), as validated by electrical measurements.
Figure 4. a) Current density vs. voltage/thickness curves with linear-fitting and a schematic diagram of a symmetric film for conductivity studies. The thickness of films were 10 μm. EIS of the control and plasmonic DSSCs with Au NPs and Au@GO NPs under the one-sun illumination and at an open-circuit voltage: b) Nyquist plots and c) corresponding Bode phase plots. d) Electron diffusion length versus $J_{sc}$ and e) electron collection efficiency (%) versus $J_{sc}$ of control and plasmonic DSSCs with Au and Au@GO NPs obtained from IMPS/IMVS measurements.

In summary, a thin layer of GO was introduced on the surface of Au NPs to demonstrate plasmon-enhanced dye-sensitized solar cells. The inclusion of Au@GO NPs resulted in broad absorption over the entire visible spectrum, which contributed to a remarkable improvement in the photocurrent generation and performance of the fabricated solar cells. When Au@GO core–shell structures were deposited in the optimum amount, a $J_{sc}$ of 17.2 mA·cm$^{-2}$ and an efficiency of 9.1%, were achieved, which is superior to both the pristine Au plasmonic device and plasmon-free
control devices. Based on the comprehensive investigations, we concluded that a thin GO shell on Au NPs plays a significant role in enhancing the performance of DSSCs by synergistically improving light absorption and facilitating charge transport through reduction of charge recombination. In the relevant society, DSSCs with ~13% efficiency have been achieved by M. Grätzel group through molecular engineering of porphyrin dye.\textsuperscript{41} In our study, a plasmon-mediated high performance DSSC was proposed based on a more conventional architecture with standard and widely available dye and electrolyte. The protocol established in this study can be employed as a generalized strategy to develop other types of high-performance solar cells.

\section*{Experimental Methods}

\textit{Synthesis of gold nanoparticles (Au NPs):} Citrate-capped 55 nm-diameter Au NPs were synthesized following a previously reported method.\textsuperscript{42} 200 mL of an aqueous solution of 0.01 wt\% chloroauric acid was added to a round bottom flask and then boiled up to 130 °C using hot oil-bath. 1.4 mL of 1 wt\% sodium citrate was then quickly added to the boiled solution and stirred for 30 min, yielding a bold-pink Au NP solution.

\textit{Synthesis of Au@graphene oxide nanoparticles (Au@GO NPs):} Negatively-charged graphene oxide (GO-COO\textsuperscript{−}) was initially prepared by the modified Hummer method.\textsuperscript{32} To encapsulate the citrate-capped Au NPs with GO, positively-charged GO (GO-NH\textsubscript{3}\textsuperscript{+}) was prepared by attaching an amine functional group on the surface of GO-COO\textsuperscript{−}, as reported previously.\textsuperscript{43} 50 mL of the as-prepared GO aqueous solution with negative charge was stirred for 4 h with 500 mg of N-ethyl-N\textprime-(3-dimethyl aminopropyl)carbodiimide (EDC), 5 mL of ethylenediamine, and 1 mL of triethylamine. The as-synthesized Au NPs were centrifuged, and their precipitate was dispersed into a positively-charged GO solution with the same volume, followed by gentle stirring overnight. The solution obtained was washed \textit{via} centrifugation to remove the residual reactants.
Fabrication of the plasmonic photoanode and devices: Glass covered with fluorine-doped tin oxide (FTO, 2.2 mm thick and sheet resistance of 6-9 Ohms sq.\(^{-1}\)) was used as the transparent conducting oxide (TCO) substrate. Before use, the FTO substrate was cleaned by sonication in acetone and isopropyl alcohol sequentially for 20 min. Commercially available TiO\(_2\) paste (TTP-20N, ENB KOREA Co., Ltd.) was printed onto the FTO substrate by the doctor-blade method and sintered at 550 °C for 2 h to obtain a uniform TiO\(_2\) film. To control the thickness of TiO\(_2\) film, three-layered 3M tape was used as thickness guide. The thickness of photoanodes was 11 ± 0.5 μm, as measured by surface profiler (Alpha step). To immobilize the plasmonic NPs onto the TiO\(_2\) film, the latter was first immersed in 10 vol% of 3-aminopropyltriethoxysiliane (APTES) ethanolic solution. The APTES-modified TiO\(_2\) film was then immersed in the GO-modified Au NPs colloidal solution with different dipping time (30 min, 60 min, and 180 min), followed by DI washing and drying with nitrogen. Finally, ruthenium dye (\(\text{cis}\)-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) bis(tetrabutylammonium), N-719, Solaronix) was sensitized on the TiO\(_2\)/Au@GO film to constitute the plasmonic photoanode by immersing into dye solution (5 mM in ethanol) for 24 h. The plasmonic photoanode was assembled with Pt-coated FTO as the counter electrode using 50-μm thick hot-melt spacer (SX1170-25, Solaronix) and an ionic liquid electrolyte 0.60 M BMIM-I, 0.03 M I\(_2\), 0.50 M TBP, and 0.10 M GTC in acetonitrile/valeronitrile 85/15 (v/v) (no. ES-0004), purchased from io.li.tec (Germany), was then injected between the two electrodes through capillary force.

Electromagnetic simulation: For the electromagnetic simulation of Au and Au@GO NPs, a three-dimensional finite-difference time-domain (FDTD) method was used. The absorption spectrum was obtained from near-field calculation, in which the total absorbed power was calculated from the following Equation 1
\[ P_{\text{abs}} = \frac{\omega}{2} \int \text{Im} [\varepsilon(\omega)] |E|^2 dv \]  

(1)

where \( \omega \) is the frequency of the incident radiation, \( \varepsilon \) is the permittivity of the medium, and \( E \) is the electric field amplitude. For the absorption simulation, symmetry boundary conditions were imposed at the center of nanoparticles in the yz and zx planes with a linearly polarized plane wave incident along the z direction. Grid size was set to 2 and 1 nm\(^3\) for Au NP and Au@GO NP, respectively. Near-field distribution was obtained without symmetry boundary conditions, in which case the grid size was set to 1 nm\(^3\) for both Au NP and Au@GO NP. A perfectly matched layer with 10-nm width was used for the entire simulation. The refractive indices of Au and GO were taken from the literature.\(^{44-45}\)

**Conductivity measurement and calculation:** For the conductivity measurement, the electrode layers, consisting of \(~40\) nm of thermally evaporated molybdenum oxide, \(~50\) nm of electron-beam deposited gold, and \(~100\) nm of thermally evaporated silver (MoO\(_3\)/Au/Ag), were deposited on the top of the photoanode films using an Angstrom Engineering Åmod deposition system in an Innovative Technology glovebox. Current–voltage characteristics in dark conditions were measured using a Keithley 2400 source meter. Conductivity calculation is based on Equation 2 (Ohm’s law)

\[ J = \sigma \frac{V}{d} \]  

(2)

where \( J \) is the current density (mA·cm\(^{-2}\)), \( \sigma \) is the conductivity (\( \Omega^{-1}\cdot\text{cm}^{-1}\)), \( V \) is the applied voltage (V), \( d \) is the thickness of the TiO\(_2\) or TiO\(_2\)/Au NPs, or TiO\(_2\)/Au@GO NPs films on the FTO substrate (10 \( \mu \)m).

**Characterization of materials and device performance:** The amine-functionalization of GO (GO-NH\(_3^+\)) was shown using an X-ray photoelectron spectroscopy (XPS, ESCALab spectrometer (Thermo VG, U.K.) equipped with mono-chromated Al-K\(\alpha\) radiation) and zeta-potential
measurement (ZETASIZER 3000, Malvern). To characterize the GO shell on Au NPs, Raman spectroscopy was performed using HORIBA Jobin Yvon at an excitation wavelength of 630 nm. The structure of Au@GO NPs was thoroughly examined by transmission electron microscopy (TEM, JEOL JSM2100-F, at 100 kV). The optical properties were measured by UV–Vis absorption spectroscopy (Cary 5000, Varian Inc.). Photocurrent-voltage (J–V) curves and EIS were measured under a simulated AM 1.5 G illumination intensity of 100 mA cm\(^{-2}\) (Polaronix K201, McScience Inc.) using an electrochemical measurement system (InviumStat.XR, Invium Technologies). EIS measurement was performed by applying a 20 mV AC signal in the range of frequency from 50 mHz to 10 kHz. For IMPS/IMVS measurements, a green light emitting diode (525 nm) was used as the light source, and its intensity was modulated using a sinewave generator with the frequency set from 0.1 to 100 Hz (Invium ModuLight-module, Invium Technologies). Scanning Kelvin probe microscopy (SKPM) measurement was carried out using a KPTechnology KP020 system. The work functions of the photoanode films were measured sequentially in the dark and under Xenon light illumination (770 W·cm\(^{-2}\)) for 380 sec at each step.

ASSOCIATED CONTENT

**Supporting Information.** Characterizations of positively charged graphene oxide and Au NPs, additional J–V curves and photovoltaic parameters of plasmonic DSSCs with varying amount of Au and Au@GO NPs. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

**Corresponding Author**

*Edward H. Sargent: ted.sargent@utoronto.ca*
Present Address

Photo-Electronic Hybrids Research Center, Korea Institute of Science and Technology (KIST), 5, Hwarang-ro, 14-gil, Seongbuk-gu, Seoul, 02792, South Korea

Material Science and Engineering, Mahidol University, 272 Rama 6 Rd., Ratchathewi District, Bangkok, 10400, Thailand

Notes

The authors declare no competing financial interest.

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