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1 Scanning transmission X-ray microscopy studies of chromium hydroxide hollow spheres
2 and nanoparticles formed by gamma-radiation

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Abstract: Amorphous chromium-containing solid nanoparticles and hollow spheres were formed as the intermediate product during the synthesis of Cr_2O_3 by gamma radiolysis of dichromate solution. Scanning transmission X-ray microscopy (STXM) is applied to investigate the electronic structure and chemical composition of this intermediate product (solid nanoparticles and hollow spheres). STXM result obtained at O K-edge and Cr $L_{3,2}$ -edge confirms that chromium in the sample exists as Cr^{3+} , and the solid nanoparticles and hollow spheres are both $\text{Cr}(\text{OH})_3$. Combined with other techniques, a mechanism for gamma-radiation-induced formation of Cr_2O_3 nanoparticles via $\text{Cr}(\text{OH})_3$ intermediates from dissolved dichromate is proposed.

Keywords

Chromium hydroxide, hollow spheres, gamma radiolysis, Scanning transmission X-ray microscopy, X-ray absorption near edge structure

Introduction

Chromium (III) oxide, one of the principal oxides of chromium, is an antiferromagnetic insulator below the Néel temperature 307 K.¹ Cr_2O_3 adopts the corundum structure, consisting of a hexagonal close packed array of oxide anions with 2/3 of the octahedral holes occupied by chromium. Cr_2O_3 nanoparticles have been used in a broad range of applications, such as green pigments,² heterogeneous catalysts,³ coating materials for thermal protection,⁴ coatings for wear resistance,⁵ and electrochromic materials.⁶ Different applications require different crystalline particle size and morphology. Cr_2O_3 nanoparticles have been synthesized by various techniques including hydrothermal reduction,⁷ solution combustion synthesis,⁸ sonochemical reaction,⁹ laser-induced pyrolysis,¹⁰ hydrazine reduction and thermal treatments,¹¹ supercritical alcohol

42 synthesis,¹² condensation-polymerization,¹³ precipitation-gelation,¹⁴ gas condensation,¹⁵
43 microwave plasma chemistry,¹⁶ and sol-gel methods.¹⁷ The major drawbacks of most of these
44 fabrication methods are a wide particle-size distribution, a low yield, and agglomeration of the
45 particles. The fabrication methods also tend to be complex and require chemically harsh
46 conditions and/or high processing temperatures.

47 Radiolysis is a promising new technique for generating nanoparticles with a narrow size
48 distribution. Radiation-induced nanoparticle formation also does not require the chemical
49 additives and stabilizers for particle size control that are used in other conventional methods. It
50 eliminates undesired effects of these chemicals on the structure and chemical composition of
51 nanoparticles. This method has been successfully used to fabricate γ -FeOOH,¹⁸ Co_3O_4 ¹⁹ and
52 Cr_2O_3 nanoparticles.²⁰⁻²¹ However the mechanistic studies of the nanoparticle formation process
53 via radiolysis are very limited.^{18, 20} In the case of Cr_2O_3 nanoparticles, the
54 precipitations(intermediate product)obtained from $\text{Cr}_2\text{O}_7^{2-}$ solution show different morphologies
55 and sizes (solid nanoparticles with different diameters and hollow spheres) and very poor
56 crystallinity.²⁰⁻²¹ Therefore it is hard to determine the chemical composition of this intermediate
57 product (the solid particles and hollow spheres) via conventional techniques such as X-ray
58 diffraction (XRD), laboratory X-ray photoelectron spectroscopy (XPS) and transmission electron
59 microscopy (TEM). This information is important for the understanding ofthe mechanism and
60 therefore to better control the morphology and size of thefinal product Cr_2O_3 .

61 Using the brilliant, undulator-based and polarization-controlled third-generation synchrotron
62 sources, scanning transmission X-ray microscopy (STXM) provides an excellent combination of
63 chemical speciation (X-ray absorption near edge structures, XANES) and microscopy with a

spectral resolution and a spatial resolution of 0.05 eV and of 30 nm, respectively. STXM employs a nano-sized X-ray beam and provides spectral-microscopic information by measuring the absolute absorption of the specimen in transmission mode; thus both chemical images and detailed absorption spectroscopic features of a single nanostructure (including its thickness) can be revealed. STXM has been successfully applied to study an individual nanostructure and microstructure with different phases and compositions.²²⁻²⁵ Hereby using STXM, we reported the electronic structures of chromium hydroxide hollow spheres and solid nanoparticles that were formed as the intermediate product during the synthesis of Cr_2O_3 via gamma-irradiation. STXM result at O K-edge confirms that the hollow spheres and the solid nanoparticles with different diameters are both $\text{Cr}(\text{OH})_3$. After a dehydration process, amorphous $\text{Cr}(\text{OH})_3$ hollow spheres and solid nanoparticles were transformed to crystalline Cr_2O_3 nanoparticles.

Experimental

The chromium sample was prepared by gamma-irradiation of dichromate solution (0.1 mM) containing 0.1 M *tert*-butyl alcohol (purity $\geq 99\%$, Sigma-Aldrich) under deaerated condition (Argon). Chromium solution was prepared by dissolving high-purity potassium dichromate ($\geq 99\%$, Sigma-Aldrich) in water purified using a NANO pure Diamond UV ultrapure water system (resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$). The pH of the test solution was adjusted to 6.0 using NaOH solution. Using a syringe, 10 mL of the chromium solution was transferred to a pre-sealed 20-mL vial (Agilent Technologies) purged with argon gas. To the capped vial the appropriate volume of *tert*-butyl alcohol was injected to get the desired concentration (0.1 M). The test vial was irradiated in a ^{60}Co γ cell (MDS Nordion) for 300 min as described in a previous paper.²⁰ The γ radiation source provided a uniform absorption dose rate of $4 \text{ kGy}\cdot\text{h}^{-1}$ in the water samples at the time of

this study. After that the test solution was extracted with a syringe, and then was centrifuged and washed with distilled water a few times.

The morphology of the as-prepared sample was first characterized by TEM (Philips CM10). STXM measurement was carried out at the SM beamline of the Canadian Light Source (CLS), which is equipped with a 25 nm outermost-zone zone plate (CXRO, Berkeley Lab). The diffraction-limited spatial resolution for this zone plate is 30 nm. We measured the same copper grid that was previously used for TEM. Image sequence (stack) scans over a range of photon energies were acquired for the same sample region at the Cr $L_{3,2}$ -edge and O K-edge. STXM data were analyzed using the aXis2000 software package, which allows for detailed interactive processing of the images and fitting of the X-ray absorption spectra contained in the image stacks. More details of STXM measurement and data analysis can be found elsewhere.^{23, 25}

The Cr $L_{3,2}$ -edge and O K-edge XANES of pure $\text{Cr}(\text{OH})_3$ and Cr_2O_3 powders were collected at the SGM beamline of CLS using total electron yield (TEY) mode. All TEY-XANES were normalized with respect to the intensity of the incoming beam (I_0).

Results and discussions

The morphology of the as-prepared sample is first characterized by TEM. As shown in Figure 1, with irradiation time of 300 min, the sample is composed of large hollow spheres with diameter of 100-170 nm and wall thickness of about 14-18 nm and small solid nanoparticles (the small solid nanoparticles with light contrast have a diameter of 8-20 nm, while those bigger ones with dark contrast have a diameter of 40-50 nm). Previously it is proposed that the large hollow spheres were $\text{Cr}(\text{OH})_3$ and the small solid nanoparticles were Cr_2O_3 .²⁰ XANES is an element- and site-specific technique, which is sensitive to the local chemical environment of a specific element (no matter the sample is amorphous or crystalline). STXM is a

spectromicroscopy technique that allows for the acquisition of XANES spectrum from a specific region of interest (ROI) on an individual nanostructure. By comparing the XANES collected from the hollow spheres and solid nanoparticles, it will help us determine their composition. Figure 2a is a STXM optical density image of the sample that shows the same area as in the TEM image (see Figure 1). One can see clearly the hollow spherical structures. Because the spatial resolution of the 25 nm zone plate is 30 nm, the morphology of the small nanoparticles is not well resolved.

Since STXM can determine the absolute thickness of the sample based on X-ray absorption, the thickness distribution of the hollow spheres and solid nanoparticles has been obtained and is shown in Figure 3. The thickness was obtained from stack fitting with the quantitatively scaled reference spectra of 1 nm thickness at O K-edge (Figure S1 in Supporting Information). The wall thickness of the hollow spheres is determined to be about 15-20 nm, which agrees well with the TEM observation. The thickness of the solid particles in the red, blue and green dashed circles are 5-10 nm (nanoparticles with small diameter), 25-40 nm (nanoparticles with medium diameter) and 60-75 nm (nanoparticles with large diameter), respectively. The brightest area marked with purple dotted circle shows thickness of 120-138 nm, which is due to the aggregation of solid particles (the darkest area in Figure 1).

Now let us compare the XANES collected from the large hollow spheres and small solid particles to determine their composition. Figure 4 shows Cr $L_{3,2}$ -edge XANES spectrum isolated from the colored regions of interest (ROIs) in Figure 2b, which probes the electron transitions from Cr $2p$ to the previously unoccupied Cr $3d$ and $4s$ states.²⁶ The $2p$ core hole spin-orbit interaction splits the absorption spectrum by approximately 8 eV into an L_3 -edge ($2p_{3/2}$) and L_2 -edge ($2p_{1/2}$). Let us first look at the spectrum of pure $\text{Cr}(\text{OH})_3$ and Cr_2O_3 . The XANES of

Cr(OH)₃ shows almost the same line shape as that of Cr₂O₃. The only difference is that the feature *B* in the spectrum of Cr₂O₃ locates at slightly lower energy than that of Cr(OH)₃ ($\Delta E = 0.25$ eV). The XANES collected from hollow spheres (ROI-1, ROI-2, ROI-3, ROI-4, ROI-5 and ROI-6 marked in Figure 2b) show the same features as that from solid particles (ROI-7, ROI-8 and ROI-9 marked in Figure 2b). The feature *B* in these nano-XANES is closer to that in Cr(OH)₃ than Cr₂O₃. At Cr L_{3,2}-edge, due to the subtle difference between the XANES of Cr(OH)₃ and Cr₂O₃, it is hard to determine the composition of hollow spheres and solid nanoparticles. But it can be concluded that the Cr in the sample only exists as Cr³⁺, because that Cr⁶⁺ (from the precursor Cr₂O₇²⁻), Cr⁴⁺ (possible reduction product) and Cr²⁺ (possible reduction product) have very different XANES features.²⁶⁻²⁷

Let us move to the O K-edge. Figure 5 displays O K-edge nano-XANES isolated from the same ROIs labeled in Figure 2b as well as XANES of pure Cr(OH)₃ and Cr₂O₃. These spectra probe the transition from O 1s to unoccupied states with at least partial O 2p character hybridized with Cr 3d states.²⁸ Taking the O K-edge XANES of Cr₂O₃ for example, the spectrum is divided into two regions. The first region shows a sharp peak *a'* near energy threshold E_0 followed by a weak shoulder *b'*. The sharp peak *a'* can be assigned to a superposition of the $t_{2g}\downarrow$ state and the $e_g\uparrow$ state with a total number of five electrons.²⁸ The shoulder *b'* relates to the remaining two $e_g\downarrow$ electrons.²⁸ The second region, typically 5-15 eV above E_0 , is attributed to O *p* character hybridized with Cr 4s and 4p states.²⁸ In the spectrum of Cr(OH)₃, feature *a* and *b* locate at higher energy compared to feature *a'* and *b'* of Cr₂O₃. The energy difference between peak *a* of Cr(OH)₃ and peak *a'* of Cr₂O₃ is about 0.8 eV. Moreover, the peak *a* of Cr(OH)₃ is much less intense than the peak *a'* of Cr₂O₃. The presence of the OH bonding significantly reduces the unoccupied states of *p* character at the O K-edge whiteline. With such spectroscopic differences

between these two compounds, it provides an opportunity to identify the composition of the hollow spheres and solid nanoparticles.

As shown in Figure 5, O K-edge XANES collected from hollow spheres (ROI-1, ROI-2, ROI-3, ROI-4, ROI-5 and ROI-6 marked in Figure 2b) shows similar features as that from solid particles (ROI-7, ROI-8 and ROI-9 marked in Figure 2b). The peak *a* and *b* in these spectra locate at the same energy as that of $\text{Cr}(\text{OH})_3$. Furthermore, the intensity ratio between peak *a* and *b* in these spectra is much closer to that of $\text{Cr}(\text{OH})_3$ than Cr_2O_3 . All the above evidence indicate that both the hollow spheres and the solid nanoparticles with different diameters are of dominantly $\text{Cr}(\text{OH})_3$ character. One can see that feature *a* is broadened and slightly weaker than feature *b* in the spectrum of some hollow spheres (such as ROI-1, ROI-2 and ROI-3) compared to that of standard $\text{Cr}(\text{OH})_3$. Since the sample thickness is about 30-40 nm (the wall thickness of hollow spheres is estimated to be 15-20 nm based on the thickness distribution shown in Fig. 3), self absorption effect that usually leads to the peak broadening in the XANES spectrum (especially for soft X-ray) will not account for this broadening. Here the broadening of feature *a* is proposed to be due to the presence of some Cr_2O_3 (feature *a'* in the spectrum of Cr_2O_3 locates at lower energy). The “*b*” feature at ROI 1-3 appears to be more intense than that expected in the $\text{Cr}(\text{OH})_3$ standard. This may be due to texture effect resulting from the higher strain of the spheres. The “*b*” feature becomes more $\text{Cr}(\text{OH})_3$ like in ROI 4-6 where the spheres get larger and in ROI 7-9 where solid particles are examined (Figure 2). The O K-edge XANES also confirms that Cr^{4+} does not exist in the sample (Cr^{4+} has a sharp peak just below 530 eV²⁹), which is consistent with Cr L_{3,2}-edge XANES results (see Figure 4).

Combined STXM result with TEM, FTIR and XPS results,²⁰ a mechanism for gamma-radiation-induced formation of Cr_2O_3 nanoparticles from dissolved dichromate is proposed. The radiation-

induced formation of Cr_2O_3 nanoparticles occurs in four stages. Stage I involves radiolytic reduction of $\text{Cr}^{\text{VI}}(\text{aq})$ to $\text{Cr}^{\text{III}}(\text{aq})$ species in the solution phase, followed by spontaneous condensation of $\text{Cr}(\text{OH})_3$ particles. This provides sites onto which Cr^{VI} and Cr^{III} coprecipitate and form mixed $\text{Cr}^{\text{VI}}/\text{Cr}^{\text{III}}$ oxide/hydroxide particles. In stage II, radiolytic interconversion of $\text{Cr}^{\text{VI}}(\text{aq})$ to $\text{Cr}^{\text{III}}(\text{aq})$ in solution reaches a steady state, while the adsorption of Cr^{VI} on particles continues, growing mixed $\text{Cr}^{\text{VI}}/\text{Cr}^{\text{III}}$ oxide/hydroxide particles. In stage III, solid-state conversion of Cr^{VI} and Cr^{III} in the particles slowly converts the oxide from a mixed $\text{Cr}^{\text{VI}}/\text{Cr}^{\text{III}}$ oxide/hydroxide to mainly $\text{Cr}(\text{OH})_3$. At this stage, the sample (as collected/unwashed) consists of large amount of nanoparticles with different sizes. The small particles are $\text{Cr}(\text{OH})_3$ with a diameter ranging 10-50 nm. While the large ones with size of 140-200 nm is proposed to be of core/shell structure. Chromium hydroxide is the shell and some Cr^{VI} species that was not yet converted to $\text{Cr}(\text{OH})_3$ is the core. Therefore, once the sample was washed with distilled water, TEM and STXM image show small solid nanoparticles and large hollow spheres that are both $\text{Cr}(\text{OH})_3$. At the last stage, $\text{Cr}(\text{OH})_3$ solid nanoparticles and hollow spheres were converted to Cr_2O_3 nanoparticles after dehydration process (heated at 400 °C for 5 h in air). It should be noted that it has been reported that hexagonal hollow $\text{Cr}(\text{OH})_3$ pellets have been observed, which upon heating converts to Cr_2O_3 .³⁰

Conclusion

The electronic structures of chromium hollow spheres and solid nanoparticles prepared from dissolved dichromate via gamma-radiation have been obtained by STXM at Cr $L_{3,2}$ -edge and O K-edge. Although whether or not the hollow spheres and solid particles are $\text{Cr}(\text{OH})_3$ or Cr_2O_3 can not be conclusively identified at the Cr $L_{3,2}$ -edge, it is confirmed that Cr only exists as Cr^{3+} . However, the O K-edge nano-XANES collected from big hollow spheres (single sphere) and

small solid nanoparticles (particle assembly) shows solid evidence that both the hollow spheres and the solid particles are $\text{Cr}(\text{OH})_3$, which is consistent with the XPS results (Here STXM with transmission mode gives both surface and bulk information of the sample, while laboratory XPS only surface information). Thus STXM results help better understand the structure and bonding of the products, hence the mechanism of radiation-induced formation of Cr_2O_3 nanoparticles from dissolved dichromate.

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Figure Captions

Figure 1 TEM image of the chromium nanoparticles formed by gamma radiolysis of dichromate solution. The scale bar is 200 nm.

Figure 2 (a) STXM optical density image of the chromium nanoparticles (the image was averaged from all stack images at the O K-edge and Cr $L_{3,2}$ -edge). (b) STXM optical density image at Cr $L_{3,2}$ -edge ($E = 578$ eV). The colored masks were created on different regions of interest (ROIs, e.g.: big hollow spheres and small solid nanoparticles).

Figure 3 Thickness distribution of the chromium hollow spheres and nanoparticles obtained at O K-edge. The vertical bar tracks the thickness.

Figure 4 Cr $L_{3,2}$ -edge XANES spectra extracted from the ROIs shown in Fig. 2b. Cr $L_{3,2}$ -edge XANES of standard Cr_2O_3 and $\text{Cr}(\text{OH})_3$ is also shown for comparison. The spectra are up shifted on the y axis for clarity.

Figure 5 O K-edge XANES spectra extracted from the ROIs shown in Fig. 2b. O K-edge XANES of standard Cr_2O_3 and $\text{Cr}(\text{OH})_3$ is also shown for comparison. The spectra are up shifted on the y axis for clarity.

Figure 1 TEM image of the chromium nanoparticles formed by gamma radiolysis of dichromate solution. The scale bar is 200 nm.

85x85mm (300 x 300 DPI)

Figure 2 (a) STXM optical density image of the chromium nanoparticles (the image was averaged from all stack images at the O K-edge and Cr L3,2-edge). (b) STXM optical density image at Cr L3,2-edge ($E = 578$ eV). The colored masks were created on different regions of interest (ROIs, e.g.: big hollow spheres and small solid nanoparticles).

87x48mm (300 x 300 DPI)

Figure 3 Thickness distribution of the chromium hollow spheres and nanoparticles obtained at O K-edge. The vertical bar tracks the thickness.

82x80mm (300 x 300 DPI)

Figure 4 Cr L3,2-edge XANES spectra extracted from the ROIs shown in Fig. 2b. Cr L3,2-edge XANES of standard Cr_2O_3 and Cr(OH)_3 is also shown for comparison. The spectra are up shifted on the y axis for clarity.

67x54mm (300 x 300 DPI)

Figure 5 O K-edge XANES spectra extracted from the ROIs shown in Fig. 2b. O K-edge XANES of standard Cr_2O_3 and $\text{Cr}(\text{OH})_3$ is also shown for comparison. The spectra are up shifted on the y axis for clarity.

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