Electronic Structures and Optical Properties of $\alpha$-Al$_2$O$_3$ Nanowires

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Abstract. The electronic structure and optical properties of $\alpha$-Al$_2$O$_3$ nanowires (NWs) have been investigated using X-ray absorption near-edge structures (XANES) and X-ray excited optical luminescence (XEOL). The XANES were recorded in total electron yield (TEY) and total fluorescence yield (TFY) across the K- and L$_{3,2}$-edges of aluminium and the K-edge of oxygen. The results indicate that the NWs are of a core/shell structure with a single-crystalline core and an amorphous shell. The XEOL spectra of the NWs show an intense peak at 404 nm, which comes from the F centre located in the amorphous shell of the NWs. The implication of these findings and the sensitivity of XEOL for defect detection are discussed.

1. Introduction
Aluminum oxide (Al$_2$O$_3$), an insulator with a wide band gap (9 eV), has many promising properties such as high radiation resistance, high thermal conductivity, high optical transparency, low dielectric loss, and low permeability of alkali ions and other impurities [1]. Recently, $\alpha$-Al$_2$O$_3$ (corundum) nanostructures have drawn much attention due to their excellent optical and mechanical properties and thermal stability. Various $\alpha$-Al$_2$O$_3$ nanostructures, such as nanowires [2], nanobelts [3], nanotubes [4], and nanosheets [3], have been synthesized and have shown excellent dielectric and unique optical properties. The optical properties of $\alpha$-Al$_2$O$_3$ nanostructures depend on the structure and properties of color centers (such as F, F$^+$, F$_2$, F$_2^-$, and F$_{2}^{2-}$ centers) associated with oxygen vacancies in them, which are strongly related to their morphology, crystallinity and electronic structure. In this work, we studied the electronic structure and optical properties of $\alpha$-Al$_2$O$_3$ nanowires (NWs) using X-ray absorption near-edge structures (XANES) in combination with X-ray excited optical luminescence (XEOL). A detailed XANES analysis of the NWs as well as the standard samples (metallic Al and $\alpha$-Al$_2$O$_3$ powders) indicates that the NWs are of a core/shell structure with a crystalline core and an amorphous shell, which is consistent with TEM observation. The XEOL spectra of the NWs show a strong emission at 404 nm, which is attributed to the F center located in the amorphous shell of the NWs and the core-shell interface.

2. Experimental

2.1. Sample preparation and characterization
Standard $\alpha$-Al$_2$O$_3$ (0.8-1 μm, 99.98%) and Al (17-30 μm, 99%) powders were purchased from Alfa Aesar. The synthesis of $\alpha$-Al$_2$O$_3$ NWs was carried out in a horizontal tube furnace, which has been
reported elsewhere [5]. The morphologies of the product were characterized by transmission electron microscopy (TEM; JOEL JEM 3000F).

2.2. Synchrotron measurements
Synchrotron measurements were carried out at the variable line spacing plane grating monochromator (VLS PGM) and high-resolution spherical grating monochromator (SGM) beamline at the Canadian Light Source (CLS), the University of Saskatchewan. The samples were mounted on conventional carbon tapes with an angle of 45° facing toward the photon beam. XANES were recorded in total electron yield (TEY), total fluorescence yield (TFY), and photoluminescence yield (PLY) where applicable. The TEY was detected with the specimen current and the TFY was measured by detecting the X-ray fluorescence photons using a micro channel plate. XEOL spectra were collected using a dispersive optical spectrometer (QE65000, Ocean Optics). All XANES and XEOL spectra were normalized to the incident photon flux collected on a refreshed Au grid.

3. Results and Discussion

3.1. Morphological and microstructural characterization
A TEM image of α-Al₂O₃ NWs is shown in Figure 1a. Tens of the NWs with the diameter of about 10-15 nm were grown on the aluminium particle (the upper-left corner of Figure 1a) and spread out from that like a bunch of grass. Figure 1b shows a typical high-resolution TEM (HRTEM) image of a single NW. It is interesting to point out that the NW is of core/shell structure. The core with a diameter of ~10 nm is single crystalline with an inter-planar spacing of 0.43 nm, in agreement with the d value (d = 0.433 nm) of the (003) planes of the α-Al₂O₃ crystal, which indicates that the NW grew along the <001> direction. While, a shell with a thickness of ~3 nm is found on the surface of the core showing poor crystallinity (or amorphous-like).

![Figure 1. TEM (a) and HRTEM (b) images of the as-prepared α-Al₂O₃ NWs.](image)

3.2. XANES of α-Al₂O₃NWs: Al L₃,2-edge, K-edge, and O K-edge
Al L₃,2-edge XANES of α-Al₂O₃NWs and standard α-Al₂O₃ and metallic Al powders are shown in Figure 2a. Let us first look at the α-Al₂O₃ powders. The TEY of α-Al₂O₃ powders exhibits two sharp peaks at 79.5 and 80.0 eV, and four broad peaks with the centre at 81.2, 83.9, 86.4, and 88.7 eV, which are the characteristic features of α-Al₂O₃. The two sharp peaks with higher intensity are attributed to the excitation from Al 2p³/₂ and 2p½ to 3s (3d), respectively. The four broad peaks at higher energies correspond to the unoccupied density of states (DOSs) of s (d) character due to multiple scattering. The TFY shows similar features as the TEY but the first two peaks are much shaper, indicating that the bulk of the NW is more order than that of the surface.

Next, we move to the XANES of the as-prepared NWs. At first glance the TEY of the NWs does not show any characteristic features of α-Al₂O₃. At the Al L₃,2-edge, the X-ray attenuation length is 30-40 nm. However, the TEY, which is very surface sensitive, can only detect the chemical information of the shell in the NWs. For standard metallic Al powders, their surfaces were easily oxidized in air and...
formed a thin layer of amorphous Al₂O₃. The surface sensitive TEY of the NWs exhibits similar features to that of metallic Al powders. It indicates that the shell of the NWs is amorphous Al₂O₃, which is in agreement with the observation by TEM. The bulk sensitive TFY of the NWs shows the features from both the α-Al₂O₃ core (feature b and c) and the amorphous shell (feature a and d) but the spectrum is partially inverted due to self-absorption (thickness effect) [6]. For thick samples, as the excitation energy increases abruptly at the edge, the absorption of the element increases but the effective penetration depth of the X-ray in the sample decreases, which tends to compensate for the increase in a total absorption situation. This results in a nonlinear distortion of the TFY spectra. Therefore, there is an energy shift on feature b and c in the TFY of the NWs.

Figure 2. Al L₃,₂-edge (a), K-edge (b), and O K-edge (c) XANES of α-Al₂O₃ MPs, NWs, and Al powders. The solid and dash-dot lines are TEY and TFY, respectively.

With the excitation energies increasing to Al K-edge, the XANES explores more “bulk” information of the samples. The Al K-edge XANES of α-Al₂O₃ NWs and standard α-Al₂O₃ and Al powder are shown in Figure 2b. The TEY of α-Al₂O₃ powders shows a shoulder at 1566.4 eV and six peaks at 1568.8, 1572.8, 1577.6, 1580.8, 1583.1, and 1588.5 eV. The intense absorption at 1568.8 eV (white line) is attributed to the Al 1s - 3p transition. Here, it should be noted that the TEY of the core/shell NWs displays some differences to that of α-Al₂O₃ powders. In the TEY of the NWs, the intensities of the two main peaks at 1568.8 and 1572.8 eV (feature e and f) drop off a lot, and a new shoulder at 1564.3 eV (feature g) appears. This shoulder is associated with some Al³⁺ in the shell and the interface between the core and shell being reduced to Al⁵⁺ or Al¹⁺, which results in that the main peak intensity decreases, and at the same time a shoulder at lower energy appears. The TFY of α-Al₂O₃ NWs and standard α-Al₂O₃ and Al powder show similar features as TEY but the peaks are broadened and strongly attenuated due to self-absorption (thickness effect) [6]. Metallic Al signal was found in the TFY of the NWs, which comes from the residual Al particles that were used as starting materials for the synthesis of NWs (e.g. the large particle in the upper-left corner of Figure 1a).

The O K-edge XANES of α-Al₂O₃ NWs, powder and Al powder are shown in Figure 2c. Both TEY and TFY of α-Al₂O₃ NWs and powder exhibit a pre-edge peak at 533.4 eV which corresponds to adsorbed O species [7], a main peak with the center at 542.6 eV which is attributed to O 1s-2p transition, and a few weak peaks at higher energies due to multiple scattering. Ino-Al₂O₃ powder, feature h(540.5 eV) has the maximum intensity. However, in NWs, feature i(543.5 eV) is the strongest. Compared to Al L₃,₂-edge and K-edge, O K-edge has moderate energies which still can give us some information of the surface (e.g. the shell of NWs and surface of Al powders). In the case of NWs, O K-edge XANES shows the information of both the amorphous shell and single-crystalline core. The amorphous shell contributes more on feature i (see the XANES of Al powders), therefore, feature i is more intense than feature h in NWs.
3.3. XEOL of $\alpha$-Al$_2$O$_3$NWs

The XEOL spectra of the NWs with excitation energy tuned across Al L$_{3,2}$-edge are shown in Figure 3. With different excitation energies, NWs emit bright luminescence at 404 nm, which is attributed to F center (oxygen vacancy with two electrons). The intensity of luminescence decreases when approaching the edge jump and increases above the edge jump. As shown in the inset of Figure 3, the zero order PLY of the NWs was recorded to monitor the absorption across Al L$_{3,2}$-edge. The TEY of standard $\alpha$-Al$_2$O$_3$ and Al powders are also displayed for comparison. We can clearly see that the PLY of the NWs is nearly identical to the TEY of Al powders (although inverted) but very dissimilar to that of $\alpha$-Al$_2$O$_3$ powders, indicating that the photoluminescence in the NWs originates from the oxygen site of the amorphous shell and the interface, not the single-crystalline core. It is understandable that large amounts of oxygen vacancies were generated on the surface of the NWs and the core-shell interface in an oxygen-deficient environment, which leads to the strong luminescence in XEOL. The inversion of PLY indicates that the energy transfer from Al L$_{3,2}$-edge absorption to the optical channel is less efficient when the edge turns on, but it may also be due to the residual Al particles with the size of 0.5-1 $\mu$m.

![Figure 3. Al L$_{3,2}$-edge XEOL spectra of $\alpha$-Al$_2$O$_3$ NWs with different excitation energies. Inset is the PLY of the NWs and TEY of standard Al$_2$O$_3$ and Al powders.](image)

4. Conclusion

Electronic structures and optical properties of $\alpha$-Al$_2$O$_3$ NWs were examined using XANES and XEOL. The XANES results indicate that the NWs are of a core/shell structure with a single-crystalline core and an amorphous shell. The XEOL spectra of the NWs show an intense emission at 404 nm, which comes from the F center located in the amorphous shell of the NWs.

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