

## Phase Determination of Black TiO<sub>2</sub> Nanoparticles

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The increased photocatalytic activity of black TiO<sub>2</sub> nanoparticle [1,2] is attributed to the bandgap narrowing in the surface layer produced by crystallization of amorphous material in a reducing atmosphere. These nanoparticles were found to have unique crystalline core-amorphous shell structures of TiO<sub>2</sub> stoichiometry. Here we report a form of black TiO<sub>2</sub> nanoparticles with different core-shell structure characterized by highly spatially resolved characterization methods. These particles were transformed from amorphous materials by post annealing. Spectra of monochromated electron energy-loss spectroscopy (EELS) show significant deviations of reference rutile Ti-L<sub>2,3</sub> and O-K energy-loss near edge structure (ELNES) in the near surface area (2.5nm-1nm away from vacuum) of a rutile nanoparticle, while no clear deviations are observed in the interior (7nm-4nm away from vacuum). Through a linear combination and linear least-square fits of these spectra, we find that deviation of ELNES originates from high concentration of Ti<sub>2</sub>O<sub>3</sub>. This result indicates a stoichiometric rutile core-Ti<sub>2</sub>O<sub>3</sub> shell structure.

Fig 1a shows the HRTEM image of black TiO<sub>2</sub> (rutile with diameter>15nm) nanoparticle. EELS spectra were taken from 7nm to 1nm away from surface along the direction highlighted by the arrow. As shown in Fig 1b, spectrum taken from 7nm to 4nm looks similar with each other, showing rutile characteristic. However, a significant changes of the EELS spectra taken at 2.5 nm and 1nm is evident: the two L<sub>3</sub>-e<sub>g</sub> peaks have roughly the same maximum intensity (2.5nm away from vacuum), but ELNES from spectra taken at 1nm away from vacuum further changed into smeared out anatase signature. These smeared out feature have been attribute to the existence of Ti<sup>3+</sup> component [3, 4]. In order to explore these structure changes quantitatively, we use the linear combinations of pure rutile and pure Ti<sub>2</sub>O<sub>3</sub> reference EELS spectra to fit the experimental data, as shown in Fig 1c. We use the linear least-square fitting to find the best fit between experimental and these reconstructed spectra yielding the TiO<sub>2</sub> concentrations as coefficients. The fit errors are very close to the noise level (max<13%). From the fit, Ti<sub>2</sub>O<sub>3</sub> component in this nanoparticles are responsible for the deviations of rutile ELNES: 33% Ti<sub>2</sub>O<sub>3</sub> at 2.5nm, 60% Ti<sub>2</sub>O<sub>3</sub> at 1nm. Even though deviations of Ti-L<sub>2,3</sub> ELNES are not easily observed in the range of 7nm-4nm, the least-square fits show a low Ti<sub>2</sub>O<sub>3</sub> concentration in the particle inner (11%-18%). This is consistent with a core-shell structure.

The ratio of the maximum intensity of the first two peaks (a and b for Ti<sub>2</sub>O<sub>3</sub>, and a' and b' for TiO<sub>2</sub>) uniquely identifies Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Specifically, for Ti<sub>2</sub>O<sub>3</sub> a/b<1, while for TiO<sub>2</sub> a/b>1, as

shown in Fig 2a. No obvious changes were observed in O-K ELNES at each location except near surface area where the high  $\text{Ti}_2\text{O}_3/\text{TiO}_2$  ratio gives rise to a slight change in the ratio of the maximum intensities of the first two peaks in the O-K edge at 2.5nm and a significant change 1nm away from the vacuum, as shown in Fig 2b and f.  $\text{Ti}_2\text{O}_3$  coefficients from fitting the O-K ELNES are consistent with those of Ti-L<sub>2,3</sub> ELNES within a 2% error at each location except 1nm where signal-to-noise ratio of O-K edges signals is high. Thus, the fit of ELNES is highly reliable, showing a  $\text{Ti}_2\text{O}_3$  shell and stoichiometric rutile core of a form of black  $\text{TiO}_2$  nanoparticles not reported previously.

## References

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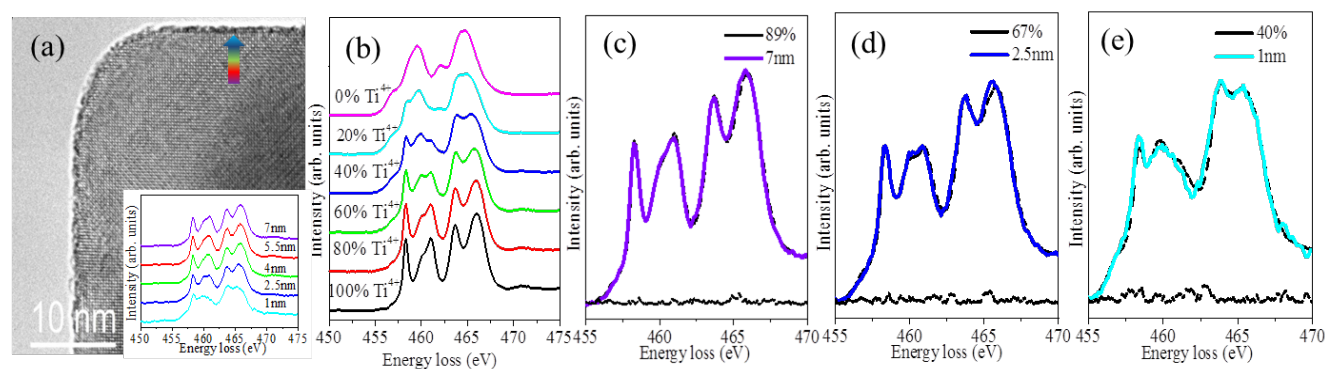


Figure 1(a) HRTEM image of rutile particle viewed in [001] zone axis. EELS spectra (inset) taken from particle inner to surface along the direction highlighted by the arrow. (b) Linear combination of Ti-L<sub>2,3</sub> ELNES from pure rutile and  $\text{Ti}_2\text{O}_3$  at different ratios. (c)-(e) Linear least-square fit of EELS spectra taken from 7nm (represent for particle inner), 2.5nm and 1nm. The difference between the experimental and reconstructed EELS spectra are given at the bottom of each image.

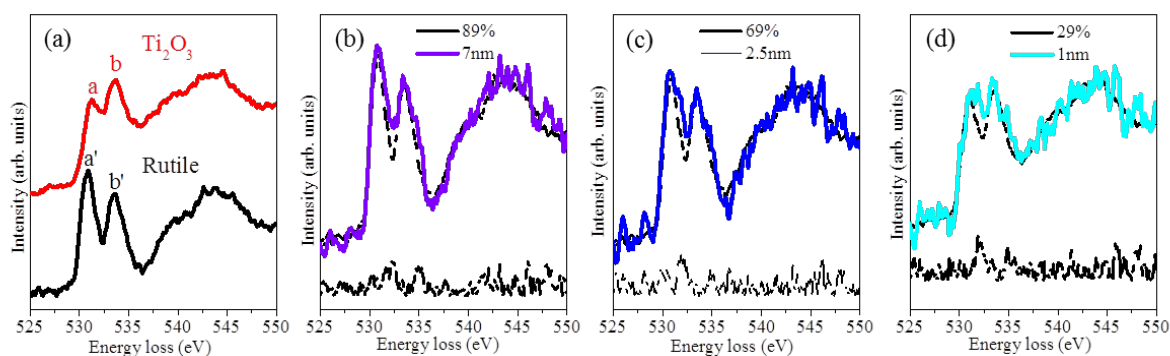


Figure 2 (a) O-K ELNES from pure rutile and  $\text{Ti}_2\text{O}_3$ . (c)-(e) Linear least-square fit of EELS spectra taken from 7nm, 2.5nm and 1nm. Difference between the experimental and reconstructed EELS spectra are given at the bottom of each image.