Local characterization of CeO_{2-x}-TiO_2 mixed metal oxide interfaces

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High energy conversion efficiency for solar fuel generation through photocatalytic water splitting necessitates visible light absorbing, high quantum efficiency materials. In 2009, photocatalytic degradation of methylene blue under visible light using TiO_2-supported CeO_2 was demonstrated and attributed to a 'coupled semiconductor' mechanism.[1] More recent experimental evidence showing Ce^{3+} enrichment at the CeO_2-TiO_2 interface suggests a mixed-metal-oxide (MMO) mechanism wherein partially occupied Ce-4f levels introduce a donor state into TiO_2's bandgap, effectively reducing the bandgap energy.[2] However, structure-activity relationships regarding the impact of increasing Ce^{3+} content on O_2/H_2 evolution rates remain inconsistent.[2-3] By utilizing monochromated electron energy-loss spectroscopy (EELS), the electronic structure about mixed metal oxide interfaces may be directly characterized to elucidate the impact of Ce^{3+} species on the light absorbing properties.

To create the composite nanoparticles, Ce precursor was loaded via wet impregnation onto large (L) and small (S) TiO_2 anatase nanoparticles. Figure 1(a) compares the powder X-ray diffraction (XRD) patterns of as-synthesized and as-loaded nanoparticles. All XRD patterns are consistent with phase-pure TiO_2 anatase and Scherrer analysis yielded average particle sizes of 66 and 14 nm for L-TiO_2 and S-TiO_2, respectively. After loading/calcination, the anatase support grows to >90 nm and the presence of CeO_2 nanoparticles ~8 nm in size are detected in 6 wt% Ce/L-TiO_2 whereas no size changes are seen in the XRD patterns from 6 wt% Ce/S-TiO_2. Figure 1(b) tracks the ultraviolet-visible absorption spectra for both composites wherein 6 wt% Ce/S-TiO_2 undergoes a significant increase in visible-light absorption evidenced by the red-shifted bandgap edge and white to yellow color change (inset, Figure 1(b)). No significant change in bulk optical absorption is observed for 6 wt% Ce/L-TiO_2.

Annular-dark field scanning transmission electron microscopy (ADF-STEM) was applied to reveal unique supported CeO_2 morphologies dominating the differently-sized TiO_2 supports. Figure 2(a) shows a Z-contrast image of an L-TiO_2 nanoparticle decorated with relatively large (>10 nm) CeO_2 nanoparticles. Smaller CeO_2 rafts and Ce single atoms (Ce_1) populate the surface of S-TiO_2, as shown in Figure 2(b). Using monochromated EELS, we aim to directly characterize the electronic structure of these different CeO_x-TiO_2 morphologies. For example, similar to previous work by our research group looking at Pr-doped CeO_2, a joint density of states approach could be applied to valence EELS data to deduce the energy position and width of bandgap states.[4] By applying this technique to valence EELS at the CeO_x-TiO_2 interface, we may be able to elucidate the electronic structure of these MMOs and correlate it with Ce^{3+} concentration providing insight into their enhanced photocatalytic activity.

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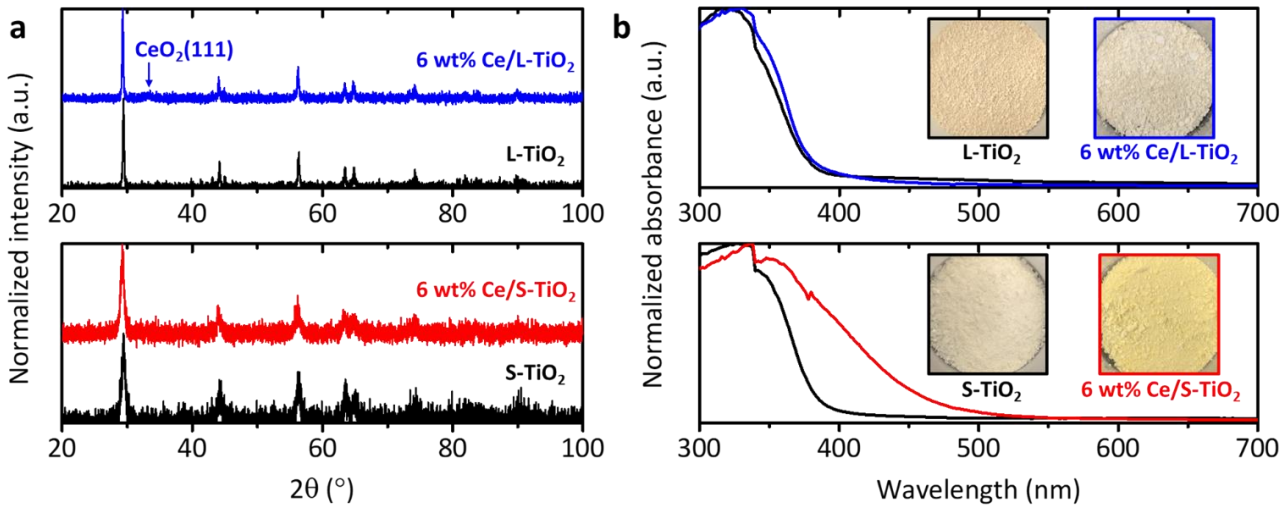

Figure 1: (a) Powder XRD and (b) UV-VIS absorption spectra of as-synthesized and Ce-loaded TiO_2 anatase composite nanoparticles.

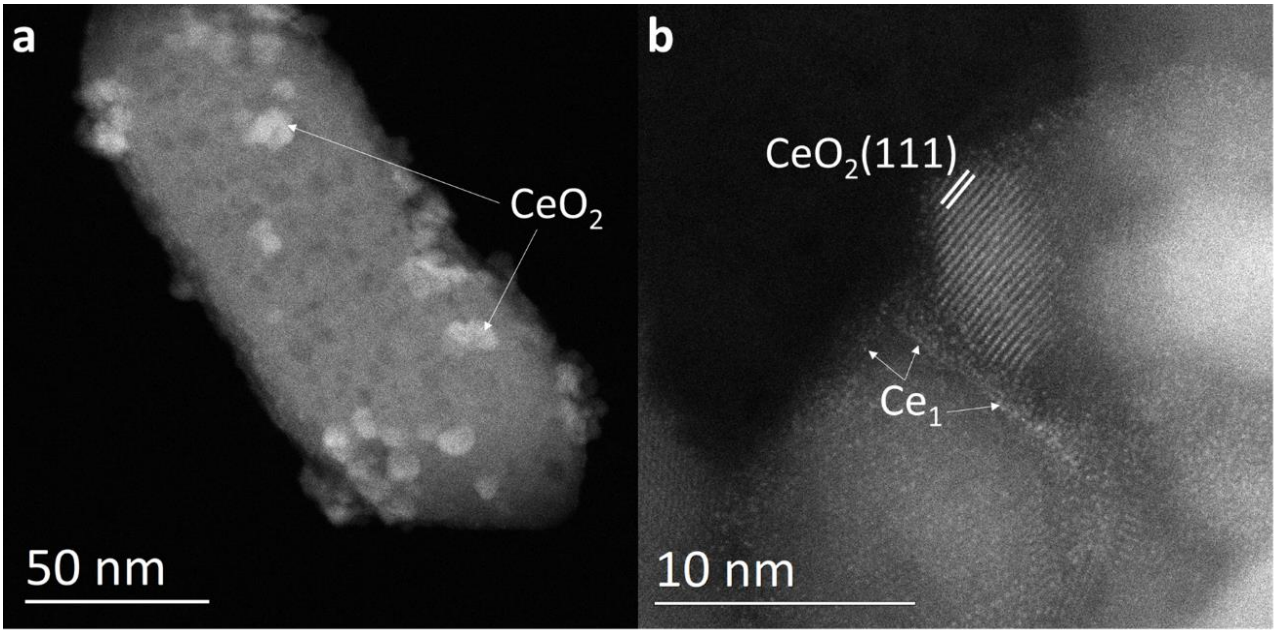

Figure 2: Representative ADF-STEM images of (a) 6 wt% Ce/L-TiO_2 and (b) 6 wt% Ce/S-TiO_2.

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