

## Characterization of Mixed Metal Oxide Interfaces Based on TiO<sub>2</sub>-supported CeO<sub>2-x</sub> Nanoparticles

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High energy conversion efficiency for solar fuel generation through photocatalytic water splitting necessitates visible light absorbing, high quantum efficiency materials. Historically, TiO<sub>2</sub> has become a widely studied ‘model’ system for this application at the expense of visible light absorption. In 2009, photocatalytic degradation of methylene blue under visible light using TiO<sub>2</sub>-supported CeO<sub>2</sub> was demonstrated and attributed to a ‘coupled semiconductor’ mechanism [1]. Here, the supported CeO<sub>2</sub> absorbs visible light photons (due an enrichment of Ce<sup>3+</sup> at the grain boundaries) and transfers photoexcited electrons to TiO<sub>2</sub> due to its more negative conduction band minimum. More recent experimental evidence showing Ce<sup>3+</sup> enrichment at the CeO<sub>2</sub>-TiO<sub>2</sub> interface suggests a mixed-metal-oxide (MMO) mechanism wherein partially occupied Ce-4f levels introduce a donor state into TiO<sub>2</sub>'s bandgap, effectively reducing the bandgap energy [2]. However, structure-activity relationships regarding the impact of increasing Ce<sup>3+</sup> concentration on O<sub>2</sub>/H<sub>2</sub> evolution rates remain inconsistent, possibly due to the inability to distinguish Ce<sup>3+</sup> at the interface vs. in the bulk of CeO<sub>2</sub> particles [2,3]. By utilizing monochromated EELS, the electronic structure about mixed metal oxide interfaces may be directly characterized to elucidate the impact of Ce<sup>3+</sup> species on the light absorbing properties.

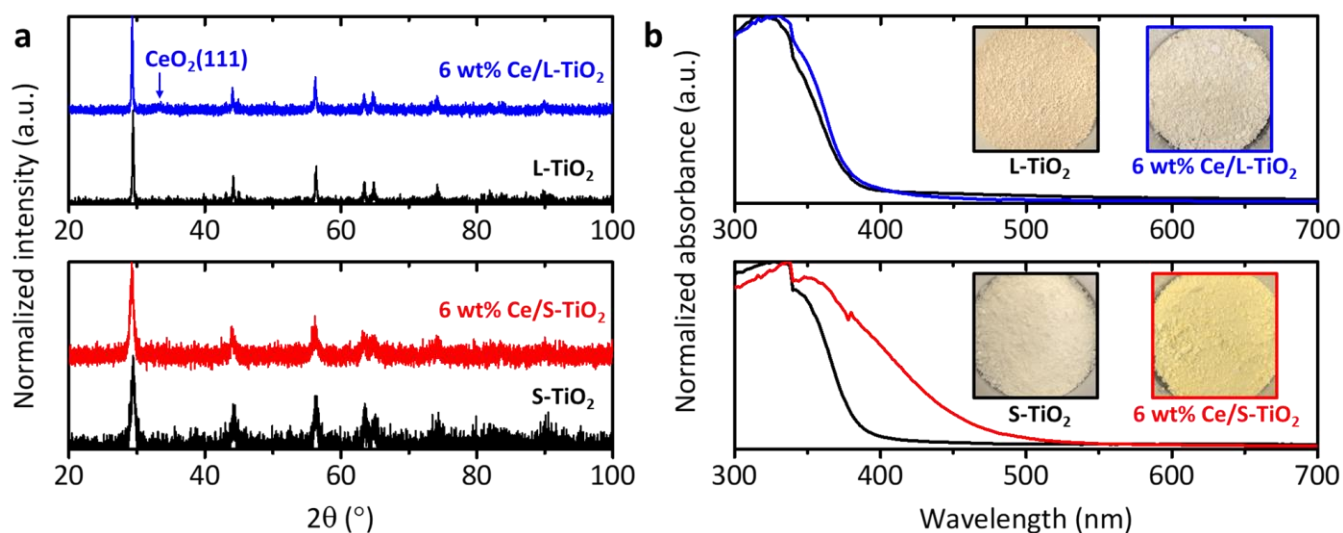
To create the composite nanoparticles, Ce precursor was loaded onto differently-sized TiO<sub>2</sub> anatase nanoparticles. Synthesis of TiO<sub>2</sub> nanoparticles involved a two-step hydrothermal route in which P25 powder (80% anatase, 20% rutile) was first transformed into sodium titanate via reaction with 10-M NaOH followed by treatment at different pH's to control the final average particle size to give large (L) and small (S) TiO<sub>2</sub> anatase [4]. Each support was impregnated with aqueous Ce(NO<sub>3</sub>)<sub>3</sub> to give 6 wt% Ce loading then calcined to remove precursors. Figure 1(a) compares the powder X-ray diffraction patterns of as-synthesized and as-loaded nanoparticles. All XRD patterns are consistent with phase-pure TiO<sub>2</sub> anatase and Scherrer analysis yielded average particle sizes of 66 and 14 nm for L-TiO<sub>2</sub> and S-TiO<sub>2</sub>, respectively. Upon loading, the anatase support grows to >90 nm and the presence of CeO<sub>2</sub> nanoparticles ~8 nm in size are detected in 6 wt% Ce/L-TiO<sub>2</sub> whereas no change is seen in the XRD pattern from 6 wt% Ce/S-TiO<sub>2</sub>. Figure 1(b) tracks the ultraviolet-visible absorption spectra for both composites wherein 6 wt% Ce/S-TiO<sub>2</sub> undergoes a significant increase in visible-light absorption evidenced by the 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<sub>2</sub>.

Aberration-corrected, annular-dark field scanning transmission electron microscopy (ADF-STEM) was applied to reveals unique supported CeO<sub>2</sub> morphologies dominating the differently-sized TiO<sub>2</sub> supports. Figure 2(a) shows a Z-contrast image of an L-TiO<sub>2</sub> nanoparticle decorated with relatively large (>10 nm) CeO<sub>2</sub> nanoparticles. On the other hand, smaller CeO<sub>2</sub> nanoparticles and Ce single atoms (Ce<sub>1</sub>) populate the surface of S-TiO<sub>2</sub>, as shown in Figure 2(b). Using monochromated electron energy-loss spectroscopy (EELS), we aim to directly characterize the electronic structure of different CeO<sub>x</sub>-TiO<sub>2</sub> morphologies and correlate these properties to photocatalytic performance. For example, similar to previous work by our research group looking at Pr-doped CeO<sub>2</sub>, a joint density of states approach could

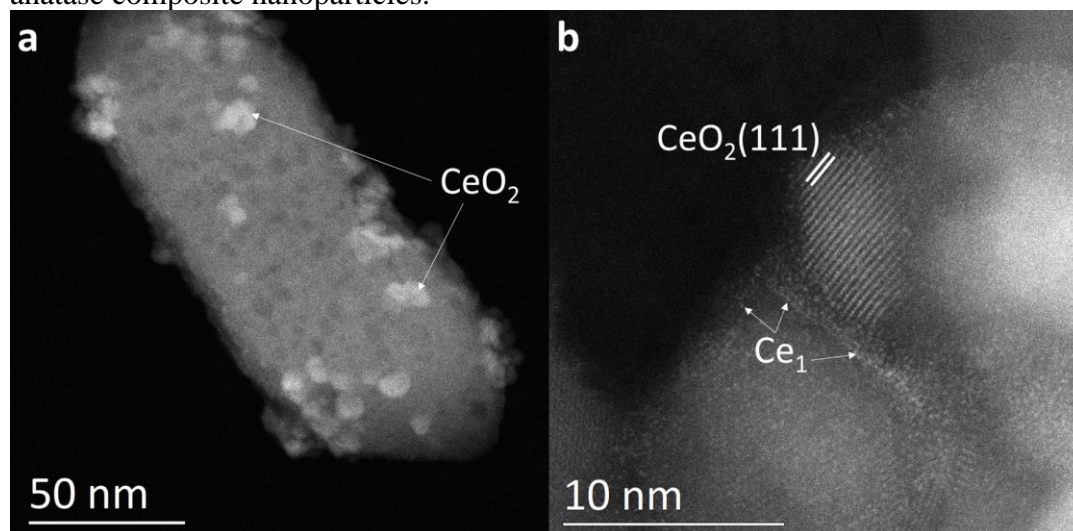
be applied to valence EELS data to deduce the energy position and width of bandgap states [5]. By applying this technique to valence EELS at the  $\text{CeO}_x\text{-TiO}_2$  interface, we may be able to elucidate the electronic structure of these MMOs and correlate it with  $\text{Ce}^{3+}$  concentration providing insight into their enhanced photocatalytic activity.

#### References:

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**Figure 1.** (a) Powder XRD and (b) UV-VIS absorption spectra of as-synthesized and Ce-loaded  $\text{TiO}_2$  anatase composite nanoparticles.



**Figure 2.** Representative ADF-STEM images of (a) 6 wt%  $\text{Ce/L-TiO}_2$  and (b) 6 wt%  $\text{Ce/S-TiO}_2$ .