Characterization of Mixed Metal Oxide Interfaces Based on TiO$_2$-supported CeO$_{2-x}$ 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$_2$ 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$_2$-supported CeO$_2$ was demonstrated and attributed to a ‘coupled semiconductor’ mechanism [1]. Here, the supported CeO$_2$ absorbs visible light photons (due an enrichment of Ce$^{3+}$ at the grain boundaries) and transfers photoexcited electrons to TiO$_2$ due to its more negative conduction band minimum. 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$^{3+}$ concentration on O$_2$/H$_2$ evolution rates remain inconsistent, possibly due to the inability to distinguish Ce$^{3+}$ at the interface vs. in the bulk of CeO$_2$ 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$^{3+}$ species on the light absorbing properties.

To create the composite nanoparticles, Ce precursor was loaded onto differently-sized TiO$_2$ anatase nanoparticles. Synthesis of TiO$_2$ 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$_2$ anatase [4]. Each support was impregnated with aqueous Ce(NO$_3$)$_3$ 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$_2$ anatase and Scherrer analysis yielded average particle sizes of 66 and 14 nm for L-TiO$_2$ and S-TiO$_2$, respectively. Upon loading, 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 change is seen in the XRD pattern 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 shifted bandgap edge and white to yellow color change (inset, Figure 1(b)).

Aberration-corrected, annular-dark field scanning transmission electron microscopy (ADF-STEM) was applied to reveals 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. On the other hand, smaller CeO$_2$ nanoparticles and Ce single atoms (Ce$_1$) populate the surface of S-TiO$_2$, as shown in Figure 2(b). Using monochromated electron energy-loss spectroscopy (EELS), we aim to directly characterize the electronic structure of different CeO$_{2-x}$-TiO$_2$ morphologies and correlate these properties to photocatalytic performance. 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 [5]. 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.

References:
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![Figure 1](https://doi.org/10.1017/S1431927618002787)

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

![Figure 2](https://doi.org/10.1017/S1431927618002787)

**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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