

Sensing Interfacial Visible Light Absorption in TiO₂-supported CeO_{2-x} Photocatalyst Nanoparticles

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Generating solar fuels such as H₂ from water will require photocatalysts that can absorb visible light and facilitate charge separation/migration for surface electrochemical reactions. Photocatalysts containing mixed metal oxide (MMO) interfaces between TiO₂ and CeO₂, both of which are UV-absorbers on their own, have garnered attention due to their ability to drive H₂/O₂ evolution from water under visible light [1,2]. Visible light absorption is hypothesized to originate from partially-occupied Ce-4f states that arise from an enrichment of Ce³⁺ at the MMO interface and act as donor levels within TiO₂'s bandgap [2]. In this view, TiO₂-supported CeO_{2-x} photocatalysts may offer a unique hierarchical geometry that confines visible light harvesting (and charge generation) near the surface. Local probing of the optical properties about such MMO interfaces would provide insights into the unique supported CeO_{2-x} morphologies that produce strong, and potentially tunable, visible light absorption.

We have created MMO interfaces by dispersing CeO_{2-x} onto the surface of size-controlled TiO₂ anatase particles. TiO₂ anatase support particles are synthesized through a two-step hydrothermal process [3]. Particle size can be controlled by varying the pH during the second hydrothermal treatment yielding average particle sizes ranging from 15 to >100 nm, as determined by powder X-ray diffraction. Subsequently, both were loaded with 6 wt% Ce via wet impregnation followed by appropriate calcination heat treatments to remove precursors. Each powder was photodeposited with Pt from PtCl₄ at a nominal loading of 0.5 wt% under visible light ($\lambda > 400$ nm) in the presence of 20 vol% aqueous triethanolamine to place active sites near MMO interfaces. Following this, H₂ production was measured under UV+visible light to maximize product formation for measurement by gas chromatography. Annular dark field scanning transmission electron microscopy (ADF-STEM) was employed to image the as-synthesized powders with atomic resolution. Diffuse reflectance spectroscopy and monochromated electron energy loss spectroscopy (EELS) were performed to yield bulk and local optical absorption spectra from each powder, respectively.

The diffuse reflectance spectra (Figure 1a) show no change in the bulk optical properties upon Ce loading onto large TiO₂ particles. A red-shifted bandgap from 3.2 to 2.7 eV is observed on smaller TiO₂ particles upon addition of Ce which is accompanied by a white-to-yellow color change. The HER of the MMO powder containing the smaller support particles is >2x that of the large TiO₂ particles owing to its increased visible light absorption (Figure 1b). ADF-STEM imaging reveals unique CeO_{2-x} morphologies dominating each support. On the large support particles, larger CeO₂ nanoparticles (*e.g.*, ~10 nm) are ubiquitous. In contrast, the small TiO₂ supports are decorated by Ce single atoms and smaller CeO₂ nanoparticles. Monochromated EELS was then applied to the sample based on small TiO₂ particles to obtain local valence EEL spectra from regions containing MMO interfaces (Figure 2). From all regions, the characteristic bandgap onset for TiO₂ at ~3.5 eV is apparent. When the probe is placed near areas containing MMO interfaces, a broad peak centered at ~1.5 eV emerges. This preliminary evidence suggests the presence of “interfacial” bandgap state(s) that facilitate absorption of visible light as low as 1.5 eV. Future work will extend this analysis to more regions of the sample and attempt to correlate the

nanoscale optical properties with local Ce^{3+} concentration and CeO_{2-x} morphology.

References:

- [1] S. Luo et al., *J. Phys. Chem. C* **119** (2015), p. 2669.
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 [3] J.N. Nian & H. Teng., *J. Phys. Chem. B* **110** (2006), p. 4193.
 [4] We gratefully acknowledge the support from the Department of Energy (DE-SC0004954) and the National Science Foundation (CHE-1508667), ASU's John M. Cowley Center for High Resolution Electron Microscopy and ASU's Eyring Materials Center.

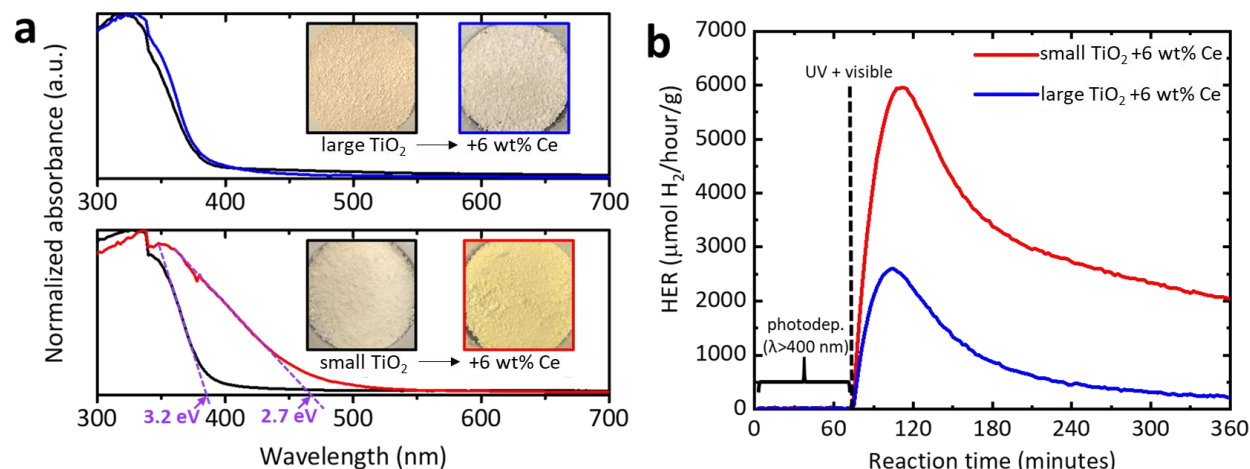


Figure 1. (a) UV-Visible absorption spectra of large TiO_2 (top) and small TiO_2 (bottom), both with and without the addition of Ce to the surface. (b) H_2 evolution rates (per mass of photocatalyst) of the $\text{TiO}_2/\text{CeO}_{2-x}$ composite nanoparticles; each were initially loaded with 0.5 wt% Pt via photodeposition under visible light ($\lambda > 400$ nm) irradiation.

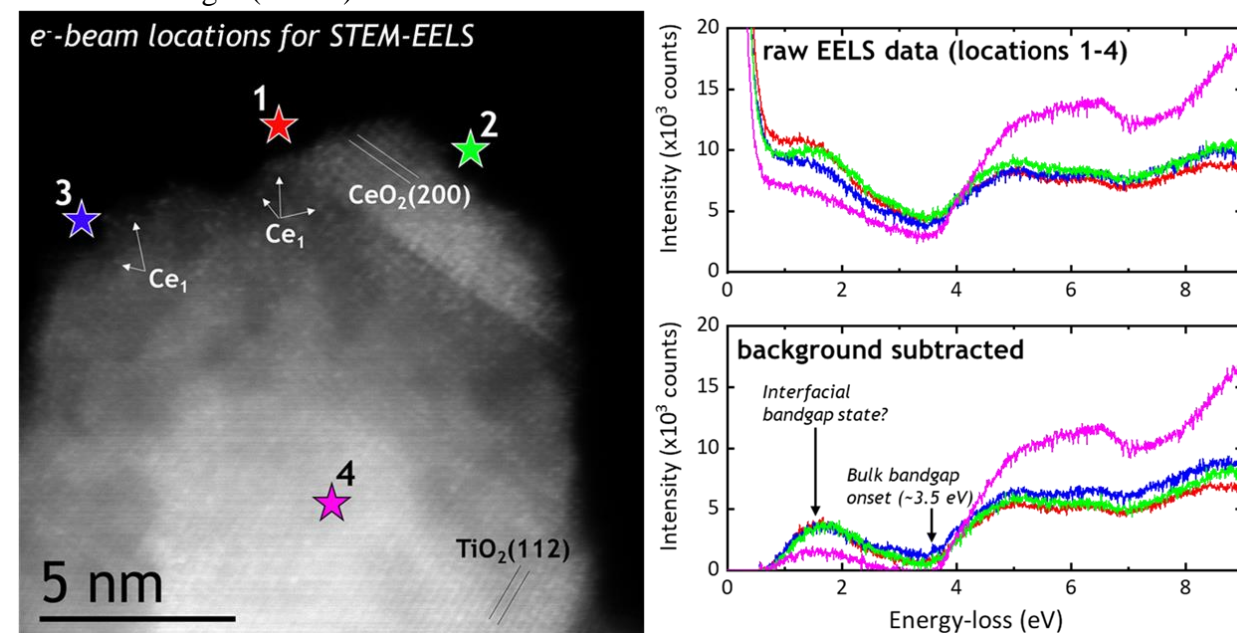


Figure 2. Valence EELS spectra from different regions of small TiO_2 loaded with Ce were acquired by placing the e^- beam at positions 1-4 (left). The raw (top right) and background-subtracted (bottom right) spectra show an “interfacial” bandgap peak suggesting interfacial visible light absorption.