

Probing Elementary Photochemical Events in Cerium Oxide by Steady-State and Ultrafast Spectroscopy

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This project seeks to understand the dynamics of photogenerated carriers or redox equivalents in nanocrystalline ceria (CeO_2), an important catalyst used in petroleum refining and other applications. In Year 1, we synthesized and characterized three different types of ceria (CeO_2) nanoparticles, discovered that CeO_2 nanoparticles undergo photoreductive dissolution in acidic conditions, and conducted broadband femtosecond transient absorption (TA) measurements with probing in the UV-Vis-mid-IR spectral regions. In Year 2, we refined our CeO_2 nanoparticle syntheses, characterized the photoreductive dissolution efficiency, performed the first TA measurements in the NIR, and began electron injection experiments using adsorbed dyes. These experiments have provided the first time-domain observations of photogenerated carriers in ceria. A manuscript describing this work will be submitted soon for publication.

Broadband ultrafast TA experiments were performed on CeO_2 and TiO_2 nanoparticles in acidic aqueous solution with excitation at 265 nm and 320 nm (**Figure 1**). We confirmed that TiO_2 carrier dynamics do not depend on excitation wavelength for pump energies above the 3.2 eV bandgap of anatase- TiO_2 . In contrast, the ceria signals depend sensitively on pump wavelength as is apparent from the time traces probed at 350 nm and 550 nm (**Figure 2**).

The signal half-life at 550 nm increases nearly tenfold when pumped at 265 nm vs. 320 nm. The slower signal decay seen with the shorter excitation wavelength is consistent with recombination of low-mobility charge carriers. On the other hand, the faster decay of the 350 nm signal observed with the 265 nm vs. 320 nm pump wavelength suggests that this signal decays due to trapping at defect sites, which are thought to be present at crystal grain boundaries and at the nanoparticle surface. Preliminary TA results on nanoparticles with larger crystalline domains reveal even slower dynamics at 350 nm, supporting this conclusion.

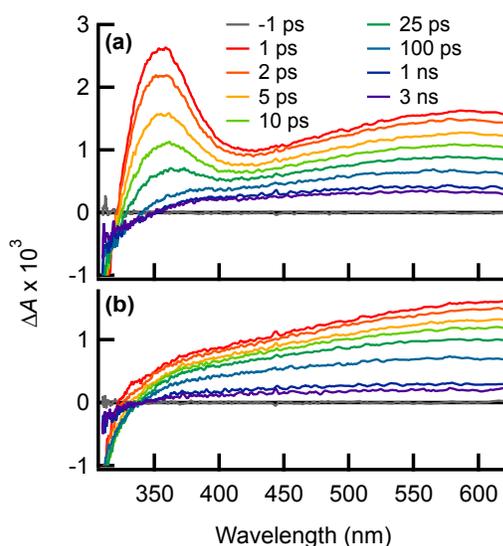


Figure 1. Transient absorption spectra of (a) CeO_2 and (b) anatase- TiO_2 recorded following 265 nm excitation at the indicated delay times.

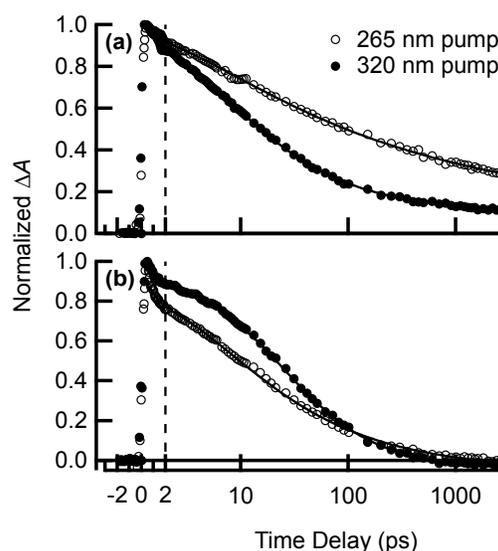


Figure 2. Transient absorption signals of CeO_2 in pH 2 aqueous solution pumped at 265 nm (open circles) and 320 nm (filled circles) and probed at (a) 550 nm and (b) 350 nm.

We assign the 350 nm signal to interband absorption by electron small polarons. While TiO_2 has a wide valence (VB) and conduction band (CB), CeO_2 has a more complicated band structure (**Figure 3**). In ceria, electrons are photoexcited to a narrow band of 4f states from where they can undergo interband absorption to the CeO_2 conduction band built primarily from Ce 5d orbitals.

The energy of the 350 nm band is higher than the calculated energy difference between the 4f states and the conduction band edge. Together with the lack of IR signal and the narrowness of the 350 nm band, this suggests that electrons self-trap, forming small polarons. When the electron polarons are trapped at defect sites, their absorption shifts to still higher energy, explaining the decay in the 350 nm signal. In order to confirm these results, we are preparing larger, single-crystal nanoparticles with fewer defects.

During the past year, we also demonstrated charge injection into CeO₂ nanoparticles from adsorbed coumarin-343 dye molecules. This is important for visible light photocatalysis and for confirming the electron and hole assignments discussed above. Whereas direct excitation of CeO₂ nanoparticles shows no evidence of mobile electrons, electron injection from coumarin-343 leads to a broad signal in the mid-IR, similar to that seen in TiO₂ (Figure 4).

UV-Vis TA experiments show a prompt bleaching of the dye absorption and spectral signatures of the oxidized dye. This suggests that electrons are injected from coumarin-343 into the CeO₂ conduction band with high efficiency.

Our results demonstrate that crystallinity profoundly influences charge carrier dynamics and reactivity in CeO₂. Our observation that Ce³⁺ ions are released at pH < 4 is a strong indication that ceria is fully oxidized in acidic conditions. To pursue our original objective of determining how Ce³⁺ defects and oxygen vacancies influence carrier recombination, we will investigate non-stoichiometric ceria (i.e., CeO_{2-x}) thin films and colloidal suspensions in nonaqueous solvents.

The spectroscopy accomplished under this award with the clear assignments of localized, polaronic states, and the ability to distinguish charge recombination from trapping, make ceria an excellent model system for fundamental studies of charge migration in metal oxides and their use in photocatalysis.

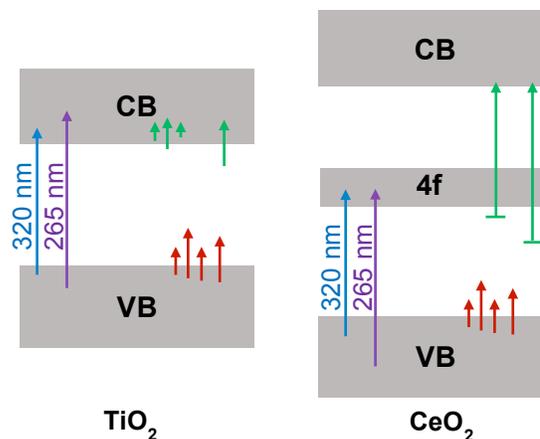


Figure 3. Band structures of TiO₂ vs. CeO₂ showing the pumped transitions (blue and purple arrows) and the probed transitions due to electrons (green arrows) and holes (red arrows).

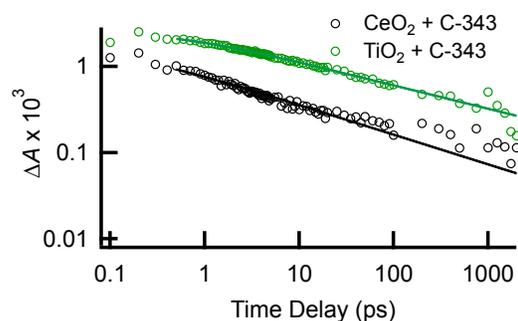


Figure 4. TA signals of coumarin-343 sensitized CeO₂ (black circles) and TiO₂ (green circles) pumped at 430 nm and probed at 3070 cm⁻¹. Solid curves are power law fits.

Impact on the PI's Research Group. This award has supported two graduate students, one of whom presented a talk with the title "Photoreductive dissolution of cerium oxide nanoparticles upon UV irradiation" in the symposium on Energy & Charge Transfer at nanoscale interfaces at the ACS National Meeting in March 2018. The funding has also allowed the Kohler Group to develop new expertise in the synthesis and characterization of metal oxide nanoparticles that will be a key to obtaining future funding.