ULTRAFAST CHARGE CARRIER DYNAMICS OF HYDROGEN TREATED AND QUANTUM DOT SENSITIZED METAL OXIDE NANOROD ARRAYS

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Introduction

Nanocomposite materials are promising for photoelectrochemical (PEC) hydrogen generation [1-4]. In one system, TiO_2 nanowire arrays were annealed in a H_2 atmosphere resulting in black TiO_2 with significantly enhanced incident photon to current conversion efficiency (IPCE) [1]. In another system, oblique angle co-deposition (OACD) was used to prepare aligned nanorod arrays composed of mixed TiO_2 and CdSe in varying compositions. The OACD method was previously utilized for the synthesis of Cr-doped TiO_2 nanorods [2]. The mixed TiO_2/CdSe nanorod arrays have a very large interfacial area between CdSe and TiO_2 which promotes charge transfer between the two materials.

We have utilized ultrafast laser spectroscopy, in conjunction with other techniques, to probe the fundamental charge carrier dynamics, including transfer, recombination, and relaxation in both the H_2 treated and CdSe sensitized TiO_2. By understanding these processes at a fundamental level we hope to improve the design of PEC water splitting materials to achieve higher efficiency.

Experimental

The primary tool used for this investigation is femtosecond (fs) transient absorption/reflection spectroscopy based on an amplified fs Ti-sapphire laser system with optical parametric amplification (OPA) for excitation and while light generation for probe with about 100 fs time resolution, and picosecond (ps) time-resolved fluorescence based on a fs Ti-sapphire oscillator and time-correlated single photon counting (TCSPC) with about 50 ps time resolution. Conventional microscopy and spectroscopy techniques, and ample synthesis and preparation have been reported previously [1-2].

Results and Discussion

Hydrogen treatment of TiO_2 nanowire films was found to increase the visible light absorption of the films rendering them black after annealing in H_2 gas at 450°C. IPCE of these samples showed little photocurrent in the visible range but dramatic enhancement of the in the UV range [1].

In the current study we are focusing on using fs transient absorption to understand the nature of the visible light transitions in H_2-treated TiO_2. **Figure 1** shows preliminary transient absorption decay profile of H_2-treated TiO_2 nanowires following a 470 nm pump excitation with a white-light continuum monitoring probe. Following the initial 180 fs excitation pulse, a small amplitude fast decay with a lifetime of ~5 ps was observed, indicative of fast electron-hole recombination as well as electron trapping into trap states. This is followed by slower trapping/recombination events persisting to tens of picoseconds. The fast initial decay suggests that the recombination is efficient, which is undesired for PEC or similar applications for which long-lived charge carriers promote efficient photocurrent generation. The effect of hydrogen treatment on the early time dynamics is significant, suggesting that hydrogen treatment has important effect on trap states within the bandgap. Even given the significant recombination, excellent photocurrent has been observed, which is partly due to the improved donor density as a result of H_2 treatment and 1-D structures that facilitate charge transfer and transport [1]. A more detailed and systematic study is currently underway.

The dynamics of CdSe/TiO_2 nanorod arrays were compared to equivalent arrays composed of CdSe alone using a pump pulse of 580 nm. It was found that the addition of as low as 28% by mass of TiO_2 drastically changed the transient absorption dynamics. The CdSe signal was dominated by a strong first exciton bleach peak centered at 700 nm and a second exciton bleach feature at 565 nm. With the addition of TiO_2 the bleach appears throughout the visible spectrum and the recovery of the bleach is much faster than in pure CdSe.

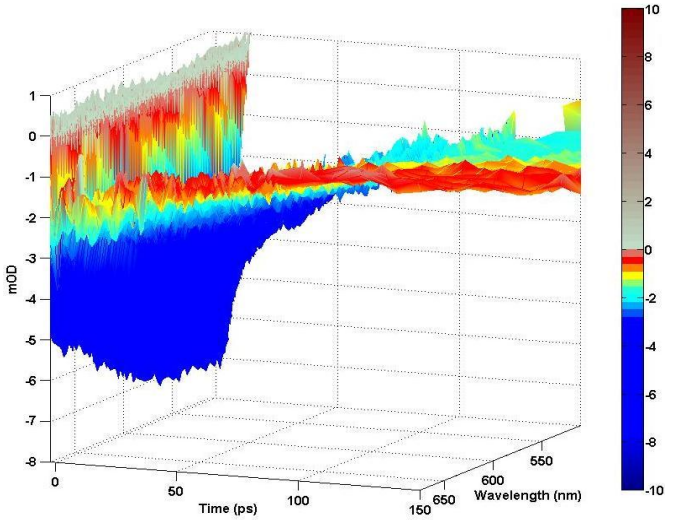

Figure 1. Transient absorption decay profile of H_2-treated TiO_2 nanowires following a 470 nm pump excitation with a white-light continuum monitoring probe. Following the initial 180 fs excitation pulse, electron-hole recombination as well as electron trapping into trap states occur quickly (~5 ps), which is followed by slower trapping/recombination events persisting to tens of picoseconds.

Conclusions

Hydrogen treated TiO_2 nanowire arrays show improved photocurrent over untreated samples. Ultrafast studies provided insights into the charge carrier dynamics in relation to PEC. In the CdSe/TiO_2 nanocomposite films, the effect of TiO_2 on the CdSe bleach dynamics shows clear charge injection from CdSe into the metal oxide. The results demonstrate that 1-D nanocomposite structures are promising for PEC and related applications.

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References

(1) Wang, G.; Wang, H.; Ling, Y.; Tang, C.; Yang, X.; Fitzmorris, B.; Wang, C.; Zhang, J.; Li, Y, *Nano Lett.,* **2011**, *11*, 3026.
(2) Larsen, G.; Fitzmorris, B.; Zhang, J. Z.; and Zhao, Y. *J. Phys. Chem. C*, **2011**, *115* , 16892.
(3) Vayssieres, L.; Beermann, N.; Lindquist, S.E.; Hagfeldt, A., *Chem. Mater.,* **2001**, *13*, 233.
(4) Tilley, S.D.; Cornuz, M.; Sivula, K.; Gratzel, M, *Angew. Chem., Int. Ed.* **2010**, *49*, 6405.