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Decoupling Bulk and Surface Contributions in Water-Splitting Photocatalysts by *In Situ* Ultrafast Spectroscopy

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By performing ultrafast emission spectroscopy in an operating, bias-controlled photoelectrochemical cell, we distinguish between bulk (charge transport) and surface (chemical reaction) recombination processes in a nanostructured photocatalyst and correlate its electronic properties directly with its incident-photon-to-current efficiency.
OCIS codes: (300.6500) Spectroscopy, time-resolved; (350.6050) Solar Energy; (310.6628) Nanostructures

Photocatalysts that harvest solar energy to convert water into hydrogen and oxygen in a photoelectrochemical water-splitting cell have been investigated for decades [1]. However, generating hydrogen-fuel by splitting water still remains a particularly complex materials science problem because the photocatalyst must simultaneously satisfy several requirements. These include restriction on its (i) bulk electronic properties for maximum light absorption and transport of photogenerated carriers to the interface (ii) band alignment and surface properties for efficient interaction with the water molecules and (iii) stability to strongly acidic or alkaline environment for prolonged performance. Furthermore, although it is generally assumed that efficient water splitting requires both a high quantum yield for charge carrier transport and for interfacial charge transfer, few studies have actually attempted to quantify each individual process selectively – including charge separation, transport and chemical reaction steps.

Here, we present a novel experimental method to measure charge carrier losses during charge separation and interfacial charge transfer in order to understand their individual impacts on the overall photocatalyst efficiency. To observe charge separation and recombination processes, which take place on the fs-to-ps timescale, we built a high-efficiency transient emission spectrometer based on the optical Kerr effect [2], connected to an operating PEC cell. Importantly, since transient emission spectroscopy can probe photoexcited species directly – in contrast to transient absorption – we can assess changes in the dynamics of the light-absorbing material even when coupled to an additional surface layer. As a proof-of-principle, the optical and electrical properties of *as-grown* zinc oxide nanowires (*ag*-ZnO) are compared to its treated counterpart, which has in addition been conformally coated with 1 nm surface layer of titania (ZnO/TiO_2) [3]. Since both samples are grown at the same time, they have the same average dimensions (diameter of ~50 nm; length of ~500 nm) and have the same initial charge carrier density.

Results and Discussion

As shown in Fig. 1, both current *vs.* voltage, impedance and emission spectroscopy can be performed in the operating PEC cell, under the same experimental conditions. Here, the ZnO/TiO_2 sample clearly shows marked improvement in performance with an incident-photon-to-current efficiency of 83%, as compared to 41% from the ag-ZnO. Although these improvements can be quantitatively evaluated (increase of 42%) and the time-integrated

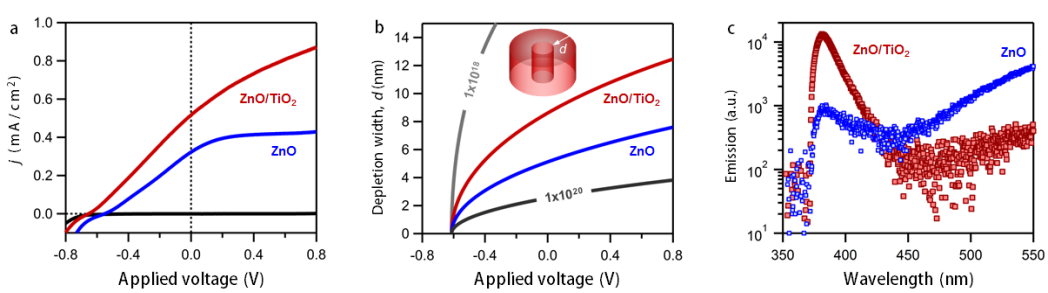

Figure 1. Characterizing electrical and optical properties of photocatalysts in the working PEC cell. (a) Current density versus applied voltage for *ag*-ZnO (blue) and ZnO/TiO_2 (red). **(b)** Depletion width as a function of voltage, obtained by Mott-Schottky analysis on the impedance spectroscopic data. **(c)** Comparing emission at flat-band potential with the band-edge emission at ~ 380 nm and the defect states emitting in the visible range.

emission suggests that a greater number of defects may be present [4], this data neither provides spatial nor temporal information about the percentage of free carriers that is lost due to defect states in the absorbing core or because of surface layer, making further improvement such heterostructured oxides difficult.

In order to provide insights about the physical mechanism of such nanostructured photocatalyst, we conduct broadband ultrafast emission spectroscopy at various applied voltages as well (Fig. 2a, b). Together with knowledge of the depletion volumes for both samples obtained by performing impedance spectroscopy (Fig. 1b), we can account for the various loss mechanisms, based on the spatial location of the minority carriers, i.e. holes for the case of ZnO (see inset of Fig.2b, c). As shown in Fig.2c, when the nanowire is biased such that holes move towards the NW core this result in a longer emission lifetime. However, when the holes are driven at the surface, a marked decrease in the lifetime is observed.

Since carrier interaction with the water molecules occurs on a much longer timescale (ns-us), this means that high-crystallinity is essential for generating the maximum number of free carriers that are involve in the chemical reaction *within* the first tens of picosecond. We note that this is despite the nanowire sizes being well below the diffusion length (~500 nm for bulk ZnO) and that both the *ag*-ZnO and *t*-ZnO/TiO_2 shows no perceivable change in their x-ray spectra. Moreover, comparing the change in lifetime – that is emission lifetime at -1V and +1V – between the *ag*-ZnO and the t-ZnO/TiO_2 reveals that the TiO_2 surface layer provides an additional source of enhanced photocatalytic activity, here about 14%, in addition to protecting the absorbing ZnO-core.

In summary we have shown that performing ultrafast emission spectroscopy in an operating PEC cell is vital to understanding the properties of nanostructured photocatalyst as charge separation that occurs during this ultrafast time frame contributes to the overall free carriers that will be later involved in the water-splitting process. Importantly, this comparative study shows the efficacy of heterostructure designs where each step critical for the water-splitting process can potentially be addressed by materials having specific, desired properties.

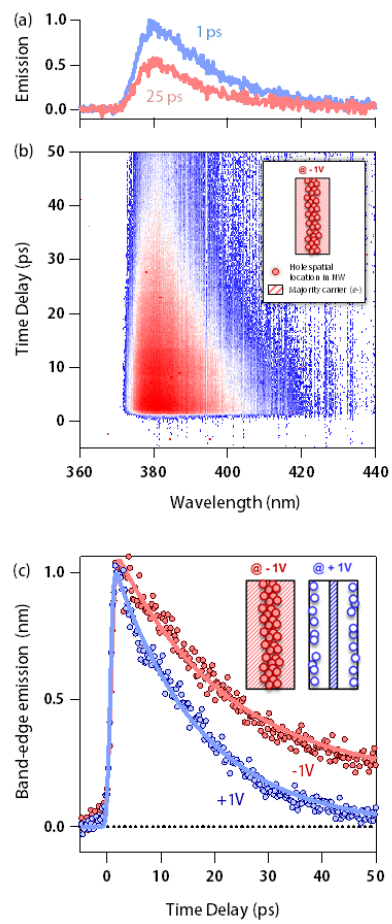

Figure 2. In situ ultrafast characterization of high-performing ZnO/TiO_2 photocatalyst. (a) Spectral emission slices at t = 1ps (red) and t = 25 ps (blue), obtained from 2D-TR emission of ZnO/TiO_2 at -1V **(b)**. **(c)** Comparing the kinetics of ZnO/TiO_2 at the band-edge emission under -1V and +1V. Inset shows the location of the holes minority carrier with respect the NW, when electrically biased.

Acknowledgements

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