

Using Time-Resolved THz Spectroscopy to Study Carrier Dynamics and Solar Energy Conversion in Nanostructured Materials

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Abstract—Terahertz (THz) spectroscopy has emerged over the last two decades as a versatile probe of a large variety of materials and processes. Because the transient THz electric field rather than its power is measured, frequency-dependent material properties such as absorption coefficient, refractive index, and complex conductivity in the far-infrared region of the electromagnetic spectrum are determined in a very straightforward manner. Optical-pump THz-probe studies characterize the photo-induced response of a material with sub-picosecond temporal resolution. One of the most important applications of time-resolved THz spectroscopy (TRTS) has been to probe transient photoconductivity and carrier dynamics in a variety of nanomaterials of interest in renewable energy research.

I. INTRODUCTION

TERAHERTZ spectroscopy has proven itself to be an excellent non-contact probe of charge injection and conductivity with sub-picosecond time resolution. One may exploit this capability to study a variety of materials, and here we choose to probe the transient photoconductivity of

dye-sensitized nanostructured wide band gap semiconductors photosensitized by high-potential chromophores. These systems are of interest in the area of renewable energy research and artificial photosynthesis.

II. RESULTS AND DISCUSSION

The charge injection time scale and efficiency for a selection of high-potential photoanodes (HPPAs) for photoelectrochemical cells (Fig. 1) will be presented. The anodes consist of tris-pentafluorophenyl free-base and metallo-porphyrin sensitizers anchored to TiO_2 and SnO_2 nanoparticles either directly or axially. THz spectroscopic studies demonstrate the sensitizers used in these HPPAs are capable of injecting electrons into the conduction band of the metal-oxide materials in those cases where the energies of the donor (excited state dye) and acceptor (metal oxide conduction band minimum) components are appropriate [1]. Importantly, the potentials photogenerated at the anode surface are high enough to permit the oxidation of high-potential electron sources.

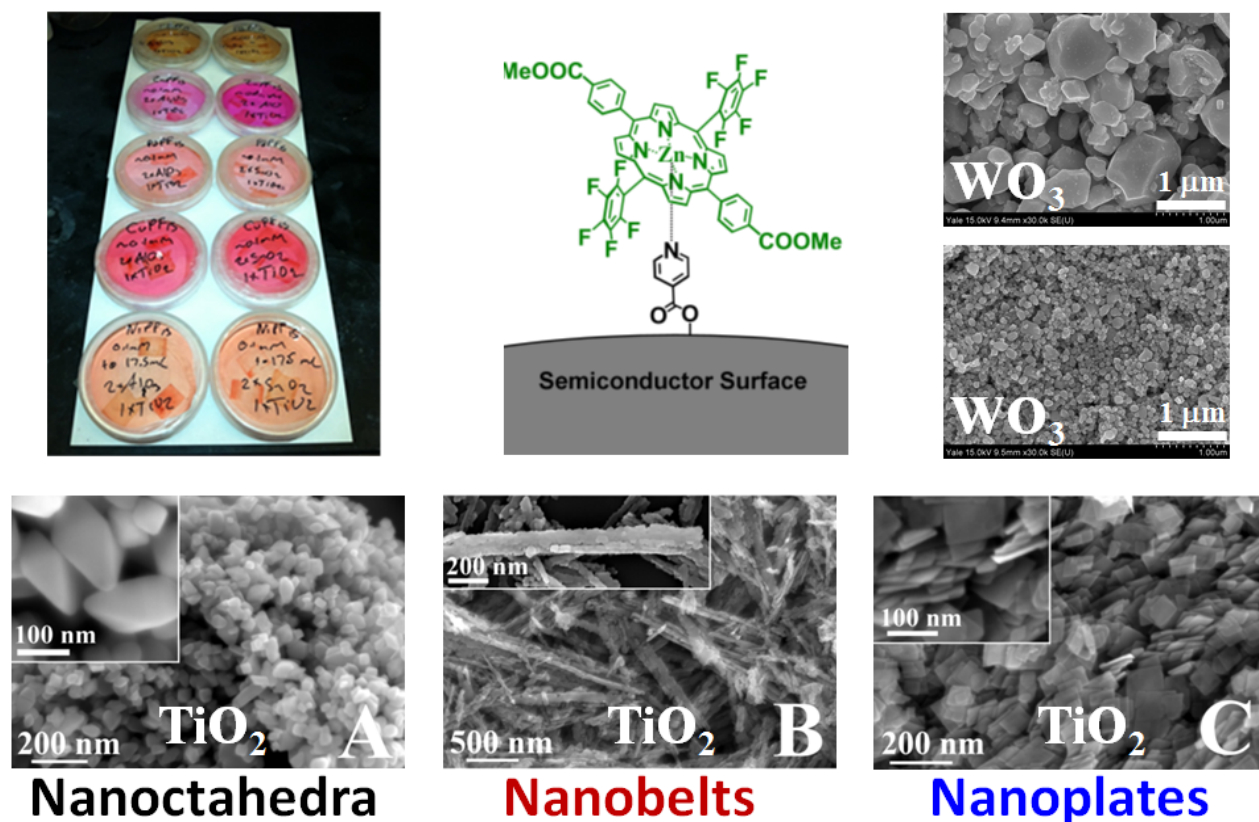


Fig. 1. Upper-left image shows dichloromethan solutions of tris-pentafluorophenyl metallo-porphyrins where $M = \text{Ni}^{2+}$, Cu^{2+} , Pd^{2+} , Zn^{2+} , and H_2 in going from the bottom to the top. Upper-center shows a high-potential Zn porphyrin axially complexed to isonicotinic acid that is anchored to a metal oxide surface. Upper-right displays WO_3 granular particles and nanoparticles. Bottom row displays anatase TiO_2 nanoparticles with different facets exposed. $\{101\}$ on the left, $\{010\}$ in the center, and $\{100\}$ on the right.

We have also investigated axially complexing bis- and tri-pentafluorophenyl Zn-porphyrin sensitizers to an isonicotinic acid anchor or variants thereof rather than binding them directly to the metal oxide surface. I will compare their binding stability in water, as well as their photoexcited interfacial electron transfer efficiency when using carboxylic acid, hydroxamate, acetylacetonate and phosphonate the anchoring group [2]. High performance dye-sensitized solar cells (DSSCs) rely upon molecular linkers that allow efficient electron transport from the photoexcited dye into the conduction band of the semiconductor host substrate. We have studied photoinduced electron injection efficiencies from modular assemblies of a Zn-porphyrin dye and a series of linker molecules which are axially bound to the Zn-porphyrin complex and covalently bound to TiO₂ nanoparticles. Experimental measurements based on terahertz spectroscopy are compared to the calculated molecular conductance of the linker molecules. We find a linear relationship between measured electron injection efficiency and calculated single-molecule conductance of the linker employed. Since the same chromophore is used in all cases, variations in the absorptivities of the adsorbate complexes are quite small and cannot account for the large variations in observed injection efficiencies. These results suggest that the linker single-molecule conductance is a key factor that should be optimized for maximum electron injection efficiencies in DSSCs. In addition, our findings demonstrate for the first time the possibility of inferring values of single molecule conductance for bridging molecules at semiconductor interfaces by using time-resolved THz spectroscopy.

The ability of WO₃ particles to photoelectrocatalytically oxidize water depends strongly on the particle dimensions. Specifically, commercially available WO₃ nanoparticles (NP) and granular particles (GP) with diameters of 77 ± 34 nm and 390 ± 260 nm, respectively, were examined. The TRTS measurements revealed that the majority of photogenerated mobile carriers are trapped within the first 50 ps after photoexcitation in both the NPs and GPs. The average diffusion lengths of the photoinduced charge carriers in the WO₃ NPs and GPs were determined to be 36 nm and 56 nm, respectively. The NPs achieved an 85-fold higher photocatalytic current than the GPs, since holes can be more efficiently transported to the WO₃/H₂O interface for catalytic oxidation.

Finally, the behavior of crystalline nanoparticles depends strongly on which facets are exposed. Some facets are more active than others, but it is difficult to selectively isolate particular facets. This study provides fundamental insights into photocatalytic and photoelectrochemical performance of three types of TiO₂ nanoparticles with predominantly exposed {101}, {010}, or {001} facets, where 86% to 99% of the surface area is the desired facet. Photodegradation of methyl orange reveals that {001}-TiO₂ has 1.79 and 3.22 times higher photocatalytic activity than {010} and {101}-TiO₂, respectively. This suggests that the photochemical performance is highly correlated with the surface energy and density of under-coordinated Ti⁴⁺ sites. In contrast, the photoelectrochemical performance of the faceted TiO₂ nanoparticles sensitized with the commercially available MK-

2 dye was highest with {010}-TiO₂ which yielded an overall cell efficiency of 6.1%, compared to 3.2% for {101}-TiO₂ and 2.6% for {001}-TiO₂ prepared under analogous conditions [3].

Measurement of desorption kinetics and accompanying computational modeling suggest a stronger covalent interaction of the dye with the {010} and {101} facets compared with the {001} facet. Time-resolved THz spectroscopy and transient absorption spectroscopy measure faster electron injection and recombination dynamics when MK-2 is bound to {010} compared to other facets, consistent with extensive computational simulations which indicate that the {010} facet provides the most efficient and direct pathway for interfacial electron transfer. Our experimental and computational results establish for the first time that photoelectrochemical performance is dependent upon the binding energy of the dye as well as the crystalline structure of the facet, as opposed to surface energy alone.

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