

## Self-Assembled Monolayers of Porphyrin Derivatives on Semiconductor Surfaces: Photoinduced Reactions at the Interface

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Photoinduced reactions at organic-semiconductor interface is the field of increasing research activities which are motivated by a wide range of existing and future applications, e.g. organic and hybrid organic-semiconductor photovoltaics and molecular sensor devices [1,2]. Among different approaches to construct such interfaces the self-assembled monolayer (SAM) method based on covalent or other strong bonding of organic compounds to semiconductor surfaces has advantages of (i) the potential ability to deposit molecular layers with well defined orientation of the photoactive molecules on the surface, and (ii) to cover semiconductor surfaces with complex morphologies such as nanoparticles, nanorods and mesoporous films. The latter is an important property for fabrication of hybrid nanodevices. At the same time it opens an opportunity to study the primary photoinduced phenomena at the interface by using ultrafast optical spectroscopy techniques, in which case the high specific surface area of the nanostructured semiconductor materials allows to prepare samples with sufficiently high absorption.

SAMs of porphyrin derivatives were deposited using carboxylic acid and triethoxysilane anchors [3, 4]. Semiconductors were hydrothermally grown arrays of ZnO nanorods and films of TiO<sub>2</sub> nanoparticles. The ZnO nanorods were further modified by atomic layer deposition (ALD) of metal oxides, such as TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> [4]. The insulating Al<sub>2</sub>O<sub>3</sub> layer allows to study photophysics of organic SAMs in conditions when the interaction with semiconductor is strongly prohibited, and these samples can serve as reference for investigations of the interfacial interactions between the SAMs and ZnO or TiO<sub>2</sub> surfaces.

The transient absorption response of zinc porphyrin SAMs deposited on a few different types of semiconductor surfaces are presented in Figure 1. The rise of the absorption at the monitoring wavelength (660 nm) can be attributed to the formation of the porphyrin cation, i.e. to the electron transfer (ET) from the porphyrin to the semiconductor. Noticeably, the slowest ET (~1 ps) and, at the same time the slowest charge recombination was observed for TiO<sub>2</sub> nanoparticles. At the surface of ZnO nanorods the ET takes place in subpicosecond time domain (~0.3 ps). The fastest ET was observed at the surface of the ZnO nanorods covered by 5 nm of TiO<sub>2</sub>, and its time constant was at the limit of the instrument time resolution (0.05-0.1 ps).

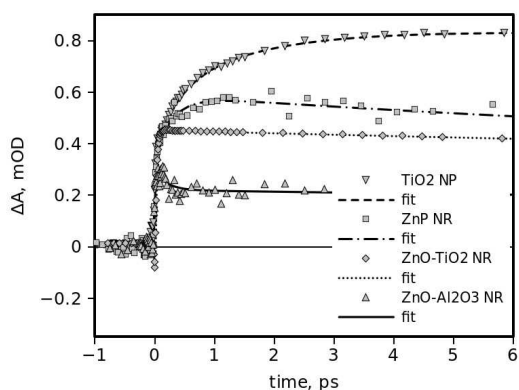


Figure 1. Transient absorption response of zinc porphyrin SAM on ZnO nanorods (ZnO NR), nanorods covered by 5 nm layers of TiO<sub>2</sub> (ZnO-TiO<sub>2</sub> NR) and 5 nm of Al<sub>2</sub>O<sub>3</sub> (ZnO-Al<sub>2</sub>O<sub>3</sub> NR), and on TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub> NP). The monitoring wavelength was 660 nm, the excitation was at 540 nm.

The band gaps of bulk ZnO and TiO<sub>2</sub> semiconductors are very close to each other. Therefore the difference in electron transfer at the surfaces can be attributed to either (1) the surface effects, such as surface defects, surface dipoles and electrostatic potential, or (2) the difference in internal electronic properties of the materials, such as density of states and carrier mobilities. Comparison of TiO<sub>2</sub> nanoparticles and nanorods covered by TiO<sub>2</sub> thin layer shows that the crystallinity and surface defects are important factors for the primary charge separation at the interface. At the same time, the interfacial charge recombination processes are virtually identical at the surfaces of ZnO nanorods and nanorods covered by a thin TiO<sub>2</sub> layer. This indicates that the bulk properties of the nanorods are determining factors for the recombination process.

## References

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