

Ultrafast dynamics at the zinc phthalocyanine/zinc oxide nanohybrid interface for efficient solar light harvesting in the near red region



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ABSTRACT

Phthalocyanine-based light harvesting nanomaterials are attractive due to their low cost, eco-friendly properties and sensitivity in the red region of the solar spectrum. However, for any practical application, phthalocyanines need to be chemically modified for anchoring groups with wide-band semiconducting nanomaterials. In this paper, zinc phthalocyanine (ZnPc) was functionalized with two carboxyl groups containing a biologically important ligand, tartrate, using a facile wet chemistry route and duly sensitized zinc oxide (ZnO) to form nanohybrids for application in photocatalytic devices. The nanohybrids have been characterized using a high-resolution transmission/scanning electron microscope (HRTEM, FEG-SEM), X-ray diffraction (XRD), steady-state infrared/UV–vis absorption and emission spectroscopy for their structural details and optical properties, whereas the ultrafast dynamical events, which are key for understanding the photocatalytic activities, were monitored using picosecond resolution fluorescence techniques. More specifically, vibrational spectroscopy (FTIR) revealed the covalent connection of ZnPc with the host ZnO nanoparticles via the tartrate ligand. The efficiency of the material for photocatalysis under red light irradiation was found to be significantly enhanced compared to bare ZnO. A mechanistic pathway for the formation of photo-induced reactive oxygen species (ROS) in an aqueous medium for the photocatalytic efficacy was investigated. To make a prototype for a potential application in a flow device for water decontamination, we have sensitized ZnO nanorods (ZnO NR) with tartrate-functionalized ZnPc. The molecular proximity of ZnPc to the ZnO surface has been confirmed by picosecond resolution Förster Resonance Energy Transfer (FRET) from the intrinsic emission of surface defects of ZnO NR to the attached ZnPc. The excited-state electron transfer dynamics, as revealed by a picosecond resolution fluorescence study (TCSPC), is in good agreement with the enhanced charge separation at the interface of the nanohybrid. The enhanced photoresponse, wavelength-dependent photocurrent of the sensitized nanorods and photodegradation of a model water pollutant in a prototype device format confirmed the potential use of the nanohybrids in water purification.

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1. Introduction

The choice of photo-sensitizers in solar light-harvesting applications, including dye sensitized solar cells (DSSC) and visible light photocatalysis (VLP) is very important. In most cases, polypyridyl ruthenium complexes are likely choices for such applications [1–4]. While the complexes work reasonably well in visible light, the main drawback of such complexes is a lack of reasonable absorption in the near-IR region. Given that IR energy accounts for 49% of the

solar spectrum, an extended red response of the sensitizers is necessary to improve the device efficiency [5]. Phthalocyanines (PCs) have been used in light-harvesting applications, including in polymer-based hybrid DSSC [6], to complement the optical absorption of the polymer in the red region of the solar spectrum. The chemical structures of the PCs are characterized by an aromatic monocyclic ligand carrying clouds of delocalized π -conjugated electrons and a central metallic atom with typically 2+ oxidation states playing the role of electron donor to the ligands. Zinc phthalocyanines (ZnPc) are a class of PCs whose main electronic features are explained in detail using DFT [7] and are represented schematically in Fig. 1. ZnPc is usually modified by the addition of anchoring groups for light-harvesting applications [8–13].

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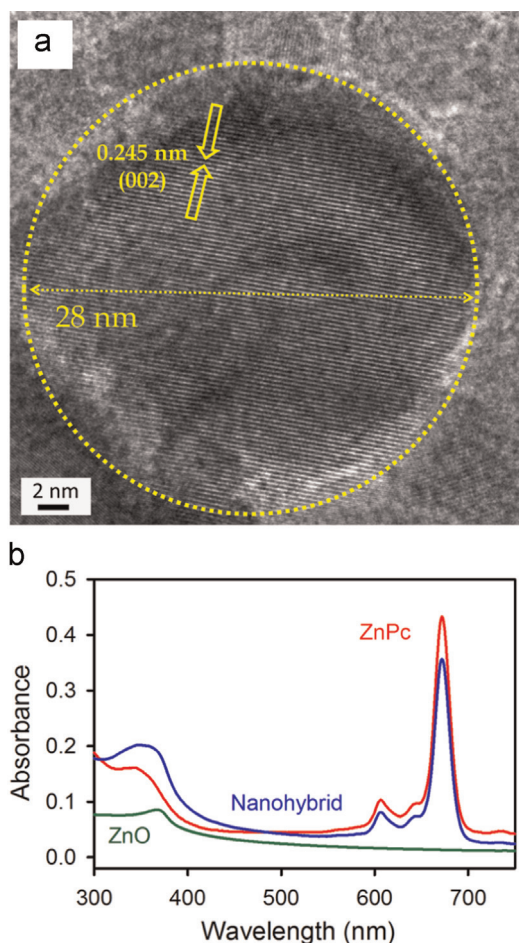


Fig. 1. (a) High-resolution transmission electron microscopy (HRTEM) of ZnO NP. Inter-fringe distance of 0.245 nm is consistent with (002) planes of the ZnO crystal. (b) UV-vis absorption spectra of ZnPc in DMSO and the nanohybrid are shown. The absorption spectrum of the suspended NPs without sensitization is shown for comparison.

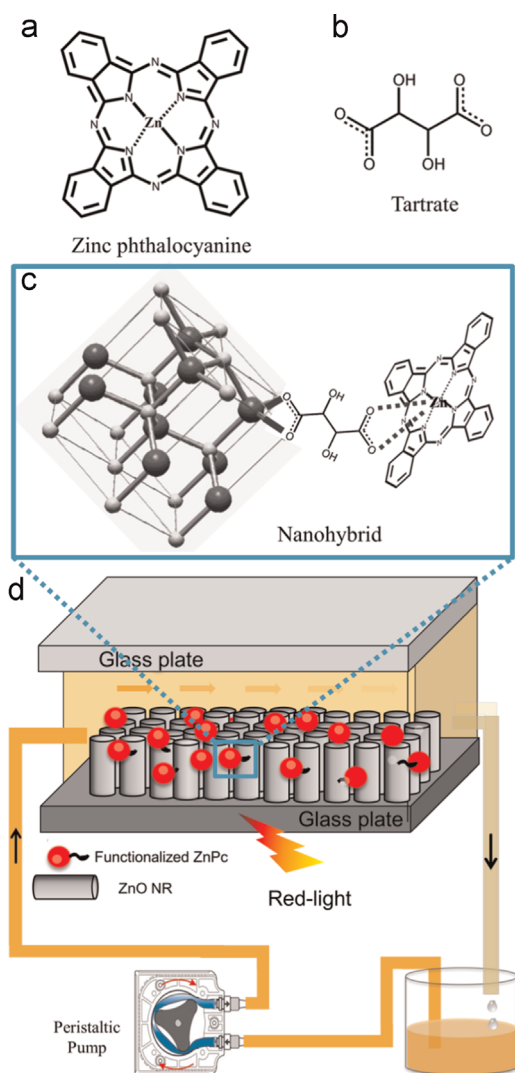
In this manuscript, a facile means to attach a biologically important ligand, tartrate, to the central metal of ZnPc using simple wet chemistry was employed. We have made nanohybrids of tartrate-functionalized ZnPc with zinc oxide (ZnO) of different morphologies (particles and nanorods) for light-harvesting applications or red light photocatalysis. Although titania (TiO_2) was reported to be a more efficient charge separator from the excited sensitizer in light harvesting, recently DSSC based on ZnO have attained efficiency that is comparable to titania [6]. Moreover, ZnO has emerged more recently in the framework of light-harvesting devices as an alternative to titania because of its flexibility in materials synthesis and significant electron mobility [14]. While Fourier transform infrared (FTIR) spectroscopy reveals attachment of the tartrate ligand through a carboxylate end to the ZnO NP, X-ray diffraction (XRD) confirms the intactness of the crystal structure of ZnO upon functionalization with tartrate. We have also studied the photocatalytic activity of the nanohybrid under red light illumination with a model water pollutant, methyl orange (MO), and found significant enhancement, which is found to be a manifestation of enhanced ROS formation from the nanohybrid in aqueous solution. To use the functional material (nanohybrid) in a flow device for the decontamination of polluted water, we have used ZnO nanorods (ZnO NR) on a glass plate duly functionalized with tartrate-ZnPc. The intrinsic emission of the ZnO NR and its spectral overlap with the absorption spectrum of ZnPc reveals Förster Resonance Energy Transfer (FRET) from the surface of the NR to the

attached ZnPc, confirming the close proximity between the sensitizer ZnPc to the host ZnO NR. We have confirmed enhanced photocurrent under visible light and measured the wavelength-dependent photocurrent in the sensitized ZnO NR. A prototype of the flow device has also been made and tested for potential application in decontamination of the model water pollutant (MO).

2. Experimental section

2.1. Reagents

Zinc acetate dihydrate, ZnO (~ 30 nm), methyl orange, zinc phthalocyanine (ZnPc), tartaric acid, zinc nitrate hexahydrate, and hexamethylenetetramine were purchased from Sigma-Aldrich. All compounds were of the highest commercially available purity and used as received. Ultrapure water (Millipore System, $18.2 \text{ M}\Omega \text{ cm}$) and ethanol ($\geq 99\%$ for HPLC, purchased from Sigma-Aldrich) were used as solvents. Analytical-grade chemicals were used for synthesis without further purification. Dimethyl sulfoxide (DMSO) and sodium hydroxide (NaOH) were purchased from Merck.



Scheme 1. (a, b) Molecular structure of the sensitizer zinc phthalocyanine (ZnPc) and the ligand tartrate are shown. (c) The nanohybrid: possible molecular attachment of ZnPc with ZnO crystal through the tartrate ligand is indicated. (d) Schematic of the prototype flow device using the nanohybrid as the functional material is shown.

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