Surface Modification of Zinc Oxide Nanorods with Zn-Porphyrin *via* Metal-Ligand Coordination for Photovoltaic Applications

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We modify ZnO nanorods with Zn-porphyrin to obtain the improved characteristics of energy transfer, which is further investigated for the applicability to photovoltaic devices. A nitrogen heterocyclic ligand containing a thiol group is covalently grafted onto the surface of finely structured ZnO nanorods with a length of 50-250 nm and a diameter of 15-20 nm. Zn-porphyrin is then attached to the ligand molecules by the mechanism of metal-ligand axial coordination. The resulting energy band diagram suggests that the porphyrin-modified ZnO nanorods might provide an efficient pathway for energy transfer upon being applied to photovoltaic devices.

Key Words : Zinc oxide, Nanorods, Porphyrin, Surface modification, Solar cells

Introduction

For organic-based photovoltaic devices including dye-sensitized solar cells (DSSCs) and organic-inorganic hybrid polymer solar cells, ZnO nanocrystals has received much attention for a new anode or n-type semiconductor material. In particular, when the surface of the metal oxide is modified with light-sensitive dyes bearing surface reactive functionalities of carboxylates,[1] thiols,[2] hydroxylates[3] and phosphates,[4] one can expect the enhanced light absorption, efficient charge separation and transport to electrodes.[5]

The key to the improved efficiency of the solar cells is suitably manipulating the size and electronic structure of the dye-modified ZnO. In DSSCs, the dye-modified ZnO nanocrystals on the anode can enhance the photoconversion efficiency when a high surface area is attained by the nanocrystals or when an efficient energy transfer from the dyes to the electrode is realized by adjusting the lowest unoccupied molecular orbital (LUMO) of the dye to the conduction band of the metal oxides.[6] The dye-coated ZnO nanorods are also similarly advantageous in exploiting for polymer-based solar cells. The typical bulk heterojuction-structured polymer solar cells formed by blending a polymer donor and a fullerene acceptor often suffer from low efficiency, low-charge mobility and exciton recombination prior to reaching the electrodes due to the short exciton diffusion length of about 10-20 nm.[7] Therefore, metal oxide nanorods with a diameter less than 20 nm and a length in a range of 100-200 nm might provide an efficient, stable pathway for the transport of photo-generated charge carriers to electrodes as a channel when hybridized into the active layer of polymer-based solar cells.[8] Furthermore, it has been suggested that the dyes grafted at the nanorod surface might also improve the characteristics of light absorption and charge carrier separation when their energy levels are optimized with those of the metal oxides.

Up to now, thiol ligands have been known for its good chemisorption property on ZnO surfaces in comparison to the other kinds of ligands.[2] Thiol-functionalized ruthenium dyes[9] and tetra(4-carboxyphenyl)porphyrin (TCPP)[10] have been examined for the surface modification of ZnO nanorods. However, concerned issues still remain, such as the mismatch in energy levels or severe nanorod aggregations due to multifunctionalities in dyes like TCPP. In this study, we demonstrate that the ZnO nanorods attached with Zn-porphyrin *via* metal-ligand coordination can be beneficially utilized for photovoltaic applications. We first prepare ZnO nanorods whose length and diameter are designed to be smaller than 250 nm and 20 nm, respectively. Then the nanorod surface is encapsulated by an alkyl thiol (but-anethiol, BT) and a nitrogen heterocyclic ligand bearing a thiol group (5-(4-Pyridyl)-1*H*-1,2,4-triazole-3-thiol, PTT), and Zn-porphyrin is attached to the surface *via* metal-ligand coordination[11] (Scheme 1). Investigation to the electronic structure by employing ultraviolet photoelectron spectroscopic (UPS) analysis reveals that the ZnO nanorods modified by Zn-porphyrin can provide well-aligned energy levels
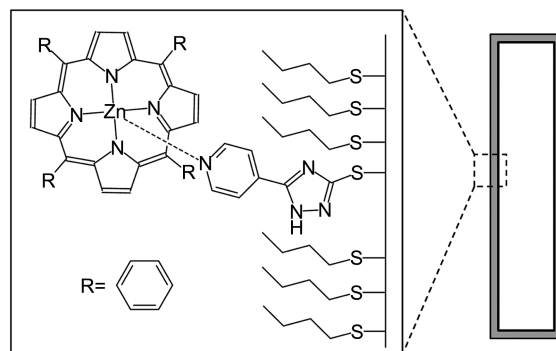
Scheme 1. Surface modification of ZnO nanorods with butane thiols (BT) and 5-(4-Pyridyl)-1*H*-1,2,4-triazole-3-thiols (PTT), followed by metal-ligand coordination with Zn-porphyrin.

to enhance the energy transfer from the dye to the ZnO, which might be useful for solar cells.

Experimental

ZnO nanorods with a controlled length and diameter were synthesized referring to a literature procedure[12] (see the supplementary information for details). To encapsulate the ZnO nanorods with organic thiols, ZnO nanorods were first dried at 200 ºC in a vacuum oven overnight and 20 mg of the dried ZnO nanorods were suspended in 10 mL of a solvent mixture (95% ethanol/5% H_2O) for 3 min with sonication and stirred for 1 hr at 65 ºC. To this solution, 10 mg (0.11 mM) of BT and 10 mg (0.056 mM) of PTT were added and sonicated for 3 min, and stirred for another 1 h at 65 ºC. The nanorods were centrifuged, washed twice with ethanol, and dried in a vacuum oven. In the last step, the nanorods were dissolved in 10 mL of 1,2-dichlorobenzene and 10 mg of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine zinc (Zn-porphyrin) was added with stirring for Zn-ligand coordination. After 1-24 h stirring, the final products were recovered by centrifugation, washed twice with 1,2-dichlorobenzene, and re-dispersed in 1,2-dichlorobenzene or dried for characterization. The details for characterization are provided in the supplementary information.

UV-vis absorption spectra and photoluminescence spectra were obtained using spectrophotometer (JASCO V-670). The crystallinity and crystal structures were investigated by X-ray Diffractometer and a high-resolution transmission electron microscope (HRTEM; TECNAI, G2 F30 S-Twin, operated at an acceleration voltage of 300 kV), for which samples are prepared by drop casting a diluted solution on a carbon coated copper grid. X-rays photoelectron spectroscopy (XPS, $h\gamma$ = 1486.6 eV AlKα) and ultraviolet photoelectron spectroscopy (UPS, $h\gamma$ = 21.23 eV He(I)) experiments were carried out on a ULVAC-PHI 5000 VersapProbe.

Results and Discussion

Since the polymer solar cells are utilizing the active layer with a thickness typically smaller than 200 nm and a domain size narrower than 20 nm to facilitate the excitons for reaching the donor/acceptor interfaces with a short diffusion length, it is significant to adjust the dimensions of ZnO nanorods for this thin film solar cell application. In our study, ZnO nanorods with a length less than 250 nm and a diameter less than 20 nm were successfully synthesized *via* two step solvothermal routes (Figure 1(a) and S1). The X-ray diffraction data (Figure S2) implies that the ZnO nanorod crystals have a hexagonal wurzite structure (a = 0.3251 nm, c = 0.5206 nm, JCPDS card no. 75-0576, Figure S2).[13-15]

To attach Zn-porphyrin onto ZnO nanorod surface by metal-ligand coordination, the surface of the nanorods was first modified with thiol molecules by using a chemisorption reaction onto the metal oxide. The metal-ligand coordination can occur between the zinc center in the porphyrin dye and the nitrogen atom in the heterocyclic molecules. However, if
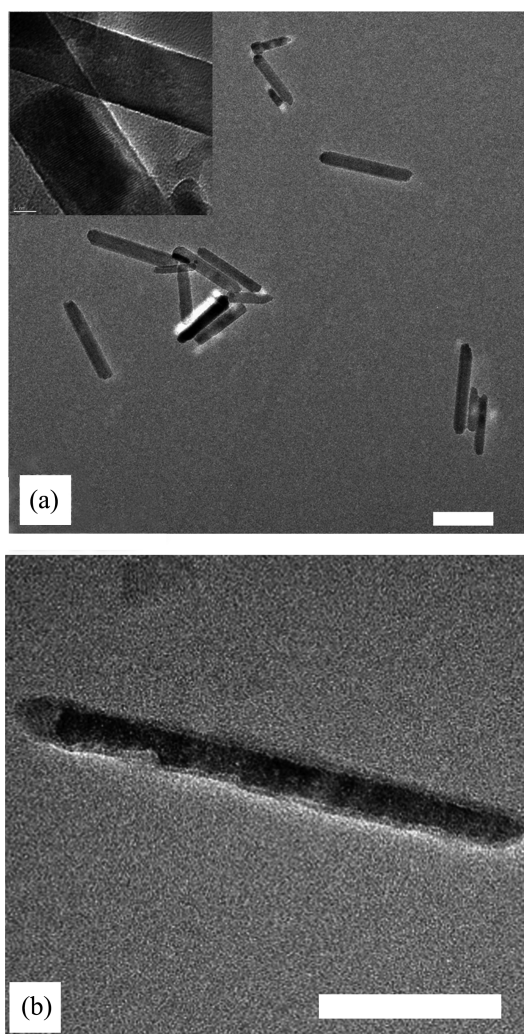

Figure 1. TEM images of ZnO nanorods (a) as prepared and (b) after modification by BT, PTT and Zn-porphyrin (The scale bar is 100 nm).

the PTT is solely located on the nanorod surface, the coordination reaction might be uncontrollable because both of the pyridyl and triazole moieties in the PTT enable the coordination reaction. To avoid this situation, we concomitantly chemisorbed an alkyl thiol, BT, whose length is suitable to sterically shield the triazole moiety in the PTT from the coordination reaction.

The attachment of thiol molecules, followed by grafting Zn-porphyrin was discerned by the observation using HR-TEM. Figure 1(b) clearly shows a thin layer with a thickness less than 5 nm which coats the ZnO nanorod surface. One can also observe that the ZnO nanorod surface morphology became irregular, compared to the pristine nanorods in Figure 1(a). We think that such a slightly roughened surface morphology originates from the dissolution of the Zn-thiol complex during the thiol grafting reaction. The mechanism of this dissolution was recently suggested by Singh *et al.*[16] In brief, hydroxyl groups can be bonded to zinc atoms on the zinc oxide lattice (ZnO-OH) and thiol molecules (RSH) react at the hydroxylated sites, forming a zinc-thiol complex

(ZnO-SR) and liberating a water molecule. This complex can readily be dissolved out into solution (Zn-SR+) and the freshly exposed ZnO surface further react with thiol molecules, which should be accelerated upon heating. As a result, the molar ratio of the PPT to BT can varies from the original recipe. Although we used twice the amount of BT than PTT, the EDS data (Figure S3), averaged over 5 different positions, reveals that 59.5 mol % of PTT-Zn-porphyrin and 40.5 mol % of BT exist on the nanorod surface. It can be attributed to the higher reactivity of PTT over BT in the grafting reaction on the ZnO surface due primarily to the electron rich moieties of pyridine and triazole in PTT and the resulting replacement reaction between thiols upon heating. Eventually, it leads to the increased molar ratio of the PTT

and irregular surface morphology, proving the dissolution mechanism experimentally.

The ZnO nanorod surface modified with BT and PTT was further characterized by X-ray photoelectron spectroscopy (XPS) and UV absorption spectra. Figure 2(a) displays XPS data of ZnO nanorods modified with the BT and PTT. The thiol molecules are known to bind to ZnO by covalent linkages, forming Zn-S bonds. It should be mentioned that the nanorods were intensively washed with ethanol to remove the unbound thiols prior to the XPS characterization. As shown in the S 2p spectrum of the Figure 2(a), a strong peak appeared at 163.1 eV agrees to the Zn-S covalent bond signal in literatures.[16-19] The existence of PTT on the nanorod surface was also verified with the UV-absorption spectrum (the thick solid line in Figure 2(b)). The strong absorption at 244 nm originates from PTT while the strong absorption peak at 362 nm is characteristic for ZnO nanorods. The attachment of Zn-porphyrin is finally confirmed by the strong Soret band maximum at 424 nm as shown by the thin solid line in Figure 2(b) and also by the strong C-N
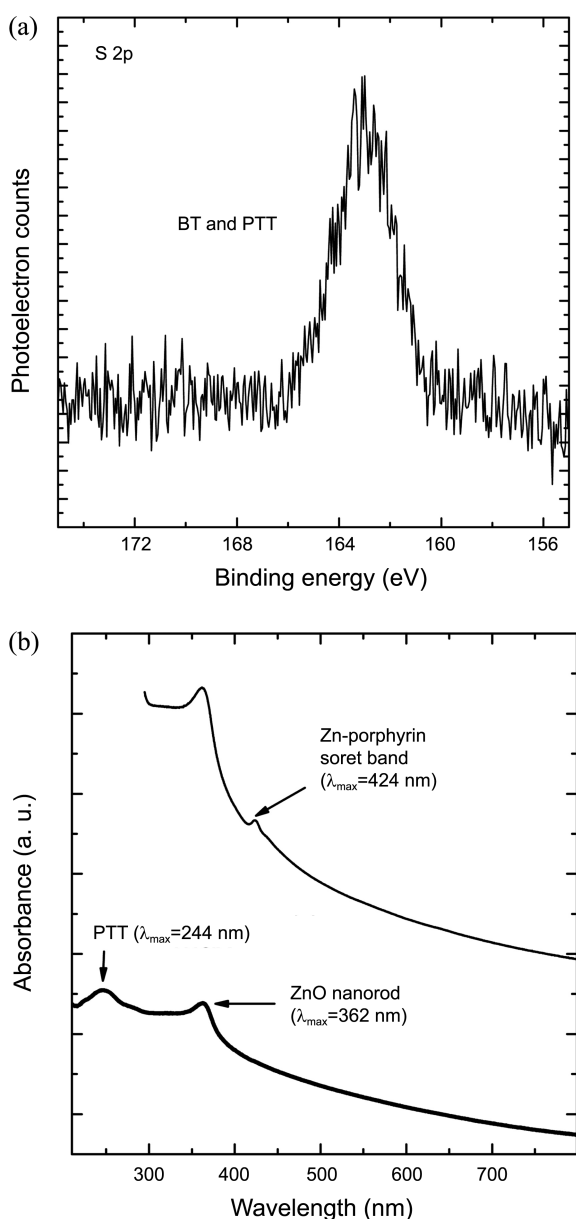

Figure 2. (a) XPS spectrum of the S 2p for ZnO nanorods modified by BT and PTT, and (b) UV-vis spectra of ZnO nanorods modified by BT and PTT (the thick solid line) and by BT, PTT, and Zn-porphyrin (the thin solid line).
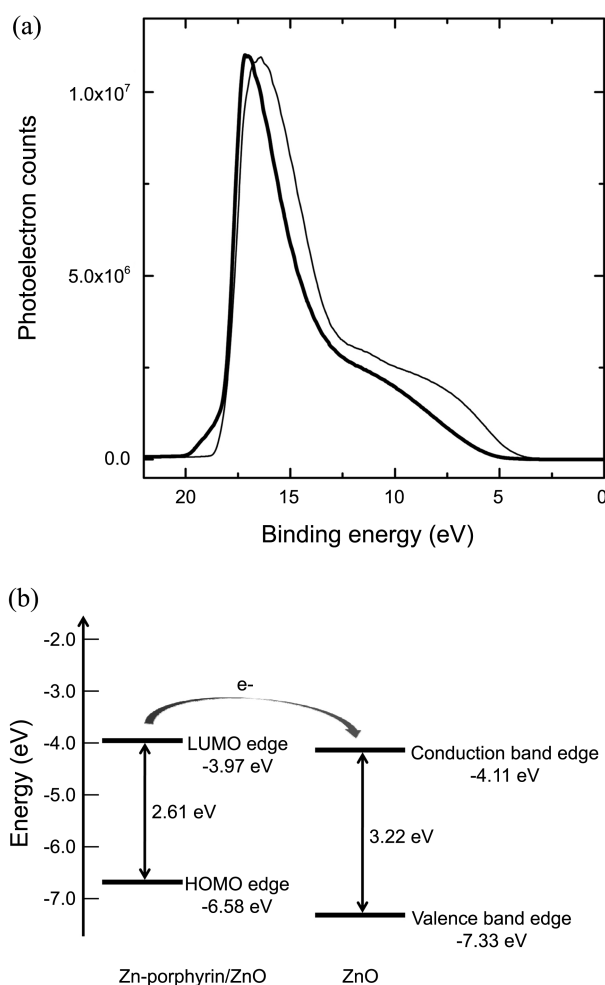

Figure 3. (a) UPS spectra of ZnO nanorods modified by BT, PTT and Zn-porphyrin (thick solid line), and pristine ZnO nanorods (thin solid line). (b) The energy level diagram of the pristine ZnO nanorods and the Zn-porphyrin-modified ZnO nanorods constructed by using the HOMO edge gained from the UPS results and the optical band gaps from the UV-vis spectra.

stretching peak at 1331 cm^{-1} in the FT-IR spectra which is distinct for Zn-porphyrin (Figure S4).

To investigate if the Zn-porphyrin-modified ZnO nanorods are optimized for photovoltaic applications, we estimated the ionization potential by measuring a UPS spectrum. The thick solid line in Figure 3(a) represents the UPS spectrum of ZnO nanorods modified by BT, PTT, and Zn-porphyrin. The edge of the highest occupied molecular orbital (HOMO) was determined by extrapolating the edges to the intersection of the baseline (Figure S5). The obtained HOMO edge is 6.58 eV which is significantly varied from the valence band edge of the pristine ZnO nanorods (7.33 eV, the thin solid line in Figure 3(a)) and the HOMO edge of Zn-porphyrin dye (5.23 eV).[20] This result clearly indicates that the valence states of the ZnO nanorods were strongly influenced by the orbital of the Zn-porphyrin.

Together with the HOMO edge value, a full scheme of the energy level diagram could be constructed by using the optical band gaps gained from the band edges in the UV-vis absorption spectra of the Zn-porphyrin-modified ZnO nanorods and pristine ZnO nanorods. In the resulting energy level diagram in Figure 3(b), the LUMO edge of the Zn-porphyrin-modified ZnO nanorod is placed at 3.97 eV below the vacuum level and at 0.14 eV above the conduction band edge of the pristine ZnO nanorod. Thus it is strongly suggested that the Zn-porphyrin-modified ZnO nanorods *via* metal-ligand coordination can be a suitable candidate for photovoltaic applications because the energy levels are well-matched, thus, the charges in the Zn-porphyrin dye can effectively be transferred to the ZnO nanorods upon light sensitization. The efficient energy transfer from the light-sensitized Zn-porphyrin to the ZnO nanorods was demonstrated by comparing the steady-state fluorescence spectrum of isolated Zn-porphyrin dyes to that of Zn-porphyrin attached to the ZnO nanorods (Figure 4). When the Zn-porphyrin was excited at 424 nm, the spectrum displays the

strong fluorescence with maxima at 599 and 646 nm. In comparison, the 93% of photoluminescence was quenched when the Zn-porphyrin grafted to the ZnO nanorods was sensitized. When we consider the emission spectrum range of the Zn-porphyrin with the absorption range of ZnO, the two ranges are not overlapped at all so that we can safely exclude the possibility of fluorescence resonance energy transfer and Dexter energy transfer. Also, it is expected that the co-chemisorption of two thiols and the Zn-porphyrin attachment *via* the metal-ligand coordination can minimize static quenching due to dye aggregation on the ZnO nanorod surfaces. Thus, we attribute this photoluminescence quenching to the efficient photoinduced electron transfer from Zn-porphyrin to the ZnO nanorods owing to the well-matched LUMO of Zn-porphyrin with the conduction band of ZnO nanorods. A similar photoluminescence quenching has also been reported for Zn-porphyrin attached to titanium oxide.[20]

Conclusion

We showed that the encapsulation of the ZnO nanorods with ligand thiols and the metal-ligand coordination with Zn-porphyrin could be a useful strategy to modify the ZnO nanorod surface. The interaction between the metal-centered porphyrin and ZnO resulted in the well-aligned energy levels for the efficient electron transfer from the Zn-porphyrin dye to the metal oxide semiconductor, as proven by the significant photoluminescence quenching. It is highly expected that the ZnO nanorods grafted with Zn-porphyrin might enhance the photocurrent generation when applied to DSSCs and hybridized into polymer solar cells.

Figure 4. The photoluminescence spectra of Zn-porphyrin (thin solid line) and Zn-porphyrin grafted to ZnO nanorods (thick solid line) in 1,2-dichlorobenzene, excited at 424 nm and at the same optical density.

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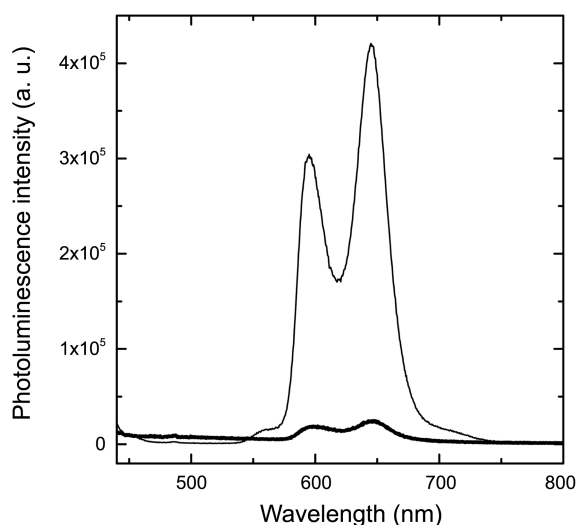
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