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## Inorganic Nanotube/Organic Nanoparticle Hybrids for Enhanced Photoelectrochemical Properties

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Inorganic/organic nanohybrids composed of arrayed TiO<sub>2</sub> nanotubes (TiNTs)/porphyrin nanoparticles (NPs) have been fabricated via a wet chemical approach. The inorganic component, particularly the arrayed one-dimensional (1D) nanostructures, provides high charge-carrier mobility and rapid charge transport. The organic component exhibits extensive visible light absorption and good solution processability. Additionally, the geometric restraint by supramolecular assembly renders an improved photostability. A combination of these two components could thus allow for an efficient solar energy conversion. In this work, a colloid of porphyrin NPs prepared by a solvent exchange method is coated on anodic TiNTs by means of a dip-coating treatment to form inorganic/organic hybrids. The hybrids exhibit an improvement on solar absorption and a significant enhancement on photocurrent generation at a small bias compared with individual component. Herein, the inorganic/organic nanohybrids are proved to be excellent photoanodes highly responsive to visible light and thus pave a way to discover new inorganic/organic assemblies for high-performance optoelectronic applications, as well as for device integration.

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### 1. Introduction

Photoelectrochemical (PEC) water splitting to produce hydrogen is considered as one of the most promising ways to achieve solar-to-fuel conversion. A number of semiconductors with controlled nanostructures have been assembled to be applied as photoelectrodes. An ideal photoelectrode used for PEC applications is required to possess sufficient active sites, broadened light absorption, and high spatial photocharge separation efficiency<sup>[1]</sup>. However, single material can hardly meet all of the above criteria. Thus, considerable efforts have been carried out on the design and fabrication of heterojunctions to gain a collective behavior to improve solar energy conversion efficiency<sup>[2,3]</sup>. Among them, inorganic semiconductors such as TiO<sub>2</sub><sup>[4,5]</sup>, Bi<sub>2</sub>WO<sub>6</sub><sup>[6-8]</sup>, BiVO<sub>4</sub><sup>[9-11]</sup>, Ag<sub>3</sub>PO<sub>4</sub> based<sup>[12-14]</sup> heterojunctions have been widely exploited. The advances of inorganic semiconductors are associated with their photostability, high charge-carrier mobility and weak electron-hole binding. However, they may suffer from low light absorption efficiency. Organic counterparts, on the other hand, exhibit wide structural diversity and remarkably enhanced UV-visible absorption<sup>[15,16]</sup>. Accordingly, heterojunctions with organic semiconductors are considered to have promising applications as cost-effective

and wide-spectrum-responsive photocatalysis<sup>[17]</sup>. It has been recently demonstrated that photocatalytic systems consisting of organic p/n bilayers or nanohybrids could be applied for highly-efficient PEC water splitting or pollutant degradation across wide or full visible light spectrum<sup>[18-20]</sup>. But their low charge-carrier mobility still shows a limit on the overall photocatalytic efficiency<sup>[21]</sup>. In this context, fabrication of novel inorganic/organic heterojunctions is necessary to take advantage of the superior carrier mobility of inorganic component, as well as the strong sunlight absorption of organic counterpart.

Among inorganic semiconductor materials, TiO<sub>2</sub> remains a favorable choice as photoelectrode. Until now, various attempts have been made to extend its photoelectrical conversion to longer wavelength. Particularly, TiO<sub>2</sub> nanotubes (TiNTs) outperform themselves in terms of light confinement, efficient charge separation, and high carrier mobility properties due to their highly ordered, unidirectional electrical channels<sup>[22]</sup>. On the other hand, one of the promising candidates for organic semiconducting materials is porphyrin that can perform essential light-harvesting and photo-induced electron transfer reaction. Because of their distinguished  $\pi$ -conjugated structure, porphyrin molecules endow an extensive absorption feature and nice assembly properties. Thus, a variety of porphyrin nanostructures have been assembled as visible-light photocatalysts, including nanowires (NWs), nanorods (NRs), nanotubes (NTs) and nanoparticles (NPs)<sup>[23-25]</sup>. Although previous efforts have been made to employ porphyrin derivatives to sensitize TiO<sub>2</sub> electrodes<sup>[26-30]</sup>,

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TiNTs hybridized with porphyrin NPs are still rarely studied. Therefore, an exploration of such inorganic/organic hybrids is also highly sought.

In this work, the inorganic nanotube/organic nanoparticle hybrids were facilely fabricated for PEC water splitting. Briefly, TiNTs were prepared via an anodization process, and colloids of meso-tetra (p-hydroxyphenyl) porphyrin (TPP) NPs were assembled by a solvent exchange method. TPP NPs were subsequently anchored on TiNTs by dip-coating to obtain the arrayed inorganic/organic nanohybrids. Given the advantages of this structure, the resultant hybrids exhibited broadened light absorption for enhanced sunlight utilization. More importantly, a remarkably high photocurrent generation has been achieved by the hybrid compared with that by its single component counterpart. These results provide a path for employing arrayed inorganic/organic nanohybrids as an efficient photoanode in PEC water splitting.

## 2. Experimental

### 2.1. Sample preparation

#### 2.1.1. Preparation of TiNTs

A Ti foil with a thickness of 0.25 mm was cut into 1 cm × 1.5 cm pieces and ultrasonically rinsed with acetone, ethanol, and deionized water in sequence for 20 min. The Ti specimen was then rinsed in HF/HNO<sub>3</sub>/H<sub>2</sub>O with volume ratio of 1:4:2 for 10 s to remove the natural-formed oxide film before anodization. The anodization was performed using a two-electrode cell with Ti foil as the working electrode and a platinum foil as the counter electrode under a constant applied voltage of 60 V at room temperature for 30 min. The distance between the two electrodes was kept at approximately 2 cm. The electrolyte contained 0.2 wt.% NH<sub>4</sub>F in ethylene glycol and H<sub>2</sub>O mixture in the volumetric ratio of 50:1. The as-prepared TiNTs were then rinsed with DI water, dried, and annealed at 450 °C for 3 h in air using a furnace with a heating rate of 10 °C/min.

#### 2.1.2. Preparation of TPP NPs colloid

TPP NPs colloid was prepared by a solvent-exchange method. TPP is soluble in ethanol and insoluble in water. In a typical process, 1 mL of TPP in ethanol solution (2.5 mg/mL) was injected into 20 mL of water to obtain TPP NPs colloid, as shown in Fig. 1. Driven by the amphiphilic molecular structure that contains hydrophilic hydroxyl groups and hydrophobic residual section (Fig. 1(a)), TPP tends to form micellar supramolecular structures that will be homogeneously dispersed in water<sup>[31]</sup>, as shown in Fig. 1(b).

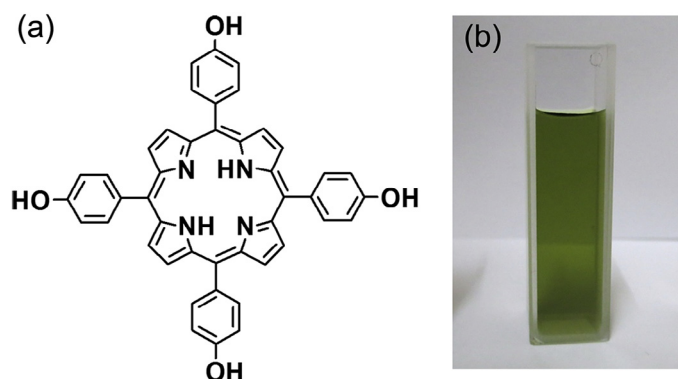


Fig. 1. (a) The molecular structure of TPP and (b) the photograph of TPP NPs colloid.

#### 2.1.3. Preparation of TiO<sub>2</sub>/TPP nanohybrids

Anodic TiNTs were dipped into the dispersion of TPP NPs, and finally dried in the vacuum oven at 100 °C for 1 h. Due to the electrostatic attraction between the rich OH-functionalized TPP and TiNTs, TPP NPs could be chemically bonded onto TiNTs. Different loadings of TPP NPs on TiNTs were allowed by repeating the dipping and drying processes. By increasing the dipping times, the as-prepared nanohybrids were denoted as hybrid I (once), II (twice), III (three times), IV (four times), and V (five times), accordingly.

### 2.2. Materials characterization

Morphologies of hybrids were observed using a Hitachi S-4800 scanning electron microscope (SEM), operated at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were taken with a JEM 2100F TEM, by using an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of specimen were obtained with a Bruker D8 Focus under CuK<sub>α</sub> radiation with a scanning speed of 10 deg./min. Raman spectra were recorded using a Renishaw Raman spectrometer (Invia reflex Raman microscope) equipped with a semiconductor-cooled CCD detector and a confocal Leica microscope. The spectrograph uses 1800 g/mm gratings and a linearly polarized Nd:YAG laser (532 nm). UV-vis absorption spectra were recorded with a Cary 5000 Varian spectrophotometer.

### 2.3. PEC measurement

The PEC measurement was carried out using a CHI 660E potentiostat/galvanostat with a three-electrode cell, in which the as-prepared samples were employed as the working electrodes, a platinum wire and a saturated calomel electrode (SCE) were employed as a counter and a reference electrode, respectively. The electrolyte was 1 mmol/L NaOH aqueous solution. The sample films (1 cm × 1.2 cm) were vertically dipped into the electrolyte and illuminated with AM 1.5 light (100 mW/cm<sup>2</sup>). The photocurrent was recorded by alternately opening and shutting the path of the incident light. The light was produced by an Oriol Sol3A solar simulator (Newport). The impedance was measured at the frequency range of 0.1 Hz–1.0 MHz using an amplitude of 10 mV at 0.05 V vs. SCE under illumination of 100 mW/cm<sup>2</sup>.

## 3. Results and Discussion

Surface and side morphologies of the as-formed TiNTs are shown in Fig. 2(a) and (b), with the pore diameters around 50 nm, wall thicknesses around 30 nm, and length up to 4 μm. For TPP colloids, as shown in Fig. 2(c), nanoscale spheres with an average diameter of ~30 nm are formed, which could be ascribed to the intermolecular π–π interaction along with hydrogen bonding interaction between TPP and water. Fig. 2(d–h) presents SEM images of the TiO<sub>2</sub>/TPP hybrids I–V where TiNTs are coated with different amounts of TPP NPs. It can be observed that the hybridized TPP NPs are dispersed evenly on the surface of TiNTs (Fig. 2(d)). With the growing loading of TPP NPs, the opening of the pores gradually narrows until the surface pores are totally covered by TPP NPs (Fig. 2(h)). As can be seen, with more TPP NPs coverage, the size of the NPs coated on TiNTs increases probably due to the aggregation of TPP NPs during the repeated drying processes. Furthermore, EDX measurements compared the relative content of the C element of the samples. As shown in Fig. S1, the bare TiNTs have a carbon content of about 4.96 at.%, and a gradual increasing of carbon content is observed for the hybrids with the loading content of TPP NPs increasing. It demonstrates that the amount of organic component has an impact on the final structure. As suggested by other researchers<sup>[32,33]</sup>, dissociative anchoring modes with chemical bonding between unsaturated

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