



Feature Article

Assembly and electron transfer mechanisms on visible light responsive 5,10,15,20-*meso*-tetra(4-carboxyphenyl)porphyrin/cuprous oxide composite for photocatalytic hydrogen production

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ABSTRACT

With 5,10,15,20-*meso*-tetra(4-carboxyphenyl)porphyrin (TCPP) and cuprous oxide nanosheet as main reactants, a novel composite (TCPP/Cu₂O) was prepared via a facile method. The assembly mechanism of TCPP and Cu₂O was investigated by UV–vis spectroscopy and FTIR. The results indicated that not only peripheries of TCPP but also the central of TCPP macrocycle interacted with Cu₂O. Furthermore, with the obtained composite as the photocatalyst, the photocatalytic activity for hydrogen production was investigated. The composite showed more excellent performance for hydrogen production than that of pure TCPP or pure Cu₂O, and also higher than that of 5,10,15,20-*meso*-tetraphenylporphyrin (TPP)/Cu₂O composite. By means of fluorescence spectra, electrochemical impedance spectra and photoelectronic performance measurement, the mechanism of electron transfer in the composite was explored. The results showed that the introduction of TCPP can enhance the light absorption of Cu₂O, and the strong interaction between TCPP and Cu₂O can quicken the transfer of photo-generated electrons. It hoped that this work can open up a new perspective for the assembly and application of dye-functionalized semiconductor nanoparticles.

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1. Introduction

The search for green energy has become hot topic because of increasing energy crisis and environmental pollution [1]. Hydrogen is considered to be a promising and environment-friendly energy with zero-carbon emission and high energy density. In technologies of hydrogen production, the technology by semiconductor-based photocatalytic water reduction for hydrogen evolution has attracted much attention.

Since some researchers concerned photocatalytic water reduction for hydrogen production, the low-cost and high-yield nanostructured photocatalysts have attracted considerable interest [2–7]. Among those reports about photocatalysts, metal oxides have attracted great attention due to their high theoretical specific capacity, and narrow band gaps [8]. Cu₂O has great advantages due to its low toxicity and favorable conduction/valence band energies

[9]. However, the application of Cu₂O is limited because of its easy corrosion and lower activity. Many efforts have been focused on solving the problems, including construction of hybrid composite structures [10], coupling with wide band-gap semiconductor [11] and morphology control [12]. Cu₂O with octahedral, cubic, spherical, multishelled spherical, and nanocage shapes have been prepared [13,14]. It is shown that the controlled syntheses of cubic and octahedral structures are vital because many other structural forms of Cu₂O crystals could derive from the two shapes [15].

In order to improve light absorption, many research groups have extensively studied on metal oxide based photocatalysts for visible light active materials. It is found that the coupling of metal oxide and dye molecule has an important influence on electron transfer efficiency and rate [16]. As a dye molecule, porphyrins are excellent building blocks because of their unique and multiple molecular structures and high visible light absorption. The porphyrins assembled on solid surfaces are widely employed to inhibit porphyrins aggregation and obtain stably functional materials for energy harvesting, water splitting, pollutant photodegradation, sensing, and photodynamic therapy [17–19]. It is reported that Rh porphyrin on

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carbon black gives higher conversion of CO than that dissolved in solution [20]. Electron transfer from photo-excited porphyrins to a variety of acceptor moieties has been interested [21]. Although the concept of dye sensitization is not new, examples of photo-functional systems composed of porphyrin with special structure attached to cubic Cu_2O are critically lack. In addition, using porphyrin molecules for surface functionalization of metal oxide will provide additional control for surface loading and attachment stability of porphyrins.

Among porphyrin molecules containing carboxyl, hydroxyl or sulfonic acid groups, those containing carboxylic groups can be combined strongly onto the metal oxides, and possess higher solar-energy conversion efficiency [22]. Meso-tetra(4-carboxyphenyl)porphyrin (TCPP) molecules have excellent photostability and heat stability, and its excited state and oxidation state have good renewable ability. Importantly, TCPP molecules easily combine with metal oxides. It is found that, with the CuTCPP sensitized TiO_2 nanotubes as the photocatalyst, the photocatalytic activity for degradation of methylene blue is improved due to the enlarged response range and effective separation of photo-generated electron-hole pairs [23]. Although many studies concerning the porphyrin-sensitized semiconductors have been carried out, the effect of functional groups located at porphyrins on the assembly and the electron transfer of the cubic Cu_2O have not been investigated in detail.

In this study, TCPP is chosen as an assembly unit and a sensitizer of the cubic Cu_2O . By a facile method, the TCPP/ Cu_2O composite is prepared. The combination mechanism between TCPP and Cu_2O is studied by various means. Moreover, photocatalytic hydrogen production and electron transfer mechanism for the obtained TCPP/ Cu_2O composite are investigated in detail.

2. Experimental section

2.1. Preparation of Cu_2O with cubic structure

All chemicals were of analytical grade and used without further purification. Typically, the Cu_2O were synthesized as follows: 1.6 g of polyethylene glycol (PEG, 10000) and 612 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were added into 200 mL of H_2O , respectively, and were stirred until PEG and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved. Then, 1.15 g of NaOH was added dropwise into the above solution. After being stirred for 15 min, 0.73 mL of N_2H_4 solution was added dropwise into the mixture. When the color of the mixture became from blue to brownish red, the mixture was filtered, washed with distilled water for several times, and dried in a vacuum oven at 60°C for 3 h.

2.2. Preparation of the TCPP/ Cu_2O composite

Typically, 1 mg of meso-tetra(4-carboxyphenyl)porphyrin (TCPP) (purchased from J&K Scientific Ltd) was dissolved into 1 mL of ethanol solution, and refluxed for 1 h with continuous stirring. Then, a certain amount of Cu_2O was added into the solution. The reaction was monitored by a UV-vis spectrophotometer. When the UV-vis spectra of the mixture did not change any more, the reaction was stopped. Subsequently, the mixture was transferred into a culture dish, and dried in a vacuum oven at 60°C . Substituted TCPP with TPP (5,10,15,20-meso-tetraphenylporphyrin, purchased from J&K Scientific Ltd), TPP/ Cu_2O composite was obtained by similar procedure.

2.3. Characterizations

Absorption spectra of all samples were recorded with a UV-3900 spectrophotometer (Japan). Fourier transform infrared spectra (FTIR) were measured using a Nicolet 6700 FTIR spectrometer

(USA). The morphology of the samples was studied using a JEOL JEM-2100F transmission electron microscope (Japan). The sample was pre-outgassed at 60°C under vacuum. X-ray powder diffraction (XRD) was recorded on a Bruker D8 Advance X-ray diffractometer equipped with $\text{Cu K}\alpha$ irradiation (Germany). Steady state emission was measured by a Hitachi F-4600 fluorescence spectrophotometer using the correction function supplied by the manufacturer (Japan).

2.4. Photoelectrochemical measurements

The photoelectrochemical performance of the samples was measured by a CHI660E electrochemical system using a three-electrode cell (Shanghai Chenhua Instruments, China). Fluorine-doped tin oxide (FTO) glasses coated with the sample were utilized as working electrodes (FTO were cleaned by sonication in ethanol, acetone, chloroform and double distilled water for 15 min, respectively, and then dried in the atmosphere), which were prepared via impregnation and subsequent calcination. In brief, 1 mg of the sample was mixed with 5 mL of alcohol, and the obtained mixture was sonicated for 30 s. After that, the FTO glass ($1 \times 1.5 \text{ cm}^2$) was soaked into the mixture for 5 min, and then was blow-dried. Repeated that for five times, and then heat-treated at 60°C for 1 h. An Ag/AgCl electrode was used as the reference electrode, and a platinum wire as the counter electrode. A 300 W Xenon lamp was used as the light source. The distance between lamp and the FTO electrode was 7 cm. The electrolyte solution was 0.5 mol L^{-1} of Na_2SO_4 aqueous solution, and the air in the solution was removed by purging N_2 for 15 min.

2.5. Measurement of photocatalytic activity

The photocatalytic activity for hydrogen evolution over the samples was performed through a CEL-SP2 N water splitting system (Zhongjiao Jinyuan Instruments, China). For photocatalytic hydrogen evolution, 10 mg of photocatalyst powder was dispersed by a magnetic stirrer in an up-irradiated photocatalytic reactor containing an aqueous solution of triethanolamine (60 mL, volume ratio of water to triethanolamine is 5:1). The reaction cell was connected to a gas circulation system, and the hydrogen evolved was analyzed by an online gas chromatograph (NaX zeolite column, high-purity N_2 as carrier gas, thermal conductivity detector). The photocatalysts were irradiated with a 300 W Xe lamp. The reaction temperature was kept at about 8.5°C by a circulating water jacket. The gas produced was automatically sampled and analyzed by the online gas chromatography. Before the photocatalytic reaction, the reactor was alternatively evacuated by a vacuum pump and flushed by nitrogen for several times to ensure complete removal of oxygen.

3. Results and discussion

Various spectroscopies are important to understand the interaction at the interface, surface composition and coordination geometry. UV-vis spectroscopy is one of the important means. Generally, porphyrin base consists of two types of characteristic absorption bands, a Soret band at about 410 nm and four Q bands in the range of 500–700 nm.

As shown in Fig. 1A (a), the TCPP in ethanol solution displays a strong Soret band at 416 nm and four weaker Q bands at 513 nm, 547 nm, 590 nm and 645 nm, respectively. After adding Cu_2O into the TCPP solution and reacting for 6 h, the UV-vis spectrum of the solution changes obviously. The Soret band is blue-shifted 3 nm, and the numbers of Q bands are reduced to one. It is the characteristic of the symmetry change from D_{2h} to D_{4h} after metal ions incorporate into porphyrin macrocycle [24]. Therefore, it is

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