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One-dimensional Z-scheme TiO_2/WO_3/Pt heterostructures for enhanced hydrogen generation

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ABSTRACT

One-dimensional Z-scheme TiO_2/WO_3/Pt heterostructures were fabricated by integrating a facile electrospinning technique and subsequent annealing in air. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and UV–vis diffuse reflectance spectroscopy, were used to characterize the as-fabricated samples. The results showed that the H_2-generation of the as-fabricated one-dimensional Z-scheme TiO_2/WO_3/Pt heterostructures (S2) was greatly enhanced compared with pure TiO_2 nanofibers (S0) and TiO_2/WO_3 nanofibers (S1). The enhanced photocatalyst activities were mainly attributed to the solid-state Z-scheme photosynthetic heterojunction system with Pt nanoparticle as an electron collector and WO_3 as a hole collector, leading to effective charge separation on these semiconductors, which were evidenced by electrochemical impedance spectroscopy (EIS) and photocurrent analysis.

1. Introduction

Utilizing solar energy to drive the semiconductor photocatalysis for production of renewable source like hydrogen is an ideal strategy to solve the growing world energy crisis and environment pollution [1–4]. Given the high photoactivity and chemical inertness, TiO_2 has been extensively used as an efficient photocatalyst for water splitting ever since its first utilization on photoelectrochemical (PEC) electrodes [5,6]. However, there are several shortcomings have limited the application of TiO_2: (1) TiO_2 can only absorb UV because of the wide band gap (Eg: ~3.2 eV) [3,7,8]; (2) low quantum yield of TiO_2 due to the rapid recombination of photogenerated charge carriers [9]; (3) large overpotential for hydrogen production [5].

Recently, Z-scheme photocatalytic system has been developed using two different semiconductors and a redox couple to achieve the overall photocatalytic [10–12]. Thus, a large number of Z-scheme nanomaterials have been investigated and used for photocatalytic, such as CdS/WO_3, g-C_3N_4/Bi_2MoO_6, g-C_3N_4/ZnO, Ag_3PO_4/MoS_2 [13–16]. In our previous work, we found that coupling WO_3 with TiO_2 can form an artificial solid-state Z-scheme photocatalytic system, promoting the separation of photogenerated electron-hole pairs by transferring photoelectrons from CB of WO_3 to VB of TiO_2. In this system, WO_3 could act as a hole collector. On the other hand, how to further improve the quantum yield of TiO_2 is another challenge. Previous research have found that loading TiO_2 photocatalysis with metal cocatalysts is an effective method to promote the quantum yield and lower the overpotential of TiO_2 because the metal cocatalysts can work as an electron-sink and active reaction sites for H_2 production [17–19]. Among all the metal cocatalysts, platinum (Pt) has been most widely used because of its small work function and low overpotential for solar-harvesting fuel production [20,21].

Besides, electrospinning is a simple, flexible and efficient technology to deal with polymers, polymer/inorganic hybrid materials and inorganic materials into one-dimensional nanofibers with controllable composition, diameter and porosity [22–25]. And, the functional electrospun nanofibers have been concerned in the photovoltaics, chemical sensors, and photocatalysis field owing to the three-dimensional (3D) open structure, large surface areas, and high porosity [26–29].

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In this work, we report the successful fabrication of the one-dimensional Z-scheme TiO_2/WO_3/Pt heterostructures through facial electrospinning technique. The investigation of photocatalytic ability indicated that the as-fabricated nanocomposites exhibited enhanced photocatalytic H_2-evolution rates under solar-light irradiation, Which might be attributed to the solid-state Z-scheme photosynthetic heterojunction system with Pt nanoparticles as an electron collector and WO_3 as a hole collector, leading to effective charge separation on these semiconductors.

2. Materials and methods

2.1. Fabrication of one-dimensional Z-scheme TiO_2/WO_3/Pt heterostructures

One-dimensional Z-scheme TiO_2/WO_3/Pt heterostructures were fabricated by electrospinning technique. Typically, 2 g tetrabutyl titanate (TBOT) (Aladdin, CP, 98.0%), 0.15 g ammonium tungstate (Aldrich, 99.95%) (Our previous study showed a higher photocatalytic activity in this proportion), an amount of $HPtCl_4$ absolute alcohol solution were dissolved in a mixture containing 10 ml ethyl alcohol (Sinopharm Chemical Reagent, 99.7%) and 6 ml acetic acid (Sinopharm Chemical Reagent, 99.5%), after magnetic stirring for 20 min, 1.1 g Polyvinyl Pyrrolidone (PVP, Mw = 1,300,000) were slowly added into the solution under vigorous stirring, the resulting solution was magnetic stirred for 12 h at room temperature. The mass concentration of H_2PtCl_6 is 0.45%. Subsequently, the above precursor solutions were drawn into a hypodermic syringe. The positive terminal of a variable high voltage power supply was connected to the needle tip of the syringe while the other terminal was connected to the collector. The distance between the needle tip and collector was ~15 cm, and the voltage was set at 15 kV. The as-collected nanofibers were calcined at a heating rate of 5°/min and remained for 30 min at 520 °C to form Z-scheme TiO_2/WO_3/Pt heterostructures (S2). As a comparison, we also prepared the TiO_2 nanofibers (S0) and TiO_2/WO_3 nanofibers (S1) use the same method.

2.2. Characterization techniques

SEM morphologies of the electrospun nanofibers were performed on a FESEM, JSM–7500F scanning electron microscope at 20 kV. TEM images were taken by a FEI Tecnai G2 F20 with an accelerating voltage of 200 kV, and samples were prepared by directly electrospinning on to the copper grid X-ray diffraction (XRD, Rigaku Ultima IV), X-ray photoelectron spectroscopy (XPS, Thermo Scientific Ltd. England), the diffuse reflectance spectra of all samples were recorded on a UV/vis spectrophotometer (Shimadzu, model UV 3600) equipped with an integrating sphere in the range of 300–800 nm and standard $BaSO_4$ powder was used as a reference.

2.3. Electrochemical experiments

Photoelectrochemical measurements were carried out in a quartz cubic urn with a conventional three-electrode process on an electrochemical workstation (AMETEK, PARSTAT 4000, America). The as-synthetic photoanode was the working electrode, and a Pt wire and Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. The electrolyte was a 0.2 M Na_2SO_4 aqueous solution. The photoanode surface has an illuminated area of $1.5 \times 1.5\ cm^2$. All the samples (0.1 g) mixing with polyethylene glycol (0.05 g) and water (0.35 ml) were deposited on the FTO conducting glass, with thin transparent cover glass to seal avoiding samples fall off. The light source was a 300 W Xe lamp (Beijing Perfectlight Co. Ltd, PLS-SXE-300). The photocurrent response spectroscopy was carried out at a constant potential of +0.9 V to the working photoanode. Electrochemical impedance spectra (EIS) were measured at an open-circuit voltage. A sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of 100 mHz to 10 kHz. All measurements were carried out at room temperature.

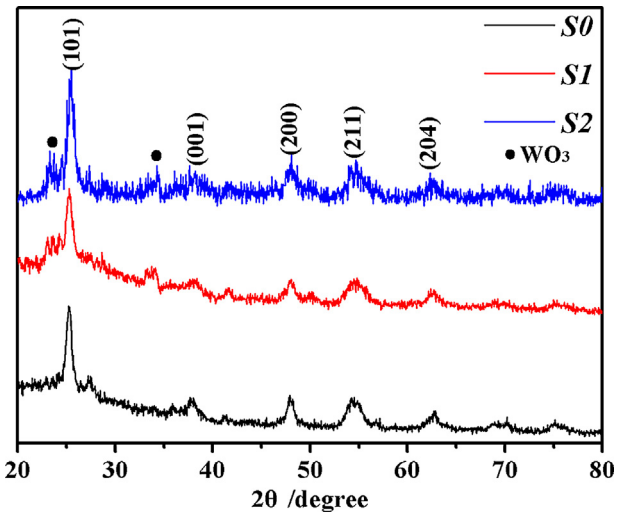

Fig. 1. XRD patterns of the as-fabricated composite nanofibers.

2.4. Photocatalytic water splitting for hydrogen production evaluation

Photocatalytic water splitting for hydrogen production was proceed on an equipment of online analysis system (LabSolar-III AG, Beijing Perfectlight Co. Ltd.) directly connected with gas chromatography (GC-7860). A 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd) was used as the light source. 0.05 g as-prepared sample was mixed with 45 ml deionized water and 25 ml methyl alcohol (anhydrous, Sinopharm Chemical Regent, 99.5%) under strong magnetic stirring for sufficient mixing. The advantage of online analysis system for hydrogen production is that we could test the amount of H_2 by real-time monitoring and the generated gas was pumped to gas chromatography every 1 h to get the in situ average hydrogen production rate.

3. Results and discussions

3.1. X-ray diffraction (XRD) patterns

X-ray diffraction (XRD) patterns (Fig. 1) of all the as-fabricated samples showed the diffraction peaks of anatase TiO_2 (ICSD: 01-070-7348) and WO_3 (ICSD: 00-001-0486). The peaks at 25.3°, 38.5°, 48.4°, 55.1° and 62.7° can be indexed to the (101), (001), (200), (211) and (204) crystal planes of the anatase phase of TiO_2, and it is in very good agreement with previous reports [30]. And the peaks of 22.9° and 33.9° can be indexed to the (002) and (220) crystal planes of the tungsten oxide. It's interesting to note that the XRD signals of Pt nanocrystals were hardly observed on the XRD patterns of TiO_2/WO_3/Pt composite nanofibers due to the low concentrations and small sizes of Pt nanoparticles.

3.2. SEM of the as-fabricated composite nanofibers

It is shown in Fig. 2a that the scanning electron microscopy (SEM) images reveal that the one-dimensional Z-scheme TiO_2/WO_3/Pt heterostructures have continuous fibrous structures with diameters of ~300 nm. These nanofibers have lengths

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