Preparation of ZnS/conductive polymer fiber composites for generation of hydrogen from water via photocatalytic reaction

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This paper focuses on the preparation of ZnS/conducting polymer fiber composites and their performance for hydrogen evolution from splitting of water via photocatalytic reaction. The nano-graphite as electrically conductive fillers were added into polyvinylidene fluoride (PVDF) and styrene-maleic anhydride copolymer (SMA) solutions, which was electrospun to make the electrically conductive polymer fibers. ZnS particles were uniformly formed on the surface of conductive polymer fibers by hydrothermal method. The rising rate of H_2 generation of ZnS/conductive polymer fiber composites was quicker than that of ZnS/non-conductive polymer fiber composites. In the third run, the average rate of H_2 evolution of ZnS/conductive polymer fiber composites was 1.35 times that of ZnS/non-conductive polymer fiber composites and 1.95 times that of ZnS powders. The electrical conductivity of carriers had an obvious effect on enhancing the photocatalytic efficiency of ZnS.

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1. Introduction

Since the discovery of hydrogen evolution through the photoelectrochemical splitting of water on TiO_2 by Fujishima in 1972, [1] photocatalytic generation of hydrogen had been considered as one of the most promising avenue for the conversion of solar energy into environmentally friendly fuels, notably by the production of hydrogen from water. [2] However, pure semiconducting photocatalyst powders are facing the challenge in large-scale application due to their low H_2 generation rate from water because of the fast recombination of photo-generated electron/hole pairs and the aggregation of semiconducting particles [3]. Therefore, semiconducting photocatalyst powders had been widely grafted onto organic, [4-5] inorganic, [6-8] and metallic [9-10] carriers. It was proved that the carriers could improve the photocatalytic activity as well as the stability of semiconducting photocatalysts [2].

Metallic carriers, such as foam nickel [11] and porous stainless steel, [12] improved electron/hole separation ability of semiconducting photocatalysts. It showed that conductive carriers were beneficial to improve photocatalytic activity. However, metal carriers were inclined to be oxidized through lost electrons, while inorganic and organic carriers were considerable stable but usually were insulated.

In our previous work, polymer fiber mats carriers were proved to inhibit the loss and aggregation of semiconducting photocatalysts and improve the photocatalytic activity efficiently [3,5,13]. In this paper, conductive polymer fiber composites were prepared by adding conductive nano-graphites to polymer fiber mats. In addition, ZnS/conductive polymer fiber composites were prepared by loading ZnS particles to the conductive polymer fiber mats, and the effect of conductive polymer fiber composites on the photocatalytic efficiency of generation of hydrogen of ZnS was studied.

2. Experimental

2.1 Materials

Polyvinylidene fluoride (PVDF) was purchased from Solvay Solexis Inc. Nano-graphites (40 nm) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Styrene-maleic anhydride copolymer (SMA), zinc acetate dihydrate ($Zn(Ac)_2{\cdot}2H_2O$), thiourea ($(NH_2)_2CS$) and other chemicals were purchased from Shanghai Chemicals Ltd. All the materials were used without further purification.

2.2 Electrospinning of conducting polymer fiber mats

A typical electrospinning process prepared conducting polymer fiber mats. PVDF (3.6 g), SMA (0.41 g) and conductive nano-graphite (0 – 0.6g) were added into the mixture solvent of acetone (14.0 ml) and N, N-dimethylacetamide (20.0 ml). After 24 h stirring, the solution was electrospun at 25 kV positive voltage, 18 cm working distance (between the target and the needle tip), and 1.2 mL/h flow rate. All process steps were operated at room temperature. Conducting polymer fiber mats were cut into strips of 5.0 cm × 5.0 cm in dimension for the succedent experiments.

As a comparative experiment, non-conducting polymer fiber composites were synthesized by the similar method without adding conductive nano-graphite.

2.3 Preparation of ZnS/conducting polymer fiber composites

The as-prepared electrospun conducting polymer fiber mats were put into the aqueous solution of zinc acetate dihydrate (25 mL, 0.25 mol/L) for 12 h to form the complex between carboxyls of electrospun conducting polymer fiber mats and the Zn^{2+}. Then the fiber mats were removed from the solution, washed with distilled water for three times, and dried in a vacuum for 2 h at 60 ^{o}C. Subsequently, the fiber mats were put into a 50 mL sealed teflon-lined stainless steel autoclave, which include desired concentration of $(NH_2)_2CS$ (50 mL, 0.25 mol/L). The autoclave was placed in an oven for 12 h at 120 ^{o}C, and then it was cooled to room temperature. The ZnS/conducting polymer fiber composites were washed with distilled water under ultrasonic vibrations in order to remove the byproducts and unreacted precursor, and were dried in vacuum for 3 h at 60 ^{o}C.

As a comparative experiment, ZnS/non-conducting polymer fiber composites and ZnS powders were synthesized by the similar method, while the latter is not loaded on electrospun fiber mats.

2.4 Photocatalytic reaction

Photocatalytic activities of the as-prepared samples for generation of hydrogen were carried in SGY-IB multi-purpose chemical reactor from Nanjing Sionetech Electrical Equipment Co., Ltd., the light source was Hg lamp (300 W, 225 nm), and the reaction system temperature was kept at 25 ± 1 ^{o}C using flowing cool water to remove the heat generated by Hg lamp. The ZnS/conducting polymer fiber composites (0.170 g containing 0.0298 g ZnS) and ZnS/non-conducting polymer fiber composites (0.169 g containing 0.0298 g ZnS) were added separately in an aqueous solution (250 mL) containing Na_2SO_3 (0.35 mol/L) and Na_2S (0.30 mol/L), while the ZnS powders (0.0298 g) were dispersed in the same solution with a magnetic stirrer. The system was initially purged by N_2 in dark environment to exclude the oxygen. The amount of H_2 production were measured by Gas chromatography (SP-6801, N_2 carrier).

2.5 Characterization

Field-emission scanning electron microscopy (FE-SEM) was carried out with a JSM-6490LV, and the transformer comprehensive test instrument was conducted with a Zentech 3302. The X-ray diffraction (XRD) (Rigaku D/max-β B, Rigaku Corporation, Japan) measurement was carried out using a Cu-Kα radiation source. X-ray photoelectron spectroscopy (XPS) spectra were detected by the ESCALAB-MK-II. Ultraviolet–visible (UV-Vis) absorption spectra were obtained on a Shimadzu Solidspec-3700 DUV spectrophotometer at room temperature. The thermo-gravimetric analysis (TGA) was applied to evaluate the content of ZnS of ZnS/conducting polymer fiber composites and ZnS/non-conducting polymer fiber composites on a Netzsch TG-209-F3.

3. Results and discussion

3.1 Structure and morphology of composites

PVDF, SMA and nano-graphite mixtures with different amounts of nano-graphite were prepared. The electrospun conductive polymer fibers had many beads when the amount of nano-graphite exceeded 0.5 g. So 0.4g nano-graphite was used during the preparation of the conductive polymer fiber mats. The SEM images of ZnS/conductive polymer fiber composites and ZnS/non-conductive polymer fiber composites were shown in Fig. 1*a* and Fig. 1*b*, respectively. The spherical ZnS particles with the diameter of about 600 nm grew on the surface of conductive polymer fibers uniformly. The dimension of ZnS particles of ZnS/non-conductive polymer fiber composites was smaller than that of ZnS/conductive polymer fiber composites. The content of ZnS in ZnS/conductive polymer fiber composites and ZnS/non-conductive polymer fiber composites, which confirmed by TGA, were 17.5% and 17.6%, respectively. And the electrical conductivity of fibers, which detected by transformer comprehensive test instrument, was 2.6×10^{-2} $S\cdot m^{-1}$.

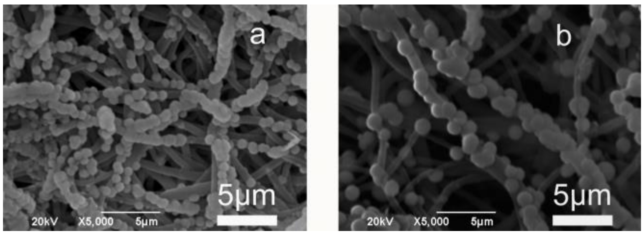

Fig. 1. SEM images of (a) ZnS/conductive polymer fiber composites and (b) ZnS/non-conductive polymer fiber composites.

Fig. 2 showed the XRD patterns of ZnS/conductive polymer fiber composites, ZnS/non-conductive polymer fiber composites and ZnS powders. The diffraction peak located at 26.48° (2θ value in Fig. 2*b* and Fig. 2*c*) corresponded to (002) graphite phase (PDF NO. 26-1079). The diffraction peaks at 2θ = 28.47°, 47.58°, 56.22° corresponded to (111), (220), (311) planes of the sphalerite structure of ZnS (PDF NO. 05-0566). Comparing with ZnS powders in Fig. 2*a*, the diffraction peaks in ZnS/conductive polymer fiber composites and ZnS/non-conductive polymer fiber composites, which corresponding to (220) and (311) planes, are not so obvious. This may be resulted from the interaction of chemical bond between Zn^{2+} and the carboxyl on the surface of the conductive and non-conductive polymer fibers.

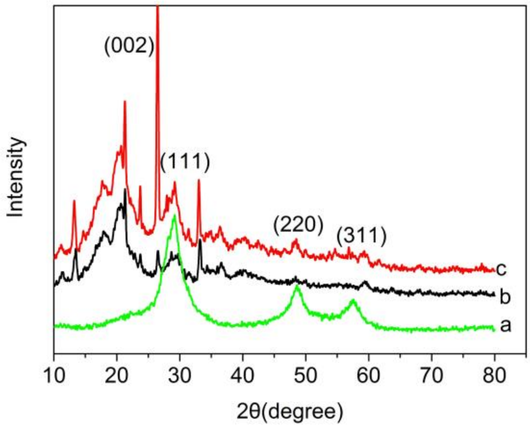

Fig. 2. The XRD patterns of (a) ZnS powders, (b) ZnS/non-conductive polymer fiber composites and (c) ZnS/conductive polymer fiber composites.

XPS spectra of ZnS/conducting polymer fiber composites and ZnS/non-conducting polymer fiber composites were shown in Fig. 3*a* and Fig. 3*b*, respectively. The spectra demonstrated that ZnS/conducting polymer fiber composites and ZnS/non-conducting polymer fiber composites were composed of C, O, F, Zn and S elements, which were corresponding to ZnS/conducting polymer fiber composites and ZnS/non-conducting polymer fiber composites.

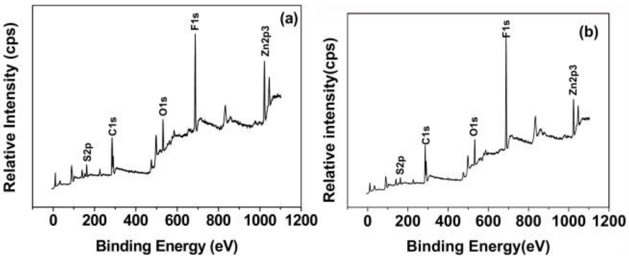

Fig. 3. XPS spectra of (a) ZnS/conducting polymer fiber composites, (b) ZnS/non-conducting polymer fiber composites.

3.2 Ultraviolet-Visible absorption spectra

The non-conducting polymer (SMA/PVDF) electrospun fibers have no evident absorption above 250 nm. It was showed that the conductive polymer electrospun mats have no evident absorption above 250 nm (Fig. 4*a*). The UV/Vis absorption edges of ZnS/non-conductive polymer fiber composites (Fig. 4*b*) and ZnS/conductive polymer fiber composites (Fig. 4*c*) were at round 360 nm, which corresponded to the band gap value of sphalerite ZnS [14].

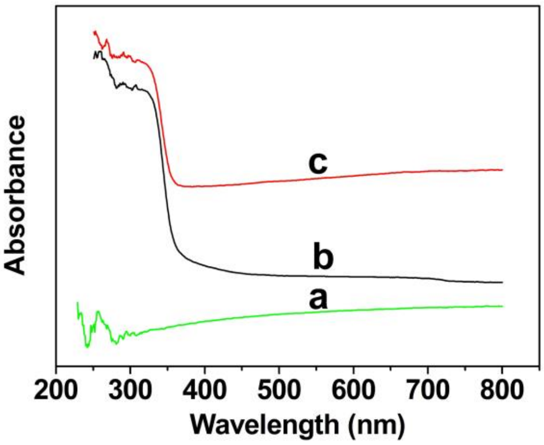

Fig. 4. UV/VIS absorption spectra of (a) conductive polymer fibers, (b) ZnS/non-conductive polymer fiber composites, (c)ZnS/conductive polymer fiber composites.

3.3 Photocatalytic activity measurements

The photocatalytic generation of hydrogen from water was determined using ZnS/conductive polymer fiber composites as photocatalyst, and compared with ZnS/non-conductive polymer fiber composites and ZnS powders. The up-take rate of H_2 from water experiments were carried out based on the average value obtained from 3 respective runs. For every run, the photocatalytic reaction was made for 30 h and the concentration of sacrificial agents (Na_2SO_3 and Na_2S) was kept identical. The experiment results were shown in Fig. 5. The average rate of H_2 generation of ZnS/conductive polymer fiber composites was higher than that of ZnS/non-conductive polymer fiber composites and ZnS powders. Furthermore, the average rate of H_2 generation of ZnS/conductive polymer fiber composites and ZnS/non-conductive polymer fiber composites gradually increased, while the average rate of H_2 generation of ZnS powders decreased in the three runs. The rising rate of H_2 generation of ZnS/conductive polymer fiber composites was quicker than that of ZnS/non-conductive polymer fiber composites. In the first run, the average rate of H_2 evolution of ZnS/conductive polymer fiber composites was higher than that of ZnS powders. In the third run, the average rate of H_2 evolution of ZnS/conductive polymer fiber composites was 1.35 times that of ZnS/non-conductive polymer fiber composites and 1.95 times that of ZnS powders. There are three possible reasons for this phenomenon (Fig. 6). Firstly, when ZnS particles were loaded on the surface of the fibers, they have large specific surface area and high-energy efficiency of UV irradiation. Secondly, the carrier can prevent the loss and degradation of the powdery catalyst. Thirdly, the photo-generated electron-hole pairs within ZnS were produced in the light, the electron migrate to the surface of ZnS and generate hydrogen by the reduction of water. Because the fiber has some electrical conductivity, it is easy for holes to migrate to the fiber, which result in the separation of the electron-hole pairs and therefore improve the photocatalytic efficiency.

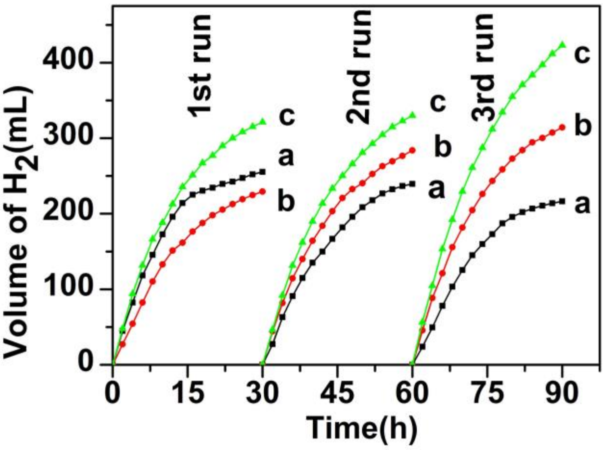

Fig. 5. Photocatalytic H_2 evolution of (a) ZnS particles, (b) ZnS/non-conductive polymer fiber composites and (c) ZnS/conductive polymer fiber composites.

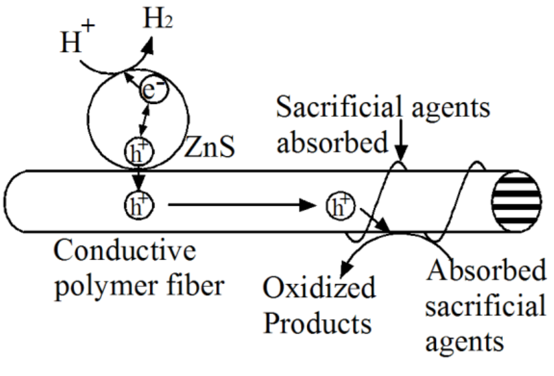

Fig. 6. Structure and catalytic mechanism diagram of ZnS/conductive polymer fiber composites.

4. Conclusion

In summary, novel composite photocatalysts – ZnS/conductive polymer fiber composites were successfully synthesized and the conductivity of carriers had an obvious effect on enhancing the photocatalytic efficiency of semiconducting photocatalysts. The average rate of hydrogen evolution from water using ZnS/conductive polymer fiber composites was higher than that using ZnS/non-conductive polymer fiber composites and ZnS powders from the first run to the third run. The conductivity of carriers had an obvious effect on semiconducting photocatalysts. The average speed of H_2 generation of ZnS/conductive polymer fiber composites and ZnS/non-conductive polymer fiber composites gradually increased, while the average speed of H_2 generation of ZnS powders decreased from the first to the third run. In the third run, the average rate of H_2 generation of ZnS/conductive polymer fiber composites was 1.35 times that of ZnS/non-conductive polymer fiber composites and 1.95 times that of ZnS powders.

Acknowledgments

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