In_2S_3-TiO_2 heterojunction/electrospinning fiber composites for efficient photocatalytic hydrogen production

HAIFEI CHEN, JIE YANG*, HAIQUN CHEN, YIHAO JIN, JINGJING GUO, FUJIANG CHEN, NIANYONG ZHOU
School of Petroleum Engineering, Changzhou University, Changzhou, Jiangsu 213016, China

An electrospun fiber with micro - nano - sized structure and carboxyl group was prepared by high - voltage electrospinning technology. In_2S_3-TiO_2 particles were formed on the surface of the electrospun fibers by the hydrothermal method. The In_2S_3-TiO_2 heterojunction/electrospinning fiber were characterized by SEM, XRD, XGA, TGA and UV-Vis. The In_2S_3-TiO_2 heterojunctions can be evenly distributed on electrospun fibers. The photocatalytic hydrogen production performance of the composites was studied by using xenon lamp in the visible light source. Na_2S / Na_2SO_3 was used as the sacrificial agent. The results show that the composite material has better photocatalytic hydrogen production capacity than the powder catalyst, and the average hydrogen production capacity is 15.29ml every two hours.

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1. Introduction

Solar energy is the most abundant energy available on the earth. Renewable energy is the potential way to answer the needs of more energy [1-3]. In recent years, the application of semiconductor materials in photocatalytic hydrogen has become a hot topic for scholars all over the world [4, 5]. In order to find out efficient photocatalyst, many scholars have made a lot of research, and achieved good photocatalytic effect [6-8]. However, the powder photocatalyst still has some practical problems such as easy recombination of electron-hole pairs, small surface areas, poor dispersibility, easy floating sticky wall, and difficulty of recycling. The semiconductor was loaded on a specific carrier and In_2S_3-TiO_2 / electrospun fiber composites were prepared, which can improve the dispersion of the photocatalyst, increase the specific surface areas, and be readily recovered.

TiO_2 has been extensively studied for its excellent chemical stability in a variety of photocatalysts, such as non-toxicity, optical and electronic properties, and low cost [9-11]. However, TiO_2 absorbs ultraviolet light only due to its wide band gap of 3.2 eV. Since the UV region occupies only near 4% of the entire solar spectrum, while 45% of the energy belongs to visible light which most solar energy cannot be used. Thus, the development of efficient photocatalysts with visible-light response has become the focus of research [12-14].

In order to efficiently utilize solar energy, a number of attempts have been made to extend the photo-response of TiO_2 to visible region, such as sensitizing with dyes or narrow band-gap semiconductors and doping with transition metal ions [13-15].

Indium sulfide (In_2S_3) is a typical chalcogenide with a narrow-band-gap of 2.0-2.2 eV, has attracted interest as a promising photocatalyst under visible-light irradiation for its high photosensitivity, stable chemical composition at ambient conditions, and low toxicity [15-18].

2. Experimental

2.1. Materials

N, N-dimethylacetamide (DMAC) was obtiained from Shanghai Pilot Chemical Co., Ltd. Styrene-maleic anhydride coelectrospinning (SMA) was purchased from Shanghai SpecTek petrochemical high tech Co., Ltd. Polyvinylidene Fluoride (PVDF) was purchased from Shanghai 3F New Material Co., Ltd. Acetone was purchased from Dandong Zhongxing Chemical Plant. Titanyl sulfate was brought from Rugao Chemical Reagent Factory. Indium nitrate and thioacetamide were supplied from Sinopharm Shanghai Chemical Reagent Co., Ltd.

2.2. Characterization

The morphologies of the products were characterized by scanning electron microscopy (JSM-6490LV), which

was bought from JEOL Co., Ltd. ESCALAB 250 X-ray photoelectron spectroscopy bought from Thermo Electron Co., Ltd was applied to study the structure of composites. The thermo-gravimetric analysis (TG-209-F3) purchased from NETZSCH-Gerätebau GmbH was utilized to estimate the weight loss of composites. The crystal structure was detected through the X-ray diffraction (D/MAX2500V) bought from Rigaku Co., Ltd. Ultravioletevisible (UV/Vis) absorption spectra was obtained on a Shimadzu-2550 spectrophotometer purchased from Shimadzu Co., Ltd at room temperature. The amount of hydrogen production was measured by gas chromatography (SP-6801), which was purchased from Shandong Lunan Ruihong Chemical Instrument Co., Ltd. Photocatalysis experiment was conducted by Multifunctional chemical reaction instrument (SGY-IB) bought from Nanjing East Branch Electric Equipment Co., Ltd.

2.3. Electrospinning of PVDF/SMA

A certain mass ratio of SMA and PVDF were weighed into a three-necked flask with stirring and N_2, and then they were dissolved with acetone and DMAC as solvent to prepare a spinning solution with a certain concentration. PVDF/SMA was prepared by high voltage electrospinning device.

2.4. Preparation of In_2S_3-TiO_2 heterojunction/ electrospinning fiber composites

The PVDF/SMA fiber mats were immersed in 50 mL titanyl sulfate aqueous solution at room temperature for 24 h, enabling Ti^{4+} and the carboxyl groups on the surface of the PVDF/SMA fibers were fully complexed. The fiber mats containing Ti^{4+} were placed in a hydrothermal reaction kettle with the volume of 50 mL, and reacting for 14 h at 120 °C. After being cooled to room temperature, the fibers were ultrasonically shaken and rinsed three times. Afterwards, the fibers are dried for 12 h at 60 °C. The as-prepared fiber mats were immersed in indium nitrate aqueous solution for 24 h at room temperature. The fiber mats containing In^{3+} were placed in a hydrothermal reaction kettle with the volume of 50 mL, and then 25 mL, 0.25 mol L^{-1} thioacetamide aqueous solution was added, reacting for 14h at 120 °C. After being cooled at room temperature, the reaction product was removed and washed by ultrasonic deionized water for three times. Finally, In_2S_3-TiO_2 heterojunction/electrospinning fiber composites were prepared after being dried in vacuum for 12h at 60°C. Also, the In_2S_3-TiO_2 powders were prepared by the same conditions.

2.5. Production of H_2

250 mL of deionized water was measured in a photochemical reaction apparatus. The complex system of Na_2S / Na_2SO_3 (0.10mol / L Na_2S, 0.32 mol / L Na_2SO_3) was used as the sacrificial agent in the photochemical reaction instrument. In order to allow the catalyst to better receive light, the electrospun fiber composites (including In_2S_3-TiO_2 heterojunction 0.15g) were spread in water. Under the same conditions, In_2S_3-TiO_2 powder (0.15g) was used for photocatalytic hydrogen production. A xenon lamp was used to simulate visible light as a light source. The hydrogen volume is quantified by the drainage method to collect the gas generated which was measured once every two hours. N_2 was used as the carrier gas and the collected gas was analyzed by a gas chromatograph.

3. Results

Fig. 1(a) showed the SEM image of TiO_2 heterojunction/electrospinning fiber composites produced by electrospinning, we can see that In_2S_3/electrospun fiber composites can be formed after the hydrothermal reaction, because fluorine fibers with carboxyl can complex zinc ions. Fig. 1(b) showed that many In_2S_3-TiO_2 particles grew on the surface of electrospinning fibers. As shown in the inset in Fig. 1(b), In_2S_3/electrospun fiber composites were immersed in zinc nitrate solution, there are numerous acicular In_2S_3 particles after hydrothermal reaction. The In_2S_3 particles on the surface distributed evenly.

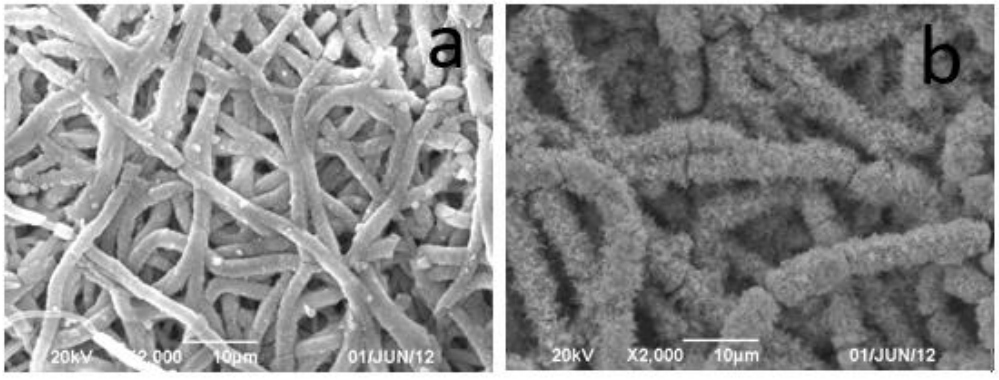

Fig. 1. SEM images of (a) TiO_2 heterojunction/ electrospinning fiber composites, and (b) In_2S_3-TiO_2 heterojunction/ electrospinning fiber composites

4. Discussions

4.1. Characterization of In_2S_3-TiO_2 heterojunction/electrospinning fiber composites

The phase structures of the In_2S_3-TiO_2 heterojunction/electrospinning fiber composites and PVDF/SMA heterojunction/electrospinning fiber composites were investigated by XRD method and the results were shown in Fig. 2. In Fig. 2(a), the curve revealed that the crystal phase of In_2S_3 was anatase with the diffraction peaks at about 25.7°,37.8°,48.2°,53.8° and 64.2°, which could be perfectly indexed to the (101), (004), (200), (105) and (211) crystal faces of TiO_2 (PDF card 32 - 0456, JCPDS) respectively [19]. This proved that the TiO_2 supported on the fibers were anatase structure, and the absorption peak of TiO_2 was insignificant because In_2S_3 cocooned TiO_2.

The composition and the valence state of the elements in In_2S_3-TiO_2 heterojunction/electrospinning fiber composites were analyzed by XPS (Fig. 3a). The characteristic signals for C, O, F, S, In, and Ti are clearly detected in the composites, and the XPS spectra are exhibited in Fig. 4b-d. The S2p peak (Fig. 3b) is belong to the S-In bond at 161.78eV. The In 3d XPS curve of the composites (Fig. 3c) presents In $3d_{5/2}$ at 444.98eV and In $3d_{3/2}$ at 452.58eV. The 7.6 eV splitting of the In 3d doublet indicated a normal state of In^{3+} in the prepared composites. The Ti 2p XPS curve of the composites (Fig. 4e) presented at 452.8 eV.

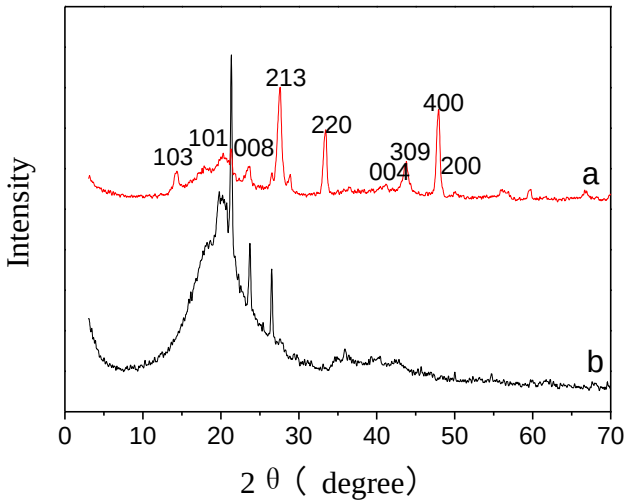

Fig. 2. The XRD patterns of (a) In_2S_3-TiO_2 heterojunction/electrospinning fiber composites, and (b) PVDF/SMA heterojunction/electrospinning fiber composites

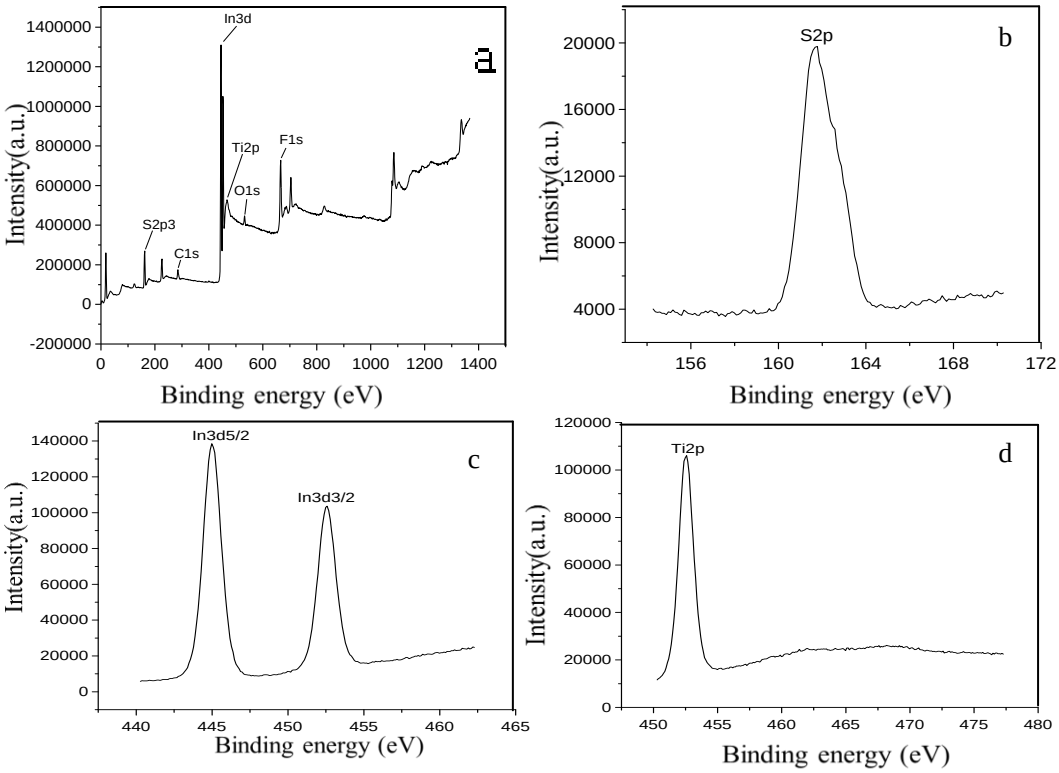

Fig. 3. XPS spectra of In_2S_3-TiO_2 heterojunction/electrospinning fiber composites: (a) survey scan spectrum and high-resolution spectra of (b)S 2p, (c) In 3d, (d) Ti 2p

In Fig. 4 (a), the unsupported electrospinning fibers have no evident absorption between 250 and 800 nm, while composites have absorption peak sat round 630 nm, and the Xe lamp has a wavelength in the range of 320 to 800 nm. This reveals that the unsupported fibers do not interfere with the light absorption during the photocatalytic reaction. Fig. 4 (b) shows the absorption peak of In_2S_3-TiO_2/electrospinning fiber composites sat round 630 nm, which indicates red shift occured, because of the quantum effect.

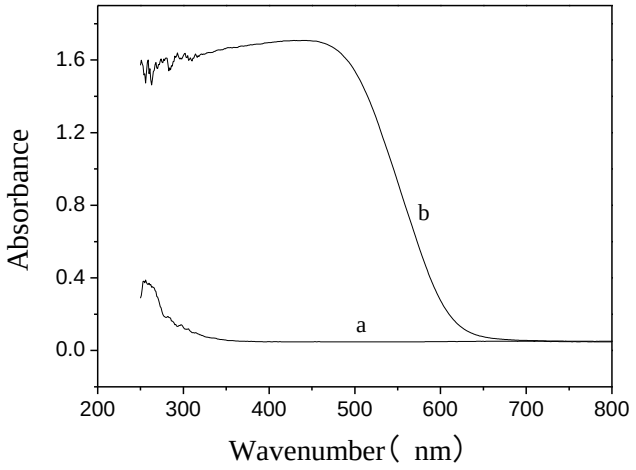

Fig. 4. UV/Vis absorption spectra of (a) PVDF/SMA electrospinning fiber and (b) In_2S_3-TiO_2 heterojunction/electrospinning fiber composites

4.2. Photocatalytic H_2 evolution

Fig. 5 summarized H_2 evolution from splitting of water under Xe lamp irradiation using In_2S_3-TiO_2 heterojunction/electrospinning fiber composites and In_2S_3--TiO_2 powders as photocatalysts, respectively. The experiments were operated for three runs, with the aqueous solution of 0.1 mol L^{-1} Na_2S (1.95g) and 0.32 mol L^{-1} Na_2SO_3 (10.08g) as sacrificial agent. For every run, the reaction time kept 20 h, and the concentration of sacrificial agents was also identical. From the first to the third run, the amount of hydrogen produced by the In_2S_3-TiO_2 powders is almost constant. While under the same conditions, the hydrogen production of In_2S_3-TiO_2 electrospun fiber composites is obviously increased, which indicates that the catalyst has good recycle stability. And the amount of hydrogen produced by the composites in the third run is 1.49 times of In_2S_3-TiO_2 heterojunction powders, this is due to the large specific surface area of In_2S_3-TiO_2 supported by the electrospun fibers, and high utilization of the light source. Also, the hydrogen production rate of the In_2S_3-TiO_2 powders decreased obviously from 12h, while the hydrogen production rate of the composite materials remained basically unchanged, which indicated that the composite materials had higher utilization efficiency of the sacrificial agent due to its larger specific surface area. Fan studied the reason for the increase of hydrogen production rate, and found that the interaction between the organic and inorganic phases increased as the reaction proceeding, and the hydrogen production rate increased.

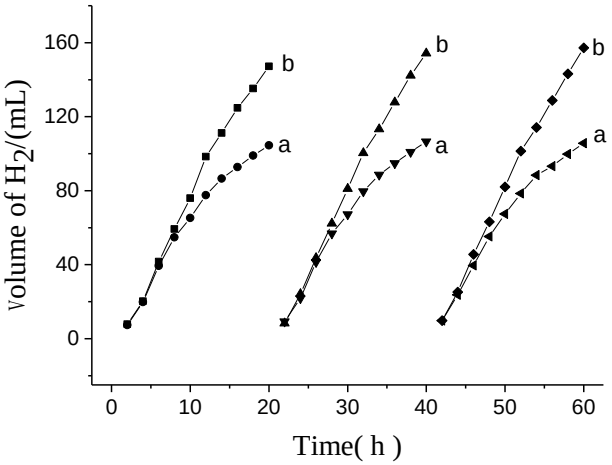

Fig. 5. Photocatalytic H_2 evolution of (a) In_2S_3-TiO_2 heterojunction/electrospinning fiber composites, and (b) In_2S_3-TiO_2 powders

5. Conclusions

The In_2S_3-TiO_2 / electrospinning fiber composites were uniformly supported on the surface of the flanged electrospinning fibers by hydrothermal synthesis. The UV-Vis absorption spectra of In_2S_3-TiO_2 / electrospinning fiber composites show that the materials have good absorption under visible light, and electrospinning fiber absorption peak in the xenon lamp simulated sunlight catalytic hydrogen water does not affect the light absorption of the composite. In the process of photocatalytic hydrogen production, In_2S_3-TiO_2 / electrospinning fiber composite material has higher stability and activity relative to the powder catalyst, and the average hydrogen production capacity is 15.29 ml every two hours.

Acknowledgements

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*Corresponding author: chfs@cczu.edu.cn