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Hydrothermal fabrication of Ni₃S₂/TiO₂ nanotube composite films on Ni anode and application in photoassisted water electrolysis



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Hongbo He, Aiping Chen*, Hui Lv, Haijun Dong, Ming Chang, Chunzhong Li

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, PR China

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ABSTRACT

Nanostructured films of rhombohedral Ni₃S₂ were hydrothermally synthesized on Ni and TiO₂ nanotube layer, as substrates. A possible mechanism is proposed to explain the formation of rhombohedral Ni₃S₂ nanostructures. The results of UV-vis spectrophotometric studies indicate that optical absorption spectrum of Ni₃S₂/TiO₂ nanotube composites could be extended to the visible region. As-synthesized Ni₃S₂/TiO₂ nanotube composite films on Ni substrate had better (by about 40%) hydrogen production performance under the visible light irradiation, in comparison with the Ni anode modified by TiO₂ nanotubes.

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1. Introduction

TiO₂ has been widely applied as photocatalyst during the past decades due to its low cost, nontoxicity and photostability [1–4]. However, TiO₂ with a wide band gap (3.2 eV) can only responsive to ultraviolet [5–8], resulting in the poor conversion efficiency in solar applications. Therefore, development of visible light-responsive TiO₂-based photocatalysts is an important goal to achieve in this active research area [9,10]. Many metal sulfides attract much attention due to their appropriate direct energy band gaps [11–15]. Nickel sulfides have received widespread attention due to their excellent electric, magnetic and optical properties [16–21]. However, sulfides tend to be display photocorrosion. In all synthetic methods for preparing metal sulfide–TiO₂ composite films reported, TiO₂ nanoparticles, nanostructures or porous films are produced firstly, followed by coating of a thin metal sulfide layer onto the TiO₂ matrix [22].

In this paper, rhombohedral Ni_3S_2 nanostructures were first hydrothermally fabricated directly on Ni substrate. Then TiO_2 nanotubes films were deposited onto the Ni_3S_2/Ni substrate. The stability of nickel sulfide was improved. Photoassisted electrolysis of water for hydrogen evolution was used to evaluate the performance of modified Ni anode. The result shows that hydrogen production efficiency of Ni substrate modified by Ni_3S_2/TiO_2 nanotube composite is remarkably increased under visible light in comparison with the Ni anode modified by TiO₂ nanotubes.

2. Experimental

2.1. Ni₃S₂ film

Ni₃S₂ nanostructures were directly fabricated on Ni substrate by a simple hydrothermal method [23]. First, 5 mmol thiourea (CH₄N₂S) and 20 mmol sodium dodecyl sulfonate (SDS, $C_{12}H_{25}SO_4Na$) were added into 40 ml ethylenediamine (EN) to form a solution. And the solution was transferred into a Teflon-lined stainless steel autoclave. A piece of Ni substrate, which has been cleaned for 30 min using an ultrasonicator in a mixed solution. The autoclave was sealed, maintained at 180 °C for 10 h, and then allowed to cool to room temperature. The Ni foil was collected and washed with absolute ethanol followed by DI water three times. The sample was then dried at 60 °C in vacuum.

2.2. TiO₂ nanotube film

In a typical fabrication process, P25 TiO₂ powder was dispersed into 40 ml of an aqueous NaOH (10.0 M). And the slurry of P25 was transferred into a Teflon-lined stainless steel autoclave. A piece of pretreated Ni foil was immersed in the slurry. The autoclave was sealed and held at 110 °C for 48 h without stirring in an oven. The obtained products were washed with DI water followed by 0.1 M HCl and finally annealed at 450 °C for 1 h in air. The TiO₂ nanotube is marked as TiO₂NT.

2.3. Ni₃S₂/TiO₂ nanotube film

About 0.5 g P25 were first added into 50 ml of 10.0 M NaOH solution to form a suspension and transferred into a Teflon-lined stainless steel autoclave. The obtained Ni anode modified with Ni₃S₂ film as described in 2.1 was immersed in



^{*} Corresponding author. Tel.: +86 21 64250996; fax: +86 21 64250624. *E-mail address*: apchen@ecust.edu.cn (A. Chen).

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the suspension. The autoclave was heated at 110 °C for 48 h. The obtained products were washed with DI water followed by 0.1 M HCl and finally annealed at 450 °C for 1 h in air.

2.4. Characterization and analysis

X-ray diffraction (XRD) analysis of the as-prepared samples was carried out at room temperature with a Rigaku D/max 2550 VB/PC apparatus using Cu K α radiation ($\lambda = 1.5406$ Å). Energy Dispersive Spectrometer (EDS) (Falion) was used to get the information about the elemental composition of materials. The structure and morphology were investigated using Field Emission Scanning Election Microscopy (FESEM, a JEOL JSM-6700F apparatus). UV-vis absorption spectra were obtained using a scanning UV-vis-NIR spectrophotometer (Varian Cary 500).

2.5. Photoassisted electrolysis of water for hydrogen evolution

The hydrogen evolution experiments were conducted in a home-made U-type alkaline electrolytic cell quartz reactor. The cathode material was a Ni–Cr alloy. The anodic and cathodic compartments were separated by a nanofiltration (NF) membrane. Each of the cylindrical-shaped compartments had a volume of 135 ml (gaseous volume of ca. 75 ml) and contained 60 ml of 30 wt.% NaOH electrolyte. All the tests were performed under the conditions of 2.0V external voltage and room temperature. The relation between the evolved hydrogen and reaction time was recorded by a gas chromatograph with a thermal conductivity detector.

3. Results and discussion

3.1. XRD and EDS

In Fig. 1a, the diffraction peaks at $2\theta = 44.47^{\circ}$, 51.78° and 76.40° can be attributed to the Ni substrate (JCPDS Card No. 65-2865). Fig. 1b shows the XRD patterns of as-prepared Ni₃S₂/Ni structures. The peaks of $2\theta = 21.64^{\circ}$, 30.80° , 50.08° and 55.07° represent diffraction lines of rhombohedral Ni₃S₂ (JCPDS Card No. 44-1418), with the cell constant a = 5.678 Å, c = 7.135 Å, which suggests the very crystalline feature of the Ni₃S₂ phase. In Fig. 1c, the diffraction peaks at 25.30° , 27.36° , 37.76° and 48.03° confirmed the presence of anatase and rutile TiO₂ (JCPDS Card No 21-1272). The XRD pattern of a typical Ni₃S₂/TiO₂ nanotube/Ni sample from Fig. 1d is characteristic for a rhombohedral Ni₃S₂, TiO₂ and Ni composite.

Fig. 2a shows the EDS patterns of Ni_3S_2 powder (the Ni_3S_2 film was scraped off from the Ni substrate and ground to a fine powder). It can be seen that the film contains only two elements sulfur and nickel, and the Ni/S molar ratio is about 3:2, which proves the film is Ni_3S_2 and is consistent with the XRD analysis. A small impurity peak derived from the analytical system of carbon or oxygen is also present, which confirms the high purity of the Ni_3S_2 film. The EDS spectrum of the as-prepared Ni_3S_2/TiO_2 nanotube composite powder is shown in Fig. 2b. These spectra reveal that S, Ni, Ti, and O are the main elements, with peaks observed at 2.31 keV,



Fig. 1. XRD pattern of the as-prepared samples.

 $0.86\ keV,\ 4.51\ keV$ and $0.50\ keV,\ respectively$ [24] in the $Ni_3S_2/$ TiO_2 nanotube composite.

3.2. SEM

Fig. 3 shows the FESEM images of Ni foil anodes modified by Ni₃S₂, TiO₂NT and Ni₃S₂/TiO₂NT. These images provide a perspective of the overall surface morphology of Ni substrate. The microstructure of the rhombohedral Ni₃S₂ can be seen in Fig. 3a and b, with crystallite sizes in the range of about 900 nm-3.5 µm. The TiO₂ nanotube (TiO₂NT) has a tubular structure with an outer diameter of about 10 nm and wall thickness of approximately 2 nm (Fig. 3c and d). From Fig. 3e, it is clearly seen that the Ni₃S₂/TiO₂ nanotube composite film has been formed from TiO₂ nanotubes and rhombohedral Ni₃S₂ particles, the TiO₂ nanotubes were randomly deposited on Ni₃S₂ with tangly and cross morphologies. Ni₃S₂ was uniformly enclosed or overlapped by TiO₂ nanotubes. Fig. 3f shows a high magnification SEM image of the $Ni_3S_2/$ TiO₂ nanotube film, in which the films are fully covered by TiO₂ nanotube without seeing rhombohedral Ni₃S₂, and the structure of TiO₂ nanotube is similar to that indicated by the results in Fig. 3d. Thus, in the composite film, most of the rhombohedral Ni₃S₂ crystallites are wrapped by TiO₂ nanotubes.

3.3. UV-vis absorbance

UV-vis absorption spectra of the as-prepared samples are shown in Fig. 4. The magenta line (Fig. 4b) obtained from sole Ni substrate shows only a very weak absorption in the UV region. It can be seen that TiO_2 nanotube films mainly absorb ultraviolet light with absorption wavelength below 400 nm(Fig. 4a). Ni₃S₂ films exhibit a visible-light absorption (Fig. 4d). The energy band gap (Eg) of Ni₃S₂ film is about 2.5 eV, which corresponds to a semiconducting material. A red shift of the intense absorption band of Ni₃S₂/TiO₂ nanotube composite photocatalyst films (Fig. 4c) with respect to that of TiO₂NT was observed. So the Ni₃S₂/TiO₂ nanotube composite photocatalyst could be excited to produce more electron-hole pairs under visible light illumination in comparison with TiO₂NT, which could result in higher photocatalytic activities.

3.4. Photoassisted electrolysis of water for hydrogen evolution

Fig. 5 shows the hydrogen evolution rates in photoassisted electrolysis of water, for the examined samples under visible light irradiation. Our work was based on the traditional water electrolysis, Ni and Ni–Cr alloy were used as anode and cathode respectively, 30% NaOH solution was used as an electrolyte, and 2 V value was selected for the test voltage. With visible light irradiation, as shown in Fig. 5, no notable difference was observed between the sole Ni and the Ni anode modified with TiO₂ nanotubes. As shown in Fig. 4, Ni and pure TiO₂ nanotubes cannot be excited by visible light irradiation. Therefore, the visible light has almost no effect on the hydrogen evolution for sole Ni anode and Ni anode modified by TiO₂ nanotubes. In the process of photoassisted water electrolysis, the maximum rate of hydrogen production is 1.72 ml/(h cm²) when the anode modified by Ni₃S₂. Fig. 5 shows the hydrogen evolution rate of Ni_3S_2/TiO_2 nanotube films (ca.1.63 ml/h cm²) increased by 40.5% in comparison with that of the Ni anode modified by TiO_2 nanotubes (ca.1.16 ml/h cm²). With visible light irradiation of the anode, the Ni₃S₂ and Ni₃S₂/TiO₂ nanotube films could improve the water electrolysis process effectively in a photoelectrochemical way. The average magnitude of visible light absorption of the Ni₃S₂/TiO₂ nanotube films is 76.3% of that of the Ni₃S₂ film, but the hydrogen production rate of the composite film is 94.8% of that of the Ni₃S₂ film. These results could be attributed to the following reasons. Under visible-light irradiation,

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