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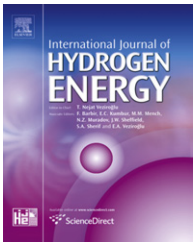

Solvothermal synthesis $ZnS-In_2S_3-Ag_2S$ solid solution coupled with $TiO_{2-x}S_x$ nanotubes film for photocatalytic hydrogen production

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ABSTRACT

$ZnS-In_2S_3-Ag_2S$ solid solution coupled with $TiO_{2-x}S_x$ nanotubes film catalyst has been successfully prepared by a two-step process of anodization and solvothermal methods for the first time. The as-prepared photo-catalysts are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–Visible diffuse reflectance spectra (UV–Vis DRS), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. The results show that the $ZnS-In_2S_3-Ag_2S$ solid solution are deposited on the surface of TiO_2NTs nanotubes under the solvothermal conditions, by which S atoms are incorporated into the lattice of TiO_2 through substituting the sites of oxygen atoms. Such $ZnS-In_2S_3-Ag_2S@TiO_{2-x}S_x$ nanotubes composite presents the enhanced absorption in visible region and the efficient transfer of photoelectron between the solid solution and $TiO_{2-x}S_x$ nanotubes, which determines the excellent photocatalytic activity for the photocatalytic hydrogen evolution from aqueous solutions containing the sacrificial reagents of Na_2S and Na_2SO_3 under 500 W Xe lamp irradiation.

1. Introduction

The photocatalytic splitting of water into H_2 using solid solution photo-catalysts would be an environmentally friendly way of producing clean and renewable hydrogen on a large scale. Since the Honda-Fujishima effect was first reported [1], all kinds of photo-catalysts for H_2 production have been studied. Over the last few years, considerable efforts have been made to improve visible light response of photocatalysts. The recently prepared solid solution photocatalysts such as $(AgIn)_xZn_{2(1-x)}S_2$ [2], ZnS-$CuInS_2$-$AgInS_2$ [3], $ZnS-In_2S-Ag_2S$[4], $Cd_{1-x}Zn_xS$[5–8], $(CuIn)_xZn_{2(1-x)}S_2$ [9], $ZnS-In_2S-CuS$[10], $Zn_mIn_2S_{3+m}$ [11], Sr-doped CdS-ZnS[12] and ZnS–CuS–CdS[13,14]have shown excellent performance for photocatalytic hydrogen production under visible light irradiation because of their controllable band structures and high quantum yield. Besides, it is reported that $ZnS-In_2S_3-Ag_2S$ solid solution shows a high apparent yield (19.8% at 420 nm) of hydrogen production from water containing sacrificial reagents of Na_2S and Na_2SO_3 without a cocatalyst [4].

Due to the problems of the separation and the recycle of the powder particles, the immobilization of solid solution has attracted increasing attentions [15,16]. In recent years, self-

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organized, well-ordered TiO_2 nanotubes arrays (TiO_2NTs) on titanium plate fabricated in situ by electrochemical anodization present the large surface-to-volume ratio, high orientation and excellent electron percolation pathways for charge transfer between interfaces [17–20]. The high cation-exchange character and the particular open mesoporous morphology as well as more free space make nano-particles easily bond on the surface of TiO_2NTs [21–30]. Especially, when a photocatalyst with a higher conduction band level is coupled with TiO_2NTs, efficient electron transfer from the sensitized semiconductor to a host titania matrix can reduce recombination of photo-induced electrons and holes and improve the photocatalytic activity of photocatalyst [31–35]. These properties make TiO_2NTs suitable to be used as a promising support material for loading solid solution.

However, to our best knowledge, $ZnS–In_2S_3–Ag_2S$ solid solution coupled with TiO_2NTs for photocatalytic hydrogen production has not been reported yet. Moreover, sulfur doping TiO_2 exhibited higher photocatalytic activity than TiO_2 [36–40], especially when introducing S at the O sites which could significantly modify the electronic structures of TiO_2 because S has a large ionic radius. Therefore, in this work, $ZnS–In_2S_3–Ag_2S$ is selected as a coupling material and meantime big atomic size sulfur is expected to be incorporated into the crystal lattice of TiO_2 to prepare $ZnS–In_2S_3–Ag_2S$ solid solutions coupled with $TiO_{2-x}S_x$ NTs.

2. Experimental sections

2.1. *Synthesis of samples*

Highly ordered TiO_2NTs were prepared by electrochemical anodic oxidation. Prior to anodization, the pure titanium sheet (purity 99.5%) of 0.5 mm thickness was pretreated by mechanically polishing and acid bright pickling, the detailed operating methods was presented in our previous paper [29]. Then, titanium sheet (reaction area 25 mm × 40 mm) was anodized in 0.14 M NaF and 1 wt. % H_3PO_4 aqueous solution at 20 V for 90 min. After anodization, the obtained TiO_2NTs were rinsed with the deionized water and subsequently calcined at 400 °C for 1 h.

A solvothermal method was employed to prepare the $ZnS–In_2S_3–Ag_2S$ solid solution coupled with TiO_2NTs ($ZnS–In_2S_3–Ag_2S$@TiO_2NTs) [4]. The mixture of $Zn(Ac)_2 \cdot 2H_2O$ (2.1 mmol), $In(NO_3)_3 \cdot 4H_2O$ (0.3 mmol) and thioacetamide (TAA) (10.8 mmol) were dissolved in 23.5 ml pyridine together. After $Zn(Ac)_2$, $In(NO_3)_3$ and TAA dissolved completely, 1.5 ml of 0.05 M $AgNO_3$ pyridine solution was then added dropwise into the above mixture solution under constant stirring. The TiO_2NTs was perpendicularly mounted into the Teflon-lined stainless steel autoclave of 50 ml capacity and 25 mm in diameter containing the prepared solution, which was maintained at 180 °C for 18 h. Before the solvothermal reaction, the solution was purged with Ar for 3 min in order to evacuate the air in the solution. When the solvothermal reaction ended, the TiO_2NTs was taken out from the autoclave and washed with ethanol and dried in air. In addition, the powders product ($ZnS–In_2S_3–Ag_2S$ solid solution) in the autoclave was collected by centrifugation, washed several times with absolute ethanol and finally air-dried. For comparison, ZnS-In_2S_3@TiO_2NTs sample was similarly prepared under the same conditions, except that $AgNO_3$ pyridine solution was not used in the experiment.

2.2. *Characterization of samples*

Morphology of as-prepared samples was observed using a scanning electron microscope (SEM; JSM-6480A, Japan). The mass of $ZnS–In_2S_3–Ag_2S$ and ZnS-In_2S_3 solid solution on the surface of TiO_2 nanotubes can be obtained quantitatively by the weight growth of TiO_2NTs after the solvothermal synthesis, which was measured by electronic analytical balance with the accuracy of the 10^{-5} g (CP 225D, Sartorius, German). The X-ray diffraction (XRD) patterns of as-prepared samples were obtained on an X-ray diffractometer (D/max-rB, Ricoh, Japan, Cu Kα, $\lambda = 1.5418$ Å, 45 kV, and 40 mA), X-ray photoelectron spectroscopy (XPS) analysis was conducted on Phi5700 spectroscopy (ESCA system, U.S.A.) using a monochromated Al Kα X-ray source (1486.6 eV) operating at 15 kV. The amounts of metal ions were determined by inductively coupled plasma emission spectrometry (ICP; Perkin Elmer, Optima 5300DV). Raman spectra were recorded using a Raman spectrometer (Jobin-Yvon Labram HR 800) to study the fine structure of the specimens. The photoabsorption property was recorded with a diffuse reflectance UV–Vis diffuse reflectance spectrophotometer (UV-2400; Shimadzu, Japan). $BaSO_4$ was used as the reflectance standard.

2.3. *Evaluation of photocatalytic properties of samples*

Photocatalytic activities of the as-prepared film catalysts were conducted in a closed gas circulation system by using a 500 W high-pressure ball-shaped Xe lamp (XHA500 W, Shanghai Ruizi Co. China) supplying the wavelength illumination from 300 to 800 nm. The film catalysts (the effective area for the film catalysts is 10 cm^2) were immersed in 40 ml aqueous solution containing Na_2S (0.1 M) and Na_2SO_3 (0.02 M) in a side-irradiation quartz reaction cell which was placed 10 cm away from the Xe lamp. The solution was continuously stirred with a magnetic stirrer. Nitrogen was purged through the cell for 10 min before irradiation to remove oxygen in the solution. The amount of H_2 was determined using thermal conductivity detector (TCD) gas chromatography (SP2100A, Beifen instrument, China).

3. Results and discussion

3.1. *Composition and structure of samples*

Fig. 1a shows the top view and cross sectional view (inset part) of as-prepared TiO_2NTs, it can be seen that the highly ordered and porous TiO_2 nanotubes with tube length of ∼600 nm and pore diameter ∼ 100 nm are formed on the Ti substrate. Fig. 1b is morphology of the powders of $ZnS–In_2S_3–Ag_2S$ solid solution, a large number of nanorods with needle-like structure appear and aggregate randomly. Fig. 1c is the SEM image of $ZnS–In_2S_3–Ag_2S$@TiO_2NTs, it can be observed that TiO_2 nanotubes still kept their tube-like structures after