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Preparation of titania nanotube-$Cd_{0.65}Zn_{0.35}S$ nanocomposite by a hydrothermal sulfuration method for efficient visible-light-driven photocatalytic hydrogen production

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ABSTRACT

Titania nanotube-$Cd_{0.65}Zn_{0.35}S$ nanocomposite ($Cd_{0.65}Zn_{0.35}S$-TiO_2) was synthesized from titanate nanotubes for ion change of Cd^{2+} and Zn^{2+} followed by hydrothermal sulfuration treatment using thiourea as sulfur source. The $Cd_{0.65}Zn_{0.35}S$-TiO_2 with enhanced crystallinity of TiO_2 nanotube can be obtained by increasing hydrothermal temperature from 90 °C to 120 °C. And further increasing hydrothermal temperature to 150 °C, TiO_2 nanotubes collapse and transform into irregular shaped particles. The photocatalytic activity for hydrogen production of the prepared $Cd_{0.65}Zn_{0.35}S$-TiO_2 with different hydrothermal temperature was investigated under visible-light irradiation. The result shows that the $Cd_{0.65}Zn_{0.35}S$-TiO_2 with hydrothermal temperature of 120 °C presents the highest hydrogen evolution rate and photostability, which can be attributed to a rapid charge transfer at the interface between $Cd_{0.65}Zn_{0.35}S$ and TiO_2 nanotube due to the increased crystallinity and unique 1-D nanotubular structure of TiO_2.

1. Introduction

Photocatalytic H_2 production from water splitting using semiconductors under solar light has attracted significant attention because of the global problems in energy and environment [1–4]. Among the visible-light-sensitive photocatalysts reported, CdS has been widely used for water splitting because its band gap (2.4 eV) corresponds well with the solar spectrum and its conduction band edge is more negative than the H^+/H_2 reduction potential [5]. However, the photocatalytic properties of CdS are limited as a consequence of its low efficiency and serious photocorrosion under a long-term light irradiation [6]. Numerous efforts have been made to improve the hydrogen evolution capability and the stability of CdS, for example, by loading the noble metal (Pt) on the surface of CdS [7,8], incorporating the nanoparticles of metal sulfides into the interlayer photocatalysts [9,10], coupling CdS with wide band-gap semiconductor [11,12], and designing the nanostructures, such as CdS nanorods or nanowires [13,14].

Some researchers also reported that photocatalytic properties of CdS could be modified by incorporation of ZnS into CdS to form $Cd_{1-x}Zn_xS$ ($0 < x < 1$) solid solution with a continuous controllable band gap [15–18]. For the $Cd_{1-x}Zn_xS$ solid solution, the conduction band (CB) and valence band (VB) would shift to more negative and positive positions with the increase of ZnS amount [15,18], ensuring sufficient power for water reduction to generate hydrogen. However, the activity and stability of the prepared $Cd_{1-x}Zn_xS$ solid solution materials are far from being satisfactory for practical application of photocatalytic hydrogen production technique. Recently, ternary semiconductor materials such as CdS-ZnS/TiO_2 [19], ZnO-ZnS-CdS [20], CdS-ZnS/Fe_2O_3 [21], reduced graphene oxide-$Zn_xCd_{1-x}S$ [22], multiwalled carbon nanotubes/$Cd_{0.8}Zn_{0.2}S$ [23], and $Cd_{0.5}Zn_{0.5}S$/titanate nanotubes [24] etc. have been reported to exhibit higher photocatalytic activity in comparison to their constituent sulfides or dual semiconductor system. Especially, one-dimensional titanate nanotube has attracted considerable attention in the structure of composite photocatalyst because of high specific surface area and fast charge transfer properties [24,25]. However, the crystallinity of titanate nanotube is poor, which is disadvantage to efficient charge separation and hydrogen generation. Calcination treatment is an efficient way to make titanate nanotube transform to anatase TiO_2 with enhanced crystallinity, but high temperature annealing usually results in the collapse of TiO_2 tubular structure [25]. The electron transfer at the interface between $Cd_xZn_{1-x}S$ solid solution and TiO_2 plays an important role in the photoactivity of the composite system. In order to maximize the interfacial areas and

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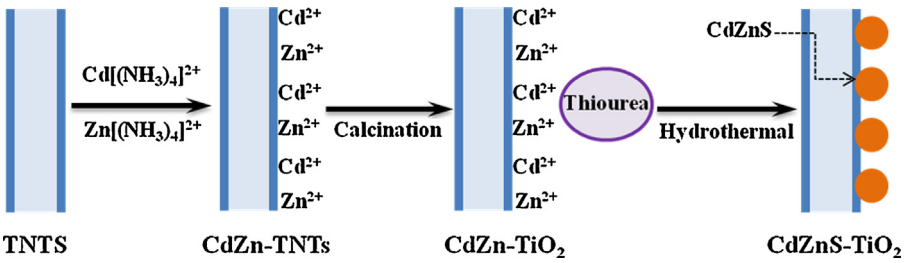

Scheme 1. Synthetic route for titania nanotube-$Cd_{0.65}Zn_{0.35}S$ nanocomposite.

physical or chemical contact among semiconductor materials, the fabrication method of these composite photocatalysts is critical for the improvement of their performances. The fabrication of titania nanotube-$Cd_xZn_{1-x}S$ nanocomposite via in-situ hydrothermal sulfuration method can ensure high crystallinity and the close contact between the ternary components, which would provide some insights for the design of highly efficient visible light catalysts.

Herein, titania nanotube-$Cd_{0.65}Zn_{0.35}S$ nanocomposite with good crystallinity was prepared from titanate nanotubes through ion exchange followed by hydrothermal sulfuration treatment using thiourea as sulfur source. The effects of hydrothermal temperature on crystal structure, the morphology, optical property of the composite photocatalyst and the photocatalytic activity for H_2 evolution under visible-light irradiation were investigated.

2. Materials and methods

2.1. Photocatalyst preparation

Titanate nanotubes (TNTs) were prepared using a hydrothermal method according to our previous report [26]. In a typical procedure, 180 mL NaOH solution (10 M) and 3 g TiO_2 powder were put into a 250 mL Teflon-lined flask, and the mixture was refluxed at 110 °C under atmospheric pressure for 48 h. The hydrothermally treated powder was recovered and washed thoroughly with deionized water. The resultant precipitate was immerged into 0.1 M HCl solution for 5 h, rinsed with deionized water until the pH value of the filtrate was about 7, and then dried at 60 °C for 24 h.

The preparation procedure of titania nanotube-$Cd_{0.65}Zn_{0.35}S$ nanocomposite is shown in Scheme 1. The salts of $Cd(NO_3)_2{\cdot}4H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ were dissolved in distilled water and then ammonia was added to obtain metal-ammonium complex solution. 1 g TNTs were dispersed in a 50 mL metal-ammonium complex solution with the Cd^{2+} concentration of 0.16 M and the Zn^{2+} concentration of 0.04 M. The resulting suspension was stirred for 2 h at room temperature under reduced pressure. The product was washed with deionized water to remove residual ion, and calcined at 500 °C for 2 h after drying. The solid obtained was named as CdZn-TiO_2. The sulfurization of the CdZn-TiO_2 precursor was carried out by hydrothermal method. 0.4 g CdZn-TiO_2 precursor was dispersed in 70 mL deionized water containing a certain amount of thiourea. Then the mixture was hydrothermally treated in a Teflon-lined stainless autoclave with a volume of 100 mL at 90 °C, 120 °C and 150 °C for 12 h, and named as CdZnS90-TiO_2, CdZnS120-TiO_2 and CdZnS150-TiO_2, respectively. The light yellow powder was obtained after washing and drying at 60 °C. For comparison, the CdS120-TiO_2 and the ZnS120-TiO_2 were prepared in the same conditions as the CdZnS120-TiO_2.

2.2. Photocatalyst characterization

The specific surface areas of the catalysts were calculated by a multipoint Braunauer–Emmett–Teller (BET) analysis of the N_2 adsorption isotherm measured at liquid nitrogen temperature on a Quantachrome SI-MP-10 apparatus. Before the measurements, the samples were degassed at 90 °C for 16 h. The X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert Pro powder diffractometer with Cu Kα radiation source operated at 40 kV

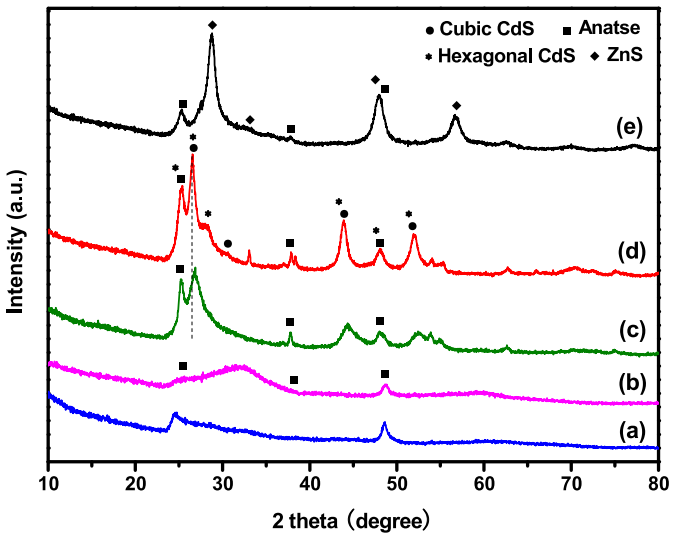

Fig. 1. XRD patterns of (a) TNTs, (b) CdZn-TiO_2, (c) CdZnS120-TiO_2, (d) CdS120-TiO_2 and (e) ZnS120-TiO_2.

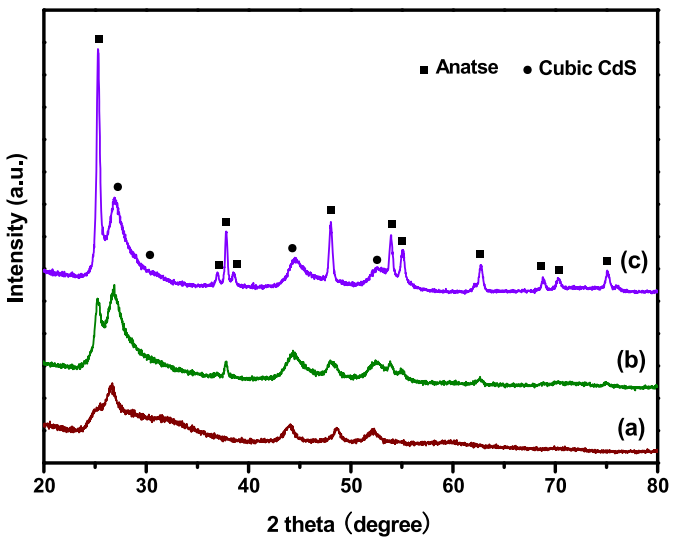

Fig. 2. XRD patterns of (a) CdZnS90-TiO_2, (b) CdZnS120-TiO_2 and (c) CdZnS150-TiO_2.