

Study of ZnO-ZnS Composite as Photocatalyst in the Water Splitting Reaction

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A Novel One-step Hydrothermal Method for the Preparation of Cd_{1-x}Zn_xS/Titanate Nanotubes Composites for Photocatalytic Hydrogen Production

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Photocatalytic water splitting over semiconductors has attracted much attention as a promising route for hydrogen production [1-3]. Taking the solar spectrum into account, it is indispensable to develop visible-light-driven photocatalysts. One of the most well-known semiconductor photocatalyst, CdS, has been widely used for hydrogen evolution. However, pure CdS is usually not very active and prone to photocorrosion. Combining CdS with the wide band gap semiconductor ZnS to form the solid solution Cd_{1-x}Zn_xS is demonstrated to be an effective way to solve the above problems [4-6]. By adjusting the value of x , the conduction band and the band gap of Cd_{1-x}Zn_xS can be modified to well meet the requirement of the photocatalytic reaction. Thus the efficient photocatalytic hydrogen production is achieved over Cd_{1-x}Zn_xS photocatalyst even without cocatalyst loaded. As known, CdS has been extensively used to form nanocomposite photocatalysts with other semiconductors so that the efficient charge separation can occur [7-9]. And yet the nanocomposites of Cd_{1-x}Zn_xS are not common, partly because it is difficult to exactly control the metal compositions of Cd and Zn and to obtain the intimate contacts between two components in the composites.

In 1998, Kasuga et al [10] developed a simple method to prepare nanotubes by the hydrothermal treatment of TiO₂ powder in 10 M NaOH solution, which are generally considered as titanate nanotubes (TNTs) [11]. Titanate nanotubes combine many properties of conventional TiO₂ nanoparticles with their distinguishing feature of one-dimension nanostructure, large surface-to-volume ratio, high sedimentation rate and ion-exchangeable ability. These interesting properties make TNTs suitable to form efficient composite photocatalysts with other semiconductors [12,13].

Here, a novel one-step hydrothermal method was developed to prepare series of Cd_{1-x}Zn_xS/titanate nanotubes(TNTs) composite photocatalysts, where the exact metal compositions of Cd and Zn were obtained. Meanwhile, it was discovered that the Cd_{1-x}Zn_xS nanoparticle with high crystallinity was surrounded by a network of well-developed TNTs in the nanocomposites, resulting in the well dispersed Cd_{1-x}Zn_xS nanoparticles and the intimate multipoint contacts between Cd_{1-x}Zn_xS and TNTs. The activity was evaluated by photocatalytic hydrogen evolution from aqueous solution containing Na₂SO₃/Na₂S as sacrificial reagents under visible light irradiation. In detail, the photocatalytic reaction was performed in a side irradiation Pyrex cell with stirring. The efficient irradiation area for the cell was 15.90 cm². 190 mL of aqueous solution containing 0.2 g of catalyst, as well as 0.25 M Na₂SO₃/0.35 M Na₂S as sacrificial reagents, was added into the cell. A 500 W Xe lamp

equipped with a cut-off filter ($\lambda > 430$ nm) was used as the light source, and the irradiation power after the filter was monitored by an irradiatometer to be 55 mW cm^{-2} . In the research, the value of x was optimized, and compared with the single $\text{Cd}_{1-x}\text{Zn}_x\text{S}$, the composite photocatalysts showed much higher activity for hydrogen production.

Table 1 summarizes series of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{TNTs}$ photocatalysts with various compositions. It can be seen that the metal compositions of Cd and Zn in each composite catalyst didn't change much compared to its stoichiometric ones. During the process of preparation, $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles were first formed, which could successfully avoid the loss of the metal compositions.

Table 1: The composition of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{TNTs}$.

Photocatalyst	The stoichiometric composition	The composition
a	$\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}/\text{TNTs}$	$\text{Cd}_{0.12}\text{Zn}_{0.88}\text{S}/\text{TNTs}$
b	$\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/\text{TNTs}$	$\text{Cd}_{0.34}\text{Zn}_{0.66}\text{S}/\text{TNTs}$
c	$\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{TNTs}$	$\text{Cd}_{0.57}\text{Zn}_{0.43}\text{S}/\text{TNTs}$
d	$\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}/\text{TNTs}$	$\text{Cd}_{0.74}\text{Zn}_{0.26}\text{S}/\text{TNTs}$
e	$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}/\text{TNTs}$	$\text{Cd}_{0.91}\text{Zn}_{0.09}\text{S}/\text{TNTs}$

Fig. 1 shows the XRD patterns of various photocatalysts. The XRD traces of single TNTs were similar to those of alkali or hydrogen titanates, which exhibited an orthorhombic structure [14]. For the composite photocatalysts, XRD patterns of TNTs and crystalline $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ appeared. It can be discovered that the diffraction peaks assigned to TNTs in all the composites were the same. However, the diffraction peaks of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ changed a lot. As the value of x increased, the diffraction peaks shifted to higher angles indicating that the crystals obtained were not simple physical mixture of CdS and ZnS but the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions. Further analysis revealed that the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions exhibited both cubic phase and hexagonal phase, which can be clearly seen through the XRD pattern of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$. And with the increase of x , the major crystal structure of the solid solution changed from the hexagonal wurtzite structure to the cubic zinc-blende one [5].

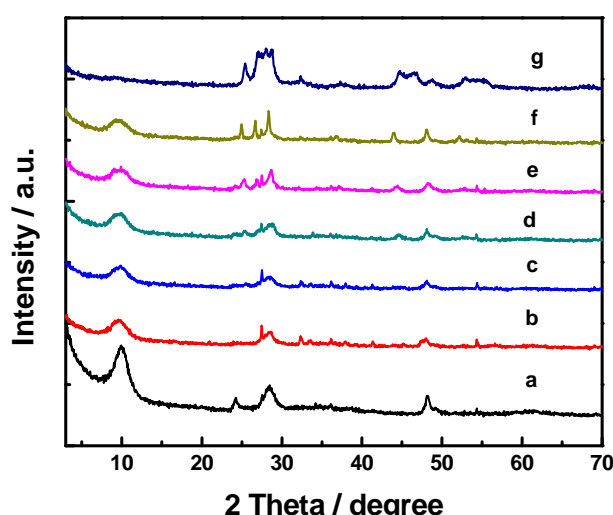


Figure 1: The XRD patterns of photocatalysts: (a) TNTs, (b) $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}/\text{TNTs}$, (c) $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/\text{TNTs}$, (d) $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{TNTs}$, (e) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}/\text{TNTs}$, (f) $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}/\text{TNTs}$, (g) $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$.

Fig. 2 shows the TEM images of the obtained products. As shown in Fig. 2a, titanate nanotubes have been successfully synthesized and presented uniform distribution, in accordance with the literature [11]. Fig. 2b showed the TEM image of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{TNTs}$ prepared by our one-step hydrothermal method. Interestingly, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles of ca. 100nm were well dispersed and enwrapped by the network of titanate nanotubes tightly in the composites. This unique architecture successfully avoided the agglomeration of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles and finally led to the intimate multipoint contacts between the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ primary particle and the surrounding titanate nanotubes (Fig. 2c). During the hydrothermal treatment, titanate nanotubes were obtained by transformation of TiO_2 nanoparticles and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles grew further. Some titanate nanotubes would grow along the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticle. Hence, CdS and TNTs well accreted in the hydrothermal process and the intimate lattice contacts between the nanocrystallines were achieved.

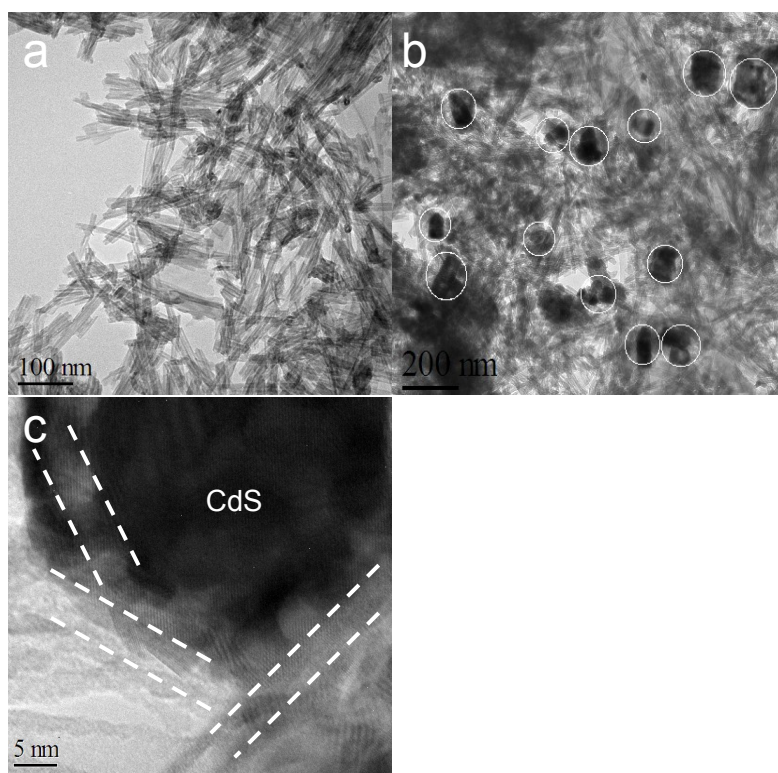


Figure 2: TEM images of various samples: (a) TNTs, (b) Cd_{0.5}Zn_{0.5}S/TNTs, (c) the multipoint contacts between Cd_{0.5}Zn_{0.5}S and TNTs.

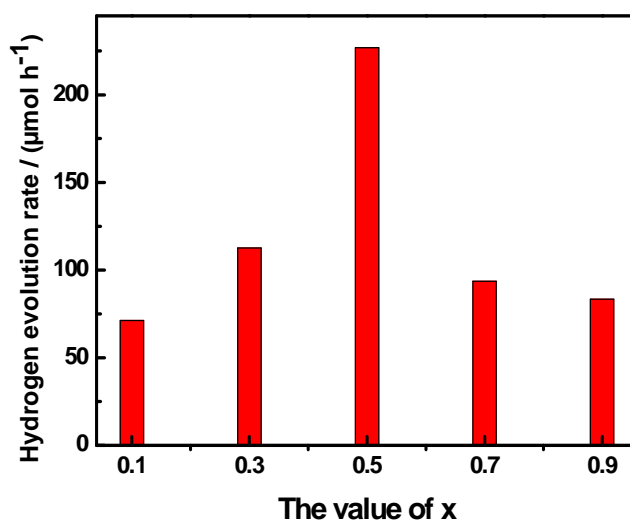


Figure 3: Photocatalytic H₂ evolution over different Cd_{1-x}Zn_xS/TNTs samples.

Fig. 3 shows the photocatalytic H₂ evolution over different Cd_{1-x}Zn_xS/TNTs samples. With the increase of x, the hydrogen production rate initially increased and then underwent a decrease. Cd_{0.5}Zn_{0.5}S/TNTs displayed the best photocatalytic activity, probably due to the suitable band gap and the favorable conduct- ion band of Cd_{0.5}Zn_{0.5}S. XRF analysis result

confirmed that the content of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ in the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{TNTs}$ sample is as small as 8.7 wt%. This is important from an environmental point of view because of the toxicity of Cd^{2+} . The comparison between the photocatalytic activities of single $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{TNTs}$ have been displayed in Fig. 4. Corresponding to the unit gram of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{TNTs}$ exhibits significantly higher activity.

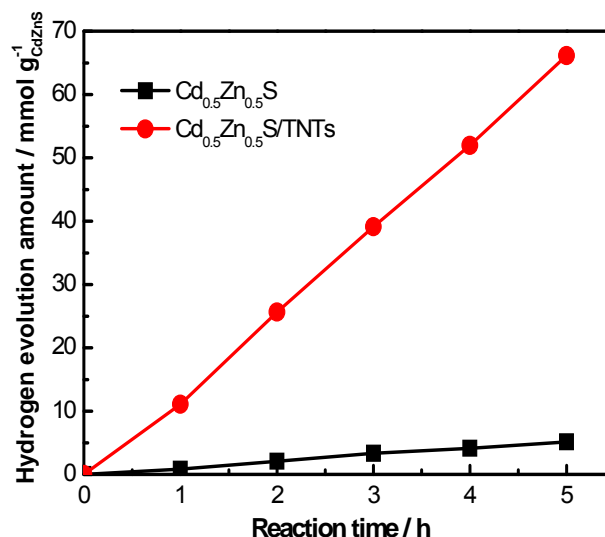


Figure 4: The time courses of hydrogen evolution over $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{TNTs}$ and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$.

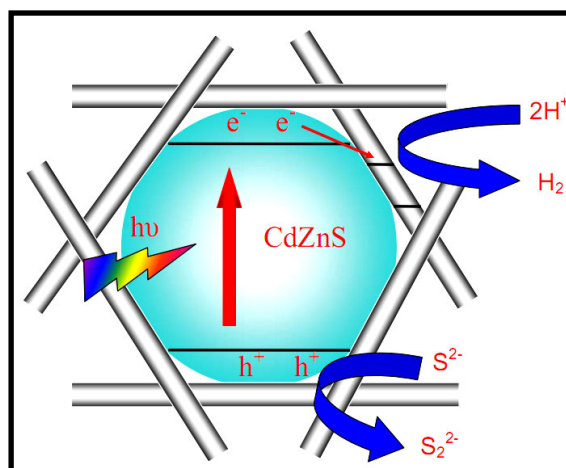


Figure 5: The schematic model of charge separation in $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{TNTs}$ composites.

For a photocatalyst to be highly active, the separation of photoinduced electrons and holes should be effective. As illustrated in Fig. 5, the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticle was surrounded by a network of titanate nanotubes in $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{TNTs}$ composites, which could avoid the agglomeration of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles and lead to the intimate multipoint contacts. The appropriate dispersion of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles could reduce the recombination of photogenerated charges, contributing to the highly efficient charge separation. The multipoint

contacts mean that when $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticle was irradiated with light, more paths could be used to transfer photogenerated electrons to the surrounding TNTs, and more efficient charge separation could be achieved. In addition, the one-dimensional tubular structure of titanate nanotubes was beneficial for enhanced mobility of electrons transferred from CdS, and their large surface area could offer more photocatalytic active sites to facilitate the photoexcited electrons reacting with the water molecule for hydrogen evolution. In summary, the efficient composite photocatalysts have been achieved through the novel one-step hydrothermal method. Both the conclusions drawn from this research and the novel preparation method itself can be extended to the preparation of other composite photocatalysts with even higher efficiency.

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