

Preparation of CdS/TiO₂NTs Nanocomposite and Its Activity of Photocatalytic Hydrogen Production

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Abstract: The CdS/TiO₂NTs nanocomposite was prepared through ion-exchange and precipitation reactions. The nanostructure properties of the composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), diffuse reflectance UV-visible absorption spectra (DRUVAS), fluorescence emission spectra (FES) and X-ray fluorescence analyzer (XRF). SEM results revealed that the lamellar sodium trititanate originating from the TiO₂ particles individually curled to form the sodium trititanate nanotubes by self-assembled mechanism. The results of XRD, TEM and DRUVAS demonstrated that hexagonal phase CdS with about 8 nm particle size were homogeneously loaded on the surface of anatase TiO₂NTs and the absorption edge of the composite was extended to the visible region. The CdS/TiO₂NTs composite exhibited the highest activity of hydrogen production (1708 μL/g) by photocatalytic water decomposition in comparison with TiO₂NTs and TiO₂ powder under visible light irradiation ($\lambda > 400$ nm) for 6 h.

Key words: CdS/TiO₂NTs nanocomposite; TiO₂ nanotubes; hydrogen production; photocatalytic water splitting

In recent years, titania nanotubes (TiO₂NTs) have received much attention due to their attractive characteristics of one-dimension nanostructure nature for applications in the areas of solar cells and photocatalysis^[1]. However, the wide band gap of them only has a photocatalytic activity of ultraviolet light. To extend the light response region, some authors reported the successful photosensitization of TiO₂NTs coupled with CdS nanoparticles by means of ion-exchange reaction in Cd-EDTA solution^[2], bubbling H₂S gas through the aqueous TiO₂ nanotubes suspension^[3], employed sulfur powder and CdCl₂ in tetrahydrofuran^[4]. But, H₂S and organic solvent employed in those synthetic routes as above mentioned are not friendly for environment.

In this paper we report a simple route via ion-exchange and precipitation reactions for the direct transformation of trititanate nanotubes to TiO₂NTs and simultaneous formation of CdS/TiO₂NTs composite by cheap chemicals of Cd(NO₃)₂ and thiourea as reactants. The TiO₂NTs coupling with a narrow band gap semiconductor of CdS nanoparticles not only can be able to extend its optical response from the UV towards visible region,

but also improve the photocatalytic activity of visible light.

Hydrogen energy is an ideal candidate for its some advantages, such as clean, storable and renewable properties as well as zero emission of pollutants. It can be expected to become a major energy source instead of fossil energy in the future. To explore a new application, the CdS/TiO₂NTs composite is firstly employed as a photocatalyst for production of hydrogen by photocatalytic water splitting under visible light irradiation to our knowledge.

1 Experimental

Sodium trititanate nanotubes (Na₂Ti₃O₇) were prepared by hydrothermal method. Typically, 0.5 g of TiO₂ powder was mixed with 100 mL aqueous solution of 10 mol/L NaOH and was treated with ultrasonic for 1 h. The reactant was put in a Teflon-lined autoclave and held in an oven at 140 °C for 12, 16, 20 and 24 h, respectively. A white flocculent precipitate was filtered, washed with a little amount of anhydrous ethanol and dried at 60 °C for 6 h.

The CdS/TiO₂NTs composite was synthesized by a simple

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two-step chemical solution route. $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes (1 g) was put into a solution of 0.1 mol/L $\text{Cd}(\text{NO}_3)_2$ (50 mL) and ion-exchange reaction was carried out to make Cd^{2+} substitute for Na^+ at 40 °C for 2 h. The product was filtrated and washed with deionized water. Subsequently, the filtrate cake was added into 0.4 mol/L $\text{SC}(\text{NH}_2)_2$ (thiourea, 50mL) and stirred at 70 °C for 3 h. After filtration and washing, the yellow powder was dried at 60 °C for 6 h. X-ray fluorescence (XRF) monitored that the sample contained 19.02% (mass fraction) CdS with 15.21%(mass fraction) Cd and 3.81% (mass fraction) S.

The X-ray diffraction (XRD) patterns of samples were measured on an X'pert MPD Pro X-ray diffractometer with Cu K α irradiation. Diffuse reflectance UV-Visible absorption spectra of the samples were recorded on a HITACHI UV-4100 spectrophotometer. Elemental analysis was carried out on a Bruker S4 PIONEER X-ray fluorescence analyzer (XRF). The morphology analysis was carried out using a Quanta 200 environmental scanning electron microscope (SEM). The high resolution image of the sample was obtained on a JEM-2010 transmission electron microscopy (TEM). The fluorescence emission spectra (FES) were recorded with F-4500 fluorescence spectrophotometer, and a 150 W xenon lamp was used as excitation source with an excitation wavelength of 250 nm.

The experiments of hydrogen production by photocatalytic water splitting were performed under visible light irradiation. About 0.1 g of sample was put into a Pyrex flask with a flat window which contained 50 mL aqueous solution of Na_2S and Na_2SO_3 . A 350 W xenon lamp equipped with a special cut-off filter to remove ultraviolet illumination ($\lambda < 400$ nm) was used as the light source. The solution was purged with nitrogen for 30 min to remove the dissolved oxygen before the visible light irradiation. The gas products were analyzed by a gas chromatograph (Agilent, HP 6890) equipped with a C-2000 capillary column and a thermal conductivity detector (TCD)^[5,6].

2 Results and Discussion

Fig.1 displays XRD patterns of samples. From curve a it can be observed that the TiO_2 nanoparticles synthesized in our lab are pure anatase TiO_2 (JCPDS No. 01-078-2486). The distinctive peaks in curve b are found at 10.5°, 25.3°, 29.9°, 34.3°, 35.6°, 38.5°, 48.1°, 52.7°, 54.4°, 60.9° and 62.9° corresponding to (001), (011), (300), (-203), (103), (-310), (020), (-413), (501), (123) and (205) crystal planes of monoclinic sodium trititanate nanotubes ($\text{Na}_2\text{Ti}_3\text{O}_7$) (JCPDS No. 00-031-1329). For the XRD pattern of $\text{CdS}/\text{TiO}_2\text{NT}_s$ composite, both CdS and TiO_2 diffraction peaks can be found in curve c. The peaks located at 24.6°, 26.6°, 28.3°, 36.8°, 43.9°, 48.1°, 52.1° and 61.2° could be indexed to the reflection from the (100), (002), (101), (102), (110), (103), (112) and (104) planes of hexagonal phase CdS (JCPDS No.01-080-0006) and the additional peaks are observed at 25.2°, 38.1° and 47.9° corresponding to (011), (004) and (200) planes of anatase TiO_2 . All of peaks in curve c broaden and weaken implying that $\text{CdS}/\text{TiO}_2\text{NT}_s$ composite

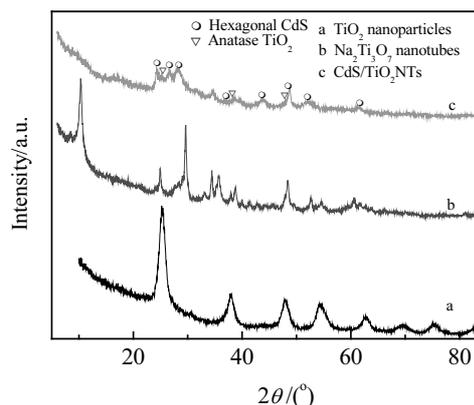


Fig.1 X-ray diffraction patterns of samples

includes TiO_2NT_s and CdS nanoparticles belonging to low-dimensional states.

During the synthetic process of $\text{CdS}/\text{TiO}_2\text{NT}_s$ composite, Cd^{2+} ions were substituted for Na^+ ions via ion exchange reaction at 40 °C to produce CdTi_3O_7 , and TiO_2NT_s and CdS quantum dots were continuously formed via a hydrolysis reaction of thiourea in a medium of water at 70 °C. In the preparation of $\text{Na}_2\text{Ti}_3\text{O}_7$, some Na^+ ions could be replaced by H^+ to derive from the compound of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$, if the $\text{Na}_2\text{Ti}_3\text{O}_7$ resultant was washed with a dilute acid^[7]. The synthesis of TiO_2NT_s through the reaction of layered $\text{Na}_2\text{Ti}_3\text{O}_7$ and H_2O was reported by Wei et al^[8].

The evolvement mechanism of sodium trititanate nanotubes can be seen from SEM images of samples for different reaction time, as shown in Fig.2. When the reactants were put in a Teflon-lined autoclave and held in an oven at 140 °C for 12 h, some sheet-shaped products surrounding the orbicular particles of TiO_2 were generated in Fig.2a. Subsequently, a large number of sheet-shaped sodium trititanate were formed after reaction between spherical TiO_2 and sodium hydroxide for 16 h in Fig.2b. Those lamellar sodium trititanates curl individually to grow into a considerable number of sodium trititanate nanotubes by self-assembled route due to no additional template in the reaction system after reaction time for 20 h in Fig.2c, and finally all of TiO_2 particles completely transferred into trititanate nanotubes after reaction time for 24 h in Fig.2d.

Yang et al^[9] considered that swelling stripes and the peel-off from the spherical surface of TiO_2 particles formed the tubular structure. This mechanism was further emphasized by Tsai and Teng^[10] who indicated that the replacement of Na^+ by H^+ will cause a peel-off of individual layers from TiO_2 particles owing to the variation of the surface charge during acid washing.

Fig.3 shows the TEM images of sodium trititanate nanotubes and $\text{CdS}/\text{TiO}_2\text{NT}_s$ composite. It can be found from Fig.3a that the sodium trititanate nanotubes display curly

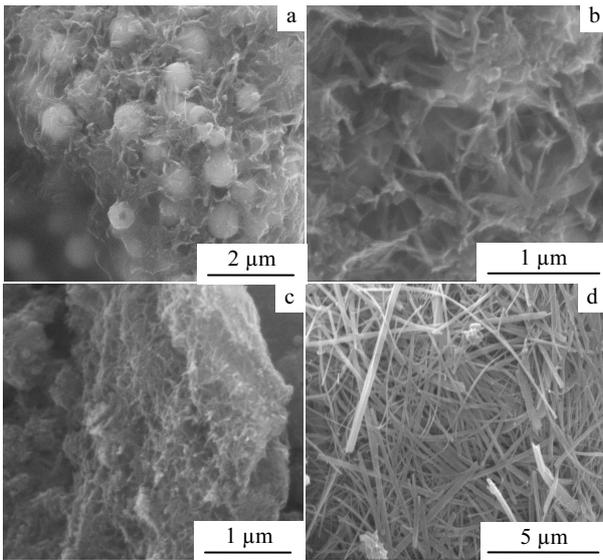


Fig.2 SEM images of samples for different reaction time: (a) 12 h, (b) 16 h, (c) 20 h, and (d) 24 h

morphologies and disordered orientation with an average diameter of about 15 nm. For the CdS/TiO₂NTs composite, CdS with particle sizes of about 8 nm are homogeneously loaded on the surface of TiO₂NTs in Fig.3b.

Fig.4 presents the diffuse reflectance UV-visible absorption spectra of samples. It can be seen that the Na₂Ti₃O₇ nanotubes exhibit an absorption edge at 361 nm in curve a, and the absorption edge of TiO₂ powder is located at 400 nm in curve b. Whereas, the absorption edge of CdS/TiO₂NTs composite falls into the visible region at the wavelength of 541 nm as shown in curve c and it is red-shifted by about 180 nm in comparison with that of trititanate nanotubes, demonstrating that the absorption spectrum of TiO₂NTs can be sensitized with CdS nanoparticles.

Fig.5 shows the fluorescence emission spectra for the samples of trititanate nanotubes, TiO₂ powder and CdS/TiO₂NTs composite. All of samples exhibit an emission peak with a maximum about 394 nm, but the photoluminescence peak of CdS/TiO₂NTs composite is much lower than those of Na₂Ti₃O₇

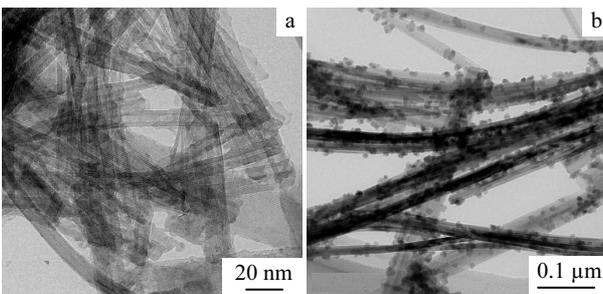


Fig.3 TEM images of samples: (a) Na₂Ti₃O₇ nanotube and (b) CdS/TiO₂NTs composite

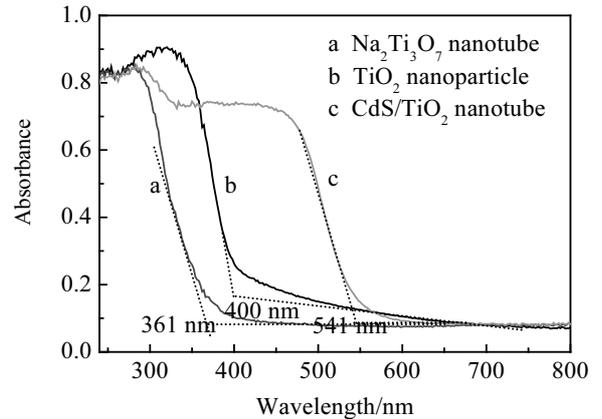


Fig.4 Diffuse reflectance UV-visible absorption spectra of samples

nanotubes and TiO₂ powder. It means that the transition frequency of electrons is quickened up and the recombination probabilities of photogenerated electron-hole pairs are decreased in the interface of CdS nanoparticles and TiO₂NTs.

Fig.6 expresses the activity of hydrogen production by photocatalytic water decomposition for the samples under visible light irradiation. The sample of CdS/TiO₂NTs composite exhibits an excellent H₂ evolution activity to the amount of 1708 μL/g for 6 h. However, a small amount of H₂ is produced for the samples of TiO₂ powder (230 μL/g) and trititanate nanotubes (48 μL/g) for 6 h, respectively.

Lower H₂ evolution for the samples of trititanate nanotubes and TiO₂ powder in Fig.6 probably results from a little amount of visible light absorption at the toes of the curves a and b in Fig.4, respectively and it is also attributed to higher fluorescence intensities of curves b and c in Fig.5. Whereas the activities of hydrogen production for the sample of CdS/TiO₂NTs composite can be primarily ascribed to strong visible light absorption at wavelength of 541 nm in Fig.4c, and then, the heterostructure formed in the interface of CdS and

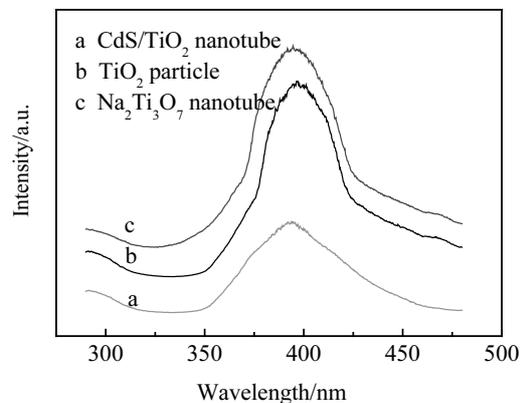


Fig.5 Fluorescence emission spectra for samples excited with $\lambda=250$ nm

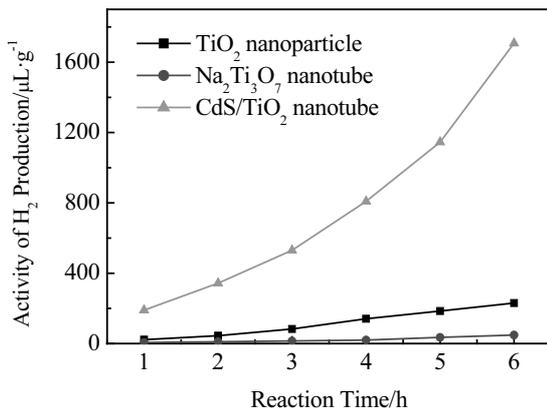


Fig.6 Activities of H₂ evolution for samples under visible light irradiation for 6 h

TiO₂NTs is efficient for separation of photogenerated electron-hole pairs and accelerate the photogenerated electron transformation from the conduction band of CdS nanoparticles with narrow band-gap (2.3 eV) to the conduction band of TiO₂NTs with broad band-gap (TiO₂ anatase, 3.2 eV). To enhance the photocatalytic activity and improve the quantum yield of hydrogen production, some authors^[11] proposed an electron transfer process in the interface by coupling two semi-conductors with different redox energy levels to improve the efficiency of charge separation.

3 Conclusions

1) The CdS/TiO₂NTs composite can be prepared by a simple two-step chemical solution routes to directly transfer trititanate nanotubes to TiO₂NTs and simultaneously load CdS nanopar-

ticles over TiO₂NTs.

2) CdS/TiO₂NTs composite consists of uniform anatase nanotubes in average tubular diameter of about 15 nm with homogenously loaded hexagonal phase CdS quantum dots in average particle size of about 8 nm.

3) The sheet-shaped sodium trititanate nanotubes generated from the TiO₂ particles curled to form the sodium trititanate nanotubes.

4) The highest activity of hydrogen evolution for CdS/TiO₂NTs composite is associated with the efficient separation of photogenerated electron-hole pairs in the interface of CdS and TiO₂NTs.

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纳米复合材料 CdS/TiO₂NTs 的制备及光催化产氢活性

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摘要: 通过离子交换和沉淀反应制备纳米复合材料CdS/TiO₂NTs。采用X射线衍射(XRD)、扫描电镜(SEM)、透射电镜(TEM)、漫反射紫外-可见吸收光谱(DRUVAS)、荧光光谱(FES)、X射线荧光分析(XRF)等手段对该复合材料的结构进行表征。SEM结果表明: 钛酸盐纳米管的形成经由TiO₂颗粒-片状的钛酸盐-卷曲的钛酸盐纳米管的自组装过程。XRD、DRUVAS、FES和FES结果表明: 平均粒度大约 8 nm 的六方相CdS均匀的负载于锐钛矿型TiO₂纳米管表面, 其吸收边扩展到可见区。与TiO₂纳米管及TiO₂粉末相比, CdS/TiO₂NTs 纳米复合材料展示了较高的可见光催化分解水产氢活性。

关键词: CdS/TiO₂NTs纳米复合材料; TiO₂纳米管; 产氢; 光催化分解水

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