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CHEMICAL DEPOSITING OF CdS/ZnS COMPOSITION NANOSTRUCTURE MODIFIED TiO_2 THIN FILM

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ZnS-CdS/TiO_2 composite nano-structure thin films are prepared using a facile chemical bath deposition method. The optical properties of samples are analyzed by XRD, Raman and Photoluminescence spectra. The analyzing results show that the film should be the combination film composed of the composition of CdS and ZnS. In order to clearly understand the forming processes and the growth mechanism of the ZnS-CdS/TiO_2 composite thin film, we discussed the competition mechanism of Zn^{2+} and Cd^{2+} with the complexing agent NH_3 during the forming of CdS-ZnS thin film. It was found that PL peak experiences a redshift with the increasing of growth time, which could arise from the increasing of the nanocrystals size and changing of composition. The samples could absorb visible light and the absorption range increased up to 500 nm.

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1. Introduction

Titania nanomaterials have been extensively investigated due to its high stability, favorable band gap energy, abundant availability, and inexpensive cost for applications in the areas of solar cells and photocatalysis [1-6]. It is more important job to extend its light response to the visible light region among areas with relation to the application of solar energy. Some efforts have been paid to develop the composite semiconductor photocatalyst systems for improving the light response region and photocatalytic activities of TiO_2 [7]. When wide bandgap semiconductor is coupled with a small bandgap one with a more negative conduction band, electrons in conduction band can be injected from the small bandgap semiconductor into the large bandgap one [8]. The binary compounds have been mostly extensivley investigated as the important candidate for wide band gap material to absorb light in the visible region. CdS is a promising candidate for TiO_2 sensitization because of its suitable bandgap energy of 2.42 eV at room temperature.

Recently, Yu et al. fabricated photoactive ZnS/TiO_2 nanocomposites via microemulsion-mediated solvothermal method. Compared with the solitary anatase TiO_2, the visible-light photocatalytic activity of the ZnS/TiO_2 was improved greatly [9]. Franco et al. prepared distinct nanocrystalline TiO_2 capped ZnS samples by chemical deposition method. ZnS/TiO_2 composite materials showed a red shift of the material band edge compared with TiO_2, and the material with the best catalytic activity towards the methylene blue photodecolorization for certainTiO_2/ZnS ratio [10]. Lee et al. coated on TiO_2 nanoparticles with ZnS in nano-scale through a simple one pot reaction, which easily controlled in nano-scale by adjusting the amount of reactants and/or the sonication time [11]. Tachibana et al. prepared CdS/nanocrustalline TiO_2 film by an in situ chemical bath deposition stated that an efficient electron injuction occurs from CdS to

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a TiO_2 conduction band [12]. The above investigations suggested that CdS and ZnS are the important materials to improve the visiable reponsing range and photocatalytic activity.

Chemical bath deposition (CBD) technique is a very attractive method for producing chalcogenide semiconductor thin films. This method could easily controlled release of the metal ions (M^{2+}) and sulphide ions (S^{2-}) in an aqueous bath [13, 14]. It is generally thought that the metal ions and sulphide ions were slowly released owing to the controllable of the complexing agents to form the thin film on the substrate. The composition of the ternary semiconductor thin film is difficultly controlled due to the great difference growth characteristics of ZnS and CdS films. Only a few investigations have been focused on the influence of growth parameters on the optical properties of CdS/ZnS films prepared by CBD [13, 15, 16].

In this paper, CdS and ZnS were co-deposited on TiO_2 thin film by chemical bath deposition with different grow time. The competition mechanism of Zn^{2+} and Cd^{2+} with the complexing agent NH_3 plays a critical role in the forming of ZnS-CdS thin film. The optical properties such as raman spectra, photoluminescence spectra and optical transmission of the films with mixed phases were further investigated. Moreover, the forming mechanism and competitive mechanism of the ZnS and CdS samples was also discussed.

2. Experiments

All reagents were used as received. Commercial glass (16 mm×76 mm) were thoroughly cleaned by detergent solution, acetone, ethanol washed, and deionized water. The TiO_2 paste was dipped on the commercial glass and sintered at 450 ℃ for 60 min. The thickness of the TiO_2 film can be controlled by the number of layers of spin-coating.

CdS-ZnS compostion nanostructures were co-deposited on TiO_2 thin film by chemical bath deposition. Aqueous solutions contain 0.396 M ammonium nitrate, 0.357 M KOH, 3.64×10^{-3} M $CdCl_2$ and $ZnSO_4$, and all solutions were mixed in a beaker without further adjusting the pH. The solution was stirred for few minutes and heated at 85℃. Next, the 3.64×10^{-3} M thiourea solution was added in the solution and the cleaned glass substrate was inclined vertically to the walls of beaker for 2 h under the constant temperature of 85℃. The reaction solution was no stirred during the deposition process. The glass substrates were removed from the beaker after reaction, and washed in running tap water, and then dried in air before characterization.

The samples were characterized by X-ray diffraction (XRD), using a Bruker Advance D8 diffractometer equipped with graphite-mono-chromatized Cu Ka radiation (k=1.54062). The diffraction angle was scanned from 10^o to 80^o with the scanning rate of 0.18/s. The room PL spectra of the as-prepared samples were measured using a Xe lamp with an excitation wavelength of 325 nm. The Raman scattering was performed in the near backscattering geometry using an Ar^+ laser and the power of 20 mW. The UV-vis absorption spectra of the samples were recorded on a New Century T6 photospectrometer with rated power 120 W and AC 220 V.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CdS-ZnS composite nanoparticles prepared on TiO_2 film surface by CBD for different deposition times. From the XRD data, we could observe that as-prepared and 450 ℃ air-annealed samples have the anatase TiO_2 diffraction peaks. Besides the diffraction peaks coming from the TiO_2 film, another three strong diffraction peaks are observed at 2θ=26.54°, 44.04°, 52.16°, which can be indexed as (111), (220) and (311) diffraction peaks of the cubic phase CdS, respectively. All the diffraction peaks in Fig. 1 are attributed to cubic phase CdS

according to the standard JCPDS card No. 80-0019. It is also clearly seen that the intensity of the diffraction peaks weakly changes with extended deposition time, which indicates that the effect of deposition time on crystallinity. As deposition time reached 90 min, three diffraction peaks (111), (220) and (311) can be observed and the intensity of peaks has almost no change, which indicates that the as-deposited CdS film is well crystallized and the number of CdS nanoparticles only increases with increasing of the deposition time. The diffraction peak originated at 2θ=29.31°corresponding to the (008) reflections of the hexagonal phase of ZnS, which can be ascribed to the weak crystallinity and a small numer of ZnS nanopartiles formed.

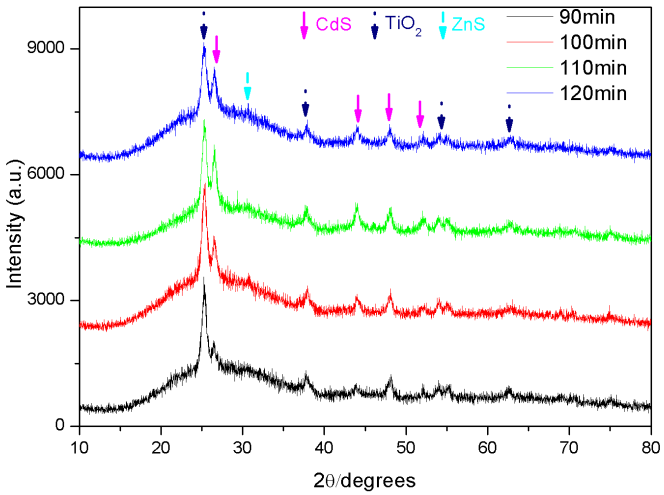

Fig. 1 The XRD patterns of the CdS-ZnS composite nanoparticles prepared on TiO_2 film surface by CBD for different deposition times.

The forming mechanism of CdS-ZnS thin film on TiO_2 substrate by CBD has been further investigated. The Cd^{2+} and Zn^{2+} exist predominantly in the form of ion complex due to the NH_3 as complexing agents during the CBD growth process. The formation rates of ZnS and CdS are determined by the concentration of Zn^{2+} and Cd^{2+} provided by $[Zn(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$, and the concentration of S^{2-} from the hydrolysis of $SC(NH_2)_2$, respectively [14]. In addition, the film chemical composition can depend on the preparing conditions. The $[Zn(NH_3)_4]^{2+}$ is more stable than $[Cd(NH_3)_4]^{2+}$ in an alkaline solution and the solubility product of CdS is lower than that of ZnS, which can lead to the growth rate of CdS is much more rapid than ZnS. $[Cd(NH_3)_4]^{2+}$ can be adsorpted on the substrate and reacted with S^{2-} to form CdS film, which can accelerate the reaction rate[14]. As the depostion time increases, the concentration of Cd^{2+} decrease in the solution, which can result in the S^{2-} combining with Zn^{2+}. Thus, we thought that CdS first was formed, then ZnS was formed on the surface of CdS nanocrystals.

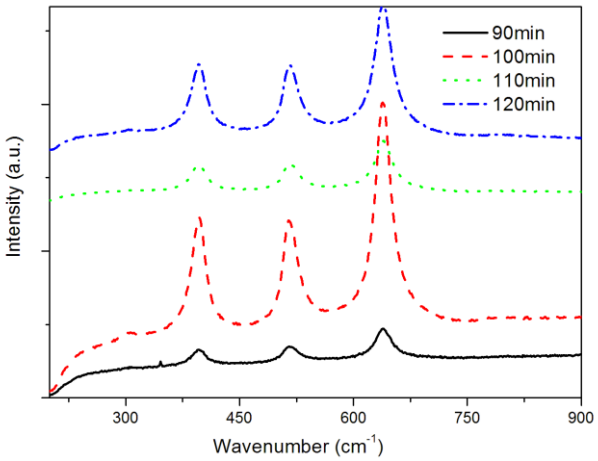

Fig. 2. Room temperature Raman spectrum of ZnS-CdS/TiO_2 composite nanostructure.

The room temperature Raman spectra of ZnS-CdS/TiO_2 composite nano-structure are shown in Fig. 2. It can be seen that there are three obvious peaks which are belong to Raman vibration peaks of the anatase TiO_2 and they are identified as the vibration mode of B_{1g}, A_{1g} and E_g, respectively. The intensity of the Raman peaks change as the growth time increases, which demonstrates that the thinkness of the ZnS-CdS nanofilm deposited on the TiO_2 have the effects on the Raman vibration mode of the as-prepared samples. The peaks at 302 cm^{-1} are attributed to CdS longitudinal optical modes A_1 mode. However, the Raman peaks of ZnS and other products are no observed.

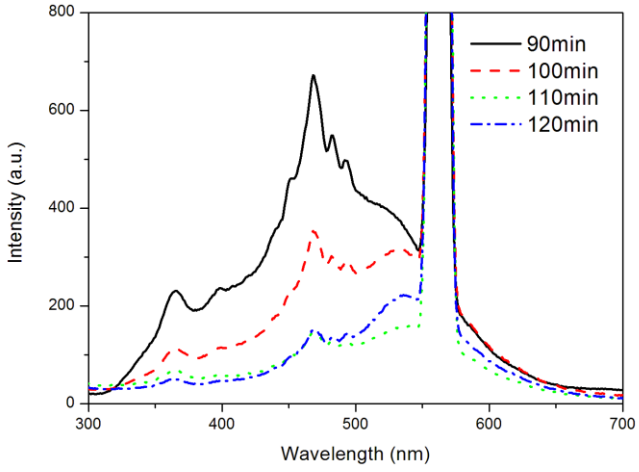

Fig 3. Photoluminescence spectra of as-prepared ZnS-CdS/TiO_2 composite nano-structure film with the different growth time.

The PL spectra of the as-prepared samples were measured using a Xe lamp with an excitation wavelength of 325 nm at room temperature. Fig 3 shows the PL spectrum consisting of

a broad green band at around 373 nm in wavelength and a very broad band located in the green-blue region. The ultraviolet emission may be ascribed to the near band edge emission of TiO_2. We believe that the green-blue luminescence band arises from transitions of electrons or the hybrid energy level transition in ZnS-CdS composition nanocrystal grains [17].

It is worthwhile to note that the overall features of PL spectrum differ from the previous investigation results. The peak is weaker and experiences a redshift with the increasing of growth time, which could result from the increasing of the nanocrystals size and changing of composition.

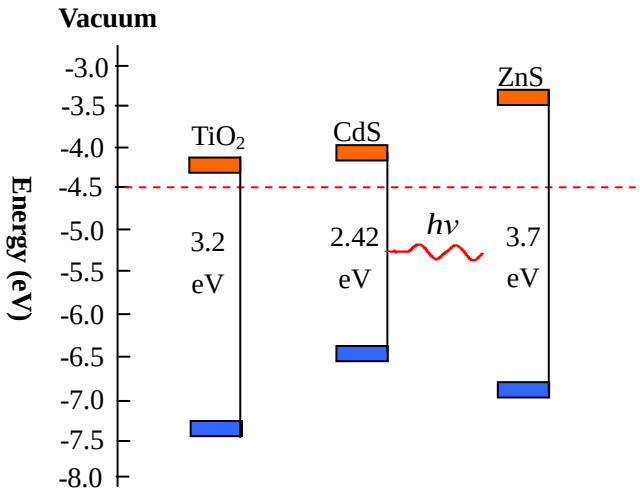

Fig. 4. Relative energy levels of TiO_2, CdS and ZnS in bulk phase based on the vacuum level.

The relative energy levels of TiO_2, CdS and ZnS in bulk phase, the lower edge of the conduction band and upper edge of the valence band are presented at Fig. 4. It can be seen clearly that the conduction band of CdS is higher than TiO_2 conduction band. After the CdS excitation, an electron-hole pair is generated. The electron is injected from conduction band of CdS to that of the TiO_2, the injected electron is trapped in the TiO_2 nanocrystal and the recombination rates depends on the CdS nanocrystal size[12]. The CdS sensitized TiO_2 is beneficial to separate the electron and hole, which not only could enhance the photocatalysis of the TiO_2 , but also coule absorb the visible light to improve the ultization of the sunlight. ZnS composition of the prepared complex film could be helpful of increasing the photocurrent of the solar cell [18].

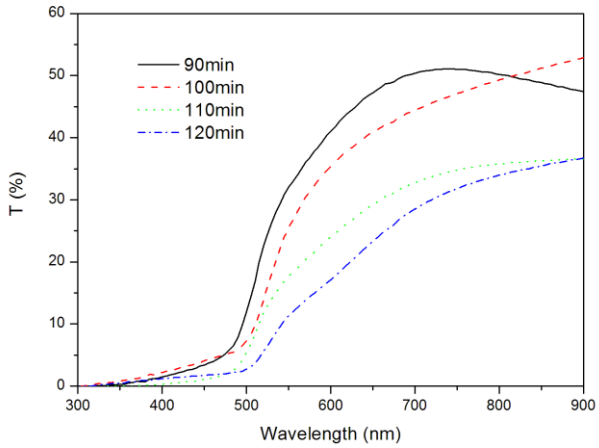

Fig. 5 The optical transmission spectrum of ZnS-CdS/TiO_2 composite nano-structure recorded for the different growth time of 90 min, 100, 110, and 120 min, respectively.

Fig. 5 shows the optical transmission spectrum recorded for the different growth time of 90 min, 100, 110, and 120 min in the range 200-800 nm, respectively. It is clearly seen that ZnS-CdS sensitized TiO_2 thin film samples could absorb visible light and the absorption range increased up to 500 nm. What's more, it is observed that the transmittance properties of thin films were influenced by the growth time. The absorbe edge performs a redshift with the increasing of growth time, which can be ascribed to the increasing of the nanocrystal size and growth of CdS [19]. Another possible reason is the formation of CdZnS, Because ZnS has a wider energy band gap E_{bg} =3.7eV and that of CdS is 2.4 eV [20]. In addition, with the increasing of growth time, the transmittance intensity decreased due to the increasing of ZnS-CdS nanocrystal density. The pure CdS thin film is with excellent transmittance in the 500-800 nm range, while for pure ZnS thin film in the 300-800 nm range. The ZnS has photostability under irradiation and could prevent the CdS from photocorrosion [18].

4. Conclusion

In summary, ZnS-CdS/TiO_2 heterostructure arrays were prepared using a facile chemical bath deposition method. The analyzing result shows that the film should be the combination film composed of the composition of CdS, ZnS. This made it able to clearly understand the forming processes and the growth mechanism of the ZnS-CdS/TiO_2 composite thin film. It was found that PL peak experiences a redshift with the increasing of growth time, which can arise from increasing of the nanocrystals size and changing of composition. The samples could absorb visible light and the absorption range increased up to 500 nm. It can be interesting that the ZnS-CdS sensitized TiO_2 heterostructure thin film will offer promising applications as photocatalysts and solar-energy conversion materials.

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