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Ultrasound-assisted microwave preparation of Ag-doped CdS nanoparticles

Jun Ma, Guo'an Tai, Wanlin Guo *

Institute of Nanoscience, Nanjing University of Aeronautics and Astronautics, No. 29, Yudao Street, Nanjing 210016, PR China

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ABSTRACT

Ag-doped CdS nanoparticles were synthesized by an ultrasound-assisted microwave synthesis method. The X-ray diffraction patterns reveal a structural evolution from cubic to hexagonal with increasing molar ratios of $\text{Ag}^+/\text{Cd}^{2+}$ from 0% to 5%. It shows that the Ag-doped hexagonal CdS nanoparticles are polycrystal. The X-ray photoelectron spectroscopy of the CdS nanoparticles doping with 5% Ag^+ shows that the doped Ag in CdS is metallic. Simultaneously, the characteristic Raman peaks of the CdS nanoparticles enhance with increasing Ag^+ concentrations. The photocatalytic activity of different Ag-doped samples show a reasonable change due to different ratios of Ag which doped into CdS.

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1. Introduction

Doping is important for semiconductors, which plays a critical role in tuning their optical and electrical properties [1] for the potential applications in wavelength-controlled lasers [2], biotechnology [3], and solar cells [4]. In particular, photoluminescence emission and excitation wavelength of nanocrystals may be tuned by dopants [5]. The lasing threshold of semiconductor nanocrystals can be reduced three fold by adding extra electrons [6]. In addition, in the bioimage field, less harmful dopants can mitigate the toxic problem by producing visible or infrared emission instead of harmful elements currently used [7]. Meanwhile, doping the semiconductors with noble metals as the photoinduced electron acceptors can also enhance the ability of photocatalysis [8]. Also, some experiments have conformed that by means of small amounts of metal doping, the crystallization progress of semiconductors can be affected [9].

CdS is one of the most important II–VI semiconductors with a direct bulk phase band gap of 2.4 eV at room temperature. It is extensively used for optoelectronic devices because of its tuning emission in the visible-light range with different sizes and shapes. CdS has the great potential applications as nanoelectronics and photocatalytic materials [10,11]. In recent years, doping of CdS nanostructures has attracted intensive attentions. A new peak appears in the Mn-doped CdS nanocrystals photoluminescence spectra due to Mn d–d transitions [12]. Se doping can induce the

formation of branched CdS nanocrystals and cause the red shift of photoluminescence of CdS nanocrystals [13,14]. (Mn, Zn) co-doped CdS nanowires exhibit a room-temperature ferromagnetic behavior [15]. Particularly, Ag is a group IB element. The potential difference between the Fermi level of Ag and the conduction band of semiconductors facilitates the electron transfer between the semiconductor matrix and the doped metal [16]. Ag doping can provide a convenient way to tailor the physical properties of the intrinsic semiconductor such as Raman scattering [17] and photocatalysis [18]. However, Ag is an active metal which can be easily oxidized by the general doping method. Impurities such as Ag easily diffuse even at room temperature [19]. Therefore, it remains an important challenge to dope Ag into CdS nanocrystals.

Microwave irradiation has been proven to be a useful tool in synthesizing nanomaterials with enhanced reaction rate [20,21], but has some disadvantages such as limited thickness penetrating and poorly experimental repeatability [22]. Simultaneously, sonochemistry method has been widely used to synthesis nanomaterials [23,24]. Tai and Guo have developed a sonochemistry-assisted microwave method for controlled synthesis of semiconductor nanostructural materials [25].

Here, the ultrasound-assisted microwave synthesis method has been successfully used to dope Ag into CdS nanoparticles. It was observed that Ag doping of CdS nanoparticles can induce the evolution of crystal structure from cubic to hexagonal under the synergistic effect of ultrasound and microwave. The characteristic Raman peaks of CdS have been enhanced with increasing Ag^+ concentrations. Photocatalytic activity experiment indicated that the Ag clusters have doped into the CdS matrix.

* Corresponding author. Tel./fax: +86 25 84895827.

E-mail address: wlguo@nuaa.edu.cn (W. Guo).

2. Experimental section

2.1. Materials

Sulfur powders, cadmium acetate and thioacetamide were purchased from Shanghai Chemical Reagents Company. Silver nitrate was purchased from Shanghai Shenbo Chemical Co. Ltd. Rhodamine B was purchased from Tianjin Institute of Chemical Reagents. All chemicals are analytical grade products and used without further purification.

2.2. Synthesis of Ag-doped CdS Nanoparticles

In typical synthesis process, 2.5 mmol of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 1.25 mmol of $\text{CS}(\text{NH}_2)_2$ and 1.25 mmol of sulfur powders were dissolved into 50 ml of ethylene glycol (EG). The mixed solution was transferred to a three-necked flask, stirred for 15 min, and then was purged for 5 min with Argon gas before put into the microwave reactor. The resulting mixed solution was placed in a program-controlled ultrasound-assisted microwave reactor (see Ref. [25]) with the microwave power set at 400 W and operated at 140 °C for 15 min. In this process, a high-intensity ultrasonic probe (from Xinzhì Co., China, JY92–2D, with a 10 mm diameter titanium horn of 20 kHz and 400 W working in a pulsed mode with a duty cycle of 0.5 s) was directly immersed in the solution. The Ti horn was immersed into the solution for 1 cm. In addition, a condenser was attached to the three-necked flask. After the reaction, the resulting solution was poured into cool cyclohexylamine and preserved at 5 °C for 12 h. To obtain Ag-doped products with different concentrations, the above reaction process was repeated by just adding 0.025 mmol (1% Ag^+), 0.075 mmol (3% Ag^+) and 0.125 mmol (5% Ag^+) of AgNO_3 into the initial reaction mixtures respectively. The as-synthesized products were separated by centrifugation, washed with absolute ethanol and ultrapure water (resistivity 18 M Ω -cm) several times, and dried at 60 °C in vacuum for 12 h.

2.3. Structural characterization

The phase of the as-synthesized products was detected by a Bruker D8 Advance diffractometer which was operating at 40 kV and 40 mA ($\text{CuK}\alpha$ irradiation, $\lambda = 1.542 \text{ \AA}$). TEM, High-resolution TEM (HR-TEM) images and the typical selected area electron diffraction (SAED) patterns were recorded on a JEOL JEM-2100F microscope operating at 200 kV. For this characterization, the products were ultrasonically dispersed in ethanol, then, the resulting suspensions were dropped onto the ultrathin carbon-coated copper grids. X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermo ESCALAB 250 using a 150 W $\text{AlK}\alpha$ radiation. The Resonant Raman spectra were measured on a Renishaw Raman spectrometer system under the excitation of a 514.5 nm line out of a 20 mW Argon Ion laser. Room temperature UV–visible absorption spectra were recorded on a Vary 500 spectrometer.

2.4. Photocatalytic study

The photocatalytic activity of the as-synthesized products for degrading Rhodamine B aqueous solution was studied with a 150 W metal halide lamp ($\lambda > 380 \text{ nm}$) being used as a visible-light source. First, the suspensions containing the as-synthesized samples (100 mg) and Rhodamine B (4 mg/L, 150 mL) were stirred in the dark for 15 min to obtain an adsorption and desorption equilibrium between the catalyst and Rhodamine B. Then the suspensions were placed under the metal halide lamp. At a designed time intervals, 4 mL of the aqueous solution was taken out for analysis. The

photocatalytic activity of the catalyst was evaluated by detecting the visible absorbance characteristic of targeted Rhodamine B using a Vary 500 spectrometer.

3. Results and discussion

3.1. Structure and morphology of the Ag-doped CdS nanoparticles

Fig. 1 displays the XRD patterns of the Ag-doped CdS nanoparticles with different $\text{Ag}^+/\text{Cd}^{2+}$ molar ratios in the initial reaction system synthesized in the sonochemistry-assisted microwave reactor. The reflection peaks of pure CdS in Fig. 1a can be indexed as zincblende structure (space group $F\bar{4}3m$) with the lattice constant of $a = 5.800 \text{ \AA}$, in agreement with literature values (JCPDS Card No. 10-0454). However, the reflection peaks of CdS with 5% Ag^+ dopant in the initial reactants in Fig. 1d correspond to the hexagonal wurtzite phase (space group $P6_3mc$) with the lattice constants of $a = b = 4.141 \text{ \AA}$ and $c = 6.720 \text{ \AA}$ (JCPDS Card No. 41-1049). The crystal structure evolution of the samples from the cubic to the hexagonal phase is noticeable from the gradual enhanced hexagonal characteristic peaks such as those at 2θ equal to 28.1° and 51.9° with increasing Ag^+ concentrations. In Fig. 1b and c can be considered as the transition-state between the cubic and the hexagonal phase. No obvious diffraction peaks of any other minerals can be detected in the XRD patterns. There are no obvious characteristic peaks of Ag or Ag_2S can be observed, indicating that the Ag has immersed into the CdS nanoparticles matrixes. In order to get nanocrystalline size-change information, the Scherer formula [26] was used to calculate the average size of the nanocrystallines

$$d = \frac{0.94\lambda}{B \cos \theta}$$

Here, d is the diameter of the crystallite, λ is the wavelength of X-ray radiation, B is the corrected full-width at half-maximum (FMWH) of the peak, and θ is the angle of diffraction. The (1 1 1), (2 2 0) and (3 1 1) crystal planes were used to calculate the average size of the cubic crystallites, while the (0 0 2), (1 1 0) and (1 1 2) crystal planes were used to calculate the average size of the hexagonal crystallites. The calculated results were showed in Table 1.

The TEM images of the Ag-doped CdS (with 5% Ag^+ in the reactants) were exhibited in Fig. 2. It is found that most of the crystallites are spherical and their size of is $\sim 15 \text{ nm}$ which agrees with the XRD result (see Table 1). The corresponding selected area electron diffraction pattern (Fig. 2b) was recorded on the nanoparticles. The diffraction ring can be indexed to the (0 0 2), (1 1 0) and (1 1 2) planes, confirming the wurtzite phase. HR-TEM in Fig. 2d

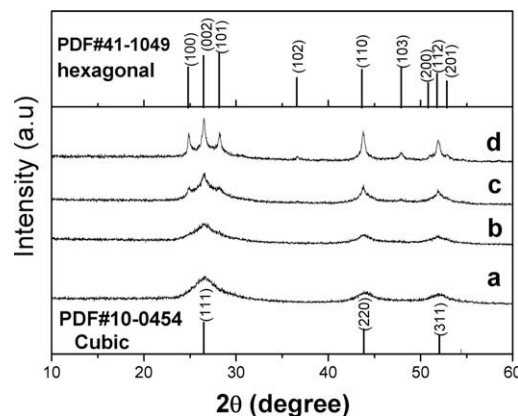


Fig. 1. XRD patterns of the as-synthesized Ag-doped CdS nanoparticles with different Ag^+ molar ratios in the reactants: (a) pure CdS; (b) 1% Ag^+ (0.025 mmol AgNO_3); (c) 3% Ag^+ (0.075 mmol AgNO_3); and (d) 5% Ag^+ (0.125 mmol AgNO_3).

Table 1

The calculated CdS nanocrystallite size from XRD patterns with different molar ratios of Ag^+ in the reactants: (a) pure CdS; (b) 1% Ag^+ (0.025 mmol AgNO_3); (c) 3% Ag^+ (0.075 mmol AgNO_3); and (d) 5% Ag^+ (0.125 mmol AgNO_3).

Sample	XRD size (nm)
a	4.07
b	4.56
c	7.35
d	16.18

also shows the preferred orientation along [0 0 1] which is consistent with the XRD result.

The XPS analysis of Ag-doped CdS (with 5% Ag^+ dopants in the reactants) nanoparticles is given in Fig. 3. From Fig. 3b and c, it is obvious that the binding energy of peaks $\text{Cd}3\text{d}_{5/2}$ and $\text{S}2\text{p}_{3/2}$ are 404.47 and 160.92 eV, respectively. The $\text{Ag}3\text{d}_{5/2}$ peak is centered at 367.45 eV; whereas, the $\text{Ag}3\text{d}_{3/2}$ is found at 373.53 eV with a spin energy separation of 6.08 eV. This is characteristic of metallic Ag [17]. It is also obtained that the real Ag-doped molar ratio is about 1.43% from XPS which is lower than the Ag^+ concentration in the initial reactants.

3.2. Investigation of the synthesis and phase evolution mechanism

In order to investigate the contributions of ultrasound and microwave, some blank tests have been taken: (1) only microwave; (2) only ultrasound; and (3) mechanical stirring. As a result, the expected products could not be obtained by the above three methods. If prepared by pure microwave, plenty of residual sulfur powders can be found in the resulting products. The reaction should last a

much longer time and the products are not ideal when only ultrasound or only mechanical stirring is used. It's indicated that ultrasound-assisted method is a convenient and quick approach to prepare Ag-doped CdS nanoparticles.

The energy of the microwave photon (0.0016 eV) is too low to break chemical bonds and is also lower than the energy of Brownian motion. It is therefore clear that microwaves cannot induce chemical reactions. Microwave-enhanced chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects [27]. On the other hand, there are two regions in sonochemical reactivity as postulated by Suslick et al. [28]: the gas phase within the collapsing cavity and the interface between the liquid and bubble. As in this experiment, microwave can be used as a quick and homogeneous heater. Simultaneously, pulsed ultrasound can offer a high energy to dissolve sulfur powder and penetrate Ag into CdS matrix. Therefore, the ultrasound-assisted microwave method can be used to prepare homogeneous doped products.

What is the phase evolution mechanism? The stacking sequence of wurtzite is ABAB and it transforms to ABCABC for zinc-blende. In both of the structures, cadmium and sulfur atoms are tetrahedrally coordinated. In thermodynamics, it is notable that zinc-blende is the most stable form at lower temperature for bulk phase, while wurtzite is more stable at high temperature. However, the situation is different in nanoscale. Banerjee et al. [29] has reported the size-dependent structural phase transformation of CdS nanoparticles. Zinc-blende to wurtzite evolution involves only a change in symmetry. The nucleation and growth of nanocrystals are primarily governed by the competition between the surface and volume free energies. During the nucleation, symmetry favors the cubic crystal structure for spherical nucleus over hexagonal structure by adopting low-energy (1 1 1) facets on the nanocrystal surface. From Table 1, the size of the crystallites grows

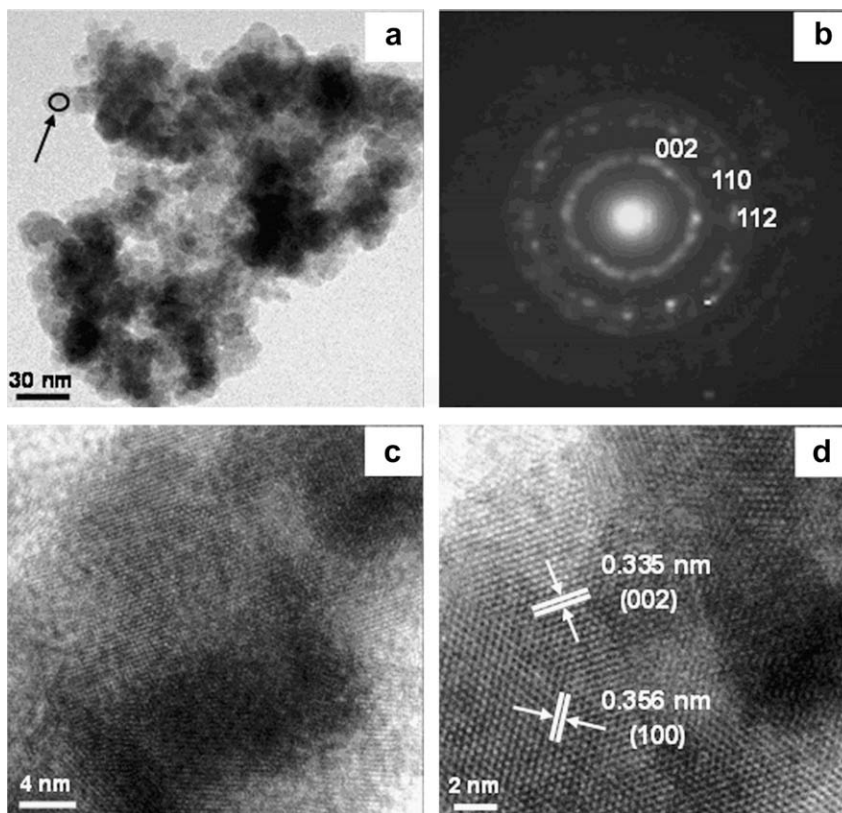


Fig. 2. TEM images of Ag-doped CdS nanoparticles with 5% Ag^+ (0.125 mmol AgNO_3) in the reactants: (a) TEM image of the sample; (b) SEAD pattern corresponds to the white ring area in (a); (c and d) high-resolution TEM images of the as-synthesized sample.

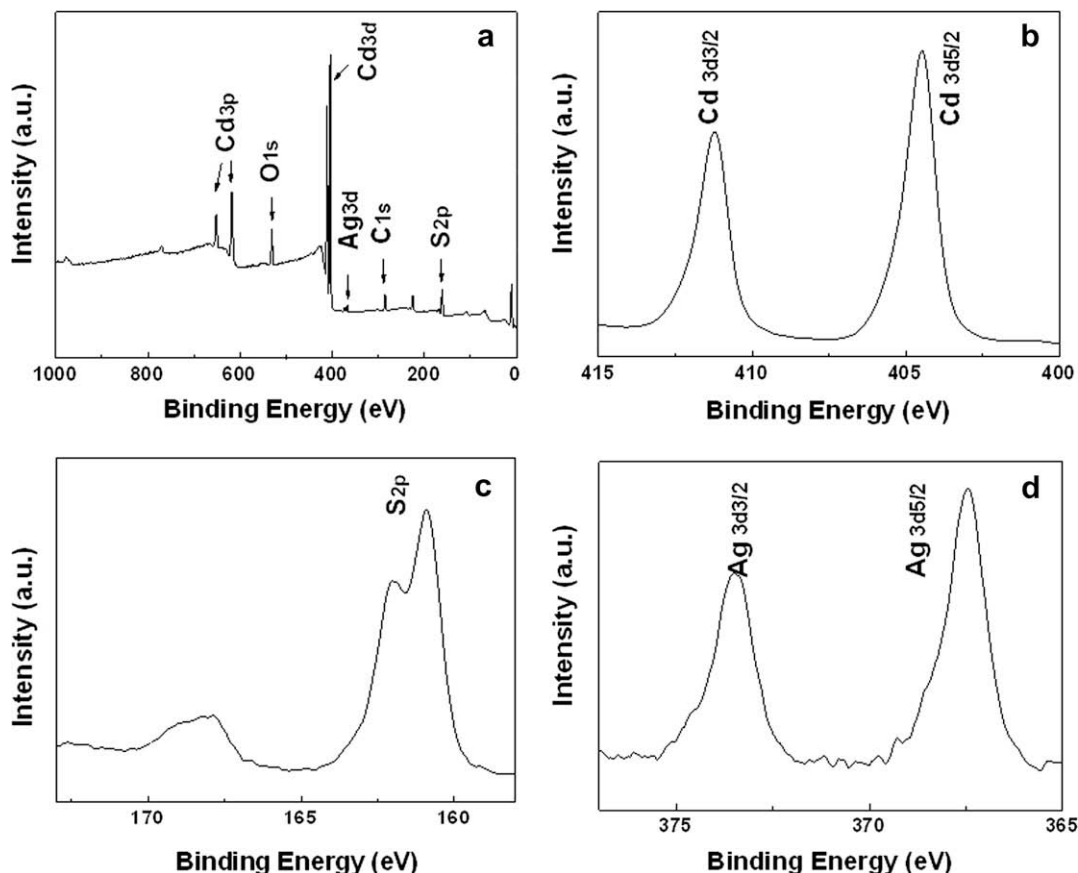


Fig. 3. XPS survey spectrum of the as-synthesized Ag-doped CdS with 5% Ag⁺ (0.125 mmol AgNO₃) in the reactants. (a) Full spectrum; (b) Cd3d spectrum; (c) S2p spectrum; and (d) Ag3d spectrum.

with increasing the Ag⁺ concentrations, therefore, the crystal structure evolves from cubic to hexagonal naturely, and the critical transformation size of CdS nanocrystallites is around 4–7 nm which agrees with Banerjee's report. It is reasonable that the CdS nanocrystallites transform from a cubic structure at the initial stage of nucleation to the stable hexagonal structure as the crystallite size increases, following Ag⁺ into the CdS matrixes with the help of ultrasound. Ag⁺ ions probably changes the free energy of the system and thus induce the fcc (face centered cubic) to hcp (hexagonal closest packed) phase transformation.

3.3. Raman investigation

To verify the Ag atomic clusters in CdS nanoparticle matrixes, the characteristic Raman spectra of CdS nanoparticles undoped and doped with different Ag concentrations were investigated. It is found that the main peaks at about 301 cm⁻¹ and 602 cm⁻¹ are obtained in Fig. 4, corresponding to 1LO and 2LO of CdS. The 1LO peak of the as-synthesized samples shows a small degree of asymmetric broadening towards the low frequency side. This can be ascribed to the contribution of the vibrational modes selected by the resonance of the exciting and the scattered light with the confined excitonic states [30]. It's easy to find out that the Ag-doped products show a gradual enhancement with increasing the Ag⁺/Cd²⁺ ratios from 1% to 5% in the initial reactants. Surprisingly, the product doping with 5% Ag⁺ shows more than 4-fold enhancement at 1LO peak compared with the pure CdS sample. And a weak 3LO peak at around 900 cm⁻¹ can be first observed the CdS nanoparticles doping with 5% Ag⁺, this peak can be observed more clearly when the Ag⁺/Cd²⁺ ratio has increased to 10% (not shown

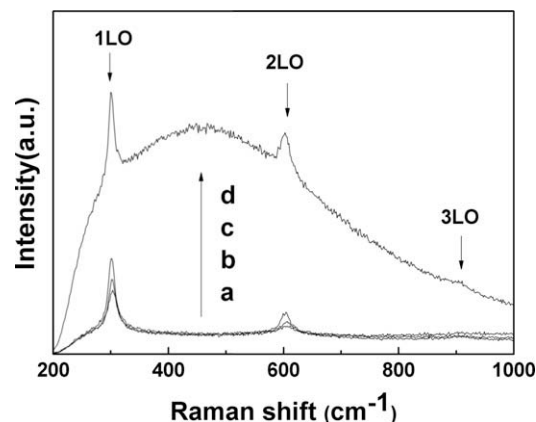


Fig. 4. Raman spectra of the as-synthesized Ag-doped CdS nanoparticles with different Ag⁺ molar ratios in the initial reactants, from bottom up: (a) pure CdS; (b) 1% Ag⁺ (0.025 mmol AgNO₃); (c) 3% Ag⁺ (0.075 mmol AgNO₃); (d) 5% Ag⁺ (0.125 mmol AgNO₃).

here). Both the theoretical and experimental studies have suggested that the enhanced signals in the characteristic Raman spectra are mainly attributed to electromagnetic excitation of localized surface plasmon of noble metals [31,32]. So, the Raman enhancement is mainly owing to the electrons transferred between CdS and Ag [17]. It's indicated that Ag has penetrated into CdS nanoparticle matrix in the form of atom clusters which agrees with the XPS patterns and the TEM figures. In addition, the background of the Raman spectra of 5% Ag-doped CdS sample should be attributed to the emission of the CdS nanoparticles [33].

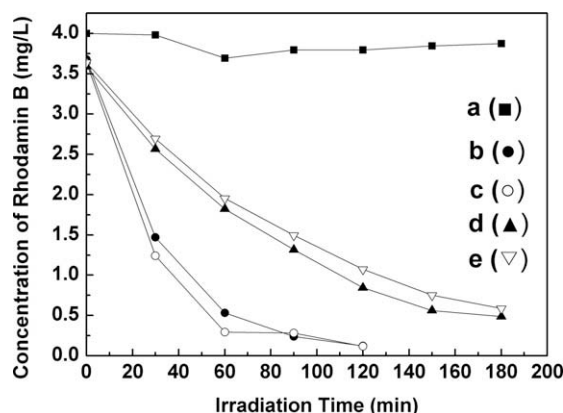


Fig. 5. Photocatalytic degradation activity for Rhodamine B obtained from the as-synthesized Ag-doped CdS nanoparticles with different Ag⁺ molar ratios in the reactants: (a) without any presence of catalysts; (b) pure CdS; (c) 1% Ag⁺ (0.025 mmol AgNO₃); (d) 3% Ag⁺ (0.075 mmol AgNO₃); and (e) 5% Ag⁺ (0.125 mmol AgNO₃).

3.4. Photocatalytic activity study of Ag-doped CdS

The photocatalytic performance of the different Ag-doped CdS nanoparticles was evaluated by photocatalytic degradation of Rhodamine B aqueous solutions. It is important that the as-synthesized samples showed an obviously photocatalytic activity for Rhodamine B degradation under the visible-light irradiation. In order to evaluate the photocatalytic activity of the as-synthesized samples, the photocatalytic experiments for the as-synthesized samples with various Ag⁺/Cd²⁺ doping ratios in the same system were carried out respectively. The concentration changes of Rhodamine B solutions versus irradiation time are shown in Fig. 5, and the fitting results of the pseudo-first order kinetics equation are listed in Table 2. No obvious change was found without presence of any catalyst (a), and this can exclude the thermal effect in the experimental progress. The results indicated the half-life time for the degradation of Rhodamine B was 23 min (sample b), 19 min (sample c), 61 min (sample d) and 68 min (sample e), respectively, which obeyed the pseudo-first order kinetics well [34]. Additionally, Fig. 5 points out that Ag-doped CdS nanoparticles (sample c with 1% Ag⁺ in the initial reactants) have exhibited nearly the same photocatalytic activity with pure CdS, but better than other doped samples. The reason has been presented as follows.

Fig. 6 shows the variation of the absorption spectra of Rhodamine B in the presence of Ag-doped CdS (with 1% Ag⁺ in the reactants) under the visible-light for various irradiation times. It is well known that Rhodamine B is stable without catalyst in visible-light region. However, Rhodamine B solution can be significantly degraded in the presence of as-synthesized CdS nanoparticles. The characteristic sharp peak at 554 nm gradually diminished and the peak shifted to lower wavelength simultaneously with time increasing. Rhodamine B was almost decomposed completely for

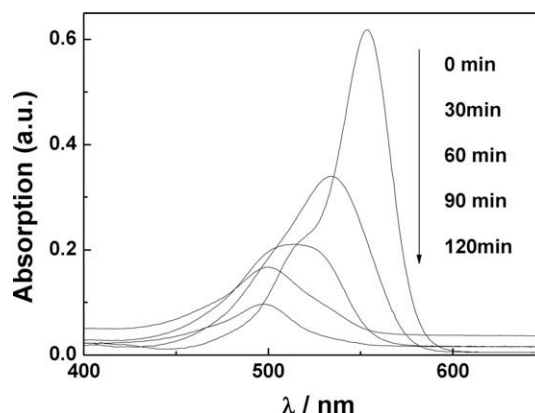


Fig. 6. Absorption spectra changes of Rhodamine B solution (4 mg/L, 150 mL) in the presence of 100 mg Ag-doped CdS nanoparticles (with 1% Ag⁺ in the reactants) under visible-light irradiation as time increasing.

about 60 min irradiation. It is ascribed the peak shift to N-de-ethylation of Rhodamine B to Rhodamine in the degradation progress, as has been confirmed by Watanabe et al. [35].

It is obviously that the CdS nanoparticles doped with 1% Ag⁺ in the initial reactants had a better photocatalytic activity than other doped samples, but nearly the same with pure CdS. The bottom of conduction band and the top of valence band (BCB and TVB) of CdS in aqueous solution is -4.0 and -6.5 eV [36]. From XRD, XPS and Raman results, the existence of metallic Ag in CdS can be ascribed to Ag atomic clusters which could be expressed as Ag_n. And the energy level of Ag atomic cluster changes from -1.3 eV ($n = 1$) to -4.64 eV of bulk phase ($n = \infty$) [37]. As Ag clusters are immersed into CdS nanoparticles, the electrons transformation schematic is displayed in Fig. 7. The photocatalytic activity can not change when the electrons could not transfer from BCB of CdS to Ag_n due to the energy level of Ag_n is much higher than BCB when the Ag doping ratios is small. As the n increasing, the energy level of Ag_n decreases gradually and starts to accept photoinduced electrons effectively from BCB when the Ag_n energy levels lie close to BCB. Photoinduced electrons would directly generate on the Ag_n energy levels when they lie lower than BCB. Simultaneously, the electrons transfer to O₂ which absorbed on CdS. The major role of the Ag atomic clusters is attributed to acceleration of O₂^{•−} formation, with effect of decreasing recombination to increase the activity of catalysis. The sample c shows a slight enhancement and nearly the same activity compared to pure CdS due to the doping ratio is not optimum to enhance the activity a lot. As n increases to a sufficient large number, when the energy level of Ag_n is lower than the energy level of O₂ which absorbed on CdS, the electron can not transfer to O₂, then the Ag_n begins to function as recombination center, therefore the photocatalytic activity of the CdS will be declined a lot such as doped CdS samples with 3% and 5% Ag⁺ in the reactants. This mechanism can be clearly implied in the following reaction equations



For small n the reaction equations are (1) and (2). When the n is sufficiently large, reaction (3) will compete with (2), and the Ag_n will become the recombination center, thus the photocatalytic activity will be declined. In this photocatalytic degradation experiment, the photocatalytic degradation activity difference between the pure CdS and Ag-doped CdS with 1% Ag⁺ in the reactants is small. This may be owing to the amounts of Ag which doped in CdS with 1%

Table 2

Photodegradation of Rhodamine B using CdS with different Ag-doped ratios as photocatalysts: (a) pure CdS; (b) 1% Ag⁺ (0.025 mmol AgNO₃); (c) 3% Ag⁺ (0.075 mmol AgNO₃); and (d) 5% Ag⁺ (0.125 mmol AgNO₃).

Sample	First-order kinetics equation ($C = C_0 e^{-kt}$)	Coefficient constant (R^2)	Half-life (min)
a	$C_t = 3.67607e^{-0.03067t}$	0.99549	23
b	$C_t = 3.63252e^{-0.036t}$	0.98549	19
c	$C_t = 3.74674e^{-0.0113t}$	0.98259	61
d	$C_t = 3.64266e^{-0.0102t}$	0.99935	68

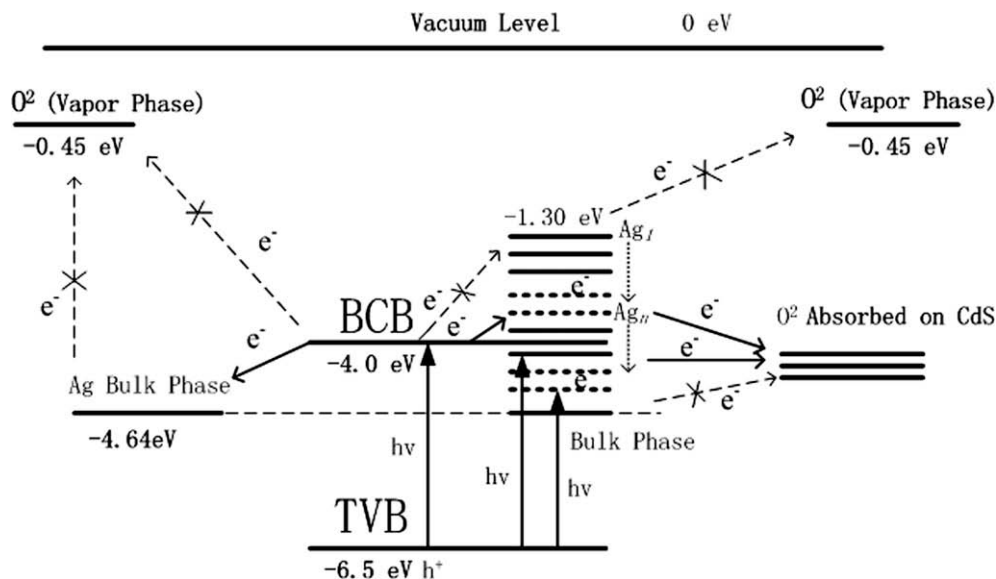


Fig. 7. Schematic diagram of the interface electron transfer of Ag-doped CdS in the photocatalytic degradation progress.

Ag^+ dopants in the reactants are not optimum for the degradation. The best Ag doping ratios for photocatalytic degradation of Rhodamine B aqueous solution has not been confirmed here and it will be studied in our further research. From the change of the photocatalytic activity of different doped samples, it is speculated that Ag clusters have doped into CdS matrix which agrees with Raman and XPS results.

4. Conclusion

In summary, Ag-doped CdS nanoparticles have been successfully synthesized by the ultrasound-assisted microwave synthesis method. Completely structural transformation from cubic to hexagonal products with increasing molar ratios of $\text{Ag}^+/\text{Cd}^{2+}$ from 0% to 5%. Simultaneously, the characteristic peaks 1LO and 2LO of CdS have been enhanced with increasing the Ag^+ concentrations and the doped Ag in CdS is metallic. The photocatalytic activity of different Ag-doped samples show a reasonable change due to different ratios of Ag have doped into CdS. These results show that the ultrasound-assisted microwave synthesis method can be applied to obtain noble metal doped semiconductor nanostructures conveniently.

Acknowledgments

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