Synthesis, structural and photocatalytic characteristics of nano-Cu$_{2-x}$Se

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Abstract
Large-scale synthesis of Cu$_{2-x}$Se nanocrystals (nano-Cu$_{2-x}$Se) with uniform size was performed via a facile hydrothermal method at room temperature and at 120 °C. Nano-Cu$_{2-x}$Se with different structures could be synthesized by changing the reaction/growth time, the Cu:Se molar ratios, and the initial concentration of the precursors. The synthesized nano-Cu$_{2-x}$Se was characterized using various techniques, including x-ray powder diffraction, scanning electron microscopy and photocatalytic activity. Systematic studies showed that the reaction time played a key role in controlling the morphology and structure leading to significant influence on the photocatalytic activity of nano-Cu$_{2-x}$Se. With increasing reaction/growth time, Cu$_{2-x}$Se could transform gradually from a cubic to hexagonal structure and from nanoparticles to nanoplate/nanorod shapes. The photocatalytic characteristics were evaluated by the photo-decoloration of Rhodamine B (RhB) in aqueous solution under visible light irradiation. As-prepared nano-Cu$_{2-x}$Se showed good photocatalytic activity under visible light irradiation, indicating potential applications in depollution technologies.

Keywords: Cu$_{2-x}$Se nanocrystals, hydrothermal synthesis, photocatalytic activity

Classification numbers: 2.03, 4.03, 5.07

1. Introduction
Solar energy can be used after transformation into heat or generating charge carriers in various semiconductors with appropriate band structures. For the latter application one can collect those charge carriers to the corresponding electrodes in a solar cell structure or use photogenerated charge carriers as direct reducer/oxidizer in photocatalytic activity [1–4]. Among various photocatalysts, TiO$_2$ has been intensively studied [5–14] because it has many advantages such as non-toxicity for the environment, the high separation rate of the photogenerated carriers contributing to redox activities, etc. However, TiO$_2$ can only absorb UV radiation, which is about 4% of sunlight, causing restriction of its practical applications [15]. To achieve higher photoconversion efficiency of a photocatalyst working under solar light, two main strategies are utilized. One is based on the chemical modification of UV-active photocatalysts to extend absorption to the longer wavelength spectral range, and the other is to directly use narrow bandgap semiconductors. The former has been mostly realized with TiO$_2$ loaded with a noble metal (Au, Ag, Pt) [5–7] or doped with a non-metal/metal (C, N, S/Fe, Cr) [8–12], or combined with narrow bandgap semiconductors (CdS, CdSe) [13, 14]. However, despite the success of this strategy in improving photocatalytic activity in the visible region, doping/loading techniques usually cause a change of stoichiometries and increase the cost of the products. For the latter approach, narrow bandgap Cu-based materials (e.g. CuO, Cu$_2$O, CuS and CuSe [15–32]) have been directly used as photocatalysts. Among the mentioned copper chalcogenides, copper selenide has attracted considerable attention because of its excellent photochemical and optical properties [17–24]. Copper selenide can exist in different stoichiometries and phases such as Cu$_3$Se, CuSe and Cu$_2$Se$_3$; therefore it is usually written as Cu$_{2-x}$Se, in which $x = 0–1$. Cu$_{2-x}$Se compounds are typically p-type semiconductors with direct bandgap energy of 2.2 eV or indirect bandgap energy of 1.4 eV, suitable for solar light sensitive photocatalytic activity [19–21]. In addition, due to their shape- and size-dependent properties, the precise controllability of Cu$_{2-x}$Se chemical composition, size, shape and surface chemistry can be considered in order to obtain...
their chemical and physical properties as desired. Much effort has been devoted recently to the synthesis of Cu$_{2-x}$Se micro- and nanocrystals with various morphologies, such as particles [21], rods [22], tubes [23] and wires [24, 25]. Nano-Cu$_{2-x}$Se has been prepared via various routes, including colloidal synthesis in hot organic surfactants, in which a solution of copper and selenium precursors was injected into the reaction solvent of tri-n-octylphosphine oxide (TOPO) or 1-octadecene (ODE) or oleylamine at a temperature of 250–300°C [21, 26, 27]; evaporation of a mixture of Cu(NO$_3$)$_2$ and alkaline selenium aequous solution at 140°C [24]; thermolysis of a copper and selenium mixed powder at 400–470°C in flowing argon [28]; mechanical alloying of Se and Cu in a high energy ball mill [29], and the reaction of Se and Cu in ethylenediamine solvent under microwave irradiation for several minutes [30]. Among the synthesis methods mentioned above, one can see that non-polar organic solvents were used as surfactants and reaction media at high temperatures usually produce nice Cu$_2$−xSe nanoparticles of high quality [21, 26, 27], while low-temperature syntheses in aqueous phase usually produce different nanospheres [20, 24, 31]. For many applications (e.g. photocatalysis and solar cells), Cu$_2$−xSe nanocrystals need to be prepared on a large scale by cost-effective means; for that purpose aqueous phase-based syntheses are shown to be promising.

In this paper, we report on the successful large-scale fabrication of high quality nano-Cu$_{2-x}$Se in water. The aqueous phase/hydrothermal method enable us to quickly produce Cu$_2$−xSe nanocrystals at room temperature with 30 nm in size. By changing the technological parameters such as the Cu:Se molar ratio, the initiation concentration of the copper precursor, surfactants, and the reaction time/temperature, we have obtained various nano-Cu$_{2-x}$Se products which are different in structure (cubic or hexagonal) and shape (particles, plates or rods) as required. Among the technological parameters used, the reaction/growth time was determined to be key in controlling the morphology and structure. Based on the experimental results, the mechanisms of structural formation of nano-Cu$_{2-x}$Se are discussed.

2. Experimental

2.1. Materials

Copper nitrate tri-hydrate (Cu(NO$_3$)$_2$·3H$_2$O) 99%, mercaptopropionic acid (MPA) 99%, sodium hydroxyl (NaOH) 99% of analytical reagent quality were purchased from Sigma-Aldrich; selenium powder (Se) 99% was purchased from Poole, England; absolute technical grade ethanol (Merck) and distilled water were used in the preparation and cleaning of samples. All chemicals and solvents were used as received without further purification.

2.2. Synthesis of nano-Cu$_{2-x}$Se

Copper selenide powders of different sizes and structures were synthesized in aqueous solution using a hydrothermal method. In a typical synthesis, 0.15 g of Se and 5.0 g of NaOH were dissolved in 20 ml of distilled water at ∼80°C to form a deep red solution (an alkaline selenium aqueous solution) after carefully stirring for 15 min. Subsequently, this solution was cooled down to room temperature and then 130 µl of MPA and 1.5 ml of 0.5 M Cu(NO$_3$)$_2$ were rapidly added. After stirring for 5 min, the reaction solution was put into an autoclave for annealing at 120°C for different lengths of time. The green black precipitate was collected by centrifugation and washed several times with hot distilled water and ethanol. The product was then dried at 60°C in air. All samples were prepared by the same method but under different experimental conditions, namely by changing the Cu:Se molar ratio, the initiation concentration of the copper precursor and surfactants and the annealing time for growing nano-Cu$_{2-x}$Se in different sizes and shapes.

2.3. Structural characterization

Powder x-ray diffraction (XRD) patterns taken from an x-ray diffractometer (Siemens D5000) using CuK$_\alpha$ (1.5406 Å) radiation at a scan rate of 0.04°/2θ s$^{-1}$ were used to identify structural phases as well as to determine the particle size using the Scherrer equation in which the full-width-at-half-maximum (FWHM) value of the diffraction peaks was corrected with the instrumental response. The morphology of the synthesized nano-Cu$_{2-x}$Se powders was studied with an S4800 field emission scanning electron microscope (FE-SEM, Hitachi, Japan) at an accelerating voltage of 5 kV. The nanocrystal size and shape were determined directly from the SEM images and compared to the values obtained from calculation using the Scherrer equation.

2.4. Measurement of photocatalytic activity

The photocatalytic activities of the prepared samples were evaluated by decolorization of the RhB aqueous solution at room temperature. Experiments were performed as follows: the prepared nano-Cu$_{2-x}$Se powders (2.0 mg) were dispersed in 1 ml of RhB aqueous solution (1 × 10$^{-5}$ M) in a quartz cell (10 × 10 × 40 mm), and then the cell was put into a supersonic bath for 5 min to homogeneously distribute the nano-Cu$_{2-x}$Se powders with RhB. Before light irradiation, the cell containing nano-Cu$_{2-x}$Se photocatalyst and RhB aqueous solution was kept in the dark for 40 min to reach an adsorption/desorption equilibrium between the photocatalyst and RhB molecules. A 150 W xenon lamp through a UV-cutoff filter (at wavelengths shorter than 420 nm), which was positioned 60 cm away from the cell to avoid additional heating effects, was used as a visible-light source for the photocatalytic reaction. The average light intensity striking on the surface of the reaction solution was ∼20 mW cm$^{-2}$. After visible light irradiation for a period of time (every 15 min), the reaction solution was measured to determine the photoluminescence (PL) intensity change of RhB in the solution by using a grating spectrometer (HR550 Horiba) equipped with a thermoelectrically cooled Si-CCD camera (Synapse). In the PL measurement, a 470-nm LED was used as the excitation source. The decoloration percentage which demonstrates the photocatalytic activity of the prepared nano-Cu$_{2-x}$Se is evaluated by PL quenching of RhB in the mixture, determined as follows:

$$\text{Percentage of the PL quenching} \,(\%) = \frac{I_0 - I}{I_0} \times 100\%,$$

(1)
demonstrates the XRD pattern of the sample obtained just after adding at room temperature the copper precursor into the reaction flask containing the alkaline selenide solution. It can be seen that all the diffraction peaks can be well indexed to the pure cubic phase of CuSe with lattice constants \( a = 9.39\text{ Å} \) and \( c = 17.25\text{ Å} \), meaning that the cubic Cu\(_{2-x}\)Se nanocrystals were completely transformed into hexagonal CuSe (curves (c) and (d) in figure 1). In addition, the obvious decrease of FWHM of the diffraction peaks with increasing growth time indicates an increase in the size of Cu\(_{2-x}\)Se nanocrystals.

From the SEM images, we see that the Cu\(_{2-x}\)Se particles prepared at room temperature for 5 min are nearly spherical nanoparticles with diameters around 30 nm (figure 2(a)). The structure of these nanoparticles was determined from the XRD patterns to be cubic. Evolution with annealing/growth time of the shape of nano-Cu\(_{2-x}\)Se obtained after annealing at 120 °C is shown in figures 2(b)–(d). For 90-min annealing/growth, the formation of CuSe nanoflakes with edge length and thickness range of 100–400 nm is clear besides spherical Cu\(_{2-x}\)Se nanoparticles with size of 20–40 nm (figure 2(b)). With increasing annealing/growth time, the CuSe plates had a tendency to stack together forming CuSe nanoflakes with diameters of 200–300 nm and lengths up to several micrometers (figures 2(c) and (d)). The XRD results are in good accordance with the SEM images; the large CuSe nanoflakes or nanorods possess a hexagonal structure and the smaller particles have a cubic structure. Large CuSe nanoflakes or nanorods could be easily deposited by centrifugation while the smaller Cu\(_{2-x}\)Se nanoparticles remained in solution that needed the addition of ethanol for precipitation before centrifugation.

The Cu:Se molar ratio as well as the \([\text{Cu}^{2+}]:[\text{Se}^{2-}]\) concentration ratio in the precursors could significantly affect the structure and constitution of the product [32]. In the present synthesis, in addition to the specific surfactant (MPA in most cases), the Cu:Se molar ratio and the \([\text{Cu}^{2+}]:[\text{Se}^{2-}]\) concentration ratio were changed in the range of 1:0.5 to 1:2.5 and 0.2 to 13, respectively. The first series of our experiments (keeping a \([\text{Cu}^{2+}]:[\text{Se}^{2-}]\) concentration ratio of 13 [24]) showed that with the low Cu:Se molar ratio (Se-rich, such as ratios of 1:2.5, 1:1.5, 1:1.2 or 1:1) the products were formed mainly in a cubic Cu\(_{2-x}\)Se structure; while with the

\[ I_0 \text{ and } I \text{ are the PL intensities of RhB aqueous solution before and after visible light irradiation, respectively. } \]

3. Results and discussion

3.1. Structural characterizations

The influence of various technological parameters, including the Cu:Se molar ratio, the reaction time/temperature, the initial concentration of the copper precursor as well as the type and amount of surfactant on the structural and photocatalytical properties of the obtained copper selenide nanocrystals have been systematically investigated. Figure 1 shows the XRD pattern of the samples prepared at different reaction temperatures and reaction times. The strong and sharp diffraction peaks indicate the good crystallinity of the samples. Curve (a) in figure 1 demonstrates the XRD pattern of the sample obtained just after adding at room temperature the copper precursor into the reaction flask containing the alkaline selenide solution. It can be seen that all the diffraction peaks can be well indexed to the pure cubic phase of Cu\(_{2-x}\)Se with lattice constant \( a = 5.739\text{ Å} \), which is in good agreement with values in the literature (JCPDF 06-0680). The average crystalline size is calculated to be 36.1 nm using the Scherrer formula, consistent with the corresponding SEM image of Cu\(_{2-x}\)Se nanoparticles (see figure 2(a) below). Curve (b) in figure 1 displays the XRD pattern of the sample obtained after growing Cu\(_{2-x}\)Se nanocrystals at 120 °C for 90 min, indicating both the cubic Cu\(_{2-x}\)Se and hexagonal CuSe phases (JCPDF 34-0171) exist. Indeed, besides the XRD peaks of the cubic Cu\(_{2-x}\)Se phase the peaks corresponding to the hexagonal CuSe phase appear more clearly, implying that a partial transformation of Cu\(_{2-x}\)Se into CuSe took place after growing Cu\(_{2-x}\)Se nanocrystals at 120 °C for 90 min. Extending the annealing/growth time to 120 min and 300 min, the XRD patterns indicate that all the peaks are exactly assigned to the pure hexagonal phase of CuSe with lattice constants

\[ a = 9.39\text{ Å} \text{ and } c = 17.25\text{ Å} \text{, meaning that the cubic Cu}_{2-x}\text{Se nanocrystals were completely transformed into hexagonal CuSe (curves (c) and (d) in figure 1). In addition, the obvious decrease of FWHM of the diffraction peaks with increasing growth time indicates an increase in the size of Cu}_{2-x}\text{Se nanocrystals.} \]
higher Cu:Se molar ratio (Cu-rich) hexagonal CuSe phases were created. This is because copper selenide can exist in different stable phases with the \( \text{Cu}_{2-x} \text{Se} \) (\( x = 0–1 \)) formula and Cu-rich synthesis makes the CuSe (Cu in the divalent state) phase favorable. In the second series of our experiments, by changing the ratio of [\( \text{Cu}^{2+} \)] : [\( \text{Se}^{2−} \)] concentrations while the Cu:Se molar ratio was kept to be constant at 1:2.5, copper selenide with different structures could be obtained through the following reactions \([32]\):

\[
\begin{align*}
3\text{Se} + 6\text{OH}^− &\rightarrow 2\text{Se}^{2−} + \text{SeO}_3^{2−} + 3\text{H}_2\text{O}, \\
(2−x)\text{Cu}^{2+} + \text{Se}^{2−} &\rightarrow \text{Cu}_{2−x}\text{Se}, \\
\text{Cu}^{2+} + \text{Se}^{2−} &\rightarrow \text{CuSe}, \\
\text{Cu}_{2−x}\text{Se} + (1−x)\text{Se} &\rightarrow (2−x)\text{CuSe}, \\
n(\text{CuSe or Cu}_{2−x}\text{Se}) &\rightarrow (\text{CuSe or Cu}_{2−x}\text{Se})_n.
\end{align*}
\]

A [\( \text{Se}^{2−} \)] concentration of 0.0375 M was kept in all cases while the [\( \text{Cu}^{2+} \)] concentration varied from 0.00625 to 0.5 M, corresponding to a [\( \text{Cu}^{2+} \)] : [\( \text{Se}^{2−} \)] concentration ratio of 0.2–13. At high [\( \text{Cu}^{2+} \)] concentration, reaction (3) could be favorable to produce \( \text{Cu}_{2−x}\text{Se} \) nanocrystals. As the [\( \text{Cu}^{2+} \)] concentration decreased, the tendency of reactions (3) and (4) would take place, leading to the formation of both cubic \( \text{Cu}_{2−x}\text{Se} \) and hexagonal CuSe crystals. Lowering the [\( \text{Cu}^{2+} \)] concentration the hexagonal CuSe nanocrystals become more and more dominant \([24]\). In addition, \( \text{Cu}_{2−x}\text{Se} \) could convert to the CuSe phase as reaction (5) by changing the ratio of chemical concentrations in precursor solutions. Freshly generated nuclei have been grown to form larger particles via reaction (6). Our results are in good agreement with the results reported in \([32]\).

Cubic \( \text{Cu}_{2−x}\text{Se} \) nanocrystals were easily synthesized at room temperature with the presence of MPA surfactant. This indicates that the cubic structure of nano-\( \text{Cu}_{2−x}\text{Se} \) is more stable than other phases at room temperature. By annealing at 120°C or changing the Cu:Se molar ratio or the precursor concentrations, \( \text{Cu}_{2−x}\text{Se} \) nanoparticles could transform gradually into CuSe nanoplates/nanorods with hexagonal structure. We have tried with other surfactant like MSA (mercapto succinic acid) but MPA helped to synthesize better nano-\( \text{Cu}_{2−x}\text{Se} \) materials.

**3.2. Photocatalytic activity**

The visible light photocatalytic activities of the samples were evaluated by measuring the decoloration of RhB in aqueous solution under visible light illumination. Figure 3 shows the degradation of the photoluminescence from the RhB aqueous solution at different intervals after visible light irradiation in the presence of typical CuSe nanoplates. The PL spectra of RhB peaking at 552 nm decreased gradually with irradiation time, proving the photocatalytic decoloration of RhB. More than 50% of the RhB was degraded after irradiation by visible light for 2 h, as shown in the inset of figure 3. In other appearances, the initial orange–red color of RhB aqueous solution was almost bleached, which indicated the chromophoric structure of the dye was destroyed. Under visible light illumination of RhB
aqueous solution without CuSe nanoplates the PL intensity of RhB did not decrease clearly (the inset in figure 3). These results suggest the degradation of RhB aqueous solution caused by photocatalytic reaction on the CuSe surface under visible light irradiation. The high photodegradation efficiency of CuSe nanocrystals can be explained from two facts. One is the visible light absorption of CuSe nanocrystals, from which the electrons and holes are generated and moved to the surface of CuSe nanoplates to participate in the photocatalytic decomposition reaction of RhB in particular and contaminants in general [15]. The other is that the water-soluble CuSe nanocrystals enable efficient contact between CuSe photocatalyst and RhB, thus improving the photodegradation activity of the CuSe photocatalyst. After four recycles for the photodegradation of RhB, the CuSe nanocrystals displayed only a very slight loss of photocatalytic activity as shown in figure 4, indicating that CuSe nanocrystals/nanoplates could be used as good photocatalytic materials.

4. Conclusion

We demonstrated a facile hydrothermal route to synthesize on a large-scale Cu$_{2-x}$Se nanocrystals with different structures and shapes by changing the reaction temperature/time, the Cu:Se molar ratios, and the initial concentration of the precursors. The reaction/growth time exhibits significant influence on the morphology and structures of nano-Cu$_{2-x}$Se. With increasing reaction/growth time, nano-Cu$_{2-x}$Se transforms gradually from a cubic to hexagonal structure and from nanoparticles to nanoplate/nanorod shapes. The prepared Cu$_{2-x}$Se nanocrystals show clear/efficient photocatalytic activity towards the photocatalytic decoloration of RhB aqueous solution under visible light. Our work on the shelling of nano-Cu$_{2-x}$Se with a large bandgap semiconductor like ZnS to resist photocorrosion is under progress. We strongly believe that nano-Cu$_{2-x}$Se and nano-Cu$_{2-x}$Se core/ZnS shell could be used efficiently in depollution technologies and in hybrid solar cells as well.

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