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The study of morphology-controlled synthesis and the optical properties of CuSe nanoplates based on the hydrothermal method

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ABSTRACT

In this study, CuSe nanoplates have been synthesized using copper sulfate and Se powder as the raw materials by a simple and rapid hydrothermal process. The edta disodium (EDTA) was used as the surface active agent to moderate the morphologies of CuSe nanoparticles. As-synthesized CuSe samples were successfully characterized by X-ray diffraction (XRD), X-ray energy dispersive spectroscope (EDS), scanning electron microscopy (SEM) and Raman spectrometer, UV–visible (UV–vis) spectroscopy and photoluminescence (PL). XRD analysis demonstrated the hexagonal klockmannite phase of CuSe nanoplates. The as-synthesized products were homogeneous and highly crystallized. The structural and compositional analysis revealed that the products were the pure phase of CuSe with corresponding atomic ratios. With sufficient reaction materials, the reaction time has an influence on the growth of large-scale CuSe nanoplates. CuSe nanoplates obtained by the described method could be a potential material in photoelectric device.

1. Introduction

Apart from zero-dimensional [1] (0D) and one-dimensional [2] (1D) nanomaterials, two-dimensional (2D) nanomaterials (nanosheets or nanoplates) are also important nanomaterial which obtained creative ideas from grapheme [3–5]. The two-dimensional nanomaterial, as a planar crystal structure, is constitutive of atomic monolayer or multilayer. The thickness of the monolayer [6] nanomaterials is an atomic diameter, such as graphene [7] and boron nitride. Graphene has many benefits chemical and physical specific properties, such as high specific ratio surface area [8], ultra-high electron mobility [9], good thermal conductivity [10] and high optical transmission rate [11]. Multilayer [12] nanomaterials have more than three atomic thickness, and mainly include the transition metal disulfide compounds, such as molybdenum disulfide [13] and tungsten disulfide [14]. The two-dimensional semiconductor nanomaterials have the characteristics introduced above, making it possess special properties in electronic [14], optical [15] and catalytic field [16]. At the same time, two-dimensional nanomaterials are easy to be integrated on their surface, because of the simple structure [17].

Because of large exciton Bohr radius of selenide nanomaterials [18,19], selenide nanomaterials have showed a strong quantum confined effect [20,21]. Therefore, a series of new features have been developed in photoelectric [22] and mechanical fields [23,24]. Copper selenide is a p-type semiconductor with broadband gap (1.2–2.3 eV) [25,26], which is very close to optimal values in solar energy utilization [27,28]. The copper selenide crystals have many different structures, which makes the copper selenide nanomaterials become the focus of scientific research [29–31].

Copper selenide appears in different composition, such as, CuSe [32], Cu_7Se_4 [33], Cu_5Se_4 [34], Cu_3Se_2 [35], Cu_3Se [36] and $Cu_{2-x}Se$ [37], as well as exists different crystal structures (monoclinic [38], hexagonal [39], tetragonal [40], cubic [41]). Meanwhile single phase synthesis of copper selenide needs harsh environmental conditions. The suitable conditions demand to do more experiments to keep exploring. Especially, researchers were attracted by the different properties of copper selenide relying on different stoichiometric forms [40]. Due to their different structures and valence states, some unique electrical properties, thermal stability and optical properties are highlighted [40]. Many studies have been developed by a variety of methods such as solvothermal method [42], electrochemical technology [43], colloidal synthesis [44], microwave-assisted nonaqueous approach [45], solution phase reaction [46], chemical bath deposition [47] and pulsed laser deposition [48]. The existing nanostructure of copper selenide includes

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nanorods [49], nanoplates [50], nanowire [43] and nanotube [51]. Zhang et al. [37] reported by adjusting the reaction parameters, especially the effective Cu/Se ratio of the reactants, the controlled synthesis of copper selenide with hexagonal nanoplates/nanowires or only hexagonal nanoplates through a green paraffin-acetate method. Li et al. [32] reported two different phases and morphology of copper – selenized films were prepared by a microwave assisted nonaqueous method using alcohol as the solvent. Liu et al. [52] reported through a microwave-assisted polyol method with careful phase control, the two-dimensional (2D) Cu_2Se nanoplates with large-scale assemblies were synthesized. Gu et al. [53] reported a concentrated alkaline hydrothermal method to synthesize hexagonal CuSe nanoflakes with a lateral size of 200–800 nm and a thickness of 15–40 nm. Ni et al. [54] reported a concentrated alkaline hydrothermal method to synthesize hexagonal $CuSe_{1-x}S_x$ with 200–600 nm edge in length and 15–20 nm thick. Zhang et al. [55] reported a selenium alkaline aqueous solution to synthesize sheet-like nanocrystalline SnSe with an orthorhombic phase. These advances have inspired us to research the new features and potential applications of two-dimensional copper selenide nanomaterials.

In this paper, a large amount of copper selenide nanoplates with large areas were successfully synthesized via the hydrothermal method. We investigated the influence of different concentration of EDTA on the nanostructure of copper selenide. When EDTA concentration was 0.01 mol/L, growing levels of material and texture was observed obviously, and hexagonal CuSe nanoplates with a uniform appearance was accomplished. In sufficient reactants, the large areas of CuSe nanoplates can be synthesized by prolonged reaction time. The CuSe nanoplates are a kind of potential materials on application of solar energy technology and all kinds of integrated processing on the surface.

2. Experimental

2.1. Materials and reagent

In the absence of further purification, all experimental reagents with analytical purity were bought and used. Se (Selenium powder, ≥ 99.7%, Sinopharm Chemical Reagent Ltd., China), $CuSO_4{\cdot}5H_2O$ (copper sulfate pentahydrate, ≥ 99.0%, Sinopharm Chemical Reagent Ltd., China), NaOH (sodium hydroxide, ≥ 97.0%, Pinghu Chemical Reagent Ltd., China), EDTA (ethylene diamine tetraacetic acid disodium, ≥ 99.0%, Sinopharm Chemical Reagent Ltd., China), C_2H_5OH (anhydrous ethanol, ≥ 99.7%, Beijing Chemical Reagent Ltd., China). In the reactions, the solvent of all the solutions was made from deionized water.

2.2. Synthetic procedures

CuSe nanoplates were prepared using the hydrothermal process. Firstly, 0.01 mol selenium powder and 10 ml 13 M NaOH were mixed in 50 ml beaker, and stirred for 30 min until selenium powder was completely dissolved. 10 ml 0.01 mol/L $CuSO_4$ was mixed with 10 ml 0.01 mol/L EDTA and stirred for 30 min. Then, selenium solution was added and stirred evenly. Finally, the NaOH solution was added in the reaction mixture until the pH of the mixture to 12. The reaction mixture was stirred at room temperature for 30 min, Afterwards, the mixture solution was put into Teflon-lined stainless steel autoclave and hydrothermally processed at 160 °C for 12 h. When the reaction mixture was cooled to room temperature, the sediment was centrifuged at 2000 rpm for 15 min and washed several times with absolute ethyl alcohol in sequence. Then the final samples were dried at 60 °C for 6 h in vacuum. Different morphologies of CuSe samples were fabricated by adjusting the amount of EDTA in the solution. The experimental conditions are shown in Table 1. Finally, hexagonal CuSe nanoplates with high quality were produced.

Table 1
A brief summary of the experiments synthesized at 160 °C.

Sample	$CuSO_4{\cdot}5H_2O$ (M)	Selenium powder (mol)	EDTA (M)	NaOH (M)	Time (h)
1	0.01	0.01	0.005	13	12
2	0.01	0.01	0.0075	13	12
3	0.01	0.01	0.01	13	12
4	0.01	0.01	0.0125	13	12
5	0.01	0.01	0.01	13	15
6	0.01	0.01	0.01	13	18

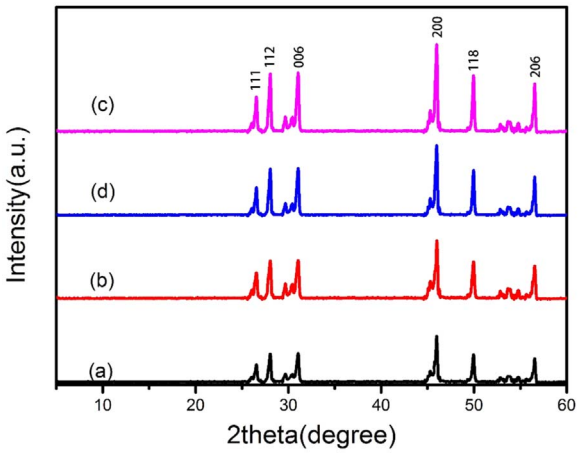

Fig. 1. The X-ray diffraction pattern of CuSe nanoplates synthesized with different EDTA: (a) 0.005 mol/L, (b) 0.0075 mol/L, (c) 0.01 mol/L, (d) 0.0125 mol/L.

3. Result and discussion

3.1. XRD analysis

The crystalline phase was characterized using an X-ray Diffraction with Cu Kα radiation scanning range was from 20° to 60°. The X-ray Diffraction patterns of the as-prepared CuSe nanoplates with different concentration of EDTA were shown in Fig. 1. All samples have six peaks at the 2θ values of 26.4°, 27.8°, 31.1°, 45.9°, 49.9° and 56.5° corresponding to the (1 1 1), (1 1 2), (0 0 6), (2 0 0), (1 1 8) and (2 0 6). All diffraction peaks of as-prepared CuSe nanoplates are indexed to the hexagonal klockmannite phase of CuSe with the lattice constants α = 1.5406 Å, which are fits well with the reported JCPDS card No. 27-0184. Diffraction peaks of other impurities are not found in the XRD pattern, indicating that the samples are pure phase CuSe. All the XRD patterns are similar, as shown in Fig. 1(a)–(d). Compared to the other three curves, the (2 0 0) diffraction peak of the (c) curve is the highest. The narrowing of the diffraction peaks and the increase of the diffraction intensity, indicate the rapid growth of CuSe nanoplates from smaller aggregates.

3.2. Component analysis

The chemical composition of CuSe nanoplates were characterized by using an X-ray energy dispersive spectroscope (EDS). The measurements of EDS supply more accurate information for evaluating the purity and composition of CuSe nanoplates. As shown in Fig. 2, all peaks are related to the Cu and Se elements of the CuSe nanoplates. The peaks of other impurities are not observed in the EDS pattern of CuSe nanoplates, demonstrating the pure phase CuSe nanomaterials have been formed. The respective weight percentage is shown in Table 2. The estimation of the results in the EDS spectra of sample 3 shows that the Cu/Se molar ratio of as-synthesized CuSe nanoplates is about 1:1. The EDS results correspond to the XRD results, indicating that the samples