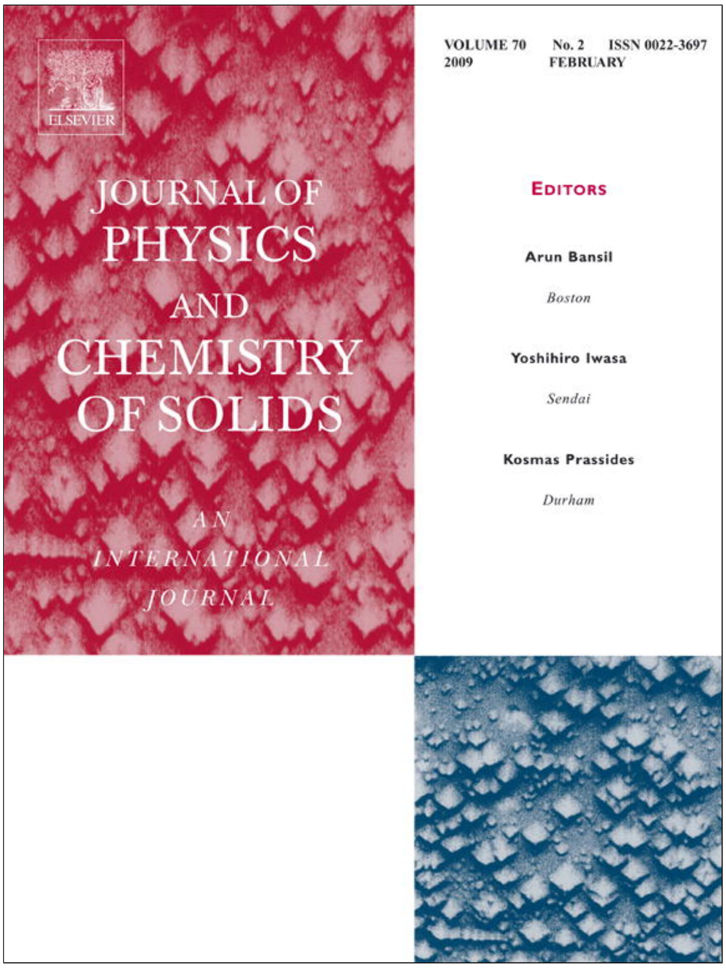

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Self-assembly of CuS nanoflakes into flower-like microspheres: Synthesis and characterization

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ABSTRACT

Using $Cu(S_2CNEt_2)_2$ as a single-source precursor and ethylamine solution (65–70%) as the reaction medium, large-scale flower-like CuS microspheres have been synthesized via a solvothermal treatment in the presence of a surfactant. The products were characterized by XRD, SEM, TEM, HRTEM, and UV-vis spectrum. The assembled microspheres, with a diameter of about 2–3 μm, were composed of single-crystalline hexagonal CuS nanoflakes with a thickness of several tens of nanometers. It was revealed that the solvent medium, the surfactant, and the reaction time have great influence on the morphology and size of the resulting CuS products.

1. Introduction

In recent years, the assembly of nano-scale building blocks into hierarchical and complex nano- and micro-structures has become the focus of a large number of studies [1–4], because it helps in a deeper understanding of the "oriented-attachment" mechanism [5,6], offers opportunities in searching for exciting new properties of materials, is useful for fabricating functional micro- and nano-devices, etc. [7,8]. In addition to one-dimensional (1D) or two-dimensional (2D) assembled structures [1–3,9], uniform spherical assembled structures, with diameters ranging from nano- to micro-scale sizes, are of great interest due to their potential applications in catalysts, drug-carriers, etc. [10–12]. As an important p-type semiconductor, copper sulfide (CuS) has wide applications in thermoelectric cooling material, optical recording material, optical filter, solar cell, and so on [13–15]. In the past decade, much work has been devoted to the preparation of CuS nanocrystals with different morphologies, such as nano-scale hollow spheres [16], wires [17], rods [18], tubes [19], and platelets [20]. However, the investigation on assembly of nano-scale CuS building blocks into a meso-scale superstructure is quite rare. Recently, we have been interested in the preparation of nanocrystals using a single-source molecular precursor (an individual reactant molecule containing all the elements required in the final product) route [21], because it not only offers the potential advantages of mildness, safety, and simplified fabrication procedure but also makes it easier to control the reaction process when compared with the use of multiple sources requiring exact control over stoichiometry. In this paper, we report on the simple and efficient single-source method for the large-scale synthesis of flower-like CuS microspheres composed of CuS nanoflakes via the solvothermal treatment of a single-source precursor of $Cu(S_2CNEt_2)_2$, and the influence of the solvent, surfactant, and reaction time on the formation of CuS nanocrystals is discussed.

2. Experimental

2.1. Preparations

All chemicals and solvents were reagent grade and were used without further purification. The ethylamine used in the experiment was 65–70% ethylamine solution.

2.1.1. $Cu(S_2CNEt_2)_2$

About 1.35 g (0.01 mol) $CuCl_2$ and 4.5 g (0.02 mol) $(C_2H_5)_2NCS_2Na \cdot 3H_2O$ were dissolved in water and methanol, respectively. The two solutions were mixed under vigorous stirring, and the resulting dark brown precipitation was filtrated, washed with water and methanol, respectively, and dried in air. The precipitation was recrystallized in ethanol and a black crystalline product was obtained. The melting point of the product is 204.5–205 °C. Elemental analysis (%): found: C 33.35, H 5.61, N 7.78, S 35.62. Calc. for $[Cu(S_2CNEt_2)_2]$: C 33.37, H 5.57, N 7.77, S 36.07. Infrared

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(IR) spectrum, $\nu_{\max}$ (cm^{-1}): 1508 [ν (C–N)], 1274 [ν (C–C)], 996 [ν (C–S)], and 481 [ν (Cu–S)].

2.1.2. CuS microspheres

In a typical experiment, 0.15 g of the single-source molecular precursor $Cu(S_2CNEt_2)_2$ and 0.1 g of a surfactant [polyvinylpyrrolidone (PVP), cetyltrimethyl ammonium bromide (CTAB), polyethylene glycol (PEG), or polyvinyl alcohol (PVA)] were first transferred into a Teflon-lined autoclave of 25 ml capacity, and then 20 ml of a solvent (65–70% ethylamine solution, H_2O or ethylenediamine) was added with vigorous stirring. The autoclave was sealed and maintained at 150 °C in an oven for some time (11–21 h). After the autoclave was allowed to cool to room temperature naturally, the resulting mixture was centrifuged, and the product was thoroughly washed with water and ethanol three times each, and dried in air.

2.2. Instrumentation

The thermoanalysis of the precursor $Cu(S_2CNEt_2)_2$ was measured by a NETZSCH STA449C differential scanning calorimeter. The IR spectrum was recorded on a Nicolet FT- ATAVAR360 spectrometer with KBr pellets in the 4000–400 cm^{-1} region. Elemental analyses were performed by an EA1112 elemental analyzer. The products were characterized by a D/MAX2500 X-ray diffractometer (XRD) with Cu Kα radiation. The morphology and the micro-structure of the products were examined by scanning electron microscopy (SEM, JSM-6480) and transmission electron microscopy (TEM, JEM-200CX and Tecnai 20). Samples for TEM were prepared by dropping the products on a carbon-coated copper grid after ultrasonic dispersion in absolute ethanol. The

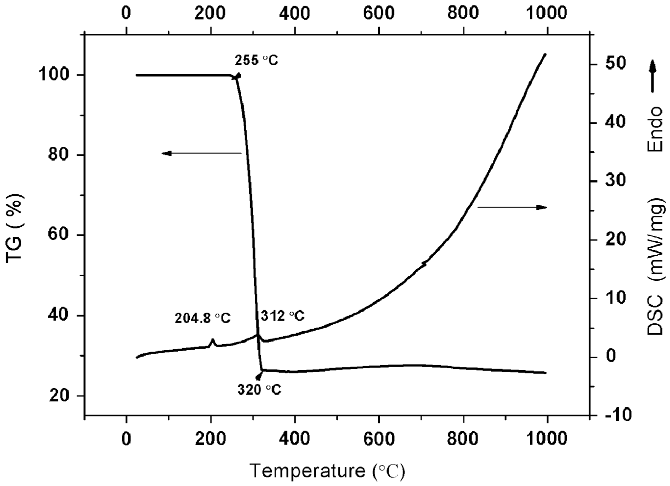

Fig. 1. TG-DSC curve of $Cu(S_2CNEt_2)_2$.

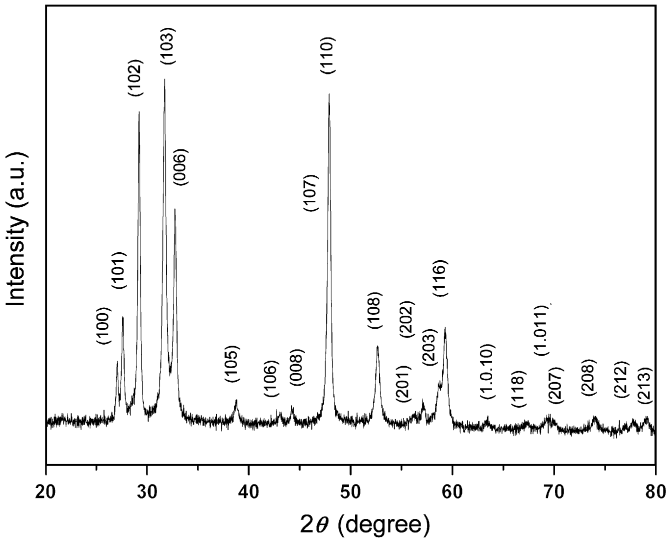

Fig. 2. XRD pattern of the CuS microspheres synthesized in ethylamine for 21 h using PVP as a surfactant.

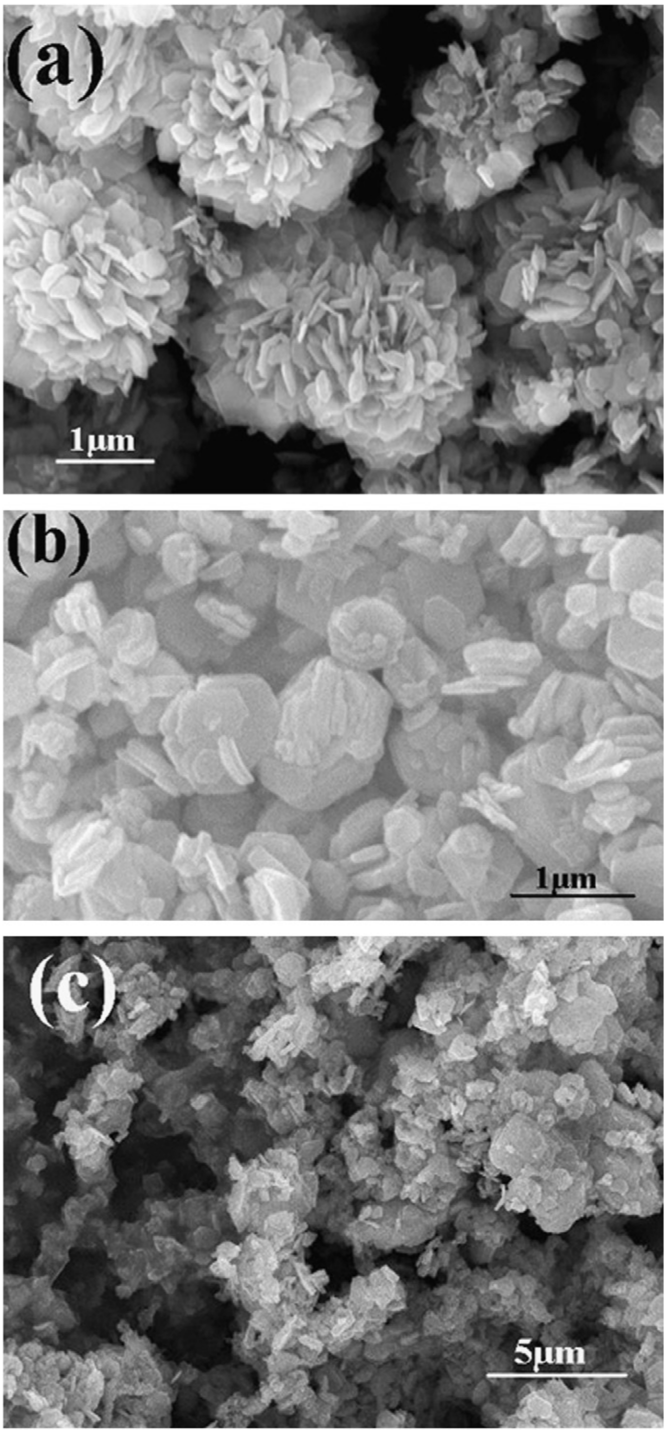

Fig. 3. SEM images of the products synthesized at 150 °C for 21 h with polyvinylpyrrolidone (PVP) as a surfactant in different reaction media: (a) ethylamine; (b) H_2O; and (c) ethylenediamine.

absorption spectrum of the sample dispersed in distilled water by ultrasonic treatment was investigated on a UV-2300 ultraviolet–visible spectrophotometer.

3. Results and discussion

3.1. Thermoanalysis of $Cu(S_2CNEt_2)_2$

Thermoanalysis was performed in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Fig. 1 shows the TG-DSC curve of $Cu(S_2CNEt_2)_2$. The complex shows a one-step weight loss between 255 and 320 °C, resulting from the thermal decomposition of the complex. The weight of the leftover at 320 °C is 26.4%, which is consistent with that of the expected CuS product (26.6%). The DSC curve shows two endothermal peaks at 204.8 and 312 °C, corresponding to the melting and thermal decomposition of the complex, respectively.

3.2. The characterization of the flower-like CuS microspheres

A systematic investigation on the synthesis of CuS nanocrystals has been made by changing the solvent, the surfactant, and the reaction time as mentioned in the experimental section. The X-ray diffraction indicates that all the products synthesized under these conditions are hexagonal-phase CuS. Fig. 2 shows a typical XRD pattern of the CuS product synthesized using ethylamine solution (65–70%) as the reaction medium and PVP as a surfactant. All diffraction peaks can be indexed to the hexagonal CuS (JCPDS 6-0464) with lattice constants $a = 3.792$ Å and $c = 16.34$ Å, and no

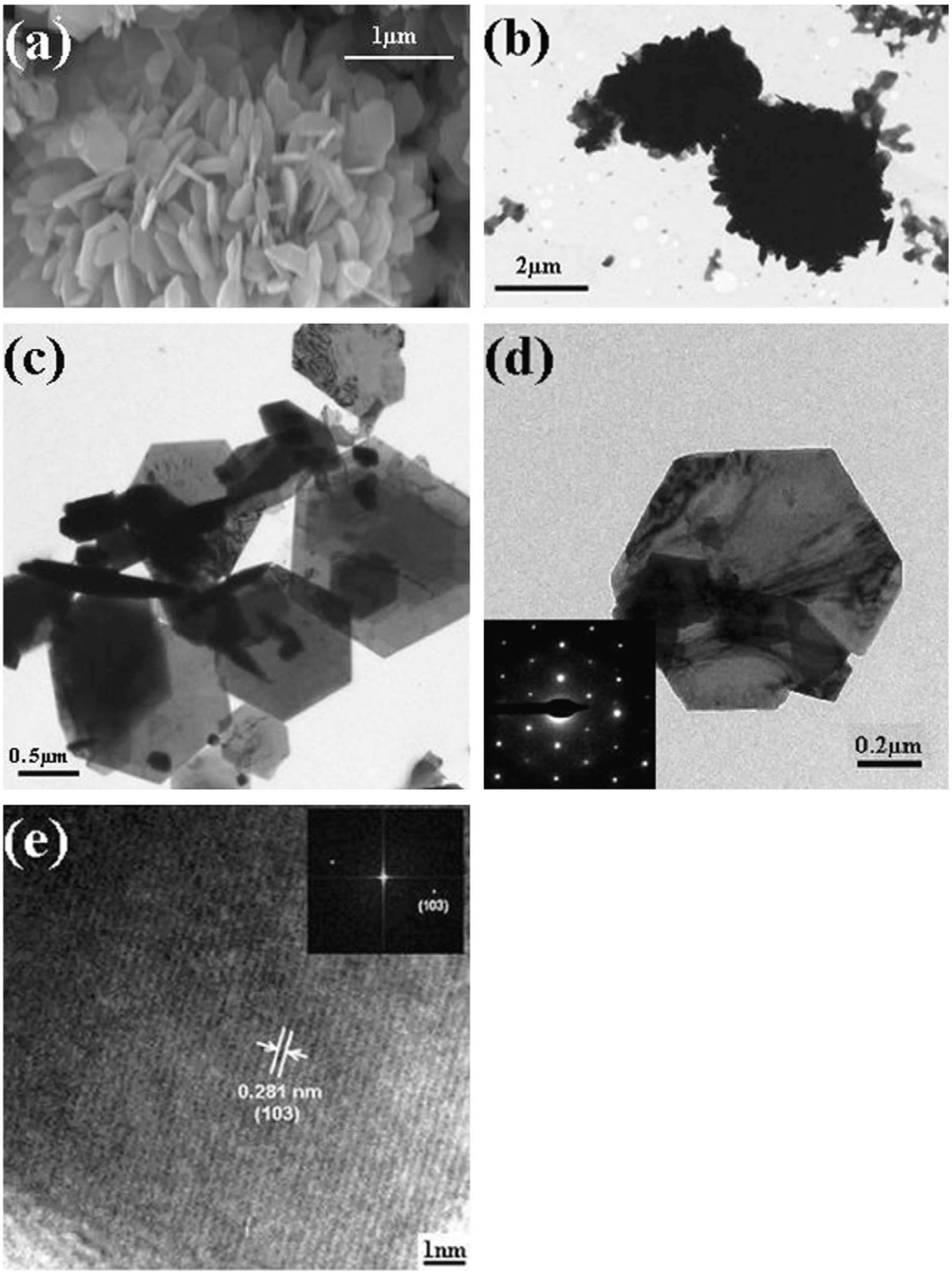

Fig. 4. SEM/TEM images of the flower-like CuS microspheres synthesized in ethylamine: (a) magnified SEM image; (b) TEM image; (c) and (d) TEM images of the nanoflakes composing CuS microspheres, the inset in (d) is the SAED pattern and (e) HRTEM image of a CuS nanoflake, the inset is a two-dimensional fast Fourier transform of the HRTEM image.

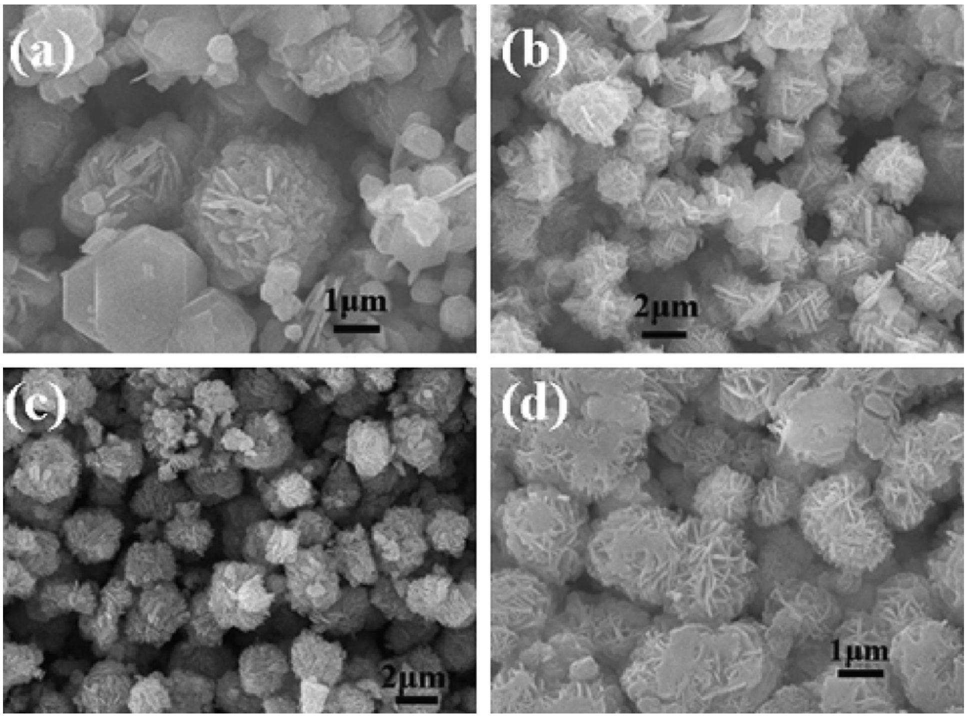

Fig. 5. SEM images of the products synthesized in ethylamine for 21 h with different surfactants: (a) without surfactant; (b) PVA; (c) CTAB; and (d) PEG.

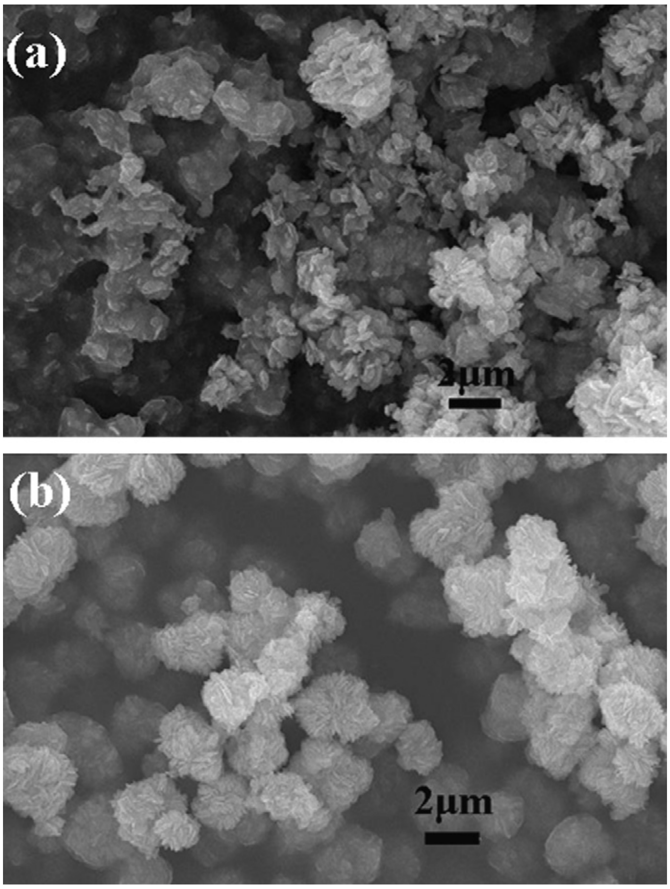

Fig. 6. SEM images of the products synthesized in ethylamine using CTAB as a surfactant with reaction time: (a) 11 h and (b) 15 h.

diffraction peaks arising from any impurities can be detected. This suggests that the precursor can be decomposed into CuS at 150 °C under a solvothermal condition. This temperature is much lower than its thermal decomposition temperature (312 °C) as shown above, probably due to the special solvothermal reaction condition such as high reaction pressure and elevated diffusion rates of the solvent and the precursor molecules, in which the precursor molecules can be decomposed more easily by the attack of the solvent molecules.

Fig. 3 shows the morphologies of the products synthesized in a different reaction medium at 150 °C for 21 h with PVP as a surfactant. It can be seen that with ethylamine as the reaction medium, CuS microspheres with a diameter of about 2–3 μm, which are composed of many nanoflakes, were obtained (Fig. 3a). With water as the solvent, CuS hexagonal flakes with a thickness of about 200 nm were synthesized, some of which congregated to form aggregates with different shapes and sizes (Fig. 3b). With ethylenediamine as the medium, CuS particles with irregular shapes and different sizes were obtained, some of which showed flake-like shape (Fig. 3c). Therefore, it can be concluded that reaction medium has great influence on the morphology and size of the CuS products, and ethylamine solution seems to be crucial for the formation of the flower-like CuS microsphere. As shown in Figs. 3a and b, the CuS flakes synthesized in ethylamine solution are not only thinner than those obtained in water but also can assemble into flower-like microspheres more easily, which suggests that the interaction between a metal ion and an organic amine molecule perhaps plays an important role in the size and morphological control of the products [22]. However, as shown above, when using ethylenediamine instead of ethylamine as the solvent, the flower-like microspheres cannot be obtained. This suggests that a suitable interaction between copper ions and organic amines is needed to form the CuS microsphere. Different from mono-dentate ethylamine, ethylenediamine is a bidentate ligand and can form a more stable chelate complex with copper ions. It was reported that the assembly functions of different organic amines are related to their coordination abilities and molecular structures [23]. In the present case, the coordination abilities of these three solvents to copper ions are ethylenediamine > ethylamine > water. Therefore, it would be possible to control the size and morphology of nanomaterials by selecting

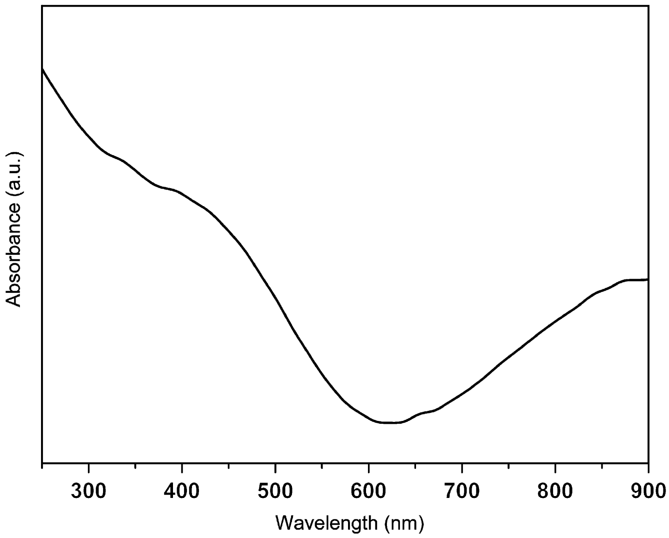

Fig. 7. UV–vis absorption spectrum of CuS microspheres synthesized in ethylamine solution for 21 h using PVP as a surfactant.

reaction solvents with suitable coordination abilities and molecular structures.

The morphology and structure of the flower-like CuS microspheres synthesized in ethylamine have been characterized in further detail using SEM, TEM, and high-resolution (HR) TEM. Fig. 4a shows the magnified SEM image of CuS microspheres. It can clearly be seen that the nanoflakes composing the CuS microspheres have a thickness of about 20–30 nm. Fig. 4b shows a typical TEM image of the CuS microspheres; it can be seen that the microspheres have solid structures with a diameter of 2–3 μm, consistent with the size observed by SEM. Fig. 4c and d are the TEM images of the nanoflakes. The flakes have a hexagonal shape with an edge length of 400–800 nm. The selected-area electron diffraction (SAED) pattern (inset in Fig. 4d) taken from an individual nanoflake shows regular diffraction spots, suggesting the single-crystalline structure of the CuS nanoflakes, which is further confirmed by the HRTEM analysis. As shown in Fig. 4e, the clear lattice fringes of the nanoflakes, with a *d*-spacing of 0.281 nm, are consistent with that of the (103) plane of hexagonal CuS. The inset in Fig. 4e is a two-dimensional fast Fourier transform (FFT) of the HRTEM image, the spots correspond to the (103) lattice plane of the hexagonal CuS.

Fig. 5 shows the effect of the surfactant on the morphology of the products synthesized in ethylamine at 150 °C for 21 h. It can be seen that when used without a surfactant, the CuS microspheres could partly transform into blocks due to the hard aggregation of the CuS flakes (Fig. 5a). When using PVA, CTAB, and PEG as a surfactant, all the products have good flower-like microspheres composed of CuS nanoflakes, and the diameter of the microspheres is about 2–3 μm (Fig. 5b–d). Thus, the surfactant, regardless of its kind, plays an important role in the formation of the flower-like microspheres because it can effectively prevent the flakes from hard aggregation. In addition, the flake-like crystals can self-assemble into steady flower-like microspheres due to minimizing the interfacial free energy by reducing the surface areas [24].

The effect of reaction time on the morphology of the products was also investigated. Fig. 6 shows the SEM images of the products synthesized in ethylamine using CTAB as a surfactant with a different reaction time. It can be seen that the formation of the flower-like CuS microspheres needs a long reaction time (more than 11 h). But the morphology of the flower-like microspheres does not obviously change when the reaction time is prolonged from 15 h (Fig. 6b) to 21 h (Fig. 5c)

As discussed above, the solvent, the surfactant, and the reaction time all have an important influence on the formation of the flower-like CuS microspheres. It is well known that hexagonal covellite CuS consists of alternating layers with compositions of CuS and Cu_2S_2. Between the layers there exists so weak van der Waals force that the crystals can easily cleave and obtain the smooth surfaces [25]. Hence the growth habit of CuS is propitious to the formation of flake-like crystals, which is consistent with the result observed in the experiment. The ethylamine solution can promote the growth of flake-like crystals, and also promote self-assembly of flake-like crystals into steady flower-like CuS microspheres. Simultaneously, the surfactant plays an important role in preventing the hard aggregation of flake-like crystals. Furthermore, only if the reaction time is long enough, flake-like crystals can self-assemble into microspheres.

Fig. 7 shows the UV-vis spectrum of CuS microspheres. It can be seen that the absorption edge is about 610 nm, which is consistent with that of CuS nanoflakes with a thickness of 20 nm [26], indicating that the CuS microspheres were dispersed into nanoflakes after ultrasonic treatment. The sample shows an increased absorption band in the near-IR region, which is a characteristic of covellite (CuS) [26–28].

4. Conclusions

In summary, this paper presents a simple single-source solvothermal route to synthesize flower-like CuS microspheres using $Cu(S_2CNEt_2)_2$ as a single-source precursor and ethylamine solution as the reaction medium. The microspheres with a diameter of about 2–3 μm are composed of hexagonal CuS single-crystalline nanoflakes with a thickness of several tens of nanometers. The effect of the solvent medium, the surfactant, and the reaction time on the formation of the flower-like CuS microspheres has been investigated systematically. This spherical superstructure self-assembled by nanoflakes can be expected to have potential applications in adsorption, catalysis, and micro- and nano-devices.

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