

Controlled synthesis of hierarchical CuS architectures by a recrystallization growth process in a microemulsion system

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Abstract Nano- and micro-sized hierarchical copper monosulfide (CuS) architectures composed of nanoplates have been successfully synthesized via a recrystallization growth process in a microemulsion system. In our method, the spatial separation of two reactants and low-reaction temperature can decrease the rate of growth of the CuS nuclei, resulting in the formation of the poorly crystallized CuS aggregates in an oil-in-water (o/w) microemulsion. The hierarchical CuS nanostructures are formed easily from poorly crystallized CuS by a recrystallization growth process at a higher temperature. Furthermore, the flower-like CuS architectures can be obtained by a kinetically controlled dissolution–recrystallization mechanism. In addition, the photocatalytic activity of the hierarchical CuS architectures has been evaluated by the degradation of methylene blue solution in the presence of hydrogen peroxide under natural light, showing that the as-prepared hierarchical CuS architectures exhibit high-photocatalytic activity for the degradation of methylene blue.

Introduction

Hierarchical architectures with nano- and micro-sizes are of interest to chemists and materials scientists due to their attractive chemical and physical properties [1–3]. Various

hierarchical architecture materials such as metal [4], metal oxide [5, 6], sulfide [7, 8], hydrate [9], and other inorganic materials [10, 11] have been successfully synthesized. A solution phase chemical method was one of the most important routes to prepare hierarchical structures because of its low cost and potential advantage for large-scale production [12–14]. However, it is still a great challenge for controlled synthesis of hierarchical architectures via the solution phase chemical methods because the control of nucleation and growth process of nanomaterials is difficult [15]. Among the solution phase chemical methods, two-phase method is a facile and effective solution phase method to synthesize hierarchical structures [16, 17]. Furthermore, the two-phase method experiences a much longer and relatively slow nucleation and growth process [18]. Therefore, it may be a feasible approach for the controlled synthesis of hierarchical nanoarchitectures by the control of growth process of nanomaterials.

Copper monosulfide (CuS) as an important p-type semiconductor has been the focus of intense interest due to not only its excellent electrical, optical properties but also its potential applications in optical recording material [19], sensors [20], solar cell [21], catalysts [22] and so on. Up to now, a variety of CuS nanostructures such as nanoparticles [23], nanorods [24], nanowires [25, 26], hollow spheres [27], and hierarchical structures [28, 29] have been fabricated. Recently, many efforts have been devoted to the synthesis of CuS hierarchical architectures. For example, Li et al. [30] have successfully prepared CuS nanomaterials with hierarchical structures by a solvothermal method in ethylene glycol. Yu's [31] group reported the synthesis of well-defined concaved cuboctahedrons of copper sulfide crystals in ethylene glycol solution system. Shen et al. [32] have synthesized flowerlike CuS microspheres by a single-source solvothermal route. Yan et al. [16] have synthesized

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CuS intersectional nanoplates via a micro-interface reaction method. Cheng et al. [17] have fabricated flowerlike CuS nanoarchitectures through a hydrothermal method. Although various CuS hierarchical architectures have been synthesized in different solution systems, there are very few studies on the control of growth process of hierarchical CuS architectures through a recrystallization growth process.

In previous works, we presented an interface reaction route in a microemulsion system for the preparation of CuS hollow spheres composed of nanoparticles [33, 34]. In this approach, the formation of stable hollow spheres must use oil/water interface as the template at higher reaction temperature. In this study, nanoplate-based hierarchical CuS architectures have been successfully fabricated via a recrystallization growth process of the poorly crystallized CuS aggregates prepared at a low temperature. The growth process of hierarchical CuS architectures can be controlled through the ripening time of the recrystallization growth process. Furthermore, this method presents a way in the synthesis of hierarchical architectures by a recrystallization growth process in a two-phase system.

Experimental methods

Materials

Dimethylbenzene, thioacetamide (TAA), *n*-butanol, and sodium dodecyl sulfate (SDS) were of analytical purity; copper naphthenate was an industrial grade reagent. All the materials were used without further purification. Deionized water was used in the experiments.

Preparation

In a typical synthesis, 1 g SDS and 3.5 ml *n*-butanol were added to 12 ml of deionized water and stirred for several minutes at room temperature (15 °C). 0.16 g of copper naphthenate dissolved in 1 ml dimethylbenzene was employed as the oil phase. The 1-ml oil phase was added to the above aqueous solution with stirring. Then a blue and transparent microemulsion could be obtained. 0.03 g TAA (the molar ratio of Cu:S \approx 1:2) dissolved in 2 ml deionized water was dropped into the microemulsion. Meanwhile, the microemulsion solution became brown immediately, indicating the formation of CuS. After 24 h, a dark brown powder was obtained. This reaction solution was kept for 90 min at 60 °C under stirring and then became dark green, leading to the formation of hierarchical CuS nanostructures. The dark green product was collected by centrifugation, washed several times with deionized water and ethanol, and then kept for 40 days at 60 °C in

5 ml ethanol without stirring, resulting in the formation of micro-sized hierarchical CuS architectures. The final products were dried in a vacuum furnace at 60 °C for 2 h. To explore the effect of copper naphthenate content on the synthesis of CuS nanostructures, control experiments were carried out by varying the amount of copper naphthenate while keeping other experimental conditions unchanged.

Characterizations

Scanning electron microscopy (SEM) images were obtained using a FEI Sirion 200 field-emission SEM. The dispersions were diluted and dried on silicon wafers. Elemental analysis of the sample was conducted using an energy-dispersive X-ray (EDX) detector (DX4, EDAX, USA) attached to the SEM. The X-ray diffraction (XRD) patterns of the products were measured using a D/max 2550VL/PC diffractometer with Cu-K α radiation ($\lambda = 0.15406$ nm) and at a scanning rate of 0.02°/s in the 2θ range from 20° to 70°. Transmission electron microscopy (TEM) images were recorded on a JEM-2100F microscope operating at 200 kV. An ultraviolet–visible light (UV–vis) spectro-photometer (Lambda 25, Perkin-Elmer, USA) was used to perform the optical measurements of the product dispersed in ethanol in the wavelength range of 400–800 nm. The Brunauer–Emmett–Teller (BET) specific surface area was performed by N $_2$ gas adsorption using a Micromeritics ASAP 2020 surface analytical instrument.

Photocatalytic activity test

The hierarchical CuS architectures were used as catalyst for the oxidation and decomposing of the methylene blue dye with the assistance of hydrogen peroxide (H $_2$ O $_2$) at room temperature. The original solution was prepared by adding 1.3 ml H $_2$ O $_2$ (30%, w/w) to 40 ml MB solution (20 mg/l), then 30 mg CuS was added into the solution to form the aqueous dispersion. At once, the dispersion was magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium of MB molecules on CuS. Afterward, the dispersion was put under the natural light. At given time intervals, the dispersion was sampled (1 ml), diluted (5 ml), and centrifuged to separate the catalyst. Then the concentration of MB was tested by the absorption spectra on a spectrophotometer (Spectrumlab PC22).

Results

Characterization of CuS by powder XRD pattern

The XRD patterns of the samples prepared with 0.16 g copper naphthenate at room temperature and after

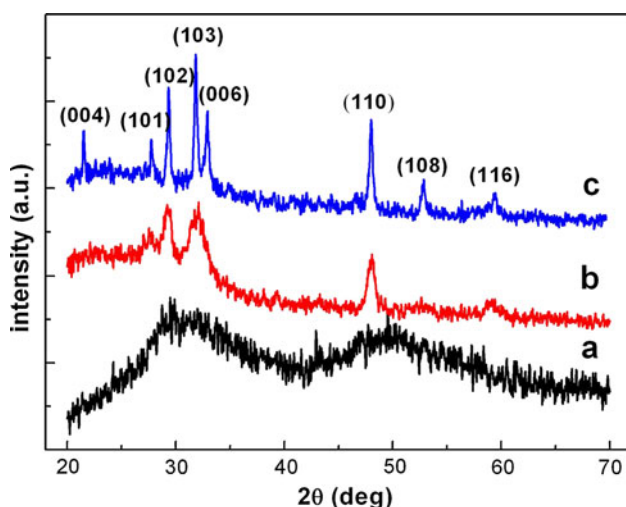


Fig. 1 XRD patterns of the samples prepared with 0.16 g copper naphthenate: (a) at room temperature for 24 h, (b) kept in ethanol at 60 °C for 40 days, and (c) after hydrothermal treatment at 60 °C for 90 min

hydrothermal treatment are shown in Fig. 1. All the patterns can be indexed as hexagonal phase CuS with lattice parameters $a = 3.79 \text{ \AA}$ and $c = 16.34 \text{ \AA}$, which are well matched with the standard values (JCPDS 74-1234). The XRD pattern of the product obtained at room temperature shows broad peaks with very low intensity (Fig. 1a). After hydrothermal treatment, the patterns became stronger and sharper (Fig. 1b, c), which indicate the increased crystallinity and grain growth as well. This is because the dark brown product obtained at room temperature is a poorly crystalline form of covellite (the green form), which can convert to crystalline covellite by increasing temperature [19]. In our experiments, no impurities are also observed in other samples obtained at different copper naphthenate contents, indicating pure CuS synthesized under excess TAA.

Effect of copper naphthenate content on the formation of hierarchical CuS nanostructures

The TEM images of poorly crystallized CuS prepared at different copper naphthenate contents at room temperature are illustrated in Fig. 2. When the content of copper naphthenate was 0.16 g, well-maintained and compact spheres with an average size of about 200 nm were obtained. The CuS spheres were composed of small nanoparticles with an average diameter of about 12 nm, as shown in Fig. 2a. When the content of copper naphthenate was decreased to 0.08 g (Fig. 2b), the resultant products were irregular aggregates which were composed of small primary nanoparticles. The average diameter of the primary nanoparticles was 5 nm and smaller than that of the

products prepared with 0.16 g copper naphthenate, as demonstrated in the inset of Fig. 2b. Moreover, some rod-shaped nanostructures can be observed particularly in the edge of the irregular aggregates, as indicated by the black arrows. When the content of copper naphthenate was further decreased to 0.04 g, the rod-shaped nanostructures of irregular aggregates were increased, but the mean size of the primary nanoparticles were not decreased (Fig. 2c). At the copper naphthenate content of 0.02 g, the rod-shaped nanostructures with lengths of about 30 nm became dense and obvious. Furthermore, it is obviously seen that the edges of the irregular aggregates became nanoplates, as indicated in the inset of Fig. 2d. In fact, the rod-shaped nanostructures are the edges of the corresponding inter-growing nanoplates which are perpendicular to the base plate [16, 35]. In the two-phase system, the nuclei grow slowly since the reactants are spatially separated in the oil and water phase. In our study, the lower reaction temperature can further decrease the rate of growth of the CuS nuclei. As the content of copper naphthenate decreases, the interfacial reaction rate becomes slower, thus forming the smaller primary nanoparticles. The CuS aggregates composed of the primary nanoparticles become looser, and the crystalline quality of the CuS aggregates is worse. Therefore, the recrystallization growth process of the aggregates becomes more obvious due to the instability of the poorly crystallized products [36]. It can be confirmed that the nanoplates could be formed because of the recrystallization growth of the poorly crystallized CuS aggregates. In a word, the poorly crystallized aggregates which were composed of primary CuS nanoparticles can be obtained in the two-phase system at the low temperature. More importantly, the primary nanoparticles can act as the “nuclei” which can grow into nanoplates by the recrystallization growth process.

To obtain the hierarchical CuS nanostructures, the reaction solution prepared at room temperature for 24 h was kept for 90 min at 60 °C. TEM images of the hierarchical CuS nanostructures prepared with different copper naphthenate contents are presented in Fig. 3. At the copper naphthenate content of 0.16 g, the products were hierarchical spheres constructed by many irregular nanoplates. The nanoplates can be observed particularly in the edge of the spheres, as demonstrated in Fig. 3a. When the content of copper naphthenate was decreased to 0.08 g, the aggregates were clear nanoplate-based nanostructures, as shown in Fig. 3b. When the content of copper naphthenate continued to decrease to 0.04 g, the nanoplate-based aggregates were looser and plate-shaped nanostructures became more apparent (Fig. 3c). As the content of copper naphthenate further decreased to 0.02 g, the intersectional nanoplates with the average thickness of 6 nm were more well-maintained and clear, as shown in Fig. 3d. The dark

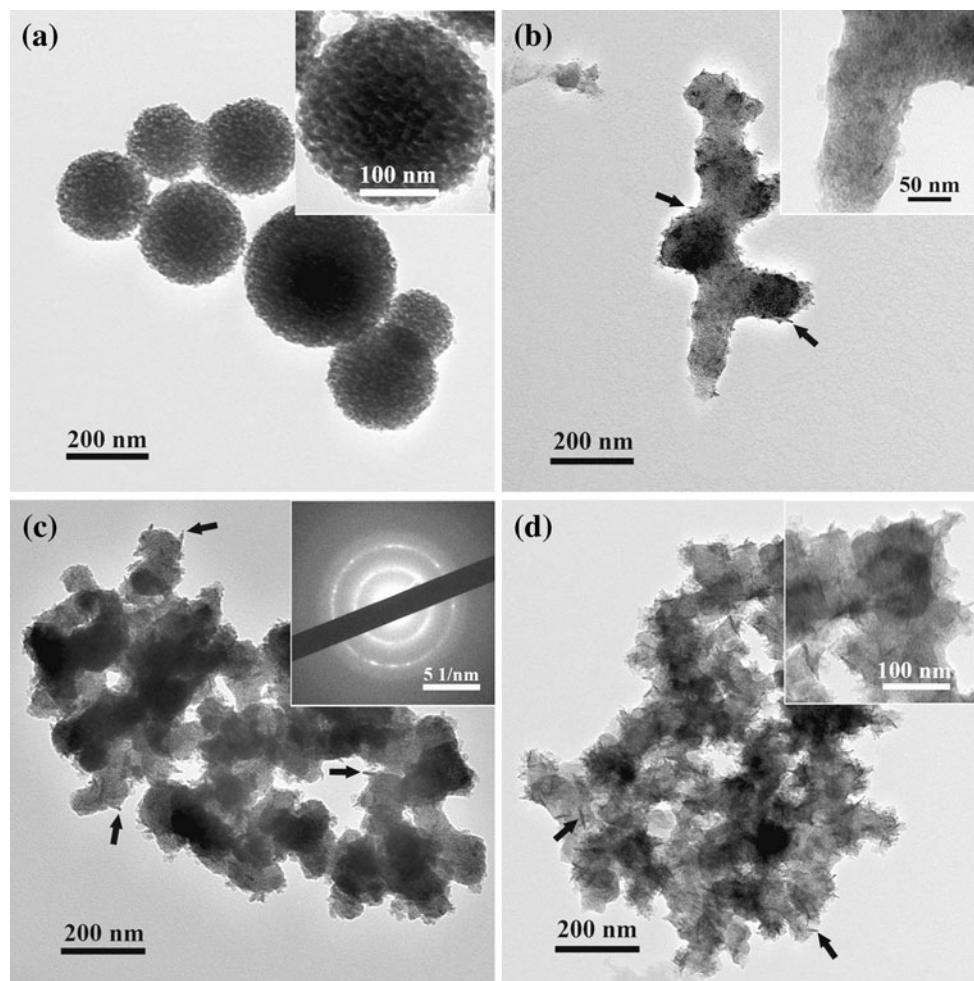


Fig. 2 TEM images of the products prepared at room temperature for 24 h with different copper naphthenate contents: **a** 0.16 g, (the *inset* shows an individual sphere at higher magnification), **b** 0.08 g, the

inset shows the irregular aggregates at higher magnification, **c** 0.04 g, (*inset* corresponding SAED pattern), and **d** 0.02 g, the *inset* shows the irregular aggregates at higher magnification

stripes that represent the edges of the nanoplates can be observed easily in the TEM image. The average edge length of the nanoplates is about 35 nm, with the edge length ranging from 20 to 50 nm. The HRTEM image and the selected area electron diffraction (SAED) pattern of the CuS nanoplate are shown in the insets of Fig. 3c and d. The lattice spacing of 0.322 nm in the HRTEM image corresponds to the separation between (101) planes of the hexagonal CuS phase. The SAED pattern indicates that the products are polycrystalline. Furthermore, the diffraction rings are clearer than the diffraction rings of the poorly crystallized CuS, indicating the formation of a highly crystalline product, which is consistent with the result of XRD analysis. As a result, the morphology of hierarchical CuS nanostructures is determined by the morphology of aggregates of poorly crystallized CuS. The nanoplates are formed easily from poorly crystallized CuS by the recrystallization growth process because of the intrinsic crystal properties of CuS [37].

To further examine the morphology of the hierarchical CuS nanostructures, the high-magnification SEM image was recorded, as shown in Fig. 4a. The products were actually composed of numerous intersectional nanoplates that were randomly arranged to form a flowerlike structure. EDS analysis (Fig. 4b) on the hierarchical CuS nanostructures shows that the atomic ratio of the element Cu versus S is about 1:1, which is in agreement with the stoichiometric ratio of CuS.

Formation of micro-sized flowerlike CuS

For the synthesis of the micro-sized hierarchical CuS architectures, the CuS hierarchical nanostructures prepared with 0.16 g copper naphthenate were kept in 5 ml ethanol at 60 °C for 40 days. The SEM images of the micro-sized hierarchical CuS architectures at different ripening times are shown in Fig. 5. When the ripening time was increased to 20 days, some big nanoplates were generated and about

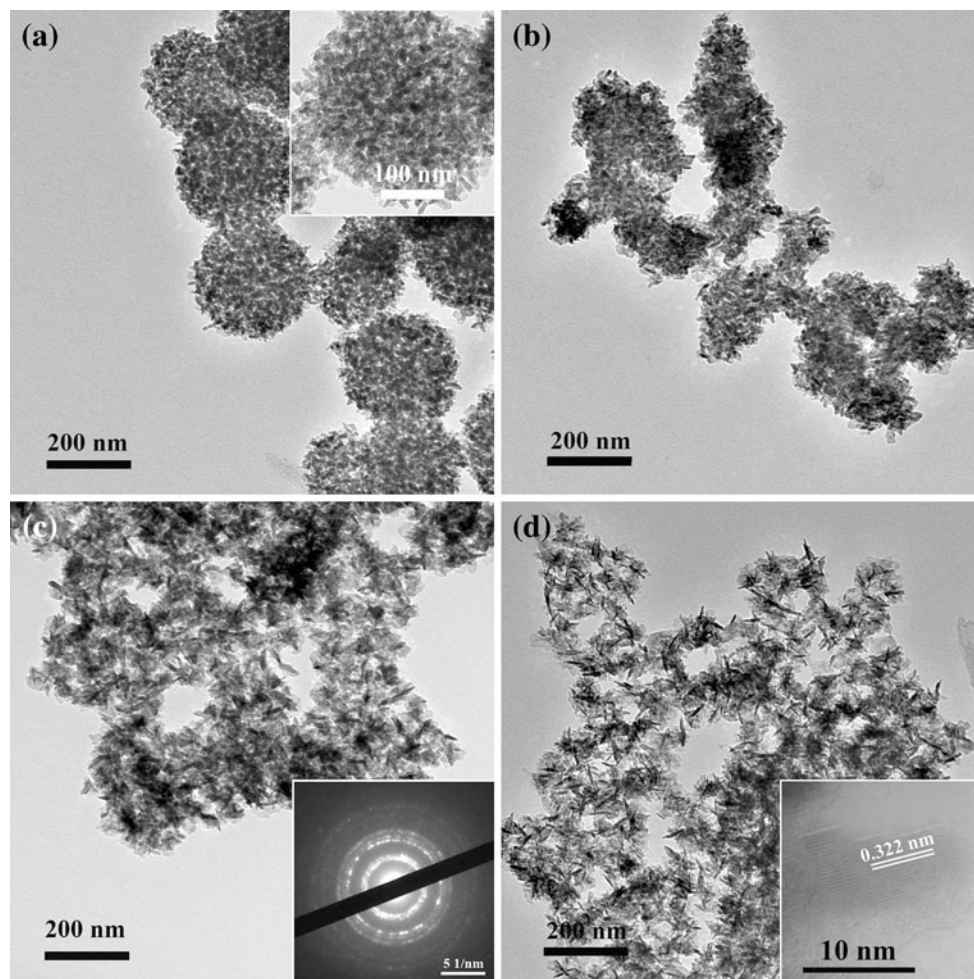
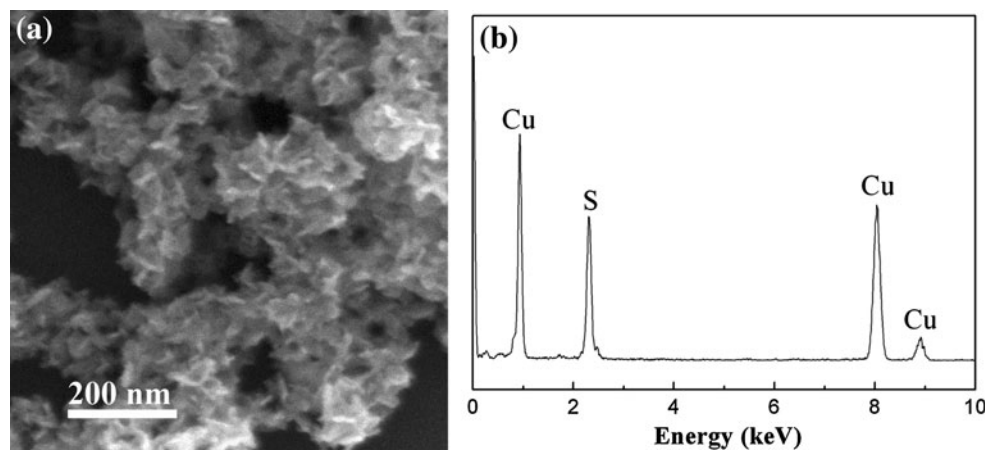


Fig. 3 TEM images of the hierarchical CuS nanostructures prepared with different copper naphthenate contents: **a** 0.16 g, **b** 0.08 g, **c** 0.04 g, and **d** 0.02 g, the *insets* show the corresponding SAED and the HRTEM image of the CuS nanoplate

Fig. 4 **a** SEM image of the hierarchical CuS nanostructures prepared with 0.08 g copper naphthenate; and **b** corresponding EDX analysis



a few hundred nanometers in size. The big nanoplates seemed to grow from the heap of the hierarchical spheres, as indicated in Fig. 5a and b. Furthermore, the hierarchical sphere became smooth, owing to the disappearance of the nanoplates of the hierarchical spheres, as demonstrated in

the inset of Fig. 5b. When the ripening time was prolonged to 40 days, many flowerlike CuS architectures were formed, as shown in Fig. 5c. The flowerlike CuS architectures have a diameter ranging from 5 to 10 μm , and almost all of them show the same morphology. It is clearly

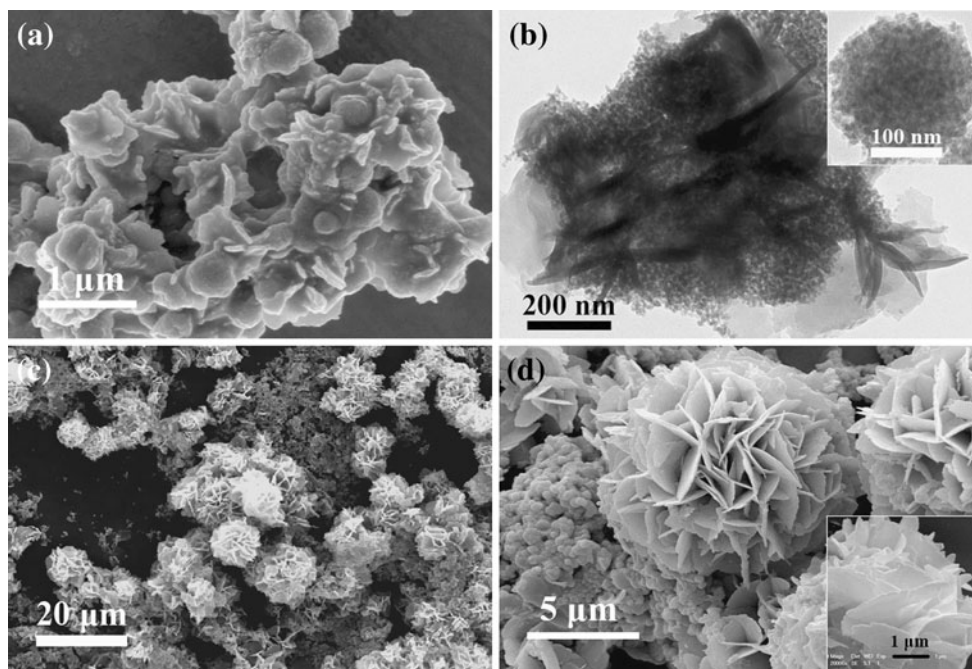


Fig. 5 SEM images of the micro-sized hierarchical CuS architectures kept in 5 ml ethanol at 60 °C for different ripening times: **a** 20 days and **c** 40 days. **b** TEM image of the micro-sized hierarchical CuS architectures kept in ethanol for 20 days; the *inset* shows an

individual hierarchical sphere at higher magnification. **d** High-magnification SEM image of the flowerlike CuS; *inset* shows the nanosheets at higher magnification

observed that the flower consists of thin nanopetals, and the petals are sheetlike (Fig. 5d). Careful examination reveals that the CuS nanopetals are 1–3 μm in size. In addition, many hierarchical spheres can still be found near the flowerlike CuS architectures or even between the petals of the flowerlike CuS architectures.

From the above experimental observations, the formation of the flowerlike CuS architectures can be rationally expressed as a kinetically controlled dissolution–recrystallization mechanism (Fig. 6). When the CuS hierarchical nanostructures were kept in ethanol, some nanoplates of CuS hierarchical nanostructures started to dissolve in the solution, and then some big nanoplates were gradually generated by recrystallization process. The dissolution phenomenon of the nanoplates can be clearly observed in ripening process of the CuS hierarchical nanostructures prepared with 0.04 g copper naphthenate (supporting information Fig. S1). In our experiments, the formation of the flowerlike CuS architectures is very slow due to the lower ripening temperature [38].

Optical properties

The UV–vis absorption spectrums of different hierarchical CuS structures prepared with 0.16 g copper naphthenate and bulk CuS powders are shown in Fig. 7. The absorption spectrums of the hierarchical CuS nanostructures and micro-sized flowerlike CuS show an increased absorption

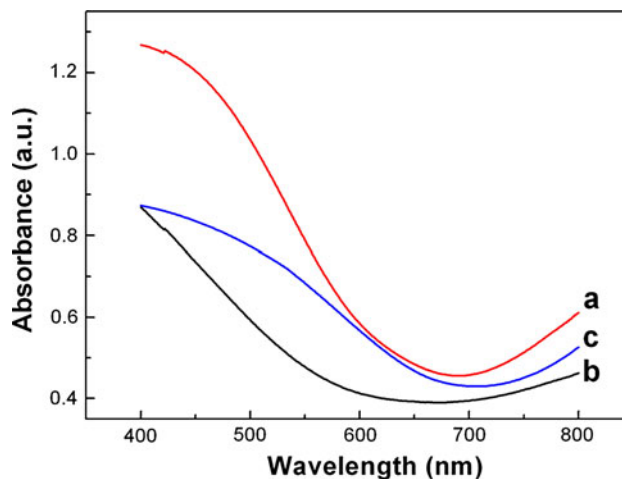


Fig. 6 UV–vis absorption spectrums of the hierarchical CuS nanostructures (*a*); micro-sized flowerlike CuS (*b*), and bulk CuS powders (*c*)

in the near-IR region, which is the characteristic band for covellite CuS [39]. Similar spectral feature has also been observed previously for CuS nanoplate-based architectures [40–42] prepared through different reaction routes. Compared with the absorption spectrum of the hierarchical CuS nanostructures and bulk CuS powders that of micro-sized flowerlike CuS was blue-shifted, which could be attributed to the strong quantum confinement of the excitonic transition for flowerlike structures. This may be because the

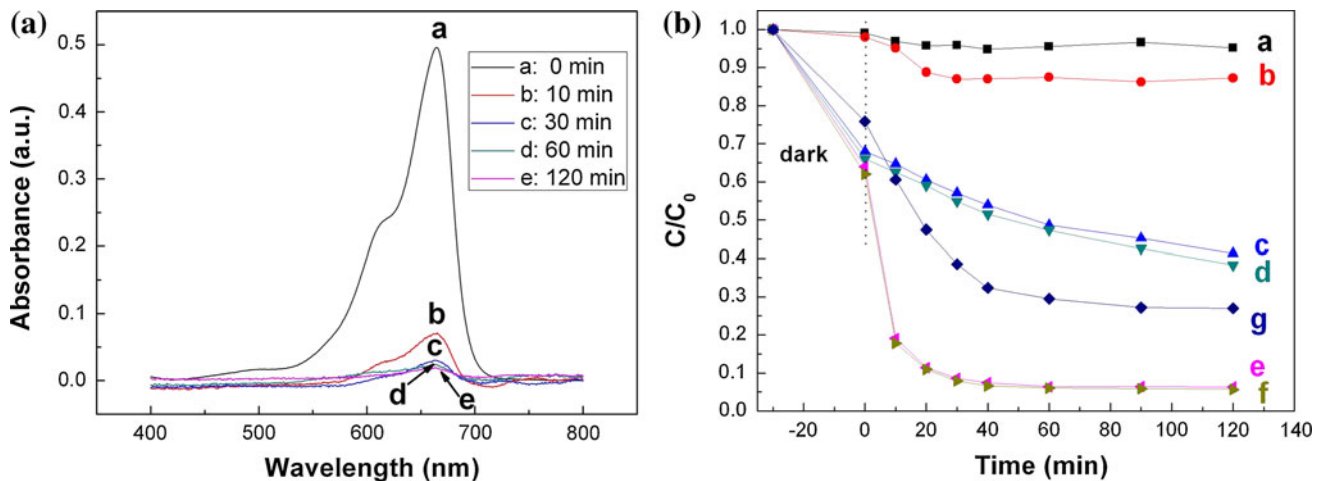


Fig. 7 **a** Time-dependent absorption spectra of MB aqueous solutions in the presence of H_2O_2 and the hierarchical CuS nanostructures prepared with 0.16 g copper naphthenate. **b** Degradation rate of MB at different intervals in the presence and absence of photocatalysts. Line *a* without any catalyst, line *b* in the presence of H_2O_2 , line *c* in

the presence of the micro-sized flowerlike CuS, line *d* in the presence of the hierarchical CuS nanostructures, line *e* in the presence of the micro-sized flowerlike CuS and H_2O_2 , line *f* in the presence of the hierarchical CuS nanostructures and H_2O_2 , and line *g* in the presence of the bulk CuS powders and H_2O_2

micro-sized flowerlike CuS composed of the smaller particles efficiently show a confinement effect [43]. In addition, the CuS with different morphologies displays the similar absorption spectrum, which may be attributed to the inherent property of covellite CuS [34].

Photocatalytic activity

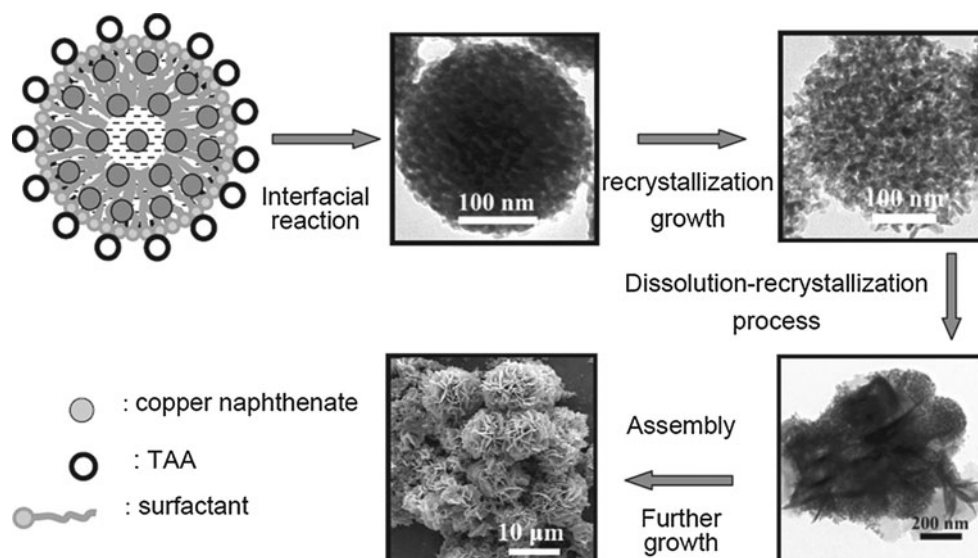
To demonstrate the potential application of as-synthesized hierarchical CuS architectures in the degradation of organic contaminants, we have investigated their photocatalytic activities by choosing the photocatalytic degradation of MB in the presence of hydrogen peroxide under natural light. Figure 7a shows the absorption spectra of aqueous solutions of MB tested at different intervals in the presence of the hierarchical CuS nanostructures prepared with 0.16 g copper naphthenate. The main absorption peak locates at 665 nm, which corresponds to the MB molecules, decreases rapidly with extension of the exposure time, indicating the photocatalytic degradation of MB.

Figure 7b shows the degradation rate of MB at different intervals. Without any catalyst, a slow decrease in the concentration of MB was detected, and the self-degradation rate of MB under natural light was only 5% (line a). When only H_2O_2 was added into MB solutions, the degradation rate of MB increased to 10% (line b). The photodegradation efficiencies of MB by the micro-sized flowerlike CuS (line c) and the hierarchical CuS nanostructures (line d) under natural light reached 40 and 42% after 120 min, respectively. However, obvious and quick degradation of MB occurs, and about 90% of the MB was degraded after

40 min by using the hierarchical CuS architectures and H_2O_2 (lines e and f) as catalysts. Furthermore, the activities of our hierarchical CuS architectures are higher than that of bulk CuS powders (line g). The improvement of degradation rate of MB using the hierarchical CuS architectures and H_2O_2 as catalysts is probably due to the following reasons. Firstly, the active sites of the surfaces of CuS may catalyze the decomposition of H_2O_2 to generate a large number of hydroxyl radicals, leading to the enhancement of photodegradation efficiency [44]. Secondly, H_2O_2 is suggested to be a better electron acceptor than oxygen. This would reduce the chances of electrons-holes recombination, resulting in the increase of photocatalyzed rate [45]. Therefore, it is concluded that the hierarchical CuS architectures play a vital role in hydrogen peroxide-assisted photocatalytic degradation of MB.

It is generally accepted that the catalytic process is mainly related to the adsorption and desorption of molecules on the surface of the catalyst. The high-specific surface area can provide more reactive adsorption/desorption sites for photocatalytic reactions [46]. The BET surface areas of the micro-sized flowerlike CuS and the hierarchical CuS nanostructures are 50.74 and 53.45 $\text{m}^2 \text{g}^{-1}$, respectively. Therefore, the micro-sized flowerlike CuS and the hierarchical CuS nanostructures exhibit similar photodegradation efficiency due to the similar specific surface area. In addition, under the same photocatalytic conditions, the activity of our samples is higher than that of Li's hierarchical CuS structures [30]. This may be because our samples have the higher surface areas compared with Li's hierarchical CuS structures.

Fig. 8 A schematic illustration of the formation of the hierarchical CuS architectures



Discussions

Based on the experimental results above, a schematic illustration of the formation mechanism of the hierarchical CuS architectures is shown in Fig. 8. Firstly, when TAA was added into the microemulsion, then the interfacial reaction started and large numbers of CuS nuclei were formed at the oil/water interface. The spatial separation of two reactants and lower reaction temperature can decrease the rate of growth of the CuS nuclei, resulting in the formation of the poorly crystallized aggregates. Secondly, when the reaction solution was carried out at 60 °C for 90 min, the poorly crystallized CuS aggregates grew into the nanoplate-based nanostructures by the recrystallization growth process due to the instability of the poorly crystallized products. Thirdly, as the CuS hierarchical nanostructures were kept in ethanol, some CuS nanoplates started to dissolve in the solution. Since the dissolution speed of crystalline CuS in solution progressed very slowly. After a longer ripening time, due to anisotropic crystal structure of CuS [37], there was an intrinsic tendency for the formation of plates-like nanostructures, and some big nanoplates were gradually generated by recrystallization process. Finally, the nanosheets gradually evolved to the flowerlike nanostructures through the self-assembly of the nanosheets.

In our previous works [33, 34], it is very important for forming stable hollow spheres to ensure the quick growth of CuS nuclei by a high-interfacial reaction rate at higher reaction temperature. The formation of nanoplates becomes very difficult, probably due to quick and discontinuous growth process of CuS nuclei. However, the relatively slow growth of the recrystallization growth process may be beneficial to the formation of nanoplates in our system. In

addition, other groups' methods [16, 17, 30, 41] in synthesis of hierarchical CuS usually require high-reaction temperatures (above 100 °C) in a solvothermal system. In comparison with those routes, hierarchical CuS architectures are formed more easily through the recrystallization growth process in the low temperature. Furthermore, the slow recrystallization growth process is very helpful for the controlled growth of primary building units of hierarchical architectures. If the different morphologically poorly crystallized products, such as hollow structure and film, are obtained in our two-phase system, we believe that the other hierarchical architectures with different morphologies will be fabricated successfully.

Conclusions

In conclusion, nano- and micro-sized hierarchical CuS architectures composed of nanoplates have been successfully prepared through a recrystallization growth process in a microemulsion system. The spatial separation of two reactants and lower reaction temperature can decrease the rate of growth of the CuS nuclei, resulting in the formation of the poorly crystallized aggregates. The hierarchical CuS nanostructures are formed easily from poorly crystallized CuS by the recrystallization growth process because of the instability of the poorly crystallized aggregates. The formation of the flowerlike CuS architectures can be rationally expressed as a kinetically controlled dissolution–recrystallization mechanism. The hierarchical CuS architectures have good photocatalytic performance on the degradation of MB under natural light. Moreover, this method presents a new avenue in the design and synthesis of hierarchical architectures.

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