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One-dimensional CuS microstructures prepared by a PVP-assisted microwave hydrothermal method

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Abstract

One-dimensional (1D) CuS microstructures of assembled chains and rods have been prepared using a facile polyvinylpyrrolidone (PVP) assisted microwave hydrothermal (MH) method. The crystallites were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and UV–vis optical absorption spectroscopy. The crystal growth and morphology evolution process have been investigated through time-dependent experiments, and the assembling of sphere into chain-like structure and the further transformation into rod-like morphology are observed. A possible formation mechanism of the as-obtained 1D structure was proposed after the investigation of the effects of the concentration of PVP and the solvent on the final products in detail. The UV–vis spectra of the spherical and rod-like CuS crystallites show a strong absorption in the visible spectrum between 500 nm and 800 nm, while the rod-like structure exhibits a distinct red shift compared to the spheres.

Keywords: Microwave hydrothermal; CuS; One-dimensional; Crystal growth

1. Introduction

One-dimensional (1D) nanomaterials such as nanorods, nanowires, nanobelts, and nanotubes are becoming more and more popular nowadays in scientific research because of their salient special properties and potential applications as compared to their bulk and zero-dimensional (0-D) counterparts [1,2]. Among them, the fabrication of 1D assemblies has drawn much attention owing to their application in electrics [3], optics [4], and sensors [5]. Some examples of 1D assemblies of Si [6], Cu [7], CdS [8], $FeNi_3$ [9] and Fe_2O_3 [10] have been reported, which were mostly based on the inherent anisotropy of the magnetic [9] or electric dipoles [11], and non-uniform distribution of ligands on the surfaces [12].

In recent years, there has also been increasing interest in transition metal chalcogenides due to their novel physical and chemical properties. Covellite copper sulfide, as a member of the chalcogenides, has been used in applications such as photothermal conversion [13], electrodes [14], solar cell devices [15], and sensors [16]. Recently, various morphologies of copper sulfide including nanowires [17], nanodisks [18], hollow spheres [19] and flower-like structures [20] have been prepared by electrosynthesis, thermolysis [21], microemulsions [22] and hydrothermal [23] (solvothermal [24]) methods. Among them, the hydrothermal method is the most common synthesis technology, because of its ease of operation with less-expensive equipment. However, the conventional hydrothermal method has disadvantages, such as long synthesis time and high energy consumption. The microwave hydrothermal (MH) method, as a modification of the conventional hydrothermal, prompts a much more rapid reaction due to the interaction of microwave field with reactant molecules. In addition, it offers further advantages, such as energy economy, simplicity of synthesis, and low cost; therefore, it has the potential of being used in large-scale commercial production [25].

In the present work, we try to adopt the microwave hydrothermal method to prepare 1D copper sulfide microstructure using PVP as the surfactant. The influence of reaction time, the PVP concentration, and the solvents on the crystallites have been systematically investigated. To the best of our knowledge, it is the first time for the synthesis of this novel

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assembled chain-like structure for CuS. And interesting crystallites growth process has been observed that the spheres assembled into chain-like structures, and then transformed into rods and microwires. We propose that these assemblies might prove useful to study and eventually model crystal growth phenomena in microparticles.

2. Experimental

In a typical synthesis process, $Cu(NO_3)_2 \cdot 3H_2O$ (0.726 g, 3 mmol), thiourea (0.456 g, 6 mmol), and PVP (0.4 g, 3.6 mmol, calculated in terms of the repeating unit C_6H_9NO FW = 111) were dissolved in deionized water (50 mL) and stirred vigorously until the solution was homogeneous. The mixture was sealed in a 50 mL Teflon-lined autoclave and was heated at 150 °C for specific lengths time (e.g., 10 min) under the temperature-controlled mode in a MDS-8 microwave hydrothermal system (Shanghai Sineo Microwave Chemistry Technology Co. Ltd., China). The working voltage of the MDS-8 is ~220 V, and the working frequency is ~2450 MHz. After the reaction was terminated and naturally cooled down to room temperature, the as-prepared black precipitates were isolated by centrifugation and purified by washing with deionized water and absolute ethanol for several times. Finally, the black precipitates were dried at 50 °C in a drying cabinet with air-blasting for 1 h.

The products were characterized via X-ray powder diffraction (XRD), field-emission scanning electron microscope (FESEM), and UV/Vis/NIR Spectrophotometer. The XRD pattern was performed on a D/MAX-2200PC X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) and a scanning rate of $8^\circ\ \mathrm{min}^{-1}$ (Rigaku, Japan). FESEM images were taken on a JSM-6700F field-emission scanning electron microscope, and UV–vis spectra were obtained by a Lambda 950 spectrophotometer (PerkinElmer, USA).

3. Results and discussion

3.1. Phase composition

Samples obtained under different reaction conditions are listed in Table 1.

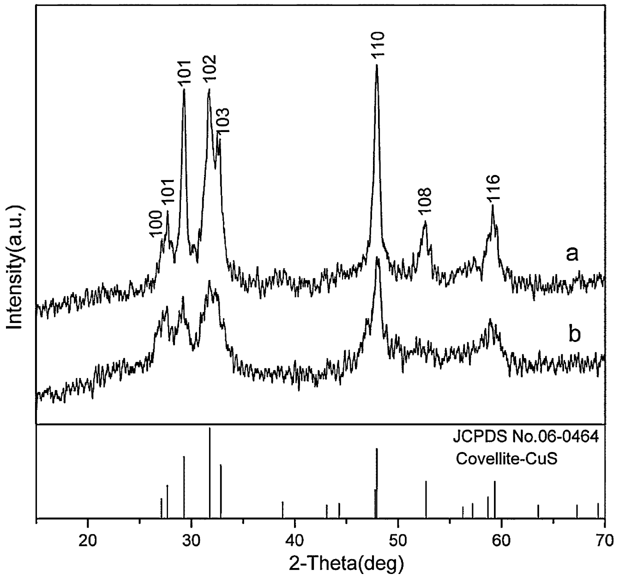

Fig. 1. Typical XRD patterns of the obtained morphology of (a) rods and (b) flower-like sphere by hydrothermal treatment at 150 °C.

Fig. 1 shows the typical XRD patterns of the CuS products with morphology of rod-like (sample 3) and flower-like (sample 9). In Fig. 1a, all the diffraction peaks could be indexed to the standard diffraction data of the corresponding hexagonal phase CuS with lattice parameters of $a = b = 3.7833$ Å and $c = 16.4266$ Å, which was consistent with the standard diffraction data (JCPDS No. 06-0464, $a = b = 3.792$ Å, $c = 16.344$ Å). No other characteristic peaks were observed, indicating that the products were pure covellite CuS. The sharp peaks reveal that the obtained sample has a good crystallization. However, in Fig. 1b, the diffraction peaks are much broader than that of Fig. 1a, which indicates that the products have a smaller size. This also has been confirmed in Figs. 2 and 5, showing that the products have a flower-like structure composed of nanoslices.

3.2. Effects of reaction time

The experiments were carried out at 150 °C for different reaction times 3, 5, 10 and 20 min. Fig. 2 shows the corresponding FESEM images of the obtained samples 1–4 in Table 1. As is shown, microwave hydrothermal treatment induces fast growth in the CuS crystallites. When the reaction time was 3 min, the product was mainly spherical, and it is interesting to note that many spheres adopt an “8” shaped

Table 1
Summary of the main results on the products obtained under different preparation conditions.

Sample	*T* (°C)	*t* (min)	PVP (g/mL)	Solvent	Phase	Main morphology
1	150	3	0.012	H_2O	Covellite CuS	Spheres
2	150	5	0.012	H_2O	Covellite CuS	Chains
3	150	10	0.012	H_2O	Covellite CuS	Rods
4	150	20	0.012	H_2O	Covellite CuS	Wound rods
5	150	15	0	H_2O	Covellite CuS	Irregular particles
6	150	15	0.008	H_2O	Covellite CuS	Spheres and rods
7	150	15	0.016	H_2O	Covellite CuS	Rods
8	150	15	0.020	H_2O	Covellite CuS	Wound rods
9	150	15	0.016	EG	Covellite CuS	Flower-like spheres

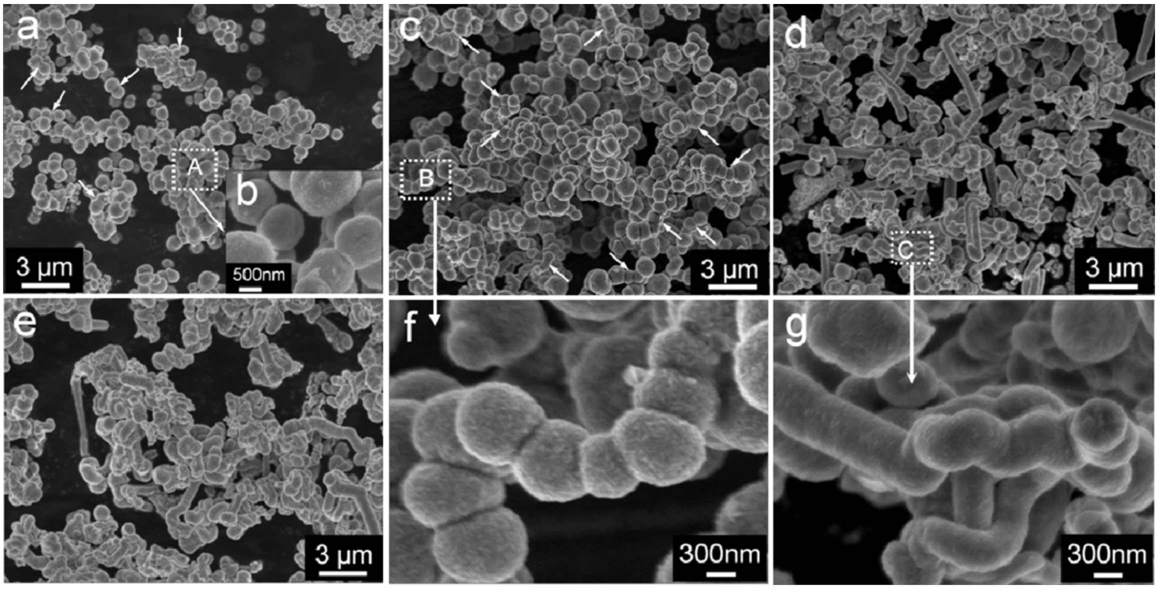

Fig. 2. FESEM images of the obtained CuS crystallites under microwave hydrothermal treatment at 150 °C for different times: (a, b) 3 min; (c, f) 5 min; (d, g) 10 min; and (e) 20 min.

structure at the interface between the crystallites, as shown in Fig. 2b. When the reaction time was increased to 5 min, most of the spheres began to assemble to chain-like structures as marked by white arrows in Fig. 2c. From Fig. 2f, it can be found that the spheres connect with each other, and some of the spheres have been compressed. When the further increase of time, many rods are obtained, and the sphere-rod transition is obviously observed (Fig. 2d and g). It can be speculated from Fig. 2g that the rods may grow by sphere–sphere assembly and rod-sphere assembly, and the bent chains will result in bent rods. These end-to-end linkages can be strengthened by increasing reaction time within a certain range. But when the microwave hydrothermal treatment was prolonged to 20 min, the twist trend of the rods is obvious (Fig. 2e).

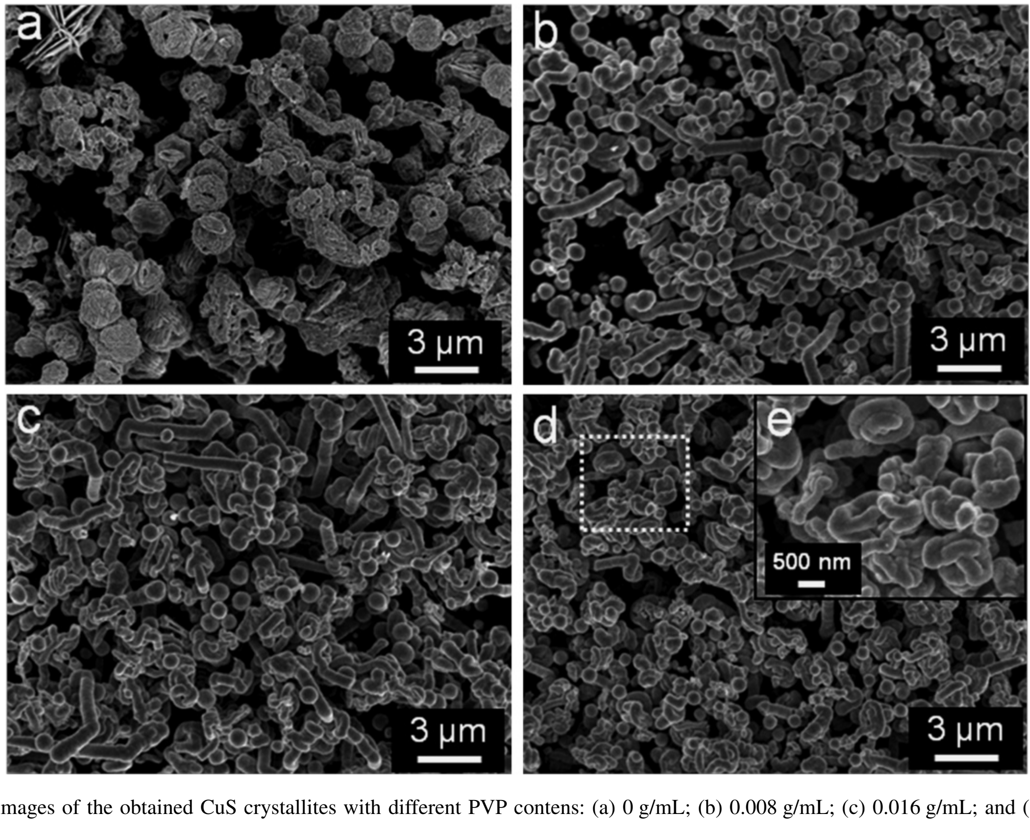

Fig. 3. FESEM images of the obtained CuS crystallites with different PVP contens: (a) 0 g/mL; (b) 0.008 g/mL; (c) 0.016 g/mL; and (d, e) 0.020 g/mL.

3.3. Effects of the concentration of PVP

In order to understand the effect of PVP on the sphere-rod transition, a series of experiments were carried out with different concentrations of PVP. Fig. 3a–d shows the corresponding FESEM images of the as-grown CuS crystallites (samples 5–8 in Table 1). Fig. 3a shows the FESEM images of CuS particles without adding PVP. Irregular particles agglomerated and no spheres or rod structures were formed. When the concentration of PVP was increased to 0.008 g/mL, the obtained particles were a mixture of spheres with a diameter of 900 nm and rods with the diameters around 700 nm and lengths of tens of micrometers (Fig. 3b). As the concentration of PVP was increased to 0.016 g/mL, the spheres became smaller, and some of the rods started to bend to form wire-like structures and wind around with each other (Fig. 3c). When PVP concentration reached to 0.020 g/mL, the wound microwires became the main morphology, and the decrease in the diameter of wires was observed (Fig. 3d and e). This phenomenon indicates that the morphology of the product is strongly influenced by the PVP concentration. It was found that higher concentrations of PVP will result in winding rods and a smaller average size of CuS crystallites.

The viscosity of the solution greatly restricts the diffusion and growth process associated with nanocrystal formation, which is why higher concentrations of PVP result in smaller average CuS crystallites sizes. The C=O of the PVP molecules might chelate with Cu^{2+} [26], preventing rapid crystal growth and resulting in a smaller size. Additionally, PVP also plays an important role in the formation of the rods, as only when high PVP concentration will result in more rod-like crystallites. The reason may be that as a number of PVP molecules absorbed on the surface of CuS sphere, driven by the minimization of the total surface energy of the system and van der Waals interactions between PVP molecules [27], the spheres tend to assemble into chains and rods.

3.4. Effects of the solvent

To further make clear the synthesis mechanism, a controlled experiment was carried out using a different solvent instead of water. It was found that water plays an important role in the formation of the chain-like and rod-like structures. In an ethylene glycol (EG) reaction system, almost no 1D structure can be observed, as shown in Fig. 4a. The products (sample 9 in Table 1) obtained in the EG have a morphology of flower-like sphere assembled by thin nanoflakes with a thickness of ~40 nm (Fig. 4b). It is important to note that the crystallites have an average size of 589 nm, which is smaller than prepared in water. This might be due to the higher viscous nature of EG, which in consequence will slow down the diffusion of ions and is helpful for the formation of new nucleus before their growth at the surface of a pre-existing nucleus [28]. Additionally, the lack of 1D structures may be attributed to the fewer hydrogen bonds absorbed on the surface of CuS spheres in ethylene glycol than in water, and the flower-like spheres have difficulty connecting with each other to form rods or microwires [29].

3.5. Formation mechanism of the as-obtained 1D structure

The copper–thiourea system has already been used to prepare copper sulfides with various forms and compositions [30]. In the reaction, thiourea (Tu) will firstly coordinate with $Cu(NO_3)_2$ to produce Tu–copper(II) complexes, which can be observed via a simple color change of the solution. In the experiment, after the introduction of Tu into the copper(II) salts solution, the color will change from blue to green, indicating the formation of Tu–copper(II). After introducing PVP to the reaction mixture, some of the Cu^{2+} ions would be attracted by the PVP to form copper(II)–PVP complex. Under microwave hydrothermal (MH) treatment, Tu in the solution will decomposed at a certain temperature to allow sulfur species to react with the copper(II)–PVP complex. The possible reaction process can be described as shown in Eqs. (1)–(4) [23,30]:

$$Cu^{2+} + n\mathrm{Tu} + xH_2O \rightleftharpoons [Cu(\mathrm{Tu})n(H_2O)x]^{2+} \tag{1}$$

$$[Cu(\mathrm{Tu})n(H_2O)x]^{2+} + n\mathrm{PVP} \xrightarrow{\mathrm{MH}} [Cu(\mathrm{PVP})n]^{2+} + n\mathrm{Tu} + xH_2O \tag{2}$$

$$NH_2CSNH_2 + 2H_2O \xrightarrow{\mathrm{MH}} 2NH_3 + CO_2 + H_2S \tag{3}$$

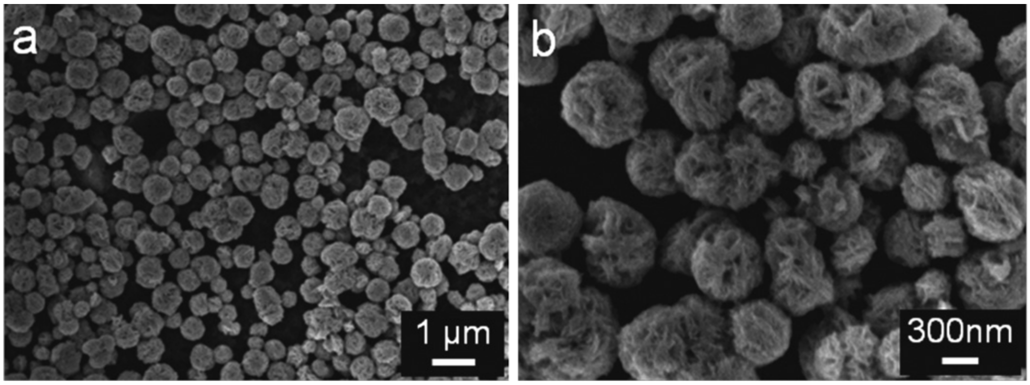

Fig. 4. FESEM images of the obtained CuS crystallites at 150 °C for 20 min in EG: (a) with low-magnification; (b) with high-magnification.

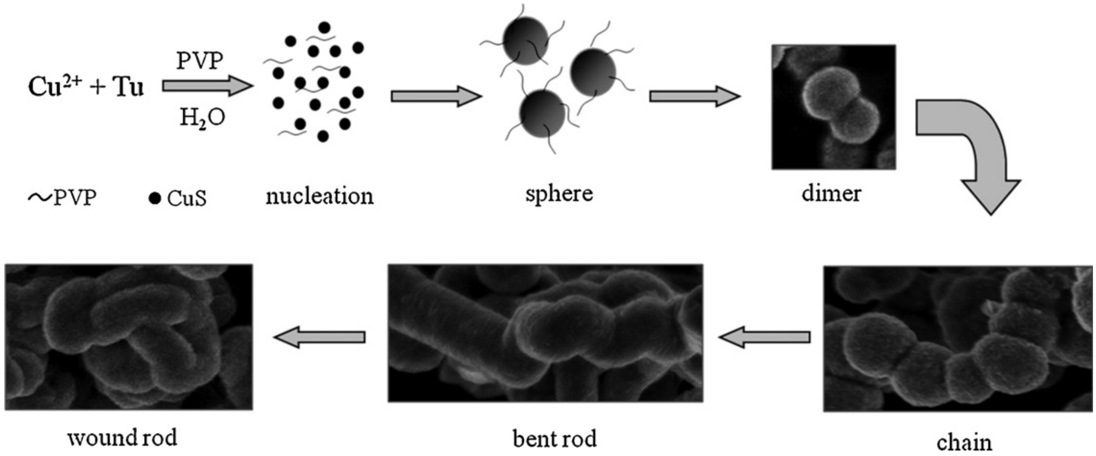

Fig. 5. Scheme of the growth process of 1D CuS structure.

$$[\mathrm{Cu(PVP)}n]^{2+} + \mathrm{H_2S} \xrightarrow{\mathrm{MH}} \mathrm{CuS(PVP)}n + 2\mathrm{H}^{+} \qquad (4)$$

The formation of ball-like, chain-like and wire-like morphology can be summarized and rationalized on the basis of the above investigations of varying the reaction time as shown in Fig. 5. At the beginning of the reaction, the CuS crystallite will nucleate with the decomposition of Tu. The particles then aggregate to form microspheres with the modification of PVP on the surfaces. In order to reduce the surface free energy, the microspheres will connect with each other to form dimers and chain-like structure through an oriented attachment mechanism, associate with Ostwald ripening [31]. As the reaction takes place in the water, the hydrogen bonding cannot be ignored. There are many hydrogen bonds absorbed on the surfaces of CuS crystallites, which will reassemble under microwave conditions [32]. As a result, the bending and knotting of the CuS rods is observed.

3.6. Optical properties of the as-obtained CuS with different structures

The optical properties of as-obtained CuS crystallites with different morphologies are characterized by UV–vis absorption spectra (Fig. 6). Both of the rods (sample 3) and spheres (sample 1) show a strong absorption in the visible spectrum between 500 nm and 800 nm, which is similar to the hierarchical tubular structures of CuS [33]. Compared with the absorption peak of rod-like CuS crystallites, the absorption peak of sphere-like CuS particles exhibit a distinct blue shift, which may result from the smaller particle size observed by FESEM. In addition, both samples show another broad at about 340 nm, which is an unusual phenomenon in the UV–vis absorption spectra. CuS particles with these unusual UV–vis absorption spectra may have potential applications in the optical field.

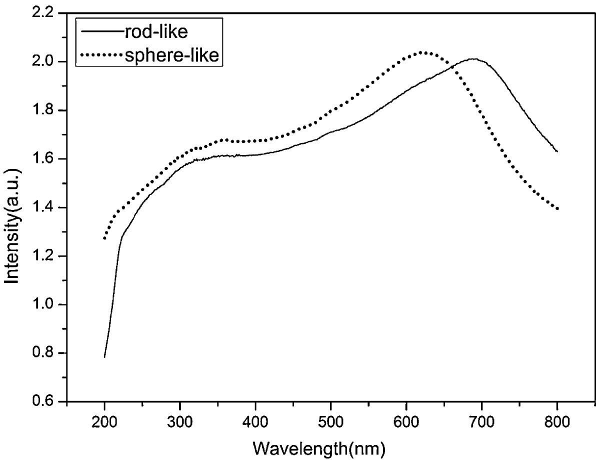

Fig. 6. UV–vis absorption spectra of rod-like and sphere-like CuS crystallites.

4. Conclusions

In summary, one-dimensional (1D) chain-like and rod-like CuS crystallites have been successfully synthesized via a simple MH method using PVP as the surfactant. After the investigation of the effects of PVP content and different solvents on the morphology of CuS crystallites, it was found that PVP and water play important roles on the formation of 1D structure. Without PVP added, only irregular particles were obtained. And the employment of ethylene glycol solvent will lead to the generation of flower-like spheres instead of 1D assembled structure. In addition, the as-found 1D assembly of spheres might be useful for the investigation and eventually modeling the crystal growth phenomena in microparticles. The UV–vis spectra of the as-prepared products with different microstructures show that both of the cases show a strong absorption in the visible spectrum between 500 nm and 800 nm, and the UV–vis spectra of spheres has a distinct blue shift, compared with rods. This one-pot process may open the new way for new routes to synthesize the self-assembled structures.

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