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Preparation and characteristics of porous CuS microspheres consisted of polycrystalline nanoslices

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ABSTRACT

This paper presents a facile method to fabricate CuS porous microspheres, which were formed by the intergrowth of CuS polycrystalline nanoslices. The obtained sample has been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electronic diffraction (SAED), X-ray diffraction (XRD), UV–vis diffusion reflection and Laser Raman. On the basis of the experimental results, we proposed a self-assemble mechanism to elucidate the formation of CuS nanoslice structure. The current–voltage characteristic under different gas atmospheres shows that the as prepared CuS polycrystalline nanoslices are sensitive to ammonia at ppm level and the electrical conductivity is found to be weaker in ammonia than that in air.

1. Introduction

Transition metal chalcogenides including CuS, CdS, ZnS and PbS have attracted considerable attention in recent decades due to their unique physical and chemical properties [1–6]. They are excellent candidates for scanning microprobe, solid lubricant and energy storage media for lithium and hydrogen [7]. As an important member of copper sulfides, CuS shows p-type semiconductor or metallic conductivity and transforms into a superconductor at 1.6 K, which makes it possible to be a promising material for solar cells, optical filters and surperionic materials and so on [8–11]. To date, CuS nanocrystals with special morphologies have been synthesized such as nanodisks, urchin-like, hollow spheres, shrub-like, microrods and chrysanthemum-like architectures [12–17]. Many methods have been developed for preparing CuS nanocrystals, including microwave, electrosynthesis, thermolysis [18–20] and so on. However, most of these synthetic methods involve template or complex equipment. Aqueous (including hydrothermal) route and nonaqueous (including solvothermal) route have been widely used to prepare inorganic materials. Qin et al. [16] reported that covellite copper sulfide submicron crystals in the shapes of ball-like, rod-like, and chrysanthemum-like architectures congregated from nanoslices with thickness of 20 to 100 nm have been prepared by hydrothermal method. Wan et al. [21] have synthesized CuS porous material with size of 50–100 μm consisted of loosely packed aggregates by solvothermal, the packed aggregates appear as a loose agglomeration of sheets irregular in size and shape, the interior holes are estimated to be about 5 μm. Nevertheless, the abovementioned CuS nanoslices are all single crystalline, and to our best knowledge, CuS polycrystalline nanoslices have not been reported so far. Nanoslices composed of nanocrystals possess large amount of nanosized rough surfaces and abundant crystal boundaries of the nanocrystals make the surface-to-volume ratio of the nanoslices higher. Therefore, this kind structure would have better physical/chemical properties than those of smooth single-crystalline nanoslices. In this paper, microspheres consisted of CuS polycrystalline nanoslices with thickness of 25–30 nm poriferous material were prepared by one-step solvothermal route at low temperature and the current–voltage curve shows that the as prepared material is sensitive to ammonia. This method might be applied in industry owning to its simple approach, innocuous reagents, benign to environment, reproducible and high yields.

2. Experimental section

2.1. Preparation of CuS

In a typical procedure, a mixture of ethylene glycol (A. R) and acetylacetone (A. R) with the volume ratio of 3:1 was put into a beaker. Then 1.3 mmol cupric chloride ($CuCl_2 \cdot 2H_2O$, A. R) was added under stirring at room temperature to ensure well dispersion of the reactant. Afterward, the mixture was transferred into a Teflon-lined autoclave which was filled with 0.04 g of sulfur powder (C. R). The autoclave was sealed into a stainless steel tank and maintained at 393 K for 12 h without shaking or stirring. After the autoclave had been cooled to room temperature naturally, the product was washed

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three times using distilled water and absolute ethanol. Finally, the products were dried at 353 K in an oven for further characterization.

2.2. Characterization of CuS

The scanning electron microscopy (SEM) images of the samples were measured on JEOL JSM-6700F SEM, Japan. Transmission electron microscopy (TEM, Hitachi-8100 transmission electron microscope, Japan) was performed to observe the microstructure of the composites. Selected area electronic diffraction (SAED) was also taken on the same apparatus. The X-ray diffraction (XRD) patterns were obtained on a powder X-ray diffractometer (D/Max 2550 V, Rigaku, Japan), using Kα radiation (λ = 1.5418). UV–vis diffusion reflection spectrum (UV–vis) was performed on a Perkin-Elmer Lambda-20 spectrometer at room temperature. The Laser Raman spectrum was obtained with a Renishaw Raman system model 1000 spectrometer. The 514.5 nm radiation from a 20 mW air-cooled argon ion laser was used as exciting source. The gas sensitivity measurements were taken in an anhydrous environment, using electrochemical interface (Solartron SI 1287) and impedance/gain-phase analyzer (Solartron SI 1260).

3. Results and discussion

Fig. 1(a) displays the low-magnification SEM image of the CuS microspheres constituted by a great deal of stagger nanoslices. Most CuS microspheres have desert rose-shape and porous structures. High-magnification SEM image (in Fig. 1(b)) indicates that the size of the individual CuS microsphere is as small as 500 nm to as large as 2 μm and the thickness of the slices is in the range of 20–30 nm.

Moreover, the typical TEM image also exhibited a rose-shape structure (Fig. 2(a)). The SAED pattern inset in Fig. 2(b) confirmed that the as prepared CuS nanoslice was of a hexagonal and polycrystalline structure. The recent prepared CuS nanoslices are all single crystalline [16,21] but polycrystalline nanoslice is rarely reported. Recently, oriented architecture has attracted a great deal of attention in the field of crystallization process. Various types of growth process and mechanism were proposed in literatures. Zeng and Liu [22] have reported that rhomb-shaped 2D building blocks (formed from 1D nanoribbons) can self-aggregate into “dandelion”-like hollow spheres. Furthermore, Zeng and Yang [23] reported another novel organizing principle-oriented attachment mechanism in which complex geometrical structures can be built by the assembly route. Individual crystal sheet forming the hollow interior and geometrical symmetry SnO_2 octahedra was elucidated. In addition, Imai and Oaki [24] synthesized manganese oxide and cobalt hydroxide nanoflakes with mosaic interiors in aqueous solutions using polymers by biomimetic approach. The mosaic nanoflakes were made by the oriented architectures of the nanocrystals with the incorporation of polymers. High-magnification of individual nanoslice was examined directly by TEM (Fig. 2(b)), irregular lines can be observed, suggesting that the CuS nanoslices may be formed by the assembly of the 0D CuS nanoparticles during the heat-treatment process.

To substantially understand the growth mechanism of porous CuS microspheres consisted of polycrystalline nanoslices, we have

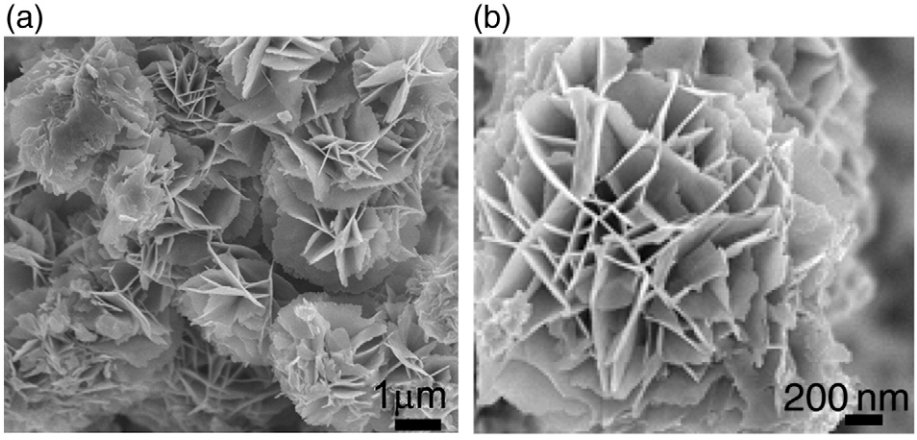

Fig. 1. SEM images of CuS microspheres at low-magnification (a) and high-magnification (b).

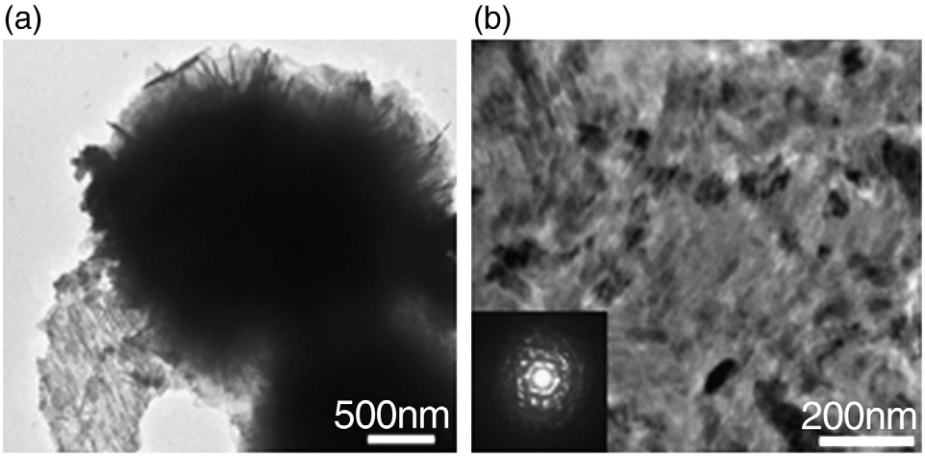

Fig. 2. TEM images of a single CuS microspheres (a) and individual nanoslice (b). The inset in (b) shows the SAED pattern.