研究简报

氧化亚铜单晶的声化学制备及表征

张 霞 陶小军 张治军* 吴志申 张平余
(河南大学特种功能材料重点实验室,开封 475001)

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Synthesis and Characterization of Cu_2O Single-Crystal by Sonochemical Method

ZHANG Xia TAO Xiao-Jun ZHANG Zhi-Jun* WU Zhi-Shen ZHANG Ping-Yu
(*Laboratory for Special Functional Materials, Henan University, Kaifeng* 475001)

Abstract: Cuprous oxide single crystal has been synthesized by sonochemical method through the thermal decomposition of copper acetate monohydrate in paraffin oil. TEM, XRD, SEM, ED and XPS techniques have been used to characterize its morphology, structure and composition. It is found that when the temperature is increased, decomposition from Cu_2O to Cu takes place.

Key words: cuprous oxide; sonochemical; single crystal; XPS

So far, many important semiconductor materials such as ZnO, SnO_2, Cu_2O, In_2O_3 have been synthesized by using a variety of techniques including sol-gel method[1], direct oxidation method[2], microwave irradiation[3,4], sonochemical method[5], solution dispersion[6] and so forth. Among them, sonochemical method has been developed very quickly. Ultrasonic is a high frequency sound waves with high energy that can generate instantaneously local high temperature as high as 5 000 K and local high pressure as high as 500 atm in a so-called "cavitation" in a solution. These transient, localized hot spots can drive many chemical reactions, such as oxidation, reduction, dissolution and decomposition *etc*[7].

As an industrially important material, Cu_2O is widely used in fields such as solar energy transformation, electronics, sensors, catalysis and so forth. The preparation of Cu_2O is limited for its instability and easy oxidization. It has been reported that Cu_2O single crystal could be fabricated using ethylene glycol as reduction agent through microwave method[8]. In this note, we present an one-step sonochemical method to synthesize Cu_2O ultrafine particles through the direct thermal decomposition of copper acetate monohydrate in paraffin oil. It is found that the morphology of Cu_2O particles could be easily controlled in the present study.

1 Experimental

All the reagents and solvents used were of analytical purity and were used without further purification. In a typical synthesis, copper acetate monohydrate (2.0 mmol) and sodium oleate (2.0 mmol) were added in 65 mL of paraffin oil. Here, sodium oleate acted as a stabilizer. The reaction mixture was exposed to high-intensity ultrasound irradiation under

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*通讯联系人。E-mail:zhangzhijun@henu.edu.cn
第一作者:张 霞,24 岁,女,硕士研究生;研究方向:无机材料的制备。

ambient air for 90 minutes at a constant temperature range of 180~220 ℃. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe immersed directly in the reaction solution. A large amount of brick-red precipitate was obtained. After cooling to room temperature, the precipitate was separated by centrifuging at a rotation rate of 12 000 rpm, washed with *n*-hexane (10 mL), ethanol (10 mL) and distilled water (10 mL) in sequence for three times and dried in air at room temperature.

The crystal structure and composition of the products were analyzed by X-ray powder diffraction (XRD). XRD measurement was performed on an X′ Pert Philips diffractometer equipped with Ni-filtered Cu $K\alpha$ radiation and operating at 40 kV and 40 mA. The composition of the products was also characterized by X-ray photoelectron spectrometer (XPS). The XPS was collected on an Axis Ultra X-ray photoelectron spectrometer, using mono-Al $K\alpha$ X-rays as the excitation sources. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate the morphologies of the sample. TEM pattern was obtained using a JEOL-JEM-100CX microscope (at an acceleration voltage of 100 kV) for samples deposited on carbon-coated copper grids. Samples for the TEM experiments were prepared by suspending the dried sample in absolute ethanol. A drop of the sample suspension was allowed to dry on a copper grid coated with a carbon film. SEM was obtained using JSM-5600 LV type scanning electron microscopy operating at a 4 kV accelerating voltage. Ultrasound irradiation was taken on a high-intensity ultrasonic probe (Ti-horn 20 kHz, 900 W·cm^{-2}).

2 Results and discussion

Fig.1 shows the typical XRD pattern of the product. All the diffraction peaks can be indexed to the cubic crystalline cuprous oxide (JCPDS card No. 75-1531). Refinement reveals that the cell contains lattice parameters a=0.426 6 nm which is consistent with corresponding literature value a= 0.426 0 nm. The peaks with 2θ values of 36.487°, 42.344°, 61.461° and 73.594° correspond to the crystal planes of 111, 200, 220 and 311 of crystalline Cu_2O, respectively.

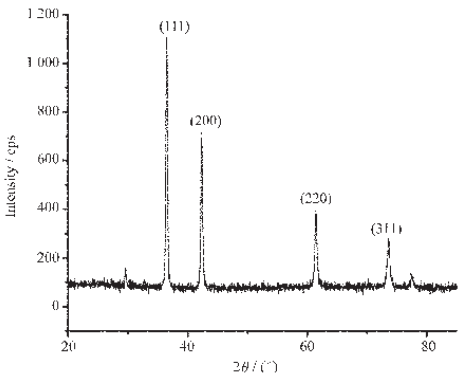

Fig.1 XRD pattern of the as-prepared cubic Cu_2O ultrafine paticles

The XPS spectrum (Fig.2) shows the composition of the sample, which is deconvoluted into two line peaks. The weak peak at 932.5 eV, which is corrected with reference to C1*s* (284.6 eV), corresponding to the binding energy of $Cu_{2p}^{3/2}$(Ⅰ), is in good agreement with the data of Cu_2O in the literature[9]. The weak peak at 934.5 eV, corresponding to the binding energy of $Cu_{2p}^{3/2}$(Ⅱ), is also observed, which is in good agreement with the data observed for $Cu(CH_3COO)_2H_2O$[10]. We infer that it may be from the starting material $Cu(CH_3COO)H_2O$. In addition, it is worth to note that the distinction between Cu(0) and Cu(Ⅰ) cannot be made from the XPS spectrum in Fig.2 only, because their band energy peaks are both at 932.5 eV. However, it is observed that the Auger spectrum shown in Fig.3 shows a peak at 916.5 eV in the CuL_3MM Auger spectrum, which is a characteristic peak of Cu(Ⅰ). The Cu (0) does not exist in the sample as shown by the absence of characteristic peak of 918.6 eV in the Auger spectrum. So according to the XPS and Auger data, we can further infer that the product is Cu_2O.

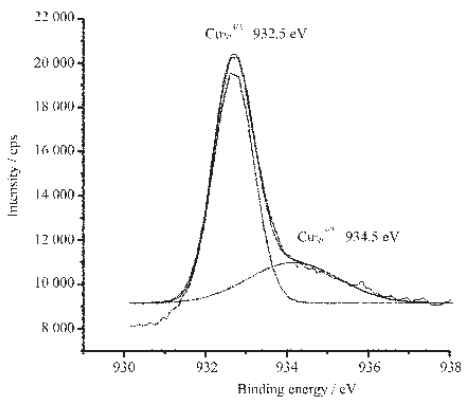

Fig.2 XPS spectrum of the Cu_2O ultrafine particles

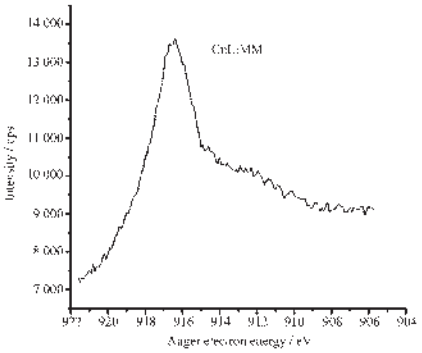

Fig.3 CuL_3MM Auger spectrum of the Cu_2O

SEM, TEM and Selected area electron diffraction (SAED) images of the sample are shown in Fig.4 (a), (b) and (c). SEM image indicates the synthesized Cu_2O particles have a large quantity of uniform cubic shape with a narrow size distribution. From Fig.4b, it can be seen that the size of most cubic shape Cu_2O is about 400~600 nm, but some small particles with size about 200 nm are also found. SAED pattern demonstrates that the ultrafine particles are single crystal and the diffraction dots can be indexed as (111), (220) crystal planes of cubic Cu_2O, which confirms the XRD results.

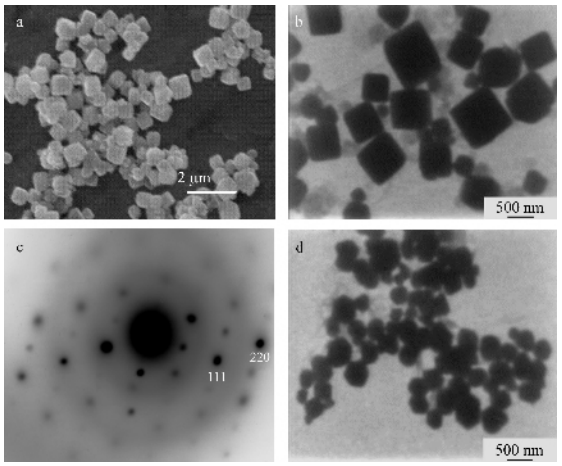

Fig.4 SEM (a), TEM (b) and SAED (c) images of Cu_2O single-crystal, TEM (d) pattern of Cu_2O synthesized with lower reagent density

In the course of the experiment, it was found that the reaction time and ultrasonic irradiation intensity had little effect on the size of the product, but when the reagent density decreased, smaller particles of Cu_2O were obtained. Fig.4d shows the TEM pattern of the product prepared with copper acetate monohydrate (1.0 mmol) and sodium oleate (1.0 mmol) as starting reagents. It can be seen the sample has a hexagonal and close-to-spherical shape with diameter of 200 ~ 300 nm.

In addition, it was found when the temperature was above 220 ℃, instead of cuprous oxide, only copper could be obtained (XRD not shown). The reduction from Cu_2O to Cu was carried out by Wang[11] who found that the reduction took place at 300~600 ℃. The low temperature reduction in our experiment was probably due to high-intensity ultrasound irradiation. According to the literature[11] the chemical reaction can be formulated as:

$$Cu(CH_3COO)_2H_2O \xrightarrow{180\sim220\ ℃} 1/2Cu_2O + 2CH_3COOH + 1/2O_2$$

$$Cu_2O \xrightarrow{\text{above } 220\ ℃} 2Cu + 1/2O_2$$

3 Conclusions

In summary, we have developed a one-step sonochemical route to synthesize Cu_2O single crystal through the thermal decomposition of copper acetate in paraffin oil. Compared with other method, this method is simple, suitable and practical for the preparation of Cu_2O ultrafine particles. Similarly, this method may be applicable for the preparation of other metal oxide particles such as ZnO, MnO *etc*.

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