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Blue Shift in the Oriented Cuprous Oxide Micro Structures Prepared *via* PEG-400 as the Soft Template by γ-Irradiation

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Cuprous oxide (Cu_2O) crystals with platelates structures were synthesized *via* γ-irradiation reducing reaction under ambient conditions, the polyethylene glycol-400 (PEG-400) as non-ionized surfactant and ethylenediamine tetraacetic acid disodium salt (Na_2EDTA) as chelator of Cu^{2+} ions. XRD and FESEM were used to illustrate Cu_2O crystals with platelates structures. The products were also been characterized by HRTEM, ED analysis and UV-VIS absorption spectrum. All the results indicated that the Cu_2O crystals with platelates were successfully prepared under γ-irradiation. The possible mechanism is that the existence of EDTA ions and polyethylene glycol may make growth rate along the <111> direction far exceeding that of the <100> direction, leading to the formation of platelate structure Cu_2O at last. Its UV-VIS absorption peak revealed blue shift phenomena, with the corresponding band gap of 2.25 eV, the size effect resulted in an obvious blue shift.

Key Words: Nanoparticels, Eectron microscopy, γ-Irradiation, Optical properties.

INTRODUCTION

The properties of nanocrystals depend not only on their composition, but also on their structure, phase, shape, size and size distribution. Furthermore, the architectural control of nanosized materials with well-defined shapes is important for the success of "bottom-up" approaches toward future nanodevice[1,2]. And such nanodevices have potential applications in nanoelectronic devices, nanooptical devices and chemical sensors[3,4], *etc*. To develop ways of tailing the nanomaterials with desired morphologies is quite important and difficult. The ability to manipulate the morphology, size and size distribution of inorganic nanomaterials remains an important goal in modern materials chemistry. The shape of inorganic nanocrystals has much influence on their widely varying physical properties[5,6]. Thus, the synthesis of inorganic nanocrystals of controlled shape arouses great interest. A series of relevant efforts has been paid on the shape' control, the synthesis of single crystalline nanocrystals with advanced structure is still in the developing stage.

Copper oxide (Cu_2O) nanostructures have attracted significant attention as it is one of the first known *p*-type direct band gap semiconductor with a band gap of 2.17 eV[7,8]. This makes it a promising material for the conversion of solar energy into electrical or chemical energy[9-11]. The growing interest in Cu_2O nanostructures is due to several reasons. Some of these are (i) Cu_2O is a potential photovoltaic material which is low cost, nontoxic and can be prepared in large quantities[12,13], (ii) excitons created in Cu_2O have been shown as suitable candidates for Bose Einstein condensate because of the large exciton binding energy of 150 meV[14] and (iii) Cu_2O has been reported to act as a stable catalyst for water splitting under visible light irradiation[15,16]. The Cu_2O nanostructures have been prepared by several methods such as (water-ethylene glycol) mixed-solvothermal route[17], seed-mediated synthesis[18], Ultrasonic radiation[19], *etc.* Based on these approaches, synthesis of Cu_2O nanostructures demands complex process control, high reaction temperatures, long reaction times, expensive chemicals and specific method for specific nanostructures.

In this paper, we developed a facile synthesis of micrometer-sized Cu_2O crystals with platelates structures *via* γ-irradiation and surfactant-assisted under ambient conditions.

We used EDTA as chelator of Cu^{2+} ions, PEG-400 (polyethylene glycol-400) as non-ionized surfactant and hydrated electrons generated by γ-radiolysis of water as reductive agents to obtain micrometer-sized Cu_2O crystals with platelate structures *via* nucleation and anisotropic crystal growth processes under room temperature and ambient pressure.

EXPERIMENTAL

All the reagents purchased from the Shanghai Chemical Company, such as cupric chloride ($CuCl_2$), ethylenediamine tetraacetic acid disodium salt (Na_2EDTA), polyethylene glycol-400 (PEG-400), sodium hydroxide (NaOH), isopropyl alcohol and *n*-propyl alcohol, were analytically pure and used without further purification. Distilled water (DI) was used for all solution preparation.

In a typical procedure, 0.31 g of $CuCl_2$, 0.40 g of Na_2EDTA and 2.56 g of PEG-400 (with the concentration of 0.40 mol/L) were dissolved in 16.00 mL of distilled water and 4 mL isopropyl alcohol (as a scavenger of oxidative radicals such as ·OH). This solution was stirred for 0.5 h to ensure that the PEG, Na_2EDTA and $CuCl_2$ dissolved completely. Then, 4.0 mol/L aqueous NaOH solution was added drop-wise to adjust pH = 12-13. Finally, the obtained blue solution was intensively stirred for 1 h at room temperature and then placed in the field of a 1.30×10^{15} Bq ^{60}Co γ-ray source at a dose rate of 38 Gy/min for different time to absorption different absorbed dose (kGy) (sample 1-5). The same recipe for sample 6 was in the absence of PEG-400 (absorbed dose 57.00 kGy). After irradiation, the brick red precipitates were collected and washed with acetone and distilled water for three times, respectively, then dried in a vacuum oven for 24 h at 5 ºC. The experimental conditions were summarized in Table-1.

TABLE-1
IRRADIATION-TEMPLATE METHOD TO FABRICATE ORIENTED CUPROUS OXIDE PLATELATES*

Sample	PEG (g)	Time (h)	Absorbed dose (kGy)	Shape	Size (μm)
1	2.56	5	11.40	Irregular	0.2-0.5
2	2.56	10	22.80	Platelates	0.4-0.7
3	2.56	15	34.20	Platelates	0.4-1
4	2.56	20	45.60	Platelates	0.5-1.5
5	2.56	25	57.00	Platelates	0.5-1.5
6	–	25	57.00	Nanocluster	0.4

*The polymerizations were carried out in $CuCl_2$ (0.31 g), Na_2EDTA (0.40 g), PEG-400 (2.56 g) distilled water (16 mL) and 4 mL isopropyl alcohol at a dose rate of 38 Gy/min for different time to absorption different absorbed dose.

The powder X-ray diffraction pattern of as-synthesized samples was recorded with a Japan Rigaku D/max λ_A X-ray diffractometer equipped with graphite monochromatized CuK_α irradiation (λ = 0.154178 nm). The scan rate of 0.06º s^{-1} allowed to record the pattern in the 2θ range of 20-80º. The selected area electron diffraction (SAED) patterns were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. FESEM (JEOL JSM-6700) with the acceleration voltage of 5 kV Ultraviolet-visible (UV-VIS) absorption spectrum was recorded by dispersing Cu_2O platelates in distilled water on a UV-2100 Shimadzu spectrophotometer at room temperature.

RESULTS AND DISCUSSION

Fig. 1. shows the XRD patterns of sample 2 and 4. All of the reflection peaks can be indexed to platelets Cu_2O (JCPDS No. 05-0667). No other diffraction peaks arising from possible impurities such as Cu and CuO were detected, indicating

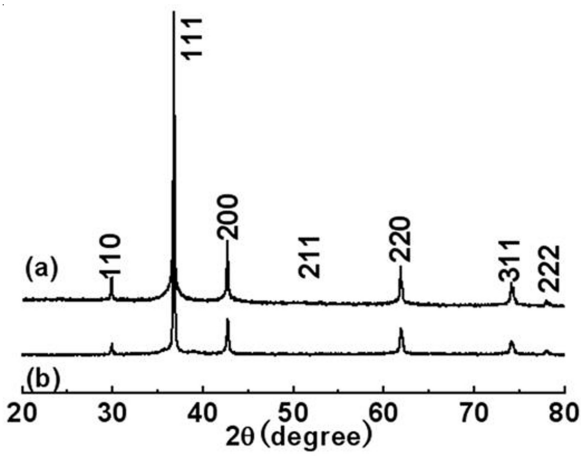


Fig. 1. XRD patterns of (a) sample 2; (b) sample 4

pure Cu_2O was obtained under this experimental condition. The high intensity of the {111} diffraction peak is probably due to the orientation of the crystals suggesting that the obtained crystals are mainly dominated by {111} facets and the {111} planes tend to be preferentially oriented parallel to the surface of the supporting substrate.

The reaction reagents and shape of Cu_2O crystals with platelate structure are summarized in Table-1. The shape and size of Cu_2O crystals with platelates structure were characterized by FESEM as shown in Fig. 2. Fig. 2. give the different shape of Cu_2O crystals according to the different absorbed dose at a dose rate of 38 Gy/min. When the absorbed dose is 11.40 KGy, the FESEM is shown in Fig. 2a. When make the absorbed dose higher and higher, there have more and more Cu_2O crystals' nano-platelates were formed, many nano-platelates assemble together to form just like a structure. Fig. 2 can give some evidences in focus. The contrastive FESEM of sample 6 is shown in Fig. 2f. There have many Cu_2O nanocrystals and not get together to form platelates.

The crystal orientation and crystallinity of Cu_2O crystals nano-platelate are further studied with SAED (Fig. 3a-b). In this measurement, SAED image was recorded by aligning the electron beam parallel to the $[1\bar{1}1]$ zone axis. From Fig. 2f, there are three sets of distinct lattice spacing of *ca*. 0.30, 0.45 and 0.26 nm, which correspond to the (001), (010) and (011) planes of Cu_2O, respectively, indicating the high crystallinity of the single nano-platelate.

The possible formation mechanism of Cu_2O may be as follows:

Radiolysis of water:

$$H_2O \xrightarrow{\gamma} e_{aq}^-,\ H^{\cdot},\ {}^{\cdot}OH, H_3O^+, H_2, H_2O_2,\ etc. \quad (1)$$

Reduction of $Cu^{2+}[Cu(II)(EDTA)]^{2-}$ $\xrightarrow{e_{aq}^-}$ Cu^+

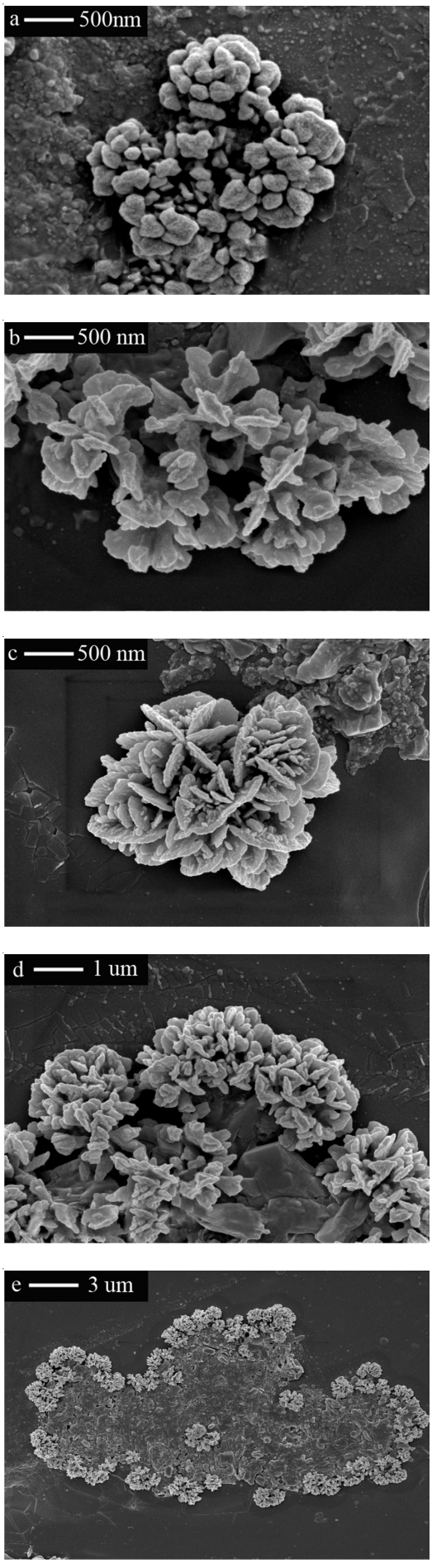
$$\xrightarrow{OH^+} CuOH \rightarrow 1/2Cu_2O + 1/2H_2O \quad (2)$$

Reduction of Cu^{2+} to Cu^+:

$$2CuO + 2e_{aq}^- + H_2O \rightarrow Cu_2O + 2OH^- \quad (3)$$

Some oxidative radicals such as ˙OH were scavenged by isopropyl alcohol.

$$^{\cdot}OH + CH_3CH(OH)CH_3 \rightarrow H_2O + (CH_3)_2(OH)C^{\cdot} \quad (4)$$



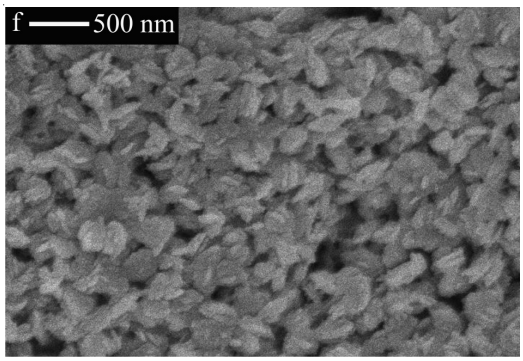


Fig. 2. FESEM of sample (1) a, (2) b, (4) d, (5) e and FESEM of a special area of sample (5) c; FESEM of sample (6) f (without PEG)

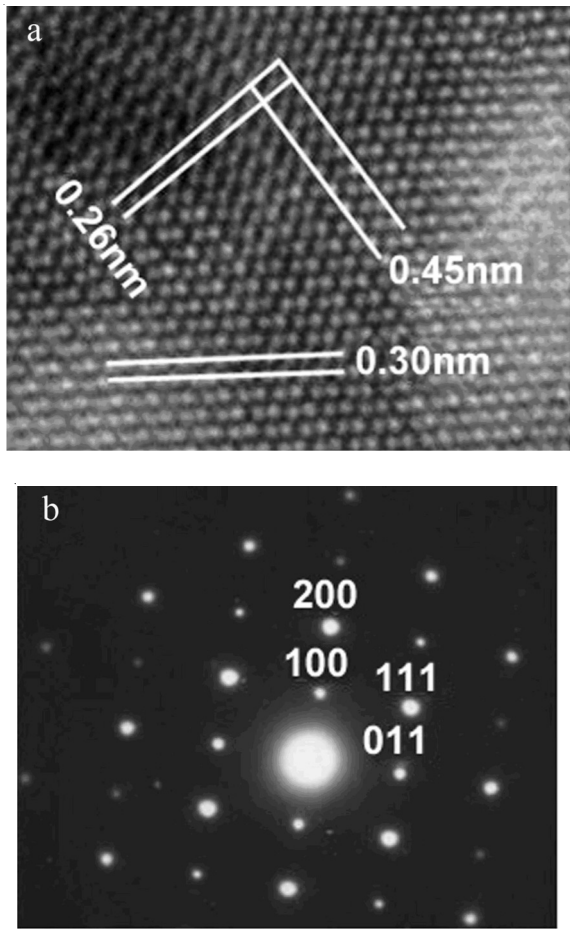


Fig. 3. (a) A lattice-resolved HRTEM image of sample 5 (b) ED pattern taken on the tip of the inset of sample 5

First, the γ-radiolysis of water produce many active intermediates, such as strong reductive hydrated electrons (-2.77 eV) and oxidative radicals ˆOH (eqn. 1). Isopropyl alcohol is introduced to scavenge ˆOH and the obtained $CH_3\dot{C}OHCH_3$ (eqn. 4) radicals also possess reducibility (-1.1 V), which keeps the system under a reductive condition[20] together with e_{aq}^-. Secondly, after Cu^{2+} has been coordinated with EDTA to form $[Cu(II)(EDTA)]^{2-}$, it would be reduced into Cu^+ by e_{aq}^- subsequently. At last, OH^- quickly combines with Cu^+ to form CuOH, which finally decomposes into Cu_2O (reaction 2). On the other hand, the CuO particles from the decomposition of $Cu(OH)_2$ are then reduced to Cu_2O by e_{aq}^-.

At the same, the non-ionized surfactant PEG-400 might be playing an important role during the fabrication of the Cu_2O nano-crystals. As illustrated by Xia and Wang *et al.*[21,22], the shape of an fcc nano-crystal was mainly determined by the ratio between the growth rates along 100 and 111 directions and the morphologies can be kinetically controlled by adding chemical capping reagents to the synthetic systems. The non-ionized surfactant PEG forms aggregate structure due to the assembly in water[23]. Then a lot of 1D liquid reaction fields could be formed when PEG and a small quantity of water are mixed together. These reaction fields are dispersed in different directions. When a high electric field is provided these reaction fields may be aligned. However, PEG assembly structures in water are flexible and aggregate. Furthermore, the strong affinity of the PEG oxygen atoms for Cu^+ results in the Cu^+ adhere to PEG aggregates. Therefore, it is reasonable that the platelateed structure Cu_2O was obtained under our experiment condition. Although the exact mechanism for the formation of the platelateed structure Cu_2O is still not fully understood, PEG plays important roles in the formation of well-defined Cu_2O nanocrystals with advanced structure.

Fig. 4a. illustrates the UV-VIS absorption spectrum of the Cu_2O platelates dispersed in distilled water. It should be noted that using the data in Fig. 4a showing a considerable blue shifts phnomena of the absorption edge in the transmission spectra of Cu_2O as the amount of platelates are increased. The center absorption peaks position of samples between 290-390 nm (sample 1 to sample 5)[8]. The band gaps of Cu_2O platelates is calculated according to the formula as below: $(\alpha Ep)^2 = K(Ep - Eg)$ (α is absorption coefficient, K is constant, Ep is photo energy, Eg is band gaps)[24]. The band gaps of Cu_2O platelates is about 2.25 eV according to the curve $(\alpha Ep)^2$ Ep (Fig. 4b) and bigger than bulk Cu_2O nanomaterials (2.17 eV).

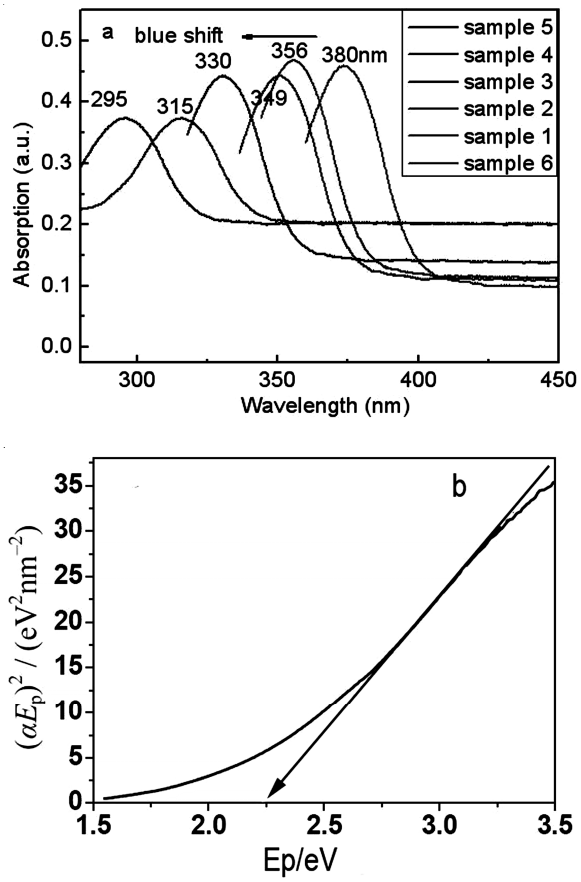


Fig. 4. (a) UV-VIS absorption spectra and (b) $(\alpha Ep)^2$-Ep curve of Cu_2O platelates

Conclusion

In summary, a facile method has been developed to prepare micrometer-sized Cu_2O crystals with platelate structure. The preparation of such Cu_2O crystals is carried out under ambient conditions and in γ-irradiation field using PEG as the non-ionized surfactant. The reaction process and shape evolution was investigated by the assistance of XRD and FESEM analyses. The chemical processes can be divided into the following steps: the Cu^{2+} ions are converted to CuO and Cu_2O in the earlier stage of the reaction, then CuO and Cu^{2+} ions are consecutively reduced to Cu_2O under our experimental conditions. At the same PEG plays an important role during the formation dendritic Cu_2O with platelate structure and the existence of EDTA ions affects the ratio of the growth rate along the <111> *versus* the <100> direction. The UV-VIS absorption peak of Cu_2O platelates appears at about 370 nm and with the corresponding band gap of 2.25 eV, reveals the quantum size effect of Cu_2O platelates.

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