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Understanding of water-assisted template-free synthesis of Cu_2O microrods

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ABSTRACT

Preparation of Cu_2O microrods was designed by a rapid water-assisted template-free method under solvothermal condition at 150 °C/2 h using copper salt, di-methyl formamide and water. Powder X-ray diffraction (PXRD) revealed the existence of Cu_2O phase in the as-synthesized samples. Morphological features showed the microrod (18–33 μm length) architecture of Cu_2O in the presence of excess amount of water (15 mL). The role of water contents on the microstructural evolution and optical features of Cu_2O microrods was demonstrated. A tentative formation mechanism for the evolution Cu_2O microrods was proposed.

1. Introduction

As p-type semiconductor cuprous oxide, Cu_2O (band gap 2.17 eV) has been fascinated remarkable curiosity in recent years due to its probable function in organic catalytic reaction [1], solar energy conversion [2], lithium ion batteries [3], gas sensors [4], photocatalysis [5], CO oxidation [6] and antibacterial application [7]. Significant effort has been employed for the fabrication of Cu_2O microstructure such as solvothermal approach [8], template-free technique [9], γ-irradiation process [10] and selective oxidative etching method [11]. The several Cu_2O architectures in literature include nanocubes [12], polyhedral [13], hexapod [14], nanosphere [15], flower-like [16] etc. Sui et al. reported recrystallization induced self-assembly (RISA) strategy for the fabrication of Cu_2O nano-frames and nano-cages by green synthetic route [17]. Recently, Sun et al. have synthesized cuboctahedral Cu_2O microcrystals using one-pot solution-phase selective-etching technique for the photocatalytic application [18]. Cu_2O is unstable in aqueous medium. However, Mishra and Pradhan synthesized Cu_2O in the presence of PVP as capping agent and $NaBH_4$ as reducing agent in aqueous medium [19]. It is a great challenge to prepare phase-pure Cu_2O and their morphological evolution by changing the sole water concentration in aqueous medium without using any templating agents. In the present report, we demonstrate a rapid template-free solvothermal synthesis of Cu_2O microrod at 150 °C/2 h using copper nitrate, di-methyl formamide (DMF) and deionized (DI) water.

In this study, the effect of water on the morphological changes of Cu_2O microcrystals has been investigated. The importance of the present work is to explore how water can play a prime role in controlling the growth of Cu_2O microcrystals with different shapes and facets. To the best of our knowledge, water manipulative investigation for transformation of hexapod microcrystal to microrod shaped Cu_2O has never been reported before.

2. Experimental

For the synthesis of cuprous oxide microrod, the procedure was employed according to our previously reported method [14]. In a typical method, 5 mmol copper nitrate trihydrate was added into 100 mmol DMF followed by adding different amounts of water (2.5–15 mL) under stirring for 30 min at room temperature. The above solution was treated at 150 °C for 2 h under solvothermal reaction, and subsequently centrifuged three times with ethanol and dried at room temperature overnight.

X-ray diffraction (XRD) was carried out by powder diffractometer (Philips X'Pert Pro PW 3050/60) using Ni-filtered Cu-K_α radiation (λ = 0.15418 nm) operated at 40 kV and 30 mA. Morphology of the samples was studied by FESEM (Zeiss, Supra™ 35VP) with 10 kV accelerating voltage. UV–VIS-NIR spectrophotometer

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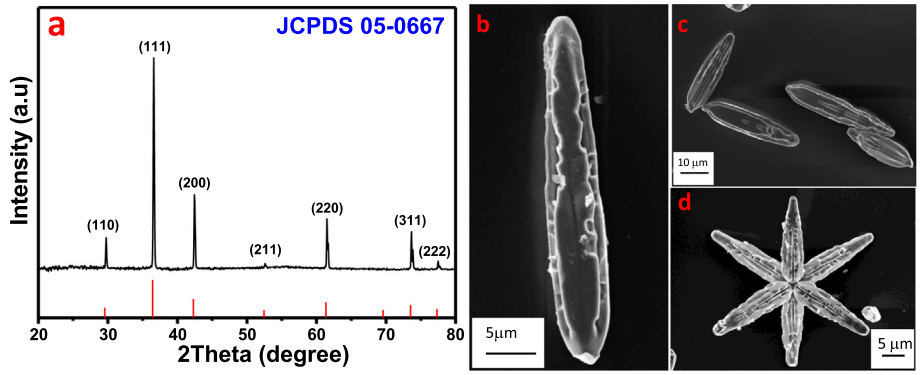

Fig. 1. (a) XRD and (b, c, d) FESEM images of Cu_2O microcrystals prepared at 150 °C/2 h in the presence of 15 mL water: (b) single microrod, (c) multiple microrods, (d) elongated hexapod.

(UV3600, Shimadzu, Japan) was used to study UV–Vis diffuse reflectance.

3. Results and discussion

The crystalline phase of the product was studied by XRD study. Fig. 1a reveals the XRD patterns of the as-prepared Cu_2O microrods obtained at 150 °C/2 h in presence of 15 mL of water. It shows the characteristic peaks of cubic Cu_2O (JCPDS No. 05-0667). The crystallization feature was further examined by the variation of water content from 2.5 mL to 15 mL at 150 °C (Fig. S1, ESI). For all the samples, the absence of signature peaks of Cu and CuO reflects the phase-pure Cu_2O in the as-prepared samples. Fig. 1b, c shows the FESEM images of as-prepared Cu_2O microrods (length 18–33 μm) obtained with 15 mL of water. However, in the presence of Cu_2O microrods, a few amount of elongated hexapod with twenty-four {1 1 1} facets (Fig. S2, ESI) were noticed. The length and width of elongated hexapods were found to be 18–26 and 4–6 μm, respectively resembling significant symmetrical stacking faults from center to the apex of each facet (Fig. 1d).

The role of water in controlling the crystal growth process of Cu_2O was further investigated. Fig. 2 shows the FESEM images of Cu_2O microcrystals obtained with (a) 2.5 mL, (b) 5 mL, (c) 7.5 mL and (d) 10 mL of water respectively. In the presence of 2.5 mL of water, Cu_2O hexapod was generated (Fig. S3a, ESI). The surface of {1 1 1} facets looked rough enough indicating lower packing density among the crystallites [20]. The length and width of the branch were found to be around 8–24 μm and 4–8 μm, respectively. Interestingly, with increase in the amount of water from 5 to 7.5 to 10 mL, the length/width ratios of each branch of the hexapod became 9–15/4–7, 10–18/4–8, and 12–22/4–8 μm, respectively (Fig. S3b,c, d, ESI). However, surface of hexapod became smoother indicating better oriented attachment and denser packing among the crystallites.

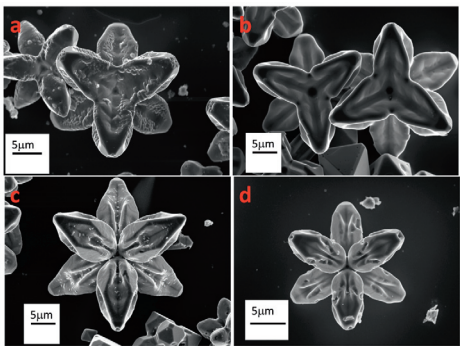

Fig. 2. FESEM images of Cu_2O microcrystals prepared at 150 °C/2 h in the presence of (a) 2.5 mL, (b) 5 mL, (c) 7.5 mL and (d) 10 mL of water.

Under solvothermal condition, formic acid (HCOOH) and di-methyl amine (Me_2NH) are formed via the hydrolysis of DMF [21]. Here, HCOOH acts as reducing agent while Me_2NH behaves as structure directing agent. In the presence of Cu^{2+} ions in solution, the hydrolysis reaction follows as:

$$HCON(Me)_2 + H_2O \rightarrow Me_2NH + HCOOH \quad (1)$$

$$2Cu^{+2} + HCOOH + 4Me_2NH + H_2O \rightarrow Cu_2O + 4Me_2NH_2^+ + CO_2 \quad (2)$$

On the basis of above observation, it is believed that with increase in water content, more hydrolyzed product (e.g., Me_2NH) is generated, which facilitated significant interaction between the polar molecules and unsaturated Cu in the {1 1 1} surface. Therefore, higher growth rate of six unstable {1 0 0} facets leads to the formation of elongated hexapod [22]. With enlargement of crystal size, the supersaturation difference between apex and center of facets become significant resulting faster growth rate of apexes [23]. Moreover, mass transport diffusion introduces a more concentrated zone on the apexes and less concentrated zone at the center of the facets rendering multilevel branching on the facet of Cu_2O microcrystal [24]. When the amount of water was further increased, the higher growth rate of apexes favors further elongation, and the highly strained-elongated hexapod microcrystal splits into separate 1D microrods (Fig. 1b,c). The symmetrical stacking faults remained in the 1D microrod which could be attributed to the existence of concentration gradient for morphological evolution of Cu_2O microcrystal [25].

The UV–Vis diffuse reflectance of Cu_2O microrods is shown in Fig. 3a. The band gap was calculated from the optical absorption diagram employing the relation;

$$(\alpha\, h\nu)^{1/n} = A(h\nu - E_g) \quad (3)$$

where A, h, hν, E_g, α and n indicate proportionality constant, Planck's constant, photon energy, band gap energy, absorption coefficient and exponent, respectively. By extrapolating the linear region of the plot $(\alpha\, h\nu)^{1/n}$ *vs.* photon energy (hν) considering direct permitted transition (n = 1/2), the band gap energy (approximate) is calculated (Fig. 3b). Fig. 4 shows (a) the UV–Vis diffuse reflectance and (b) band gap energy plot of reference Cu_2O bulk sample. The band gap energy of synthesized Cu_2O microrod and the reference sample were found to be 1.89 and 2.15 eV, respectively. The UV–Vis diffuse reflectance and $(\alpha\, h\nu)^{1/n}$ *vs.* photon energy (hν) plots of Cu_2O hexapods obtained with different water contents is shown