Versatile synthesis of rectangular shaped nanobat-like CuO nanostructures by hydrothermal method; structural properties and growth mechanism

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1. Introduction

Micro- and nanostructures with well-defined shape and inner structure have attracted great interests due to their novel properties and diverging applications [1–6]. Self-assembly driven by various interactions, such as surface tension, capillary effects, electric and magnetic forces, and hydrophobic interactions, is an effective strategy for forming versatile “soft” nanocrystal-assembly motifs [7,8]. Copper oxide (CuO) is a narrow band gap semiconductor material. It possesses unique physical properties and great potential for diverse electronic and photonic applications that require superconductivity, colossal magnetoresistivity, and piezoelectricity. [9–12].

The great diversity of applications needs the distinct morphological and functional CuO nanostructures. The tailored organization of primary building block units into curved structures represents another challenge for nanomaterial self-assembly, such as hollow spheres, and tubular structures that are highly required for newly emerging applications [15–17]. Considering the potential applications of copper based material, various kinds of morphologies have been reported, such as wires, monodisperse nanocubes, octahedral nanocages, hollow nanospheres, etc. [7,18–30].

In this work, we report a facile template-less and surfactant-free hydrothermal approach to synthesize well-defined CuO nanostructures with rectangular shaped nanobat-like CuO nanostructures. The morphology and dimensionality of CuO nanoarchitectures can be tuned by simple variation of reaction parameters.

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2. Experimental

All the reagents used in the experiments were analytically pure, purchased from Shinyo Pure Chemicals Co. Ltd. and Sigma–Aldrich. In a distinctive procedure for the synthesis of CuO nanostructures, copper (0.2 M) solution was prepared in a beaker by mixing Cu(NO$_3$)$_2$·3H$_2$O in a double distilled water, which was stirred with magnetic stirrer till the solution became transparent. The above solution was mixed with urea (0.2 M) under continuous stirring, and then it was transferred into Teflon-lined stainless steel autoclave of 100 mL capacity. The autoclave was maintained at 100–150 °C for 6–12 h and then cooled to the room temperature. The obtained black precipitates were washed several times with double distilled water to remove the impurities such as surfactants and then dried at 75 °C for 6 h. The effect of pH and reaction precursor is also investigated in details.

The crystallinity and crystal phase of the synthesized products were examined by X-ray diffraction (XRD) measured with Cu-Kα radiation. The surface morphology of the as-synthesized product was observed by field emission scanning electron microscopy (FESEM). Detailed structural properties of the obtained product were analysed by transmission electron microscopy (TEM) equipped with SAED patterns. The chemical composition was analysed by X-ray photoelectron spectroscopy (XPS). The Raman spectra measurements were performed at room temperature using the 488 nm line of an argon ion laser as the excitation source.

3. Results and discussion

3.1. Surface morphology and structural properties of CuO nanostructures

The formation of crystalline CuO nanostructures was confirmed by the use of XRD. Fig. 1 shows XRD spectrum of rectangular shaped nanobat-like CuO nanostructures.
CuO nanostructures. All the diffraction peaks can be indexed to the monoclinic phase of CuO (S.G. C2/c; with lattice constants of $a = 4.684$ Å, $b = 3.425$ Å, $c = 5.129$ Å, and $\beta = 99.47^\circ$). The broadening of all recorded peaks in the spectrum indicates the presence of nanoscale crystallites. No other impurities were detected by XRD analysis, indicating the phase purity of CuO rectangular shaped nanostructures. The synthesized powder is composed of JCPDS (05-0661, 13-0420) data of CuO with monoclinic phase.

The morphology of as-synthesized CuO products was observed by using FESEM analysis and is shown in Fig. 2(a) of a low magnification FESEM image of CuO microspheres. Interestingly, the morphology of CuO structures grown under optimized reaction conditions represents microspheres that are composed of well-organized rectangular shaped nanostructures. It can be seen that several curved rectangular shaped structures were self-organized themselves into the spherical assemblies with bulbous appearance. Fig. 2(b) shows a high magnification FESEM image of a single CuO microsphere. The rectangular shaped nanostructures are densely packed to the architecture of microsphere. Each microsphere has a diameter of $8 \pm 2$ μm. Fig. 2(c) shows its magnified FESEM image of rectangular shaped structures. The term “nanobat-like structure” in this study is used to describe the structural evolution that each CuO nanorods shows acicular growth behavior at one end and become a rectangular shaped structure as growth proceeds. It is important to note that most of the rectangular shaped nanorods show this typical morphology. The well-faceted end and side surfaces of perfectly grown rectangular shaped nanobat-like structure are also clearly observed in Fig. 2(c). Each nanobat-like CuO nanostructure has a diameter of $\sim 70$ nm, thickness of $\sim 8$ nm and length of $\sim 174$ nm. Fig. 2(d) shows a low magnification FESEM image of a single microsphere broken by ultrasonication, which demonstrates that inner part of these microspheres is empty. This inimitable nanobat-like morphology is different from other shapes and not yet reported in CuO crystals for the case of growth with or without using any surfactant and modifier polymers or organic additives. Fig. 2(e) shows a FESEM image of side faceted nanorods obtained by increasing initial pH of reaction solution to 5.36 (mild acidic). The inset shows a single microsphere composed of rectangular shaped CuO nanorods. Fig. 2(f) demonstrates nanopetal-like CuO nanostructures formed in the presence of sodium hydroxide (NaOH) at pH 6.2.

The detailed structural analysis of as-grown rectangular shaped nanobat-like CuO nanostructures was performed by TEM and high resolution TEM (HRTEM). For TEM analysis, the CuO nanobat-like nanostructures were ultrasonically (30 min) dispersed into acetone and a drop of acetone, which contains the CuO nanostructures, was placed on the TEM grid. Fig. 3(a) shows a low magnification TEM image of each microsphere composed of nanobat-like structures. In order to obtain a single rectangular shaped nanobat-like structure, the ultrasonication time was increased to 50 min. Fig. 3(b) shows a high magnification TEM image of single rectangular nanobat. In Fig. 3(b) one can observe rectangular shaped nanobat having ends with a small faceted nano-grip-like structure. It is important to note that the side facets of rectangular structure can be evidently observed in Fig. 3(b). Fig. 3(c) represents a SAED pattern taken from the center of nanobat, which indicates that these CuO nanostructures are single crystalline and grown along $[0 \ 1 \ 0]$ direction. Fig. 3(d) is the HRTEM image taken on the specific nanobat-like structure. The clear fringe spacing of 0.25 nm that is perpendicular to the long axis of the nanobat, accords well with the d value of the monoclinic CuO crystal plane, which indicates that the CuO nanobats grew along the [0 1 0] direction. The TEM results fully accord with the XRD and FESEM results.

Fig. 4 shows the Raman spectra of the rectangular shaped CuO nanostructures. CuO belongs to the $C_{2h}^{6}$ space group with two molecules per primitive cell. One can find the zone center Raman active normal modes $\Gamma_{A1} = 4Au + 5Bu + Ag + 2Bg$. There are three acoustic modes ($Au + 2Bu$), six infrared active modes ($3Au + 3Bg$), and three Raman active modes ($Ag + 2Bg$). Three Raman active optical phonons have been identified and comparable to that reported in the literature by other methods [21]. The Raman analysis of the CuO sample confirmed the three known bands like 297, 346 and 631 cm$^{-1}$, which is with good agreement with the

![Fig. 3](image-url)
reported data [29]. These significant peak intensities indicate the single phase property and high crystallinity of as-grown samples.

The phase purity and chemical composition of the as-grown sample was investigated by X-ray photoelectron spectroscopy. In Fig. 5(a), wide survey scan spectra of the as-prepared sample was carried out and it was found that only CuO and C peaks were present. In Fig. 5(b), the peaks at 932.2 and 952.9 are attributed to the Cu 2p 3/2 and Cu 2p 1/2, respectively. The satellite peaks are also produced by Cu²⁺. In Fig. 5(c), the O 1s core-level spectrum is broad, and two O 1s peaks can be resolved by using curve-fitting procedure. The peak observed at 529 is in an agreement with O²⁻ in CuO, while peak at 531.2 eV is attributed to O adsorbed on the surface of rectangular shaped structure of CuO. Thus XPS result indicates that the sample is composed of CuO. In Fig. 6, the weight loss was observed in the region between 320 and 400 °C where reduction of CuO might occur.

3.2. Growth mechanism for the formation of nanobat-like CuO nanostructures

The formation scheme of nanobat-like CuO nanostructures in this work is discussed according to the growth mechanism as illustrated in Fig. 7. In this reaction the Cu(NO₃)₂·3H₂O and urea were used as reagents. Urea acts as pH buffer to control the supply of OH⁻ ions. Before the start of precipitation reaction, the solution has pH value of 5.26. The possible chemical reaction is as follows:

\[
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3 \quad (1)
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (2)
\]

\[
2\text{OH}^- + \text{Cu}^{2+} \rightarrow \text{Cu(OH)}_2 \quad (3)
\]

\[
\text{Cu(OH)}_2 \rightarrow \text{CuO + H}_2\text{O} \quad (4)
\]

In the suggested reaction scheme, urea played key role for the formation of desired CuO nanostructures. In the initial stage, urea reacts with water and forms ammonia and carbon dioxide. The formed ammonia further reacts with water and produces ammonium ions and OH⁻ ions. This is a crucial stage in this distinctive chemical reaction since this stage controls the supply of OH⁻ ions which is most important for the formation of CuO nanostructures. The first is initiation, in which reaction slowly generates building units of solids into solution (b). The concentration of building units in the reaction solution increases continuously until a crucial super-saturation level is reached and

![Fig. 4. Raman spectrum of rectangular shaped nanobat-like CuO nanostructures.](image)

![Fig. 5. (a) Wide XPS survey scan spectra of the as-grown nanobat-like CuO nanostructures; (b) the peaks attributed to the Cu 2p 3/2 and Cu 2p 1/2; and (c) the O 1s core-level spectrum and two O 1s peaks resolved by using curve-fitting procedure.](image)

![Fig. 6. Thermogravimetric (TG) profile of nanobat-like CuO nanostructures.](image)
nucleation starts (c) [30]. It is well-known that the crystallographic structure of the nuclei and seeds, during the nucleation process and their subsequent growth stage, is the key parameters in influencing the final shapes of the nanocrystals (d). The structure of CuO nanoparticles might be changeable at this stage due to a buffer effect until the crystal kinetically locks into a well-defined shape. The variation in two different sized CuO nuclei is due to the elevating pH of reaction solution (c). With the increase of reaction time the size of CuO crystal increases and forms bigger crystals. The growth of rectangular shaped nanobat-like structure can be further understood on the basis of polar surfaces of CuO crystals and crystallographic planes. The anisotropic growth of monoclinic CuO crystal can be described as alternating planes composed of \(\text{O}^–\) and \(\text{Cu}^{2+}\) which are stacked alternately along the specific directions [31,32]. The difference in the speed of growth is caused by the crystallographic faces. The growth rate is sequenced in our rectangular shaped nanobat-like structure: \([0 \ 1 \ 0]\) length > \([1 \ 0 \ 0]\) - breadth > \([0 \ 0 \ 1]\) height.

According to Bravais–Friedel–Donnay–Harker analysis, the growth speed of CuO crystal is proportional to \(1/dhkl\), therefore, the rectangular crystals elongate along the \([0 \ 1 \ 0]\) direction [33,34]. The slowest growing phase determines morphology of crystals [35,36]. Thus, under the experimental conditions and the kinetic difference in the growth planes, the slowest growing (0 1 0) planes dominate the crystal into the typical rectangular shaped structure (e). The formation of nanobat-like structure can be attributed to oriented attachment mechanism. In the process of oriented aggregation, the single crystalline nanobat-like structure forms through oriented arrangement by rotating adjacent divergent sized rectangular structure (e) to allocate identical crystallographic orientation [37,38]. It can be realized that controlled aggregation likely takes place along \([0 \ 1 \ 0]\) direction which has highest reactivity [39]. In general, during the anisotropic crystal growth, tiny primary crystals at their high-energy surfaces are energetically favored since the formation of large crystals can greatly reduce interfacial energy. Thus, we can conclude that the ultimate crystal with well-defined shape and morphology can be attained by adjusting crystal along the three preferred directions pursued by reorganization and crystallization process. To substantiate the formation of rectangular shaped nanobat-like structure via orientation attachment, TEM study was carried out (f).

Consequently, the reorganization and assembling of microsphere-like structures comprised of nanobats was further elucidated by ultrasonically breaking the microspheres that was shown in the previous Fig. 2(d). The formed nanobat-like structure was self-assembled in a circular fashion to build hollow microspheres. This happens because a few unbalanced charge centers were formed due to dissimilarities in the surface charges [40]. These centers attract the nanobats formed in the solution by rotating adjacent structure (e) to share identical orientation and by increasing reaction time (Figs. 2(d) and 7(f)), forming the sphere-like CuO microsphere assemblies.

The pH value also has a significant influence on the morphology and dimensionality control. The concentration of \(\text{OH}^–\) can significantly affect the nucleation and growth behavior (such as the number of nuclei and the concentration of “growth units”) of the CuO nanocrystals. In our experiment, when the initial pH values are increased from 5.26 to 5.36, the nuclei formed show uniform size due to adequate quantity of \(\text{OH}^–\) in the solution (g). Thus, these CuO nuclei are further grown into a rectangular shaped nanorods (i). When the urea was replaced with NaOH and the initial reaction pH was kept at 6.5, nanopetal-like CuO nanostructures were obtained (l). Thus, the reaction precursor and pH largely affects the morphology of CuO nanostructures under the hydrothermal reaction conditions.

4. Conclusion

In summary, rectangular shaped nanobat-like CuO nanostructures were synthesized by using a simple hydrothermal chemical route. This reliable method gives a high yield of CuO nanostructures. The shape of CuO nanostructures can be tuned from rectangular nanobats to nanorods and nanopetals by tailoring initial pH of the reaction. FESEM analysis showed that the rectangular nanobat-like nanostructures have diameter of...
70 nm, thickness of ~8 nm and length ~174 nm. Detailed structural analysis revealed that the obtained CuO nanostructure exhibited a high crystal quality with monoclinic crystal structure. The Raman spectrum showed significant peak intensities, which indicate the single phase property and high crystallinity of as-grown CuO nanostructures. A plausible growth scheme was proposed for the formation of the CuO nanostructures.

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References