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Growth and structural properties of CuO urchin-like and sheet-like structures prepared by simple solution process

M. Vaseem [a], Ahmad Umar [a], S.H. Kim [a], A. Al-Hajry [b], Y.B. Hahn [a,*]

[a] School of Semiconductor and Chemical Engineering and BK21 Centre for Future Energy, Materials and Devices, Chonbuk National University, Chonju 561-756, South Korea
[b] Department of Physics, Faculty of Science, King Khalid University, Abha, Saudi Arabia

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Abstract

Urchin-like and sheet-like CuO structures have been synthesized in a large-quantity via simple solution process. Urchin-like CuO structures were obtained by the copper powder, present in the strong alkali solution of copper nitrate, in which small CuO nanosheets were nucleated and grown on the outer surfaces of copper powder moieties. Sheet-like structures, some arranged in flower-shaped morphologies, were found in the same reaction from the reactant solution. The detailed structural investigations using XRD, TEM, and IR revealed that the as-grown products are nanocrystalline pure CuO and possessing a monoclinic structure. The as-grown products are exhibiting a higher surface area hence proving an opportunity to use themselves for the fabrication of efficient devices in near future.

Keywords: Urchin-like structure; Nanosheets; Nanomaterials; Characterization methods

1. Introduction

As an important p-type transition metal oxide semiconductor with a narrow band gap (Eg = 1.2 eV), CuO has received considerable attention in recent years due to its exotic properties and wide applications ranges from heterogeneous catalysts, gas sensors, field-emission emitters to high temperature superconductors and solar cells, lithium ion electrode materials, and etc [1–3]. Therefore, due to these versatile properties and wide applications of CuO, a variety of CuO structures have been fabricated by different synthetic techniques and reported in the literature [4–10]. Regarding the synthesis of complex CuO structures, Liu et al. synthesized the dandelions-like CuO structures by using copper nitrate, ethanol, ammonia, NaOH, and $NaNO_3$ in Teflon-lined stainless steel autoclave at 180 °C in 2–24 h [4]. Self-assembled CuO monocrystalline nanoarchitectures were successfully synthesized by Liu et al. by the reaction of copper acetate, ammonia, under continuous stirring at 65–85 °C in 24 h [5]. Xu et al. reported the formation of CuO microflowers synthesized from the copper chloride and ammonia solution under continuous stirred and in Teflon-lined stainless steel autoclave at 180 °C in 2 h [6]. Liu et al. presented the synthesis of CuO honeycombs and flower-like assemblies by mixing NaOH, $(NH_4)_2S_2O_8$, Na_2WO_4, Na_2MoO_4, SDS on copper foil in Teflon-lined stainless steel autoclaves at 160 °C in 24 h [7]. Recently, Keyson et al. synthesized the urchin-like CuO structures by hydrothermal microwave route by mixing the copper carbonate, polyethylene glycol (PEG) and NH_4OH at 120 °C in 1 h [8]. Previous reports shown above revealed that higher temperature and time, and complex instrument were needed for the growth of complex CuO structures. Therefore, it is a need to develop a simple, easy and effective method to synthesize the complex CuO structures in large-quantity.

In this paper, we present a very simple and convenient solution route to synthesize the complex CuO structures, i.e. urchin-like and sheet-like structures in very short time, without the use of any complex instrument, reagent and surfactants. In

* Corresponding author. Tel.: +82 63 270 2439; fax: +82 63 270 2306.
E-mail addresses: ahmadumar@chonbuk.ac.kr (A. Umar), ybhahn@chonbuk.ac.kr (Y.B. Hahn).

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our synthesis, only Cu powder, copper nitrate and NaOH were used for the synthesis of urchin-like and sheets-like CuO structures. To the best of our knowledge, the approach employed in this paper to synthesize the complex structures of CuO is not reported yet in the literature. The high surface area of the as-grown urchin-like and sheet-like structures provides an opportunity to use these structures for the fabrication of efficient devices in near future.

2. Experimental details

All the reagents used in this synthesis were in analytical grade and used as received without further purification. The typical reaction process for the synthesis of urchin-like and sheet-like CuO structures was as follows: about 1 g of copper powder was put into 10 ml of deionized (DI) water under continuous stirring. Subsequently, 0.2 M copper nitrate ($Cu(NO_3)_2 \cdot H_2O$) solution was prepared in 50 ml of DI water and mixed with 2.0 M NaOH solution prepared in 50 ml DI water under continuous stirring. The resultant mixture (0.2 M copper nitrate and 2.0 M NaOH) was put into the previous stirred aqueous solution of Cu powder and stirred again for next 20 min. A blue colored solution was obtained, which was transferred into a three-necked flask and refluxed at 90 °C for 1 h. The solution temperature was controlled by inserting manually adjustable thermocouple in the three-necked refluxing pot. After completing the reaction in desired time, black precipitate was obtained which was collected and washed with methanol and deionized water several times and dried at room-temperature. The as-grown products were structurally characterized by various analyses tools.

3. Results and discussion

Metallic copper powder was used to synthesize urchin-like CuO structures consist of thin CuO nanosheets. Bunches of almost spherical-shaped copper particles with the diameters of about 1–2 μm were observed from the copper powder (Fig. 1(a) and (b)). These copper particles are oxidized and converted into CuO in the presence of strong alkali solution of copper nitrate. The general morphologies of as-synthesized urchin-like CuO structures were observed by the FESEM and shown in Fig. 1(c) and (d) which reveals that these structures are made by the fine arrangements of thin CuO nanosheet. It is believed that the copper particles were oxidized and converted into CuO particles in the presence of strong alkali solution of copper nitrate, and CuO sheets are arranged on these CuO particles as the reaction proceeds for longer time. Interestingly, it is seen that the sizes of the copper particles are smaller as compared to the urchin-like CuO structures; therefore it is believed that some converted CuO particles adhere each other and form the large urchin-like CuO structures. The typical diameter of urchin-like morphologies lies in between 2 μm and 4 μm (Fig. 1(c)), while some smaller urchin-like morphologies are also seen in the micrograph (Fig. 1(d)). In addition to the urchin-like morphologies, 2D sheet-like structures were also observed from the reactant solution and shown in Fig. 2. Fig. 2(a) shows the low-magnification image of the as-grown nanosheets which reveals that the sheets are grown in very large-quantity. Interestingly, it is also seen that some sheets are arranged in such a special fashion that they made flower-like morphologies with an average diameter of 2–5 μm (Fig. 2(b)) while some sheets are arranged in irregular manner (Fig. 2(c)). As revealed by high-resolution FESEM image, the thickness of the as-grown nanosheets is in the range of 40–60 nm (Fig. 2(d)). Moreover, the as-grown nanosheets are 2–4 μm wide.

For detailed structural observations, the as-grown urchin-like CuO structures were further characterized by the transmission electron microscopy (TEM) and shown in Fig. 3(a) and (b). The observed TEM

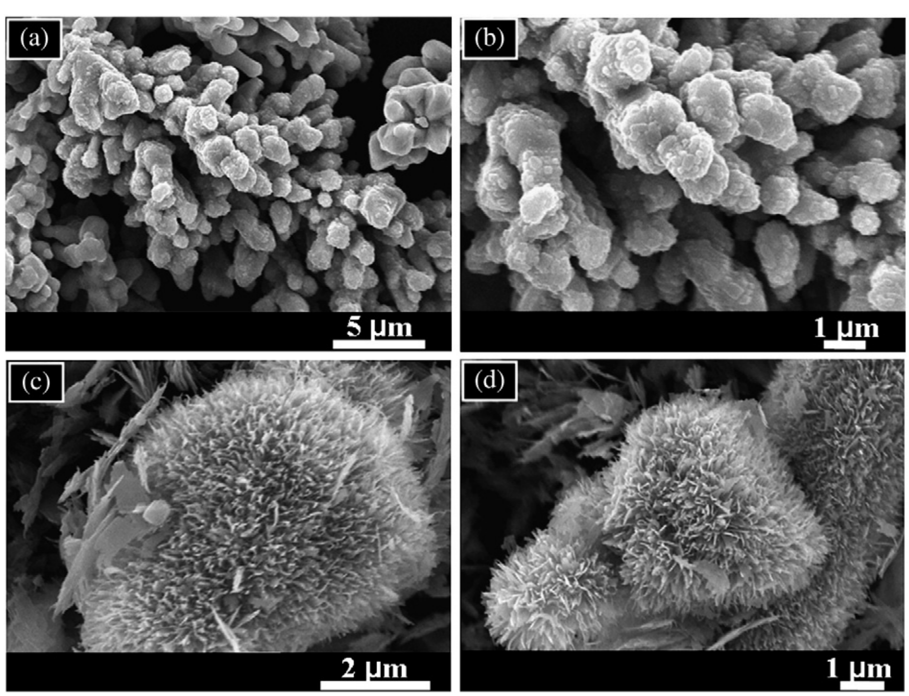

Fig. 1. (a) Low and (b) high-magnification typical FESEM images of copper powder before the experiment and (c) low and (d) high-resolution FESEM images of as-grown urchin-like CuO structures grown onto the copper powder by simple solution process.

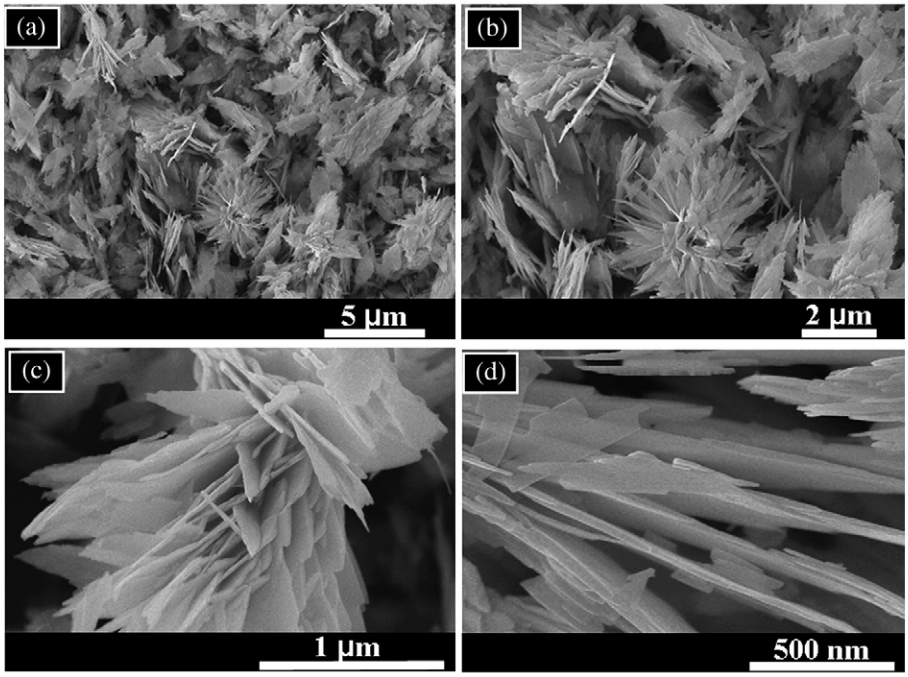

Fig. 2. (a) and (b) Low and (c) and (d) high-magnification typical FESEM images of flower-like composed of thin nanosheets and irregularly arranged sheet-like structures grown in the reactant solution.

images of as-grown urchin-like structures are exhibiting full consistency, in terms of morphology and dimensionality, with the FESEM observations shown in Fig. 1(c) and (d). It is clearly seen from the TEM image that these structures consist of small nanosheets which are arranged in very fine manner at the outer surfaces of the CuO particles. These structures are exhibiting pointed needle-like structures at the edges of microspheres. Interestingly, large urchin-like structures are also observed which seems to be formed by the accumulation of several CuO particles (Fig. 3(a) and (b)), which reveals the consistency with the FESEM explanations.

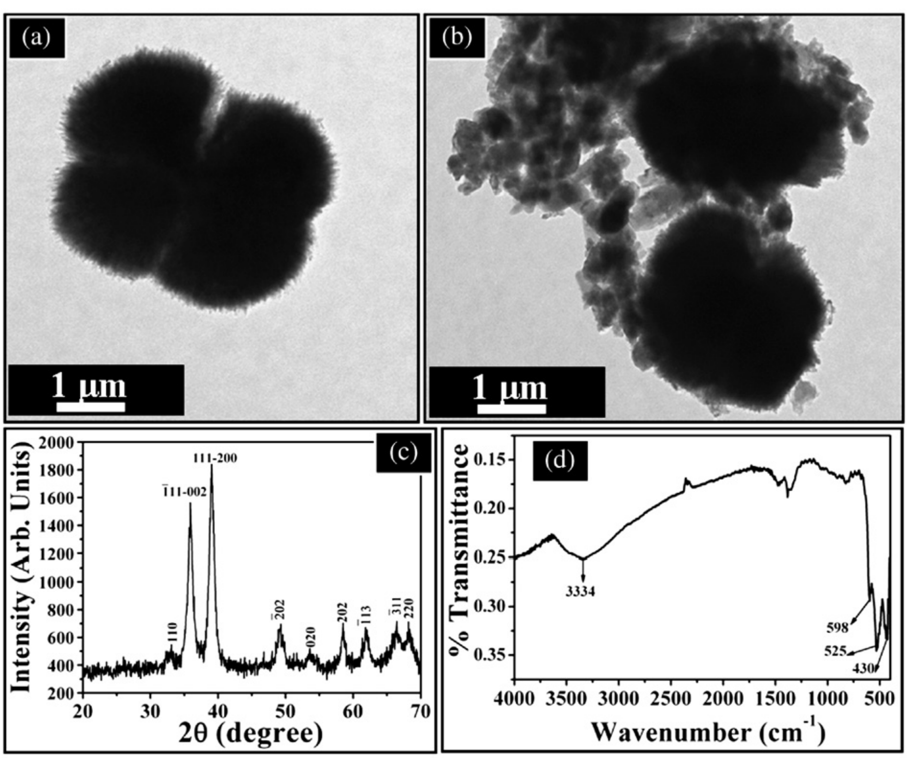

Fig. 3. (a) and (b) Typical TEM images; (c) X-ray diffraction (XRD) pattern and (d) FTIR spectrum of the as-grown urchin-like CuO structures grown by simple solution process.

The crystal phase and crystallinity were analyzed by X-ray diffractometer (XRD) measured with Cu-Kα radiations ($\lambda = 1.54178$ Å) in the range of 20–70° and shown in Fig. 3(c). The obtained XRD pattern of as-synthesized product is supported well the nanocrystalline nature of CuO and can be indexed to the monoclinic phase of CuO crystals (JCPDS 48-1548). Moreover, two dominated peaks compared to other observed peaks in the pattern, located at 2θ values of 35.6° and 38.8° indexed as $(\bar{1}11)$–(002) and (111)–(200) planes, respectively are characteristics for the pure phase monoclinic CuO crystallites. The quality and composition of the synthesized CuO structures were characterized by the Fourier transform infrared (FTIR) spectroscopy in the range of 400–4000 cm^{-1} and shown in Fig. 3(d). Several bands have been appeared in the FTIR spectrum of the as-grown sample. The presence of a weak adsorption at 3334 cm^{-1} is due to the stretching vibration of the adsorbed water and surface hydroxyls. Several other bands appeared in the FTIR spectrum at 598, 525, and 430 cm^{-1} are the characteristic for monoclinic CuO phase and confirms the monoclinic phase for the as-grown structures[1].

As two different kinds of CuO structures i.e. urchin-like and sheet-like have been obtained in our reaction, hence two types of growth mechanisms can be explained for the formation of these structures. Regarding the growth of the urchin-like CuO structures, since the urchin-like structures were grown onto the Cu particles mixed with the high alkaline solution of copper nitrate, therefore we believed that initially the outer surfaces of the copper powder were got oxidize under higher alkaline medium as evident from the previously reported results [9] and a layer of copper hydroxide was covered, depending upon the adsorption of hydroxyl ions, on the surfaces of copper particles [10]. The formation of copper hydroxide occurs according to the following chemical reaction $Cu + 2OH^- \rightarrow Cu(OH)_2$. Moreover, the copper powder in this case can provide two things, i.e. as a self source of the Cu^{2+} ions and as a template for the formation of urchin-like morphologies. Thus, with longer reaction time, the conversion of $Cu(OH)_2$ into CuO occurred according to this chemical reaction $Cu(OH)_2 \rightarrow CuO + H_2O$. Moreover, with time, the copper particles are converted into copper oxide and after saturation at a critical level, the growth over the converted CuO particles occurred and finally urchin-like structures are obtained. Furthermore, it is worth while to note that the copper nitrate may also provide Cu^{2+} ions for the growth of urchin-like structures.

In addition to the urchin-like structures, large-surface area sheet-like morphologies were also obtained from the reactant solution. Yang et al. reported that the $Cu(NO_3)_2$ in presence of higher concentration of NaOH aqueous solution produces $[Cu(OH)_4]^{2-}$ ions instead of $Cu(OH)_2$ precipitates [10] via this simple chemical reaction $Cu^{2+} + 4OH^- \rightarrow [Cu(OH)_4]^{2-}$. Therefore, with the reaction time at appropriate temperature, dehydration occurs in the $[Cu(OH)_4]^{2-}$ moieties, and finally CuO nuclei were obtained according to this reaction $[Cu(OH)_4]^{2-} \rightarrow CuO + H_2O + 2OH^-$. The grown CuO nuclei develop in their own preferred growth directions and finally sheet-like morphologies were obtained as final products in the reactant solution.

4. Conclusions

In conclusion, urchin-like composed of thin nanosheets and 2D sheet-like morphologies of CuO have been synthesized in a large-quantity via simple solution process at low-temperature of 90 °C without the use of any complex instruments and reagents. The detailed structural investigations revealed that the as-grown products are nanocrystalline pure CuO possessing a monoclinic structure. Both the structures, i.e. urchin-like composed of thin nanosheets and 2D sheet-like morphologies are exhibiting a higher surface area hence proving an opportunity to use them for the fabrication of efficient devices in near future.

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