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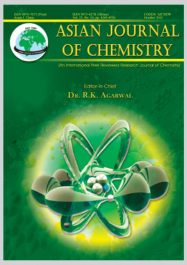

Microwave-Assisted Synthesis of Carambola-Shaped CuO with Hierarchical Nanostructures†

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High-quality uniform carambola-shaped CuO with hierarchical nanostructures have been successfully synthesized using $Cu(acac)_2$ and NaOH as starting materials through a convenient microwave heating route. Various techniques have been used to characterize the prepared products, such as X-ray diffraction, field-emission scanning electron microscopy and transmission electron microscopy. The experimental results indicated that the single carambola-shaped nanostructure is a hierarchitecture, which is intersected through the center by two nanoshuttles with thickness of 10-15 nm. The single nanoshuttle (also called as nanostrip bundle) is formed *via* orderly aggregating of tiny nanostrips with each other through van der Waals force. The morphologies of CuO products were greatly affacted by the concentration of NaOH. The possible reaction process is simply investigated.

Key Words: CuO, Carambola-shaped, Microwave heating, Nanomaterials.

INTRODUCTION

In recent years, many efforts have been devoted to self-assembling nanoscale building units (including nanoparticles, nanorods, nanobelts, nanotubebelts and nanosheets, *etc.*) into two- and three-dimensional ordered superstructures or complex functional architectures in the soulution[1-3]. Various hierarchical architectures can be produced by conjunction and integration of the self-assembled building nanostructures under nonequilibrium through a solution-phase approach.

Compared with the conventional heating methods, the application of microwave heating in synthetic chemistry is appealing, as they can offer rapid volumetric heating, higher reaction rate, short reaction time and so on. Microwave heating has been successfully used to fabricate many inorganic nanomaterials[4-8]. As an important p-type transition-metal-oxide semiconductor with a narrow band gap (1.2 eV), CuO has received much attention for their various applications, such as gas sensors[9], field-emission source[10], solar cell device[11], lithium ion electrode materials[12]. Over the past years, many methods (including hydrothermal, thermal decomposition, ultrosonic and wet chemical technique, *etc.*) have been applied to prepare CuO with special morphologies, such as bundle-like nanostructures[13], fishbone-like nanostructures[14], flower-like nanostructures[15], nanobelts[16], hollow microspheres[17], dendrite-like nanostructures[18], spongy-like nanostructures[19], pumpkin-shaped hollow submicrospheres[20] and so forth. However, most of the reported routes dealt with high treating temperature and long reaction time.

Herein, we developed a convenient microwave-assisted chemical process to synthesize carambola-shaped CuO nanostructures using self-prepared $Cu(acac)_2$ as copper source and NaOH as alkaline source by only microwave irradiating for 15 min in a domestic microwave oven. To the best of our knowledge, this is the first time for the synthesis of CuO nanocarambolas through microwave heating route.

EXPERIMENTAL

All chemicals (analytical grade reagents) were purchased from Shanghai Chemical Reagents Co. and used without further purification. Microwave-heating was performed by a domestic microwave oven (Galanz WG800SL23-K6, 2.45 GHz, maximum power 800 W).

Preparation of copper source-$Cu(acac)_2$ complexes: 10 g $CuCl_2{\cdot}H_2O$ was dissolved in 40 mL anhydrous methanol in a 100 mL flask under magnetic stirring until completely dissolved, 20 mL acetylacetone was added into the above solution. The obtained mixed solution was kept on stirring for 50 min. Then, triethylamine was added dropwise into the reactant solution to adjust pH to 8 nearby. After 2 h of stirring,

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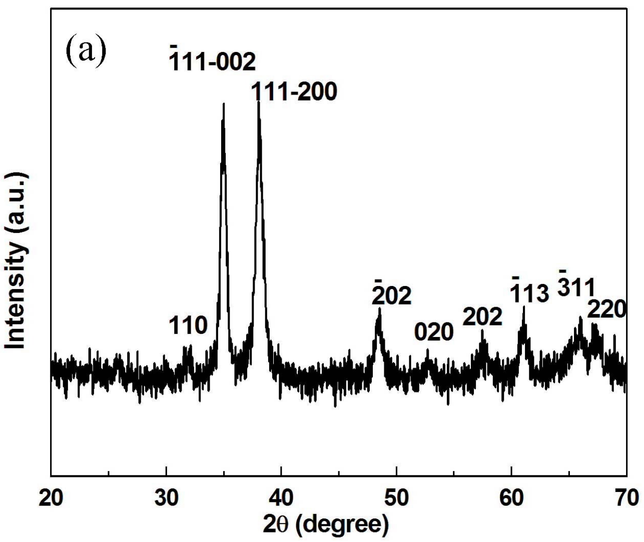
the resulting blue crystallites were filtered, washed with distilled water and dried in a vacuum.

Preparation of carambola-shaped CuO nanostructures: 1 mmol $Cu(acac)_2$ complexes was added into a 100 mL conical flask containing 30 mL deionized water, which was labeled as A. Meanwhile, 4 mmol NaOH was dissolved in 30 mL deionized water to obtain solution B. Then, solution B was added into the solution A under stirring. After stirring for 10 min, the obtained reaction solution was covered with a piece of polyethylene film, then put into a domestic microwave oven and heated for 0.5 h at low power grade. After cooling down to room temperature, the precipitation was filtered out, washed several times with chloroform, anhydrous ethanol and deionized water and then dried in a vacuum at 60 ºC for 6 h.

Detection method: The phase purity of as-synthesized products was examined by X-ray diffraction (XRD) using a Dandong Y-2000 X-ray diffractometer equipped with graphite monochromatized CuK_α radiation (λ = 1.54178 Å). Field-emission scanning electron microscope (FESEM) images of the samples were taken on a field-emission microscope (Sirion 200, 15 kV) attached with the energy dispersive X-ray spectrometry (EDX). The transmission electron microscope (TEM) images of the samples were performed on a H7650 transmission electron microscope with an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

A typical XRD pattern of as-prepared CuO products is shown in Fig. 1(a). All diffraction peaks can be indexed to the crystalline CuO with monoclinic structure (JCPDS card No. 05-0661). No characteristic peaks of any impurities such as Cu_2O, $Cu(OH)_2$ and other copper compound were detected, demonstrating that as-synthesized CuO have high phase purity. The purity and composition of as-prepared sample are also reflected by EDX analysis [Fig. 1(b)]. The result exhibits only the presence of Cu and O elements in products. The molar ratio of Cu:O obtained from the peak areas is 0.98: 1.02, which is in agreement with stoichiometry of CuO. A peak assigned to Si is due to background from the Si foil. Au peak comes from metal spraying during the process of sample preparation.



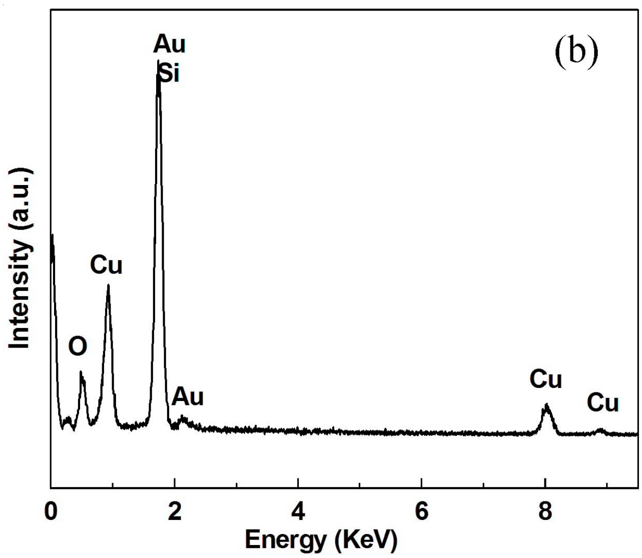
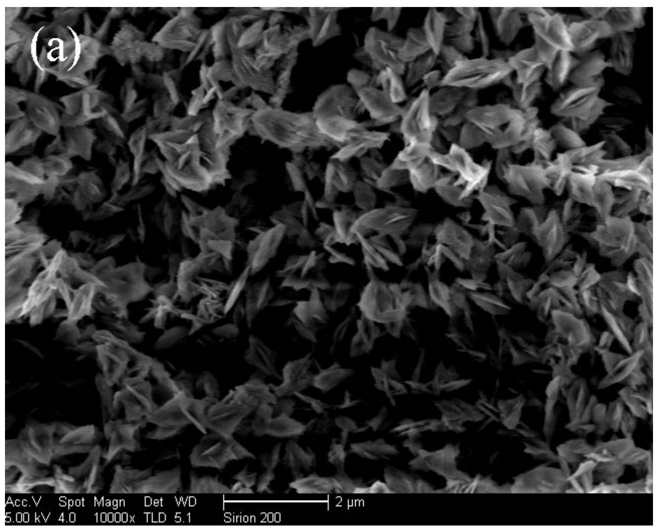


Fig. 1. XRD pattern (a) and EDX result (b) of as-prepared sample

The morphologies of as-synthesized sample were investigated through field-emission scanning electron microscopy (FESEM). The panoramic view in Fig. 2(a) and 2(b) clearly demonstrate that as-synthesized products take on carambola-shaped morphologies with the size of 0.8-1 μm and they are uniformly distributed. An individual carambola-shaped nanostructure was inserted at the lower right corner of Fig. 2(b), which distinctly reveals that the nanocarambola is mainly assembled by two shuttle-like nanoplate with the thickness of 10-15 nm and as a matter of fact, this two nanoplates intersect perpendicularly in the middle.

In order to obtain detailed information about microstructure and morphology of the as-synthesized samples, TEM observations were carried out. Fig. 2(c) and (d) show the typical TEM images of the as-synthesized sample. The carambola-like nanostructures preserve their shapes during the ultrasonic treatment, which display its good structural stability. By careful observation, we found that every single shuttle-like plate was in fact self-assembled from much more tiny building units-nanostrips (see the enlarged image of Fig. 2(c)), which can also be called as nanostrip bundle. The average diameter of the nanostrip is around 8 nm.



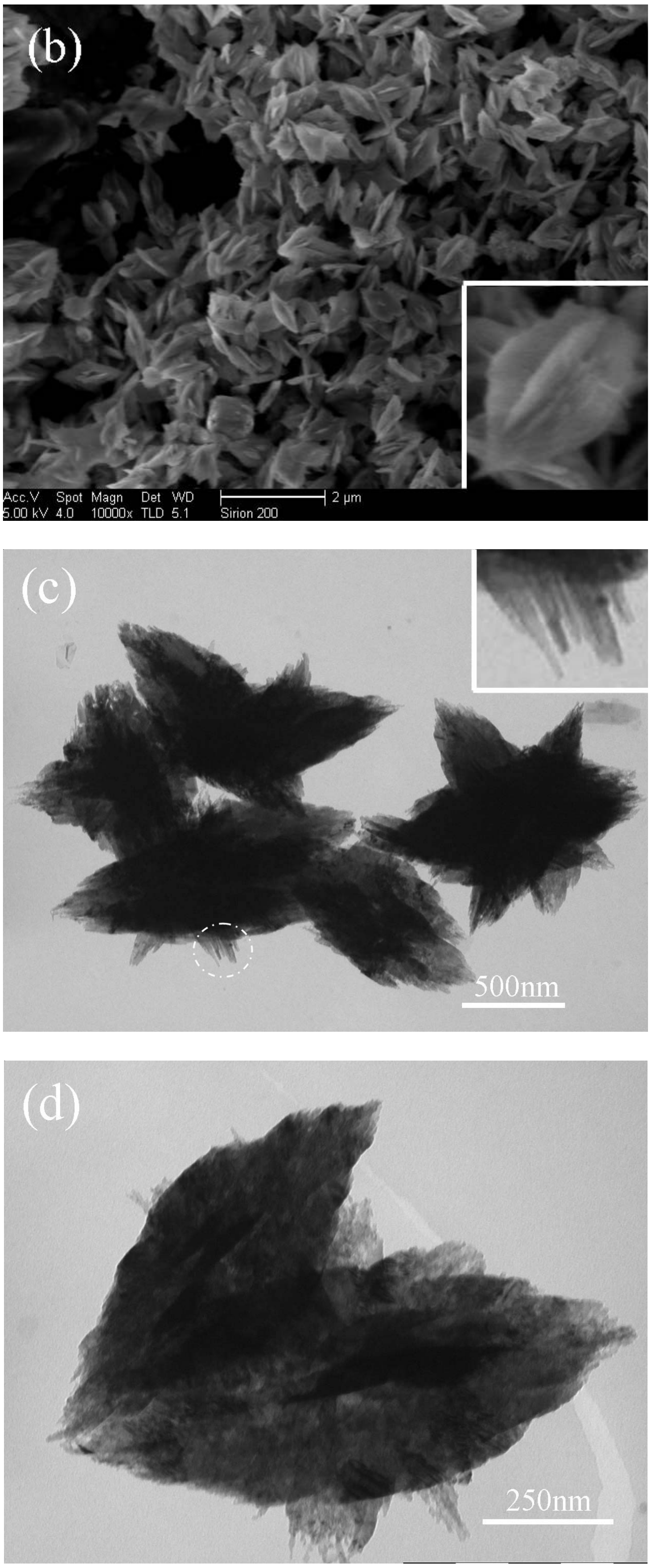


Fig. 2. Morphologies of the as-prepared CuO products: (a,b) FESEM image, (c,d) TEM image

Under the condition of microwave irradiation, the preformed $Cu(acac)_2$ complexes decompose to release dissociative meta ion Cu^{2+}. Meanwhile, as a alkaline reagent, NaOH can dissociate OH^-. Then, meta ion Cu^{2+} in the solution combine with OH^- to form $Cu(OH)_2$. Finally, the newly-produced $Cu(OH)_2$ dehydrolyze quickly to generate primary CuO monomers. With crystal growing and Ostwald ripening, hierarchical CuO nanocarambola assembled by nanostrip bundles may be formed. The related chemical reaction process can be described as follows:

$$Cu(acac)_2 \rightleftharpoons Cu^{2+} + acac \quad (1)$$

$$Cu^{2+} + OH^- = Cu(OH)_2 \quad (2)$$

$$Cu(OH)_2 = CuO + H_2O \quad (3)$$

During the process of experiments, we discovered that the concentration of NaOH would seriously affect the morphology of CuO products. Parallel experiments were carried out by only changing the adding dose of NaOH and keeping other conditions constant, which was checked with FESEM as indicated in Fig. 3. Fig. 3(a) presents the image of CuO products when the adding amount of NaOH was 16 mmol, which reveals that the nanocarambola was enlongated to growth into leaf-like nanostructure. When the adding amount of NaOH was add up to 64 mmol, mutilayer nanoplates were obtained (the enlarged image inserted in Fig. 3(b)).

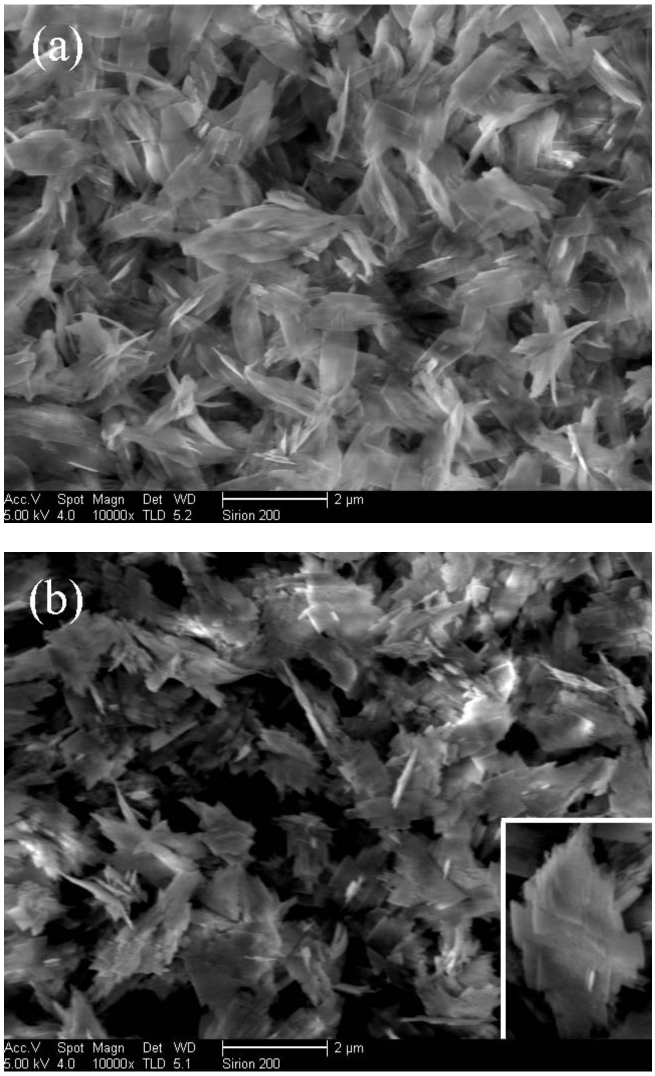


Fig. 3. FESEM images of CuO products obtained with adding different dosage of NaOH: (a) 16 mmol NaOH, (b) 64 mmol NaOH

Conclusions

In conclusion, three dimensional (3D) carambola-shaped CuO hierarchical superstructures were successfully prepared by employing a microwave irradiation method without any surfactant. FESEM and TEM images indicate that the single nanocarambola is composed of two intersectional nanoshuttles which is assembled by tens to hundreds of nanostrips with average diameter of 8 nm. The microwave-assisted method is a quick, simple and green method, which may be used to synthesize other metal oxide with especial morphology.

ACKNOWLEDGEMENTS

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