

† Electronic Supplementary Information (ESI)

Efficient microwave-assisted hydrothermal synthesis of CuO sea urchin-like architectures via a mesoscale self-assembly

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I. Synthesis

Cupric oxide (CuO) samples were synthesized as follows: 0.5 mmol of copper (II) chloride dihydrate (CuCl₂·2H₂O, 99.9% Aldrich, USA) were added to 100 mL deionized water, and this solution was stirred for 10 minutes. Then, 5 mL of ammonium hydroxide (NH₄OH, 30%) was dripped into the copper (II) (Cu²⁺) solution under stirring for 15 min. The light blue solution developed an intense blue color in the tetramminecuprate (II) ([Cu(NH₃)₄]²⁺). The derived solution was transferred to a microwave-hydrothermal system (MHS) (see Figure S1) (2.45 GHz/800 W) with a polytetrafluoroethylene vessel 120 mL capacity autoclave and kept at 100 °C for 30 seconds and for 15 min under autogenous pressure. The resulting CuO black precipitates were collected and washed with deionized water several times and then dried at 60 °C in air.

II. Experimental Setup

In a typical design appeared in a Brazilian patent (2008-PI0801233-4), one hole was drilled into the wall of a domestic oven (2.45 GHz/800 W) for a polytetrafluoroethylene (PTFE) vessel in the oven top. The magnetron was monitored to a very efficient proportional–integral–derivative (PID) external controller. Intuitive software enables the user to control everything from process conditions (temperature, time and heating rate). The user simply defines the desired temperature–time profile, and the MHS will automatically carry out the programmed cycle.

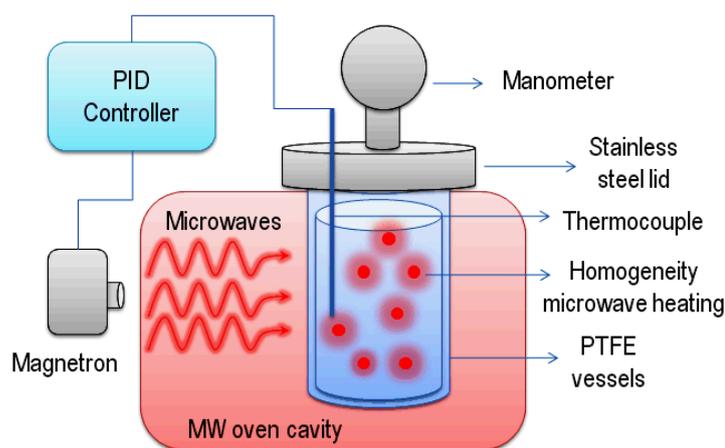


Fig.S1 A schematic diagram of the experimental setup.

III. Characterizations details

The samples were characterized by X-ray powder diffraction (XRD) on a Rigaku DMax 2500PC, 40kV, 150mA, using Cu $K\alpha$ ($\alpha = 1.5406 \text{ \AA}$). The 2θ range used was from 25 to 75° in steps of 0.02° with a count time of 1 s . The field emission scanning electron microscopy (FESEM) images were performed on a microscope (Zeiss SupraTM 35) operating at 15 kV . The structural formation of CuO structures was measured by select-area diffraction (SAD) and transmission electron microscopy (TEM) and high resolution (HRTEM) on a Jeol JEM-3010 microscope at 300 kV . FTIR transmittance spectra were recorded by using a Bruker Equinox 55 spectrometer at $400\text{--}4,000 \text{ cm}^{-1}$ frequency range. Solid samples were prepared using 1% by weight in potassium bromide (KBr) pellet at room temperature. The RS were obtained using a micro-Raman Renishaw spectrograph model inVia equipped with a Leica microscope ($50\times$ objective with $\sim 1\mu\text{m}^2$ spatial resolution) and CCD detector. The scan ranges of 100 to 1400 cm^{-1} , using the 633nm wavelength of a He-Ne laser.

IV. FTIR spectroscopy

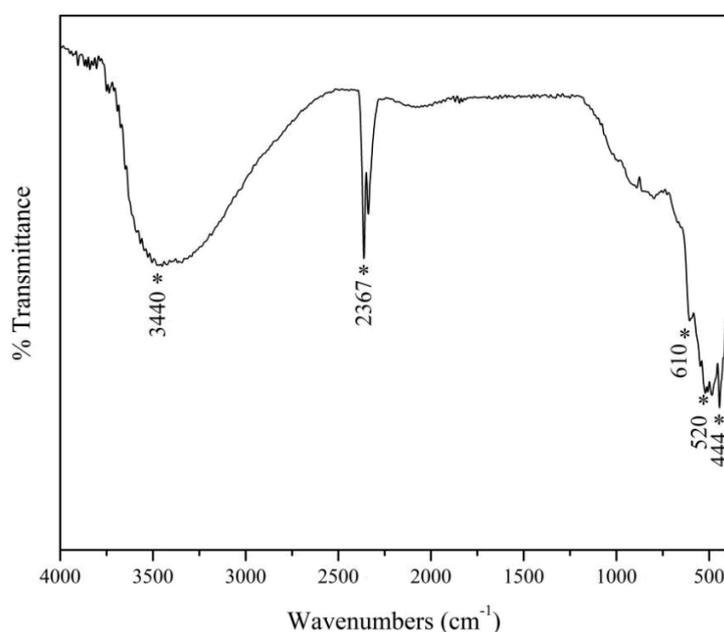


Fig.S2 FTIR spectrum of the CuO urchin-like grown by simple MAH process.

V. Micro-Raman spectroscopy

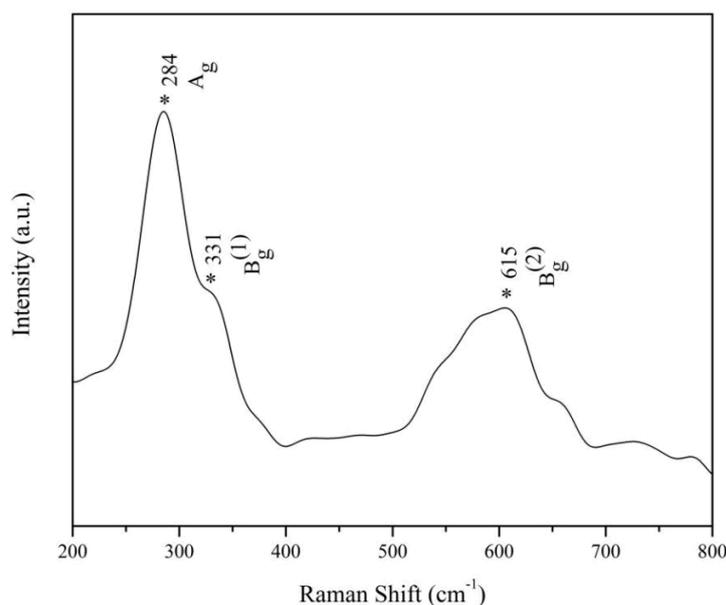


Fig.S3 Raman spectrum of the CuO urchin-like obtained by MAH method.

VI. Chemical equations

The arrangement of CuO crystals during an aqueous solution reaction is an equilibria of complex ions in solution. At the first stage, the dissociation for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ shown in equation (1) occurs. Then Cu^{2+} ions form the hexaaqua ions $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, according to equation (2). The acid equilibrium step is given generically as equation (3). Moreover, ammonia is a stronger ligand than water, and the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex is readily formed in solution, according to equation (4). However, the base equilibrium also occurs in an ammonia solution, as seen in equation (5). The copper (II) hydroxide ($\text{Cu}(\text{OH})_2$) is not formed before any ammonia solution is added because the hydroxide concentration is insufficient to remove NH_3 groups from the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex. With the elimination of NH_3 , the solution is heated by microwave radiation and the increase of hydroxyl ions in solution produces $\text{Cu}(\text{OH})_2$, see equation (6). Finally, the dehydration of $\text{Cu}(\text{OH})_2$ yields CuO primary crystals, according to equation (7). Thus, the crystallization appears to proceed through the aggregation of these CuO particles.

