

An Efficient Synthetic Route towards Sea Urchin-like CuO Mesocrystals

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Abstract – For the first time, we provide evidence both for nucleation at macroscopic scale and for progression of the crystallization process during synthesis of CuO with sea urchin morphology. This work sheds light on the general mechanism of CuO mesocrystals synthesis. The strategy reported is an important advancement in the microwave synthesis technology to synthesize other kinds of metal oxide mesocrystals, such as perovskite and scheelite based materials.

In recent years, copper oxides have attracted considerable attention because of their vast technological applications, such as solar energy materials, gas sensors, batteries, including a promising catalyst [1]. According to Cölfen,[2] the three-dimensional (3D) case of oriented attachment leads to mesocrystals. Thus, CuO whiskers, urchins, flowers, and other 3D architectures can be described as typical mesocrystals. In this work, the entire sequence of crystallization events of CuO was monitored by scanning electron microscopy (SEM) in combination with transmission electron microscopy (TEM) and X-ray diffraction (XRD) patterns. For the first time, we provide evidence both for nucleation at macroscopic scale and for progression of the crystallization process during synthesis of CuO with sea urchin morphology. This work sheds light on the general mechanism of CuO mesocrystals synthesis.

Microwave-Assisted Hydrothermal (MAH) is a greener approach to synthesize materials, and has shown several advantages: i) lower energy consumption, ii) rapid heating process, iii) fast kinetics of crystallization compared to conventional hydrothermal process, and iv) new phases can be produced [3]. The experimental details were described by Volanti et al. [4].

XRD was used to study the phase purity of the obtained copper oxide, and the pattern is shown in Figure 1a. No impurity peaks were observed. All peaks in the diffractogram can be indexed by the tenorite phase of CuO with monoclinic structure (JCPDS 48-1548; $a = 4.6883 \text{ \AA}$, $b = 3.4229 \text{ \AA}$, $c = 5.1319 \text{ \AA}$, and $\beta = 99.506^\circ$). The labels above the peaks are the respective (hkl) indexes. Figure 1b shows the SEM images of the as-obtained CuO, composed of urchin-like architectures with diameters of around $2.2 \mu\text{m}$. A closer observation of the sea urchin-like morphology is shown in the insert of Figure 1b. The image showing that the architectures are composed of strips. Figure 2 shows the TEM image of the extremities for the obtained sea urchin-like CuO, illustrating that the architecture is composed of triangular plates. Figure 2b is a HRTEM image of just one plate, showing that the plates have the same crystallographic orientation, like a single crystal, which is in agreement with the concept of mesocrystals. In addition, the planes (110) and (002) are indexed in the HRTEM image, and this means that the [11-2] direction is the bisector of the triangle. The inset in the image of Figure 2a shows the selected area electron diffraction (SAD) pattern that can be indexed by the monoclinic structure of CuO. Thus, we developed a rapid and facile synthetic route to synthesize sea urchin-like CuO mesocrystals.

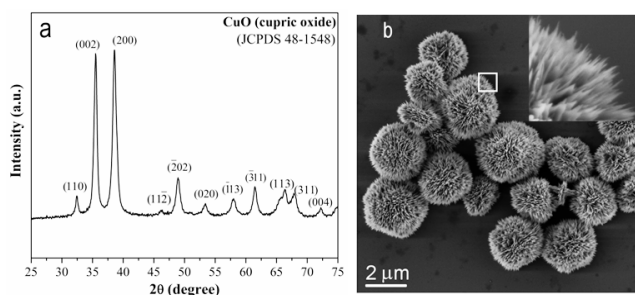


Figure 1: (a) Powder XRD pattern recorded for CuO synthesized in this work, and (b) SEM image of sea urchin-like CuO mesocrystals.

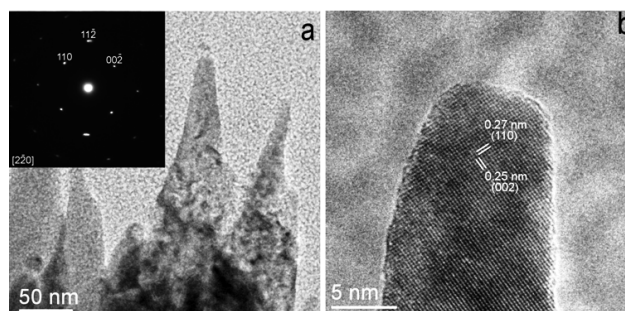


Figure 2: (a) TEM image, inset a SAD pattern, and (b) HRTEM image of a single plate of the CuO mesocrystals.

[1] L. Rout, T.K. Sen, T. Punniyamurthy, *Angew. Chem. Int. Ed.* 46 (2007) 5583-5586.

[2] H. Cölfen, S. Mann, *Angew. Chem. Int. Ed.* 42 (2003) 2350-2365.

[3] S. Komarneni, *Nanophase Curr. Sci.* 85 (2003) 1730-1734.

[4] D.P.Volanti, E.Longo, J.A.Varela, P.S.Pizani, A.G.Souza, *J. Alloys Compd.* 459 (2008) 537-542.