

## Synthesis of Ultrathin-Wall Mesoporous Cu<sub>2</sub>O Nanotubes for Low-Temperature Carbon Monoxide Oxidation

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Hollow nanostructures with mesoporous walls provide readily accessible high-surface-area materials that allow high mass transport rate for heterogeneous catalysis and sensing [1]. Since Cu<sub>2</sub>O is a low-cost and environmentally friendly p-type semiconductor various types of Cu<sub>2</sub>O nanostructures have been utilized for broad applications including energy conversion and storage. It has been a challenge to synthesize small diameter Cu<sub>2</sub>O nanotubes (NTs) with ultrathin walls because of the delicate synthesis conditions that are required. The search for a mild and facile synthetic route to prepare hollow Cu<sub>2</sub>O nanostructures with controllable morphology and high surface area is highly desired. We report here the development of a low-temperature synthesis process to facilitate fabricate mesoporous Cu<sub>2</sub>O NTs with ultrathin walls and the catalytic evaluation of the synthesized Cu<sub>2</sub>O NTs for low-temperature CO oxidation.

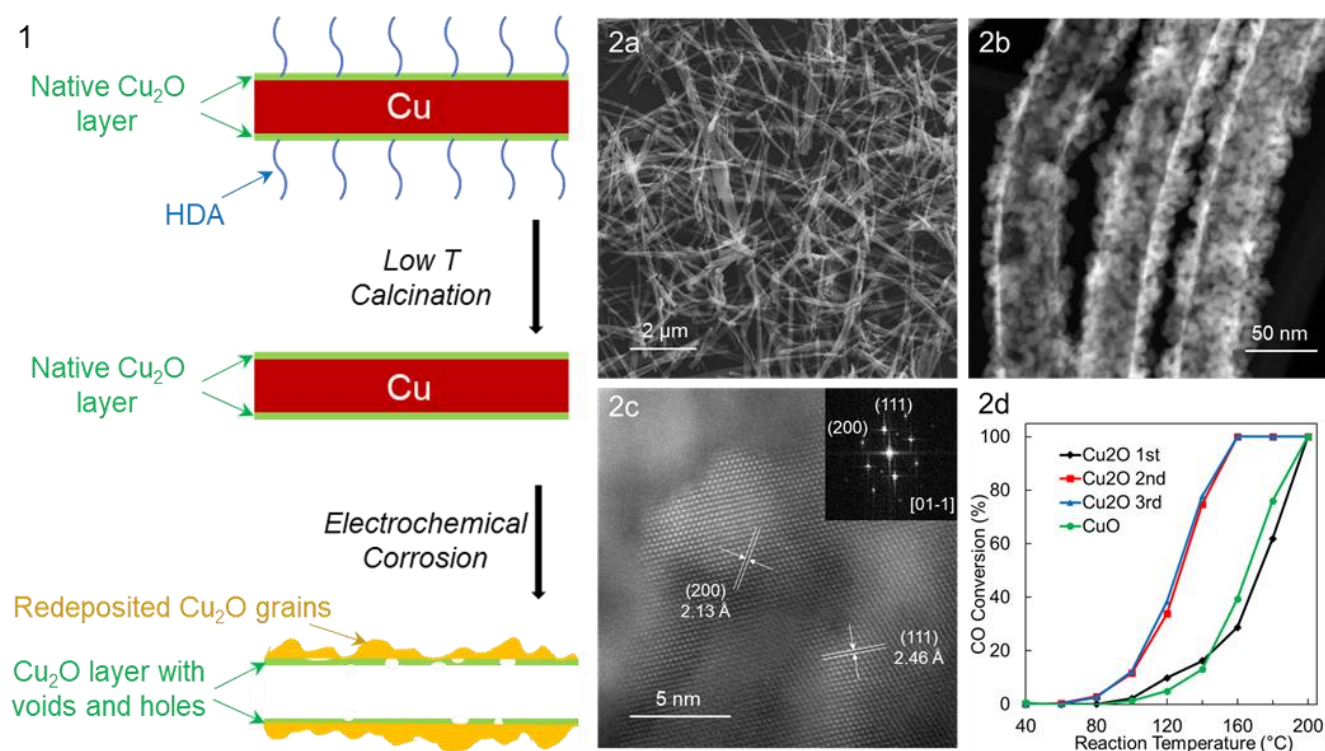
The synthesis protocols are based on the utilization of native oxide layer of fabricated Cu nanowires (NWs) (Fig. 1). Briefly, pentagonal Cu NWs were produced via a surfactant (HDA) assisted hydrothermal approach [2]. The as-synthesized Cu NWs are usually encapsulated by a thin layer of conformably grown Cu<sub>2</sub>O which are coated with surfactants. An electrochemical corrosion process was used to etch away the Cu core from the Cu<sub>2</sub>O layer. Prior to the electrochemical process the as-prepared Cu NWs were calcined at 100 °C to remove the HDA coating layer so that the native or newly grown Cu<sub>2</sub>O surfaces are exposed. A modified electrochemical corrosion process [3] was performed by mixing CTAB and calcined Cu NWs in aqueous solution and stirring for 15 min in a water-bath to obtain the mesoporous tubular structure. CuO NTs were then obtained by calcining the Cu<sub>2</sub>O NTs at 300 °C for 1h. The morphology and structure of the as-synthesized Cu<sub>2</sub>O NTs was examined by SEM and aberration-corrected HAADF-STEM techniques. For the CO oxidation reaction, the reactant gas mixture, consisting of 1 vol% CO, 2 vol% O<sub>2</sub> and balance with He, was introduced into the inlet of a continuous plug-flow reactor at a flow rate of 6 mL/min. The outlet gas composition of the catalytic reactor was on-line analyzed by a gas chromatograph.

Figure 2a shows a representative SEM image of the as-synthesized Cu<sub>2</sub>O NTs with lengths ranging from 1 to 10 μm and an average diameter of ~35 nm. The HAADF-STEM image of the as-prepared Cu<sub>2</sub>O NTs (Fig. 2b) clearly confirmed their tubular nature. The average inner diameter of the Cu<sub>2</sub>O NTs was ~29 nm with an average wall thickness of ~6 nm. The walls of the Cu<sub>2</sub>O NTs consist of numerous Cu<sub>2</sub>O nanograins with an average size of ~6 nm and they form interconnected networks. The average pore size, formed among the individual Cu<sub>2</sub>O nanograins, was ~5 nm. The atomic resolution HAADF-STEM image (Fig. 2c) shows that most of the NT walls possess lattice fringes with the same crystal plane. Image analyses suggest that the electron beam was along the Cu<sub>2</sub>O [01-1] zone axis. CO oxidation was conducted over the as-prepared Cu<sub>2</sub>O and CuO NTs (Fig. 2d). The 1<sup>st</sup> run of the as-prepared Cu<sub>2</sub>O NTs demonstrated an activity similar to that of the CuO NTs. The CO conversion rate the Cu<sub>2</sub>O NTs, however, was significantly increased during the 2<sup>nd</sup> cycle and maintained its stability during the subsequent reaction cycles. It is not

fully understood why the CO oxidation activity was significantly increased after the first reaction cycle and maintained stable for the subsequent reaction cycles although it has been reported that transformation of some of the  $\text{Cu}_2\text{O}$  grains into  $\text{CuO}$  during the CO oxidation reaction may have generated unique interfacial sites [4]. Detailed investigation on the CO oxidation processes over the synthesized  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  NTs will be discussed [5].

#### References:

- [1] G Prieto et al, *Chem. Rev.* **116** (2016), p. 14056.  
 [2] M Jin et al, *Angew. Chem.* **123** (2011), p. 10748  
 [3] Q Wang et al, *J. Phys. Chem. C* **119** (2015), p. 22066.  
 [4] B Wei et al. *J. Phys. Chem. C* **122** (2018), p.19524.  
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**Figure 1.** Schematics illustrate synthesis processes for fabricating ultrathin wall  $\text{Cu}_2\text{O}$  nanotubes.

**Figure 2.** SEM image of as-prepared  $\text{Cu}_2\text{O}$  NTs (a); HAADF image of as-prepared  $\text{Cu}_2\text{O}$  NTs showing tubular and mesoporous structure (b); atomic resolution HAADF image showing crystal nature of tube walls (c). The inset in (c) is the digital diffractogram obtained from the HAADF image (c) with the electron beam along the  $\text{Cu}_2\text{O}$  [01-1] zone axis. Figure 1d shows conversion rates vs temperature for CO oxidation over the as-synthesized  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  NTs. After the first reaction cycle, the CO conversion over the  $\text{Cu}_2\text{O}$  NTs was significantly increased and stabilized. CO oxidation reaction condition:  $[\text{O}_2] = 2\%$  and  $[\text{CO}] = 1\%$  balance with He at a gas flow rate of  $6 \text{ mL min}^{-1}$ , temperature ramping at  $2^\circ\text{C/min}$ , and ambient pressure.