



Short communication

# Formation of Cu nanostructured electrode surfaces by an annealing–electroreduction procedure to achieve high-efficiency CO<sub>2</sub> electroreduction

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## ABSTRACT

An effective fibrous Cu electrode surface, created using a procedure combining high-temperature annealing and electroreduction, is explored for CO<sub>2</sub> reduction to produce useful fuels. The nanostructure of this Cu electrode surface contains a layer of nanofibers or nanofibers surrounded by kernels with 30–100 nm diameters. With a specific surface area as high as 458 cm<sup>2</sup> per geometric electrode surface area, this nanostructured electrode is found to have a high activity toward CO<sub>2</sub> reduction, indicated by its more positive reduction potentials and higher catalytic current density than a smooth Cu electrode. The Faradaic efficiency for HCOO<sup>−</sup> production is 43%, and the electrode surface remains stable during 19 h of electrolysis – better results than with smooth Cu under identical conditions.

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## 1. Introduction

The key technological challenge in the electrochemical reduction of CO<sub>2</sub> into low-carbon fuels is the insufficient performance of electrocatalysts in terms of both catalytic activity and stability [1–4]. Polycrystalline Cu-based materials have been explored as one kind of the unique metal catalysts for CO<sub>2</sub> electroreduction studies because of their low cost and chemical robustness compared to Pb and Hg [5–8]. However, the activity of Cu is still insufficient, signaled by its large overpotential (almost 1 V); in addition, a fairly broad mix of major and minor products is formed, including hydrogen, ethylene, and methane [9,10]. Also, Cu electrodes have been found to deactivate rapidly during CO<sub>2</sub> reduction, especially in aqueous solutions [6]. To address these issues, nanostructured catalyst materials are very promising candidates as they possess unique properties, such as high specific surface area as well as 1-, 2-, and 3-dimensional structures, which can provide more active sites different from those on the surface of a polycrystalline Cu electrode [5,11–13]. It has been reported that the electrochemical reduction of metal oxides is an efficient route to obtain metal particles with altered surface structures, and that the Faradaic efficiencies for this reaction are strongly affected by the synthesis method and the pretreatment of the copper electrode [5,11–13]. However, the underlying reasons for the influence of the

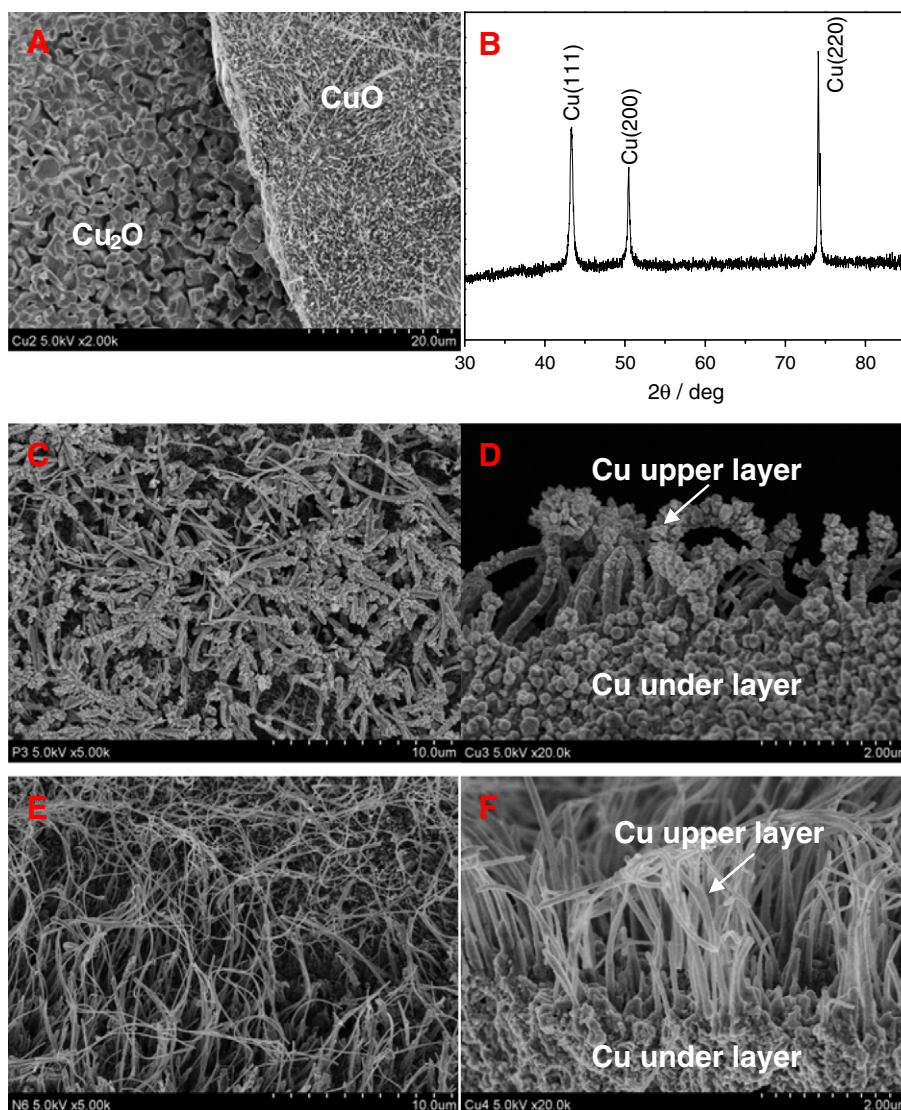
pretreatment are still not clearly understood [11,14–16]. Even starting with the same Cu-oxide material, different pretreatments can yield different surface structures and morphologies, which then exhibit different catalytic activities, stability, and selectivity [17,18].

In this communication, we present a combined thermal-electroreduction approach for preparing hybrid nanostructured Cu electrode surface from Cu oxide film on Cu substrates. The special morphology of such an electrode surface can effectively catalyze CO<sub>2</sub> reduction with high selectivity and is stable against the deactivation phenomena that plague bulk metal electrodes.

## 2. Experimental

To prepare the Cu nanostructured cathodic electrode surfaces, Cu oxide film was first subjected to a thermal procedure. Cathodic electrodeposition of this film to form nanosphericity-nanofibers was then performed in NaOH or H<sub>3</sub>PO<sub>4</sub> solution using a constant potential method. Typically, square pieces of smooth copper foil (99.99% purity, 10 mm × 10 mm, thickness 0.02 mm), used as the working electrodes, were first cleaned by electropolishing at 4.0 V for 5 min in 85% phosphoric acid. The electrodes were then annealed in air at a selected temperature for 12 h. In this way, the Cu oxide film, containing a mixture of CuO and Cu<sub>2</sub>O, was formed on the Cu foil surface as shown in Fig. 1A. The electrodes were further electrochemically reduced by applying a potential of −3.0 V in 1 M NaOH or H<sub>3</sub>PO<sub>4</sub> aqueous solution for 10 min. All of these preparations

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**Fig. 1.** (A) SEM image of Cu oxide nanostructure covered surface, which was obtained from Cu foil annealed at 500 °C for 12 h; (B) XRD pattern of Cu nanostructure covered surface; (C), (D) SEM image of Cu nanostructure covered surface, which was obtained after electrochemically reduced in 1 M H<sub>3</sub>PO<sub>4</sub> aqueous solution; (E), (F) SEM image of Cu nanostructure covered surface, which was obtained after electrochemically reduced in 1 M NaOH aqueous solution. (D) and (F) are the cross-section views.

were performed in a three-electrode cell vs. Ag/AgCl, and the nanostructured electrode surfaces formed at different annealing temperatures then served as catalysts for CO<sub>2</sub> electroreduction.

The catalytic activity of the Cu nanostructured surface for CO<sub>2</sub> electroreduction was tested using a conventional three-electrode electrochemical H-type cell, in which a piece of Nafion® 117 membrane (H<sup>+</sup> form) was used as a separator. An Ag/AgCl electrode saturated with KCl was the reference electrode, and a Pt foil (99.999% purity, 10 mm × 10 mm) was the counter electrode. An aqueous electrolyte of 0.5 M KHCO<sub>3</sub> was used as the measurement solution, which was bubbled with 1.0 atm CO<sub>2</sub> (99.99%) to remove dissolved air before the test. The kinetics and electrocatalytic activity of the Cu working electrodes were measured using cyclic voltammetry at a potential scan rate of 50 mV s<sup>-1</sup> from -0.2 V to -1.5 V. For comparison, a smooth Cu foil measured under the same conditions was used as the baseline. Electrolysis for product identification was performed potentiostatically, during which CO<sub>2</sub> was constantly bubbled into the cell. For CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> solution, the pH was about 7.4, so the calculated CO<sub>2</sub> concentration was about  $2.2 \times 10^{-2}$  M, using the equilibrium equation  $[H^+][HCO_3^-]/[CO_2] = 10^{-6.1}$  for a rough estimation.

XRD patterns were obtained with a Philips PW3830 X-ray diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm). SEM images were taken using a Zeiss Ultra Plus thermal field emission SEM instrument (Carl Zeiss SMTAG, Germany), coupled with EDX. <sup>1</sup>H NMR was employed to quantify the concentration of formate product in aqueous solutions. The NMR data was obtained using a Varian Mercury/VX 400 MHz spectrometer with the WET solvent suppression pulse sequence. Sodium 3-(trimethylsilyl) propionate 2,2,3,3-d<sub>4</sub> (TSP) was used as the internal standard.

### 3. Results and discussion

To test the composition and morphology, a Cu surface generated by annealing Cu foil then reducing it in a 1.0 M solution of NaOH or H<sub>3</sub>PO<sub>4</sub> was analyzed using both XRD patterns and SEM images. As shown in Fig. 1B, only three narrow, pure crystalline peaks can be seen, centered at 43.3°, 50.4°, and 74.1°. These peaks correspond to metal Cu (Card No. 04-0836) (111), (200), and (220), respectively. No diffraction peaks corresponding to other phases can be observed, indicating that the Cu oxides produced by the annealing process were all reduced to metallic

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