Novel Electrochemical Milling Method To Fabricate Copper Nanoparticles and Nanofibers

D. W. Zhang, C. H. Chen,* J. Zhang, and F. Ren

Department of Materials Science and Engineering,
University of Science and Technology of China,
Anhui Hefei 230026, People's Republic of China

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In the past few years, nanosized metal materials have attracted much technological and scientific attention as a result of their interesting size-dependent chemical and physical properties and wide applications in catalysis, electronics, magnetism, and optics.[1−4] Among all metals copper is the most commonly used because of its high electrical conductivity.[5] A number of methods have been developed to fabricate nanosized copper, such as reduction of copper compounds[6−9] and electrochemical deposition.[10,11] Though these methods were successful to fabricate nanosized copper with uniform and controllable dimensions, the complicated synthesis process and the low yield are the main disadvantages. Other methods such as vacuum vapor deposition,[12] vapor−solid reaction growth,[13] and hydrothermal reduction[14] have also been used to fabricate copper nanowires. However, the requirements for special instruments or harsh conditions in these processes represent the drawbacks of these methods.

Recently, copper oxide (CuO) has been explored to be used as a new class of electrode materials for rechargeable lithium-ion batteries.[15−18] Tarascon et al. studied the discharge mechanism of a CuO electrode and demonstrated that the final reduction product was metallic copper grains dispersed in a Li_2O matrix.[16,17] An unusual feature of this electrochemical reduction is that many nanometer-sized copper domains are formed out of a micrometer CuO particle. Thus, we are motivated to develop a novel "top-down" synthesis route for nanosized metal particles. Here we refer to this reduction process as an electrochemical milling (ECM) method. This paper reports for the first time this novel ECM method and its application to prepare copper nanoparticles with a high yield. By controlling the current density, we can elegantly tailor the size and morphology of the nanoparticles. Surprisingly, we have synthesized dentritic copper nanofibers by the ECM method.

The first step of the ECM process is the fabrication of an electrochemical cell with a CuO electrode versus a Li counter electrode. The electrochemical discharge process was carried out on a multichannel battery test system (NEWARE BTS-610) using two-electrode coin cells (CR2032) of the Li/1 M $LiPF_6$ (EC/DEC = 1:1)/CuO, where EC and DEC stand for ethylene carbonate and diethyl carbonate, respectively. The CuO electrode laminate was prepared by casting a slurry consisting of 90 wt % active oxide and 10 wt % poly(vinylidene fluoride) (PVDF) binder onto a copper foil. PVDF served as the binder owing to its wide electrochemical stability window already proved in the lithium-ion battery industry. Copper was used as the electrode base because it was stable in the whole voltage range involved in this study.[19] Celgard 2400 microporous polypropylene membrane was used as the separator, and lithium served as the reference electrode. These cells were discharged galvanostatically between 3.0 and 0 V at room temperature and at different current densities between 0.032 and 0.32 mA/cm^2.

The fully discharged cells were disassembled in a glovebox to recover the tested powder, which was then washed with pure DEC to remove the electrolyte residue. After being taken out of the glovebox, the obtained electrode film was washed with 1-methyl-2-pyrrolidone (NMP) and a dilute hydrochloric acid to remove PVDF, Li_2O, and the residual CuO and Cu_2O. The resulting solid product was washed with ethanol and finally separated in a centrifuge. The obtained powder was also characterized by X-ray diffraction (XRD; Philips X′Pert Pro Super, Cu Kα radiation), field-emission scanning electron microscopy (FESEM; JEOL JSM-6700F), transmission electron microscopy (TEM; Hitachi 800), and high-resolution transmission electron microscopy (HRTEM; JEOL-2010).

The electrochemical reduction of the CuO electrode composed of micrometer-scaled CuO particles and a polymer binder took place in the first discharge process, as illustrated in the voltage profile (Figure 1). The potential of the CuO electrode rapidly drops to a long 1.2-V plateau followed by a sloping decrease down to the cutoff voltage of 0 V. Independent of the discharge current density, the total amount of lithium inserted in 1 mol of CuO, that is, *x* in the nominal

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* Corresponding author. E-mail: cchchen@ustc.edu.cn. Fax: 86-551-3602940.

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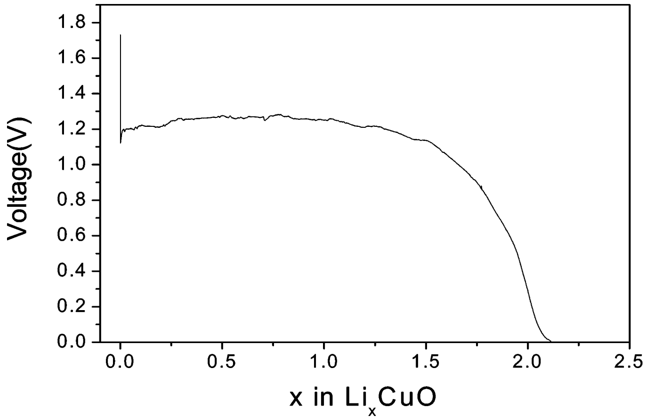

Figure 1. Voltage profile of the CuO/Li cell in the first discharge process. The discharge current density was 0.065 mA/cm^2.

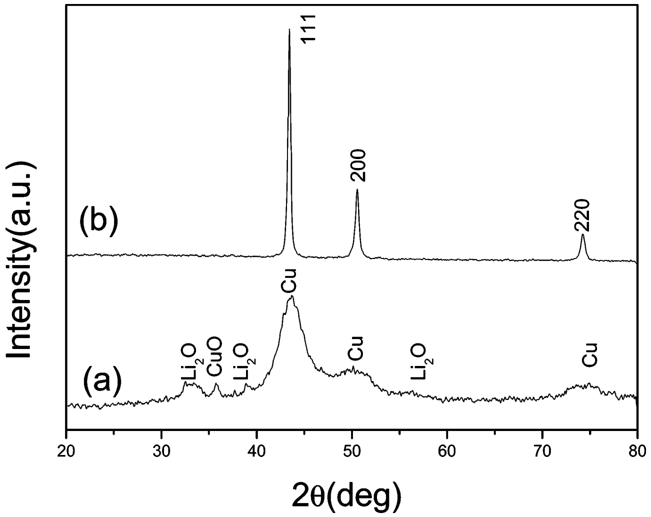

Figure 2. XRD patterns of the fully discharged CuO after the first discharge process: the as-prepared CuO electrode film (a) and the solid product obtained by washing the discharged CuO electrode with NMP and dilute hydrochloric acid (b).

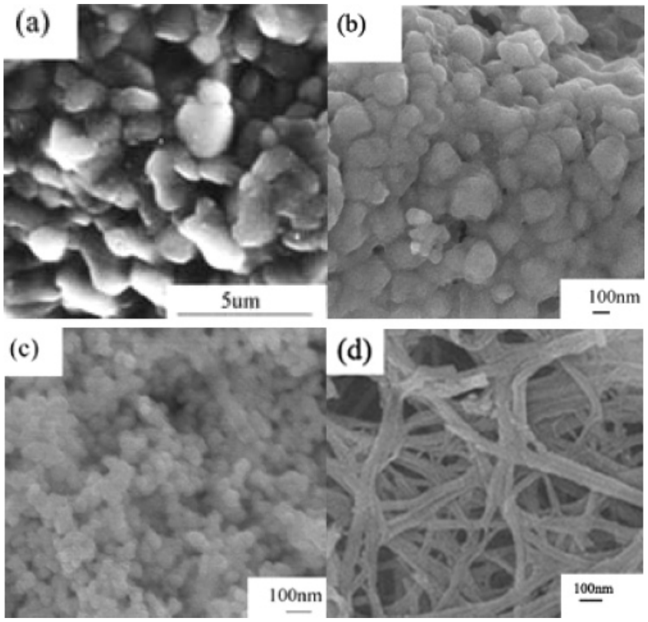

Figure 3. Scanning electron micrographs of the starting CuO powder (a) and the discharged products (metallic copper) obtained at the current density of 0.32 mA/cm^2 (b), 0.065 mA/cm^2 (c), and 0.032 mA/cm^2 (d).

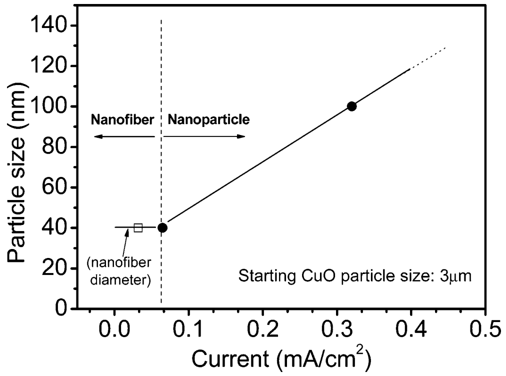

Figure 4. Relation between the current density and the particle size of the copper nanograins and nanofibers produced by ECM of CuO.

composition "Li$_x$CuO", is about 2.11. According to Tarascon et al., this discharge step corresponds to the formations of first Cu$_2$O and then Cu nanoparticles.[16,17] The consumption of 2.11 stoichiometric Li per CuO formula is larger than the theoretical value of 2 that is predicted by the complete reduction of CuO by Li. The extra amount of Li is attributed to the growth of an organic-type coating in the discharge process.[16]

The fully discharged CuO electrode film from a disassembled cell was directly transferred to the sample chamber of an X-ray diffractometer without exposure in air. The XRD pattern (Figure 2, pattern a) shows that the final product after the electrochemical discharge is metallic copper, lithium oxide, and a small quantity of residual copper oxide. This result proves that the electrochemical reduction reaction can be easily realized in a Li cell.

After the discharged CuO electrode was treated with NMP and hydrochloric acid, lithium oxide and residual copper oxide were "washed" away as impurities. Pure metallic copper powder with face-centered cubic crystal structures was obtained as shown in the XRD pattern of the isolated copper particles (Figure 2, pattern b). The rather sharp diffraction peaks suggest a high crystallinity of these copper particles with an average crystallite size of 35 nm, which is calculated with the Scherrer equation. The lattice parameter (a) of a unit cell is estimated to be 0.361 nm, which is very close to the reported data (JCPDS 4-836, $a = 0.3615$ nm). This result indicates that pure metal copper is obtained under the synthetic conditions.

To investigate the influence of the current density on the structure of the discharged product, CuO/Li cells were discharged at different current densities. The morphology of the obtained copper products was examined by FESEM. The FESEM images (Figure 3) show that a large scale of nanosized copper has been fabricated by the electrochemical reduction. Note that in these Li cells the CuO electrode is composed of a commercial CuO powder with a particle size around 3 μm (Figure 3a). The current density has obviously a large influence on the morphology and size of the nanosized copper products. When the current density is 0.32 mA/cm^2, the final product copper consists of a large quantity of uniform nanoparticles with a diameter of about 100 nm (Figure 3b). When the current density is 0.065 mA/cm^2, the final product copper consists of a large quantity of spherical nanoparticles, but the diameter decreases to about 40 nm

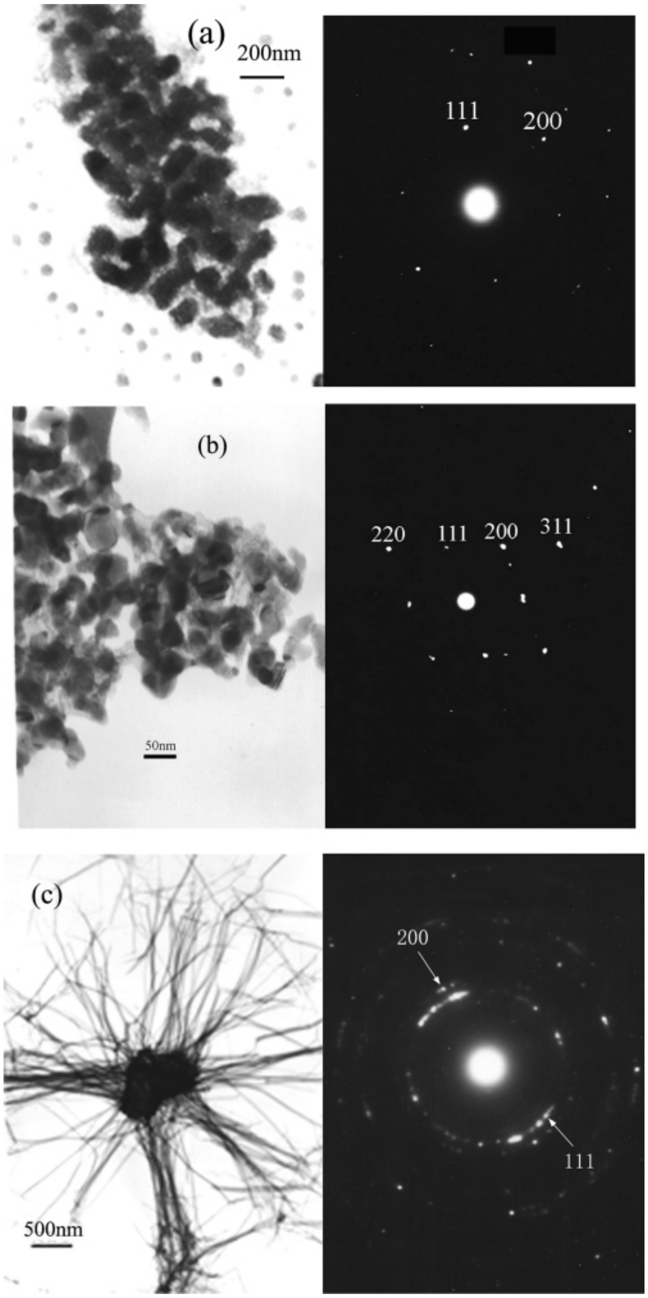

Figure 5. TEM images (left) and SAED patterns (right) of the discharged products (metallic copper) obtained at the current density of 0.32 mA/cm^2 (a), 0.065 mA/cm^2 (b), and 0.032 mA/cm^2 (c).

(Figure 3c). When the current density is decreased to 0.032 mA/cm^2, the obtained copper nanoparticles are unexpectedly composed of nanofibers with a rather uniform thickness of about 40 nm (Figure 3d). The relationship between the current density and the particle size is also plotted in Figure 4.

TEM was employed to extract more details of the morphology and structures of the nanosized copper products obtained via the ECM technique. The TEM images (Figure 5) reveal similar morphologies as detected by the FESEM measurement (Figure 5a,b), except that each of the copper nanoparticles obtained at 0.032 mA/cm^2 is found to be composed of many dentritic nanofibers originated from a core (Figure 5c). The corresponding selected-area electron diffraction (SAED) patterns to the right of each TEM image indicate that the copper particles obtained at the current densities of 0.32 and 0.065 mA/cm^2 are single crystals while the copper nanofibers obtained at 0.032 mA/cm^2 are polycrystalline. HRTEM was used to further study the crystal structure characterization of the copper nanofibers formed at 0.032 mA/cm^2. The HRTEM image of a copper nanofiber is shown in Figure 6. The enlarged image shows that the copper nanofibers are composed of a large number of small single-crystal domains.

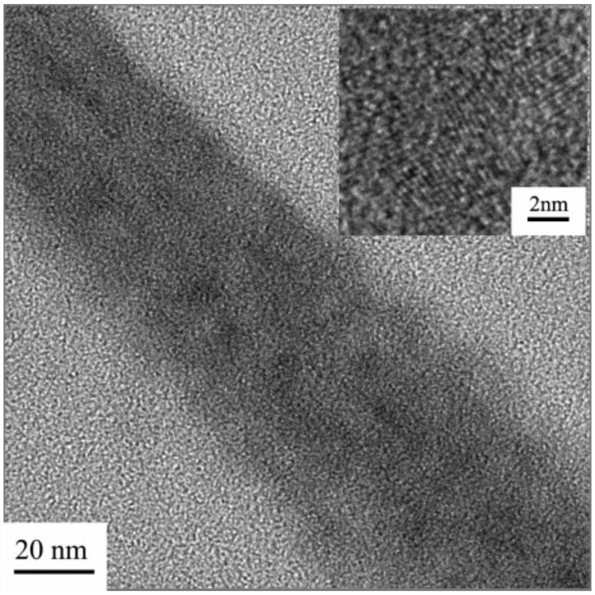

Figure 6. HRTEM image of a copper nanofiber obtained at the discharge current density of 0.032 mA/cm^2.

Compared with Tarascon et al.'s studies where they were mainly interested in the electrochemical performance and mechanisms of the CuO electrode,[16,17] this work here explores the possibility of developing the discharge step into a new synthesis route, that is, ECM, to prepare metallic nanosized particles. Thus, we investigated the effect of the discharge current density on the size and morphology of the final products (Figures 3 and 5). Also, a marked difference in the CuO electrode composition is that an electronic conducting additive (carbon black) is used by Tarascon et al. but not by us. Therefore, the growth kinetics of the copper particles here is probably controlled by the electron conduction on the CuO electrode. The electrochemical reduction must take place first on the CuO particles in the vicinity of the current collector. The intermediate products of the reduction are in turn Li_xCuO and Cu_2O.[16,20] Finally, as the result of the further reduction of Cu_2O, Cu and Li_2O are produced (Figure 2). Because Li_2O is a very poor electronic conductor, the electron conduction path for a further reduction must be the copper grown within the Li_2O matrix. Obviously, the electronic conductivity is proportional to the size of the copper particles. Hence, to maintain a fast reduction process at a high discharge current density, the copper particles produced are large. This is exactly what we have observed (Figure 3b,c). At a very small current density of 0.032 mA/cm^2 (equivalent to less than a *C*/400 discharge rate), the copper is pushed out of the Li_2O structure, forming many nanofibers emanating from a core

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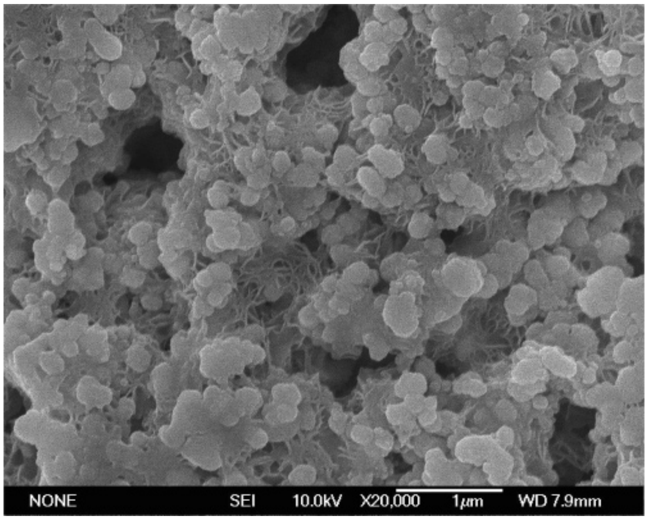

Figure 7. FESEM image of a gently washed CuO electrode after a discharge process at the current density of 0.032 mA/cm^2.

(Figures 3d and 5c). The formation of such a structure is not expected, as it does not follow the trend of forming nanograins. Nevertheless, a similarity is found between this structure and the copper dendrimers grown on the discharged product of $Cu_{2.33}V_4O_{11}$.[21] In addition, according to Tarascon et al.'s studies[16] and our FESEM observation on a 0.032 mA/cm^2 discharged CuO electrode sample that was not rigorously washed with NMP after the cell disassembly (Figure 7), the reduction products, that is, copper nanoparticles and nanofibers, are gradually formed within the electrode during the discharge process.

In conclusion, we have developed a novel ECM process to fabricate nanosized copper. This method can be realized easily and controlled elegantly via the discharge process of CuO/Li cells. The discharge current has a large influence on the morphology and size of the nanosized copper. Other metal oxide powders may also be electrochemically "milled" in the reduction reactions, indicating a new synthesis method to fabricate nanosized metals.

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