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Large-Scale Synthesis of Well-Dispersed Copper Nanowires in an Electric Pressure Cooker and Their Application in Transparent and Conductive Networks

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Supporting Information

ABSTRACT: We present a novel large-scale synthetic method for well-separated copper nanowires (CuNWs) in a commercial electric pressure cooker under mild reaction conditions. CuNWs (~2.1 g) can be prepared in a batch with the cost of \$4.20/g. Well-dispersed polyvinylpyrrolidone-capped CuNWs were obtained via a ligand-exchange method. The transparent and conductive CuNW networks with excellent electrical conductivity and high optical transmittance (30 Ω/□ at 86% transmittance, respectively) were fabricated by a spin-coating process.

1. INTRODUCTION

Transparent conducting thin films have a wide variety of applications in low-emissivity windows, liquid crystal display (LCD), light-emitting diodes (LEDs), and thin-film solar cells.[1−6] Transparent conductive oxides (TCOs), such as indium tin oxide (ITO), fluorine-doped tin oxide (FTO), and aluminum-doped zinc oxide (AZO), are the most commonly used materials in real-world applications. These TCO thin films are usually deposited by expensive vacuum-based methods, including sputtering and chemical vapor deposition (CVD).[7−10] Recently, metallic silver nanowires (NWs) have attracted considerable attention because of their potential application in the low-cost transparent conductive electrodes.[11−20] Their conductivity and transmittance are comparable with those of traditional TCOs, and they are being used in many fields such as flat-panel displays, organic LEDs, and thin film solar cells.[21−24]

Compared with silver, copper is cheaper and more abundant, which can dramatically lower the cost of nanowires.[25−30] Additionally, the conductivity of CuNWs is nearly as good as AgNWs.[31−36] Therefore, the synthesis of high-quality CuNWs is of great significance and has received more and more attention. In 2005, Zeng and co-workers first synthesized high-quality CuNWs by reducing $Cu(NO_3)_2$ aqueous solution with hydrazine in the presence of NaOH and ethylenediamine.[25] Subsequently, Wiley and co-workers utilized this approach to prepare gram-scale CuNWs and further fabricated transparent conductive films with excellent transmittance and high conductivity.[31] Additionally, Konya and co-workers as well as Xia and co-workers prepared CuNWs by reducing $CuCl_2$ aqueous solution with glucose in the presence of hexadecylamine (HDA).[26,27] Recently, Lu and co-workers have synthesized ultralong CuNWs with excellent dispersibility in a liquid-crystalline medium of HDA and cetyltriammonium bromide (CTAB) and further fabricated high-performance transparent conductive electrodes.[32] Although high-quality CuNWs could be synthesized by these approaches, these reactions were usually conducted in a traditional flask under magnetic stirring, which is not favorable to the ultralarge-scale synthesis of CuNWs.[25−30] Thus, developing a large-scale synthetic approach for high-quality CuNWs is still necessary.

2. RESULTS AND DISCUSSION

In this paper, we demonstrate a novel and facile approach to synthesize well-dispersed CuNWs by a commercial electric pressure cooker under mild reaction conditions. Figure 1a shows a picture of a commercial electric pressure cooker. Note that the electric pressure cooker is very suitable for the large-scale and low-cost preparation of CuNWs. Oleic acid (OA) and oleylamine (OM) were used as the dual capping agents, and glucose was used as the reducing reagent. CuNWs were synthesized by mixing the ethanol solution of OM and OA with the aqueous solution of $CuCl_2$ and glucose. The reaction was conducted in a 5 L electric pressure cooker at around 116 °C (~164 kPa) for different reaction times. Finally, ~2.1 g of CuNWs can be obtained in a batch (Figure 1b). The calculated cost of CuNWs is around \$4.20/g (see Supporting Information, Table S1).

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Figure 1. (a) A commercial electric pressure cooker for the synthesis of CuNWs. (b) The crude solution of as-prepared CuNWs.

Figure 2a,b shows the scanning electron microscope (SEM) images of CuNWs prepared using OM as the sole ligand for 2 and 12 h. It was observed that the aspect ratio of CuNWs dramatically increases with reaction time. Finally, the bundled CuNWs were achieved, which led to very poor dispersibility in water or organic solvents. Thereby, these bundled CuNWs cannot be used to prepare the transparent conductive networks. To obtain the well-separated CuNWs, OA was used as the secondary ligand. Optimal volume ratio of OM/OA was found to be 100. We found that the CuNWs have an average yield of 87%. Figure 2c,d displays SEM images of CuNWs prepared using OM and OA as the dual ligands for 12 h. It was clearly revealed that the CuNWs are uniform in diameter. As-prepared CuNWs have a diameter of 45 ± 3 nm, a length of 60−90 μm, and an aspect ratio of greater than 1700. Dispersibility of CuNWs is significantly influenced by the length of the NWs. These ultralong CuNWs are flexible and have a very poor dispersibility in ethanol. This is probably due to a weak binding strength of polyvinylpyrrolidone (PVP) with CuNWs. Therefore, these ultralong CuNWs are not suitable for the fabrication of transparent conductive networks. We attempt to synthesize the CuNWs with a lower aspect ratio and use them to fabricate the high-quality transparent conductive CuNW networks.

To reduce the aspect ratio of CuNWs, the reaction time was decreased to 6 h from 12 h. As a result, the aspect ratio of CuNWs was evidently decreased from 1700 to 300, as shown in Figure 3a,b. These well-separated CuNWs with a suitable aspect ratio were capped by OA and OM. Thus, these hydrophobic CuNWs cannot be well-dispersed in polar solvents such as water, ethanol, acetone, etc. Note that hydrophilic PVP is commonly used in the synthesis of AgNWs, and it can be easily removed by thermal decomposition on a hot plate, leading to a highly conductive and transparent AgNWs thin film.[11−20] Herein, PVP-capped CuNWs were obtained by a ligand-exchange process. These PVP-capped CuNWs can be well-dispersed in ethanol, and the

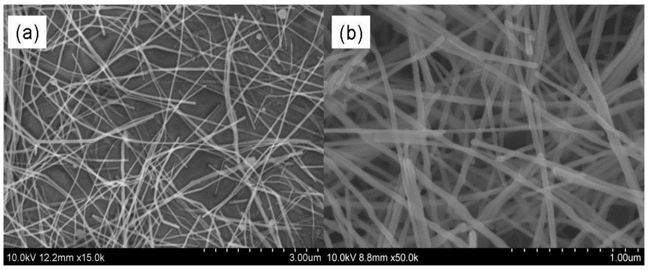

Figure 3. SEM images of CuNWs using OM and OA as the dual ligands for 6 h under magnifications of 15.0 k (a) and 50.0 k (b).

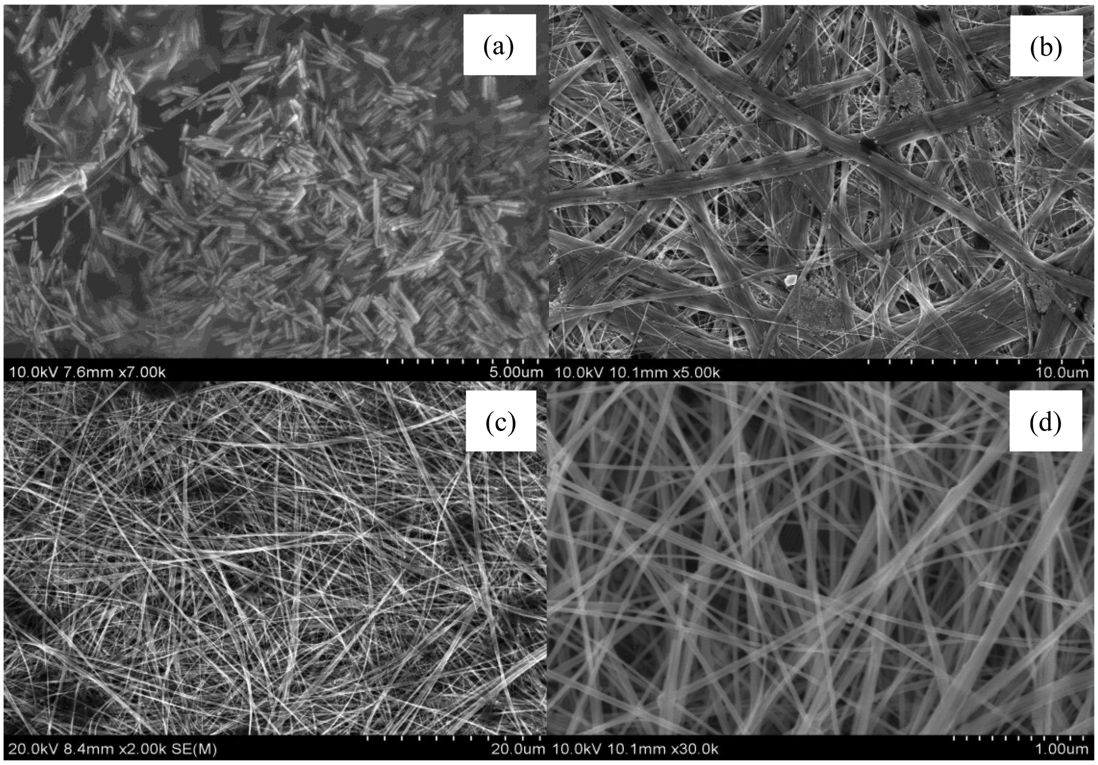

Figure 2. SEM images of CuNWs using OM as the sole ligand for 2 h (a) and 12 h (b); SEM images of CuNWs using OM and OA as the dual ligands for 12 h under different magnifications (c, d).

solution of CuNWs can be directly used to fabricate transparent and conductive CuNW networks by a spin-coating approach.

The shape and structure of the CuNWs were further studied by transmission electron microscopy (TEM). Figure 4a shows a TEM image of CuNWs synthesized for 6 h. This image revealed that CuNWs were uniform in diameter. The average diameter is 52.3 nm, which is close to the size determined by SEM. Figure 4b shows a high-resolution TEM (HR-TEM) image of the single Cu nanowire. The lattice fringe spacing is calculated to be 2.08 Å, corresponding to the (111) plane of CuNWs. CuO and Cu_2O domains were not found on the surface of CuNWs according to the HR-TEM image, confirming that the surface oxidation of CuNWs does not occur. The preferred growth direction of CuNWs was found to be [110], as shown in the inset of Figure 4b.

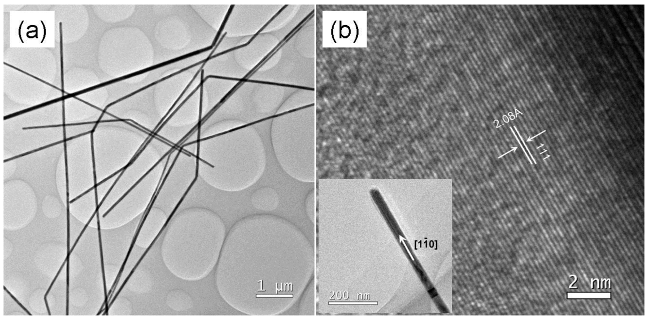

Figure 4. (a) TEM and (b) HR-TEM images of CuNWs synthesized using OA and OM as the dual ligands for 6 h.

The purity and crystal structure of CuNWs were characterized by powder X-ray diffraction (XRD). Figure 5a shows an XRD pattern of CuNWs synthesized under standard conditions. The three diffraction peaks at $2\theta = 43.5$, 50.7, and 74.48° correspond to the diffraction from (111), (200), and (220) planes, which confirmed that CuNWs have a face-centered cubic (FCC) structure (JCPDS #03−1018). Two possible CuO and Cu_2O impurity phases have not been detected in our CuNWs, which is consistent with the observation of HR-TEM. In addition, the ultraviolet−visible (UV−vis) absorption spectrum of CuNWs dispersed in ethanol was measured and shown in Figure 5b. A shoulder peak located at 578 nm was observed, which was in good agreement with those previously reported values for CuNWs.[28,30] This could be due to the plasma excitation in CuNWs.[36]

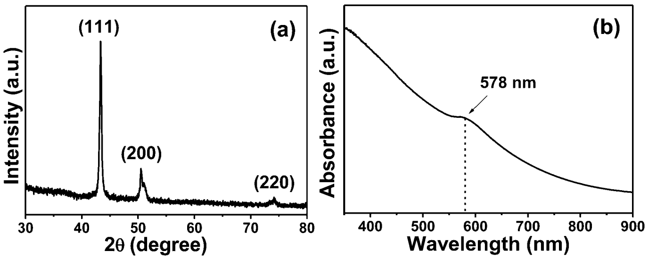

Figure 5. XRD pattern (a) and UV−vis absorption spectrum (b) of CuNWs.

PVP-capped CuNWs have a good dispersibility in ethanol solution, and thus the networks of CuNWs can be fabricated on a glass substrate by a spin-coating process. As-prepared networks of CuNWs were not conductive unless PVP was burned away. To avoid the oxidation of CuNWs, the sintering process was conducted in a nitrogen-filled glovebox on a 340 °C hot plate for 20 min to remove PVP. After sintering, the sheet resistance of CuNW films decreased dramatically. Note that the conductivity and transmittance of CuNW films are strongly dependent on the density of CuNWs on the substrate. The density of CuNWs can be controlled by changing the rate of spin-coating or by tuning the concentration of CuNWs. The inset of Figure 6a shows a series of CuNW films with different transmittances. Figure 6a shows an optical transmittance spectrum of a typical CuNW film with a transmittance of 86% and a sheet resistance of 30 $\Omega/\square$. Figure 6b exhibits the relationship between transmittance and sheet resistance of CuNW films. The optical transmittance and sheet resistance both decrease sharply with the increase of the density of CuNWs. Obviously, our CuNWs exhibited excellent performance, which is similar to those of AgNWs (De,[11] Hu[12]), CuNWs (Wiley,[31] Lu[32]), and carbon nanotubes CNTs (Lee[37]). Importantly, the cost of CuNWs is much less than AgNWs and CNTs.

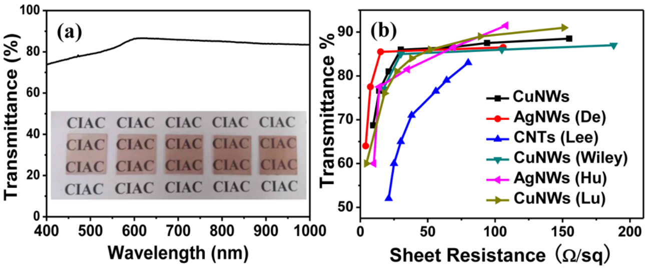

Figure 6. (a) Optical transmittance spectrum of CuNW film with a sheet resistance of 30 $\Omega/\square$. (inset) A digital image of a series of CuNW films with different transmittances. (b) Comparison of the sheet resistances and transmittances (at a wavelength of 560 nm) of CuNW thin films with literature values for CuNWs, AgNWs, and CNTs.

To further illustrate the relationship between the density of CuNWs on the glass substrate and the properties of the CuNW film, Figure 7a,b shows two SEM images of CuNW films after baking with the different transmittances and sheet resistances. Lower density of CuNW film (Figure 7a) exhibited higher transmittance (86%) and higher sheet resistance (30 $\Omega/\square$). When the density of CuNWs increased (Figure 7b), both the transmittance (76%) and sheet resistance (14 $\Omega/\square$) decreased. Furthermore, these SEM images revealed that the continuous CuNW networks were formed after baking at 340 °C.

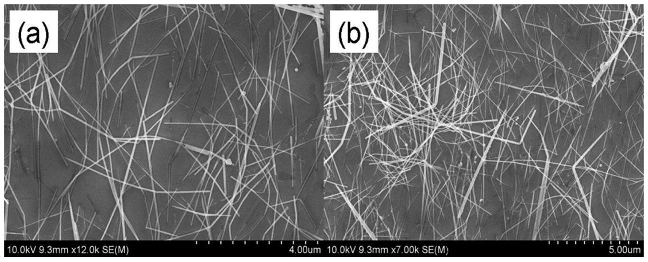

Figure 7. SEM images of CuNW films after baking, with different transmittances and sheet resistances: (a) 86% transmittance with sheet resistance of 30 $\Omega/\square$, (b) 76% transmittance with sheet resistance of 14 $\Omega/\square$.

The conductive CuNW films can be directly used in an electrical circuit. Figure 8b shows an electrical circuit connected with transparent and conductive CuNW film. As a comparison, Figure 8a shows an electrical circuit without CuNW thin film. As can be seen in Figure 8b, it was found that CuNW thin film can easily achieve enough current to power the LED, while the luminous intensity of the LED had no obvious change when compared with Figure 8a.

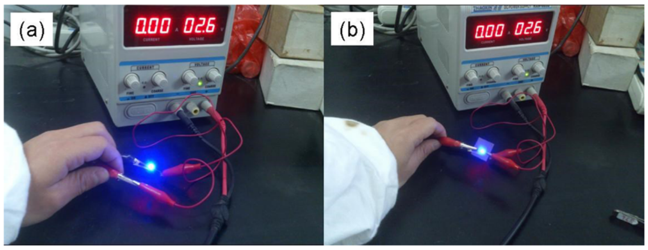

Figure 8. An electrical circuit with a power source and an LED with direct connection (a) and with a CuNW thin film connection (b).

The stability of CuNWs is a critically important issue for further application. The sheet resistance of sintered CuNW films showed an increase due to surface oxidation after the films were stored for 2 d in the open air. However, when the CuNW films were stored in a glovebox, they exhibited an excellent stability with almost constant sheet resistance after one week. The oxidation of CuNWs should be eliminated by coating a thin layer of ZnO or TiO_2 shell[22,24] on the surface of CuNWs or by synthesizing Cu/Ni core/shell NWs. These studies are currently underway in our laboratory.

3. CONCLUSIONS

In summary, we developed a novel and facile method for large-scale and low-cost synthesis of CuNWs with different aspect ratios by using a commercial electric pressure cooker under mild reaction conditions. CuNWs (~2.1 g) can be obtained in a batch with a cost of \$3.80/g. The transparent and conductive CuNW networks with excellent transmittance and sheet resistance were fabricated by a spin-coating process. These CuNW films have better transmittance and conductivity than CNTs, close to AgNWs films. Importantly, the cost of CuNWs is much less than AgNWs and CNTs; thus, CuNWs have a high potential application in low-cost displays, LEDs, and thin-film solar cells. Additionally, when this reaction is conducted in a 24 L commercial electric pressure cooker, more than 10 g of CuNWs can be obtained in a batch.

4. EXPERIMENTAL SECTION

I. Chemicals. $CuCl_2 \cdot 2H_2O$ (AR), glucose (AR), and OM (OM, 80−90%) were purchased from Aladdin. OA (90%) was obtained from Aldrich. PVP, M_W = 55 000, was purchased from Alfa. All chemicals were used as received without further purification.

II. Large-Scale Synthesis of Different Lengths of Copper Nanowires. $CuCl_2 \cdot 2H_2O$ (6.8 g, ~40 mmol) and glucose (7.92 g, ~40 mmol) were added to a 900 mL beaker containing 800 mL of H_2O under magnetic sirring. Then, 80 mL of OM, 0.8 mL of OA, and 140 mL of ethanol were loaded to a 400 mL beaker under magnetic stirring. Afterward, these two solutions were put into a 5 L plastic container and diluted to 4000 mL with water, followed by magnetic stirring for 12 h on a 50 °C hot plate. The color of the mixture changed from blue to caesious (see Supporting Information, Figure S1). Subsequently, the mixture was transferred to a 5 L electric pressure cooker. The reaction temperature was held for 2−12 h. Finally, the reddish brown CuNWs were obtained.

III. Preparation of Transparent and Conductive CuNW Films. After the reaction, 4 mL of the crude solution of CuNWs was centrifuged for 4 min at 12 000 rpm, then the precipitate was sonicated and centrifuged twice in an ethanol solution containing 2.0 wt % PVP. Afterward, CuNWs were centrifuged twice again in ethanol solution to remove the free PVP and were redispersed in ethanol for SEM, TEM, UV−vis, and XRD measurements.

CuNW films were prepared by spin coating. The ethanol solution of PVP-capped CuNWs was sonicated for 5 min and spun on a glass substrate at 2500 rpm for 10 s. Subsequently, the films were sintered in a nitrogen-filled glovebox at 340 °C for 20 min to remove the resident PVP from the surface. Finally, the CuNW films were cooled to room temperature in the glovebox to avoid oxidation.

IV. Characterizations. The powder XRD pattern was measured using a Bruker D8 FOCUS X-ray diffractometer. UV−vis transmittance spectra were measured using a Shimadzu UV-3600. The SEM images were characterized on a Hitachi-4800 field-emission SEM. TEM images were taken on a FEI Tecnai G2 F20 with an accelerating voltage of 200 kV. The sheet resistances of CuNW films were measured by a Hall effect system (ET9000, East Changing Technologies, Inc.).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Pictures of the precursor solution before and after heating at 50 °C for 12 h and the calculated cost of CuNWs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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