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Facile Synthesis of Oxidation-resistive Copper Nanowires for High-conductive Flexible and Foldable Electrodes

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Abstract

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As a promising electrode material, Copper nanowire (Cu NW) has been widely researched for next generation electronics, because of their low cost, high conductivity, flexibility and foldability. Recently, there are already several methods for the synthesis of Cu NWs. However, for reasons of rapid oxidation and high sintering temperature, these Cu NWs are difficult to use for practical applications.

In this research, a simple polyol reduction method for the growth of oxidation-resistive Cu NWs for high-conductive flexible and

foldable electrode is introduced. Potassium bromide and oleylamine play fundamental roles in the formation of Cu NWs as structure induced factors and protective antioxidant layers.

In the synthesized process, single crystalline Cu NWs with average diameter of 92 nm and length of about 30 μm were dispersed in isopropyl alcohol solution. Moreover, this synthesis of Cu NWs successfully solved the previous problems with excellent oxidation stability, well dispersibility and low sintering temperature and high conductivity.

We applied the Cu NWs for high-conductive flexible and foldable electrodes. On the basis of analysis, we confirmed that these Cu NWs based electrodes have low sheet resistance (0.11~0.66 Ω/sq) and remarkable flexible and foldable property after annealing 180 °C in the vacuum oven. We believed that this type of Cu NWs based flexible and foldable electrodes can be promising candidates for next generation electronics.

Keywords: Copper nanowire, oxidation-resistive, high-conductive, flexible and foldable

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Chapter 1. Introduction

1.1 The shapes of nanoparticles

Nanostructure is a crystal between 0 and 3 dimensions below 100 nm, and one nanometer is roughly equal to the length of 4 or 5 atoms line up.[1] Nanostructures not only have the specific structural property, such as quantum size effect, surface effect and small size effect, but possess the interaction properties of quantum coupling effect or coordination enhancement effect.[2,3]

According to the dimension, the nanostructures can be divided into three classes; and the most common shapes are shown in Figure 1. Zero-dimensional, also known as the three dimensional scale of quantum dots that material in the nanoscale, such as nanocluster and nanoparticles.[4] One-dimensional or quantum wires means that the other two dimensional of the crystals are the nanosize, such as nanowires and nanotubes.[5,6] Because of their unique electronic transmission, optical properties and mechanical properties, they have attracted enormous attentions as a new theoretical research model in the nanoscale. As a prospective electrical nanocircuit, one-dimensional nanowires, nanotubes and nanorods have effectively

applied for single electron transfer or a single nanowire light emitting diodes.[7] Two-dimensional means that one dimensional of the materials stay in the nanoscale, such as nanoplates and nanofilms. Due to some characteristic are relative to the size, their properties are significantly different with massive materials.[8] In recently, the most thin and optimal two-dimensional nanomaterial is the graphene. Because of their two-dimensional ultra-thin structure, their light absorption is only 2.3 %; it is almost completely transparent. As the most promising two-dimensional material, their coefficient of thermal conductivity is as high as 5300 W/m·K; the electron mobility is 15000 $cm^2/V·s$; and the resistivity is 10^{-6} Ω·cm, lower than that of copper or silver, because of the overlap of electron cloud in the two-dimensional structure. For their high opto-electrical property, the graphene is expected to be used for transparent touch screen, light panel and solar cell. Therefore, the research of two-dimensional nanostructure has received great attentions in recent years.

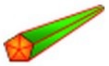
Structures	Shapes	Schematic drawings
single-crystal	perfect/truncated cube	
	perfect/truncated octahedron	
	perfect/truncated tetrahedron	
	rectangular bar	
	octagonal rod	
	rectangular or octagonal wire	
singly twinned	right bipyramid	
	beam	
multiply twinned	decahedron	
	icosahedron	
	five-fold twinned pentagonal rod	
	five-fold twinned pentagonal wire	
	triangular/hexagonal plate	
	disc	

Figure 1. A summary of different shapes of nanoparticles. Adapted from Ref [29] (Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem., Int. Ed.* **2009**, *48*, 60.)

1.2 Copper nanowires based conductive ink

Electrical circuits are essential for many flexible and foldable devices, such as displays, RFID and transistors.[18] Traditionally, photolithography is used for the fabrication of micro-patterns for conductive circuit.[19] However, the technique of photolithography requires some expensive equipment and complicated processes. In this reason, a directly ink writing of conductive patterns with simple process are researched in recent years.[20,21] As a promising alternative material, metal nanoparticle based conductive ink exhibit a very high conductivity compared to other conductive materials, such as conductive polymer and carbon. Although silver exhibits an outstanding electrical conductivity, the problem of the scarcity and high cost is limited for practical wide range applications.

For a conductive ink material, the electrical conductivity of Cu is a little lower than Ag. However, compared with Ag, Cu is not only 100 times less expensive but also 1000 times more abundant than Ag.[22] In general, the sintering temperature of conventional Cu nanoparticles for proper conductivity is more than 300 °C, because of their high contact resistance.[23] Compared with the spherical copper nanopaticles, the Cu NWs have outstanding structural advantages.

Normally, copper nanomaterial-based electrodes have a plenty of point-to-point contacts as a current pathway through the partial sintering process.[23-26] Since the spherical copper nanoparticles have large surface area compared to that of the Cu NWs with same volume, show higher sheet resistance because of their excessive contact points, thus need to be sintered at more increased temperature for exhibiting a proper conductivity. In this reason, the nanowire shapes, which need relative low sintering temperature, are more applicable to the fabrication of electrodes better than using spherical nanoparticles. Although the Cu NWs have relative low sintering temperature, they are difficult to be patterned micro size, because of their ultra-long length. Therefore, adjustment to the appropriate aspect ratio of Cu NWs through the control of synthetic conditions is a critical point in research, which can be patterned micro-size with low sintering temperature.

1.3 Solution processed flexible and foldable electrodes

Solution processed flexible and foldable electrodes have been great interest in development of next generation electronic devices with both for high electrical conductivity and flexibility.[9] For application to the smart clothes and the intelligent medical devices, various flexible and foldable electrodes have been proposed.[10,11]

In general, the traditional flexible and foldable electrodes were based on conductive polymer, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI). They have relative low conductivity (10–1000 Ω/sq) for displays and smart devices.[12] Although the conductive carbons (carbon nanotubes and graphene) are feasible to use for flexible and foldable electronics with their good electrical conductivity (1–100 Ω/sq) and mechanical strength, a wide range of their applications is mostly limited for high-priced source.[13,14] Metal NWs exhibit outstanding conductivity and promising mechanical properties compared to other conductive materials. Silver (Ag) and Cu NWs exhibit high conductivity (0.01–10 Ω/sq) and flexibility.[15-17] However, Ag NWs also have problems of scarcity and high cost. Therefore, the low-cost Cu NWs with high conductive and flexible electrodes have received more attention.

Chapter 2. Experimental process

2.1 Synthesis of copper nanowires

Cu NWs were prepared from ethylene glycol reduction of copper chloride (CuCl) (Ⅰ) with surfactants, according to salt-assisted polyol reduction method. Briefly, 2 mmol of CuCl (Ⅰ), 2 mmol of KBr, 6 mmol of oleylamine were dissolved by 30 ml of ethylene glycol in 100 ml round-bottom flask, while forming Cu-amine complex. Then, it was magnetically stirred for 10 min, and the temperature was raised up to 110 °C for degassing and enhancing the purity, kept for 0.5 h. As we already or well known, the moisture is an obstacle of the formation of pure Cu NWs in the polyol process. Finally, the reaction temperature was raised to 198 °C (heating time is 10 min), and kept it for 1 h. When temperature reached above 180 °C, the solution was changed to reddish brown of Cu nanocrystals, and the size and shape of the nanocrystals were changed continuously until it reached the steady state, so called nanowire structures. When the synthesis of Cu NWs was finished, the products must be quenched by cold water and be washed by hexane, then centrifuged for 3 min in 10000 rpm. The centrifugation was repeated for 3 times and finally the NWs were re-

dispersed and preserved in isopropyl alcohol or n-hexane. It is important that the reaction solution must be washed rapidly. As the time goes on, the Cu^{2+} ions and ambient oxygen in the solution oxidized Cu NWs to form Cu^{+} ions or Cu_2O. It is the reason that the Cu nanomaterials were oxidized during the washing process in general.

2.2 Fabrication of flexible and foldable electrodes

The flexible and foldable electrodes were prepared by vacuum filtration and sintering method. Typically, the well-dispersed Cu NWs were filtered onto a filter paper (pore size 8 μm) to form the Cu NW up-headed paper. After filtration, the Cu NW up-headed paper sintered under vacuum at 180, 200 and 220 °C for 1 h without any reduction gases. The high conductive flexible and foldable electrodes were obtained with paper substrate after sintering. Through the separation of filter paper, the free-standing electrode could be easily obtained.

2.3 Characterization

The morphology of the samle was investigated by field emission scanning electron microscope (SEM) (Hitachi S-4800 FE-SEM) and and high resolution transmission electron microscope (HR-TEM) (JEOL JEM-2100F instrument operated at 200 kV). X-ray diffraction (XRD) (Bruker D8 DISCOVER), ultraviolet-visible spectroscopy (UV-vis) (PerkinElmer Lambda 35) and X-ray photoelectron spectroscopy (XPS) (VG Multilab ESCA 2000 system) were used for the investigation of the oxidation resistance of Cu NWs. The sheet resistance of the Cu NWs films was measured by a conductivity meter (4-point probe) (AiTCo.,Ltd CMT-SR2000N).

Chapter 3. Results and discussion

3.1 Synthetic condition

3.1.1 Molar ratio of surfactants

The molar ratio of surfactants of potassium bromide (KBr) and oleylamine is a dominant factor in synthetic condition. As we known, different shapes of Cu nanoparticles were easily prepared with the control of synthetic condition. In general, the surface energy of copper is {110} > {100} > {111}.[25] To be a steady state, the lowest energy of crystal plane is prefer to be exposed a large area of surface, and various shapes of Cu nanomaterial directly depend on the different proportions of exposed planes.[27] In other words, the shape is directly related to the surface energy gap. Bromide could change the surface energy gap to prepare the metal NWs, because of their unique adsorption ability of metallic {100} plane.[28]

Figure 2 shows the effects of molar ratio variation of two type capping agents in totally fixed 8 mmol. Figure 2a showed the case of 7 mmol of oleylamine and 1 mmol of KBr, only a proportion of seeds were capped by bromide ion and grown in the [$1\bar{1}0$] direction, because

of insufficient quantity of bromide ion.[29] In addition, the [$1\bar{1}0$] direction of Cu nanoparticles was blocked in the midway of the reaction, so finally prepared the tadpole shape. In optimized synthetic condition of 6 mmol of oleylamine and 2 mmol of KBr, (Figure 2b) the bromide as the ionic capping agent was naturally adsorbed in the {100} plane of Cu nanocrystals, and grown along [$1\bar{1}0$] direction.[28,30] Figure 2c shows the case of 4 mmol of oleylamine and 4 mmol of KBr. After the synthesis, above half of the impurities were synthesized, because the exceeded bromide not only capped in the {100} plane but also capped in the {110} and {111} planes.

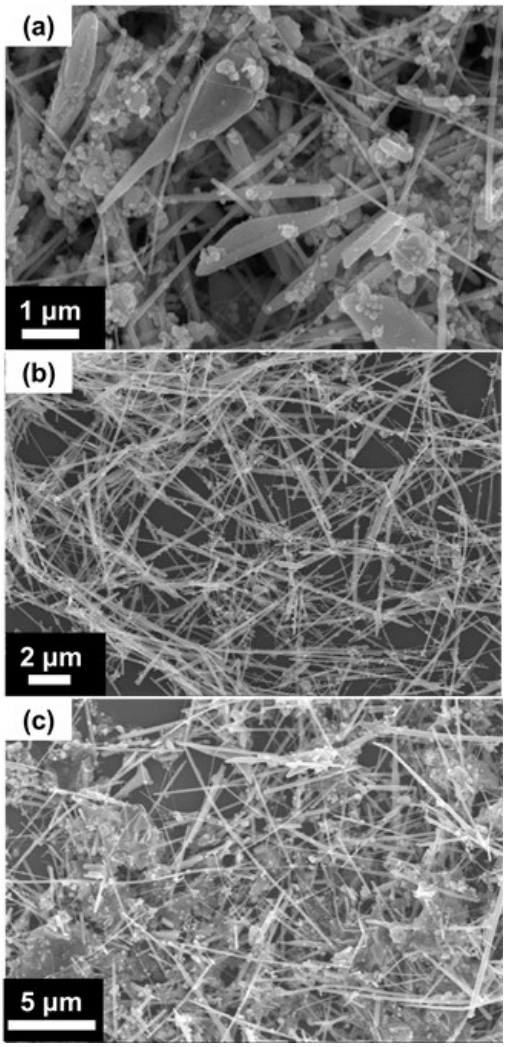


Figure 2. SEM images of Cu NWs synthesized in different molar ratio of oleylamine and KBr, (a) 7 mmol and 1 mmol, (b) 6 mmol and 2 mmol, (c) 4 mmol and 4 mmol.

In order to investigate the effect of individual capping agent, the change of molar mass of oleylamine and KBr is shown in Figure 3. In case of the lack of oleylamine, a few of big particles were prepared by little surfactants, because the capping balance of surfactants was collapsed. In case of the lack of bromide, the copper nanoparticles were grown along [$1\bar{1}0$] direction, the reaction was blocked in the midway, so finally formed the tadpole shaped copper nanoparticles. When the oleylamine or bromide is too overmuch, many of small particles were synthesized. Too much capped molecules induced to be steady state of spherical shape.

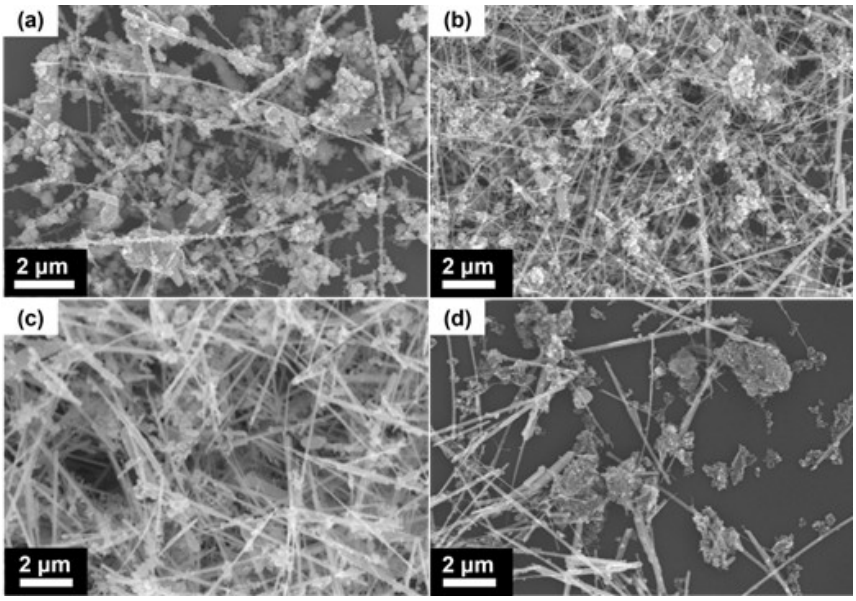


Figure 3. (a–b) SEM images of Cu NWs synthesized by fixed 2 mmol of KBr in different quantities of oleylamine, (a) 3 mmol, (b) 9 mmol. (c–d) SEM images of Cu NWs synthesized by fixed 6 mmol of oleylamine in different quantities of KBr, (c) 1 mmol, (d) 4 mmol.

To fully prove the synthetic mechanisms, we synthesized the Cu NWs without KBr, the SEM image of products was shown in Figure 4a. Although there is no KBr salt, half the proportion of Cu NWs as products was prepared, because the halide ion still existed in reagent, such as Cl^- ion in CuCl (Ⅰ). To demonstrate the effect of halide ion, we also synthesized without halide ion; the precursor of CuCl (Ⅰ) was replaced by copper acetate with same molar mass. The SEM image of products without halide ion was shown in Figure 4b, and that none of wire shape was obtained. Therefore, the KBr salt is a key factor for NWs structural formation and the control of ratio between KBr and oleylamine contents, which is a critical point in synthetic conditions of Cu NWs.

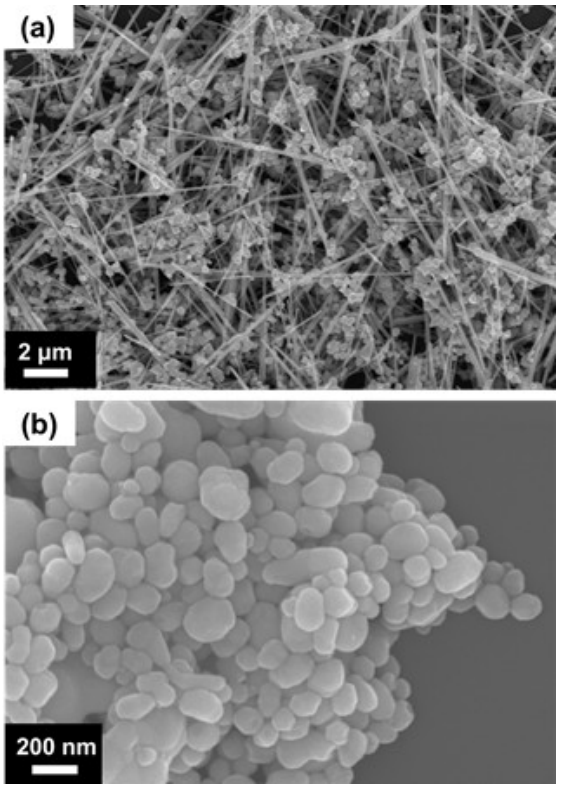


Figure 4. (a) SEM image of products synthesized in 6 mmol of oleylamine and 0 mmol of KBr (b) SEM image of products synthesized in 6 mmol of oleylamine, 0 mmol of KBr; and 2 mmol of CuCl (Ⅰ) was replaced to 2 mmol of copper acetate.

3.1.2 Nucleation rate

Nucleation rate is also a significant factor in synthesis of the Cu NWs. Controlling of nucleation rate was changed by heating rate from 110 to 198 °C. (Figure 5) The products were obtained in the fixed experimental condition of 30 ml of ethylene glycol, 2 mmol of CuCl (Ⅰ), 2 mmol of KBr and 6 mmol of oleylamine. At the heating rate of 18 °C/min, the Cu precursor was reduced rapidly by ethylene glycol before controlling the morphology of the seed. As a result, the flake-like or non-shaped copper was obtained. In the case of heating rate of 9 °C/min, the CuCl (Ⅰ) was firstly reduced to the quasi-stable decahedral shaped copper seeds.[31,32] With the effect of the capping agent, the decahedral shaped Cu seed was grown to several thousands of aspect ratio along the [$1\bar{1}0$] direction and reached to steady state. When the heating rate was 4.5 °C/min, the SEM image showed that above 60% contents of nanoparticles with a few Cu NWs were prepared, because the Cu^{+} ions were reduced to be the steady state of spherical nanoparticles with overmuch time for the nucleation.

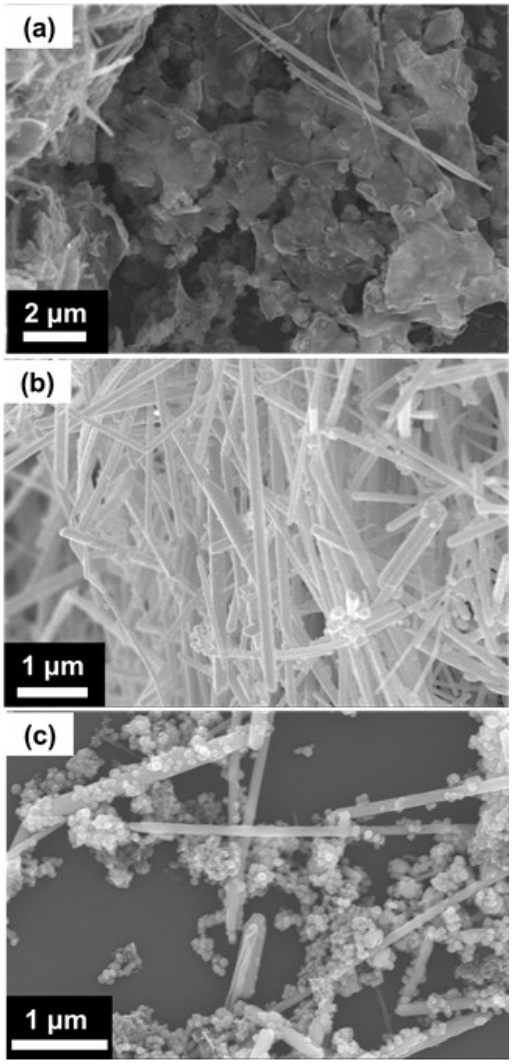


Figure 5. SEM images of Cu NWs synthesized by increasing the temperature from 110 to 198 °C with different heating rate, (a) 18 °C/min, (b) 9 °C/min, (c) 4.5 °C/min.

3.1.3 Optimized synthetic condition

We confirmed the optimum conditions for preparing of the Cu NWs as follow; 2 mmol of CuCl (Ⅰ), 30 ml of ethylene glycol, 6 mmol of oleylamine, 2 mmol of KBr, and the heating rate of 9 °C/min from 110 to 198 °C. (Figure 6) As well known, the Cu NWs were grown under unstable specific state of decahedral shaped copper seed.[28,32] Therefore, the synthetic conditions of Cu NWs are much sensitive than that of other shapes like spheres.

In the experimental process, the precursor of CuCl (Ⅰ) was reacted with the oleylamine to form the blue-color Cu-amine complex in the EG solution, and then, these Cu-amine complex were reduced by EG with a high reduction ability at high temperature (approximately 180 °C).[33] Generally, the order of the surface energy of face-centered-cubic metal is {110} > {100} > {111}.[34] When the lowest surface energy of {111} plane was exposed to the crystal surface, the decahedral shaped Cu seeds were obtained.[28,31] Simultaneously, the bromide molecules selectively capped in the {100} plane with the growth of Cu seed, and the surface energy of the {100} plane tended to be relatively stable.[35] When the growth rate of seed and the molar ratio of capping molecules reached to an optimized

point, the Cu seed began to expose as the {100} plane to crystal surface and grew along [$1\bar{1}0$] direction, because the {100} plane was more stabilized by the capping agents.[23,27]

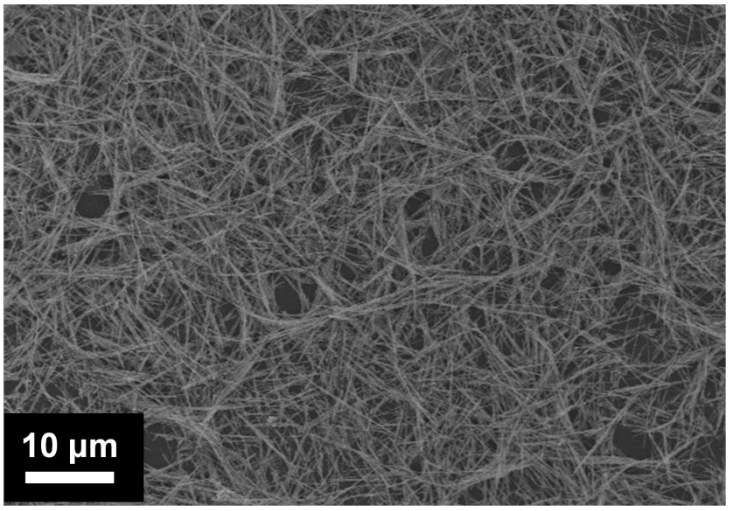


Figure 6. SEM images of Cu NWs synthesized by 6 mmol of oleylamine and 2 mmol of KBr with heating rate of 9 °C/min from 110 to 198 °C.

3.2 Structural characterizations

To demonstrate the crystal structure of synthesized Cu NWs, the high resolution transmission electron microscope (HR-TEM) and X-ray diffraction (XRD) were measured. Figure 7a shows the TEM image of representative three Cu NWs, the average 92 nm of diameter and about 30 μm of length were measured from the dozens of Cu NWs. A selected area of electron diffraction (SAED) pattern of the Cu NWs is shown in Figure 7b, which indicates that electron beam was oriented along the [110] zone axis, which means that the Cu NWs was single-crystalline structure and elongated to $[1\bar{1}0]$ direction.

The HR-TEM image of the Cu NWs in Figure 7c clearly shows the two lattices spacing of {111} and {200} and planes of copper crystals, which is 0.21 and 0.18 nm.[36] Through the fast fourier transform (FFT), the pattern also corresponds to {111} and {200} planes. Figure 7d shows the X-ray diffraction (XRD) pattern of the Cu (JCPDS # 03-1028). The three diffraction peaks at 2θ = 43.5, 50.7, and 74.4 ° respectively matches to the {111}, {200}, and {220} planes.

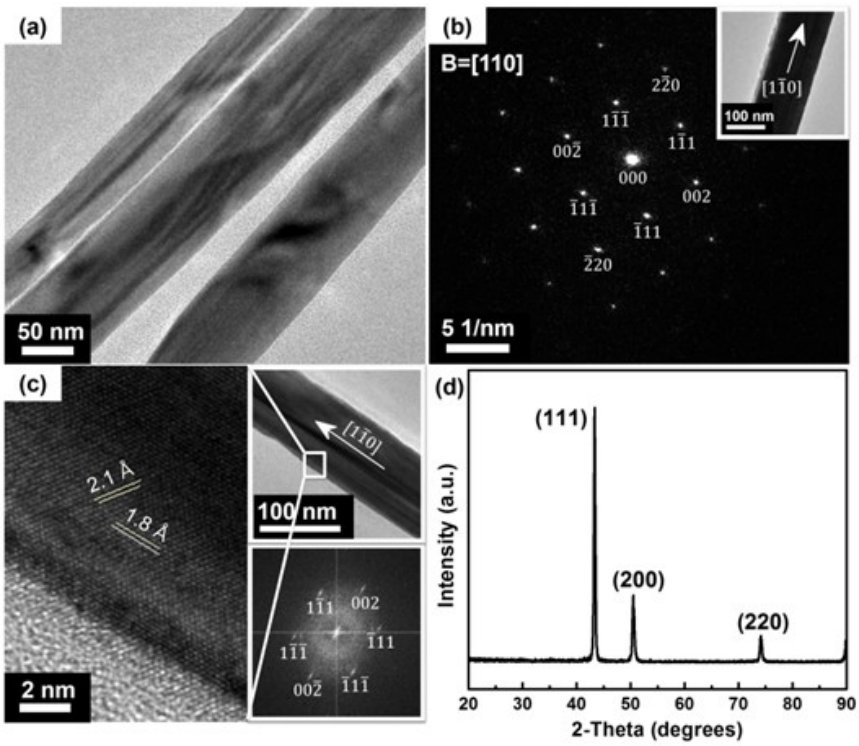


Figure 7. (a) TEM image of representative three Cu NWs. (b) SAED pattern of the Cu NWs along the [100] zone axis. (c) HR-TEM images of the top right white boxed areas, and corresponding FFT pattern of the bottom right. (d) XRD pattern of Cu NWs.

3.3 Oxidation-resistive analysis

As a copper nanomaterial based conductive ink, the oxidation-resistivity is very important for long-term preserving, because copper has activated surface and is easy to be reacted with oxygen.[37] In this study, we synthesized strongly oxidation-resistive Cu NWs through the strong capping of oleylamine and KBr on activated layer for long-term preserving. For investigation of the oxidative resistivity, we carried out XRD, UV-vis, XPS and 4 point probe to measure the change of the oxidation state and electrical conductivity with the preserved time of Cu NWs in isopropyl alcohol (IPA).

Through the analysis of XRD, UV-vis and XPS, there were no significant changes on the characteristics of the Cu NWs. The XRD and UV-vis data exhibit in Figure 8a and 8b, which preserved in 2 and 7 days. As a result, the (111), (200) and (220) of crystal structure and 585 nm of light absorbance had no changes after 7 days. The XPS peaks are shown in Figure 8c, meaning that both 2 day sample and 7 day sample show the characteristic peak of $2p_{1/2}$ and $2p_{3/2}$ with the binding energy of 952.2 eV and 931.8 eV. It was directly proven that the Cu NWs still kept the original state preserved in isopropyl alcohol solution during 7 days without any anti-oxidants.

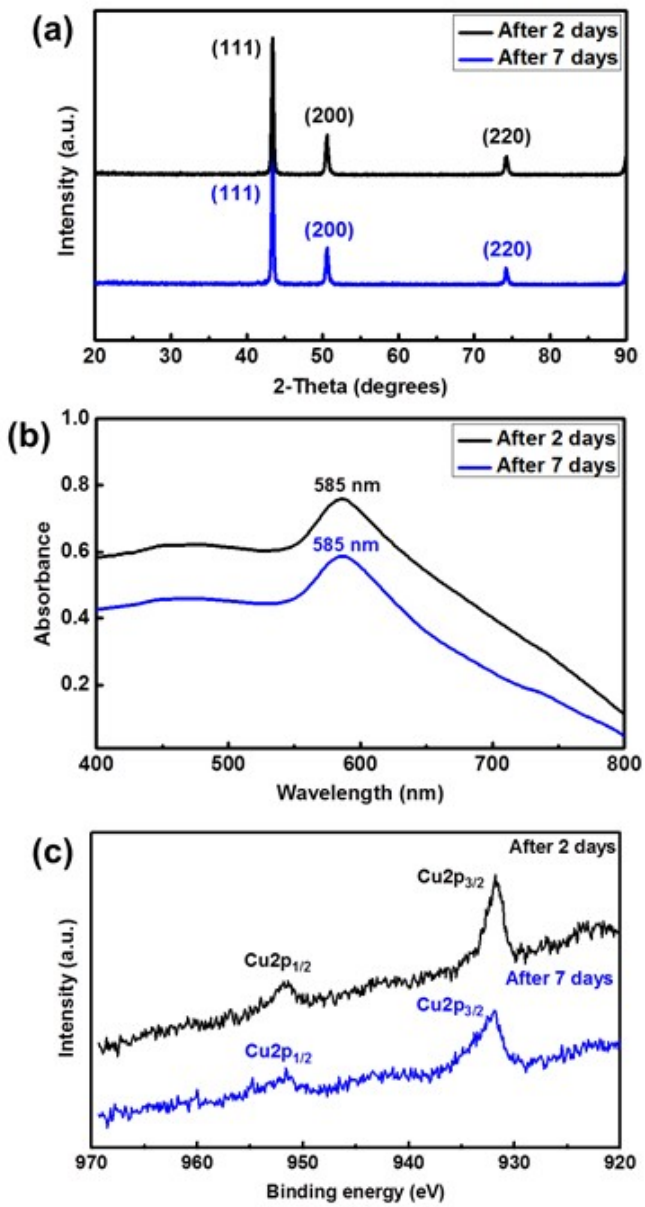


Figure 8. The analysis of Cu NWs preserved in IPA after 2 days and 7 days, (a) XRD pattern (b) UV-vis absorption spectrum (c) XPS pattern.

To further demonstrate high oxidation resistance, the sheet resistance of sintered Cu NWs was then measured by 4-point probe with preserving time. (Figure 9) Without any anti-oxidants, the 7 days preserved Cu NWs still exhibited high conductivity (0.11–0.44 Ω/sq). Certainly, any types of Cu NWs were not absolutely free from the oxidation, and the resistivity of electrode increased with the passage of preserved time. However, these Cu NWs sustained the high electrical conductivity for a relative long time with a little degradation. The strongly capped molecules of surfactants as a stabilizer could delay the oxidation.[38] In this reason, these Cu NWs as a conductive ink material had an enough potential to be used for practical applications with their high oxidation resistance.

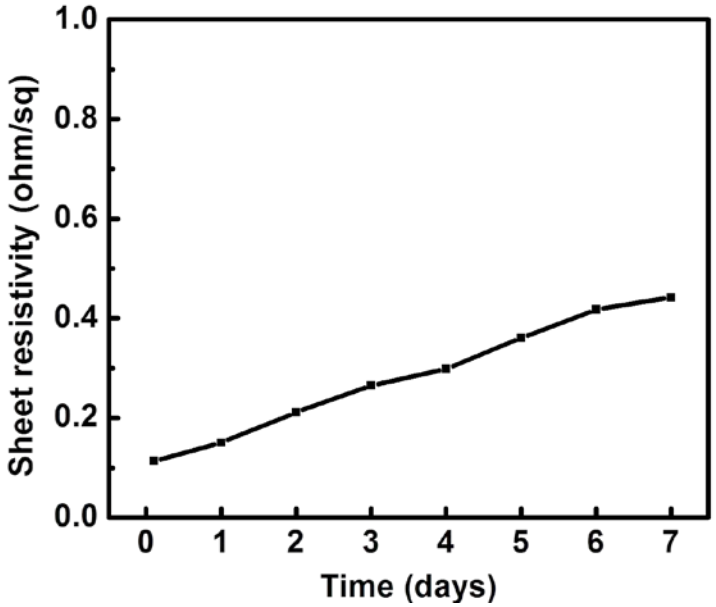


Figure 9. The sheet resistance for Cu NWs based electrode (5 mg/cm^2) preserved within 7 days and sintering at 220 °C.

Although the surface energy of Cu NWs was more higher with the increase of the reaction temperature; they were not oxidized in strong reduction condition of reaction process.[39] To be a steady state, the surface energy of the Cu NWs was lowered the strongly binding of capping molecules. Therefore, the surfactants as the capping molecules were effectively bind to the activated surface of Cu NWs at high temperature. Even the reaction temperature reached to room temperature, those Cu NWs were still remaining at relatively low surface energy. In this reason, this type of Cu NWs possessed an excellent oxidation resistance. In general, other Cu NWs were synthesized in amine, hydrazine or aqueous solution, these solutions could not provide a proper reduction potential or strong capping conditions of high temperature, further not to be an enough steady state. Hence, they were easy to be aggregated and difficult to be used for practical applications.[40] However, this type of Cu NWs has an excellent dispensability in isopropyl alcohol solution. Figure 10 shows the images of the Cu NWs dispersed with the preserved time in isopropyl alcohol solution and re-dispersed easily after a short time shaking even preserved in 7 days. This phenomenon indirectly proved that these synthesized Cu NWs were successfully stabilized by capping molecules with lower surface energy.

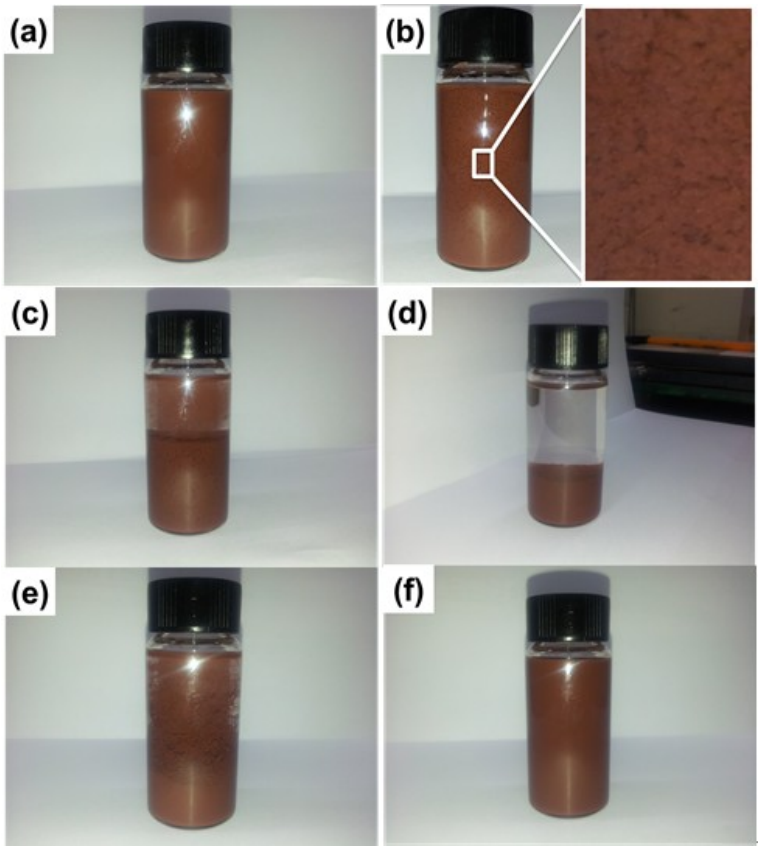


Figure 10.. Photographs of (a) well-dispersed Cu NWs solution (b) the beginning of aggregation after preserved for 1 h. (c) preserved for 2 h. (d) preserved for 3 h. (e) a little shaking after preserved for 7 days (f) re-dispersed Cu NWs solution after preserved for 7 days.

3.4 The electrical and mechanical properties

3.4.1 Electrical property

Both have the electrical conductivity and mechanical properties are the unique characteristics of flexible and foldable electrode. In this study, the Cu NWs based flexible and foldable electrodes were fabricated by filtration and sintering process; and filter paper was used as a flexible substrate.[41] After filtering the well-dispersed Cu NWs on the filter paper (pore size 1 μm, ø=55 mm), the copper up-headed filter paper was sintered at the various temperatures of 180, 200 and 220 °C in a vacuum oven for 1 h without any reduction gases. After sintering, the Cu NW up-headed paper exhibited excellent electrical conductivity, flexibility and foldability, because of enough energy for percolation.

The Cu NWs were percolated at 180 °C of sintering temperature. (Figure 11a) The connected wires were shown in Figure 11b. On the basis of analysis of sheet resistance, we confirmed that the sheet resistance of Cu NWs films are directly related to sintering temperature and surface density. The sintering temperature demonstrated the degree of the percolation; and the connecting of Cu

NWs depended on surface density and uniformity. As a result, the sheet resistance was reduced by high sintering temperature and high surface density. Through the experiments, we confirmed that the 180 °C is the minimum sintering temperature for proper conductivity of Cu NWs films without any reduction condition. In addition, the Cu NWs had good connections, because of the random filtration. The Cu NWs up-headed filter paper showed in figure 11b, and the photograph showed on the top right.

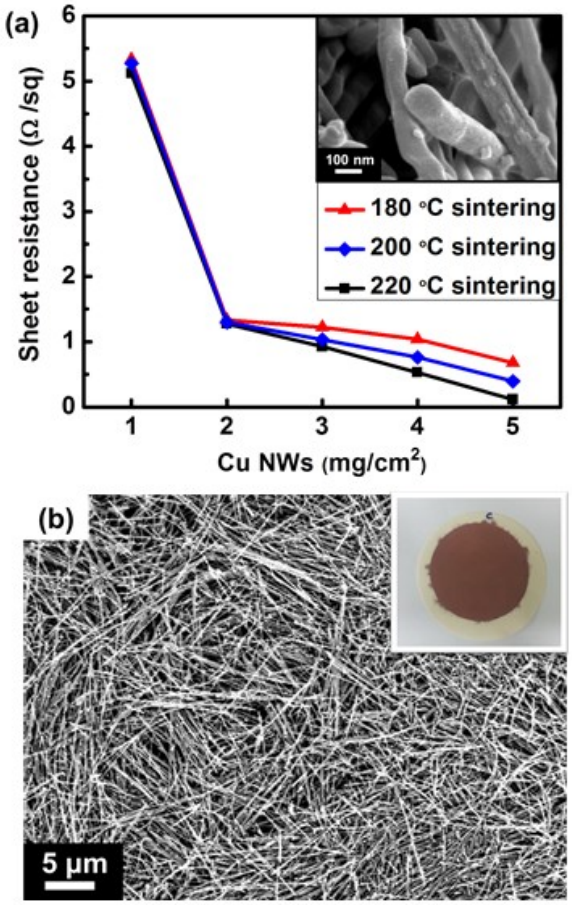


Figure 11. (a) The sheet resistance for various surface densities of Cu NWs sintering at different temperatures; SEM image of Cu NWs after sintering at 180 °C on the top right. (b) SEM images of well dispersed Cu NWs filtered onto filter paper, and photograph of Cu NW up-headed paper on the top right.

3.4.1 Mechanical property

The flexibility was measured by different bending radius and bending times of the flexible Cu NW up-headed paper (5 mg/cm^2) using a self-designed bending machine. As a result, although the sheet resistance was a little fluctuated by changing of the bending radius and the bending times, the Cu NW up-headed paper still exhibited high electrical conductivity. (Figure 12a) For general spherical copper nanoparticles, too much bending induced intergular fracture at the points of contact, because of structure and a plenty of contact points.[26] However, the Cu NWs were grown along [$1\bar{1}0$] direction to several micrometers, made current pathways via simple stacking structures, which can resist the bending effectively.[42] Most of the bending occurred at the linear parts of NWs, not the sintered contact points. Therefore, the Cu NW up-headed paper showed more stable performance under the excessive bending with inherent malleability and flexibility of copper materials. These structural advantages of Cu NWs could also be applied for folding test.

The folding test of the Cu NW up-headed paper was measured by all 90 ° folding sections. (Figure. 12b) The resistivity of the Cu NW up-headed paper was slightly changes with in-direction folding. In

contrast, the resistivity was increased by 6 times with five 90 °-out-direction folding, due to the fact that folding induced creases which develop the deformation of cracks and remain permanently.[14] In comparison of other foldable electrodes, this type of Cu NWs based foldable electrode was still exhibited high conductivity and a tiny degradation even folded several times.[43,44]

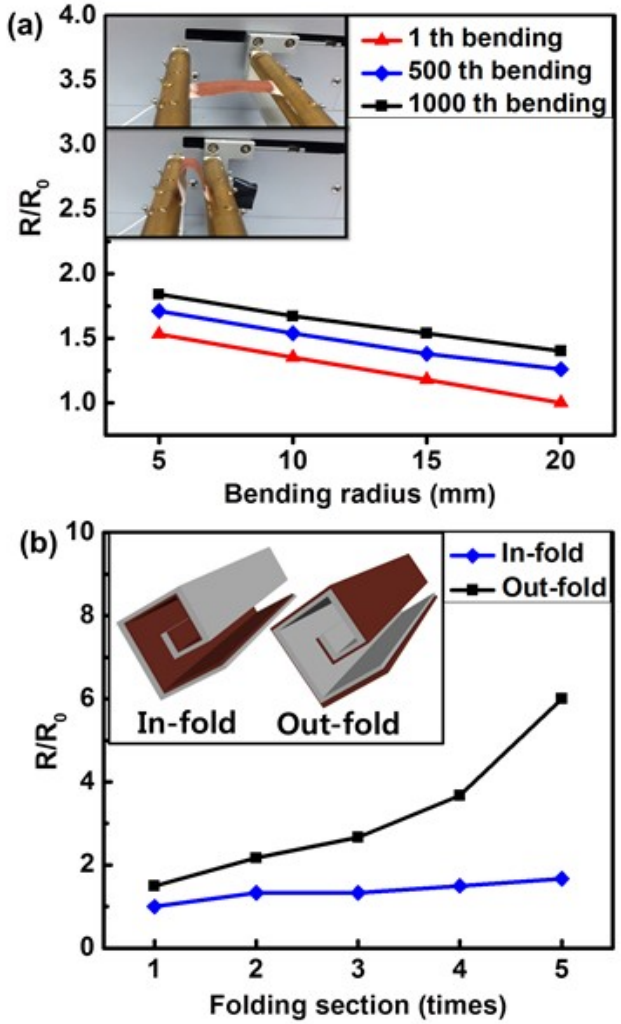


Figure 12. (a) The relative resistance of 180 °C sintered Cu NW up-headed paper (5 mg/cm^2) after 1, 500, 1000 bending test. (b) The relative resistance of 180 °C sintered Cu NW up-headed paper (5 mg/cm^2) under 1–5 folding 90 °-cross sections and the schematic images on the top left. The brown section is Cu and the white section is a filter paper.

The Cu NW up-headed paper as conductive circuit was successfully lighting of a LED with an external power supply, even bended or folded. Moreover, free-standing Cu NWs could be easily obtained by the separation of the filter paper. (Figure 13) As a special structure property of stacked nanowires, the free-standing film depended on randomly connected and supported Cu NWs, and it still maintained intrinsic high electrical conductivity, flexibility and foldability. Compared to bulk metal, these Cu NWs based conductive films had no feeling of metallic contacts, and as light as a thin paper or textile. Therefore, the flexible, foldable and free-standing electrodes had a great potential to be applied for smart clothes and wearable devices.

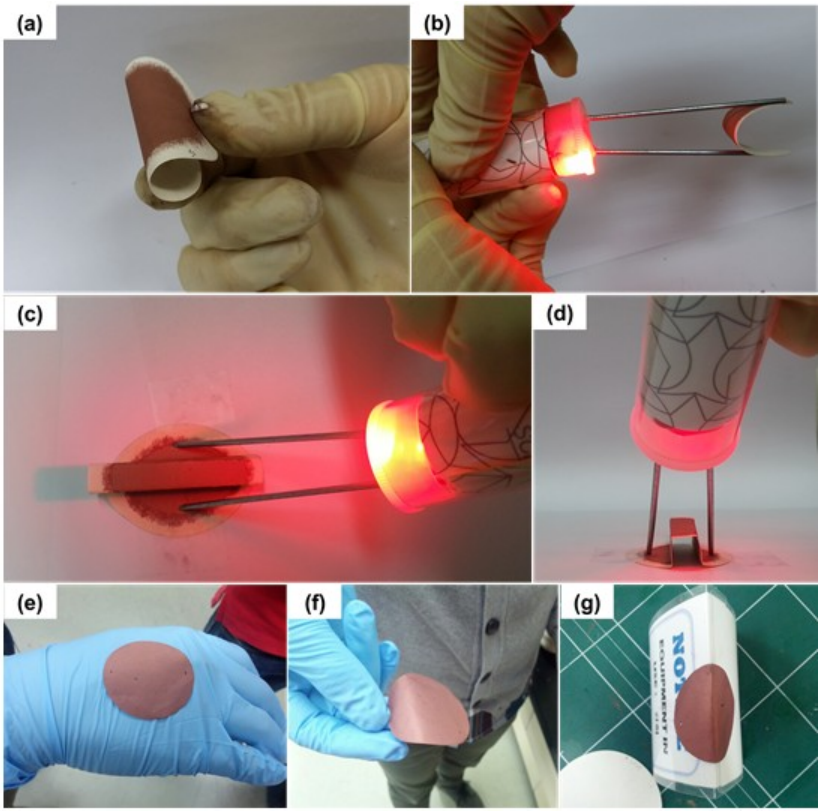


Figure 13. Photographs of (a) flexible electrode, lighting of a LED *via* (b) flexible and (c–d) foldable Cu NW up-headed paper with an external power supply, (e–g) 80 mg of free-standing Cu NWs on the back of the hand, fingers and folded surface.

Chapter 4. Conclusion

We have synthesized oxidation-resistive Cu NWs *via* salt-assisted polyol reduction method toward solution-processed high conductive flexible and foldable electrodes. This type of Cu NWs showed superior oxidation stability and well dispersibility without any anti-oxidants, because of strongly capped molecules of surfactants. Despite of relative low sintering temperature (180~220 °C), the synthesized Cu NWs based flexible and foldable electrodes exhibited a low sheet resistance (0.11 Ω/sq) with a plenty of contact areas. The Cu NWs based electrodes in this study are promisable candidate as the conductive material for flexible and foldable electrode in wide applications, because of their superior electrical conductivity, anti-oxidation property, low sintering temperature, flexibility, foldability, free-standing ability and lower cost than other conductive materials.

References

[1] H. Ohnishi, Y. Kondo, K. Takayanagi, *Nature* **1998**, *395*, 780.

[2] Y. Zhang, J. W. Tan, H. L. Stormer, P. Kim, *Nature* **2005**, *438*, 201.

[3] H. B. Bao, Y. J. Gong, Z. Li, M. Y. Gao, *Chem. Mater.* **2004**, *16*, 3853.

[4] W. C. W. Chan , S. M. Nie , *Science* **1998**, *281*, 2016.

[5] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353.

[6] G. R. Patzke, F. Krumeich, R. Nesper, *Angew. Chem. Int. Ed.* **2002**. *41*, 2446.

[7] S. De, P. J. King, M. Lotya, A. O'Neill, E. M. Doherty, Y. Hernandez, G. S. Duesberg, J. N. Coleman, *Small* **2010**, *6*, 458.

[8] Y. Sun, B. Mayers, Y. Xia, *Nano Lett.* **2003**, *3*, 675.

[9] T. Sekitani, U. Zschieschang, H. Klauk, T. Someya, *Nat. Mater.* **2010**, *9*, 1015.

[10] M. Suh, K. Carroll, N. Cassill, *J. Text. Apparel. Technol. Manage.* **2010**, *6*, 1.

[11] A. C. Siegel, S. T. Phillips, B. J. Wiley, G. M. Whitesides, *Lab Chip* **2009**, *9*, 2775.

[12] X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andersson, A. Volodin, C. van Haesendonck, M. Van der Auweraer, W. R. Salaneck, M. Berggren, *Chem. Mater.* **2006**, *18*, 4354.

[13] D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M. E. Tompson, C. Zhou, *Nano Lett.* **2006**, *6*, 1880.

[14] W. J. Hyun, O. O. Park, B. D. Chin, *Adv. Mater.* **2013**, *25*, 4729.

[15] L. Hu, H. S. Kim, J. Y. Lee, P. Peumans, Y. Cui, *ACS Nano* **2010**, *4*, 2955.

[16] C. H. Liu, X. Yu, *Nanosc. Res. Lett.* **2011**, *6*, 75.

[17] H. Guo, N. Lin, Y. Chen, Z. Wang, Q. Xie, T. Zheng, N. Gao, S. Li, J. Kang, D. Cai, D.-L. Peng, *Sci. Rep.* **2013**, *3*, 2323.

[18] A. Oprea, N. Bârsan, U. Weimar, M.-L. Bauersfeld, D. Ebling, J. Wöllenstein, *Sens. Actuators B* **2008**, *132*, 404.

[19] A. Garcia, J. Polesel-Maris, P. Viel, S. Palacin, T. Berthelot, *Adv. Funct. Mater.* **2011**, *21*, 2096.

[20] D. Kim, J. Moon, *Electrochem. Solid-State Lett.* **2005**, *8*, 30.

[21] B. Park, D. Kim, S. Jeong, J. Moon, *Thin Solid Film* **2007**, *515*, 7706.

[22] U. S. Geological Survey, Mineral Commodity Summaries. Copper. **2013**, *18*, 48.

[23] T. Ishizaki, R. Watanabe, *J. Mater. Chem.*, **2012**, *22*, 25198.

[24] A. R. Rathmell, B. J. Wiley, *Adv. Mater.* **2011**, *23*, 4798.

[25] D. Zhang, R. Wang, M. Wen, D. Weng, X. Cui, J. Sun, H. Li, Y. Lu, *J. Am. Chem. Soc.* **2012**, *134*, 14283.

[26] C. Kind, A. Weber, C. Feldmann *J. Mater. Chem.* **2012**, *22*, 987.

[27] H.-J. Yang, S.-Y. He, H.-L. Chen, H.-Y. Tuan, *Chem. Mater*, **2014**, *26*, 1785.

[28] B. J. Wiley, Y. Sun, B. Mayers, Y. Xia, *Chem. Eur. J.* **2005**, *11*, 454.

[29] Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem., Int. Ed.* **2009**, *48*, 60.

[30] X. Huang, Y. Chen, C. Chiu, H. Zhang, Y. Xu, X. Duan, Y. Huang, *Nanoscale* **2013**, *5*, 6284.

[31] Y. Zhao, Y. Zhang, Y. Li, Z. Yan, *New J. Chem.* **2012**, *36*, 130.

[32] H. Guo, Y. Chen, H. Ping, J. Jin, D.-L. Peng, *Nanoscale* **2013**, 5, 2394.

[33] Y. Shi, H. Li, L. Chen, X. Huang, *Sci. Technol. Adv. Mater.* **2005**, *6*, 761.

[34] M. Jia, Y. Lai, Z. Tian, Y. Liu, *Modell. Simul. Mater. Sci. Eng.* **2009**, *17*, 015006.

[35] A. R. Tao, S. Habas, P. Yang, *Small* **2008**, *4*, 310.

[36] M. Jin, G. He, H. Zhang, J. Zeng, Z. Xie, Y. Xia, *Angew. Chem., Int. Ed.* **2011**, *50*, 10560.

[37] M. Grouchko, A. Kamyshny, S. Magdassi, *J. Mater. Chem.*,**2009**, *19*, 3057.

[38] C. Barriere, K. Piettre, V. Latour, O. Margeat, C. Turrin, B. Chaudret, P. Fau, *J. Mater. Chem.* **2012**, *22*, 2279.

[39] Y. Sun, Y. Yin, B. Mayers, T. Herricks, Y. Xia, *Chem. Mater.* **2002**, *14*, 4736.

[40] A. R. Rathmell, S. M. Bergin, Y Hua, Z. Li, B. J. Wiley, *Adv. Mater.* **2010**, *22*, 3558.

[41] J. Lee, P. Lee, H. Lee, D. Lee, S. S. Lee, S. H. Ko, *Nanoscale* **2012**, *4*, 6408.

[42] G. D. Moon, G. Lim, J. H. Song, M. Shin, T. Yu, B. Lim, U. Jeong, *Adv. Mater.* **2013**, *25*, 2707.

[43] A. Russo, B. Ahn, J. Adams, E. Duoss, J. Bernhard, J. Lewis, *Adv. Mater.* **2011**, *23*, 3426.

[44] S. Glatzel, Z. Schnepp, C. Giordano, *Angew. Chem., Int. Ed.* **2013**, *52*, 2355.

요 약 (국문 초록)

용액 공정에 사용 가능한 구리 나노선은 유망한 전극 물질로서 차세대 전자 제품에 적용되기 위하여 많은 연구가 진행되고 있다. 이런 구리 나노선은 흔히 저가, 높은 전도도, 좋은 유연성 등 특성을 가지고 있다. 최근에 구리 나노선을 합성함에 있어서 다양한 방법이 보고 되었으나 나노 단위의 구리의 강한 산화성과 높은 소성온도로 인하여 실질적으로 사용되기에는 문제점이 있다.

본 연구에서는 간단한 다가 알콜의 환원법으로 산화 안정성이 강하고 소성온도가 낮은 구리 나노선을 합성 하였고 이를 이용하여 유연성 전극을 제조하였다. 브롬화 칼륨과 올레일 아민은 여기에서 구리의 나노선 모양을 인도하고 산화를 막아주는 주요한 역할을 한다.

합성된 물질을 볼 때 구리 나노선은 단일 결정을 가지고 있으며 평균 직경이 92 nm 이고 길이는 30 μm 이며 아이소프로필 알코올 용액에 잘 분산되어 있다. 이렇게 합성된 구리 나노선은 강한 산화 안정성, 좋은 분산성, 낮은 소성 온도 및 높은 전도성을 나타내어 기존의 문제점들은 해결하였다.

구리 나노선을 180 °C 진공 오븐에서 소성 및 제조 된 유연전극은 낮은 표면 저항값을 (0.1~0.6 Ω/sq) 보이고 훌륭

한 기계적 특성을 나타내고 있다. 이런 구리 나노선으로 제조된 유연 전극은 차세대 전자제품의 전극 물질로서 유망한 후보라고 할 수 있다.

주요어 : 구리 나노선, 산화 안정성, 높은 전도도, 유연성

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