FAST AND FACILE SYNTHESIS OF COPPER NANOWIRES AND THEIR APPLICATION AS CONDUCTIVE INK

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Abstract

Copper nanowires (Cu NWs) were synthesized by a chemical reduction method under atmospheric pressure stirring at 700 rpm using Sodium Hydroxide(NaOH), Copper (II) Nitrate ($Cu\ NO_3)_2$, Hydrazine ($N_2\ H_4$) and Ethylenediamine ($C_2\ H_8\ N_2$) at temperature 70 ℃ and the synthesis time of 5 minutes. The surface morphologies of Cu NWs are analyzed by Scanning Electron Microscopy (SEM). SEM results revealed that the lengths of CuNWs were up to 40 μm ranging in diameter from 1 μm to 2 μm. The size of synthesized nanoparticles accompanied with nanowire are in the range of 100 nm to 300 nm. Finally, the as-synthesized Cu NWs are dispersed well in a 0.5 wt % PVP-based ink and then coated onto glass by a Meyer rod. The electrodes fabricated by this technique exhibited good performance (sheet resistance) of 30 Ω/sq.

Keywords: Copper nanowire, hydrazine, low sheet resistance, copper nanowire ink

Introduction

Copper (Cu) and the compounds of gold (Au), silver (Ag), palladium (Pd) and platinum (Pt) are widely used during these days (Bell et al, 2001). Copper has an excellent electrical conductivity. Nanoparticles of these metals have been interested extensively in recent years because of their unexpected physical and chemical properties shown at nanoscale (Ozin, 1992). Owing to extremely small size, copper nanoparticles exhibit enhanced properties when compared with bulk material including large surface area relative to their volume, ability to easily interact with other particles and increased antibacterial efficiency (Song et al, 2006). Because of its excellent electrical conductivity, catalytic behaviour, good compatibility and surface enhanced Raman scattering activity, copper nanoparticles have drawn the attention of scientists to be used as essential component in the future nano-devices (Pergolese et al., 2006). The general problems like aggregation and oxidation

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of copper nanoparticles limit their usage. However, the usage of suitable separate stabilizing agent in the preparation rectifies this problem easily. Copper nanoparticles have been synthesized by different methods.

To date, thermal reduction, thermal decomposition, direct electrochemical reduction from CuO nanoparticles, mechano-chemical process, polyol process, chemical reduction, in-situ synthesis in polymers, electro-exploding wire (EEW) and ion beam radiation have all been developed to prepare nanostructured copper.

Moreover copper is only 6% less conductive than the most conductive element, silver, but it is 1000 times more abundant. Based on these facts, there has been recently a growing interest in the development of one-dimensional copper nanowires (Cu NWs). Several methods for preparing Cu NWs have been reported such as chemical vapour deposition, template assisted electrochemical synthesis or membrane processes. Surprisingly, fabrication of flexible transparent electrodes based on random networks of Cu NWs has been scarcely studied up to now. Wiley and co-workers have pioneered CuNWs based electrodes by preparing flexible films exhibiting sheet resistance of 30 Ω/sq at 85% transmittance. Transparent electrodes with remarkable optoelectronic performances were also obtained with the deposition of electrospun copper nanofibers or nanotrough networks.

In this paper, one pot synthesis of ethylenediamine-mediated processes have been used for the synthesis of ultralong copper nanowires. The stability against aggregation or precipitation of copper nanowires will be improved. Their influence on the different amount of hydrazine affects the nanowire solutions will be discussed. Moreover, optical and electrical properties of air dried ultralong CuNWs thin films are reported. Further, the structural, chemical properties of these two different structures of ultralong CuNWs were examined.

Experimental

2.1 Materials

Analytical grade (BDH, England) Copper (II) Nitrate $(CuNO_3)_2$, Sodium Hydroxide (NaOH), Ethylenediamine ($C_2H_8N_2$), Hydrazine (N_2H_4)

were used as starting precursor. All chemicals were used as purchased without further purification.

2.2 Synthesis of copper nanowire

In a typical copper nanowires synthesis Sodium Hydroxide (NaOH) (15 M, 20 mL), Copper (II) Nitrate(Cu $(NO_3)_2$) (0.15 M, 1 mL)and Ethylenediamine (EDA) (99 %, 8.5 mmol) were mixed for 3 minutes under stirring at 700 rpm. Hydrazine (N_2H_4) (50wt %,0.13 -0.22 mmol) was then added to the solution and the stirring was stopped after 5 minutes. The solution color changed from deep blue to clear and colorless to reddish cake floating on to top of the solution surface, indicating the formation of Cu NWs. Next, the Cu NWs were washed with the above solution many times with water until pH 7 was obtained. Finally the precipitation was washed with ethanol and 2 propanol by centrifuge at 2000 rpm, 5 min and stored in the same solution. The concentration of reducing agent Hydrazine (N_2H_4) is a critical parameter for anisotropic growth of NWs. Moreover, EDA is also a critical chemical. In this method, without EDA, only copper nanoparticles are achieved.

The initial mixing of $Cu(NO_3)_2$, NaOH, and EDA results in a blue complex, $Cu(OH)_4^{2-}$. After the addition of N_2H_4, the blue solution turns white and then colorless, and is comprised mainly of $Cu(OH)^{2-}$ with a small amount of Cu_2O nanoparticles. These Cu_2O nanoparticles are further reduced to metallic Cu aggregates which serve as seeds that sprout CuNWs via continuous reduction of $Cu(OH)^{2-}$. The resultant solute was centrifuged many times to obtain pure Cu Nws precipitations. The results of an EDA-mediated CuNWs synthesis before and after centrifugation are shown in Figure 1(a) and (b). Three samples were synthesized by varying the concentration volume of Hydrazine from 0.13 mmol to 0.22 mmol. The result also reveals that the amount of hydrazine used in the synthesis take part a important role to the formation of CuNWs.

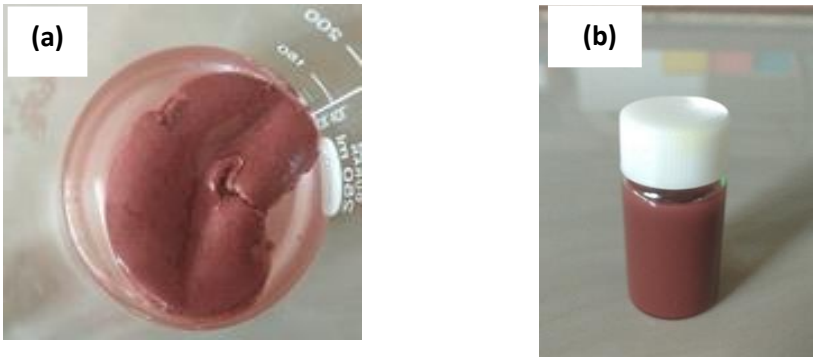


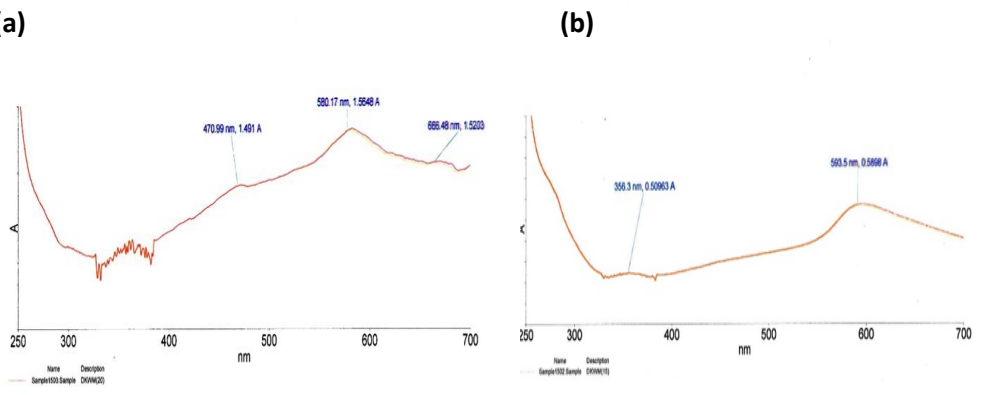
Figure1: Photograph of CuNWs growth solutions. (a) before and (b) after centrifugation

2.3 Characterization

Centrifuge machine (Kokusan H-200 series) was used to separate the colloid from the solutions. The influence of solvent on formation of Cu nanoparticles was confirmed UV _Vis spectrophotometer (Lamda35), X-ray powder diffractometer (Type: RIGAKU–RINT 2000), and Scanning Electron Microscope (Type: JEOL 15 kV).

Results and Discussions

3.1.UV-Vis Measurements



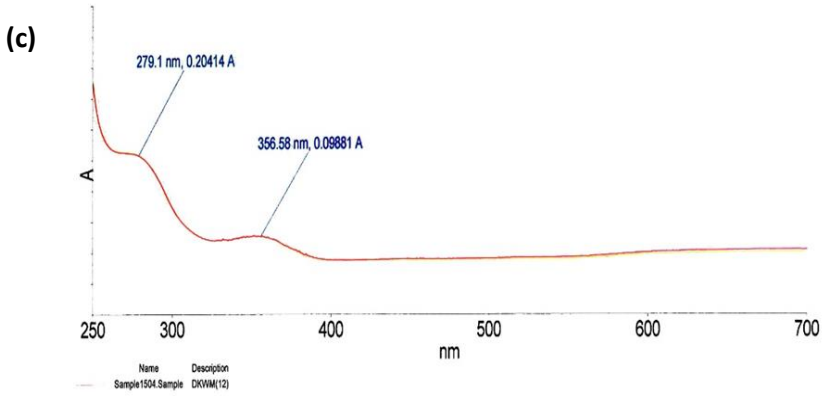


Figure2: UV- Vis spectra of Cu Nanowires solution by using ethylenediamine and hydrazine (a) 0.22 mmol (b) 0.17 mmol and (c) 0.13 mmol.

Figure 2 shows the UV-Vis spectra of the copper nanostructures in the range 250 nm – 700 nm. The results from the different amount of hydrazine (0.22 mmol, 0.17 mmol and 0.13 mmol) show a different response. At the hydrazine amount of 0.22 mmol, the absorption band in visible light region (250 nm – 700 nm, plasmon peak at 580 nm) is typical for copper nanoparticles (Hutter et al, 2001).Different peak at 666 nm and 470 nm shows that the sample has different size of nanostructure. The plasmon peak and the full-width of half-maximum (FWHM) depends on the extent of colloid aggregation (Yamamoto et al, 2004). Figure 2 (b) shows the two different absorption peak at 593 nm and 356 nm indicates that amount of copper nanoparticles decrease and the formation of nanowires are formed. The decrement of the hydrazine amount to 0.13 mmol (Figure 2c) produce a more relevant change in the response. At 0.13 mmol, the intensity of the peak is higher than the detection limit. So the dilution of the sample is needed to obtain the good UV-Vis spectrum. The good spectrum was obtained after diluting the sample to one tenth of original solution. As hydrazine at 0.13 mmol was added to synthesis procedure, the SPR peaks are around 356 nm 279 nm. The peak positioned at 356 nm could be considered as the optical signature of relatively long CuNWs. This implies that the final product synthesized under this particular condition that is using 0.13 mmol mediated gives a high of yield of Cu NWs. As it can be noted, the spectrum is broad and

asymmetric and it has been suggested that this optical feature is due to the non-uniform size of the copper nanoparticles and nanowires, Figure 2.

3.2 SEM Measurements

After the preparation of the nanowires, the suspension of nanowires in ethanol was used for microscope analysis by fabricating a drop of suspension onto a clean glass substrate and allowing ethanol to completely evaporate. The surface morphology of Cu NWs were observed by using SEM. The SEM characterizations of the as-synthesized Cu NWs are shown in Fig.3 (a) (b) and (C). In Fig 3 (a), it was obviously shown that the wire and particles were distributed throughout the sample surface. 90 % of the sample is particles and other is wire. The SEM images suggested that the length of CuNWs were up to more than 40 μm ranging in diameter from 1 μm to 2μm. The sizes of synthesized nanoparticles accompanied with copper wires are in the range of 100 nm to 300 nm.

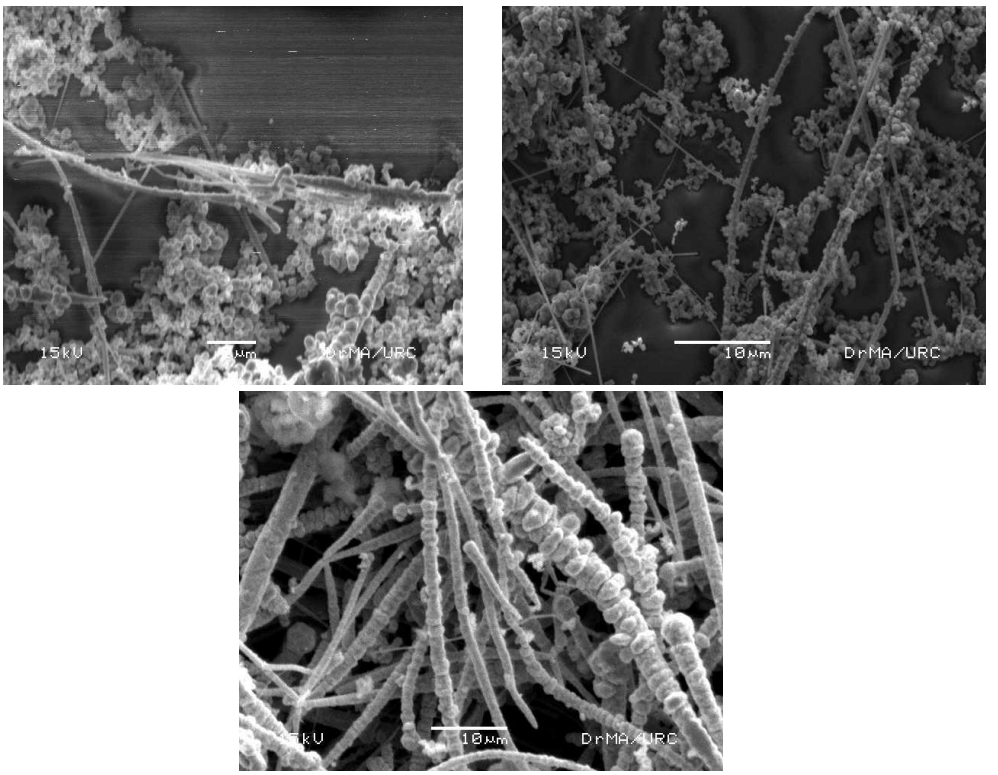


Figure 3: SEM micrograph of Cu Nanowires solution by using ethylenediamine with different amount of hydrazine (a) 0.22 mmol (b) 0.17 mmol and (c) 0.13mmol.

In Fig 3 (b), it was obviously shown that the amount of wire is increasing when the hydrazine amount decreased to 0.17 mmol Fig. 3 (C) show the lengths that could be increased by reducing amount of hydrazine 0.13 mmol. Cu NWs with particle-like structures along their lengths are also observed in this sample. Attaching Cu nanoparticles along the Cu NWs may cause the larger diameter of the wire and consequently increase the larger size distribution in the sample. According to these three experiments, a greater volume hydrazine produced CuNWs accompanied with more CuNPs. This means that there is an optimized condition in which the amount of hydrazine helping to transform the CuNPs into CuNWs.

3.3 XRD Measurements

To confirm the crystalline structure of the copper (Cu) nanostructures, the samples were analyzed on X-ray diffractometer (Model RIGAKU–RINT 2000). All samples give similar XRD spectrum. The polycrystalline properties for drop coated glass thin film of Cu nanostructure were analyzed by using Cu K-α 1 radiation (40 kV, 40 mA) in 2θ range from 10°C to 70° C on a Rigaku powder X-ray diffractometer equipped with a diffracted-beam graphite monochromator. The crystallite domain diameters D were obtained from XRD peaks according to the Scherrer equation: where λ is the wavelength of the incident X-ray beam (1.54056 Å for Cu K-α 1), θ is the Bragg's reflection angle, ΔW is the width of X- ray pattern line at peak half peak height in radians. The Miller indices in XRD pattern reference of Cu (upper) and standard CuO and Cu_2O (lower) were shown in Fig 4. This pattern showed that two XRD peaks appeared at 43.092, 50.209°due to strong Bragg reflections from (111) and (200) planes of fcc (face centred cubic) copper respectively. All reflections are agreed with standard library file (ICDD-PDF#99-0034) of pure copper metal with fcc symmetry. Based on Scherrer equation, the average crystallite size of Cu NWs was found to be 28 nm. No peaks attributed to copper oxides such as CuO and Cu_2 O could be detected.

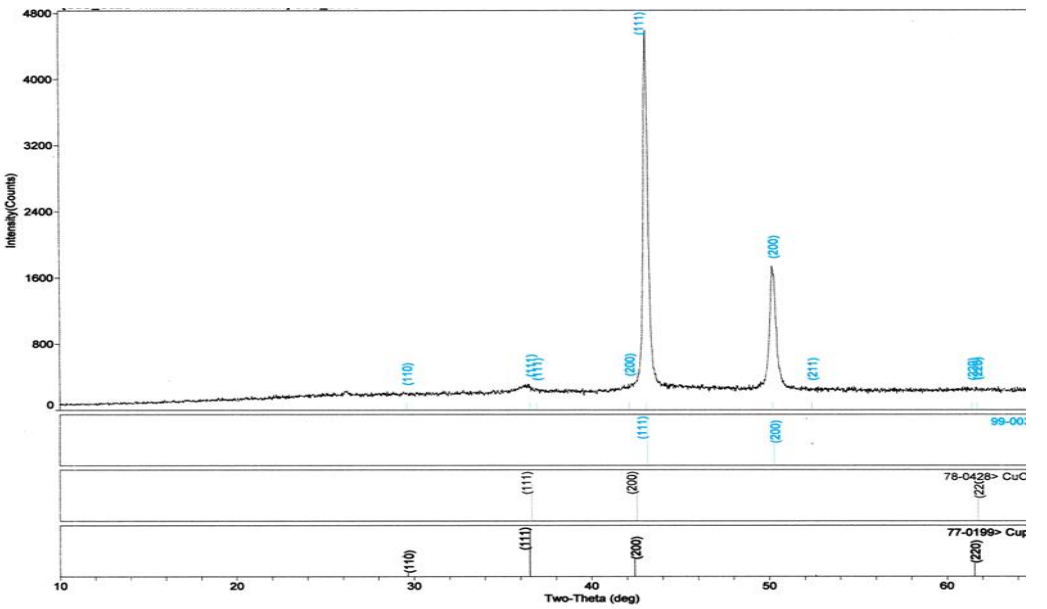


Figure 4: XRD plots obtained from CuNWs sample by using hydrazine 0.13 mmol to investigate the structures and crystallinity. Reference bulk reflections of pure Cu phases are shown at the bottom (ICDD-PDF#99-0034).

3.4 Preparation of copper nanowire ink

First, 0.5 wt % Polyvinylpyrrolidone (PVP)-based ink was prepared by dissolving 0.5 g of PVP-K30 in 100 ml of IPA. The stored Cu NWs were transferred to a 1.5 mL tube and washed once more with the 0.5 wt % PVP-based ink solution by centrifuging at 2000 rpm for 5 min. Lastly, depending on the desired concentration, there quired amount of PVP-based ink was pipetted into the tube containing the copper nanowires to make the final coating solution. Purified copper nanowire ink was deposited onto glass. The very first step before ink deposition is the washing of glass substrate in order to remove dirt and impurities that may have unknowingly settled on the glass substrate. This is done by washing in several substances, namely: acetone, distilled water, ethanol, distilled water again, hydrochloric acid (HCl) and lastly distilled water. These glass substrates are then dried in air blow at room temperature. The CuNWs ink was applied on glass substrates and then annealed at temperature 150 HC to evaporate the solvents. Finally, the coated

film is dipped into acetic acid for 1 min at room temperature and left for 3 min to self-dry. Without any post-treatment, the conductivity between the copper nanowires is greatly confined by the incomplete contact between Cu nanowires and their small contact area because of their round cross section. Interestingly, the dried copper pastes exhibited low electrical resistance of 30 Ω.

Figure 5: Copper nanowires ink deposited on glass substrate. Thin film of copper nanowires shows low sheet resistance 30 Ω.

Conclusion

In conclusion, highly dispersed Cu NWs possessing a long (entire length up to 40 μm) and fine (average diameter of 1μm, 2μm) geometric nature have been successfully synthesized through chemical reduction by using hydrazine as the reducing agent. A series of experiments were carried out to clarify role of reducing agent (hydrazine) on the formation of NWs, which demonstrates that right amount of hydrazine play a key role in forming NW elongation and meanwhile restricting the lateral diameter and production of copper nanoparticles which are bi products of synthesis procedure. Finally, the as-synthesized Cu NWs are dispersed well in a 0.5 wt % PVP-based ink and then coated onto glass by a Meyer rod and the coated film is dipped into acetic acid for 1 min at room temperature and left for 3 min to self-dry. The electrodes fabricated by this technique exhibited excellent performance (sheet resistance) of 30Ω/sq. In virtue of the superior properties, low cost and capability of mass synthesis, further improvement of the performance is believed to lead to a replacement of traditional ITO in the near future.

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References

Choi, H.; Park, S.-H. Seedless Growth of Free-Standing Copper Nanowires by Chemical Vapor Deposition. J. Am. Chem. Soc. 2004, 126, 6248–9.

Gao, T.; Meng, G.; Wang, Y.; Sun, S.; Zhang, L. Electrochemical Synthesis of Copper Nanowires. J. Phys. Condens. Matter 2002, 14, 355–363.

Molares, M. E. T.; Busch mann , V.; Dobrev, D.; Neumann ,R.; Scholz, R.; Schuchert, I. U.; Vetter, J. Single- Crystalline Copper Nanowires Produced Track Membranes. Adv. Mater.

Rathmell, A. R.; Bergin, S. M.; Hua, Y.-L.; Li, Z.-Y.; Wiley, B. J. The Growth Mechanism of Nanowires and Their Properties in Flexible, Transparent Conducting Films. Adv. Mater. 2010, 22, 3558–63.

Rathmell, A. R.; Wiley, B. J. The Synthesis and Coating of Long, Thin Copper Nanowires to Make Flexible, Transparent Conducting Films on Plastic Substrates. Adv. Mater. 2011, 23, 4798–4803.

Shengrong Ye, et al (2016), How Copper Nanowires Grow and How To Control Their Pr Wu, H.; Hu, L.; Rowell, M, W.; Kong, D.; Cha, J, J.; McDonough, J.R.; Zhu, J,; Yang, Y.; Mcghee, M. D.; Cui, Y. Electrospun Metal Nanofiber Webs as High-Performance Transparent Electrode. Nano Lett. 2010, 10, 4242-8.

Wu, H.; Kong, D.; Ruan, Z.; Hsu, P.-C.; Wang, S.; Yu, Z.; Carney, T. J.; Hu, L.; Fan, S.; Cui, Y. A Transparent Electrode Based on a Matel Nanotrough Network. Nat Nanotechnol. 2013, 8, 421-5.

Zhao, Y.; Zhang, Y.; Li, Y.; Yan, Z. Soft Synthesis of Single-Crystal Copper Nanowires of Various Scales. New J. Chem. 2012, 36, 130.