

Synthesis of Copper-Nickel Nanowires by Two-Step Method

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Abstract. Copper (Cu) nanowires were successfully coated with nickel (Ni) using a simple, low-temperature, two-step solution process. The effect of different types of solvent, e.g. ethylene glycol and water, on the deposition of Ni on Cu was investigated using a scanning electron microscope (SEM), coupled with energy dispersive X-ray spectrometer (EDX). On the other hand, the composition of the nanowires was determined by X-ray diffraction (XRD). Smoother Cu-Ni nanowires were produced using ethylene glycol due to better dispersion of Cu nanowires and more controlled Ni diffusion during coating. This can be attributed to the slower reduction of Ni(II) ions in ethylene glycol, leading to a more controlled deposition on the Cu nanowires. The as prepared Cu-Ni nanowires were confirmed to be face-centered cubic (fcc) Cu and fcc Ni. Neither oxides of Cu nor Ni were present on the nanowires produced.

1 Introduction

Flexible electronic applications in advanced fields, such as wearable electronics, medical implants, solar cells, organic light-emitting diodes (OLEDs), smart glass, and foldable displays, are recently being explored [1-2]. In these applications, it's very important to consider flexible materials with high electrical conductivity, and high transparency [1-3]. Currently, indium tin oxide (ITO) is the most commonly used transparent conducting electrode due to its high transmittance (>90%) and low sheet resistances ($10 \Omega \text{ sq}^{-1}$ on glass). However, ITO, being a ceramic, is brittle and prone to cracking. The cost of ITO is also high since indium is scarce (0.05 ppm) in the earth's crust [4-5]. Cu, next to silver (Ag), has the second highest conductivity among all metals and it is more abundant and cheaper. However, the use of Cu nanowires in flexible transparent electrodes is limited due to its high susceptibility to oxidation. As a result, its electrical conductivity suffers. Additionally, Cu is inherently reddish-orange in color, which is not desirable for transparent electronic applications [1]. To address this problem, recent studies propose coating the Cu nanowires with metals having high resistance to oxidation [1-2]. Coating the Cu nanowires with Ni not only improves its resistance to corrosion but also changes its color from reddish-orange to gray [1]. With this, Cu-Ni nanowire is a promising candidate for flexible electronic applications.

In this study, Cu-Ni nanowires were synthesized in solution by a two-step method. The effect of solvent on the quality of the coated Ni was investigated. The diameter of the Cu-Ni nanowires was observed in SEM. Elemental and phase analyses were performed by EDX and XRD, respectively.

2 Experimental

The synthesis was adopted from Wiley et al [1,3] which involved two steps to produce Cu-Ni nanowires. First, Cu nanowires were synthesized in an aqueous solution, followed by Ni coating.

2.1 Materials

Copper nitrate hemi (pentahydrate) [$\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, Sigma Aldrich] and nickel chloride hexahydrate [$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Fluka] were used as Cu(II) and Ni(II) precursor, respectively. Sodium hydroxide [NaOH, RCI Labscan], was added to raise the pH of the solution. On the other hand, ethylenediamine [EDA, Sigma Aldrich] and poly(vinylpyrrolidone) [PVP, 10,000 MW, Sigma Aldrich], and ethylene glycol [EG, JT Baker] were used as surfactants. Hydrazine [N_2H_4 , 35 wt%, Sigma Aldrich] was employed as reducing agent for both Cu(II) and Ni(II).

2.2 Synthesis of Cu nanowires

In a typical experiment, Cu nanowires were synthesized by mixing 200 mL of 15 M NaOH, 10 mL of 0.1 M $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, 1.5 mL of ethylenediamine (EDA), and 0.25 mL of N_2H_4 . The mixture was heated at 65°C for 5 min with continuous stirring at 200 rpm. Then, the solution was removed from heat and 25 mL of 0.46 mM PVP solution was gently added into the mixture. The total solution was then placed in an ice bath for 1 h. After 1 h reaction, the red precipitates were collected and washed

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three times with 3wt% N₂H₄ aqueous solution. The Cu nanowires were then stored in a solution containing 1 wt% PVP and 3 wt% N₂H₄ aqueous solution to avoid oxidation.

2.3 Ni-Coating of Cu nanowires

Cu-Ni nanowires were synthesized by adding 3.66 mL of Cu nanowire stock (1.4 mg Cu nanowires per 1 mL of 3wt% N₂H₄) solution to 6.6 mL of 2 wt% PVP, 0.785 mL of 0.1 M NiCl₂·6H₂O in water, and 0.66 mL of 35wt% N₂H₄. The PVP solution is prepared in water or EG. This resulting Cu-Ni solution was sonicated for 15 s and heated at 80°C for 10 min. During the reaction, the dispersed Cu nanowires became aggregated, floated on the surface of the mixture and changed from red to black, indicating the reduction of Ni(II) ions on the surface of Cu nanowires. After the 10 min reaction, black precipitates were magnetically collected. Similarly, the Cu-Ni nanowires were washed three times with 3wt% N₂H₄ aqueous solution and stored in 1 wt% PVP and 3 wt% N₂H₄ aqueous solution.

2.4 Characterization

Surface morphology of the nanowires was analyzed using scanning electron microscopy (SEM, JEOL 5300). Elemental analysis was performed using energy dispersive x-ray spectroscopy (EDX, JEOL 5300). Compositional analysis was done using x-ray diffraction (XRD, Shimadzu XRD-7000).

3 Results and discussion

Figure 1 shows the SEM images of Cu nanowires before and after coating with Ni using two-step method. Originally, the Cu nanowires have a mean diameter of about 71 nm and mean length of about 30 μm. The Cu nanowires have uniform diameter along its length and exhibit mechanical strength since they remain stable even after several washing. Additionally, the Cu nanowires

appear well-dispersed, suggesting limited agglomeration. High magnification SEM image in the inset of Fig. 1(a) shows that each Cu nanowire is attached to a spherical particle. This could indicate that the Cu nanowires grew from the spherical particles, which act as seeds during growth [6].

After coating with Ni, the diameter of the Cu nanowires significantly increased from 71 to 108 and 121 nm when EG and water were used as solvents for PVP, respectively as seen in Fig. 1(b)-(c). The increase in the average diameter of the nanowires indicates that Ni was coated on the surface. On the other hand, the smaller and smoother Cu-Ni nanowires obtained in the presence of EG in Fig. 1(b) can be attributed to the gradual deposition of Ni atoms on the Cu nanowires [7-8]. Additionally, the better dispersion of the initial Cu nanowires in EG also contributes to the uniform coating of Ni on Cu [7]. The reduction of Ni(II) ions occurs faster in an aqueous solution due to the enhanced oxidation of N₂H₄ in water [8]. Consequently, more Ni atoms are produced at a time leading to non-uniform deposition of Ni along the wire length. This also explains the presence of spherical particles [see inset of Fig. 1(c)] possibly Ni, attached to the surface of the Cu nanowires.

The EDX spectra, with the corresponding SEM images, of the Cu-Ni nanowires prepared in aqueous and EG solutions are shown in Fig. 2. The compositions of the Cu-Ni nanowires produced using EG were 80.74 wt % Cu and 19.26 wt % Ni, while it is 61.90 wt % Cu and 38.10 wt % Ni when water was employed. The higher amount of Ni in the Cu nanowires formed in water can be attributed to the faster reduction of Ni(II) ions, which agrees well with the larger nanowires in Fig. 1(c). It is possible that EG restrains the diffusion of Ni on the Cu nanowires due to its high viscosity. This could lead to a more controlled deposition of Ni on Cu nanowires. Consequently, lower amount of Ni is coated as determined by EDX in Fig. 2. No oxygen was also detected in the Cu-Ni nanowires, which indicates that the both oxides of Cu and Ni were not present in the nanowires.

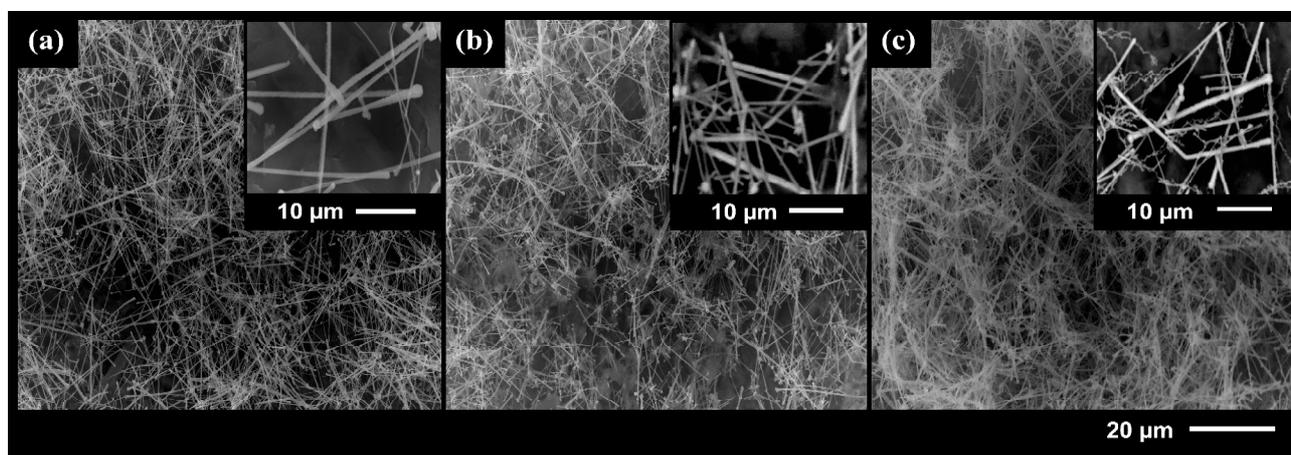


Figure 1. SEM images of Cu nanowires (a) before and after coating with Ni using (b) EG and (c) water as solvents.

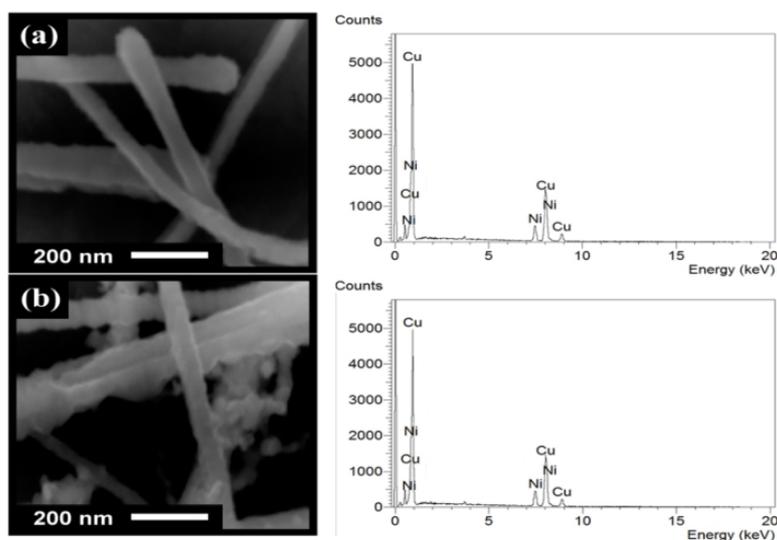


Figure 2. EDX spectra of the Cu-Ni nanowires prepared in aqueous and EG solutions with the corresponding SEM images.

Figure 3 shows the corresponding XRD patterns for the Cu-Ni nanowires prepared in EG and water. For Cu-Ni in EG, three characteristic peaks were observed at 2θ equal to 43.38° , 50.54° and 74.06° corresponding to 111, 200 and 220 peaksof metallic Cu (JCPDS 04-0836), respectively [9]. Further, peaks at 2θ equal to 44.58° , 51.84° , and 76.34° are indexed to to the 111, 200 and 220 peaksof metallic Ni (JCPDS 04-0850), respectively [10]. Similarly, for Cu-Ni formed in water, only peaks

attributed to both metallic Cu and Ni were observed [9-10]. This suggests that the Cu nanowires were successfully coated with Ni. Moreover, no peaks due to oxides of Cu and Ni were detected on the XRD patterns, which agrees with the EDX results. This also attest to the purity of the Cu-Ni nanowires prepared by the proposed method.

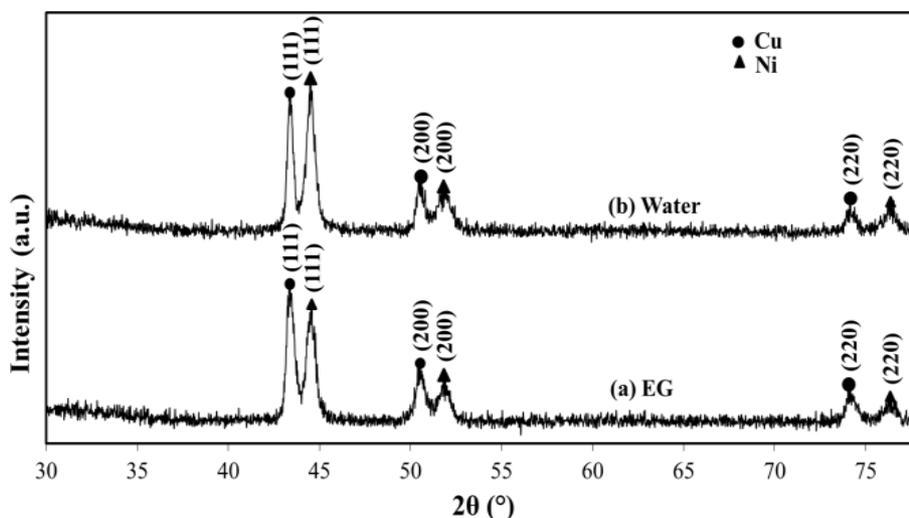


Figure 3. XRD patterns of Cu-Ni nanowires prepared using (a) EG and (b) water as solvents.

4 Conclusion

Cu nanowires, about 71 nm in mean diameter, were successfully coated with Ni using water and EG as solvents. The mean diameter of the Cu nanowires was increased to 108 and 121 nm after coating with Ni using EG and water, respectively. The use of EG prevents the agglomeration of nanowires and improves dispersion of nanowires. Thus resulted to more controlled Ni coating, which produced smaller and smoother Cu-Ni nanowires.

EDX results showed a lower percentage of coated Ni when EG is used as solvent. This is due to the slower reduction of Ni(II) ions in EG. As a result, Ni atoms deposits gradually on Cu nanowires. XRD patterns of the Cu-Ni nanowires revealed peaks of metallic Cu and Ni only. Oxides of Cu and Ni were not present based from both EDX and XRD results.

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