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Effect of Precursor Molar Ratio on the Yield of Cu Nanowires Synthesized using Aqueous Solution Method

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***Abstract*— Synthesis yield of Cu nanowires using aqueous solution method has been controlled by varying the precursor molar ratios. The main materials in this experiment consisted of (1) a precursor of copper (II) nitrate trihydrate or $Cu(NO_3)_2.3H_2O$, (2) a capping agent of ethylenediamine, and (3) a reducing agent of hydrazine. The synthesis process was carried out on the hot plate for 60 min with stirring rate of 60 rpm. For this purpose, the molar ratio of the precursor was varied from 0.012 to 0.2 M. Based on SEM images, we found that the ratio between nanowires and nanoparticles increased by decreasing precursor molar ratio. Furthermore, the Cu nanowires resulted from the synthesis were analyzed by XRD and SEAD, SEM-EDX, and UV-Vis spectroscopy to confirm crystalline properties, morphology and element distribution, and optical properties.**

***Keywords*—aqueous solution; Cu nanowires; precursor molar ratio; reducing agent; capping agent.**

I. INTRODUCTION

Copper is one of the most popular metals in recent technologies [1],[2]. Copper have generated a great deal of interest in recent years due to copper is more abundant in the earth. Copper is 1000 times more abundant than indium or silver and copper is 100 times less expensive [3]-[5]. Copper has been the metals of choice due to its high conductivity, amenability towards solution synthesis and inherent mechanical flexibility [6]. Research on Copper nanowires is continuously developing due to their wide application such as transparent conductive [7]-[10], solar cell [11]-[13], sensor [14]-[16] and electronic devices [17],[18].

Researchers have developed various synthesis Cu nanowires by modifying the capping agent and reductant. Ye *et al*. (2012), demonstrated that synthesis Cu nanowires by modifying the capping agent and reductant for increasing the aspect ratio of Cu nanowires [19]. They found that the size and shape of the Cu nanowires were controllable through adjustment of the molar ratio of ethylenediamine as capping agent and hydrazine as a reductant. Rathmel *et al*. (2010) modified synthesis Cu nanowires by decreased capping agent to result in the length to 6 µm [3]. Xia *et al*. (2011) synthesized Cu nanocrystals in aqueous solution with shape-controlling by glucose as reductant and hexadecyl amine as capping agent [20]. However, there has been a limited report controlling the synthesis yield of Cu nanowires by precursor molar ratio. In this work, we investigate the effect of various precursor molar ratio on the synthesis yield of Cu nanowires. This is significant because the point in the development of applications Cu nanowires based is the design and synthesis of appropriate materials with desirable properties.

II. MATERIAL AND METHOD

A. Material and Instrumentation

The main materials used in this experiment consisted of copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) (99%, Merck), NaOH (99%, Merck), ethylenediamine (EDA, Merck) and hydrazine (N_2H_4, Merck). Meanwhile, the instrumentations included X-ray Diffraction (XRD) and selected area electron diffraction pattern (SAED) (to investigate the crystalline properties), Uv-Vis spectroscopy (to characterize the optical properties of Cu nanowires), and the Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy or SEM-EDX (to study the morphology and size and element distribution of Cu nanowires).

B. Synthesis of Cu nanowires

The procedure of the synthesis as follows, 0.012 M in 20 mL of Cu $(NO_3)_2.3H_2O$ was mixed with 15 M in 100 mL of NaOH to the 150 mL reaction flask. After 2 min, 0.5 mL of EDA and 0.25 mL of hydrazine (35.wt %) were added. During the process, the mixtures were stirred at a speed of 60 rpm for 60 min. This process can be schematically described in Fig.1.

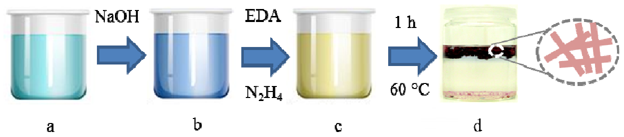

Fig 1. Schematic of synthesis Cu nanowires a. Cu $(NO_3)_2.3H_2O$ in water, b. Cu $(NO_3)_2.3H_2O$ in water + NaOH, c. Cu $(NO_3)_2.3H_2O$ in water + NaOH + EDA + N_2H_4 d. Cu nanowire in water.

Figure 1 (a) illustrates $Cu(NO_3)_2.3H_2O$ dissolved into aquadest. In the condition, the color was a light blue. Figure 1 (b) is the illustration of $Cu(NO_3)_2$ solution that was added NaOH. The addition of NaOH in the solution resulted in a deep blue color. It indicated the formation of $(Cu\ (OH)_4)^{-2}$. Meanwhile, figure 1(c) was $(Cu\ (OH)_4)^{-2}$ solution that was injected EDA and hydrazine resulted in changing the color from a deep blue to clear solution. After 60 min letter, Cu nanowire would be floated on the top of solution (Fig. 1d), and would be ready to be characterized.

III. Result and Discussion

The addition of EDA to the reaction solution is necessary to promote the anisotropic growth of Cu nanowires [3]. Without EDA, only spheres with diameters ranging from 125–500 nm were present after 1 hr.

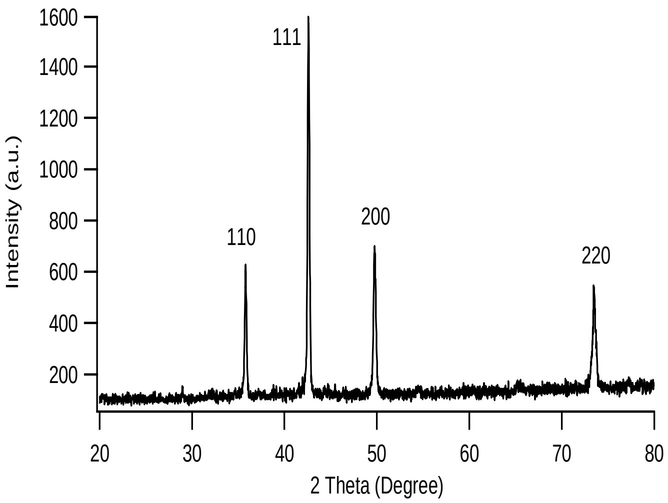

Fig 2. X-ray diffraction of Cu nanowires

X-ray diffraction patteren was performed to examine the crystallinity of the Cu nanowires. Figure 2 shows diffraction pattern of Cu nanowires with crystalline peaks (JCPDS 04-0836). The peaks at 2θ of 433.30, 50.48 and 74.13 corresponds to the peaks of 111, 200 and 220 planes. In the pattern, Cu_2O peak appears at 110 plane, the oxidation may occur during the synthesis process in air ambient.

Thr precursor molar ratio is also a necessary parameter in the formation of Cu nanowires. In this study, Cu nanowires were synthesized using 5 different precursor molar ratios under wet-chemical conditions. We used $Cu(NO_3)_2.3H_2O$ as precursor with variation of molar ratios (0.2 M, 0.1 M, 0.05 M, 0.025 M and 0.012 M).

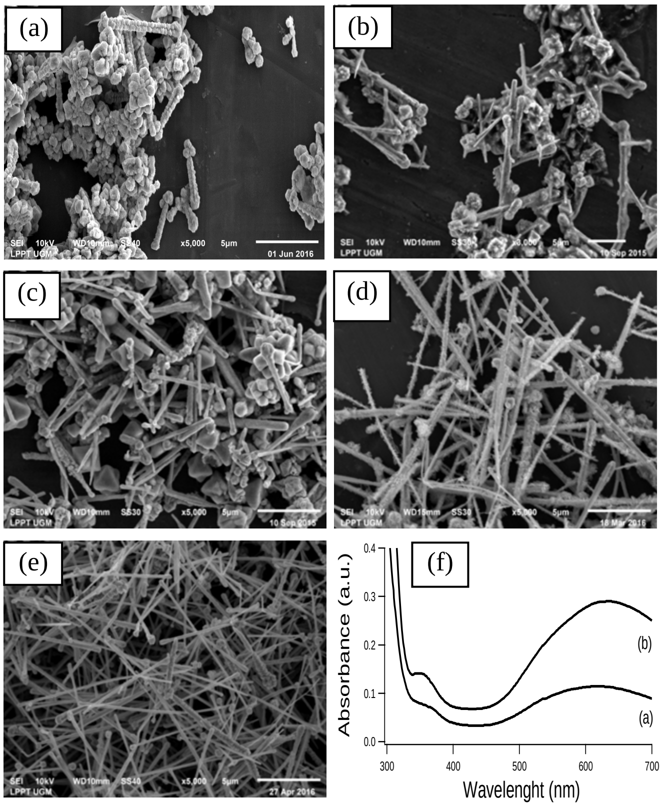

Fig 3. SEM images of Cu nanostructures with variation of the molar precursor, (a). Synthesis precursor molar 0.2 M (b). Synthesis precursor molar 0.1 M (c). Synthesis precursor molar 0.05 M (d). Synthesis precursor molar 0.025 M (e). Synthesis precursor molar 0.012 M (f). Uv-Vis spectra Cu nanowires and Cu nanoparticles.

Precursor molar ratio plays an important role in the yield of the Cu nanowires synthesized using aqueous solution technique. The condition shows the effect of variation precursor molar ratios on the morphology of the Cu nanowires. The experiments were carried out at different precursor molar ratios to change conditions. Figure 3 (a) shows the SEM image of Cu nanostructures (combination of Cu nanoparticles and Cu nanowires) synthesized with 0.2 M $Cu(NO_3)_2.3H_2O$. The image shows domination of Cu nanoparticles. The average diameters was 257 nm. After decreasing molar ratio precursor to 0.1 M, Cu nanowires grew on the among Cu nanoparticles (Fig. 3 b). From this image, it is found that the yield of Cu nanowire increase. When, the amount of precursor molar ratio was decreased to 0.05 M, ratio between Cu nanowires and Cu nanoparticles become 50:50 with diameter 140 nm and 160 nm, respectively (Fig. 3 c). If the precursor molar ratio was further decreased to 0.025 M, the image shows domination of Cu nanowires. The diameter of Cu nanowires were decreased to 125 nm (Fig. 3 d). Finally, precursor molar ratio was decreased to 0.012 M, the yield of Cu nanowire was optimum with diameter 101 nm and length 21 µm (Fig. 3 e). The results indicate that the morphology of final products could be controlled by the amount of precursor molar ratios.

UV–vis spectra of Cu nanostructure were recorded to investigate their optical property. As seen from Fig 3 (f), Cu nanoparticles have absorption spectra at 607 nm. For the nanowires, the absorption spectra shows a slight shift to 620 nm. The absorption spectrum of Cu nanostructures are in good agreement with the reported values for Cu nanoparticles and Cu nanowires.

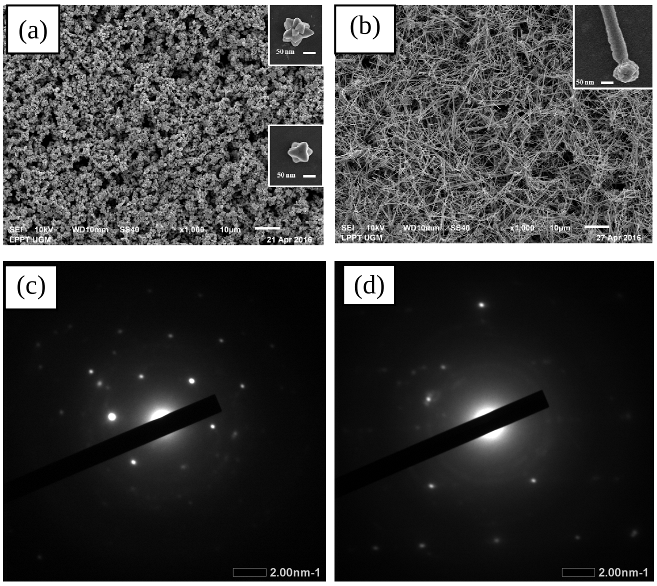

Fig 4. SEM images of Cu nanostructures, (a). Cu nanoparticles with the inset shows individual Cu nanoparticles (b). Cu nanowire with the inset shows individual Cu nanowire. (c). SAED Cu nanoparticles. (d). SAED Cu nanowires.

TABLE I
EDX PROFILE OF CU NANOSTRUCTURES

No	EDX profile	Distribution of elements			
		Cu	**O**	**C**	**Al**
1.	Cu nanoparticles	24.31%	27.15%	33.34%	15.20%
2.	Cu nanowires	89.63%	5.84%	-	4.54%

Decreasing concentration molar ratio from 0.2 M to 0.012 M can change formation of Cu nanoparticles to Cu nanowires. Figure 4 (a) shows SEM image of Cu nanoparticles with diameter 162 nm. The individual Cu nanoparticle (inset in Fig 4 a) formed single nanoparticle with difference shapes. Figure 4 (b) shows SEM image of Cu nanowires with diameter and length of 101 nm and 21 μm, respectively. The SAED pattern (Fig 4 c and 4 d) indicate that Cu nanoparticles and Cu nanowires are a single crystal. The SAED patterns indicate the electron beams are oriented along [110] plane. Table I (1) shows EDX analysis the distribution of elements in Cu nanoparticles. The relative concentrations of Cu, O, C and Al elements are around 24.31%, 27.15%, 33.34% and 15.20%, respectively. The distribution of Al presents may be because of the preparation with an aluminum grid. Table I (2) shows EDX analysis the distribution of elements in Cu nanowires. The relative concentrations of Cu, O and Al elements are around 89.63%, 5.84% and 4.54%, respectively.

IV. CONCLUSIONS

Effects of precursor molar ratio on the yield of Cu nanowires synthesized using aqueous solution method have been successfully investigated. Decreasing of precursor molar ratio from 0.2 M to 0.012 M increased the yield of ratio Cu nanowires on the Cu nanoparticles. 0.2 M of precursor molar ratio produce less Cu nanowires with bigger diameters. However, 0.012 M of precursor molar ratio produce domination of Cu nanowire with diameter 101 nm and length 21 μm.

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