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Low cost fabrication of flexible transparent electrodes using copper nanowires

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ABSTRACT

Copper nanowires have been successfully applied to produce flexible transparent electrodes with excellent performance. The techniques for the fabrication of electrodes commonly use nitrocellulose-based ink as the coating solvent. However, this ink is expensive, contains many toxic chemicals, and requires expensive equipment, such as plasma cleaners, furnace tubes, etc. for post-treatment. In this study, we demonstrate an approach using polyvinylpyrrolidone-based ink for successful fabrication of high quality copper nanowire based transparent electrodes. When compared to the nitrocellulose-base ink, this ink is 2.5 times less expensive, simple to synthesize and requires only an oven and glacial acetic acid for post-treatment. The results showed that the copper nanowire based transparent electrodes produced using our ink exhibited equivalent performance to the ones fabricated by applying the nitrocellulose-based ink. Several experiments were carried out to fully understand and optimize our approach.

1. Introduction

In recent years, there has been a growing demand for flexible transparent electrodes (FTEs), which are crucial components for various electronic devices such as flexible displays, flexible solar cells, touch screens, etc. [1–4]. As the name suggests, FTEs are flexible, transparent and highly conducting and can even withstand high levels of bending, stretching, twisting, and folding without degradation of their transparency or their electrical properties [5]. Traditional transparent electrodes utilize indium tin oxide (ITO) as a conducting material due to its excellent optical and electrical performance [2,6,7]. However, ITO is brittle and toxic, which renders it unsuitable for FTEs [8–11]. Thus, efforts have been made to develop substitutes for ITO [1,6,12,13]. Lately, copper nanowires (Cu NWs) have emerged as attractive materials for the fabrication of FTEs [2,7,11,14–16]. Copper is the second most electrically conductive metal (after silver), and is also soft and ductile [17]. Copper is 100 times more economical than both silver and ITO, as vast reserves of copper are available on earth [18]. Due to these merits, copper nanowires have been applied to fabricate remarkably flexible thin films [2,14,15].

Meyer rod coating is a simple and scalable method commonly used for fabricating transparent electrodes [19–21]. Wiley et al. developed a nitrocellulose-based ink to optimize the Meyer rod coating of copper nanowires [11,22,23]. Due to the good dispersion of copper nanowires in the nitrocellulose-based ink, it is easy to obtain a uniform coating and the coated layer has excellent adhesion to the substrate. In order to make it electrically conductive, the coated film needs to be plasma cleaned under a forming gas atmosphere (5% hydrogen, 95% nitrogen) and then annealed in a tube furnace under a pure hydrogen atmosphere at 175 °C. In 2013, Mayousse et al. discovered that the purification of Cu NWs can be achieved simply by wet treatment with glacial acetic acid [24]. Later, in 2014, Steward et al. applied glacial acetic acid to remove nitrocellulose-based ink from coated film [25]. They showed that dipping in acetic acid reduces the contact resistance between the copper nanowires to nearly the same degree as that obtained while using the combination of plasma cleaning and hydrogen annealing. However, this approach consists of 6 cycles of dipping and drying procedures; thus it is not a simple process. Moreover, this method still utilizes the nitrocellulose-based ink which is toxic, expensive and easily flammable.

In this work, we report a new facile, low-cost, and eco-friendly method for the fabrication of high quality FTEs using copper nanowires. A polyvinylpyrrolidone (PVP)-based ink was used instead of nitrocellulose-based ink, to prepare the coating solution. Furthermore, the proposed method does not require the film to be immersed in acetic acid more than once. Besides, copper (II) sulfate was replaced by copper (II) nitrate for the synthesis of Cu NWs in order to further reduce the cost of fabrication.

2. Materials and methods

2.1. Materials

Copper (II) sulfate pentahydrate and sodium hydroxide beads were purchased from Daejung Chemical & Metal (South Korea). Ethylenediamine (EDA, E1521), 35 wt.% hydrazine (N_2H_4) in water, isopropyl

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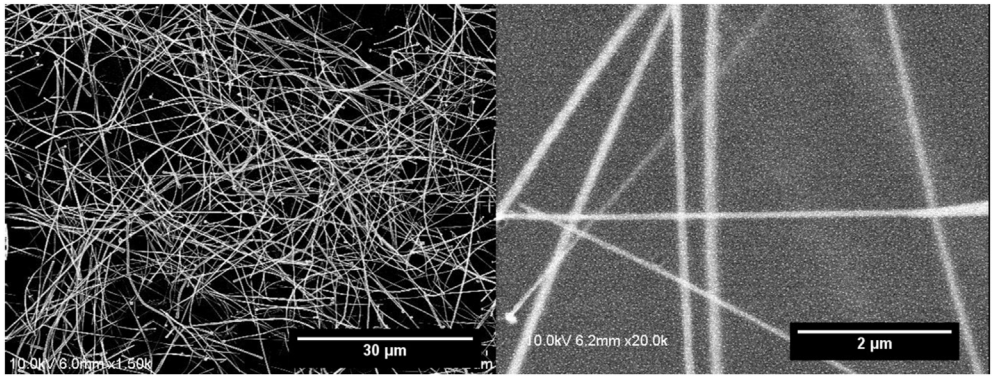

Fig. 1. SEM of CuNWs.

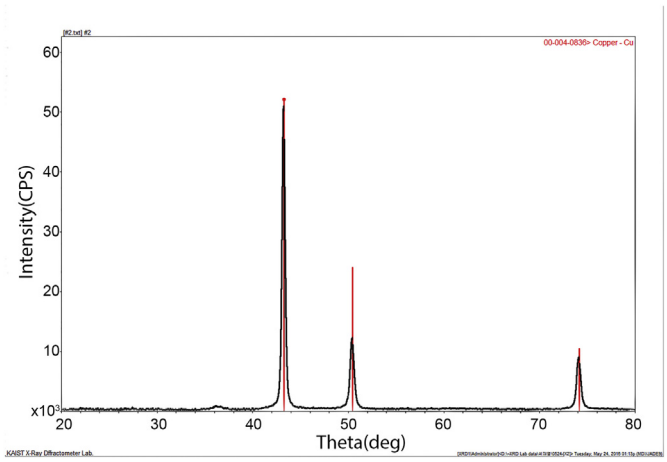

Fig. 2. XRD of synthesized CuNWs.

alcohol (IPA, W292912), *N*-diethylhydroxylamine (DEHA, 471593) and polyvinylpyrrolidone (PVP, MW = 30,000 and 360,000) were procured from Sigma-Aldrich (USA). Polyethylene terephthalate (PET) with 50 μm thickness was obtained from KAIST (Deajeon, South Korea). Meyer rods of sizes #12, 16, 20 and 24 were supplied by RD Specialties©.

2.2. Synthesis of copper nanowires

The flasks, beakers, measuring cylinders, and stir bars used for the process were cleaned thoroughly and dried at room temperature. Copper nanowires were synthesized according to the seed method of Ye et al. with several modifications [26]. First, the seed solution was prepared by pouring 10 mL of NaOH (15 M) and 2 mL of $Cu(SO_4)_2$ (0.1 M) into an Erlenmeyer flask. The solution was kept under stirring and heated to 50 °C on a hot plate. Simultaneously, growth solution was prepared by mixing 40 mL of NaOH (15 M), 0.3 mL of EDA and 2 mL of $Cu(SO_4)_2$ (0.1 M) in a flask and heated at 50 °C on another hotplate. Next, 10 μL of N_2H_4 (35 wt.%) was added to the seed solution and 2 min later, 2 mL of this seed solution was transferred to the flask containing the growth solution. Subsequently, 20 μL of N_2H_4 (35 wt.%) was added to the flask containing the growth solution. Two min later, 5 mL of PVP (0.4 wt.% K30 in deionized (DI) water) was poured gently in to the growth solution. The growth solution was placed in an ice bath for 5 min and later kept in an oven at 65 °C for 30 min. Copper nanowire disks formed on the top of the solution were removed by vortexing and washed thrice with DI water and washing solution (1% DEHA, 1% PVP-K30 in DI water), respectively. Finally, Cu NWs were stored in 1% DEHA, 1% PVP-K30 solution for further studies.

In order to weight the as-synthesized Cu NWs, the sample was dissolved completely in 2% HNO_3 solution. And then by using the PowerWave HT Microplate Spectrophotometer, the absorbance of the sample at wavelength 800 nm was measured.

2.3. Preparation of flexible transparent electrode

First, 2.5 wt.% PVP-based ink was prepared by dissolving 2.5 mg PVP-K90 in 97.5 mg IPA. Cu NWs obtained from above reactions were transferred to 1.5 mL tube. Next, this suspension was centrifuged at 2000 rpm for 5 min, the supernatant was removed from nanowires. The nanowires then were dispensed in IPA by vortex for 30 s. This centrifugation-redispersion cycle was repeated for 3 more times to remove most of PVP-K30, DEHA and water. Then the nanowires were washed one more time with the PVP-based ink solution by centrifuging at 2000 rpm for 5 min. Lastly, depending on the desired concentration, the required amount of PVP-based ink (from 0.3 to 0.6 mL) was pipetted into the tube containing the copper nanowires to make the final coating solution (concentration from 10.45 to 20.9 mg/mL).

Table 1
Comparison price chart of nitrocellulose-based ink and 2.5% PVP-based ink.

	Chemicals	Amount	Unit	Market price (KRW)	Total cost (KRW/mL)
Nitrocellulose-based ink	H_2SO_4	4	mL	164,000/100 mL	198.36
	HNO_3	4	mL	67,000/100 mL	
	Acetone	41	g	122,000/1 L	
	Ethanol	42	g	104,000/500 mL	
	Ethyl acetate	2	g	66,000/100 mL	
	Pentyl acetate	5	g	92,000/250 mL	
	Isopropanol	5	g	91,000/1 kg	
	Toluene	8	g	59,000/100 mL	
PVP-based ink	PVP	2	g	79,000/100 g	77.8
	IPA	78.5	g	84,000/1 L	
Cost ratio = nitrocellulose-based ink / PVP-based ink					2.55

All the chemical prices were collected from the website of Sigma-Aldrich website on 2nd April 2016.