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Synthesis of stable ultra-small Cu nanoparticles for direct writing flexible electronics

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ABSTRACT

In this study, pure Cu nanoparticles (NPs) have been successfully synthesized and the Cu nano-ink was prepared for direct writing on photo paper using a roller pen. The tri-sodium citrate was used as initial reducing-cum-surfactant agent followed by hydrazine as a second massive reducing agent and cetyltrimethylammonium bromide (CTAB) as extra surfactant agent. From the XRD, TEM, and HR-TEM analyses, the synthesized particles are confirmed to be Cu in spherical shape with sizes range of 2.5 ± 1.0 nm. By analyzing the FT-IR spectroscopy and TGA curves, it was found that the obtained particles capped with tri-sodium citrate and CTAB layers are stable to oxidation up to the temperature 228 °C. The reduced size and enhanced air-stability of the Cu NPs result in an improved particle density upon sintering, which is mainly responsible for the increased conductivity of the Cu patterns. The resistivity of Cu patterns sintered in Ar at 160 °C for 2 h is $7.2 \pm 0.6\ \mu\Omega$ cm, which is 4.40 times the bulk Cu resistivity. The drawn Cu lines exhibited excellent integrity and good conductivity, which were experimentally tested. Moreover, a Cu electrode and a sample RFID antenna were successfully made.

1. Introduction

The preparation of conductive patterns on flexible substrate is vital in the printed electronics and has been achieved for various applications, including flexible displays [1], flexible antennas [2], solar cells [3], transistors [4], sensors [5], batteries [6], etc. Traditionally, photolithography technology is widely used to produce very precise thin circuits in flexible electronics [7]. However, this method requires expensive facilities and involves etching, patterning, electroplating, etc., so it is an uneconomical, complicated and time consuming process. Therefore, many new manufacturing techniques for fabricating conductive patterns in flexible electronics are becoming more important and expected, such as inkjet printing [8], sputter coating [9], airbrush spraying [10]. However, these methods are either costly or some pollution and waste cannot be avoided. In this regard, the convenient and low-cost pen-on-paper approach, using a roller pen filled with conductive ink to directly write conductive patterns on paper substrate, is considered as a promising alternative technology [11,12].

Photo paper as a flexible substrate is newly explored to produce flexible patterns. This is because photo paper has a set of advantages over conventional flexible substrate (polyimide plastics) as follows: (1) paper is ubiquitous and inexpensive; (2) a photo paper, which is porous and has a good graphomotor property as well as a low surface roughness, guarantees the flexibility of the substrate and excellent adsorption ability between the ink and the substrate; (3) paper can be trimmed, rolled, folded into 3D configurations or as one part of other devices, such as micro-portable analytical devices (mPADS). For these reasons, photo paper has attracted more and more attention. Russo [11] and Tai and Yang [12] reported the fabrication of conductive electronic arts and practical circuit on paper, respectively.

Pen-on-paper approach requires conductive liquid phase materials, i.e., inks, to be printed through a pen head, from which the conductive patterns forms after sintering. Up to now, carbon [13], conductive polymers [14] or metal–organic complexes [15] as conductive ink materials have been used in the formation of conductive patterns or lines, but these materials typically exhibit low electrical conductivity and low resolution. In contrast, many metallic particles that possess high conductivity can be used as the alternative materials. Most recent studies have focused on noble metals such as gold and silver NPs [16–18]. However, their high costs limit their applications. Thus, copper is highly anticipated because it is highly conductive but much cheaper than silver and gold [19,20]. The main challenge to adopt copper NPs is that they are easily oxidized into either Cu_2O or CuO because the oxides phases are more thermodynamically stable than pure Cu. In order to obtain air stable copper particles, some previous papers have reported to synthesize

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Cu NPs in a glove box [21] or nitrogen atmosphere [22], but the copper oxide was easily formed when they exposed in air. As is well known, the presence of Cu_2O or CuO on Cu NPs surface is harmful to the pattern conductivity and results in increasing the sintering temperature of the pattern. In this regard, the synthesis of Cu NPs with anti-oxidation stability is a prerequisite to develop a highly conductive Cu pattern.

In this paper, a facile and promising approach is used to fabricate a paper-based Cu conductive pattern for flexible electronics by direct writing. First, air stable Cu NPs were synthesized using CTAB as a capping polymer layer under tri-sodium citrate and massive hydrazine, from which a conductive ink applicable for direct writing was prepared. Second, a kind of roller pen as the writing implement was designed, and prepared by filling the Cu nano-ink into the pipe of the pen. Third, ordinary photo paper as the substrate guarantees the flexibility and fold ability of the Cu pattern on photo paper. The drawn Cu lines and electrode as well as prepared RFID antenna were conductive and flexible after sintering at 160 °C for 2 h under Ar atmosphere.

2. Experimental

2.1. Materials

The cetyltrimethylammonium bromide (CTAB), diethylene glycol (DEG) were purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. Copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), tri-sodium citrate ($Na_3C_6H_5O_7$), hydrazine (($N_2H_4{\cdot}H_2O$), ethanol, ethylene glycol (EG) and glycerol were all obtained from Chemical Reagent Company, Tianjin, China. All these agents were used without further purification. The distilled water was used in all experiments.

2.2. Preparation of Cu NPs and Cu nano-ink

For a typical preparation of Cu NPs in ambient atmosphere, 0.35 g (0.96 mmol) of CTAB, 0.5 g (0.02 mmol) of $CuSO_4{\cdot}5H_2O$ were added to a single-neck round-bottom flask containing 20 ml DEG and dissolved with magnetic stirring. Then 10 ml distilled water with 1.0 g (3.8 mmol) tri-sodium citrate added. The mixture solutions were heated to 80 °C and 20 ml (1.6 M) hydrazine was successively into the solution at a rate of 9.6 ml/min. After reaction for 3 min, the solutions were cooled down to room temperature and the stirring was continued for an additional 2 h. The resulting particles were separated by centrifugation and washed with ethanol.

To build a surface tension gradient between the solvents to acquire high quality Cu nano-ink, the obtained Cu NPs were redissolved into the mixture of water, ethanol, glycerol and ethylene glycol (their corresponding surface tension were 72.8, 22.4, 63.3, 48.5 mN/m, respectively) with a corresponding vol% of about 23.0:8.0:30.5:38.5. The Cu NPs were dispersed by ultrasonic treatment to obtain 35 wt% Cu nano-ink and used for drawing flexible printed patterns.

2.3. Preparation of Cu patterns

The Cu patterns were created by directly writing on a flexible photo paper using a roller pen loaded with Cu ink. The schematic illustration is shown in Fig. 1. First, the empty pipe of the roller pen was washed and the photo paper is used as the flexible substrate without any other treatment. Second, a certain amount of Cu ink (35 wt%) was injected by a syringe. Third, the patterns we designed can be easily drawn by this roller pen on photo paper. Finally, the Cu pattern (together with the photo paper) was sintered under argon atmosphere at 80–160 °C for different time.

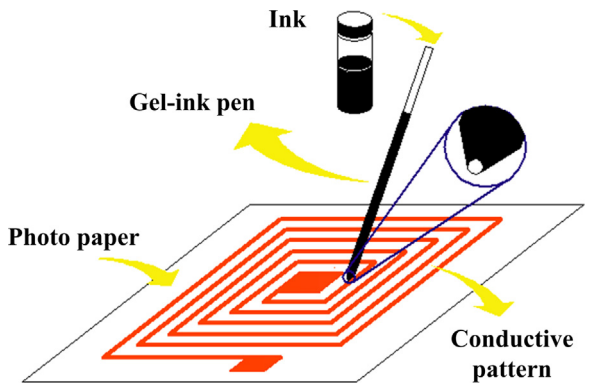

Fig. 1. Schematic illustration for the preparation of conductive patterns by writing on photo paper using a roller pen.

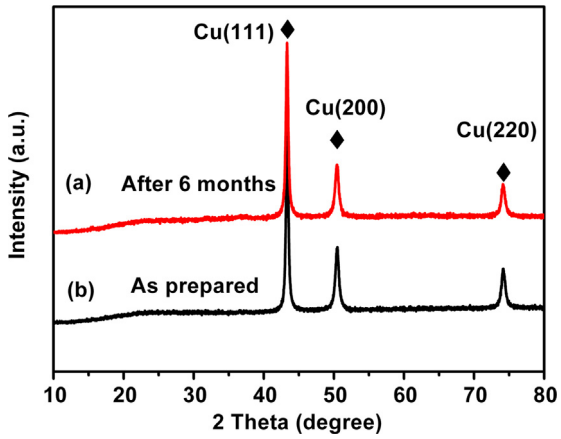

Fig. 2. X-ray diffraction patterns for Cu NPs: (a) as-prepared at 80 °C and (b) after storing in a capped bottle under atmospheric condition for 6 months.

3. Characterizations

The purity of the Cu NPs was investigated by X-ray powder diffraction (XRD, D/Max 2500pc, Rigaku, Japan) with CuKa radiation (λ = 1.54059 Å). The morphology and size distribution of the particles were characterized by transmission electron microscopy (TEM, JEM-2100, Japan) at 200 kV. The dried Cu particles were grinded with KBr and compressed into a circle flake for FT-IR analysis. FT-IR spectra were performed and recorded with a Fourier-transform infrared spectrophotometer (Nicolet 6700) between 4000 cm^{-1} and 400 cm^{-1}. Thermogravimetric study of copper NPs was performed with an NETZSCH STA 499 C thermal gravity analyzer. The particles were heated up to 600 °C at a ramped temperature of 10 °C min^{-1} in air. The resistivity of the written patterns was measured by a 4-point probe (CMT-SR200 N, Chang Min Co., Ltd., Korea). The morphology of the copper patterns after sintering was investigated by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) with a voltage of 2.0 kV.

4. Results and discussion

4.1. Characteristics of Cu nanoparticles

Fig. 2 shows the XRD patterns of the synthesized copper NPs depending on storage conditions, which were first dried in a vacuum oven at 60 °C for 3 h and then stored in a capped bottle under