Conductive Ink-Jet Inks for Plastic Electronics: Air Stable Copper Nanoparticles and Room Temperature Sintering

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Abstract

One of the greatest challenges in fabrication of plastic electronics devices by printing metallic nanoprticles is obtaining highly conductive patterns at sufficiently low temperature which will not damage the polymeric substrate. However, to date, sufficient conductivity of silver patterns was achieved only after prolonged heating at elevated temperatures, thus limiting fabrication of plastic devices only to heat resistance polymers.

We report on a discovery that assemblies of silver nanoparticles, can undergo a spontaneous two-dimensional aggregation-coalescence process, even at room temperature. The surface coalescence of the metal nanoparticles leads to sintering and eventually to electrical conductivity, much below the melting temperature of the bulk silver. This process is triggered by surface charge neutralization of the nanoparticles, by using a variety of charged flocculants, and takes place in thin layers of various substrates, such as plastic and paper. The resulting high conductivity, 20% of bulk silver, enabled fabrication of various devices, as demonstrated by a flexible plastic electroluminescent ink-jet printed device.

Introduction

Fabrication of electric circuits on flexible and heat-sensitive substrates such as paper and packages has attracted significant interest as a pathway to flexible and low-cost devices [1, 2]. Ink-jet technology can be utilized for direct printing of conductive patterns [3], overcoming disadvantages of other printing methods such as lithography [4] and screen printing [3]. The inks used for the fabrication of conductive patterns by ink-jet printing usually contain silver nanoparticles (NPs) (surfactants and polymers) dispersed in water or an organic solvent by organic stabilizers [5, 6]. After the printing and drying processes, a pattern composed of conducting metallic NPs capped with insulating organic stabilizers is formed. Due to the presence of insulating organic material within the NPs array, the number of percolation paths is limited, and the resistivity of the printed pattern is usually too high for practical applications. This obstacle is conventionally overcome by a post-printing sintering process, achieved by heating the printed substrates to temperatures usually higher than 200^{o}C in an oven [7] or by applying microwave [8] or laser radiation [9]. This sintering phenomenon is usually attributed to the reduced melting point of NPs and to the high self-diffusion coefficient of their atoms [10]. However, due to the sensitivity of paper and many plastic substrates to high temperatures, such treatments are usually not possible for these substrates. Therefore fabrication of flexible devices is limited to a small number of heat resistant polymers such as polyimide. Obviously, there is a great need for a technology that will enable sintering of the metallic NPs without heating the substrate.

Another obstacle of silver inks is their high cost due to the increasing price of bulk silver. Since copper is much cheaper than silver but possesses a very high conductivity, only 6% less than that of Ag, Cu NPs can be considered as an alternative to silver NPs. However, Cu NPs can not be used, due to their spontaneous oxidation at ambient conditions. In a previous report, we demonstrated that the formation of a thin silver shell on the Cu nanoparticles ,thus forming $Cu_{core}Ag_{shell}$ NPs, prevents their oxidation and enables their use at ambient conditions [11].

Here we report on a new technology to achieve sintering of such low cost $Cu_{core}Ag_{shell}$ NPs in a printed pattern even at room temperature, due to a spontaneous flocculation-coalescence process, which takes place on the desired substrate. The concept is based on replacing the heating step by a flocculation step which leads to the coalescence of the NPs. The result is a sintered pattern which possesses high electrical conductivity even at room temperature. In the first part of this paper, we describe the synthesis of the $Cu_{core}Ag_{shell}$ NPs. In the second part, we demonstrate a spontaneous two-dimensional coalescence process of these NPs and the high electrical conductivity obtained at room temperature.

Result and Discussion

Synthesis and Characterization of $Cu_{core}Ag_{shell}$ NPs

The core-shell structure was obtained by a two step process as schematically presented in Figure 1. At the first step Cu nanoparticles (NPs) were synthesized in an aqueous medium by reduction of $Cu(NO_3)_2$ with an excess of hydrazine hydrate in the presence of polyacrylic acid sodium salt as a polymeric stabilizer, as reported previously [12]. Due to the large excess of hydrazine hydrate which serves as an anti-oxidation agent, the oxidation of the copper NPs was prevented, but only if their dispersion was kept in closed vials. Exposure of such dispersion to air led to immediate oxidation with color change from red to bluish green.

At the second step silver ions (as a silver salt solution) were added, and by transmetalation reaction the reduction of silver ions by the metallic copper takes place directly on the surface of Cu NPs, thus leading to the formation of a silver shell on the copper core.

In order to prevent the formation of free Ag NPs at the shell formation step, the hydrazine hydrate was consumed by the titration of acetaldehyde prior to the addition of silver nitrate.

The obtained dispersion of $Cu_{core}Ag_{shell}$ NPs is characterized by an orange-reddish color. In contrast to the uncoated Cu NPs, while exposing these $Cu_{core}Ag_{shell}$ to air, their color remains unchanged even in an open vial and after drying as well.

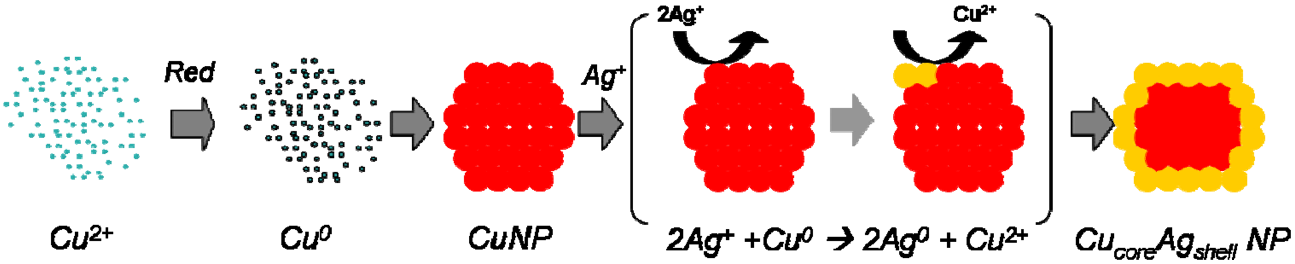

Figure 1. Schematic illustration of CucoreAgshell NPs synthesis.

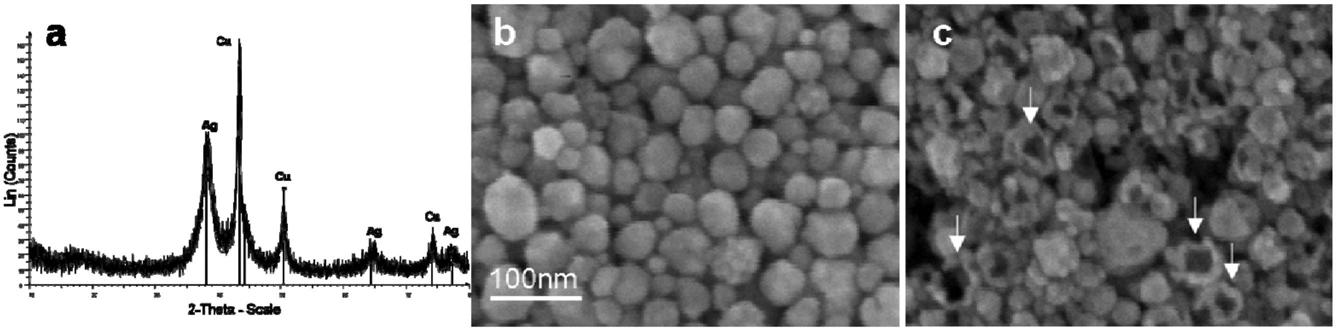

Figure 2. XRD pattern (a) and HR-SEM image (b) of the CucoreAgshell NPs, and a HR-SEM image of the NPs after the cores dissolution (c).The same scale bar for the both images

High resolution scanning electron microscope (HR-SEM) image presented in Figure 2b reveals the formation of NPs with a diameter of 20 to 50 nm. The XRD pattern of these NPs (Figure 2a) indicates the presence of both copper and silver, with fcc crystal structures (not their alloy). In order to confirm the formation of silver shells on the copper cores, ammonium hydroxide, which is capable of dissolving copper [13, 14], was added to the aqueous dispersion of the NPs. Figure 2c demonstrates that such treatment of the core/shell NPs results in the formation of some hollow silver nanoshells, probably in particles where the shell was not complete.

Sintering at room temperature

An aqueous ink containing $Cu_{core}Ag_{shell}$ NPs was ink-jet printed on a glass slide by an office Lexmark printer (Z 615) without any modification. It was found, as expected, that after drying at room temperature, the printed pattern was composed of closely packed non-sintered $Cu_{core}Ag_{shell}$ NPs and therefore, possessed a very high resistivity, more than a million times of that for the bulk copper. The polymeric stabilizer (PAA) adsorbed onto the NPs surface causes the NP to have surface charges, which enables their stabilization while in dispersion (electro-steric stabilization). Indeed, ζ-potential of the NP's was -32(±4) mV (at pH 8.9), which explains their stability in dispersion and non-contact after deposition. Figure 3 presents ζ-potential of NPs in aqueous dispersion as a function of pH. It can be seen that the negative ζ-potential of the original NPs decreases with the decrease of pH. At a pH of 2.0 or lower, the ζ-potential value is very small, and a rapid precipitation occurred due to aggregation of the NPs. Particles size measurements by dynamic light scattering (DLS) indicated a size increase from 30nm up to about 2 μm (Figure 3).

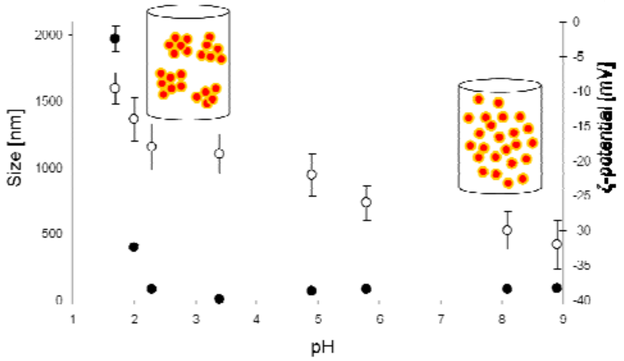

Figure 3. ζ-potential (open circles) and average particle size (filled circles) of the CucoreAgshell in aqueous dispersion, as a function of pH and a schematic illustration of the NPs in their stabilized form (left) and after aggregation (right).

The decrease in the absolute value of ζ-potential at low pHs results from protonation of the carboxylic groups of the adsorbed polymer. At pH values higher than ~4 (the pKa of acrylic acid is 4.25), the carboxylic groups are de-protonated, thus providing the NPs a large negative ζ-potential, which stabilizes the NPs. However, at a lower pH, the carboxylic groups are protonated (COOH), the ζ-potential decreases and flocculation and aggregation of the NPs occurs.

Based on the results obtained in the liquid dispersion, this flocculation process was performed directly on the printed substrate. Therefore, the ink containing $Cu_{core}Ag_{shell}$ nanoparticles was printed on an Epson photo paper, which was pre-treated with 8 wt% phosphoric acid solution (by a 6 μm application rod). Comparison of HR-SEM images of the patterns printed on the paper with or without phosphoric acid pre-treatment (Figures 4a and b), clearly shows the effect of the acid : not only that the pnanoparticles aggregated, they were even sintered, due to the close contact between the particles during the drying of the printed pattern, at room temperature. Figure 4c shows an example of an RFID antenna printed on this paper, by the Lexmark printer. As seen from SEM image of the cross-section of the pattern, (Figure 4d), the thickness of the printed pattern is about 1.2 µm.

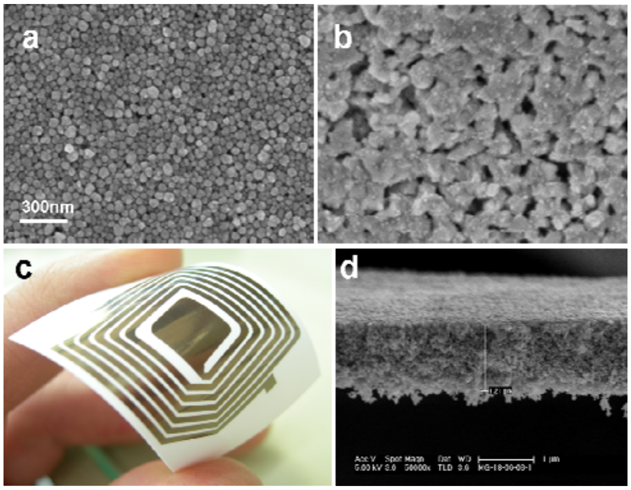

Figure 4. CucoreAgshell NPs printed on Epson photo paper (a) and on the same paper pre-treated with phosphoric acid (b). An RFID antenna printed on Epson photo paper (c) and SEM image of the cross-section of the printed pattern (d).

Sheet resistance measurements revealed, as expected, that the sintering is accompanied by a drastic decrease of the resistance down to values of 3 (±0.2) Ωsquare. It should be emphasized that such low sheet resistances were reported until now only for metallic patterns which were heated at temperatures ≥150oC for prolonged time, while in the present study it was achieved spontaneously at room temperature.

In summary, we demonstrated how the well known flocculation process, which is widely reported for colloidal systems, can be utilized on a solid surface, leading to sintering of metallic NPs without heating. This process can be simply controlled by tuning the surface properties of the NPs and the substrate and it enables obtaining conductive patterns on low cost, heat sensitive substrates. We expect that this process can be performed in various modes, such as printing the flocculation agent after printing the metal nanoparticles. This concept, combined with the formation of the low cost copper nanoparticles, may open new possibilities for applications in flexible and plastic electronics.

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