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Room Temperature Synthesis of a Copper Ink for the Intense Pulsed Light Sintering of Conductive Copper Films

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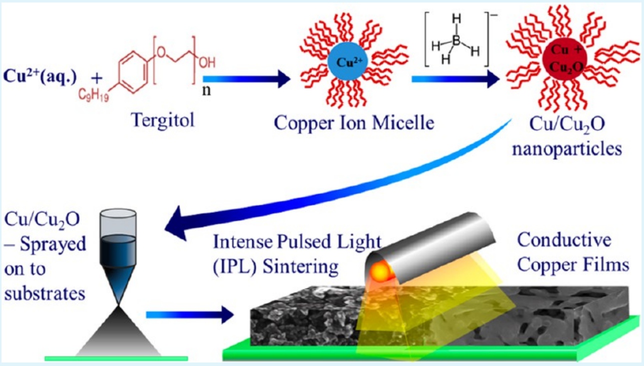
Supporting Information



ABSTRACT: Conducting films are becoming increasingly important for the printed electronics industry with applications in various technologies including antennas, RFID tags, photovoltaics, flexible electronics, and displays. To date, expensive noble metals have been utilized in these conductive films, which ultimately increases the cost. In the present work, more economically viable copper based conducting films have been developed for both glass and flexible PET substrates, using copper and copper oxide nanoparticles. The copper nanoparticles (with copper(I) oxide impurity) are synthesized by using a simple copper reduction method in the presence of Tergitol as a capping agent. Various factors such as solvent, pH, and reductant concentration have been explored in detail and optimized in order to produce a nanoparticle ink at room temperature. Second, the ink obtained at room temperature was used to fabricate conducting films by intense pulse light sintering of the deposited films. These conducting films had sheet resistances as low as 0.12 Ω/□ over areas up to 10 cm^2 with a thickness of 8 μm.

KEYWORDS: *copper nanoparticles, intense pulse light, sintering, chemical reduction process*

■ INTRODUCTION

The direct printing of conductive materials has garnered a fair share of interest from researchers and industry in the past few years. The advantages primarily stem from a cost savings over traditional techniques such as vacuum deposition and photolithography. The reduction in costs are reflected by large area scalability, efficient materials usage, reduced energy processes, and the availability of existing manufacturing capacity. The ability to process onto polymeric substrates using roll-to-roll manufacturing further improves the economics and opens up new opportunities. The conductive ink market is expected to exceed \$3 billion in the next few years in a wide array of end point uses including antennas, RFID tags, photovoltaics, flexible electronics, and displays.[1] As an example, the photovoltaic industry is expected to become a major consumer of silver for conductive current collectors that are typically deposited using screen printing techniques and sintered using thermal processing.[2]

Solution phase inks and pastes for the direct printing of conductive lines are typically composed of metallic particles (spherical, flake, and wires and may include dimensions less than 100 nm) suspended in an organic solvent or binder. Silver in the form of flakes is the most predominant material used in the direct printing of conductive lines. There have been a number of applications utilizing silver nanoparticles (NP)s in inkjet formulations and sintering using lower temperature methods such as inert gas plasmas,[3,4] microwaves,[5] and intense pulsed light (IPL).[6,7] These inks and processes reduce the overall cost of devices and have gained some advantage in the flexible electronics industry but nevertheless still rely on a relatively expensive material.

Inexpensive materials such as copper (Cu) that utilize the lower temperature sintering processes above would further reduce the costs associated with conductive patterns. Cu and silver have very similar electrical conductivity; however, Cu is significantly less expensive. Despite this, silver is commonly used in printed electronics primarily due to its stability in air. Cu tends to rapidly oxidize under ambient conditions, which significantly reduces conductivity and higher processing temperatures to sinter.[8] To overcome these shortcomings, Cu inks have been developed utilizing reducing capping agents on pure Cu NPs in order to produce conductive patterns at temperatures between 200 and 320 °C[9,10] and using inert gas plasmas.[11] However, these inks rely on pure Cu NPs using relatively complex processes that inevitably add cost.

IPL sintering is one technique that has been used to sinter pure Cu NPs dispersed in an ink formulation.[12] A fast flash, approximately a millisecond in duration, from a Xenon lamp is used to emit incoherent pulses of light from the UV to IR region. The NPs absorb the light, resulting in a localized

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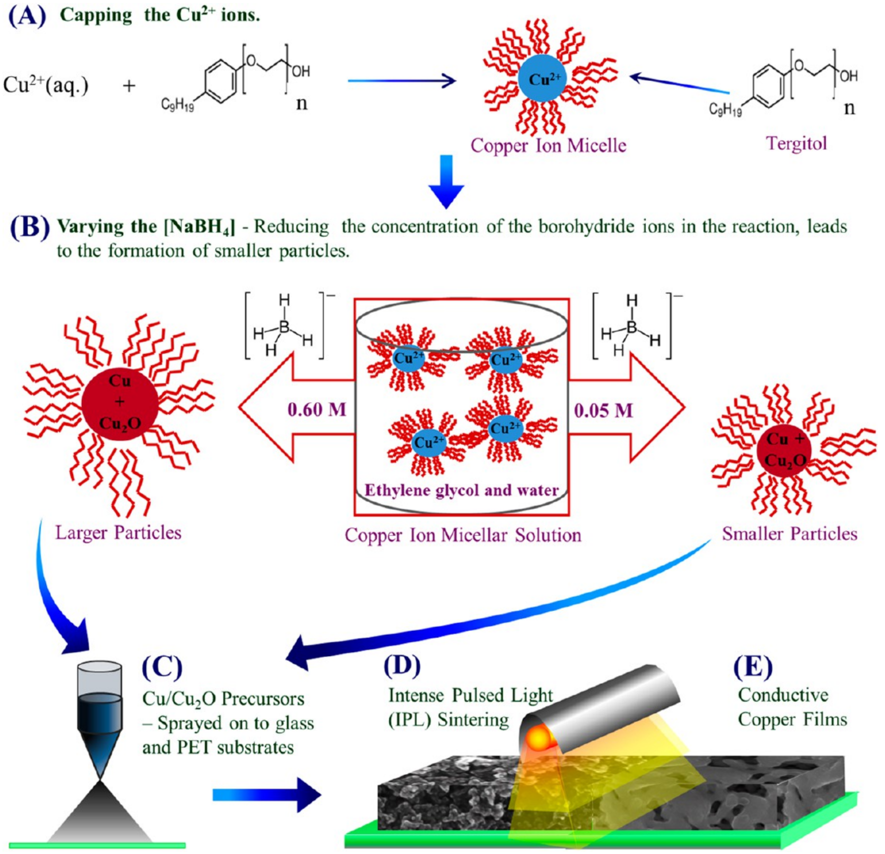

Figure 1. Schematic representation of the synthetic route for the fabrication of the copper nanoparticulate inks and the IPL sintering of the ink films to produce conductive copper films.

temperature rise at the surface that can sinter the particle to its neighbors. The outcome of the extremely short pulse time is a process having very fast kinetics, and as a result sintering can occur without oxidation.[12,13] To date, the Cu inks used with IPL sintering have been produced using commercially available Cu NPs. These particles are commonly created by an energy intensive process that includes the resistive heating of the metal precursor followed by vapor condensation, to produce spherical NPs.

Techniques for synthesizing Cu NPs include electrochemical deposition,[14] hydrothermal methods,[15] electrolysis,[16] microwave assisted polyol methods,[17] reverse micellar synthesis,[18,19] sonochemical methods,[20] thermal reduction,[21] and thermal decomposition of copper oxalate[22] that leads to the formation of the powder form of Cu rather than an ink to make conductive films. The instability of Cu even under atmospheric conditions commonly results in the formation of a Cu oxide shell on the NP. Therefore in addition to introducing additional solvents to disperse the NPs into an ink, organic stabilizers such as poly(*N*-vinyl-pyrrolidone) are commonly added in order to reduce the Cu oxide on the surface of the NPs during the IPL process.[13,23,24]

The motivation of the present work is to develop a straightforward and economical process to produce highly conducting Cu films and patterns. We present a low cost Cu/Cu_2O NP ink formulated from the simple mixing of a Cu salt (copper nitrate, $Cu(NO_3)_2$, a reducing agent (sodium borohydride, $NaBH_4$), capping agent (Tergitol), and solvents (water and ethylene glycol) at room temperature. In order to investigate the sintering performance of the inks, the ink was directly deposited onto a substrate without the need for further processing and subsequently sintered using IPL. The study involved the optimization of the synthesis and formulation of the Cu/Cu_2O NP inks for optimal performance in the large area IPL sintering. Large area films were produced on both glass and polyethylene terephthalate (PET) substrates.

EXPERIMENTAL SECTION

Materials. Commercially available Tergitol NP-9 (CAS no. 127087-87-0, Sigma Aldrich, 99%) was used as the capping agent for the synthesis of the Cu NPs. Anhydrous $Cu(NO_3)_2$ (CAS no. 10031-43-3, Alfa Aesar, 99.99%), ethylene glycol (CAS no. 107-21-1, Alfa Aesar, 99.5%), $NaBH_4$ (CAS no. 16940-66-2, Sigma Aldrich, 98%), and ammonium hydroxide (NH_4OH, CAS no. 1336-21-6, Fisher Scientific, 29.18%) were used in the synthesis of the inks.

Synthesis of Nanoparticle Ink. A total of 5 mL of Tergitol NP-9 was added to a 50 mL aqueous solution of 0.1 M $Cu(NO_3)_2$, followed by 100 mL of water. The pH of the solution was adjusted from pH 7 to 11 by the dropwise addition NH_4OH. To this solution, 50 mL of aqueous $NaBH_4$, 0.3 M, was added, and the reaction was then stirred for 2 h. This reaction was also repeated replacing 100 mL of water with 100 mL of ethylene glycol. The NP ink was optimized further at pH 11, using ethylene glycol as the solvent and by changing the concentration of $NaBH_4$ (0.05 M/0.1 M/0.3 M/0.6 M) used in the reaction. The Cu/Cu_2O NP inks obtained using ethylene glycol at pH 11 were used in the fabrication of the Cu films (see Figure 1 for more details). These inks were not further altered after the synthesis, but used directly in the solvent mixture that they were produced in and deposited or sprayed as films onto the substrate as described in the next section.

Fabrication of Cu Film Using Cu Nanoparticle Ink. Films were prepared from the NP (mixture of Cu(I) oxide and Cu) inks by decanting the excess solvent until the remaining mixture contained approximately 50 vol % solids. In order to disperse the NPs in the solution and to break up any large agglomerates, the mixture was ultrasonicated using a VirSonic Ultrasonic Cell Disrupter 100. Films were deposited by spraying the mixture onto glass substrates preheated to 160 °C, using a Nordson EFD 787MS-SS Microspray Valve. A surface profilometer (please see material characterization section) was used to measure the thickness of the as-deposited films. The films had a thickness of approximately 7−10 μm.

IPL Sintering on Glass. The films were placed in an inert nitrogen atmosphere and were sintered with pulses of light. A Sinteron 2000 (Xenon Corporation) was used to produce the pulses of intense light. The system, fitted with a linear 30 cm Xenon lamp, generates pulses of incoherent light with wavelengths ranging from 190 to 1000 nm. Pulse durations can be changed from 0.58, 1.00, and 1.50 to 2.00 ms and the interval time between pulses can be varied from a minimum time of 0.1 s to tens of minutes. The system was also equipped to generate pulses with energy of 150 to 2000 J, which corresponds to an energy density of 2.5 to 34.5 J cm^{-2}, respectively. The energy output of the pulse was changed by varying the high voltage setting. The processing area of the Sinteron 2000 is approximately 58 cm^2 with a focal length of ~2.5 cm. In this study the energy density (ED) of each pulse was varied from 10.2 J cm^{-2} to 34.5 J cm^{-2}. This required adjusting the high voltage from 1.6 to 3.0 kV. Voltage settings of 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, and 3.0 kV generate pulses with energy densities of 10.2, 12.9, 15.5, 19.0, 22.4, 26.7, 31.1, and 34.5 J cm^{-2}, respectively. Our experience using IPL also determined that more than one pulse is required to sinter films greater than 5 μm in thickness on glass; therefore, it was decided to apply 10 pulses of light at each ED setting to the films. The total energy input to the film was varied by increasing the voltage in 0.2 kV increments, in order to systematically increase the ED of the pulses. For example, a total energy input of 386 J cm^{-2} comes from 10 pulses at 1.6 kV + 10 pulses at 1.8 kV + 10 pulses at 2.0 kV. This "cumulative" method was used to sinter the Cu particles, in order to remove residual organic material in the film, before the top surface of the films could melt. If the top of the film melts before all of the volatile organic material has been removed, the film is prone to blistering, leading to delamination.

IPL Sintering on PET. Cu/Cu$_2$O films were deposited on 0.01 in. thick uncoated moisture resistant polyester (PET, McMaster-Carr). The thickness of the Cu/Cu$_2$O films was reduced to approximately 4 μm by changing the spray parameters. PET has a melting temperature of approximately 150 °C; consequently, it is unable to withstand the high temperature rise of multiple light pulses applied in a short period of time. As a result, only one pulse using an ED of 22.4 J cm^{-2} with a pulse duration of 2 ms was used to sinter the films.

Material Characterization. Powder and film X-ray diffraction (PXRD or XRD) studies were carried out on a Bruker AXS D8 X-ray diffractometer using Ni-filtered Cu Kα radiation with a step size of 0.02° and a scan speed of 1 s/step. Raw data was subjected to background correction, and Kα2 lines were removed. TEM studies were carried out using a Tecnai G^2 20 electron microscope operated at 200 kV. TEM specimens were prepared by dispersing the oxide powder in ethanol by ultrasonic treatment. A few drops were deposited onto a porous carbon film supported on a Cu TEM grid (Ted Pella) and then dried in air. The thickness of the deposited films was measured using a Technor Instruments Alpha-Step 500 surface profiler. Sheet resistance of the films was measured with a 4-point probe attached to a Keithley 2400 source-meter. The four probes were equally spaced, with two of the probes being used to apply a current across the film. The remaining two probes measured the voltage drop due to the resistance of the material; from these values the sheet resistance of the IPL treated films was determined. Topographical morphology of the films was examined by scanning electron microscopy (SEM). A FEI Nova NanoSEM 600 was used with an accelerating voltage of 15 kV and a working distance of 5−6 mm.

■ RESULTS AND DISCUSSION

This work includes both a synthesis of a NP ink and a low temperature sintering technique with the overall flow shown schematically in Figure 1. The previously cited work indicated that the IPL process would necessitate an ink with a very low concentration of oxides. Thus the initial work focused on the optimization of the NP synthesis (Figure 1A,B) and yielded a degree of control over the particle size and oxide concentration. These inks were sprayed onto a surface using an air assisted microsprayer (Figure 1C) and after evaporation of the solvent resulted in a nanoparticulate film of mixed Cu and Cu oxides (Figure 1E). This film was finally processed using IPL to sinter neighboring particles (Figure 1D) where it became apparent that the technique also reduced the surface oxides to produce a conductive thin film of Cu.

The original assumption was that inks with a high percentage of Cu would produce Cu films with the lowest sheet resistance. The optimization of the mixture of NPs for the fabrication of conductive coatings was done by varying three synthetic conditions as follows: (1) the solvent system, (2) the pH of the reaction, and (3) the concentration of the reducing agent, NaBH$_4$, used in the reaction. Aqueous inks are desirable as a low cost and environmentally friendly solution, and the synthesis of the NP ink was accomplished by dissolving a Cu(NO$_3$)$_2$ into water, creating Cu^{2+} ions in solution. Tergitol NP-9 is a nonionic surfactant with a hydroxyl functional group and a long chain (C9) hydrocarbon tail which is hydrophobic. The addition of the Tergitol NP-9 to the aqueous Cu^{2+} ion solution leads to the formation of Cu micelle structures (Figure 1A). To this dispersion was added NaBH$_4$ to reduce the Cu ion micelles to form Cu/Cu$_2$O. Initially, copper nitrate (pH = 7) was dissolved in deionized water and reacted with 0.3 M NaBH$_4$ in the presence of the capping agent, Tergitol (Figure 1A), producing a Cu/Cu$_2$O NP ink with a pH of 7. Figure 2a shows the PXRD of the NPs obtained under these conditions showing that the NPs formed are a mixture of approximately equal amounts of Cu and Cu$_2$O. (The PXRD patterns of the Cu and Cu$_2$O were indexed to the JCPDS patterns no. 851326 and no. 751531, respectively.) Both materials crystallize in cubic structure with the space group of *Fm*3*m* and *Pn*3*m*.

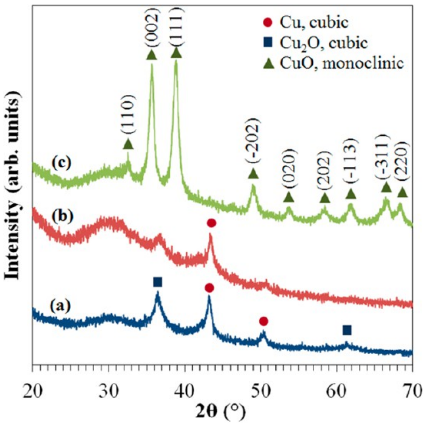

Figure 2. Powder X-ray diffraction pattern of the copper nanoparticle ink obtained at (a) pH = 7 without ethylene glycol, (b) pH = 11 with ethylene glycol, and (c) pH = 11 without ethylene glycol.

NaBH$_4$ is known to decompose rapidly at low pH, and even in neutral conditions its reactivity is low. It is also known that NaBH$_4$ acts as an efficient reducing agent at high pH due to its complex hydrolysis process.[25] Therefore in an attempt to enhance the reduction of the Cu ion micelles in the ink, the pH was adjusted to 11 by dropwise addition of NH$_4$OH. However, the PXRD patterns of the NPs formed under these conditions show the presence of pure monoclinic CuO (JCPDS pattern no. 801917) (Figure 2c).

The use of water as the solvent causes oxidation of the Cu and necessitates the addition of a cosolvent to minimize the formation of Cu oxides. Earlier reports on the synthesis of micrometer sized nickel particles in nonaqueous solvents showed that ethylene glycol is a very good solvent for obtaining oxide-free metal nanostructures.[26] Subsequently, ethylene glycol was added to the reaction to reduce the formation of oxides while increasing the Cu yield. The overall concentration of reagents was kept the same. At pH of 11, in the presence of ethylene glycol, a mixture of Cu and Cu_2O was obtained (Figure 2b) at a ratio of approximately 3:1. The increase in the yield of Cu in the ink suggests that a reducing environment was generated by the presence of the ethylene glycol cosolvent. For further optimization of the ink, there could be additional changes made to the ink formulation to alter the physical properties of the ink itself, such as viscosity or surface tension, or the Cu/Cu_2O NPs for spray deposition or other deposition or printing techniques. The viscosity and surface tension of the ink are 3.395 (1) mPa sec and 14.39 mN/m, respectively (Table 1), under these conditions at pH 11.

Table 1. Semiquantitative PXRD Analysis, Surface Tension, and Viscosity of the Copper Inks Using Various Concentration of Sodium Borohydride

	phase analysis			
sodium borohydride concentration	% Cu	% Cu_2O	viscosity (mPa/s)	surface tension (mN/m)
0.05 M	34.12(1)	65.88(2)	3.388(2)	14.39(5)
0.1 M	60.30(2)	39.70(4)	3.385(5)	14.39(2)
0.3 M	67.90(1)	32.10(3)	3.395(1)	14.39(3)
0.6 M	91.56(2)	8.44(4)	3.391(5)	14.38(2)

To reduce the primary particle size of NPs at room temperature, the concentration of reducing agent ($NaBH_4$) was varied. This also had the effect of increasing the concentration of oxides, and the ratio of the Cu/Cu_2O increases linearly as the concentration of $NaBH_4$ was adjusted from 0.6 to 0.05 molar as shown in Figure 3. All the patterns show a mixture of Cu and Cu_2O. It has been observed that as the $NaBH_4$ concentration (from 0.05 to 0.6 M) was increased, the yield of Cu in the NP ink also increased without having any effect on viscosity and surface tension (inset of Figure 3 and Table 1). It appears that the $NaBH_4$ in the presence of ethylene glycol facilitates the reducing environment further with the Cu/Cu_2O ratio more than doubling, when the $NaBH_4$ concentration was increased to 0.6 M. Under these conditions the NP ink was composed of Cu with a small amount of Cu_2O acting as an impurity. These results are in close agreement with the previous reports on the reduction of Cu.[27] The ability to manipulate the Cu/Cu_2O ratio based on the synthetic conditions for the synthesis of the NPs allows for greater latitude in the ability to find processing conditions that are scaleable for the production of low cost conductive Cu films.

Films were prepared by spraying the ink on glass substrates resulting in wide area coverage of NPs in two dimensions after the evaporation of the solvents. Although the synthesis of the inks resulted in a wide control of oxide concentration, the as-deposited films were composed of both Cu/Cu_2O NPs. Thus, the Cu_2O in the deposited films must be reduced to Cu during

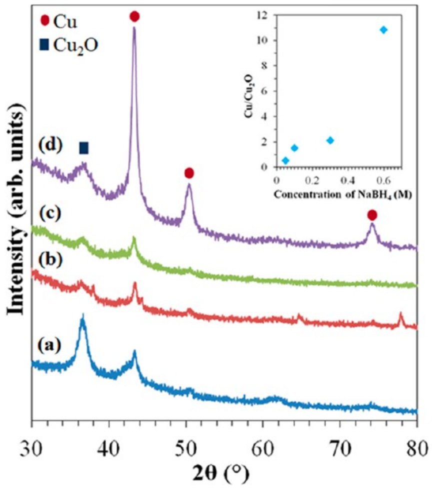

Figure 3. Powder X-ray diffraction pattern of the copper nanoparticle ink obtained at pH = 11 in the presence of ethylene glycol by the reaction of copper salt with $NaBH_4$ at concentrations of (a) 0.05 M, (b) 0.1 M, (c) 0.3 M, and (d) 0.6 M. An inset shows the variation of the ratio of Cu (111) intensity to Cu_2O (111) intensity vs $NaBH_4$ concentration.

the IPL process in order to achieve low resistance since the electrical conductivity of Cu is several orders of magnitude greater than Cu_2O or CuO. Additionally, the NPs must be sintered by increasing the temperature of the film to create a continuous network of electronic pathways, leading to a low sheet resistance (R_s).

Figure 4 shows the R_s of the Cu/Cu_2O films deposited from the 0.05, 0.1, 0.3, and 0.6 M $NaBH_4$ inks with varying energy inputs. The total energy input was changed by increasing the energy densities (ED) of the pulses. Films deposited from the ink obtained using 0.6 M $NaBH_4$ displayed R_s's greater than 100 Ω/□, even after a total energy input of 1723 J cm^{-2} was applied to the film, using pulses with a maximum ED of 34.5 J cm^{-2}. In contrast, under similar conditions, the films deposited from the 0.3, 0.1, and 0.05 M inks produced R_s's lower than 10 Ω/□. These films also display an inflection point at a total energy input of ~350 J cm^{-2}, where the R_s changes from MΩ/

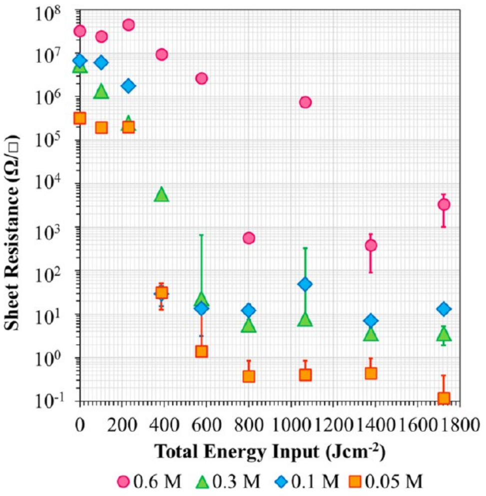

Figure 4. Sheet resistance vs total energy input during the IPL treatment. The films were fabricated from the 0.6, 0.3, 0.1, and 0.05 M $NaBH_4$ inks. The error bars were calculated using the standard error.

□ to less than 100 Ω/□. This indicates that pulses with a minimum ED of 15.5−19.0 J cm^{-2} are required to reduce and sinter the Cu/Cu_2O films. The lowest sheet resistance of 0.118 Ω/□ was obtained from the 0.05 M ink, after 1723 J cm^{-2} was applied to the film. It should be noted that the films are deposited over a wide area (10 cm^2) as we are trying to demonstrate a bulk Cu film technique. The bulk resistivity can be found by the product of the sheet resistance and the film thickness ($\rho = tR_s$); the film thickness is 7.97 μm, yielding a bulk resistivity of 9.40×10^{-5} Ω·cm.

Interestingly, the XRD patterns of the powders (Figure 3) showed that the 0.6 M ink had the highest Cu content and should have produced a lower sheet resistance. Therefore, to further understand the sintering process, TEM of the particles from the 0.05 and 0.6 M inks were studied. The TEM micrograph of the Cu NP ink obtained using 0.05 M $NaBH_4$ shows the formation of NPs 10−15 nm particles (Figure 5a, Supporting Information Figure S1a). When the $NaBH_4$ concentration was increased to 0.6 M, the particle size increased to 100−120 nm (Figure 5c, Supporting Information Figure S1b). It is well-known that the melting point at the surface is significantly lower than in the bulk of the material, due to the weak bonding of the surface atoms.[28] Thus these atoms have a lower cohesive energy than atoms found in the bulk of the material. In elemental solids, the cohesive energy has an almost linear relationship with the melting point temperature. Consequently, as the cohesive energy of the material decreases, so does the melting point. In the NP regime, the surface area becomes significantly larger than the volume. Hence the average cohesive energy of the particle is reduced.[28] This effect can result in the NPs having melting point temperatures several hundred degrees lower than the bulk material. Kim et al[12] calculated the melting point temperature vs particle size analysis for pure Cu, assuming the homogeneous melting of spherical particles. These results predict that particles less than 20 nm in diameter will have a dramatic decrease in their melting temperature. Based on Kim et al.'s results, Cu particles with a diameter greater than 30 nm will have a melt temperature similar to the bulk (1084 °C), while a particle size of 10 nm will have a melting temperature of approximately 900 °C. Therefore the smaller particles from the inks synthesized using 0.05 M $NaBH_4$ will sinter and melt more effectively than the particles produced from higher $NaBH_4$ concentrations. As a result, the films fabricated from the 0.05 M $NaBH_4$ inks showed improved conductivity as a result of improved electronic pathways and reduced porosity due to better melting, in addition to increased Cu content in the films (Figures 4 and 6).

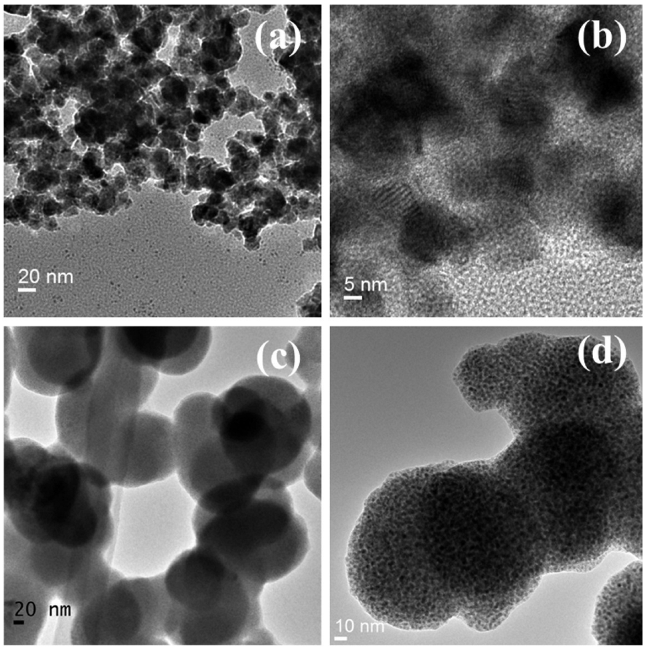

Figure 5. Cu/Cu_2O nanoparticle ink obtained at pH = 11 in the presence of ethylene glycol by the reaction of copper nitrate with 0.05 M $NaBH_4$ (a) TEM micrograph and (b) HRTEM micrographs and 0.6 M $NaBH_4$ (c) TEM micrograph and (d) HRTEM micrographs.

Further analysis of the IPL treatment on the Cu particles was carried out using films fabricated from the 0.05 M $NaBH_4$ inks. Figure 6 shows the XRD patterns of the as-deposited and IPL treated films. The as-deposited sample was indexed to the (111), (200), (220), and (311) crystalline planes of cubic Cu_2O ICDD (00-001-1142) and cubic Cu ICDD (00-001-1241). Upon IPL treatment, the reflections belonging to Cu become more crystalline and appear prominently in the XRD diffraction patterns. These Cu reflections have a significantly narrower reflection than those corresponding to Cu_2O, indicating that in addition to Cu_2O to Cu conversion, the crystallite size of Cu becomes significantly larger due to particles melting and coalescing. Figure 6c shows the ratio of the $(111)_{Cu}/(111)_{Cu2O}$ vs the energy input during the IPL process. At approximately 400 J cm^{-2}, this value exceeds 1. In other words there is more crystalline Cu than Cu_2O in the films. This transition point is consistent with the observations made during the sheet resistance study, where the transition between MΩ/□ to Ω/□ occurs in this region. When a total energy input of 1723 J cm^{-2} was applied to the films, the $(111)_{Cu}/(111)_{Cu_2O}$ ratio exceeded 45. However, it should be noted that, in addition to the melting of Cu, the temperature of the film was raised sufficiently for the oxidation of Cu to CuO to be observed.

Figure 7 shows the SEM topographical images of the as-deposited and the 576 and 1723 J cm^{-2} IPL treated films. The images show that the as-deposited Cu/Cu_2O films form very rough and porous structures. The smaller particles have agglomerated into small clusters with a width of approximately 50 nm. Applying 576 J cm^{-2} of energy to the film resulted in significant changes to the morphology, with a large amount of particle coalescence of large particles approximately 100 nm wide (Figure 7b). At an applied energy of 1723 J cm^{-2}, the NP network appears to be much smoother, as further melting of the particles has occurred (Figure 7c).

The IPL sintering of Cu on glass required EDs of 22.4 J cm^{-2} over multiple pulses to reduce Cu_2O to Cu and sinter the particles, resulting in good conductivity. This amount of energy would damage the PET substrate since PET is a low melting temperature substrate (∼260 °C). Compared to glass substrates it is unable to withstand the high temperature rise of multiple light pulses applied in a short space of time. Therefore, to sinter films on PET, either the thickness of the films must be reduced, or the interval time between pulses must be increased. For the initial fabrication of Cu films on these substrates, the thickness of the films was reduced to approximately 4 μm. As a result only one pulse with an ED of 22.4 J cm^{-2} needed to be applied in order to produce well adhered films with a R_s as low as 1.35 Ω/□. In addition the short sintering time of 2 ms (i.e., the

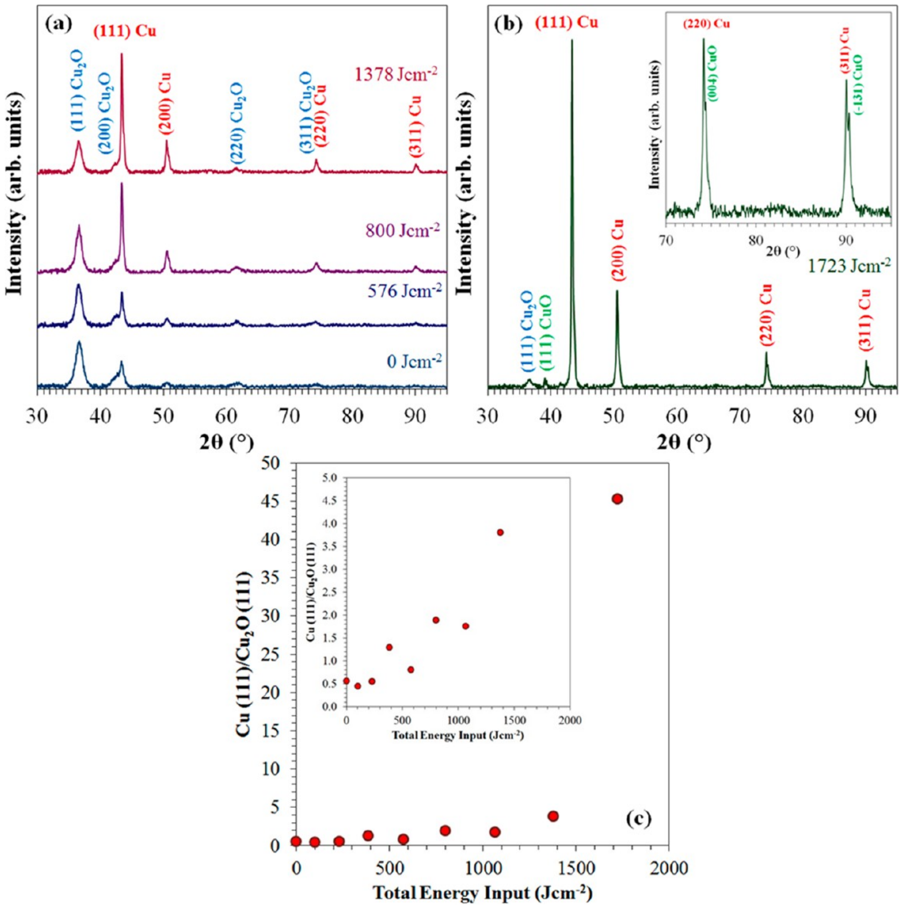

Figure 6. (a, b) XRD patterns of the Cu/Cu_2O films deposited from the 0.05 M $NaBH_4$ ink before and after IPL sintering. The XRD patterns are shown for films treated with a total energy input of 0, 576, 800, 1378, and 1723 J cm^{-2}. (c) Ratio of Cu (111) intensity to Cu_2O (111) intensity vs Total Energy Input during IPL treatment. (The insets show close-ups of the graphs.)

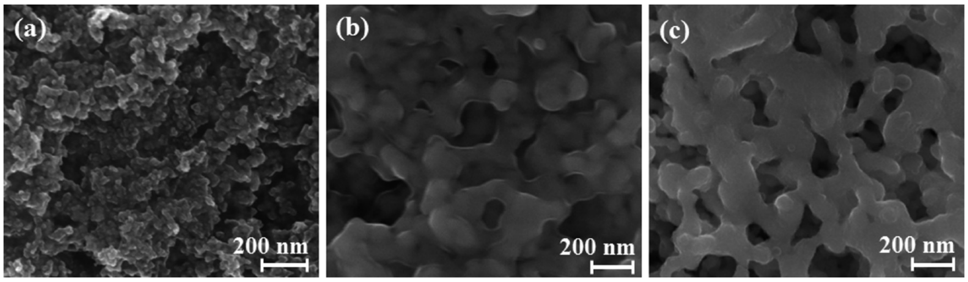

Figure 7. SEM topographical images of the Cu/Cu_2O films before and after IPL sintering. (a) As-deposited films, (b) IPL treated film with a total energy input of 576 J cm^{-2}, and (c) IPL treated film with a total energy input of 1723 J cm^{-2}.

pulse duration) allowed the films to be sintered in air. These films showed no difference in performance when compared to the films processed under nitrogen. Figure 8a displays the XRD plots of a film sintered in air. The diffraction pattern shows that not all the Cu_2O was reduced to Cu. In addition the pattern shows a significant proportion of the film was oxidized to CuO. During the fabrication of the Cu/Cu_2O films on both the glass and PET substrates, the films were initially heated to 160 °C in order to remove excess solvent. However, the boiling point of ethylene glycol is approximately 195 °C, so after heating the as-deposited Cu/Cu_2O particles will continue to be surrounded by a layer of organic material (a mixture of Tergitol and ethylene glycol). Upon IPL treatment the Cu/Cu_2O particles absorb the pulses of intense light, creating localized heating. This temperature rise (>240 °C for the decomposition of ethylene glycol) is sufficient for the organic chemicals to decompose. The products of this decomposition (e.g., H_2, CO, hydrocarbons) create a reducing atmosphere sufficient to reduce Cu_2O to Cu.[29] A similar reducing atmosphere has been observed during the spray pyrolysis of Cu NPs by Firmansyah et al.[30] The pyrolysis of a Cu salt in a water and ethanol based solution was initially found to produce particles of Cu_2O. These oxide NPs were subsequently reduced to Cu by H_2 produced during the decomposition of ethanol. The study found that, in a temperature range between 450 and 525 °C, the Cu_2O was initially oxidized to CuO before being reduced to Cu, while at temperatures greater than 525 °C the Cu_2O was directly reduced to Cu. The authors attribute the indirect route to

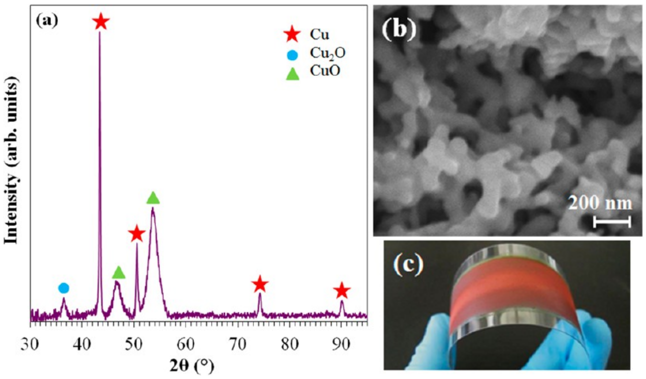

Figure 8. (a) XRD pattern, (b) SEM, and (c) photograph of the IPL sintered Cu/Cu_2O film on PET using one pulse with an ED of 22.4 J cm^{-2} in air.

producing Cu/Cu_2O NPs at lower temperatures to the relatively smaller yield of H_2 in the reducing atmosphere.

IPL treatment of the Cu/Cu_2O films on PET was conducted using one pulse with an ED of 22.4 J cm^{-2} in an open environment of air. Consequently the temperature rise in the films produced by one pulse is substantially lower than if multiple pulses were used. This may have resulted in a lower yield of the reducing gases. In addition the open environment may have led to the rapid dissipation of the reducing atmosphere, hence allowing some of the Cu_2O to be oxidized to CuO. However, the Cu content was sufficient to produce the low R_s's. The IPL sintered films also display a very porous network (Figure 8b). The reduction in the thickness of the films appears to have resulted in a higher porosity. Hence the electrical pathways are much narrower after sintering. We believe that optimization of both the deposition and sintering processes for PET will result in lower R_s's. However, these results are comparable to the R_s's obtained by Hwang et al.[23] where poly(*N*-vinyl-pyrrolidone) was used to IPL sinter Cu NPs. The need to only use 0.05 M $NaBH_4$ to develop an NP ink for conductive Cu patterns at room temperature makes this route both economical and more environmentally friendly. In addition, the use of Cu_2O NPs promises to prolong the inks' lifetime.

CONCLUSION

An economically viable method for fabricating conducting Cu films on both glass as well as flexible plastic substrates has been developed. The study involved three stages of optimization: (1) room temperature Cu/Cu_2O NP synthesis, (2) Cu/Cu_2O ratio, and (3) IPL process parameters. First, a simple room temperature Cu reduction process was explored to yield a stable NP ink by varying the solvent/cosolvent and the pH of the ink. Second, the concentration of the $NaBH_4$ was adjusted over 2 orders of magnitude to establish the ability to control the Cu/Cu_2O ratio over a wide range of concentrations. Finally, the IPL parameters were optimized to produce conductive Cu films. The films were deposited on glass and PET substrates over 10 cm^2 areas, and the complete process was performed at room temperature. The sheet resistance of the films was reduced to 0.12 $\Omega/\square$. It was noted that the IPL process could produce a highly conductive Cu film despite the large presence of Cu_2O phases. The low viscosity and moderate pH make these inks scalable to other printing techniques such as ink jet, screen printing, and gravure. In addition, the optimization of both the synthetic and processing conditions as reported here allows for greater latitude in the ability to scale up and manufacture conductive Cu films in the future.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1, size distribution plots of nanoparticle inks. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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