CHEMISTRY OF MATERIALS

COMMUNICATION

pubs.acs.org/cm

Preparation of Conductive Silver Films at Mild Temperatures for Printable Organic Electronics

Lakshminarayana Polavarapu, Kiran Kumar Manga, Hanh Duyen Cao, Kian Ping Loh, and Qing-Hua Xu*

Department Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

S Supporting Information

KEYWORDS: silver nanoparticle ink, printable electronics, organic electronics, conductive silver films

Recent developments in printable electronics have opened the door for the manufacturing of lightweight, flexible, cost-effective electronic devices that are beyond the conventional silicon-based devices.[1,2] The printable electronic devices such as field-effect transistors,[3] photovoltaics,[4] radio-frequency identification tags,[5] and displays[6] usually require electrical contacts. Various materials such as graphene,[7] carbon nanotubes,[8] polymers,[9] and metals[10,11] have been used as electrodes. Among all these conductive materials, metal electrodes have been the most widely used, because of their high conductivity. Different physical methods, such as vacuum evaporation, photolithography, and sputtering, usually are used to fabricate conductive metal electrodes for various electronic devices. The preparation of conductive electrodes by solution processing methods offers several advantages, such as mild temperature and roll-to-roll processing, flexibility and reduced cost, compared to the conventional physical deposition methods.[1,2,12,13] In addition, inkjet printing technology can be utilized to print metal contacts directly, using conductive metal nanoparticle inks, overcoming the disadvantages of physical deposition methods. A few research groups have been actively developing metal nanoparticle inks for printable electronics.[2,4,10,13−17]

The nanoparticle inks used for printing electrical contacts are usually either organic or aqueous dispersions of metal nanoparticles (NPs) protected by organic capping agents. The organic capping agents prevent electrons moving from one particle to another. The resistivity of the electrical contact printed using these metal NPs is usually high, because of the presence of insulating organic capping agents on the nanoparticle surfaces. This problem can be overcome by sintering the electrical contact after printing. The sintering can be achieved by annealing the substrates at higher temperatures,[11,14] laser irradiation,[18] microwave irradiation,[19] or chemical treatment.[13,16] So far, most of the previously reported methods[2,14,18,20,21] for the preparation of conductive films via solution processing require further treatments after printing the nanoparticle film. However, the plastic substrates and polymer films used in flexible plastic electronics are usually heat-sensitive. It is challenging to prepare electrical contacts on plastic substrates that have low glass-transition temperature (T_g) values, since further treatment procedures that make the electrodes conductive could destroy the plastic substrates or polymer films. Over the past a few years, many research groups have been making tremendous efforts in reducing the sintering temperature, to be compatible with the plastic substrates.[11,13,14,16]

Here, we report the preparation of a silver (Ag) NP ink. The preparation of large-area conductive silver films on glass and plastic substrates at room temperature, using these silver nanoparticle inks, has also been demonstrated. These films can be made conductive by a very mild annealing process that is plastic-compatible. The good conductivity was achieved because of the coalescence of silver NPs on the substrate after the solvent evaporation. This method is advantageous, compared to the previously reported methods in which the substrates were usually heated above 200 °C. We have further demonstrated the fabrication of a P3HT-PCBM solar cell via direct deposition of the cathode using these silver NP inks. A solar cell efficiency of 2.25% was achieved. The preparation of conductive silver films on flexible plastic substrates at mild temperatures is expected to have high impact on future low-cost printable electronics.

Silver NP ink was prepared by reducing silver nitrate ($AgNO_3$) with sodium borohydride ($NaBH_4$) in the presence of poly(vinyl pyrrolidone) (PVP) as a stabilizer. In a typical synthesis of silver NPs, 0.5 g of $AgNO_3$ and 0.5 g of PVP were dissolved in 100 mL of deionized water under vigorous stirring. Eight milliliters (8 mL) of a 10 mg/mL freshly prepared $NaBH_4$ solution was added dropwise to the reaction mixture, resulting in an immediate solution color change from colorless to dark yellow. The solution was kept stirring for another 5 min and then filtered to remove any undissolved impurities. The resultant solution was centrifuged at a speed of 5000 rpm to remove the excess PVP. The precipitate was collected and dispersed in ethanol for further studies.

The PVP stabilizer plays an important role in the preparation of aqueous silver NP ink. The reaction without PVP resulted in formation of an insoluble powder with micrometer-sized silver NPs (see Figure S1 in the Supporting Information). Figure 1A shows the appearance of Ag nanoparticle ink in ethanol solution with a concentration of 30 mg/mL. The transmission electron microscopy (TEM) image of the silver NPs is shown in the inset of Figure 1A. The silver NP ink contains spherical nanoparticles with diameters in the range of 15−30 nm. The extinction spectrum of the Ag nanoparticles in solution (Figure 1D) shows a sharp plasmon peak at 400 nm, which is typical for spherical silver NPs. Figures 1B and 1C show SEM images of the film formed by depositing silver NP dispersion onto the glass substrate at room temperature. The film is uniform and has a metallic shiny brightness, similar to that of a silver mirror (see Figure 1B, inset).

Received: February 15, 2011
Revised: June 21, 2011
Published: July 01, 2011

dx.doi.org/10.1021/cm200471s | Chem. Mater. 2011, 23, 3273–3276

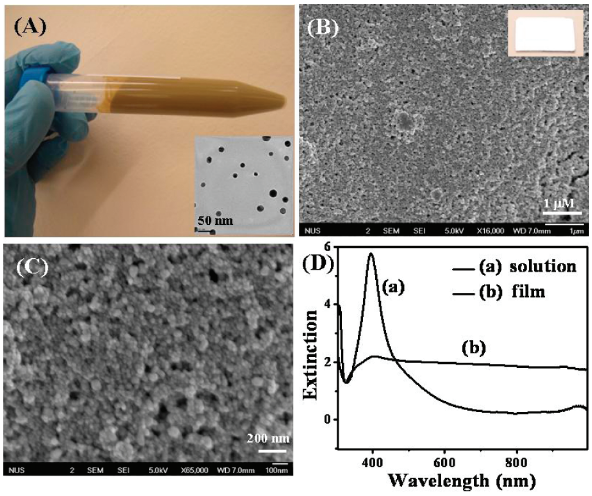

Figure 1. (A) Silver nanoparticle (NP) ink in ethanol solution with a concentration of 30 mg/mL. The inset shows the TEM image of the silver NPs. (B,C) SEM images of the silver NP film prepared by solvent evaporation. The inset in panel B shows the shiny silver film on a glass substrate. (D) Ultraviolet−visible light (UV−vis) extinction spectra of the silver NPs in ethanol and a silver film.

The formation of a shiny silver mirror after solvent evaporation indicates that the nanoparticles are closely packed in the film (see the Supporting Information for the movie of preparing a shiny silver film on a glass substrate). The SEM images clearly show that the nanoparticles were self-aggregated and formed an interconnected structure within the film. The extinction spectrum of a partially transparent film (see Figure 1D) shows a broad spectrum spanning from the visible range to the infrared region, consistent with the heavily aggregated structure revealed by the SEM image.

The self-aggregation behavior of silver NPs was utilized to fabricate conductive films on plastic substrates, which have potential applications in flexible plastic electronics. The conductive films were prepared by depositing the silver NP dispersion onto the polyethylene terephthalate (PET) plastic substrate (see Figure 2A) and then evaporating the solvent at room temperature under table light illumination. It should be mentioned that the solvent evaporation can be accelerated by heating the substrate at a slightly raised temperature (e.g. 50 °C) or by using a blow dryer. These treatments are plastic compatible and do not cause any damage to the plastic substrate. The thickness of the silver film can be adjusted by controlling the amount of nanoparticle dispersion deposited onto the substrate. Figure 2B shows the resultant shiny silver film on a plastic substrate after solvent evaporation. The AFM image of the silver film on the plastic substrate (see Figure 2B, inset) shows that the NPs were interconnected with each other. The optical microscopic image of the silver film on a plastic substrate indicates that the film is smooth without any cracks (see Figure S2 in the Supporting Information). The film exhibits low resistance (Figure S3 in the Supporting Information). The sheet resistance of the prepared silver film with a thickness of 510 nm was measured using a four-point probe. The sheet resistance of the film was measured to be 0.29 Ω/□ when it was unfolded, and increased slightly with increasing bending angles (see Figure 2C). The resistance remained almost unchanged after over 100 deformation cycles. The sheet resistance of the prepared film is comparable to that of silver film prepared by electrolyte-induced sintering (0.44−0.67 Ω/□).[22] We have also found that the resistance of the silver film remained almost constant after a month, demonstrating their potential for long-term use.

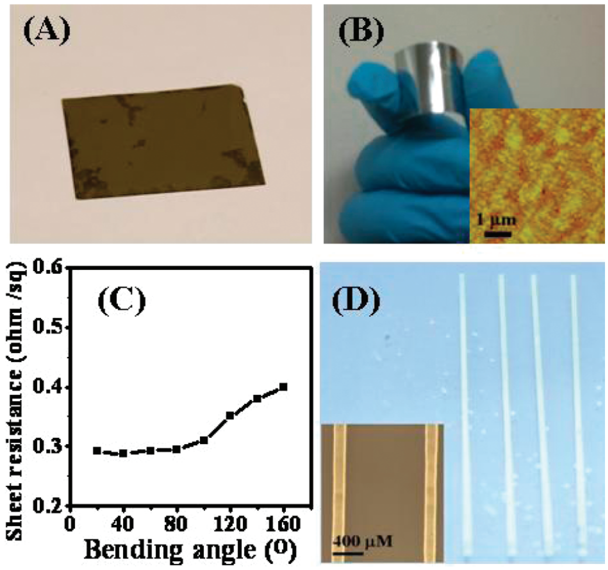

Figure 2. Photographs of the silver nanoparticle (NP) dispersion on a plastic substrate (A) before and (B) after solvent evaporation. (Inset in panel B shows the AFM image of the prepared silver film.) (C) Sheet resistance at different bending angles; the sheet resistance was obtained using four-point probe measurements. (D) Photograph of the inkjet-printed silver lines. Inset shows the optical microscope image of the printed silver lines.

Previously, Anto et al.[14] reported that silver films prepared using thiol-capped silver NPs behaved like an insulator after solvent evaporation and the film had to be annealed at 150−200 °C to become conductive. Our silver NPs are capped with PVP through the coordination of the nitrogen atom (N) in PVP.[23] Because of the steric effect, PVP binds weakly to the silver nanoparticle surface, compared to thiols and primary amines.[23] TGA showed that only 2−3 wt % of the PVP was present in the silver NP ink (see Figure S4 in the Supporting Information). The low density of PVP on the nanoparticle surface is also due to the weak binding of PVP. The weakly adsorbed PVP can desorb readily from the surface of nanoparticles and collapse after solvent evaporation. The silver NPs tend to self-aggregate to form conductive films.

We have further demonstrated the application of our silver NP ink to print silver lines onto a plastic substrate, using a GIX Microplotter II inkjet printer. The photograph and optical microscopic images of the printed silver lines are shown in Figure 2D and the inset. The printed silver lines have lengths of 1 cm and widths of 150 μm with a line spacing of ∼1 mm.

The conductivities of silver films of different thicknesses were measured using four-point probe measurements. The substrates for the measurements were prepared via the thermal evaporation of four aluminum electrodes onto the glass substrate with a line spacing of 4 mm. The dispersion of silver NPs was deposited on top of the four probes via drop casting to form films after solvent evaporation. The conductivity was obtained by measuring the resistance of the silver films using a GS 610 source measurement unit (Yokogawa). Thickness-dependent conductivity measurements (see Figure S5 in the Supporting Information) showed

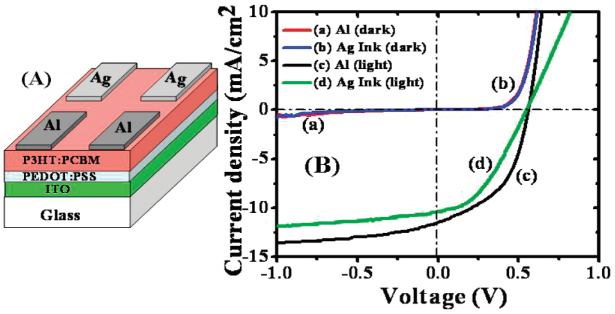

Figure 3. (A) Device structure of the solar cell. The aluminum electrode was deposited by vacuum evaporation, and the silver electrode was deposited by solution process using aqueous silver NP ink. (B) The current density−voltage ($J-V$) curves for the P3HT-PCBM organic solar cell fabricated using aluminum and silver as cathodes in darkness and under a light illumination of 100 mW/cm^2.

that the film conductivity increased rapidly with increasing film thickness and remained constant at thicknesses of >400 nm. The maximum conductivity was measured to be $\sim 0.7 \times 10^5$ S cm^{-1}, which is ~9 times lower than that of the bulk conductivity of Ag ($\sim 6.3 \times 10^5$ S cm^{-1}). The lower conductivity of the solution-processed silver film, compared to bulk silver, is due to the void space present in the silver film (see Figure 1C) that is formed during the self-aggregation processes of the silver NPs. The conductivity of films prepared via this method is comparable to that of silver films obtained by previously reported conventional sintering methods, such as chemical sintering (0.65×10^5 S cm^{-1}) and microwave irradiation (0.33×10^5 S cm^{-1}).[11,16,19,22]

To demonstrate the application of the silver NP ink for organic electronics, we fabricated a thin film solar cell, using P3HT-PCBM as the active layer and depositing the silver NP ink onto the P3HT-PCBM film as the cathode (see details in the Supporting Information). The device structure is shown in Figure 3A. The current density−voltage curves for a P3HT-PCBM solar cell using solution-processed silver electrodes in darkness and under 100 mW/cm^2 light illumination are depicted in Figure 3B. For direct comparison, the P3HT-PCBM solar cell fabricated using vacuum-evaporated aluminum as the cathode was also measured under the same conditions. The device characteristics with a solution-processed silver electrode are comparable to those of conventional vacuum-evaporated aluminum electrodes. The open-circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF), and power conversion efficiency (η) are 0.56 V, 10.4 mA/cm^2, 38.6%, and 2.25%, respectively, for the solar cell prepared using the solution-processed silver electrode. In comparison, the V_{oc}, J_{sc}, FF, and η values for a solar cell prepared using a vacuum-evaporated aluminum electrode are 0.57 V, 11.5 mA/cm^2, 47.0%, and 3.07%, respectively. Similar V_{oc} values were observed for the solution-processed silver electrode and the vacuum-evaporated aluminum electrode, which indicates that there is no chemical or structural modification of the active layer at the interface. The decrease in efficiency (η) and fill factor (FF) could be due to the slightly larger contact resistance between organic active layer and silver electrodes, compared to the evaporated aluminum electrodes. Although the overall characteristics of the solar cell using solution-processed silver electrodes are slightly lower than those using vacuum-evaporated aluminum electrodes. Considering the unique advantages of solution-processable silver inks and mild temperature annealing, they are expected to have potential applications for printable low-cost organic solar cells and other plastic electronics.

Conventional metal nanoparticle inks require additional post-annealing at high temperatures or chemical treatments to make the metal films conductive. To use these metal films as electrodes in organic electronics using an organic active layer, high-temperature annealing or chemical treatments could destroy the organic active layer. Therefore, conventional metal nanoparticle inks cannot be used to fabricate electrical contacts directly onto the organic active layer via solution processing. Recently, Gaynor et al.[4] have developed a laminated silver nanowire film electrode for organic solar cells to overcome the above-mentioned problems. Instead of depositing the silver nanowire directly onto the organic active layer, they first fabricated a silver nanowire mesh on a glass substrate by drop-casting the suspension of silver nanowires, followed by annealing at 180 °C for 1 h to make the mesh conductive. Finally, they laminated the silver nanowire mesh onto the organic active layer as the top electrode. This lengthy process limits the large-scale fabrication of organic solar cells. Here, we have successfully demonstrated the preparation of conductive silver films at very mild temperatures, using silver NP inks. The prepared silver NP ink can be deposited directly onto an organic active layer to make electrical contacts. This method allows fast and large-scale preparation of conductive silver films for organic electronics. The device characteristics obtained using the prepared silver NP ink as a cathode are comparable to those obtained using conventional vacuum-evaporated aluminum cathode electrodes.

In summary, here, we report the preparation of silver nanoparticle (NP) ink that can be used to fabricate highly conductive films on glass and plastic substrates by depositing the NP dispersion onto the substrate and drying the solvent. The high conductivity was achieved by annealing the substrate at very mild temperatures, because of the self-aggregation of NPs after drying the solvent. We have also demonstrated the printability of our silver inks. The conductive films fabricated on plastic substrates are highly flexible, and very small changes in the conductivity were observed by deforming the plastic substrate. The preparation of conductive films by annealing at mild temperatures will enable the preparation of conductive patterns on various heat-sensitive substrates. Furthermore, polymer solar cell was fabricated by depositing the cathode onto the polymer film, using the silver NP ink and an efficiency of η = 2.25% was obtained. We expect that the preparation of conductive films by self-aggregation of nanoparticles at mild temperatures would have potential applications for many low-cost printable solar cells and flexible plastic electronics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Preparation of nanoparticle ink, TEM images of the nanoparticles obtained without PVP, optical microscopic image of the silver film, thickness-dependent conductivity, solar cell fabrication procedures, TGA of Ag inks, and movie of preparing shiny silver film on a glass substrate. (PDF and AVI files.) This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chmxqh@nus.edu.sg.

■ ACKNOWLEDGMENT

This work is supported by the Faculty of Science, National University of Singapore (R-143-000-341-112).

■ REFERENCES

(1) Gates, B. D. *Science* **2009**, *323*, 1566.

(2) Ahn, B. Y.; Duoss, E. B.; Motala, M. J.; Guo, X. Y.; Park, S. I.; Xiong, Y. J.; Yoon, J.; Nuzzo, R. G.; Rogers, J. A.; Lewis, J. A. *Science* **2009**, *323*, 1590.

(3) Caironi, M.; Gili, E.; Sakanoue, T.; Cheng, X. Y.; Sirringhaus, H. *ACS Nano* **2010**, *4*, 1451.

(4) Gaynor, W.; Lee, J. Y.; Peumans, P. *ACS Nano* **2010**, *4*, 30.

(5) Fuller, S. B.; Wilhelm, E. J.; Jacobson, J. M. *J. Microelectromech. Syst.* **2002**, *11*, 54.

(6) Andersson, P.; Forchheimer, R.; Tehrani, P.; Berggren, M. *Adv. Funct. Mater.* **2007**, *17*, 3074.

(7) Kalita, G.; Matsushima, M.; Uchida, H.; Wakita, K.; Umeno, M. *J. Mater. Chem.* **2010**, *20*, 9713.

(8) An, K. H.; Kim, W. S.; Park, Y. S.; Choi, Y. C.; Lee, S. M.; Chung, D. C.; Bae, D. J.; Lim, S. C.; Lee, Y. H. *Adv. Mater.* **2001**, *13*, 497.

(9) Crispin, X.; Jakobsson, F. L. E.; Crispin, A.; Grim, P. C. M.; Andersson, P.; Volodin, A.; van Haesendonck, C.; Van der Auweraer, M.; Salaneck, W. R.; Berggren, M. *Chem. Mater.* **2006**, *18*, 4354.

(10) Bishop, P. T.; Ashfield, L. J.; Berzins, A.; Boardman, A.; Buche, V.; Cookson, J.; Gordon, R. J.; Salcianu, C.; Sutton, P. A. *Gold Bull.* **2010**, *43*, 181.

(11) Perelaer, J.; Smith, P. J.; Mager, D.; Soltman, D.; Volkman, S. K.; Subramanian, V.; Korvink, J. G.; Schubert, U. S. *J. Mater. Chem.* **2010**, *20*, 8446.

(12) Layani, M.; Gruchko, M.; Milo, O.; Balberg, I.; Azulay, D.; Magdassi, S. *ACS Nano* **2009**, *3*, 3537.

(13) Magdassi, S.; Grouchko, M.; Berezin, O.; Kamyshny, A. *ACS Nano* **2010**, *4*, 1943.

(14) Anto, B. T.; Sivaramakrishnan, S.; Chua, L. L.; Ho, P. K. H. *Adv. Funct. Mater.* **2010**, *20*, 296.

(15) Magdassi, S.; Grouchko, M.; Toker, D.; Kamyshny, A.; Balberg, I.; Millo, O. *Langmuir* **2005**, *21*, 10264.

(16) Valeton, J. J. P.; Hermans, K.; Bastiaansen, C. W. M.; Broer, D. J.; Perelaer, J.; Schubert, U. S.; Crawford, G. P.; Smith, P. J. *J. Mater. Chem.* **2010**, *20*, 543.

(17) Zhang, R. W.; Lin, W.; Moon, K. S.; Wong, C. P. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2637.

(18) Chung, J. W.; Ko, S. W.; Bieri, N. R.; Grigoropoulos, C. P.; Poulikakos, D. *Appl. Phys. Lett.* **2004**, *84*, 801.

(19) Perelaer, J.; de Gans, B. J.; Schubert, U. S. *Adv. Mater.* **2006**, *18*, 2101.

(20) Lee, H. H.; Chou, K. S.; Huang, K. C. *Nanotechnology* **2005**, *16*, 2436.

(21) Perelaer, J.; Hendriks, C. E.; de Laat, A. W. M.; Schubert, U. S. *Nanotechnology* **2009**, *20*, 165303.

(22) Long, Y. H.; Wu, J. J.; Wang, H.; Zhang, X. L.; Zhao, N.; Xu, J. A. *J. Mater. Chem.* **2011**, *21*, 4875.

(23) Wang, H. S.; Qiao, X. L.; Chen, J. G.; Wang, X. J.; Ding, S. Y. *Mater. Chem. Phys.* **2005**, *94*, 449.