Highly conductive ink made of silver nanopolyhedrons through an ecofriendly solution process

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An ecofriendly process has been successfully developed to synthesize the polycrystalline silver nanopolyhedrons with a high yield at large scale. By using tannic acid in the presence of poly (vinyl pyrrolidone) (PVP), high quality silver nanopolyhedrons were obtained in an aqueous one-pot reaction without any templates or auxiliaries. The film made from the silver nanostructures exhibits an electrical conductivity higher than 10^4 S/cm on both rigid and flexible substrates. The supreme mechanical strength of this silver film recommends its wide application in printing and flexible electronics.

With the rapid growth of printed electronics and flexible devices, conducting fluids or conductive inks become a prerequisite for large area and ultra-low-cost electronics.[1–3] The conducting elements in the inks are usually noble metal micropolyhedrons or nanopolyhedrons, such as gold and silver.[4–6] However, the high cost of gold impedes the development of application of gold-based conductive inks in low-cost electronics. Therefore, silver nanoparticle-based conductive inks become attractive in terms of cost, as well as electrical and thermal conductivity.[3,7] In addition, the applications of silver conductive materials in flexible electronics ask for low temperature processable inks that can be converted into metallic films with high electrical conductivity ($>10^4$ S/cm) by thermal treatment at a relatively low temperature (~150 °C).

Using a solution process to fabricate silver nanopolyhedrons is preferred to other methods, such as electrochemical deposition,[8] photochemical synthesis,[9] and microwave-assisted preparation,[10] due to the solution process's low cost, large-scale operation, and easily-controlled process parameters. However, most solution processing methods use organic solvents and non-ecofriendly reducing agents and auxiliaries.[11,12] Herein, we report a silver nanopolyhedron-based conductive ink that shows high electrical conductivity with low annealing temperature through a green chemistry type procedure.

In our synthesis strategy, we chose silver nitrite as the metal source, a nontoxic compound polyvinylpyrrolidone (PVP) as the capping agent, and tannic acid as an ecofriendly reducing agent. Moreover, water, the best environmentally acceptable solvent, was used as the solvent in the one-pot reaction. In a typical preparation, silver nitrate (1.0 g, 5.88 mmol) in 15 mL of deionized water was added to a solution of PVP (2.0 g, 17.7 mmol, weight-average molecular weight M_w = 55,000 g/mol) and tannic acid (2.11 g, 1.22 mmol) in 20 mL of deionized water, at a rate of 30 drops per min at room temperature. After the mixture was vigorously stirred for 30 min, it was heated in an oven at 80 °C for 24 h. Then, the mixture was cooled to room temperature in tap water, and a large amount of acetone was added followed by centrifugation. The obtained precipitates could be well redispersed in different solvents, like ethanol, n-butyl alcohol, triethylene glycol monoethyl ether, and so on, to form various kinds of conductive inks satisfying different applications' requirements. After six months' storage at room temperature, no phase separation was observed in the dispersions, showing the supreme kinetic stability of the conductive inks.

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The morphology of the silver nanopolyhedrons shown in the SEM (scanning electron microcope) image [Fig. 1(a)] indicates the ultrahigh yield of the synthesis method. It should be noted that the particles are tightly packed nanopolyhedrons with uniform size and shape. The TEM (transmission electron microscope) image [Fig. 1(b)] suggests that the nanopolyhedrons tend to aggregate even at very low concentration. A representative silver nanopolyhedron has a roughly hexagonal surface with a size of about 100 nm [Fig. 1(c)]. High resolution TEM images clearly show the polycrystalline structure of the silver nanopolyhedrons (Fig. S1). Electron microdiffraction patterns taken from both a large quantity of nanopolyhedrons [Fig. 1(b) inset] and an individual one [Fig. 1(c) inset], reveal that the crystal lattice structure of the silver nanostructures is face center cubic (fcc). The XRD (x-ray diffraction) pattern illustrated in Fig. S2 shows the Bragg reflections from the {111}, {200}, {220}, {311}, and {222} planes in an fcc lattice, with intensity ratios similar to the results obtained by other groups.[13] The lattice constant calculated from the XRD pattern is 4.091 Å, consistent with the standard data (a = 4.0862 Å, JCPES File No. 04-0783).

The conductive inks were fabricated by mixing the silver nanopolyhedrons with triethylene glycol monoethyl ether in mass fraction of around 30% by a rotor. To make silver films, rigid or flexible substrates were drop cast with the inks followed by annealing in nitrogen [Figs. 2(a), 2(b)]. It is generally accepted that upon heating, while the solvent was evaporated, the capping agents and the aggregated nanopolyhedrons melted and reorganized to form a continuous metal phase, which significantly increased the electrical conductivity. SEM images of the sintered silver film on glass substrate reveal that the film became solid and continuous after annealing

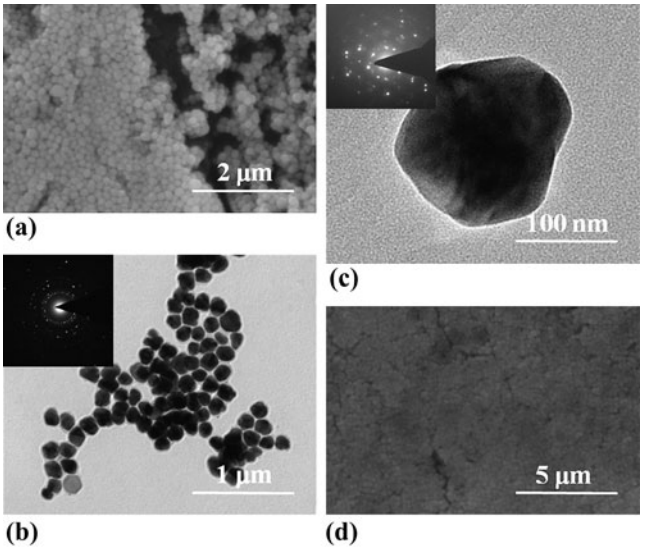


FIG. 1. (a) Large area SEM image of the silver nanopolyhedrons. (b) Small area TEM image of the self-aggregated nanopolyhedrons. Inset: electron microdiffraction pattern taken from a large amount of nanopolyhedrons. (c) TEM image of a single silver nanopolyhedron. Inset: electron microdiffraction pattern taken from a single nanopolyhedron. (d) Large area SEM image of the surface of a silver film.

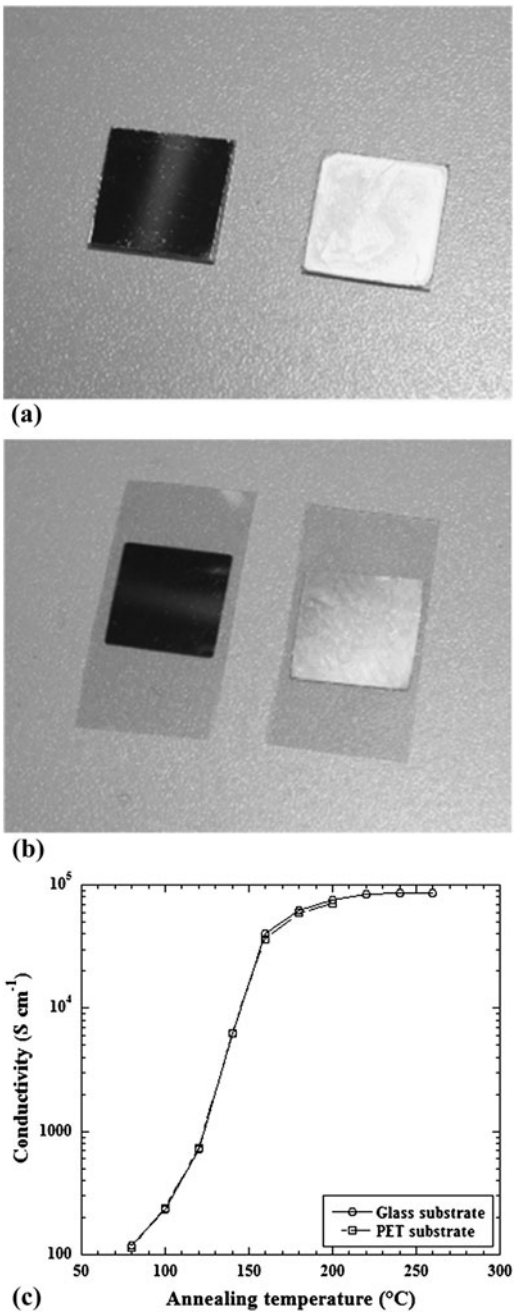


FIG. 2. (a) Picture of conductive ink formed silver film (right), and evaporated silver film (left) on glass substrate. Both devices have dimensions of 1.5 cm × 1.5 cm. (b) Picture of conductive ink formed silver film (right), and evaporated silver film (left) on PET substrate. Both devices have dimensions of 1.5 cm × 1.5 cm. (c) The dependence of the conductivity on the annealing temperature.

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at 160 °C [Figs. 1(d) and S3(b)]. As the annealing temperature reached 200 °C, the nanoparticles fused into a contiguous network [Figs. S3(c), S3(d)]. The dependence of the conductivity on the annealing temperature is plotted in Fig. 2(c). The annealing time is 15 min for all the annealing processes. The sintered film becomes conductive after annealing at 80 °C, exhibiting a conductivity of 1.2×10^2 S/cm. The conductivity increases sharply when the annealing temperature is above 120 °C. It reaches a maximum value of 8.5×10^4 S/cm at 220 °C. The saturation of the electrical conductivity at a high temperature indicates that at 220 °C, the silver nanopolyhedron aggregates are fully converted into a macroscopic network, and the structure of the bulk material will not change until the temperature reaches the melting point. Furthermore, silver films were prepared by annealing in air, and they have similar conductivity as the samples prepared in nitrogen, showing the chemical stability of the silver nanopolyhedrons against oxygen. In comparison with the drop cast silver film, the conductivity of the evaporated silver films was studied against the annealing temperature. Since the average thickness of the drop cast silver film is about 760 nm, 750 nm thick silver was evaporated onto a glass substrate in a vacuum of 8.8×10^{-4} Pa. Figure 2(a) shows the drop cast and the evaporated silver films on glass substrates. The black color of the evaporated silver film in the photo is due to the strong specular reflection from the film. The evaporated silver film exhibits a conductivity

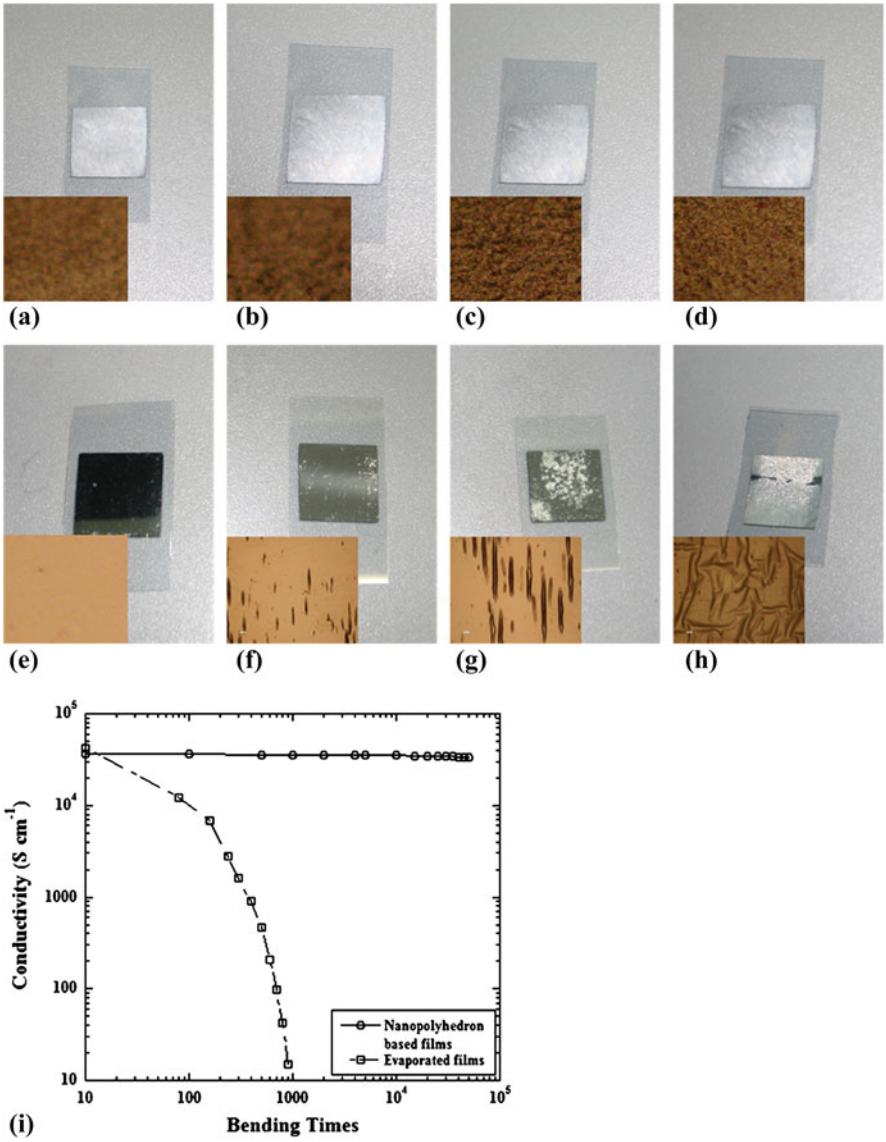


FIG. 3. Macroscopic pictures and surface morphologies of the conductive ink formed silver film: (a) pristine, (b) after 5000 bending cycles, (c) after 20,000 bending cycles, (d) after 50,000 bending cycles, and the evaporated film: (e) pristine, (f) after 80 bending cycles, (g) after 500 bending cycles, (h) after 1000 bending cycles, and (i) the dependence of the conductivity of the silver film on the bending cycles.

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of 4.2×10^4 S/cm, independent of the annealing temperature.

The conductivity achieved by our silver nanopolyhedrons is one of the highest according to literatures.[14] Even at a low annealing temperature of 160 °C, the conductivity of 4×10^4 S/cm is better than that of the most nanoparticle-based conductive inks.[3,15] The high conductivity at low annealing temperature is desirable in the applications of flexible electronics.[14] To investigate the performance of our conductive inks on flexible substrates, a PET substrate was drop cast with the ink followed by 15 min thermal treatment in nitrogen at various temperatures. As pictured in Fig. 2(b), the ink is easily spread on the PET substrate, and forms a solid film after solvent evaporation, showing its strong affinity to the flexible substrate. The dependence of the conductivity on the annealing temperature is plotted in Fig. 2(c), which is similar to that on glass. The sintered film on the PET substrate becomes conductive after being annealed at 80 °C, exhibiting a conductivity of 1×10^2 S/cm. The conductivity increases to 3.6×10^4 S/cm at an annealing temperature of 160 °C. For comparison, the film on the glass substrate shows a conductivity of 4×10^4 S/cm at the same annealing temperature. The maximum conductivity achieved on the PET substrate is 7.1×10^4 S/cm at 200 °C, limited by the temperature.

For collapsible devices, the film materials used are required to have strong mechanical strength during folding. A bending experiment was designed to investigate the mechanical strength of silver films on the PET substrate. The experimental setup can be found in Fig. S4. To make the film under test, the silver conductive ink was drop cast onto the PET substrate followed by 15 min annealing at 160 °C in nitrogen [Fig. 3(a)]. The initial conductivity of the pristine film was 3.6×10^4 S/cm. After 50,000 bending cycles, the conductivity slightly dropped to 3.4×10^4 S/cm [Fig. 3(i)]. Neither the macroscopic photos nor the microscopic images of the film after bending [Figs. 3(b)–3(d)] show any change of the silver film. The film stays strong and solid, and no cracks have been found. The excellent mechanical strength of the conductive ink silver film could be attributed to the presence of the polymer inside the annealed film. EDS analyses performed on the film before and after the annealing at different temperatures in air verified our hypothesis (Fig. S5). To further demonstrate the polymer effect, a device with an evaporated silver film was tested. The device is pictured in Figs. 2(b) and 3(e), while the photos of the device after bending are shown in Fig. 3(f)–3(h). After only 80 bending cycles, small cracks started developing on the surface of the film, which are clearly revealed by the microscopic image as well as to the naked eye [Fig. 3(f)]. The average conductivity of the whole film dropped to 1.2×10^4 S/cm from the initial value of 4.2×10^4 S/cm. As the cracks grew both in size and in number with the increase of bending times [Figs. 3(f)–3(h)], the conductivity decreased sharply [Fig. 3(i)]. After 1000 bending cycles, most parts of the silver film became torn and the film was no longer conducting. The conductivities of the evaporated silver film before and after bending prove that the polymer capping agent inside the conductive ink, on one hand, provides the necessary mechanical strength for the sintered film, on the other hand, does not severely reduce the conductivity of the film.

High quality polycrystalline silver nanopolyhedrons were synthesized through an environmentally friendly solution process with a high yield. Conductive inks were made by redispersing the silver nanopolydedrons in a variety of solvents. By annealing the drop cast inks on both rigid and flexible substrates, high conductive silver films were obtained with the highest conductivity of 8.5×10^4 S/cm$^-$ for the film on glass. On the PET substrate, even at the annealing temperature of 160 °C, the conductivity reached 3.6×10^4 S/cm. A bending test showed that the conductive ink formed film retained its conductivity after 50,000 bending cycles. The strong mechanical strength of the solid film, combined with high conductivity, low annealing temperature, and long lifetime, make the conductive ink desirable for application in printing and flexible electronics.

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APPENDIX: MATERIALS AND METHODS

Silver nitrate (analytical grade, Tianjin Fuchen Chemical Reagent Co., Ltd., Tianjin, China), polyvinylpyrrolidone (analytical grade, Shanghai Bio Life Science & Technology Co., Ltd., Shanghai, China; weight average molecular weight M_w = 55 000 g/mol), and tannic acid (analytical grade, Tianjin Qilun Chemistry Co., Ltd., Tianjin, China) were used without further purification. Deionized (DI) water was used for the entire synthesis. Ethanol (analytical grade, Guangzhou Reagent Co., Ltd., Guangzhou, China), acetone (analytical grade, Guangdong Guanghua Chemical Factory Co., Ltd., Shantou, China), and triethylene glycol monoethyl ether (analytical grade, Shanghai Jingchun Reagent Co., Ltd., Shanghai, China) were used as received. SEM and energy disperse spectroscopy were performed on a Hitachi S-3700 scanning electron microscope (Tokyo, Japan) operating at 15 kV. TEM were recorded on a Philips model Tecnai F20 electron microscope (Amsterdam, The Netherlands) operating at 200 kV. Powder x-ray diffraction was recorded on a D/max-RA high power rotating anode 12 kW x-ray diffractometer (Guangzhou, China). The conductivity of silver films was measured by a four point probe electrical measurement station (Kunde, KDY-1). By assuming that the drop cast silver films with typical thickness 670–900 nm were ideal plane thin films, the classic equation $\rho = \left(\frac{\pi}{\ln 2}\right) d \frac{V}{I} = 4.5324 d \frac{V}{I}$ was used to determine the resistivities. For detailed derivation of the equation, please check Schroder, D. K., *Semiconductor Material and Device Characterization*, 2nd ed. (John Wiley & Sons, New York, 1998). The bending experiments were performed on a precision displacement instrument (Zolix, TSA400-B, Beijing, China). The microscopic images were taken by a Nikon microscope (eclipse E600 POL, Tokyo, Japan) coupled with a DXM1200F digital camera (Tokyo, Japan). The thickness of the silver films was measured by a Dektak 150 surface profiler (New York, NY), and averaged over 10 films.

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