

Supporting Information

Facile Synthesis of Silver Nanoparticles Useful for Fabrication of High-conductivity Elements for Printed Electronics

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1. Instrumentation

UV-vis absorption spectra were obtained on a Varian Cary 5 UV-Vies NIR spectrophotometer. X-ray diffraction was recorded at room temperature on a Rigaku MiniFlex Diffractometer using Cu K α radiation (λ 1.5418 Å) with a θ -2 θ scans configuration. OTFTs were characterized using Keithley SCS-4200 characterization system in ambient conditions. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FM-SEM) measurements were performed on Philips CM20 transmission electron scope and JEOL JSM-6300F scanning electron scope at an accelerating voltage of 120 kV and 2 kV, respectively. Thin film conductivity was measured using a Keithley 237 High Voltage Source Measure Unit using a conventional four-probe technique.

2. A general synthesis of silver nanoparticles (NanoAg-C12 and NanoAg-C16)

Silver acetate (99%), 1-dodecylamine (98%), 1-hexadecylamine (technical grade, 90%), phenylhydrazine (97%), and solvents (reagent grade) were used as received from Sigma-Aldrich without further purification.

The synthesis of silver nanoparticles, NanoAg-C16 and NanoAg-C12, was successfully conducted with the silver acetate concentrations in the range of 0.001 to 1.0 M in toluene in the presence of 2.2 to 20 molar equivalents of organoamine (based on silver acetate) at 25 – 60 °C for 1 hr. The following is an illustrative example for synthesis of 1-hexadecylamine-stabilized silver nanoparticles (NanoAg-C16).

A mixture of silver acetate (0.17 g, 1 mmol) and 1-hexadecylamine (2.41 g, 10 mmol) in toluene (40 mL) was first heated at 60 °C until silver acetate was dissolved (about 5 min). To the resulting solution was added a solution of phenylhydrazine (0.11 g, 1 mmol) in toluene (10 mL) with stirring over a period of 5 min. The resulting reaction mixture was stirred at 60 °C for 1 hr before cooling down to room temperature. Subsequently, acetone (10 mL) was added to the reaction mixture to destroy excess phenylhydrazine, and the solvent was removed on a rotary evaporator (bath temperature \leq 50 °C). The resulting concentrated reaction mixture was added to a stirring methanol/acetone mixture (50 mL/50 mL) to precipitate the crude silver nanoparticle product. The crude silver nanoparticles were isolated by centrifugation, washed twice with acetone (50 mL each), and vacuum-dried at room temperature to afford a black solid. Yield: 0.13 g.

3. Conversion of silver nanoparticles to conductive films

To form a conductive thin film for conductivity measurement, a dispersion of silver nanoparticles in cyclohexane (5 - 10 wt %) was spin coated on a glass substrate at a speed of 1000 rpm to form a brownish thin film. The latter was heated on a hot plate at a

temperature of about 120-160°C under ambient conditions. The conductivity of the resulting silver film was measured using the conventional four-probe technique.

4. TFT Fabrication and Evaluation

Bottom-contact TFT test devices were fabricated using the source and drain silver electrodes generated from the silver nanoparticles. A heavily doped silicon wafer was used as gate electrode, which has a SiO₂ surface layer with a thickness of ~100 nm serving as the gate dielectric. The SiO₂ surface was first cleaned with argon plasma, and then immersed in 0.1 M solution of octyltrichlorosilane (OTS-8) in toluene at 60 °C for 20 min, followed by rinsing with isopropanol and then air dried. A dispersion of silver nanoparticles, NanoAg-C16 in cyclohexane (5 – 10 wt. %) was deposited on the modified SiO₂ surface via a mask-assisted microcontact printing in the following manner. The dispersion of silver nanoparticles in cyclohexane was spin coated on a PDMS rubber sheet at 1000 rpm for 30 sec. A stainless steel mask with a thickness of 13 μm was placed on top of the wafer, and the PDMS rubber sheet carrying a thin layer of the silver nanoparticle film was then laid on top of the mask and gently pushed to force the silver nanoparticles to make contact with the wafer surface through the electrode features of the mask. After 1-2 min, both the mask and the PDMS rubber sheet were removed from the wafer, leaving the silver nanoparticle features on the wafer. The printed features comprising of silver nanoparticles were annealed on a hotplate at 160 °C for 5-10 min, resulting in the formation of a series of silver source/drain electrode pairs with channel lengths of 90 to 400 μm and channel widths of 1000 to 5000 μm. Finally, a 30-nm thick

of PQT-12 semiconductor layer was deposited by spin coating a PQT-12 solution in dichlorobenzene, and annealed at 140 °C for 10 – 30 min.

The TFT devices were evaluated in air using a Keithley 4200 semiconductor characterization system. The mobility in the linear and saturated regimes was extracted from the following equations:

$$\text{Linear regime } (V_D \ll V_G): I_D = V_D C_i \mu (V_G - V_T) W/L$$

$$\text{Saturated regime } (V_D > V_G): I_D = C_i \mu (W/2L) (V_G - V_T)^2$$

where I_D is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are respectively the gate voltage and threshold voltage. V_T of the device was determined from the relationship between the square root of I_D at the saturated regime and V_G of the device by extrapolating the measured data to $I_D = 0$.

5. UV-vis spectra and X-ray diffraction

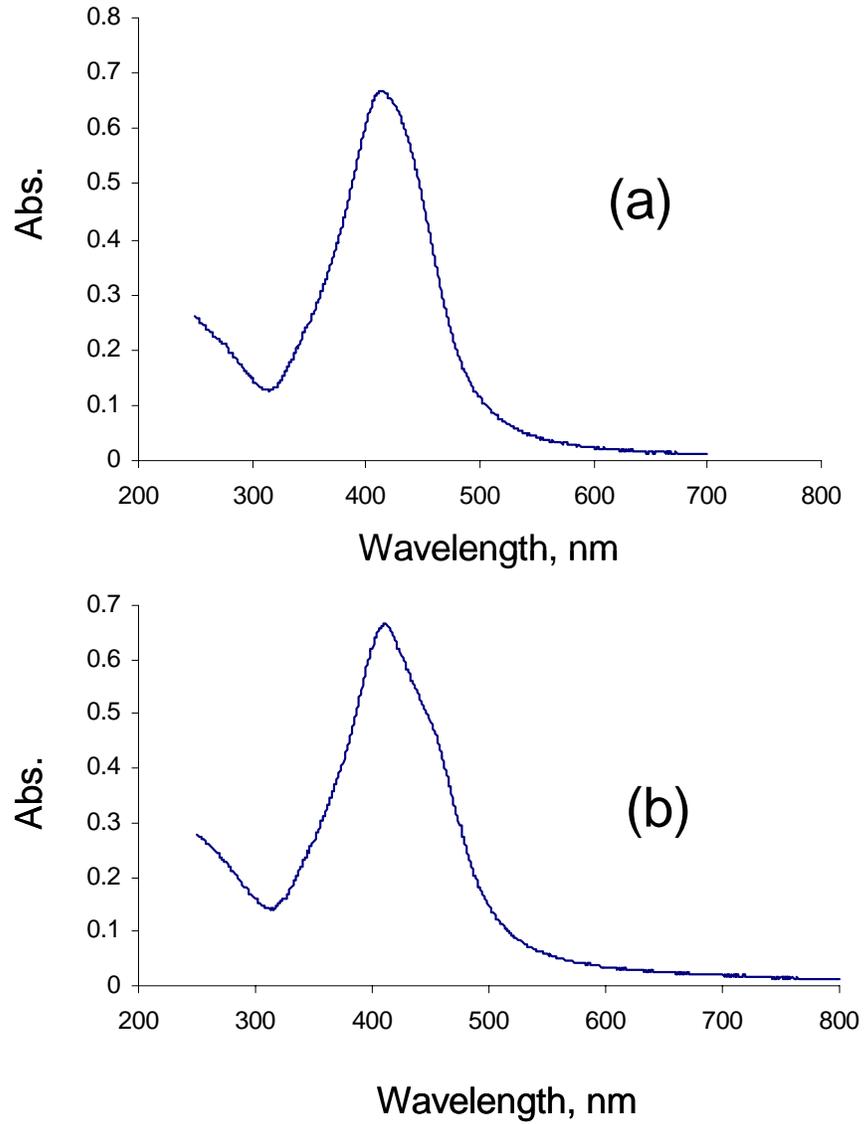
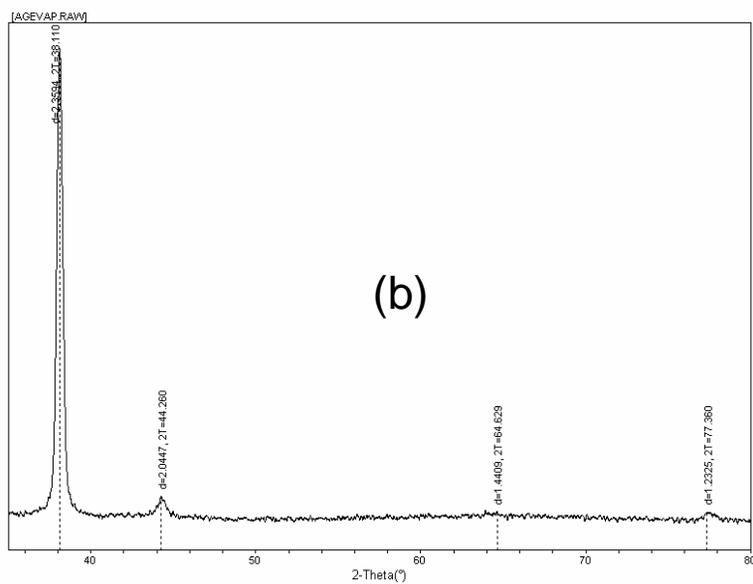
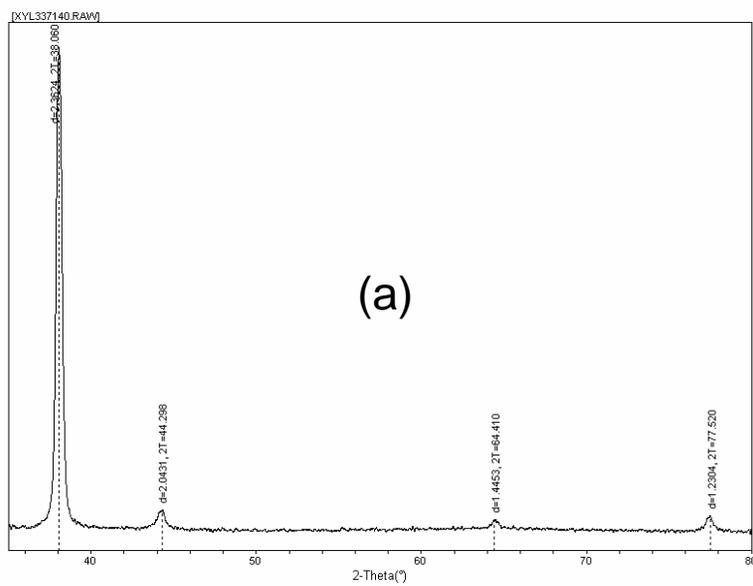


Figure 1. UV-vis spectra of (a) NanoAg-C16 and (b) NanoAg-C12 in dilute cyclohexane.



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Figure 2. X-ray diffraction patterns: (a) spin-coated NanoAg-C16 thin film annealed at 140 °C/1 min and (b) vacuum-deposited silver thin film.