

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

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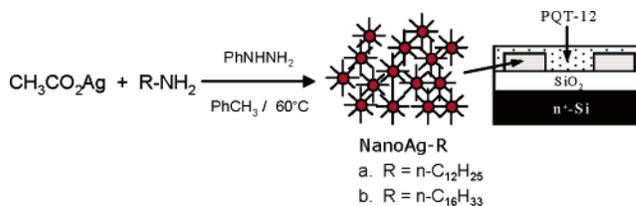
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Printed transistor circuits using liquid-based printing techniques for patterning and deposition are of great interest<sup>1–5</sup> as they represent potentially low-cost alternatives to amorphous silicon technologies for electronics. Potential applications for these circuits are diverse, ranging from large-area electronics (e.g., active-matrix LCDs, organic light emitting diodes, e-paper), where fast switching speeds are not essential, to low-end devices (e.g., wearable electronics, smart labels, radio frequency identification tags), where mechanical flexibility is required or where high cost of silicon chip packaging becomes prohibitive. While great strides have recently been achieved in designing liquid processable semiconductors for printed electronics, little progress has been made in printable conductive materials, despite their importance as electrodes, pixel pads, conductive lines, and tracks in enabling low-cost electronics. Earlier work on printable conductors focused on organic materials, such as polyaniline<sup>6</sup> and PEDOT/PSS.<sup>5b,7</sup> These are very low-conductivity materials (<3 S cm<sup>-1</sup>), aside from their potential chemical, thermal, and electrical instabilities. Noble metals, such as gold and silver, which possess high conductivity (~10<sup>4</sup>–10<sup>5</sup> S cm<sup>-1</sup>) and operational stability, require high temperature and high vacuum deposition. Gold nanoparticles have been successfully explored as a low-temperature, high-conductivity alternative,<sup>8</sup> but the high cost of gold may negate its merits. Liquid-processed silver materials accordingly represent an appealing approach if both the high conductivity and low-temperature processing requirements can be met.

Electroless deposition of silver has been used with microcontact printing to fabricate thin-film transistor (TFT) electrodes,<sup>9</sup> but this approach is too complex to be practical. Commercial silver pastes and inks generally provide thin-film conductivity up to only 2000 S cm<sup>-1</sup>, even with annealing temperatures as high as >200 °C.<sup>10</sup> Recently, conductive elements have been generated from silver nanoparticles, albeit at high annealing temperatures (>300 °C).<sup>11</sup> Since the melting points of metal particles drop drastically in the extreme nanometer regime (<10 nm),<sup>12</sup> it would thus be possible to significantly lower the annealing temperature of silver nanoparticles by reducing their particle size. However, the preparation of stabilized silver nanoparticles in the sub-10 nm range necessary to enable low-temperature coalescence to conductive elements remains a synthetic challenge. We report here a facile synthesis of stabilized silver nanoparticles with a particle size of <10 nm and demonstrate that they can be transformed at relatively low temperatures to highly conductive elements suitable for low-cost printed electronics.

A thin film spin cast from alkanethiol-stabilized silver nanoparticles (~10 nm) prepared by published procedures<sup>13</sup> yielded little conductivity upon annealing around 160 °C, a temperature which is still considered to be compatible with plastic substrates for flexible electronics. This was probably due to the strong bonding of alkanethiol to silver. Silver nanoparticles stabilized with other stabilizing agents, such as metal carboxylate,<sup>14</sup> ammonium salts,<sup>15</sup>

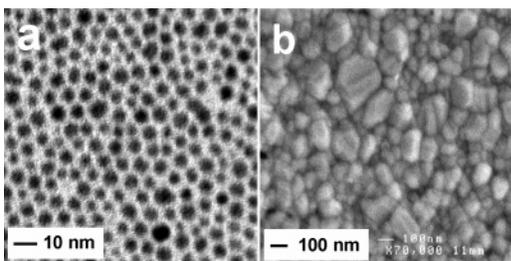
### Scheme 1



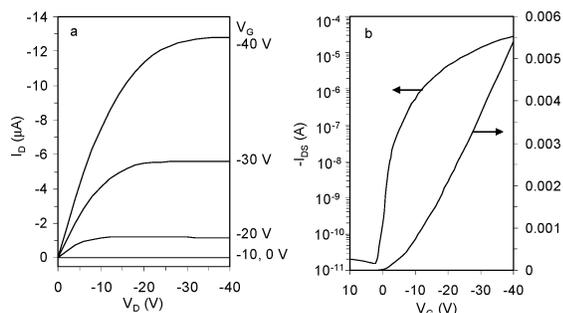
and polymer stabilizers,<sup>16</sup> are not particularly useful as they are difficult to remove at low annealing temperatures. We elected to study alkylamines as stabilizers for silver nanoparticles since they have weaker interactions with silver.<sup>17</sup> These weak interactions can potentially be broken up at significantly lower temperatures, thus enabling the “stripped” silver nanoparticles to coalesce to form a continuous conductive layer.

Oleylamine-stabilized silver nanoparticles were prepared from silver acetate and oleylamine in refluxing toluene according to Hiramatsu and Osterloh’s procedure,<sup>17</sup> but no significant conductivity was observed when a thin film prepared from these nanoparticles was annealed at 160 °C; this was likely due to the difficulty in removing the high-boiling oleylamine. Synthesis of silver nanoparticles with shorter-chain alkylamine stabilizers, such as 1-hexadecylamine or 1-dodecylamine, at refluxing toluene temperature led to silver precipitation, and at lower reaction temperatures (~60 °C), insignificant reaction.

Nonetheless, we found that the reduction of silver acetate at lower temperatures could be accelerated if an appropriate reducing agent was added. While reducing agents, such as NaBH<sub>4</sub>, hydrazine, and aldehyde, provided rapid acceleration leading to large silver aggregates, substituted hydrazines, such as phenylhydrazine, were effective in modulating the reduction to an extent which gave stable silver nanoparticles (Scheme 1). Specifically, with just 0.5 molar equiv of phenylhydrazine in the presence of an alkylamine in toluene, the reduction of silver acetate at 25–60 °C proceeded smoothly and was completed in less than 1 h, yielding a dark-brown solution without precipitation. A black solid of silver nanoparticles was quantitatively obtained upon simple precipitation from a nonsolvent, such as a mixture of acetone and methanol. Silver nanoparticles prepared in this manner were soluble in common organic solvents (e.g., hexane, toluene, THF, etc.) and were stable under ambient conditions. Transmission electron microscopic (TEM) measurements showed that the particle size was <10 nm (Figure 1a). UV–vis absorption spectrum exhibited a plasmon band at ~415 nm, indicative of metallic silver. The present synthesis is facile and offers the following advantages: (i) one-phase reaction without additional surfactants; (ii) low reaction temperature and short reaction time; (iii) less stabilizer (as low as 2.2 molar equiv to silver acetate) and high concentration of silver nanoparticle product (~0.5 M); and (iv) relatively inexpensive starting materials.



**Figure 1.** (a) TEM image of NanoAg-C16 nanoparticles on a grid; (b) SEM image of NanoAg-C16 film after annealing at 140 °C for 30 s.



**Figure 2.** (a) Drain current ( $I_D$ ) versus source-drain voltage ( $V_D$ ) as a function of gate voltage ( $V_G$ ) for a TFT with printed source/drain electrodes from NanoAg-C16 (channel length = 90  $\mu\text{m}$ ; channel width = 2250  $\mu\text{m}$ ). (b)  $I_D$  and  $(-I_D)^{1/2}$  versus  $V_G$  at a constant  $V_D = -40$  V used for calculation of the mobility and current on/off ratio.

A reddish-brown thin film with a thickness of  $\sim 70$  nm spin cast from a solution of 1-hexadecylamine-stabilized silver nanoparticles (NanoAg-C16) in cyclohexane (5–10 wt %) on a glass substrate turned to a shiny silvery film within 30 s upon heating on a hotplate at 140–160 °C. Use of a shorter alkylamine, such as 1-dodecylamine (NanoAg-C12), as a stabilizer further lowered the metalization temperature to 120–140 °C. X-ray diffraction pattern of the resulting silver film showed diffraction peaks at  $2\theta = 38.1$ , 44.2, 64.34, and 77.39°, which are identical to those of a vacuum-deposited silver thin film. SEM image revealed formation of a continuous layer comprising of larger coalesced particles of 100–500 nm (Figure 1b). The electrical conductivity of the resulting silver film was in the range of  $2\text{--}4 \times 10^4$  S  $\text{cm}^{-1}$ , which is in the same order as that of a vapor-deposited silver thin film of similar thickness ( $4\text{--}6 \times 10^4$  S  $\text{cm}^{-1}$ ). This high level of conductivity is more than sufficient for application in any electronic devices. In addition, the alkylamine-stabilized silver nanoparticles prepared by the present procedure exhibited good shelf-life stability both in powder and in solution forms, and this is of critical importance in electronic circuit manufacturing.

An organic TFT was used to validate the usefulness of the conductive elements formed from alkylamine-stabilized nanoparticles as the source/drain electrodes. Unlike single-layer conductive tracks as antennas for RFID tags or conductive lines for electronic interconnects, a multilayered TFT structure would present a more challenging environment for testing the structural integrity and functional performance of printed conductive elements. Poor interfacial contacts and/or intermixing of organic semiconductor with the printed silver electrodes would adversely affect the device performance. Bottom-contact TFTs were built on n-doped silicon wafer with a poly(3,3'-didodecylquaterthiophene) (PQT-12)<sup>4</sup>

semiconductor layer and the source/drain silver electrodes printed from NanoAg-C16 (see Supporting Information). All of the TFTs exhibited good field-effect transistor characteristics, which conformed to the conventional gradual channel model in both the linear and saturated regimes (Figure 2). The devices gave average mobility of 0.05–0.08  $\text{cm}^2$   $\text{V}^{-1}$   $\text{s}^{-1}$ , current on/off ratio of  $10^6\text{--}10^7$ , and threshold voltage of  $-8$  V. These are similar to those of reference TFTs with vacuum-deposited silver electrodes (mobility  $\sim 0.06$   $\text{cm}^2$   $\text{V}^{-1}$   $\text{s}^{-1}$ ; on/off ratio  $\sim 10^6\text{--}10^7$ ).

In summary, we have demonstrated a facile synthesis of stable silver nanoparticles with a particle size of  $<10$  nm. These nanoparticles were stabilized with easily detachable alkylamines, thus permitting their ready conversion at low temperatures to highly conductive silver elements suitable for low-cost, printed electronic applications. OTFTs with the printed silver source/drain electrodes of this nature exhibited TFT properties similar to those using vacuum-deposited silver electrodes.

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**Supporting Information Available:** Materials synthesis and characterization, OTFT fabrication. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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