

Reactive Silver Inks for Patterning High-Conductivity Features at Mild Temperatures

S. Brett Walker and Jennifer A. Lewis*

Department of Materials Science and Engineering and the Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

S Supporting Information

ABSTRACT: Reactive silver inks for printing highly conductive features ($>10^4$ S/cm) at room temperature have been created. These inks are stable, particle-free, and suitable for a wide range of patterning techniques. Upon annealing at 90 °C, the printed electrodes exhibit an electrical conductivity equivalent to that of bulk silver.

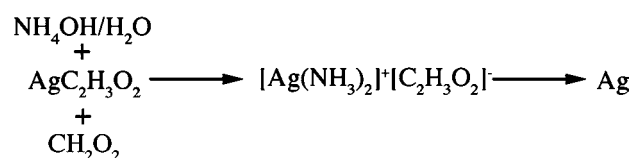
Printed electronics constitute an emerging class of materials with potential applications in photovoltaics,¹ transistors,^{2,3} displays,⁴ batteries,⁵ antennas,⁶ and sensors.⁷ Recent efforts have focused on the design of conductive inks for integration on plastic,^{2,8} textile,⁹ and paper substrates.^{10,12} To date, conductive polymer,² carbon,^{5,9} and metallic nanoparticle inks^{11,12} have been demonstrated. However, organic inks typically exhibit low conductivity, whereas metallic nanoparticle inks often require high annealing temperatures (>200 °C) to decompose stabilizing agents and other polymeric additives that inhibit electrical conductivity.¹³

Recent exploration into silver precursor inks has yielded promising results. For example, silver compounds with carbamate or other relatively low molecular weight ligands (compared to polymer stabilizers) have been synthesized that decompose at temperatures near 150 °C, yielding electrical conductivities approaching that of bulk silver.¹⁴ Unfortunately, even these temperatures render the ink incompatible with many plastic¹⁵ and paper^{12,16} substrates used in flexible electronic and biomedical devices. Hence, there is a need to develop particle-free silver inks that possess high conductivity under ambient conditions.

An optimal ink design would meet the following requirements. First, the ink synthesis procedure should be both simple and high-yielding. Second, the ink should possess low viscosity to make it compatible with a broad range of patterning techniques, including direct ink writing, inkjet printing, and airbrush spraying. Third, the patterned features should be highly conductive at room temperature and achieve bulk conductivity upon annealing at mild temperatures (<100 °C). Finally, the ink should remain stable at room temperature for months without particle precipitation.

To meet the above criteria, we synthesized a reactive silver ink by a modified Tollens' process.¹⁷ Specifically, we first dissolved silver acetate in aqueous ammonium hydroxide. Formic acid was then titrated into the solution, which was mixed thoroughly. Scheme 1 shows the key constituents present in the initial solution (left), the reactive silver ink

Scheme 1. Key Constituents in the Initial Solution, Ink, and Printed Features



(middle), and the patterned silver features (right). The chemical reactions occurring at each step are shown in the Supporting Information (SI). Silver particles formed during initial mixing and were removed by sedimentation over a period of 12 h, yielding a stable, clear supernatant constituting the reactive silver ink.

This modified Tollens' process has several inherent advantages. First, by using silver acetate in place of silver nitrate, we are able to create a stable, nonexplosive silver precursor ink. Second, the use of formic acid results in the formation of carbon dioxide and water, leaving no residual reducing agent.¹⁸ Third, by using excess ammonia in water, we directly create the diamminesilver(I) complex without the need for a silver oxide intermediate. The excess ammonia in solution complexed preferentially with formic acid, leading to the in situ synthesis of ammonium formate (see the SI). The resulting ink is composed of 22 wt % silver, which is comparable to other silver-precursor-based inks.¹⁴ When stored in a sealed vial, this solution is stable for months under ambient conditions without further precipitation. However, upon ink patterning and evaporation, silver particles rapidly form.

The reactive silver ink is highly transparent and can be printed through highly flexible, ultrafine nozzles (100 nm diameter) via direct ink writing (Figure 1a,b; also see the movie in the SI). This ink can also be inkjet-printed and airbrush-sprayed upon the addition of 2,3-butanediol (10% by volume) as a humectant and viscosifying aid (see the SI). The UV-vis absorption spectrum showed a lack of absorption in the 400–425 nm range typically associated with the presence of silver particles (Figure 1c), thus confirming the ink to be particle-free.¹⁹ Thermogravimetric analysis (TGA) indicated that the ink contains a solids loading of 26 wt % when dried at 23 °C and a final silver content of 22 wt % after annealing at 90 °C for 15 min (Figure 1d). The maximum silver content is limited by the solubility of the diamminesilver(I) cation in water.²⁰ Under

Received: October 1, 2011

Published: January 5, 2012

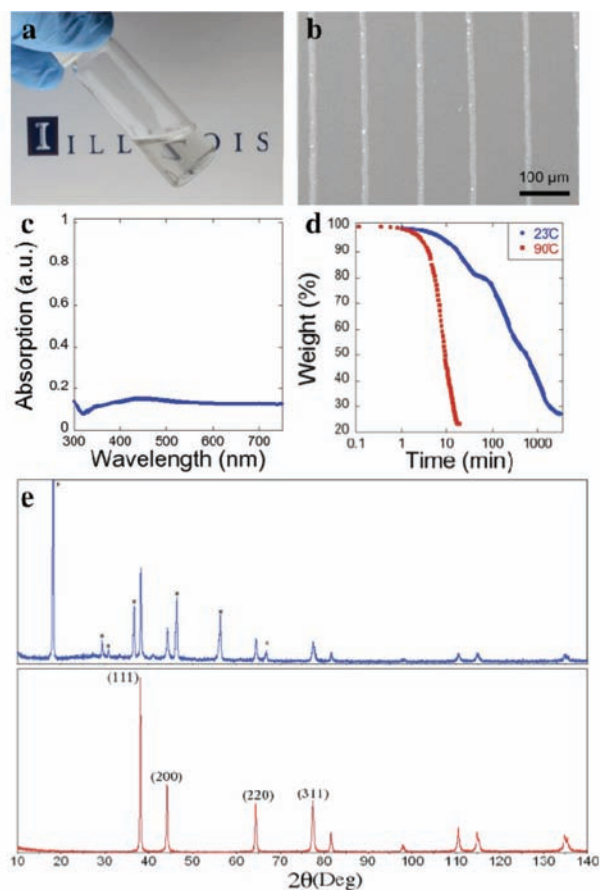


Figure 1. (a) Optical image of the reactive silver ink in a scintillation vial. (b) 1D array of conductive silver lines ($\sim 5 \mu\text{m}$ wide) printed on a silicon substrate via direct-write assembly using a 100 nm nozzle. (c) UV-vis spectrum of the reactive silver ink. (d) TGA curves for the reactive silver ink held at 23 and 90 °C in air. (e) XRD patterns of films patterned from the reactive silver ink dried at 23 °C for 24 h (top) and annealed at 90 °C for 15 min (bottom). Asterisks denote peaks corresponding to silver acetate.

ambient conditions, residual acetate groups are present, which are removed upon heating to 90 °C. X-ray diffraction (XRD) revealed the presence of both silver and silver acetate peaks in drop-cast films produced from this ink and dried at 23 °C for 24 h, while only silver peaks were observed when these films are heated to 90 °C for 15 min (Figure 1e). On the basis of these data, we estimate that the dried ink is composed of approximately 57 wt % silver and 43 wt % silver acetate. Notably, diamminesilver(I) complexes exist only in solution, reverting back to their constituent salts upon drying when the complex is not reduced to metallic silver. Scanning electron microscopy (SEM) images of the top surfaces of printed silver electrodes dried at 23 °C and annealed at 90 °C for 15 min, respectively, are provided in the SI. Unlike drop-cast films, which required drying times of ~ 24 h, the printed features dry nearly instantaneously, yielding fine particles at 23 °C and after annealing at 90 °C.

An important advantage of this reactive silver ink is that particle formation occurs only after patterning, as evaporation ensues. The ink possesses a low initial viscosity of 2 mPa·s (Figure 2a), enabling it to flow through ultrafine nozzles. However, it undergoes significant wetting and spreading on the substrate, resulting in minimum feature widths ($\sim 5 \mu\text{m}$) that

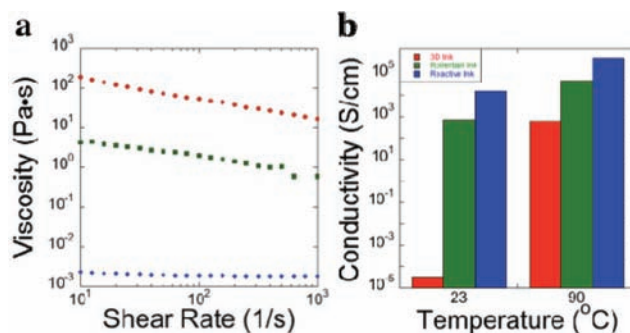


Figure 2. (a) Log–log plot of ink viscosity as a function of shear rate and (b) semilog plot of electrical conductivity as a function of temperature for the reactive silver ink (blue), the silver particle ink developed for pen-on-paper printing (green), and the silver nanoparticle ink developed for omnidirectional (3D) printing (red).

are considerably larger than the nozzle size (Figure 1b). By comparison, silver particle inks developed for omnidirectional printing¹¹ and pen-on-paper writing¹² have apparent viscosities roughly 3–5 orders of magnitude higher at low shear (Figure 2a). Because of the presence of silver particles, those inks cannot be printed through nozzles that are less than $\sim 30 \mu\text{m}$ wide without intermittent clogging.

The electrical conductivity of printed features produced using the reactive silver ink is shown in Figure 2b. For comparison, data are also provided for electrodes produced from silver particle inks developed for omnidirectional printing¹¹ and pen-on-paper writing.¹² Upon drying at 23 °C, the electrical conductivity of electrodes printed from the reactive silver ink exceeded 10^4 S/cm, which is 8 orders of magnitude higher than that of electrodes produced from silver nanoparticle inks formulated for omnidirectional printing, which contain a polymer capping agent and a humectant to enable in- and out-of-plane printing of self-supporting filaments.¹¹ Moreover, their conductivity was an order of magnitude greater than that observed for the silver particle ink developed for pen-on-paper writing.¹² Upon annealing of the electrodes printed from this reactive silver ink at 90 °C for 15 min, their electrical conductivity was identical to that of bulk silver (6.25×10^5 S/cm), while those produced from either of the silver particle inks exhibited at least an order of magnitude lower conductivity despite their substantially higher initial silver contents (75 and 55 wt %, respectively). Importantly, the reactive silver ink adheres very well to poly(ethylene terephthalate) and polyimide substrates and moderately well to other substrates such as glass and cellulose-based materials (see the SI).

In conclusion, we have demonstrated a unique and facile synthesis route for producing reactive silver inks that are particle-free, low-viscosity, and highly conductive at room temperature. These inks flow readily through ultrafine nozzles, enabling patterning of conductive microelectrodes for flexible electronics, displays, and photovoltaics. The ability to achieve bulk silver conductivity upon annealing of the printed electrodes at 90 °C for several minutes opens new avenues for integrating printed electronic devices on low-cost substrates such as plastic, paper, and textiles.

■ ASSOCIATED CONTENT

📎 Supporting Information

Experimental methods for ink synthesis, assembly, and characterization, a movie (MPG) showing direct ink writing, and complete ref 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

jalewis@illinois.edu

■ ACKNOWLEDGMENTS

This material is based on work supported by the U.S. Department of Energy, Materials Sciences and Engineering Division, under Award DEFG-02-07ER46471 (ink synthesis) and the NSF Center for Nanoscale Chemical-Electrical Mechanical Manufacturing Systems (DMI-0328162) (ink patterning). We gratefully acknowledge the Center for Microanalysis of Materials in the Frederick Seitz Materials Research Laboratory as well as Dr. Bok Ahn for experimental assistance, Vania Petrova for SEM imaging, Scott McLaren for AFM assistance, and the Murphy and Sottos groups for use of their experimental facilities.

■ REFERENCES

- (1) Li, L.; Coates, N.; Moses, D. *J. Am. Chem. Soc.* **2010**, *132*, 22–23.
- (2) Siringhaus, H.; Kawase, T.; Friend, R.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. *Science* **2000**, *290*, 2123–2126.
- (3) Okimoto, H.; Takenobu, T.; Yanagi, K.; Miyata, Y.; Shimotani, H.; Kataura, H.; Iwasa, Y. *Adv. Mater.* **2010**, *22*, 3981–3986.
- (4) Comiskey, B.; Albert, J. D.; Yoshizawa, H.; Jacobson, J. *Nature* **1998**, *394*, 253–255.
- (5) Hu, L.; Choi, J.; Yang, Y.; Jeong, S.; Mantia, F.; Cui, L.; Cui, Y. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 21490–21494.
- (6) Subramanian, V.; Fréchet, J. M. J.; Chang, P. C.; Huang, D. C.; Lee, J. B.; Molesa, S. E.; Murphy, A. R.; Redinger, D. R.; Volkman, S. K. *Proc. IEEE* **2005**, *93*, 1330–1338.
- (7) Lim, S.; Kemling, J.; Feng, L.; Suslick, K. *Analyst* **2009**, *134*, 2453–2457.
- (8) Bok, A.; Lorang, D.; Lewis, J. *Nanoscale* **2011**, *3*, 2700–2702.
- (9) Hu, L.; Pasta, M.; La Mantia, F.; Cui, L.; Jeong, S.; Deshazer, H.; Choi, J.; Han, S.; Cui, Y. *Nano Lett.* **2010**, *10*, 708–714.
- (10) Dennuelin, A.; Blayo, A.; Neuman, C.; Bras, J. *J. Nano. Res.* **2011**, *13*, 3815–3823.
- (11) Ahn, B.; Duoss, E.; Motala, M.; Guo, X.; Park, S.; Xiong, Y.; Yoon, J.; Nuzzo, R.; Rogers, J.; Lewis, J. *Science* **2009**, *323*, 1590–1593.
- (12) Russo, A.; Ahn, B.; Adams, J.; Duoss, E.; Bernhard, J.; Lewis, J. *Adv. Mater.* **2011**, *23*, 3426–3430.
- (13) Pan, H.; Ko, S.; Grigoropoulos, C. *Appl. Phys. Lett.* **2008**, *93*, No. 234104.
- (14) U.S. Patent Application 20090120800A1.
- (15) Kim, D.; et al. *Nat. Mater.* **2010**, *9*, 511–517.
- (16) Martinez, A.; Phillips, S.; Butte, M.; Whitesides, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 1318–1320.
- (17) Yin, Y.; Li, Z.; Zhong, Z.; Gates, B.; Xia, Y.; Venkateswaran, S. *J. Mater. Chem.* **2002**, *12*, 522–527.
- (18) Lawson, A. *J. Catal.* **1968**, *11*, 295–304.
- (19) Kumbhar, A.; Kinnan, M.; Chumanov, G. *J. Am. Chem. Soc.* **2005**, *127*, 12444–12445.
- (20) Fox, B.; Beyer, M.; Bondybey, V. *J. Am. Chem. Soc.* **2002**, *124*, 13613–13623.