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(54) **METAL NANOPARTICLE INKS**

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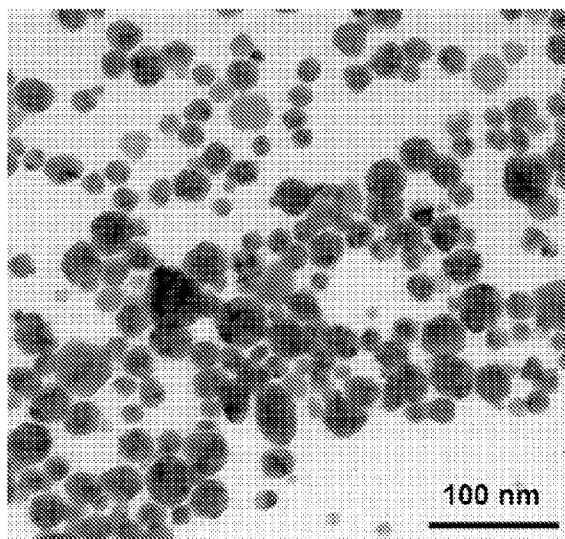
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(57) **ABSTRACT**

Stabilized silver particles comprise particles comprising silver, a short-chain capping agent adsorbed on the particles, and a long-chain capping agent adsorbed on the particles. The short-chain capping agent is a first anionic polyelectrolyte having a molecular weight (Mw) of at most 10,000, and the long-chain capping agent is a second anionic polyelectrolyte having a molecular weight (Mw) of at least 25,000. The stabilized silver particles have a solid loading of metallic silver of at least 50 wt %.

20 Claims, 13 Drawing Sheets



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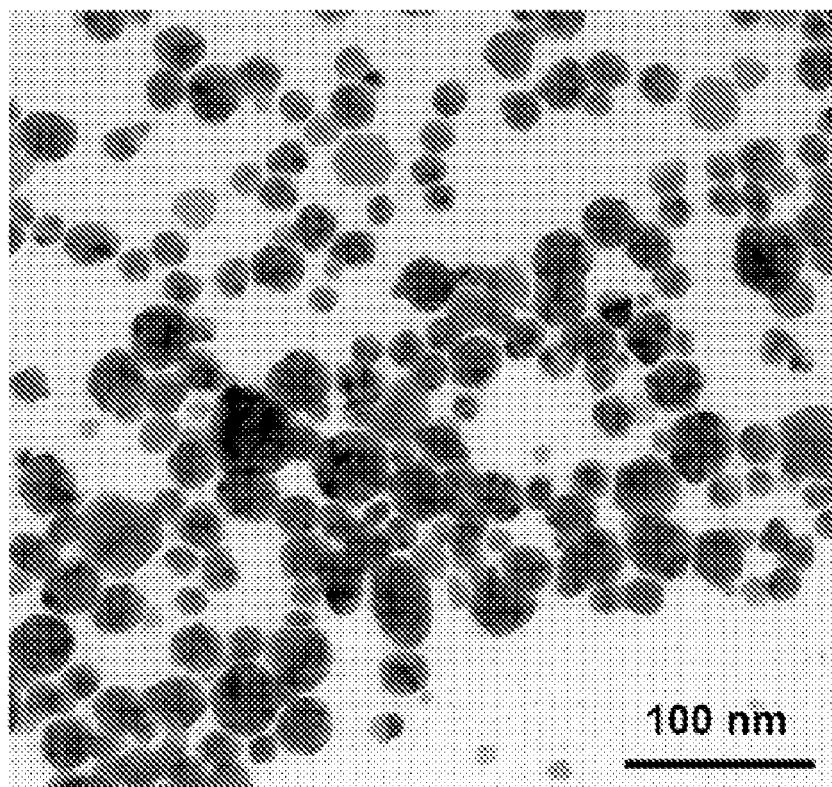


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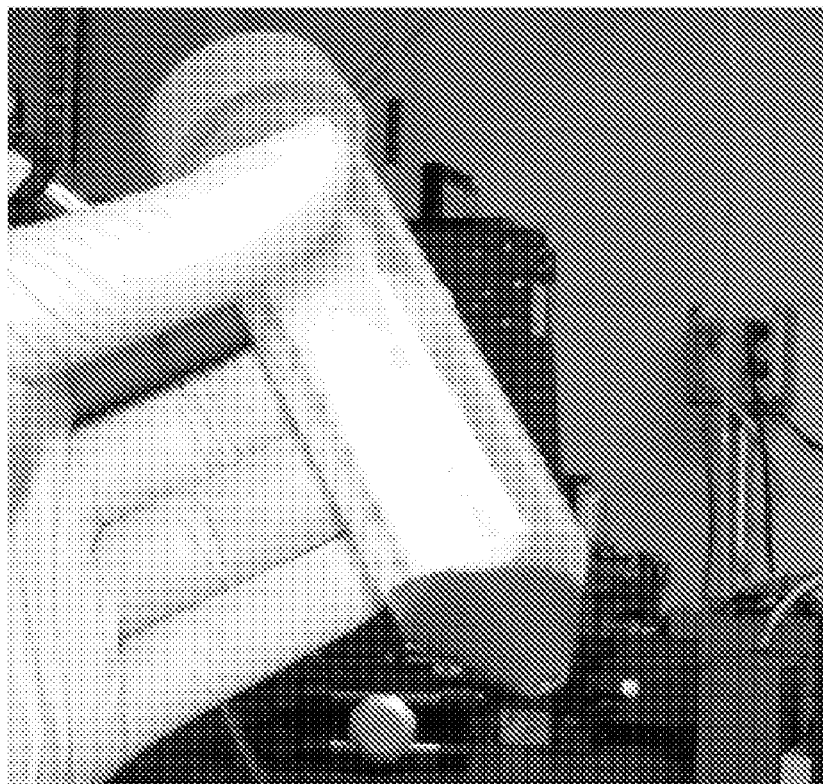


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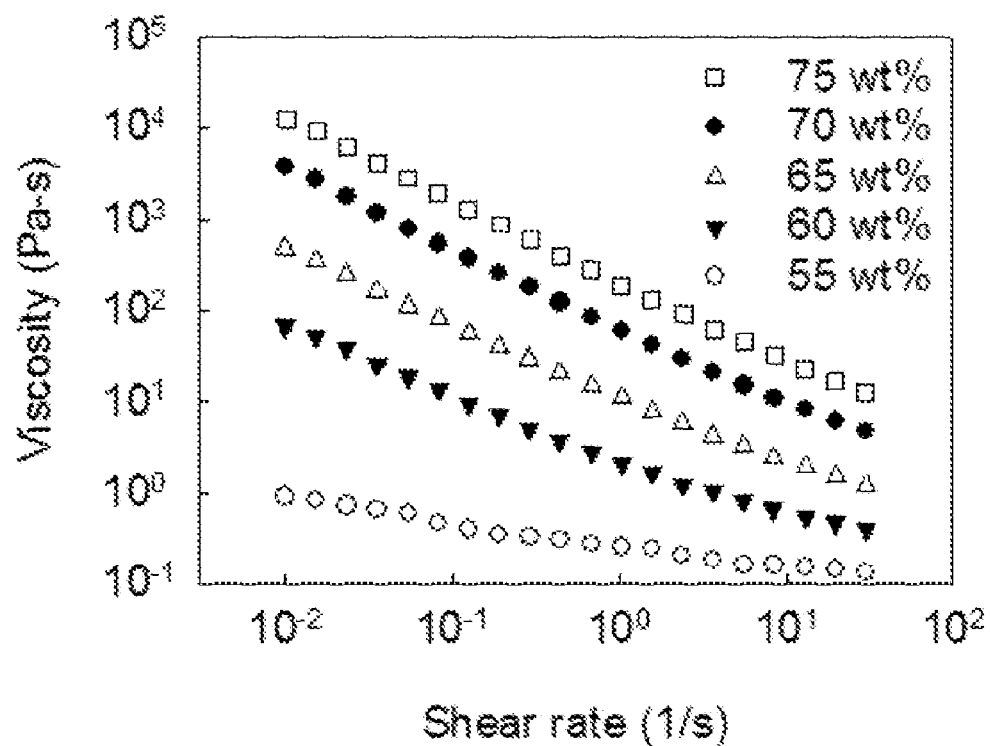


Figure 3

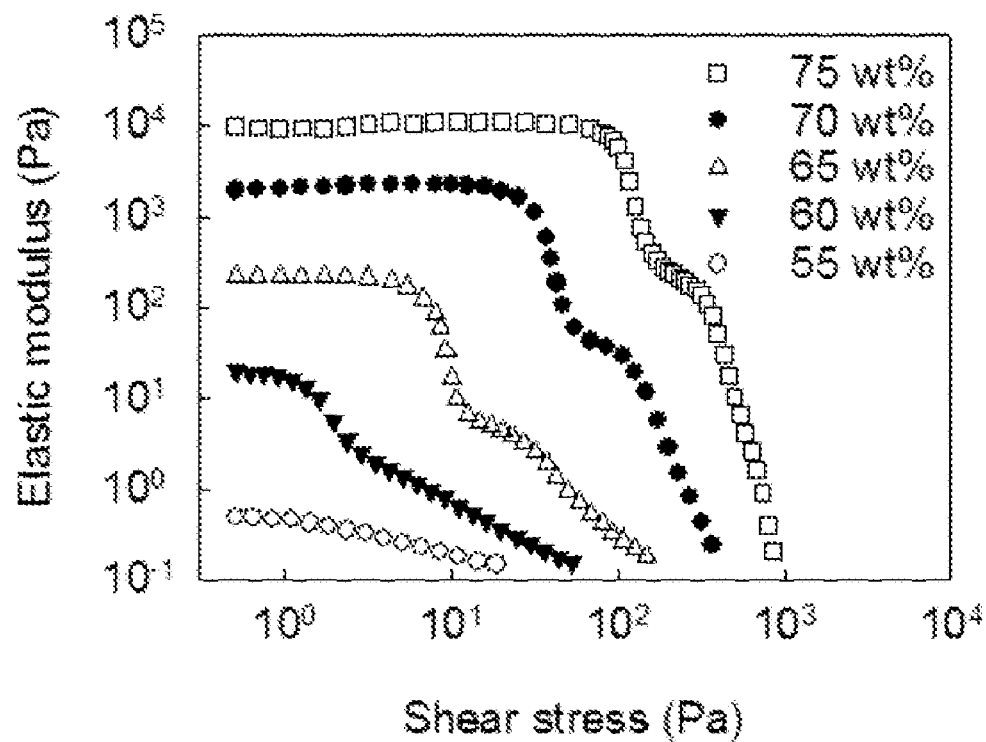


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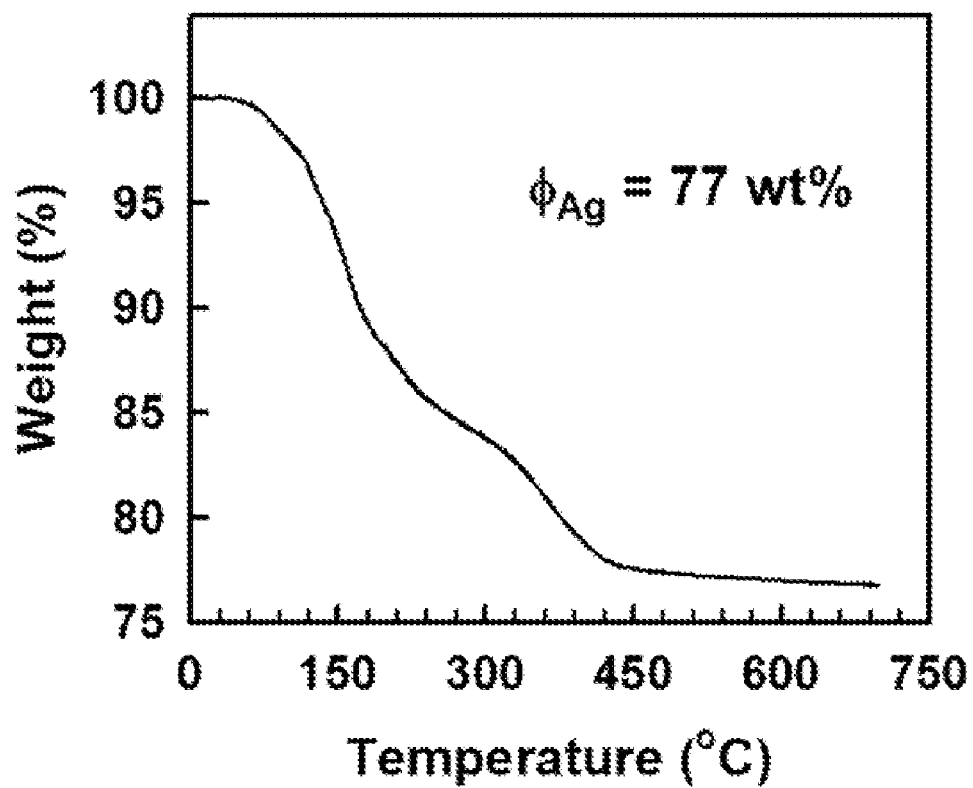


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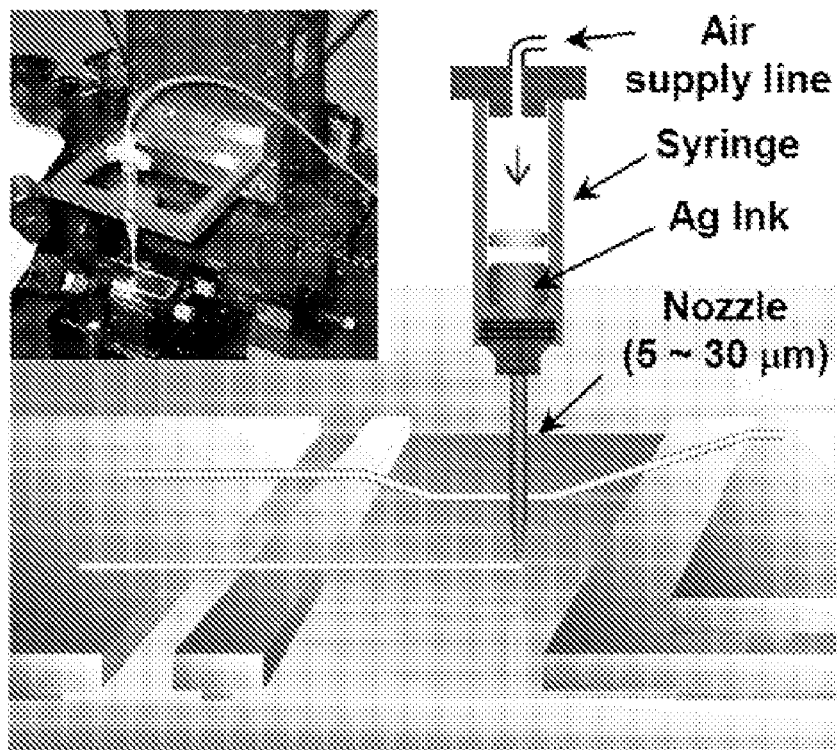


Figure 6

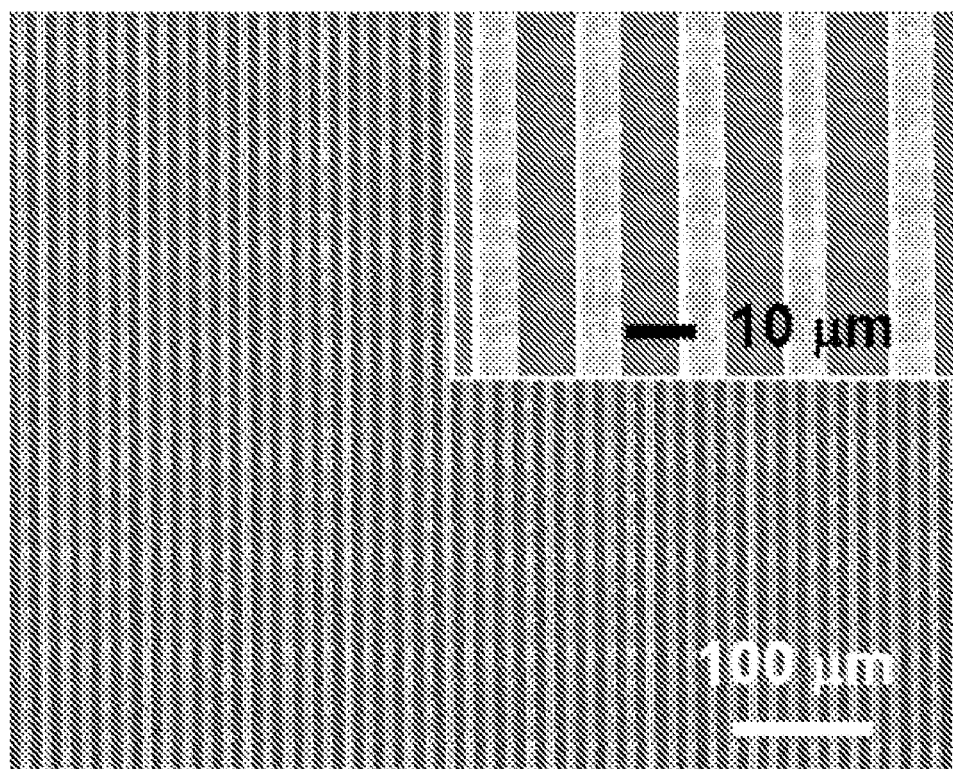


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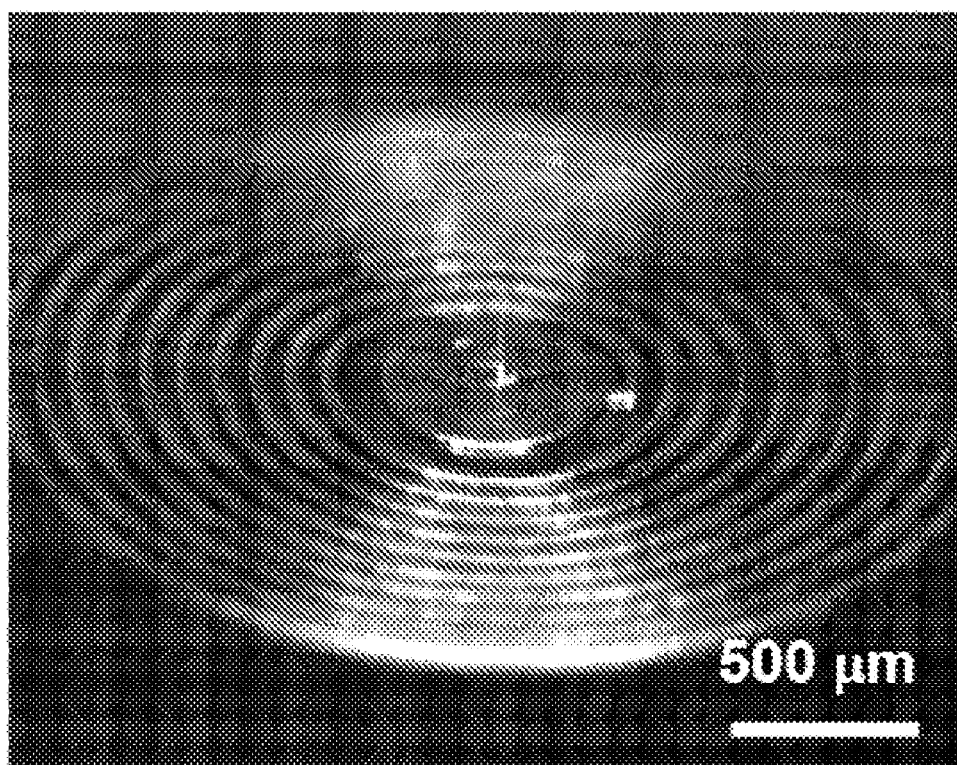


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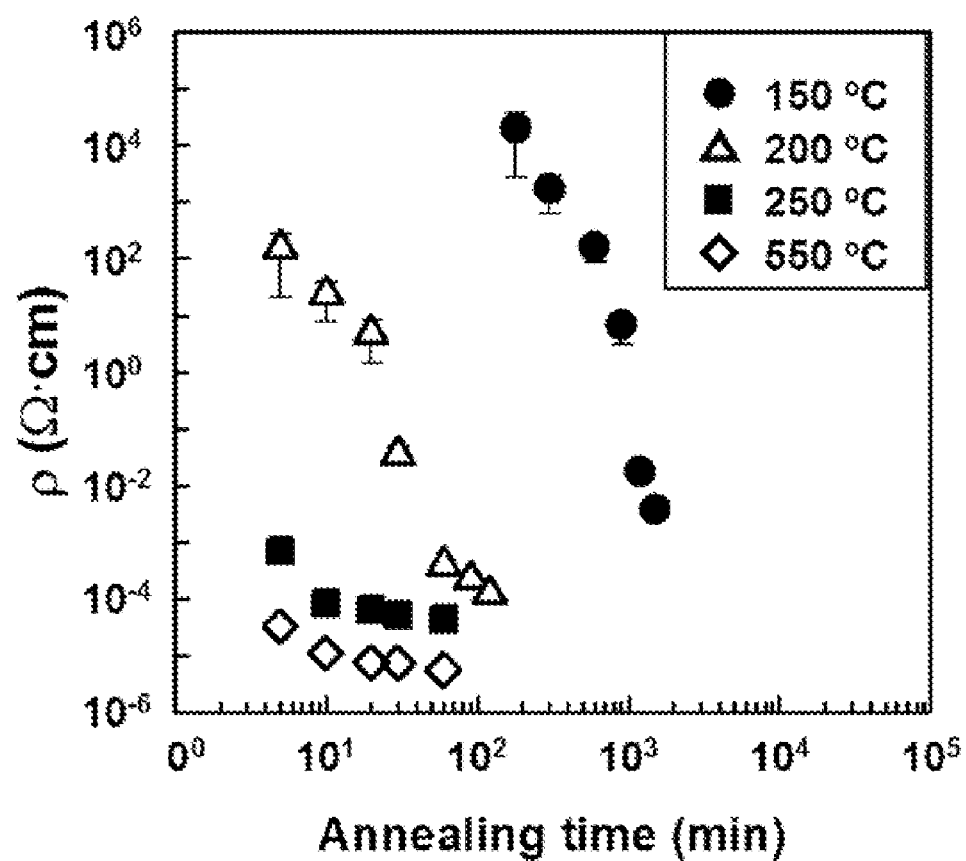


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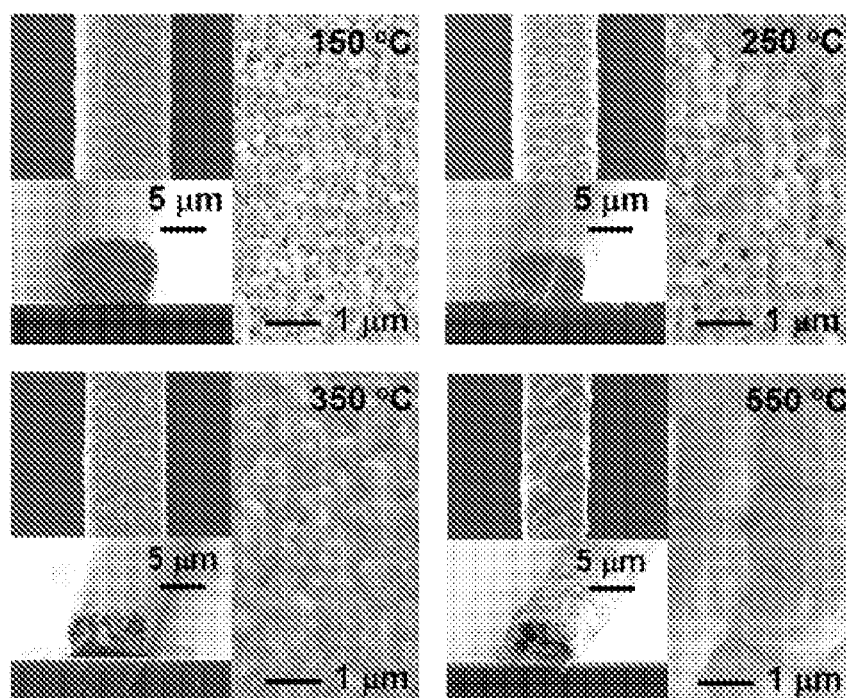


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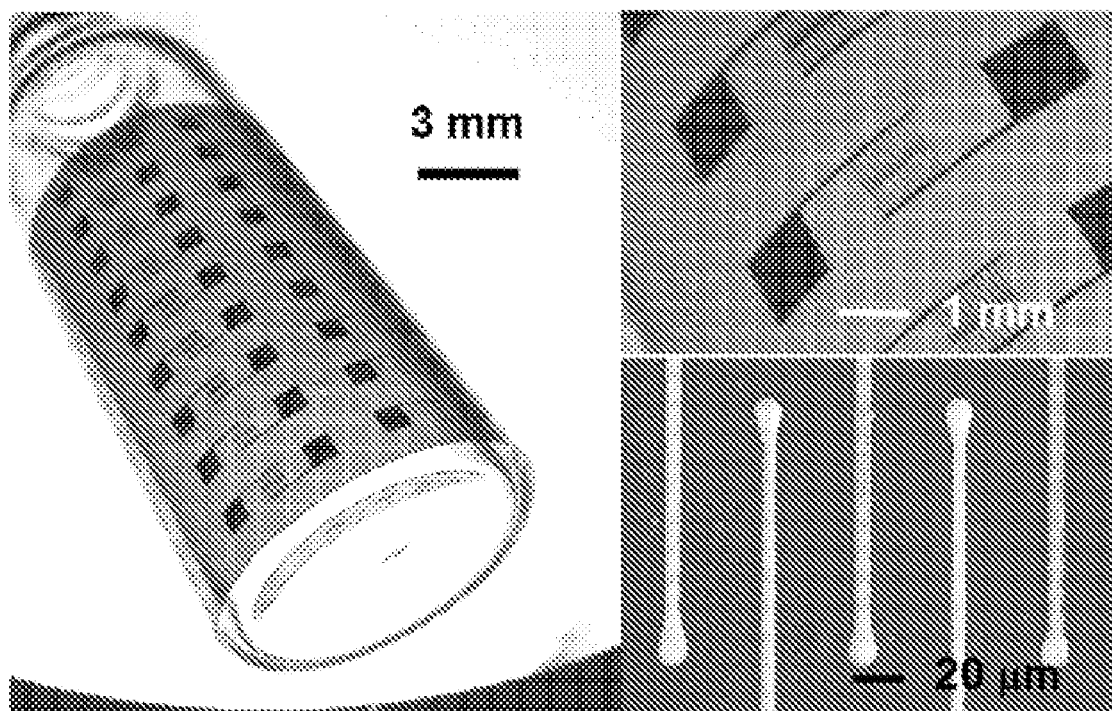


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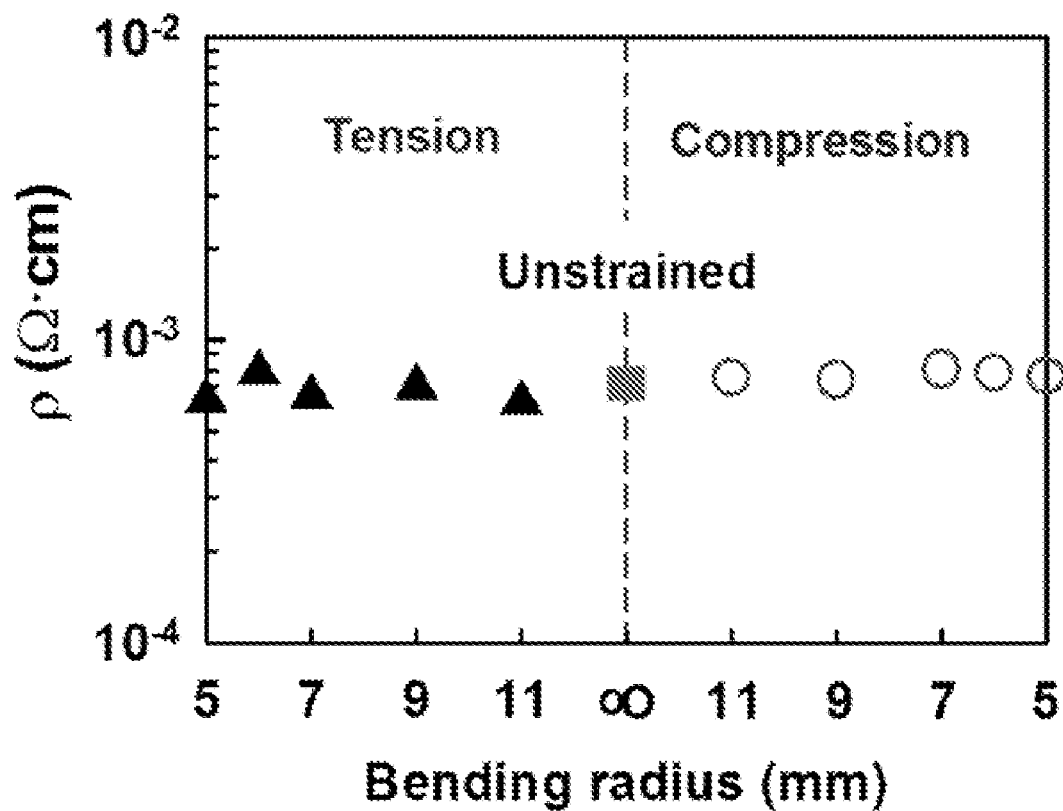


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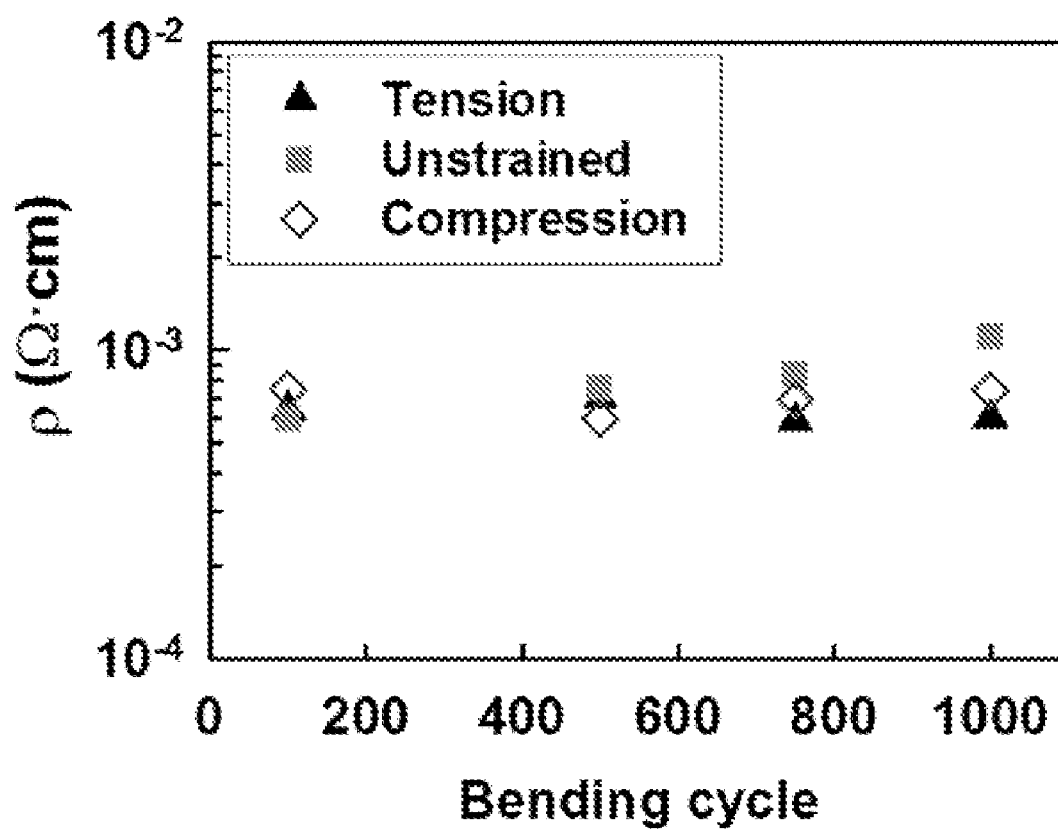


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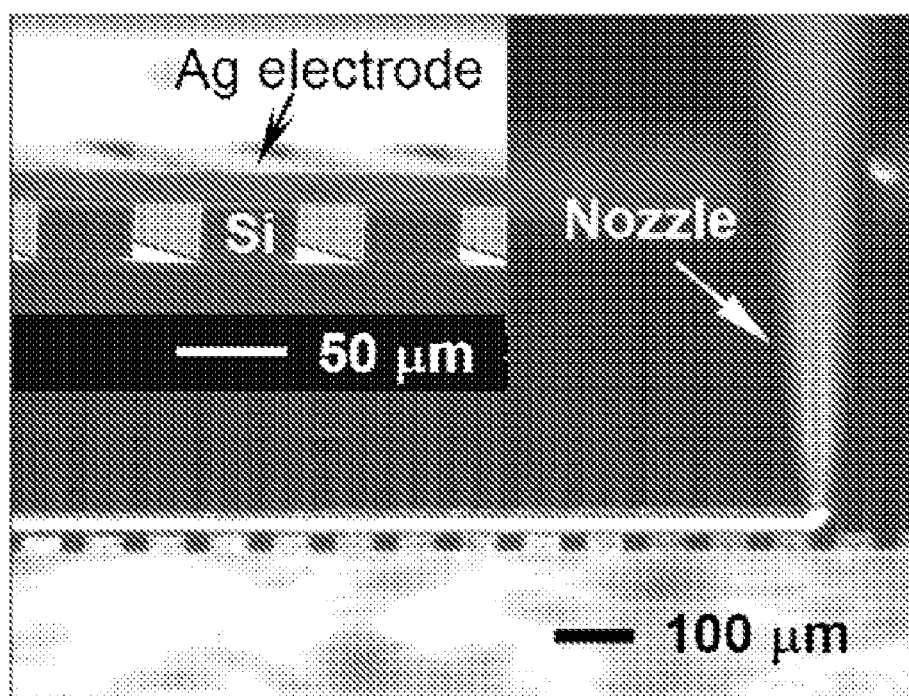


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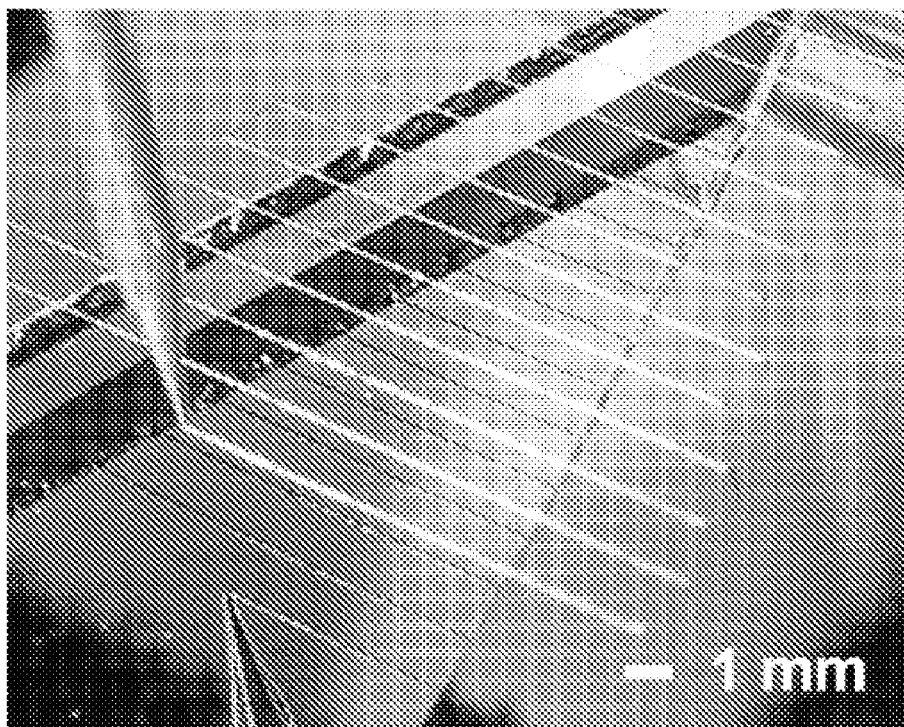


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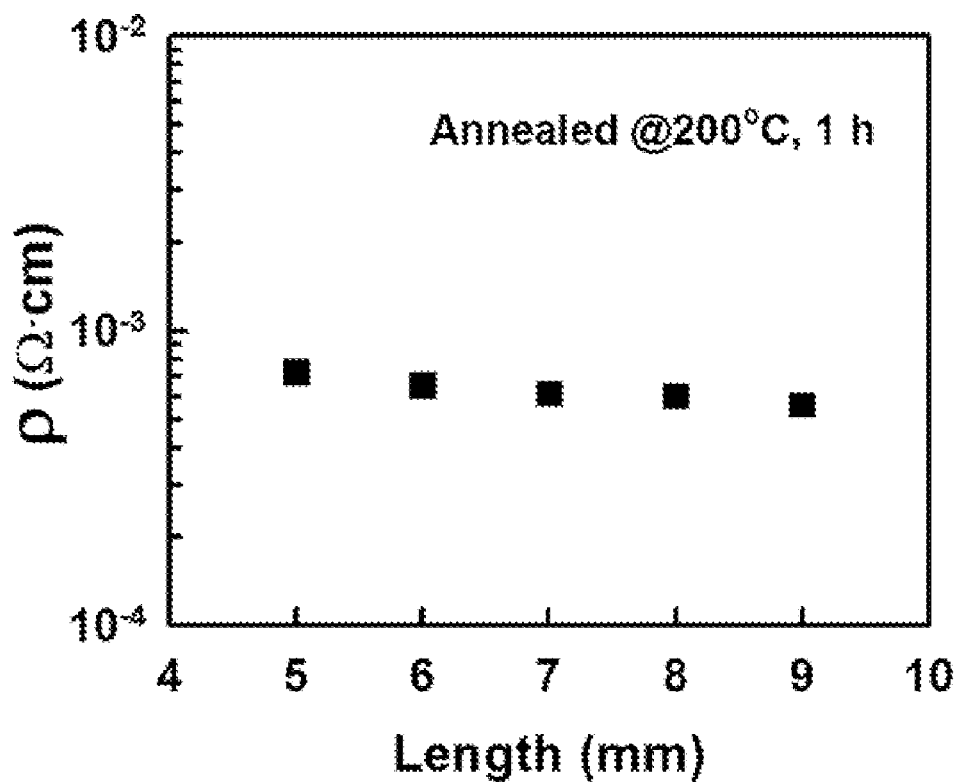


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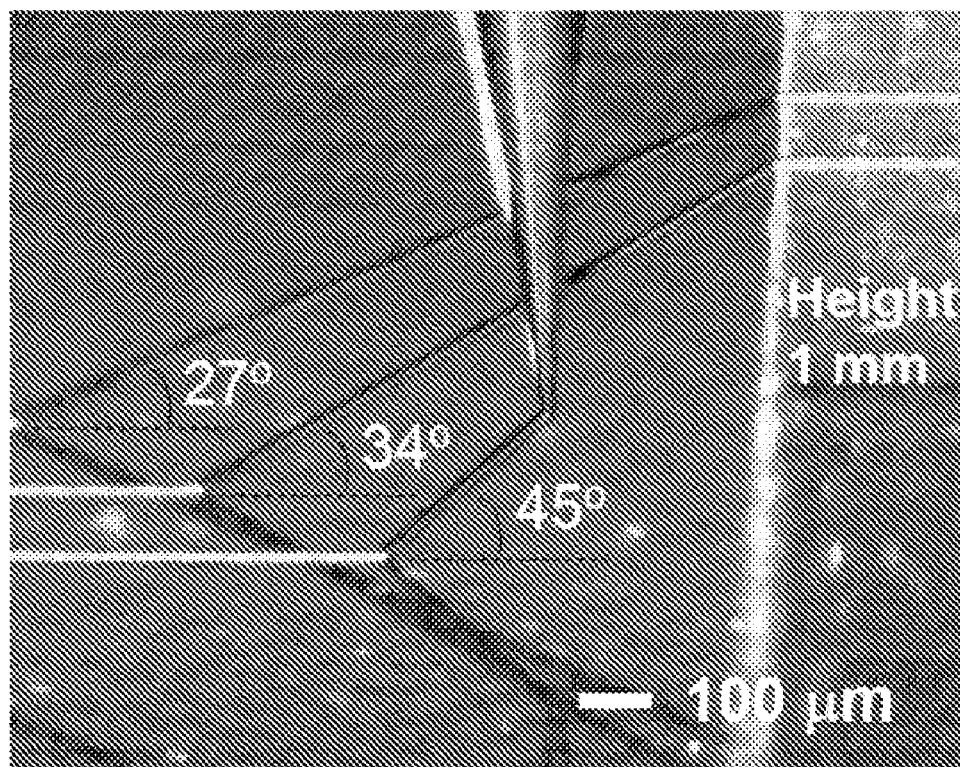


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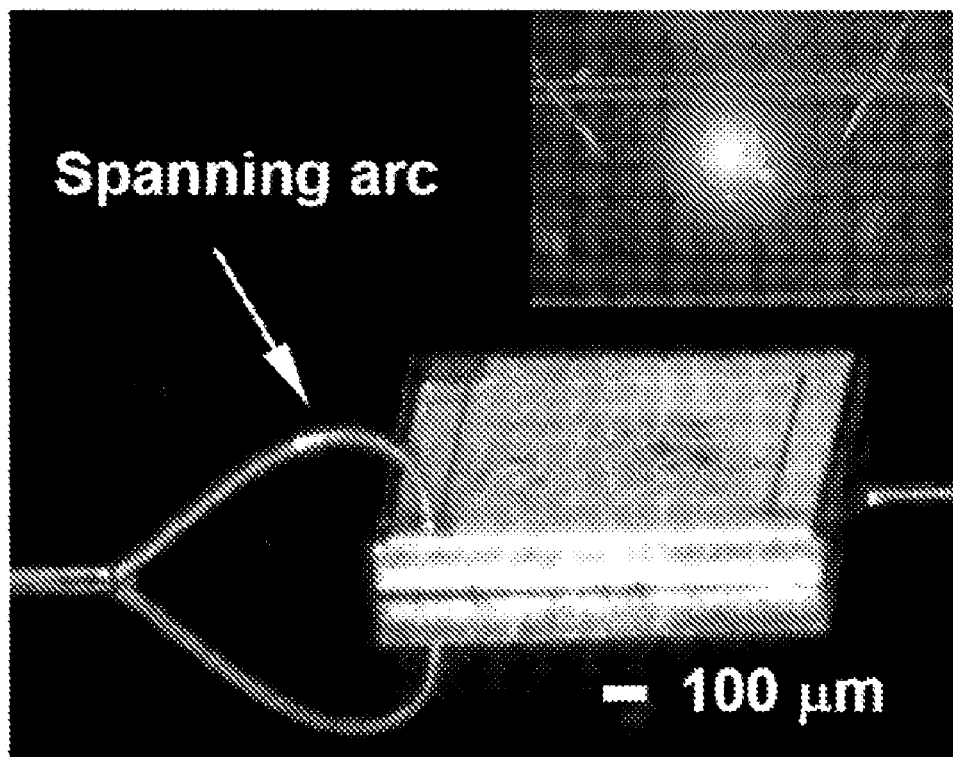


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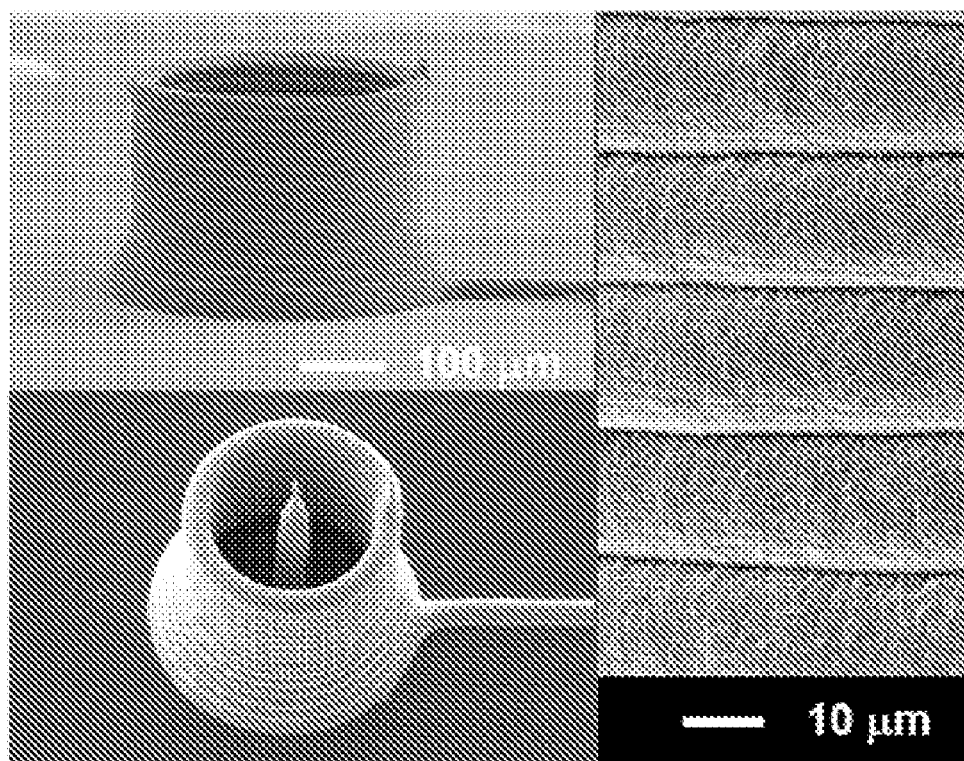


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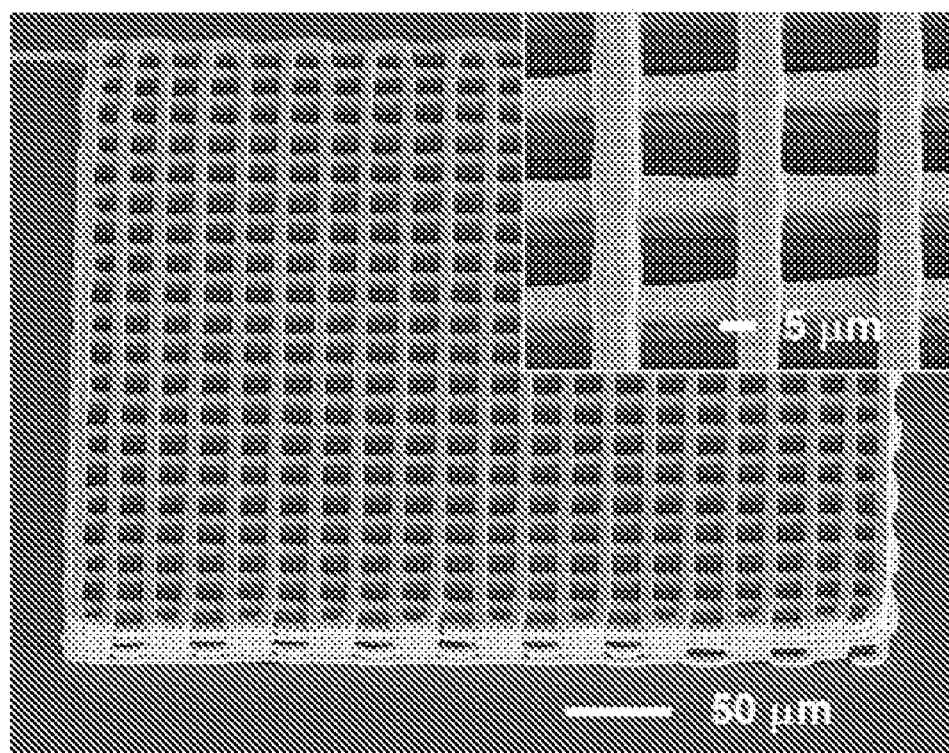


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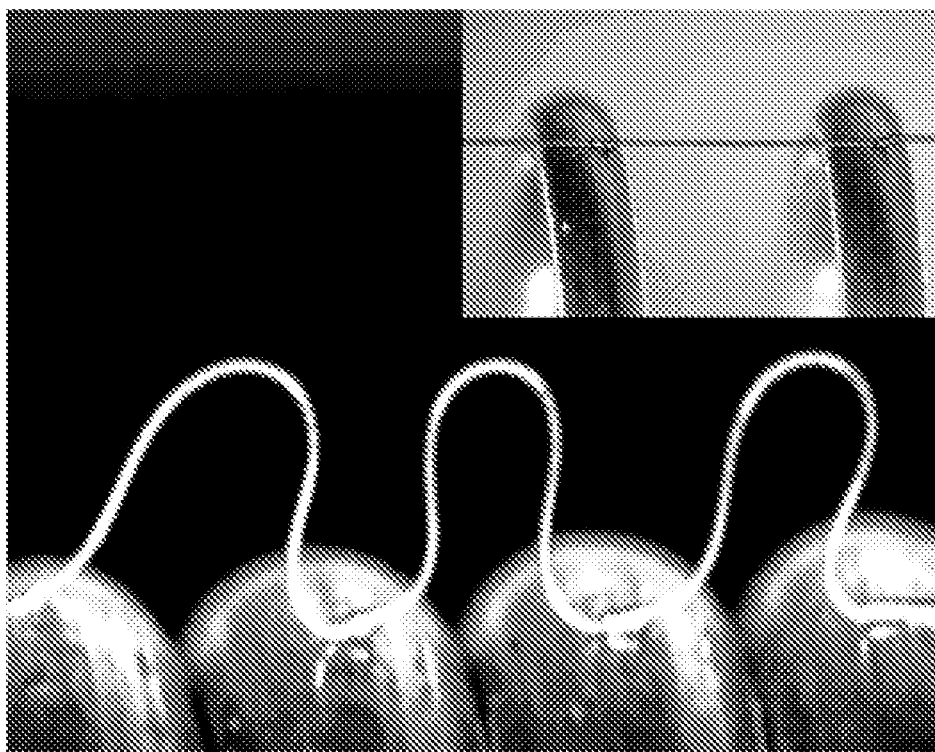


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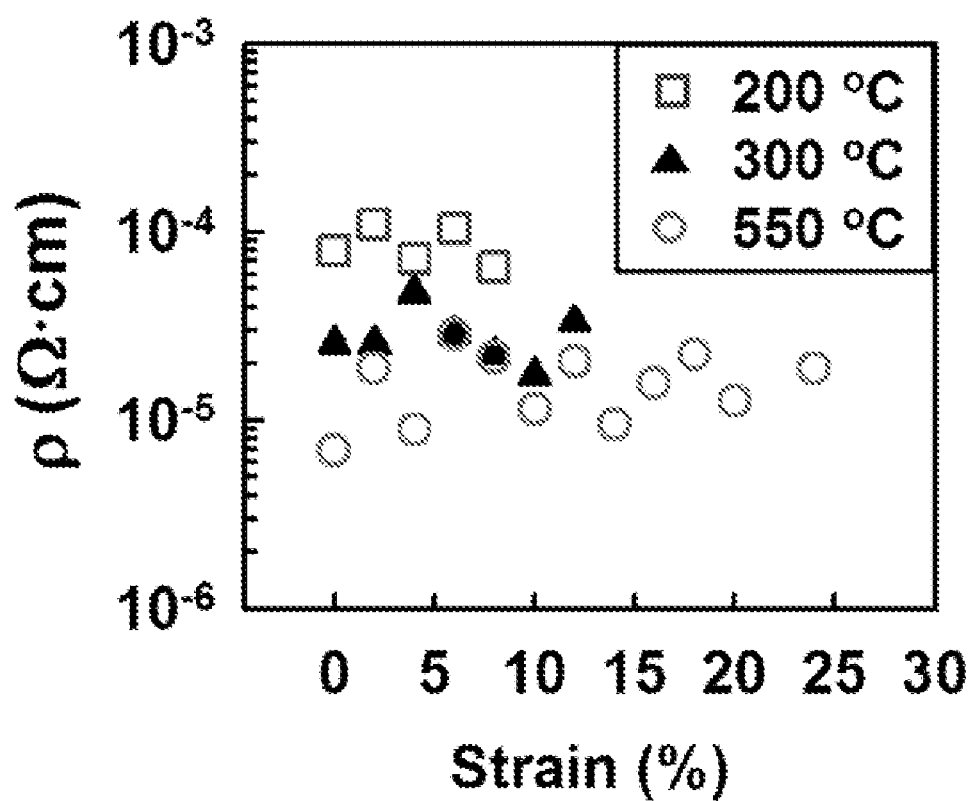


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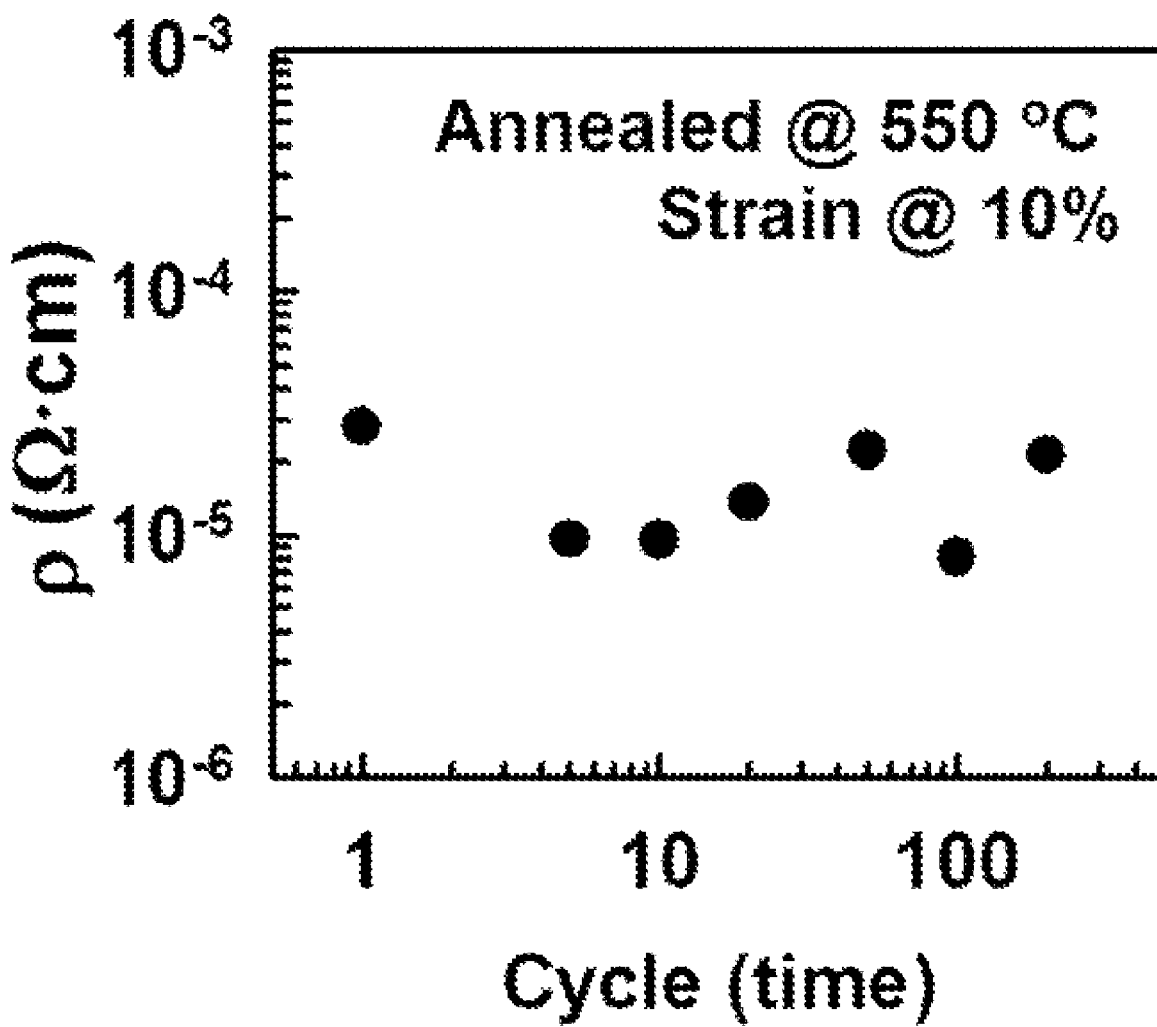


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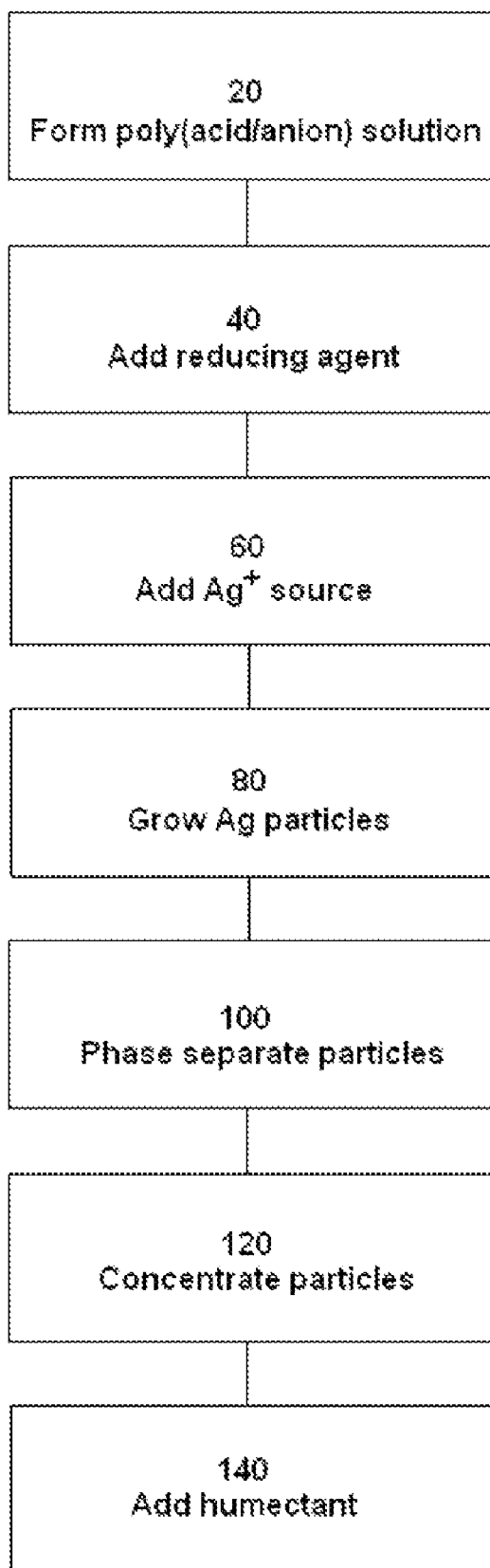


Figure 24

METAL NANOPARTICLE INKS

FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

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BACKGROUND

Printing techniques such as screen printing, flexography, gravure, and offset lithography have been widely used throughout history for both graphics arts and, more recently, materials assembly. However, the push towards smaller feature sizes has focused attention on other print-based approaches, such as inkjet printing¹ and direct ink writing (DIW),²⁻⁴ where ink is deposited through fine nozzles onto a substrate. Inkjet printing is a droplet-based approach primarily limited to low aspect-ratio features (for example, 100 nm thick and 100 μ m wide) geometries for single pass and supported features in multipass printing due to the diluted solids content of the liquid-like inks. Alternatively, DIW is a filament-based approach that affords the creation of continuous, fine scale, high aspect ratio, and self-supporting electrodes due to the high concentration and stiffness of silver particle inks expressly engineered for these properties.

The design of metallic inks for self-supporting printed electronics poses considerable challenges. Several requirements must be met simultaneously, including careful control over particle size and solids loading, appropriate rheological behavior to facilitate deposition, low resistivity at modest curing temperature, and compatibility with a variety of substrate materials. While some commercial metallic pastes (or paints) are conductive under ambient conditions, they typically contain large particles (0.1~10 μ m) and, hence, are not suitable for patterning at the microscale due to nozzle clogging.

To date, solution based synthetic methods have yielded stable silver dispersions with relatively low solids loading (typically ~10 wt %) that are not suitable for printing self-supporting electrodes. Typically, silver nanoparticles are synthesized in solution via the reduction of silver precursors in the presence of surface capping and reducing agents. The surface capping agents usually contain functional groups, such as thiol (~SH), carboxyl (~COOH), or amine (~NH) groups, whereas sodium borohydride (or citrate), hydrazine, or polyol are used as reducing agents. It is challenging to synthesize stable and highly concentrated (>50 wt %) nanoparticle inks due to their strong tendency to agglomerate.

PAA, a water-soluble polyelectrolyte is a well-known effective capping agent for stabilizing silver particles. Hydrophilic silver particles are produced by this method. The carboxyl (~COOH) group in PAA provides an active site for capping in the presence of reducing agents, such as NaBH₄, H₂NNH₂, and light irradiation. B. H. Ryu, et al. demonstrated silver nanosol with high silver content (50 wt %) using an aqueous AgNO₃/PAA-Na salt/NaBH₄ system.⁵ X. Xu et al. reported metal nanocomposites using an aqueous AgNO₃/Acrylic acid/ γ -ray system.⁶ N. Toshima, et al. investigated silver nanoclusters using an aqueous AgClO₄/PAA-Na salt/UV-ray system.⁷

Other carboxyl (~COOH) group functionalized compounds have also been used as capping agents. S. Magdassi, et al. demonstrated an aqueous silver nanocolloids stabilized

by carboxymethyl cellulose as a capping agent in the presence of trisodium citrate as a reducing agent.⁸ In contrast, long-chain carboxylates provide hydrophobic silver particles that are dispersible in toluene or hexane.⁹⁻¹²

Alkyl amines have commonly been used as reducing agents (short-chain amines), as well as capping agents (long chain amines). The silver particles obtained from this method are generally hydrophobic and only dispersible in organic solvents.¹³⁻¹⁶

Direct printing of self-supporting electrodes, such as spanning and three-dimensional (3-D) structures is challenging. The conventional ink-jet printing method uses droplet based printing, which is not suitable for producing self-supporting electrodes due to a spreading issue of liquid-like inks. S. B. Fuller, et al. demonstrated 3-D silver electrodes by ink-jet printing using reiteration of printing and curing process for each layer.¹⁷

SUMMARY

In a first aspect, the present invention is stabilized silver particles, comprising particles comprising silver, a short-chain capping-agent adsorbed on the particles, and a long-chain capping agent adsorbed on the particles. The short-chain capping agent is a first anionic polyelectrolyte having a molecular weight (Mw) of at most 10,000, and the long-chain capping agent is a second anionic polyelectrolyte having a molecular weight (Mw) of at least 25,000. The stabilized silver particles have a solid loading of metallic silver of at least 50 wt %.

In a second aspect, the present invention is a silver particle ink, comprising the stabilized silver particles, and water. The silver particle ink has a solid loading of metallic silver of at least 50 wt %.

In a third aspect, the present invention is a silver particle ink, comprising particles comprising silver, and an ink solvent. The silver particle ink is shear thinning, and the silver particle ink has an elastic modulus, G', and viscous modulus, G'', such that G'>G''. The silver particle ink has a solid loading of metallic silver of at least 50 wt %.

In a fourth aspect, the present invention is a method of forming a conductive structure, comprising forming a structure from the silver particle ink, and heating the structure at a temperature of 150-550° C., to form the conductive structure.

In a fifth aspect, the present invention is a method of forming stabilized silver particles, comprising forming a solution comprising a reducing agent, a short-chain capping agent, a long-chain capping agent, and Ag⁺ ions, to form silver particles; and growing the silver particles to a mean particle size of 10-50 nm. The short-chain capping agent is a first anionic polyelectrolyte having a molecular weight (Mw) of at most 10,000, the long-chain capping agent is a second anionic polyelectrolyte having a molecular weight (Mw) of at least 25,000, and the reducing agent comprises a hydroxyl group terminated amine containing 2-10 carbon atoms.

In a sixth aspect, the present invention is a method of forming a silver particle ink, comprising forming stabilized silver particles; and dispersing the stabilized silver particles in an ink solvent.

DEFINITIONS

The symbol ϕ_{Ag} means the solid loading of metallic silver as weight percent of the composition.

The term "particle size" means the average of all diameters of the particle. The term "mean particle size" refers to the mean of the particles sizes for a collection of particles. Fur-

thermore, the term "nanoparticle" means a particle have a particle size of less than or equal to 500 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a transmission electron microscopy (TEM) image of silver particles (mean particle size of about 20 nm) grown in an aqueous AgNO_3 solution in the presence of poly (acrylic) acid as a stabilizing agent and diethanolamine (DEA) as a reducing agent.

FIG. 2 is an optical image of the silver particle ink ($\phi_{Ag}=77$ wt %, PAA/(Ag+PAA)=10 wt %).

FIG. 3 is a graph of apparent viscosity as a function of shear rate for silver particle inks of varying solids loading ($\phi_{Ag}=55$ -75 wt %, PAA/(Ag+PAA)=10 wt %).

FIG. 4 is a graph of shear elastic modulus (G') as a function of shear stress for the silver particle ink of varying solids loading ($\phi_{Ag}=55$ -75 wt %, PAA/(Ag+PAA)=10 wt %) as a function of shear stress.

FIG. 5 is a graph produced from thermogravimetry analysis (TGA) of the silver ink ($\phi_{Ag}=77$ wt %, PAA/(Ag+PAA)=10 wt %) measured in air.

FIG. 6 is a schematic diagram illustrating direct ink writing (DIW) of the silver particle ink. The inset shows an optical image of a DIW apparatus.

FIG. 7 is a scanning electron microscopy (SEM) image of an array of silver microelectrodes (width 6 μm , height 3.7 μm , spacing 15 μm) printed on a silicon wafer by a nozzle with 5 μm orifice. DIW conditions: 50 $\mu\text{m/s}$, 40 psi, RH 23%, 24° C. Inset shows the magnified SEM micrograph.

FIG. 8 is an optical micrograph of a resonant inductive coil printed on a silicon wafer by 30 μm nozzle.

FIG. 9 is a graph of resistivity of the printed silver electrodes as function of heat treatment time and temperature.

FIG. 10 is a set of SEM micrographs of silver electrodes heat treated to: (from top left) 150° C., 250° C., 350° C., and 550° C. Each image shows the electrode width (top left), height (bottom left), and surface morphology (right) for a sample heated to the indicated temperature.

FIG. 11 is optical images of the bendable silver electrodes printed on polyimide sheet, heat treated to 200° C. for 3 h, and wrapped around a vial with bending radius of 14 mm. (Top right) Optical image of electrode pads, conducting features, and interdigitated conducting hairs. (Bottom right) Magnified SEM micrograph of the fine interdigitated silver hairs.

FIG. 12 is a graph of resistivity of the silver electrodes as a function of bending radius under tension, compression, and the unstrained state.

FIG. 13 is a graph of resistivity of silver electrodes as a function of bending cycle. One cycle is defined as bending through a series of tension, unstrained, compression, and unstrained states.

FIG. 14 is an optical micrograph of the spanning silver electrode (width 15 μm , height 13 μm) printed on an array of unplanarized silicon microribbons (width 45 μm , height 26 μm , spacing 33 μm). DIW conditions: $\phi_{Ag}=77$ wt %, 10 μm nozzle, 70 $\mu\text{m s}^{-1}$, 65 psi, RH 23%, 24° C.). The inset shows the magnified SEM micrograph.

FIG. 15 is an optical image of the spanning silver electrodes printed over a wedge-shaped gap with 1 mm height difference between top and bottom surfaces.

FIG. 16 is a graph of resistivity (ρ) of the spanning silver electrodes as a function of length.

FIG. 17 is an optical micrograph acquired during vertical printing between two substrates with 1 mm height difference at varying printing angles.

FIG. 18 is an optical micrograph of an LED chip (1 mm \times 1 mm \times 200 μm) connected to a voltage source via a spanning arc (top contact) and linear wire (bottom contact) printed with silver ink (heat treated to 200° C. for 3 h). Inset shows blue emission after connecting to a voltage source with an applied bias of 2.0 V.

FIG. 19 is SEM micrographs of a cylinder (top left), a cylindrical microcapacitor with a vertically printed spike in the center (bottom left), and the magnified surface morphology (right).

FIG. 20 is SEM micrographs of an 8 layer square lattice (400 \times 400 μm , wire width 6 μm , center-to-center spacing 20 μm) printed by a 5 μm nozzle. Inset shows high magnification SEM image of the square lattice.

FIG. 21 is optical micrographs of stretchable silver arches printed on a spring. Stretchable arches form after printing a linear electrode on to a pre-strained spring (inset) and subsequently releasing the spring tension (main image).

FIG. 22 is a graph of resistivity of the stretchable silver arches as a function of strain (%) and heat treatment temperature.

FIG. 23 is a graph of resistivity of stretchable silver arches as a function of strain cycle.

FIG. 24 is a flow chart of a process for preparing a silver particle ink.

DETAILED DESCRIPTION

The present invention makes use of the discovery of stabilized silver particles, and a concentrated silver particle ink containing the stabilized silver particles. Stabilized silver particles are silver particles containing adsorbed anionic polyelectrolytes. The silver particle ink contains the stabilized silver particles dispersed in an ink solvent. The silver particle ink may be used to form an ink filament or droplet by printing through a nozzle. A conductive electrode may then be formed by curing the ink. Preferably, the silver particle ink exhibits reliability in printing through fine nozzles (1-100 μm diameter) to form self-supporting conductive electrodes. The silver particle ink of the present invention makes possible, for the first time, the ability to prepare spanning, bendable, and stretchable electrodes and interconnect.

Stabilized silver particles are silver particles that preferably have a mean particle size of 5-500 nm, more preferably 10-50 nm, for example 15-25 nm, including 20 nm, which are stabilized by an adsorbed short-chain capping agent and an adsorbed long-chain capping agent. The capping agents are polymers containing anionic and/or acidic repeating units, preferably carboxylic acid and/or carboxylate moiety containing repeating units, such as poly(acrylic acid), poly(methacrylic acid), copolymers thereof and salts thereof. These polymers are referred to as anionic polyelectrolytes, which include both the anionic and protonated forms. Examples of anionic polyelectrolytes includes poly(acrylic acid), poly(methacrylic acid), poly(methyl methacrylate), poly(lauryl methacrylate), carboxymethyl ether, carboxyl terminated poly(butadiene/acrylonitrile), poly(butadiene/maleic acid), poly(butyl acrylate/acrylic acid), poly(ethylene glycol) monocarboxymethyl ether monomethyl ether, poly(ethylene/maleic acid), poly(maleic acid), poly(methyl methacrylate/methacrylic acid), poly(vinyl methyl ether/maleic acid), poly(vinyl methyl ether/monobutyl maleate), poly(vinyl methyl ether/monoethyl maleate), poly(vinyl methyl ether/monoiso-propyl maleate), copolymers thereof and salts and mixtures thereof. The anionic polyelectrolytes, such as poly(acrylic acid) $[(\text{CH}_2\text{C}(\text{O})\text{OH})_n]$, PAA, is used not only as a stabilizing agent but also as a binder, providing adhesion of

inks on the substrates. The steric stabilization and multiple capping by the anionic groups, such as carboxyl ($-\text{COOH}$) groups from the PAA, provide long lifetime stability for the inks.

The short-chain capping agent has a molecular weight (Mw) of at most 10,000, such as 1,000-10,000, preferably 2,500-7,500, more preferably 4,000-6,000. The long-chain capping agent has a molecular weight (Mw) of at least 25,000, such as 25,000-100,000, preferably 30,000-80,000, more preferably 40,000-60,000. The weight ratio of the short-chain capping agent to the long-chain capping agent is preferably 5:95 to 95:5, including 10:90 to 90:10, and 20:80 to 80:20.

The silver particle ink contains the stabilized silver particles dispersed in an ink solvent. The ink solvent preferably contains water, and more preferably also contains a non-aqueous solvent which is soluble in water and has a higher boiling point than water, such as polyols, for example ethylene glycol, propylene glycol and glycerin. Preferably, the ink solvent contain a weight ratio of water:non-aqueous solvent of 5:1-1:5, more preferably 3:1-1:3. Preferably, the silver particle ink has a silver content (solid loading of metallic silver as weight percent of the composition) of at least 50 wt %, more preferably at least 60 wt %, and most preferably at least 70 wt %, such as 70-85 wt %, including 75 wt %, 77 wt %, and 82 wt %. The silver particle ink is shear thinning, i.e., apparent viscosity decreases with increasing shear rate. Furthermore, the silver particle ink has elastic (G') and viscous (G'') moduli, such that $G' \geq 1.5 G''$. Example silver particle inks are stable for at least two months at room temperature and are readily re-dispersible in water or ethylene glycol.

A silver particle ink may be prepared by forming stabilized silver particles, concentrating the stabilized silver particles, and forming an ink from the particles. An example of the process is shown schematically in FIG. 24, with additional details below.

The stabilized silver particles may be formed, for example, by forming a solution of the short-chain and long-chain capping agents (20), adding a reducing agent (40), adding a source of Ag^+ (60), and growing the silver particles (80). The reducing agent is hydroxyl ($-\text{OH}$) group terminated amines, which are effective for producing stable silver particles with high concentration. Preferably short-chain hydroxyl group terminated amines, containing 2-10 carbon atoms, are used, since they are easy to evaporate during a curing step at low temperature ($\leq 250^\circ \text{C}$). Examples of short-chain hydroxyl group terminated amines include diethanolamine (DEA), 2-(methylamino)ethanol, 2-(butylamino)ethanol, bis(2-hydroxypropyl)amine, n-(2-hydroxyethyl)trifluoroacetamide, 2-(propylamino)ethanol, n-(2-hydroxyethyl)ethylenediamine, 2-(3-aminopropylamino)ethanol, ethanolamine, 2-(2-aminoethoxy)ethanol, 1-amino-2-propanol, 3-aminophenol, and 3-amino-1-propanol. Chemical formulas of these short-chain hydroxyl group terminated amines are shown in the table, below.

Diethanolamine	$\text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{OH}$
2-(Methylamino)ethanol	$\text{HO}(\text{CH}_2)_2\text{NHCH}_3$
2-(Butylamino)ethanol	$\text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{CH}_3$
Bis(2-hydroxypropyl)amine	$[\text{CH}_2\text{CH}(\text{OH})\text{CH}_2]_2\text{NH}$
N-(2-Hydroxyethyl)trifluoroacetamide	$\text{HO}(\text{CH}_2)_2\text{NHCOCF}_3$
2-(Propylamino)ethanol	$\text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{CH}_3$
N-(2-Hydroxyethyl)ethylenediamine	$\text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$
2-(3-Aminopropylamino)ethanol	$\text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{NH}_2$
Ethanolamine	$\text{HO}(\text{CH}_2)_2\text{NH}_2$
2-(2-Aminoethoxy)ethanol	$\text{HO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{NH}_2$
1-Amino-2-propanol	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$

-continued

3-Aminophenol	$\text{HOC}_6\text{H}_4\text{NH}_2$
3-Amino-1-propanol	$\text{HO}(\text{CH}_2)_3\text{NH}_2$

Hydroxyl group terminated amines, such as DEA, are effective in modulating the nucleation and particle growth in the stabilized silver particles, while the strong reducing agents, such as sodium borohydride (NaBH_4), hydrazine (NH_2NH_2), and aldehydes result in rapid large particle growth and aggregates. It is also expected that hydroxyl group terminated amines acts as a charge modulator of the carboxyl ($-\text{COOH}$) groups in PAA, which enables the highly concentrated ink to be stable and re-dispersible in water or ethylene glycol.

The source of Ag^+ may be any water-soluble silver compound, such as AgNO_3 , CH_3COOAg , or AgClO_4 . Growing the silver particles may be carried out by agitation of a dispersion of the particles, such as by stirring and/or sonicating, with or without heating.

For example, stabilized silver particles may be formed by (1) making an aqueous poly(acrylic) acid (PAA) solution by dissolving PAA with a molecular weight (Mw) of 5,000, and PAA with a molecular weight (Mw) of 50,000; (2) adding hydroxyl group terminated alkyl amine to the PAA solution; (3) adding AgNO_3 solution dropwise to the PAA solution; and (4) stirring at room temperature for 1-24 hours, followed by sonication for 2-5 hours at $60-100^\circ \text{C}$. to grow the silver particles.

Concentrating the stabilized silver particles may be carried out by addition of a solvent which does not wet the stabilized silver particles, but does form solutions with water. Examples include organic solvents such as ethanol, propanol and acetone. After addition, the stabilized silver particles will precipitate, and the particles may be separated from the supernatant (100 in FIG. 24). Further concentrating of the particles may be carried out by centrifugation (120 in FIG. 24). After concentrating, preferably the stabilized silver particles have a silver content of at least 50 wt %, more preferably at least 60 wt %, and most preferably at least 70 wt %, such as 70-85 wt %, including 75 wt %, 77 wt %, and 82 wt %. Addition of the ink solvent (such as a humectant, 140 in FIG. 24), followed by homogenization, and optionally vacuum treatment and/or aging for 1-3 days, completes formation of the silver particle ink.

Each part is now described in further detail.

(1) It is known that the ink resistivity increases with increasing PAA content. Less than 10 wt % PAA is sufficient for stability and is recommended. Molecular weight (Mw) of PAA plays an important role on the ink properties, such as printability, resistivity, drying mechanics, and adhesion. Molecular weight of 5,000 (5K) to 50,000 (50K) is recommended. Particle size of inks decreases with increasing Mw of PAA due to steric hindrance during particle growth but more than 50K shows sponge-like bulky networks resulting in bad printability and conductivity. Inks from 50K PAA show good printability, good adhesion to substrate but they result in higher resistivity than that from 5K PAA. Inks from 5K PAA display high conductivity but poor adhesion to a substrate, as well as crack formation during drying, and bad printability due to nozzle clogging by rapid drying. Nozzle clogging occurs even after adding a high content (~ 10 wt %) of high boiling point solvent like ethylene glycol (EG). The best case is obtained from a mixed PAA system of 5K:50K=80:20 in wt %. In this case, 5K gives high conductivity and 50K regulates ink flow properties, adhesion, drying, and elasticity.

(2) PAA ionizes in an aqueous solution at pH 8.5-10. Inhomogeneous precipitates result when using pH below 8.5. pH ≥ 9.5 is recommended. Hydroxyl group terminated alkyl amine is used as a pH controlling agent as well as a mild reducing agent. Advantages of this kind of reducing agent include (1) easy control of particle size by slow growth rate, (2) free of alkali metal impurities, and (3) good solubility in both water and alcohol. Diethanolamine (DEA) is ideal.

(3) AgNO_3 is an inexpensive and soluble precursor in aqueous solution. 25-65 wt % solution is recommended. The ink product reduces below this range or inhomogeneous coagulates may result above this range during addition due to high concentration. Drop-wise addition is recommended because fast addition may cause large agglomerates. The reaction is exothermic, so the use of a water bath is recommended.

(4) Particle growth at room temperature halts at ~ 5 nm size upon stirring ~ 24 h. Further growth of particles to 10-500 nm mean particle size is enhanced by elevated reaction temperatures up to 100°C . Sonication is useful for homogeneous particle growth. Stirring on a hot-plate causes inhomogeneously grown precipitates to segregate along the reactor wall. Reaction for 2-5 h at 60°C . is recommended to obtain ~ 20 nm. High temperature may shorten reaction time but longer reaction time may cause inhomogeneous, large particles. Particle size plays an important role on electrical resistivity of the inks. Inks composed of small particles less than 10 nm show high resistivity due to strong capping and steric hindrance, preventing percolation. A particle size more than 20 nm is recommended to obtain ink with high conductivity that maintains a low sintering temperature ($\leq 250^\circ\text{C}$.). Large particles above 50 nm suffer from nozzle clogging through nozzles ≤ 5 μm , because of jamming effects, but can be printed through larger nozzles.

(5) Because fine particles are dispersed in viscous solution, it is not possible to collect them even using high speed centrifugation ($\geq 10,000$ rpm). Phase separation by liquid extraction is used to collect the particles. Ag particles are highly soluble in water but they are phase-separated with addition of poor solvents, such as alcohol or acetone. Titration is recommended to control uniform formation of flocculants.

(6) The flocculated particles precipitate within 30 min. They are collected by decanting supernatant, followed by centrifugation at 9,000 rpm for 20 min. A highly concentrated ($\phi_{\text{Ag}} \geq 75$ wt %) bluish precipitate is obtained. High speed centrifugation at more than 4,000 rpm is recommended to get high solid content.

(7) It is important to carefully tune the ink chemistry for good printability, redispersibility, and stability at room temperature. The centrifuged precipitate can be used as an ink itself, but further optimization is required for producing a more reliable ink. The precipitate is homogenized by adding preferably 2-10 wt % of wetting solvent (ink solvent; H_2O :EG=1:1-3:1 in wt ratio), vacuumed ~ 30 min to remove trace amount of nonwetting solvents and fine bubbles, followed by aging at room temperature ~ 3 days. After optimization, the bluish inks turn to purple and provide better printability and reliable ink flow.

Factors affecting the properties of the silver particle inks include the following: silver concentration affects self-supporting behavior, conductivity and viscosity. Molecular weight of surface capping agent affects viscosity, stability, and drying dynamics of printed electrodes. The amount and type of reducing agent affects the pH, particle growth size and speed, and stability.

Filaments, droplets and other structures may be formed by DIW. The filaments, droplets and other structures may be cured by heating to enhance conductivity, forming a conduc-

tive structure. Preferably, curing is carried out by heating at temperatures of 150 - 550°C ., preferably 150 - 250°C . The silver particle ink has a wide range of application in the field of microelectronics, and can be used to form various electronic devices, such as displays, chemical reactors, solar cells, RFIDs, antennas, metamaterials, and sensors.

EXAMPLES

A highly concentrated ($\phi_{\text{Ag}}=77$ wt %), poly(acrylic acid)-stabilized (PAA/(Ag+PAA)=10 wt %) silver particle ink in aqueous solvent (FIG. 2) was formed as follows. 1.99 g poly(acrylic acid) (PAA) (Mw 5,000, 50 wt % aqueous solution), 1.0 g PAA (Mw 50,000, 25 wt % aqueous solution), and 40 g diethanolamine (DEA) are dissolved in 50 ml of H_2O by stirring 2 h in a water bath at room temperature (DEA/Ag=2.65 in molar ratio, PAA/(Ag+PAA)=10 wt %). The pH of the solution is 9.5, in which PAA is fully ionized. Silver nitrate solution (20 g AgNO_3 in 20 ml H_2O) is added to the PAA solution under vigorous stirring. The resulting reddish yellow solution is gently stirred for 24 h at room temperature. The solution exhibits gradual color change from reddish yellow to dark black, indicating a mean particle size ~ 5 nm. Particles are grown further by sonicating the solution in a heated water bath (60°C .) for 2 h. After this treatment, the mean particle size is $\sim 20 \pm 5$ nm with a total size distribution between 5-50 nm. The particles are concentrated by titrating (10 ml/min) 240 ml ethanol. Ethanol is a nonwetting solvent which causes the particles to coagulate and precipitate from solution. After decanting the supernatant, the coagulated mass is centrifuged (9,000 rpm, 20 min) to remove remaining solvent and recover the precipitate. The process yields a highly concentrated ($\phi_{\text{Ag}}=77$ wt %, see TGA in FIG. 5) and stable paste of silver particles. The resultant paste is homogenized by adding ~ 5 wt % of wetting solvent (H_2O :EG=2:1 in wt) and vacuuming ~ 30 min to remove trace amount of nonwetting solvents and fine bubbles. The ink is typically aged for 3 days at room temperature prior to use. After homogenization, the bluish paste turns to purple. Homogenized ink displays extremely reliable printability through fine nozzles 5 μm -30 μm . The silver particle ink is stable at room temperature for at least two months and it is readily re-dispersible in water or ethylene glycol.

Particle size is tuned by adjusting pH and PAA molecular weight, but the dominant effects are temperature and reaction time, which are both carefully controlled upon addition of reducing agent to silver salt (AgNO_3). FIG. 1 shows silver particles extracted from the ink for TEM imaging, exhibiting a mean particle size $\sim 20 \pm 5$ nm with a size distribution between 5-50 nm. This range of particle sizes appears to be optimal for high conductivity and good printability through fine nozzles. The ink is synthesized at pH ≥ 9 to ensure the adsorbed PAA chains are charged, which inhibits formation of particle aggregates that would jam the nozzle orifice. The ink is concentrated and collected from aqueous solution by coagulating in a poor solvent (e.g. acetone or EtOH) for PAA and then centrifuging. After centrifugation, a small amount of poor solvent remains in the inks, thus creating an ink that consists of stabilized particles with a globular coating of polymer that adds stiffness. Finally, a small amount of humectant (e.g., ethylene glycol) is incorporated to prevent drying induced clogging commonly observed in inkjet inks. Under these conditions, the sealed ink has been stored at room temperature for over two months without any noticeable decline in printing behavior.

The ink is well suited for producing fine scale (widths=5-30 μm) self-supporting microelectrodes by DIW (FIG. 6).

DIW is carried out using a robotic deposition apparatus (ABL 900010 x-y-z motion stage, Aerotech Inc., Pittsburgh, Pa.) controlled with custom computer-aided design software (RoboCAD, 3D Inks, Stillwater, Okla.). The silver ink is housed in a syringe (3 mL barrel, EFD Inc., East Providence, R.I.) attached by luer-loc to a borosilicate micronozzle (diameter=5-50 μm , P-2000 laser based micropipette puller, Sutter Instrument Co., Novato, Calif.). An air-powered fluid dispenser (800 ultra dispensing system, EFD Inc.) is used to pressurize the barrel and control ink flow rate. The required pressure depends upon ink viscosity, nozzle diameter, and printing speed, but typically ranges from 10-100 psi at 50-500 $\mu\text{m s}^{-1}$. The deposition process is performed under ambient conditions with a relative humidity of ~20-30% at room temperature (23-26° C.).

Unlike inkjet printing, direct ink writing relies on air pressure (10~100 psi) driven extrusion of inks. Both the ink viscosity and elasticity under shear flow are critical parameters that must be optimized to enable patterning of self-supporting, filamentary microelectrodes. FIG. 3 shows the apparent viscosity (η) as a function of shear rate for inks of varying solids loading. The low-shear, apparent viscosity (η) rises nearly four orders of magnitude as the solids loading (ϕ_{Ag}) increases from 55-75 wt %. Concomitantly, there is a pronounced increase in the shear thinning behavior observed. A similar rise in the elastic modulus (G') is observed with increasing solids loading, as shown in FIG. 4. To produce self-supporting features via DIW, the ink preferably contains a minimum solids loading of 70 wt %, which corresponds to a minimum G' of 2,000 Pa. From experimental observation, it is known that $G' > G''$, preferably $G' \geq 1.5 G''$, is required to produce self-supporting features. Upon exiting the nozzle, the ink rapidly solidifies as the aqueous solvent evaporates, forming a continuous filamentary shape, and therefore preventing wetting or spreading that are deleterious to achieving small feature sizes.

To demonstrate fine scale and high aspect ratio printing, a planar pattern of silver microelectrodes (width 6 μm , height 3.7 μm , spacing 15 μm) is printed onto a silicon wafer from a nozzle with 5 μm orifice (FIG. 7). The high aspect ratio (height/width ≥ 0.6) is obtained by single-step deposition, unlike droplet-based printing methods which would require multi-step printing and heat treatments to achieve similar aspect ratios.¹⁷ Furthermore, the deposited electrodes display uniform drying and solidification with a notable absence of any "coffee ring effect",¹⁸ which commonly plagues ink-jet printing.

With this approach, it is possible to fabricate conductive structures of arbitrary complexity whose geometries are applications driven. For some relevant applications, the conductive architecture may itself be the desired device (e.g., antennas, metamaterials). For others, direct ink writing of silver particle ink may be used in conjunction with other processes (e.g., photolithography, transfer printing, etc.) for heterogeneous integration of dissimilar materials. An example of the former case is shown in FIG. 8, wherein a resonant inductive coil is printed onto a silicon wafer by a 30 μm nozzle, demonstrating feasibility for printing of RFIDs. An example of the latter case is shown in FIG. 14, wherein silver microelectrode interconnects are printed onto an array of silicon ribbon solar cells (width 45 μm , height 26 μm , spacing 33 μm) planarized by photocurable polymer (NOA-61).

The resistivity of printed silver traces as a function of heat treatment time and temperature is shown in FIG. 9. The volume resistivity of the electrodes is obtained via the equation $\rho = (R \cdot A) / L$, where ρ is volume resistivity ($\Omega \cdot \text{cm}$), R is resis-

tance (Ω), A is cross-sectional area (cm^2), and L is length of the electrode (cm).¹⁹ The resistivity of the electrodes decreases with increasing heat treatment time. A resistivity (10^{-5} $\Omega \cdot \text{cm}$ range) close to the value of bulk silver (10^{-6} $\Omega \cdot \text{cm}$) is obtained by short cure times (≤ 10 min) above 250° C. By contrast, long cure times (≥ 30 h) are required to obtain 10^{-3} $\Omega \cdot \text{cm}$ range of resistivity at 150° C. Low resistivity after heat treatment at low temperature is attributed to the high concentration of metallic silver, low content of stabilizing agent (PAA), as well as the size effect of particles which enables consolidation at low temperature due to diffusion.²⁰ Resistivity results correspond well with the morphology characteristics as a function of curing temperature (FIG. 10). Width and height of the electrode reduce up to 30% and grain sizes increase from nanometer scale to several microns after heat treating to 550° C. The high magnification SEM images display a transition to a sintered surface morphology after heat treating to temperatures above 250° C.

One important advantage of using highly concentrated silver nanoparticle inks to create printed microelectrodes is their compatibility with both wetting and non-wetting substrates, including silicon, polyimide, and silicone surfaces. Unlike, inkjet printing, which greatly suffers from dewetting phenomena,⁵ these inks exhibit infinite viscosity under zero-shear conditions (i.e., after exiting the deposition nozzle) thereby suppressing this phenomena.

Low temperature heat treatment indicates this ink and printing approach are compatible with flexible polymer substrates such as polyimide. FIG. 11 shows optical images and an SEM micrograph of a bendable silver pattern printed onto a 25 μm thick polyimide sheet, followed by heat treatment to 200° C. for 3 h, and subsequent wrapping onto a scintillation vial with a bending radius of 14 mm. Stop and run ink flow is employed to create disconnected architectures as well as patterned areas of different feature sizes. Contact pads (1 mm \times 1 mm) are printed with a 30 μm nozzle by programming the line spacing \leq nozzle diameter, resulting in a continuous region of merged ink (FIG. 11 top right). Fine interdigitated electrodes are printed by a 5 μm nozzle onto an electrode backbone of 30 μm width, illustrating the ability to produce elaborate structures with stop and run printing (FIG. 11 bottom right).

To examine the bendability of silver microelectrodes printed onto flexible substrates, bend tests using a specially designed mechanical stage were performed on a silver electrode (width 21 μm , height 15 μm , length 2 cm) cured at 200° C. for 3 h in ambient air. Resistivity of the electrode as a function of bending radius is shown in FIG. 12, for tension (convex surface), the unstrained state (flat surface), and compression (concave surface). No significant variations of resistivity are observed, even upon bending from a radius of 11 mm to 5 mm. Fatigue studies of repetitive bending up to 1,000 cycles (one cycle-flat-tension-flat-compression-flat) at the smallest bending radius of 5 mm confirm the bendable nature of conductive silver microelectrodes (FIG. 13).

To demonstrate the self supporting capacity of silver particle inks as well as heterogeneous integration with other patterning approaches, interconnects (width 15 μm , height 13 μm) are printed onto silicon ribbons (width 45 μm , height 26 μm) separated by periodic gaps of 33 μm width (FIG. 14). The high magnification SEM micrograph (FIG. 14 inset) confirms the electrode spans the unsupported regions between ribbons without sagging. In addition, direct ink writing of silver particle ink exhibits the capacity to span extraordinarily long unsupported regions (> 1.0 cm), as shown in FIG. 15. The electrical resistivity as a function of span length is shown in FIG. 16. Moreover, the incredibly stiff nature of the ink enables vertical printing between two substrates with differ-

ent heights. For example, a set of electrodes are patterned onto two substrates with a 1 mm height difference at varying printing angles of 27°, 34°, and 45° (FIG. 17). In another case, vertically printed arched electrodes are used to connect a voltage source to a commercial GaN LED chip (1 mm×1 mm×200 μm) to illustrate the conductivity of these structures (FIG. 18). After heat treating at 200° C. for 3 h, the LED shows blue emission under an applied bias of 2 V (FIG. 18 inset). Furthermore, elaborate 3-D structures have been printed, such as hollow cylinders, cylindrical microcapacitors (FIG. 19), and micropatterned lattices using layer-by-layer assembly (FIG. 20).

Ultrathin metal films and ribbons deposited onto pre-strained, stretchable substrates have been shown to form wavy buckles and arches upon release of the substrate from the stretched to the relaxed state.²² These configurations even form in brittle materials such as silicon, due to the change in mechanical behavior of ultrathin materials compared to the bulk.²³ The built-in slack enables mechanical stretching while preserving the desired optoelectronic properties. Stretchable wavy and arched architectures can be created out of non-brittle materials that are not ultrathin, this is particularly true for ductile metals. For example, stretchable arches have been formed by printing a linear silver electrode onto a pre-strained spring (FIG. 21 inset), followed by strain release to form the arches (FIG. 21), and subsequent heat treatment. To ensure good adhesion and accurate resistivity measurements, a silicone adhesive is printed onto the spring at the silver contact positions as an insulation and adhesion layer both before and after printing of the silver ink. It is noteworthy that the arch amplitude increases with increasing magnitude of pre-strain (ϵ_{pre}). The resistivity of the arches as function of strain (%) is shown in FIG. 22 at different heat treatment temperatures. The stretchability increases with increasing temperature from 8% at 200° C. and 12% at 300° C. to 25% at 550° C. This result is expected, since the grain size increases with temperature (FIG. 10), so the electrodes will more closely resemble the ductile, bulk material. Notably, straining the arched electrodes up to 200 cycles does not result in fatigue-induced failure of the connection, as exhibited by resistivity measurements acquired through the electrode (FIG. 23).

Characterization was carried out as follows. Silver electrode morphology is measured by a scanning electron microscope (JOEL 6060LV, JEOL Ltd.) after sputtering with Au/Pd for 30 s (Emitech K575 Sputter Coater). Ink particle size is obtained by transmission electron microscope (JOEL 2010Lab6 TEM, JEOL Ltd.). Viscosity and modulus of the inks are measured by a rheometer (C-VOR, Malvern Instruments, Melvern, UK) using a cone and plate geometry (CP 4/40, cone diameter 40 mm with a 4° angle and gap width of 0.15 mm) at 25° C. in the presence of water trap to prevent solvent evaporation during measurement. Ink solid content is determined by thermogravimetric analysis (Mettler Toledo TGA/SDTA851, Columbus, Ohio) with a heating rate of 10° C. min⁻¹ to 800° C. in air. Resistivity is measured using micropositioners (Signatone) with tungsten tips (SE-T, Signatone) attached to a source meter (Keithley 2400).

Mean particle size of the stabilized silver particles by transmission electron microscope (TEM) is about 20±5 nm with a size distribution between 5–50 nm. With the thermogravimetric analysis (TGA), weight changes are 7.0 wt % (150° C.), 12 wt % (200° C.), 15 wt % (250° C.), and 23 wt % (700° C.), respectively. The ink has rheological properties of viscosity (η =900 Pa·s), elastic modulus (G' =2670 Pa), and viscous modulus (G'' =1450 Pa). The resistivity obtained from I-V characteristics and geometries of the electrodes after curing

for 3 h results in 1,100 Ω·cm (150° C.), 1.77×10⁻³ Ω·cm (175° C.), 2.2×10⁻⁴ Ω·cm (200° C.), and 2.1×10⁻⁵ Ω·cm (250° C.).

The research outlined here demonstrates synthesis of a silver particle ink that possesses many new properties, heretofore unseen in other inks for printed electronics. In summary, DIW of silver particle ink has been used to create fine scale, self-supporting, and 3-D metallic structures of arbitrary complexity. Low temperature processing ensures compatibility with flexible and stretchable substrates, enabling the creation of printed silver microelectrodes that are both bendable and stretchable. DIW of silver particle inks is a simple and low cost approach for the production and heterogenous integration of devices for high performance applications, such as photovoltaics, LEDs, RFIDs, antennas, and metamaterials.

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13

The invention claimed is:

1. Stabilized silver particles, comprising:
particles comprising silver,
a short-chain capping agent adsorbed on the particles, and
a long-chain capping agent adsorbed on the particles,
wherein the short-chain capping agent is a first anionic
polyelectrolyte having a molecular weight (Mw) of at
most 10,000,
the long-chain capping agent is a second anionic polyelec-
trolyte having a molecular weight (Mw) of at least 25,000, and
the stabilized silver particles have a loading of metallic
silver of at least 50 wt %.
2. The stabilized silver particles of claim 1, wherein the
first and second anionic polyelectrolytes both have carboxy-
lic acid and/or carboxylate moiety containing repeating units.
3. The stabilized silver particles of claim 2, wherein the
first and second anionic polyelectrolytes are both selected
from the group consisting of poly(acrylic acid), poly(meth-
acrylic acid), copolymers thereof and salts thereof.
4. The stabilized silver particles of claim 3, wherein the
particles have a mean particle size of 10-50 nm.
5. The stabilized silver particles of claim 3, wherein the
first anionic polyelectrolyte has a molecular weight (Mw) of
1,000-10,000.
6. The stabilized silver particles of claim 3, wherein the
first anionic polyelectrolyte has a molecular weight (Mw) of
4,000-6,000.
7. The stabilized silver particles of claim 3, wherein the
second anionic polyelectrolyte has a molecular weight (Mw)
of 25,000-100,000.
8. The stabilized silver particles of claim 3, wherein the
second anionic polyelectrolyte has a molecular weight (Mw)
of 40,000-60,000.
9. The stabilized silver particles of claim 6, wherein the
second anionic polyelectrolyte has a molecular weight (Mw)
of 40,000-60,000.
10. A silver particle ink, comprising:
particles comprising silver,
a short-chain capping agent adsorbed on the particles,
a long-chain capping agent adsorbed on the particles, and
water,
wherein the short-chain capping agent is a first anionic
polyelectrolyte having a molecular weight (Mw) of at
most 10,000,
the long-chain capping agent is a second anionic polyelec-
trolyte having a molecular weight (Mw) of at least
25,000, and
the silver particle ink has a solid loading of metallic silver
of at least 50 wt %.

14

11. The silver particle ink of claim 10, further comprising
a solvent which is soluble in water and has a higher boiling
point than water.

12. The silver particle ink of claim 11, wherein the first and
second anionic polyelectrolytes both have carboxylic acid
and/or carboxylate moiety containing repeating units.

13. The silver particle ink of claim 12, wherein the first and
second anionic polyelectrolytes are both selected from the
group consisting of poly(acrylic acid), poly(methacrylic
acid), copolymers thereof and salts thereof.

14. The silver particle ink of claim 13, wherein the particles
have a mean particle size of 10-50 nm.

15. The silver particle ink of claim 13, wherein the first
anionic polyelectrolyte has a molecular weight (Mw) of
1,000-10,000.

16. The silver particle ink of claim 13, wherein the first
anionic polyelectrolyte has a molecular weight (Mw) of
4,000-6,000.

17. The silver particle ink of claim 13, wherein the second
anionic polyelectrolyte has a molecular weight (Mw) of
25,000-100,000.

18. The silver particle ink of claim 13, wherein the second
anionic polyelectrolyte has a molecular weight (Mw) of
40,000-60,000.

19. A silver particle ink, comprising:
particles comprising silver, and
an ink solvent,
wherein the silver particle ink has a solid loading of metal-
lic silver of at least 60 wt % and an apparent viscosity of
at least about 100 Pa·S at a shear rate of 10^{-2} 1/s,
the silver particle ink is shear thinning, and
the silver particle ink has an elastic modulus, G' , and vis-
cous modulus, G'' , such that $G' > G''$.

20. A method of forming stabilized silver particles, com-
prising:
forming a solution comprising a reducing agent, a short-
chain capping agent, a long-chain capping agent, and
 Ag^+ ions, to form silver particles; and
growing the silver particles to a mean particle size of 10-50
nm;
wherein the short-chain capping agent is a first anionic
polyelectrolyte having a molecular weight (Mw) of at
most 10,000,
the long-chain capping agent is a second anionic polyelec-
trolyte having a molecular weight (Mw) of at least
25,000, and
the reducing agent comprises a hydroxyl group terminated
amine containing 2-10 carbon atoms.

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