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Facile and Scalable Preparation of Solid Silver Nanoparticles (<10 nm) for Flexible Electronics

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ABSTRACT

Metal conductive ink for flexible electronics has exhibited a promising future recently. Here, an innovative strategy was reported to synthesize silver nanocolloid (2.5 ± 0.5 nm) and separate solid silver nanoparticles (<10 nm) effectively. Specifically, silver nitrate (AgNO_3) was used as silver precursor, sodium borohydride (NaBH_4) as reducing agent, fatty acid ($\text{C}_n\text{H}_{2n+1}\text{COOH}$) as dispersant agent, ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) and hydrochloride (HCl) as pH regulator and complexing agent in aqueous. The main mechanism is the solubility changes of fatty acid salts ($\text{C}_n\text{H}_{2n+1}\text{COO}^-\text{NH}_4^+$) and fatty acid ($\text{C}_n\text{H}_{2n+1}\text{COOH}$) coated on the synthesized silver nanoparticles (NPs) in aqueous. This change determinates the suspension and precipitation of silver NPs directly. The results show that when n in dispersant is 12, and molar ratio ($\text{C}_{12}\text{H}_{24}\text{O}_2/\text{AgNO}_3$) is 1.0, the separation yield of silver NPs is up to 94.8 %. After sintered at 125 °C for 20 minutes, the as-prepared conductive silver nanoink (20 wt. %) presents a satisfactory resistivity (as low as 6.6

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3 $\mu\Omega\cdot\text{cm}$ on polyester-PET substrate), about 4 times the bulk silver. In addition, the efficacy of the
4
5 as-prepared conductive ink was verified with the construction of radio frequency antenna by
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7 inkjet printing and conductive character pattern (Fudan-Fudan) by direct wiring, showing with
8
9 excellent electrical performance.
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12 13 14 **KEYWORDS**

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16 Metal conductive ink, flexible electronics, solid silver nanoparticles (<10 nm), radio frequency
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18 antenna, conductive character pattern.
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21 22 23 24 **1. Introduction**

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26 Recently, many research efforts are being devoted to many kinds of functional inks for
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28 flexible electronics, like conductive metal ink,^{1,2} dielectric ink,^{3,4} magnetic ink,^{5,6}
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30 ceramic ink,^{7,8} semi-conductive ink,^{9,10} optically active ink,^{11,12} thermal sensitive ink,¹³
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32 etc... These functional inks can be applied for electronic skin (E-skin) sensor, organic
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34 light-emitting diode (OLED), organic photovoltaic (OPV), flexible battery &
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36 supercapacitor, artificial muscles, radio frequency identification (RFID) tags, etc.^{14,15,16,17}
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38 This is mainly because the diverse printing technologies like inkjet printing, screen
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40 printing, gravure printing, directing writing etc. are very promising as additive methods.
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42 They will be an important alternative to the production of electronic devices with micro-
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44 scale or millimetre scale, compared with traditional silicon based photolithography
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46 process. However, these functional inks, especially nano-based inks, are still the main
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48 barrier for the application of flexible electronics widely due to its high cost, unstability,
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50 dilemma of scale production (though some commercial inks, but high price), etc.^{18,19}
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Based on these, it is necessary to develop conductive nanometal ink with cost effective, high quality, easily large-scale production.

Compared with solid phase method, liquid phase method is more efficient to prepare metal NPs with small size (<10 nm in diameter) and various geometrical morphologies.^{20,21,22} Presently, long-chain fatty acid salts (such as capric acid, lauric acid, myristic acid, oleic acid, etc...) are widely used as dispersants to synthesize metal NP in aqueous solution. This is because they can be attached onto the surface of metal NPs proficiently by coordinated action between the carbonyl group from fatty acid salts and metal NPs.^{18,23,24} Thus, a stable structure of electric double layer can be constructed accordingly, inhibiting the congregation of Metal NPs and further forming a steady colloidal solution. However, it is very difficult to separate the nanoparticles from the colloid, and high energy consumption and pollution will be brought based on the present ways, such as centrifugation,²² nonsolvent precipitation,^{25,26} evaporation.^{27,28} Thus, new strategies have to be considered. To the best of our knowledge, there is few research reporting this work.

Herein, a facile and scalable strategy was demonstrated to separate protosomatic metal NPs from its colloid solution effectively. In specific, silver nitrate (AgNO_3) was chosen as silver precursor, sodium borohydride (NaBH_4) as reducing agent, fatty acid ($\text{C}_n\text{H}_{2n+1}\text{COOH}$) as dispersant agent, ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$) and hydrochloride (HCl) as pH regulator and complexing agent in aqueous solution. In this strategy, on one hand, silver ammonium complex ion $[\text{Ag}(\text{NH}_3)_2^+]$ can be got from the reaction between AgNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$, which can keep the concentration of silver ion (Ag^+) stable in solution like a reservoir of Ag^+ , as well as can regulate the reaction rate well; Meanwhile, fatty acid

ammonia ($C_nH_{2n+1}COO^-NH_4^+$) can be get from the reaction between $C_nH_{2n+1}COOH$ and $NH_3 \cdot H_2O$, which is one kind of stronger electrolyte and a good dispersant agent in aqueous. Noted that $C_nH_{2n+1}COOH$ is insoluble in aqueous solution. On the other hand, if pH value of the silver nanocolloid was adjusted from alkalinity to acidity by HCl, namely $C_nH_{2n+1}COO^-NH_4^+$ can change to $C_nH_{2n+1}COOH$. Thus, silver NPs coated by $C_nH_{2n+1}COOH$ precipitate accordingly in aqueous. If restoring the pH to alkaline, the precipitated metal nanoparticles can be re-dispersed. A schematic illustration of the separation process is shown in Scheme 1.

Scheme 1. a) Schematic illustration for the separation process of $C_nH_{2n}O_2$ -coated silver NPs (Step-A: stable silver nanocolloid; Step-B: the separation process; Step-C: the re-

dispersion process; Step-D: the protosomatic dispersion); b) The real-separation process; c) The as-separated solid silver NPs.

This method is very promising and offers the following advantages: (i) green and environment friendly preparation and separation process; (ii) relatively inexpensive starting materials; (iii) excellent electrical properties and well processing adaptability; (iv) easy to accomplish large-scale production. Therefore, this paper will exhibit this promising strategy about the preparation and separation of solid silver NPs. Its efficacy of the as-prepared conductive ink was also verified with the construction of radio frequency antenna by inkjet printing and conductive character pattern (Fudan-Fudan) by direct wiring. Moreover, we envision that this approach can be extended to the synthesis of other metal or nonmetallic nanomaterials and functional application.

2. Experimental

2.1 Materials

Silver nitrate (AgNO_3 , ACS, 99.9+ %) was purchased from Alfa Aesar. Polyester (PET) was got from Teonex with the thickness of 125 μm . All the other chemicals were obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd, and were used without further treatment. Deionized water was used in all experimental processes.

2.2 Preparation and separation of silver NPs

Preparation of silver nanocolloid: the new prepared $[\text{Ag}(\text{NH}_3)_2^+]$ solution was mixed with fatty acid, with the pH value of 8-9 adjusted by $\text{NH}_3 \cdot \text{H}_2\text{O}$, under the vigorous stir at 60 $^\circ\text{C}$ for 15 min until the solution became transparent. Then, NaBH_4 solution was quickly injected into the above mixture by a syringe. After strongly stirred for 10 min, the colour

of the solution gradually changed from colourless to light yellow to black, and aged for 24 h at room temperature, the desired silver colloid was obtained.

Separation of Ag NPs: typically, pH value of the silver nanocolloid was adjusted from alkalinity (8-9) to acidity (6-7) using HCl (0.1 wt. %) drop by drop under vigorous stirring at room temperature, flocculent precipitate appeared. Then filtered by buchner funnel, along with washing by DI water for several times, then vacuum drying for 10 h at room temperature.

2.3 Preparation of silver nanoink (20 wt. %)

The method has been reported before.¹⁸ Briefly, 2 g of the obtained silver NPs were dispersed in 8 ml of an aqueous medium containing ammonia, isopropanol, and ethylene glycol. These solvents were used to adjust to pH = 8, viscosity 10–20 cps and surface tension 25-40 dyn.cm⁻¹ of the silver nanoink, mixing at high speed for 10 min. The prepared conductive ink (20 wt. %) can be seen in Section 3.3. For information, the prepared silver ink with lauric acid as dispersant is very stable at least for ten days without any precipitation.

2.4 Instrumentation

The prepared silver nanocolloid was investigated by ultraviolet-vis spectrophotometer (UV-vis 3150, Shimadzu, Japan); Size analysis (SA, Zeta Nanosizer, Malvern, England); Transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan); Differential scanning calorimetry (DSC-60, Shimadzu, Japan); X-Ray Diffraction (XRD, max 2550 PC, Rigaku-D, Japan); The conductive patterns on polyethylene terephthalate (PET) substrate (125 μ m) were fabricated by piezoelectric drop-on-demand inkjet printer (Fujifilm Dimatix DMP-3000) with the inkjet head of 16 nozzles, 25 μ m drop distance, and the

nozzle voltage of 24-28 volts. The printed conductive pattern was measured by a 4-point probe (BD-90, Shanghai Power Tool institute, China); Scanning Electronic Microscopy with Energy dispersive X-ray (EDX) analysis (SEM, S-360, Cambridge, England); PNA network analyzer (Agilent N5225A, 10 MHz-50 GHz) with a coaxial cable and a sub-miniature version A (SMA) connector.

3. Results and discussion

3.1 Mechanism consideration

According to the description above, the whole preparation process of solid silver nanoparticles (NPs) in our strategy can be divided into three procedures, incl. synthesis process, separation process, and re-dispersion process, respectively.

For synthesis process, silver NPs with homogeneous size of 2.5 ± 0.5 nm can be obtained finally through the present method (Section 2.2). This has been confirmed in our previous research.¹⁸ The main chemical reaction during this process can be seen in chemical equations (1), (2) and (3), in which R_0 is the carbon chain. Noted that

1) After the addition of $NH_3 \cdot H_2O$, not only it can complex Ag^+ to $[Ag(NH_3)_2]^+$ improving its concentration and stability in aqueous solution, but also it can react with $C_nH_{2n+1}COOH$ to generate fatty acid ammonia ($C_nH_{2n+1}COO^-NH_4^+$) which is one kind of stronger electrolyte and a good dispersant agent in aqueous compared with the poor solubility of $C_nH_{2n+1}COOH$ in water.

2) Fatty acid or fatty acid salt (normally $10 < n < 18$) can be used as dispersant to synthesize metal nanoparticles due to their strong emulsification ability.^{29,30,31} These are because that, on one side, they can form a stable structure of electric double layer in the

relevant solvents due to their amphiphilic groups (carbon chain and carboxyl group); On the other side, they can attach onto the surface of Ag NPs proficiently by chemisorption, and the two oxygen atoms in the carboxylate are coordinated symmetrically to the Ag atoms, leading to the formation of the covalent Ag-O bond.

For separation process, how to separate the metal NPs from its colloid is the key point here. The main mechanism is built on the solubility changes of fatty acid salts and fatty acid in aqueous solution. In specific, $C_nH_{2n+1}COOH$ almost can't dissolved in water only converting to its relevant salt (like $C_nH_{2n+1}COO^-NH_4^+$) by the adjustment of pH value to alkalinity. On the contrary, when the pH value is back to acidity, $C_nH_{2n+1}COO^-NH_4^+$ will convert to $C_nH_{2n+1}COOH$, precipitating accordingly in water due to its solubility, as shown in Scheme 1b and chemical equation (4). The results indicated that this variation of dispersant dissolution and precipitation does not affect the interaction between carboxyl group and silver NPs basically. This have to ascribe to the stronger interaction between fatty acid and silver NPs through the covalent Ag-O bond.

For re-dispersion process, the obtained silver NPs coated $C_nH_{2n+1}COOH$ can be re-dispersed into aqueous solution if restoring the pH to alkaline, which can be seen in Scheme 1b and chemical equation (5). Noted that high temperature will quick this re-dispersing process. Moreover, this kind of silver NPs also can be re-dispersed into other solvents, which can dissolve fatty acid ($C_nH_{2n+1}COOH$). The solubility of dominant

saturated fatty acid in various solvents was summarized in Table. S1. Other fatty acids which can exhibit the similar performance also can be used to the preparation of re-dispersible solid metal NPs.

Conclusively, based on this synthesis, separation and re-dispersion mechanism of solid metal NPs, the following experiments (n=12 as example) will provide a further verification and optimization systematically.

Figure 1. a) UV-vis absorption spectra of (A) original silver NPs with molar ratio (0.5) and (B, C, D, E) separated silver NPs with molar ratio (3.0, 2.0, 1.0, 0.5, respectively); b) Size distribution of silver NPs before and after separation with different molar ratios; c) UV-vis absorption spectra of the separated silver NP with molar ratio (1.0) re-dispersed in DI water (A), ethanol(B), tetrahydrofuran(C), dimethylbenzene (D). Inset images are the relevant silver nanocolloids and the default solvent is DI water. All the molar ratio is $C_nH_{2n+1}COOH / AgNO_3$.

3.2 Preparation of solid silver NPs

To verify the previous mechanism description, silver nanocolloids with different molar ratios of lauric acid ($C_{12}H_{24}O_2/AgNO_3$) were prepared.

UV-vis spectrum was used to discuss the influence of the dispersant dosage on the preparation and separation process. It has been well-known that transition-metal NPs typically exhibit a characteristic surface plasmon absorption band which superimposes onto the exponential decay Mie scattering profile. This band intensity is usually proportional to the particle size (volume).³² As for silver element, the absorption band at about 310 nm occurs because of Ag^+ ions. Whereas, surface plasmon resonance of nano-silver will be at 400 nm or above.

From Figure 1a, it can be seen that all the spectrums showed a narrow and intense absorption at 408 nm, 410nm, 415 nm, 420 nm, 440 nm corresponding to A, B, C, D, E, respectively. From the gradually increase of the peak values from A to E, it can be found that the size of the silver NPs is increasing along with the decreasing dosage of $C_{12}H_{24}O_2$. Specially, when the molar ratio is 0.5, the absorption peak of the separated silver

nanocolloid shifts to 440 nm. This phenomenon manifests that Ag NPs have the chance to congregate during the conversion process between $C_{12}H_{24}O_2^-NH_4^+$ and $C_{12}H_{24}O_2$. The less the dosage of $C_{12}H_{24}O_2$ is, the larger the chance is.

In addition, size distribution was also used to characterize these processes to present a further confirmation, as shown in Figure 1b. With the decreasing of molar ratio ($C_{12}H_{24}O_2/AgNO_3$) from 3 to 0.5, the size of silver NPs after the separation progress increases progressively from 2.69 nm to 15.70 nm, compared with the original size (2.5 nm) with the molar ratio (0.5). This result is well consistent with that from UV-vis characterization.

The separated silver NPs can be easily re-dispersed in various solvents which are good for lauric acid ($C_{12}H_{24}O_2$, incl. ethanol, tetrahydrofuran, dimethylbenzene, etc...) or laurate ($C_nH_{2n+1}COO^-NH_4^+$, incl. water, etc...), as seen in Figure 1c. Results present that surface plasmon resonance of nano-silver in different solvents from A to D almost emerge in the scope of 412 nm - 417 nm, confirming the above comments. Besides, this phenomenon also should have a relationship with the small size of Ag NPs. Hence, this performance provided a guarantee for the formula optimization of conductive ink to improve its printing suitability.

According to Table S1, different fatty acid ($C_nH_{2n+1}COOH$) displays different solubility, depending on the number of “n”. Therefore, it is very necessary to select the optimal solvent to optimize the concentration and stability of the final conductive ink in practical application.

Generally, these results manifest that this strategy is very facile and effective to obtain small size, narrow distribution and solvent-adaptable Ag NPs.

Figure 2. a) and b) TEM image of silver NPs before and after separation; c) XRD of solid silver NPs; d) DSC of $C_{12}H_{24}O_2$ and $C_{12}H_{24}O_2$ coated silver NPs (All molar ratio is 1.0).

3.3 Characterization of the solid silver NPs

Figure 2a and 2b displays the representative TEM images of silver NPs before and after separation with molar ratio (1.0). It can be seen that the original silver nanoparticle is very uniform with an average size of 2.5 ± 0.5 nm. After the separation and re-dispersion process, the size of silver NPs become a little inhomogeneous, some bigger particles appear, but the average size is still in the range from 4 nm to 10 nm. It can be concluded

that under this molar rate (1.0), the intact bilayer structures of $C_{12}H_{24}O_2$ can inhibit the agglomeration of silver NPs well.

In addition, XRD was used to characterize the crystalline structure of silver NPs as shown in Figure 2c. From the XRD pattern, the prominent peaks at respective 2θ values were exhibited, which presented the (111), (200), (220), (311) and (222) crystal planes of zero-valent fcc silver, respectively, according to Bragg's reflections. Usually, the broadness of the diffraction peaks reflects the size of silver NPs, and the smaller nanoparticles tend to show the broader XRD patterns. Therefore, the line broadening of the X-ray diffraction peaks here was primarily due to the small particle size. These results are consistent with the particle sizes determined by TEM images and size distribution analysis images.

Besides, DSC was also used to investigate the sintering properties of the prepared silver NPs (Figure 2d). It is widely accepted that metal-particle size plays a significant impact on its melting point. The smaller the size is, the lower the melting point is. Especially, when the size is down to below 10 nm, the melting point decreases sharply.³³ Based on the results, $C_{12}H_{24}O_2$ has two endothermic peaks, at around 58 °C and 206 °C, which can be indexed as the melting point and boiling point respectively. Apart from the former peaks, $C_{12}H_{24}O_2$ coated silver NPs have another narrow peak at 105 °C, which can be seen as the melting point of silver NPs. So, it can be inferred that silver NP prepared by this method is below 10 nm with a narrow distribution.

Figure 3. a) Relationship between resistivity, yield of silver NPs and the number of carbon atoms in the dispersant (yield = the molar of silver after sintered /that of silver ion, sintering condition: 125 °C for 20 minutes); Insets are SEM images of Ag films with different dispersants; b) Resistivity variations of silver ink (20 wt. %) sintered at different temperature and time; Inset is the as-prepared silver nanoink of 20 wt. %; c) Optical and SEM images with different magnifications of silver film; d) EDX spectrum (taken with SEM). The default dispersant is $C_{12}H_{24}O_2$.

3.4 Characterization of conductive silver ink

To demonstrate electrical properties of the synthesized silver NPs, silver nanoink with solid content 20 wt. % was prepared, and the resistivity variation and the relationship between resistivity, yield of silver NPs and the number of carbon atoms in the dispersant were investigated systematically.

From Figure 3a, the dispersant plays an important role to both the synthesis yield of solid silver NPs and the resistivity of silver nanoink. Specifically, when the number of carbon atoms in the dispersant increased from 8 to 18, the yield increased from 86 % to 99.5 % and the resistivity from 7.2 $\mu\Omega\cdot\text{cm}$ to 112 $\mu\Omega\cdot\text{cm}$ after sintered at 125 °C for 20 minutes. This can be explained that, with the decrease of the carbon number in the dispersant, it is not easier to accomplish the dissolving and precipitating process along with the change of acidity and alkalinity. But it will be easier to remove the dispersant with shorter carbon chain during the sintering process. This hypothesis can be confirmed from the inset images. The clear and large silver NPs can be seen when carbon number = 10, compared with the smaller and caking silver NPs when carbon number = 18. In brief, when the number of carbon atoms in the dispersant is between 10 and 12, the resistivity and the yield can be balanced well.

Besides, the electrical properties of conductive ink (20 wt. %) with carbon number of 12 was further evaluated. From Figure 3b, the resistivity of silver films is coming to stable after 20 minutes. The resistivity was decreased to 10.6 $\mu\Omega\cdot\text{cm}$ at 100 °C, to 6.6 $\mu\Omega\cdot\text{cm}$ at 125 °C, even to 5.1 $\mu\Omega\cdot\text{cm}$ at 175 °C for 20 minutes, which is 3.2 times the bulk silver. The microstructure of silver film with different magnifications can be seen from Figure 3c.

The single small particles were melting into larger particles with an average size of 300 nm-600 nm during sintering process. These large particles connect with each other to fabricate a continuous conductive track, avoiding the scattering of electrons effectively. Moreover, from the chemical composition curve identified by EDX, it also can be obtained that almost all the dispersant has volatilized (Figure 3d). Only three elements (C, O, Ag) can be detect on the surface of the silver thin film: Ag-98.79 wt. %, C-0.39 wt. %, O-0.82 wt. %.

3.5 Fabrication and application of conductive pattern

To evaluate the efficacy of the as-prepared silver nanoink (20 wt. %) for flexible electronics, two designed radio frequency antennas (A-1 and A-2) were fabricated by inkjet printer with two layers, as shown in Figure 4a and 4b.^{34,35} After sintered at 125 °C for 20 minutes, the resistance of A-1 (total length $L_t = 49.2$ cm, turn = 8) and A-2 (total length $L_t = 24.8$ cm, turn = 4) with line width (500 μ m) and line spacing (500 μ m) is 43.6 ohm, 21.2 ohm respectively. The working frequency of A-1 and A-2 was also measured by network analyzer (Agilent N5225A) with a SMA connector. Results, summarized in Figure 4c, show that the working frequency peaks are very sharp and clear, 35.1 MHz for A1 and 93.5 MHz for A-2, indicating the excellent electrical performance.³⁶ In addition, the efficacy was also demonstrated through the construction of conductive circuit pattern by direct wiring. A normal gel pen with the diameter of pen head (0.75 mm) was filled with the as-prepared silver nanoink (20 wt. %) by syringe. It was used to construct the designed pattern by directing wiring. As show in Figure 4 d and e. a character pattern (Fudan-Fudan) was presented as an example. After three LEDs were integrated into the

character pattern and 2.5 volt voltage was provided, the LED device can working well.
37,38 Generally, from the above successful exhibitions, it can be concluded that the as
prepared conductive inks can be used for the fabrication of conductive patterns through
inkjet printing or direct writing.

Figure 4. a) and b) Digital images for the fabrication of radio frequency antennas (A-1 and A-2) by inkjet printing on PET substrate; c) Working frequency characterization of two designed radio frequency antennas; d) and e) Digital images for fabrication of

conductive character pattern (Fudan-Fudan) by direct writing (diameter of pen head is 0.75 mm); f) Working LED device based on the as-prepared character pattern. All the scale bar is 1 cm.

Conclusions

A facile and scalable strategy has been demonstrated to synthesize silver nanocolloid (2.5 ± 0.5 nm) and separate solid silver NPs (<10 nm) successfully, with the main mechanism of the solubility changes of fatty acid salts ($C_nH_{2n+1}COO^-NH_4^+$) and fatty acid ($C_nH_{2n+1}COOH$) in aqueous solution. The results show that when n in dispersant is 12, and molar ratio ($C_{12}H_{24}O_2/AgNO_3$) is 1.0, the separation yield of silver NPs is up to 94.8 %. After sintered at 125 °C for 20 minutes, the as-prepared conductive silver nanoink (20 wt. %) presents a satisfactory resistivity (as low as $6.6 \mu\Omega \cdot cm$ on polyester-PET substrate), about 4 times the bulk silver. Moreover, the construction of radio frequency antenna by inkjet printing and conductive character pattern (Fudan-Fudan) by direct wiring were exhibited to further verify the efficacy of the as-prepared silver nanoink. Generally, this strategy has provided a very promising approach to prepare solid silver NPs (< 10 nm) and conductive ink for flexible electronics, which is low cost, environment friendly, easy large-scale production, in addition to its excellent electrical properties and well processing adaptability. In this fashion, this strategy not only can be used to metal NPs but also other metal or nonmetallic nanomaterials and functional application.

ASSOCIATED CONTENT

Supporting Information.

It was found that the solubility of the common fatty acid in main solvents is presented, which can be well used to explain the preparation, separation, and re-dispersion mechanism of silver NPs coated by fatty acid described in this manuscript. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Table of contents (TOC)

Schematic illustration and real-demonstration for the separation and re-dispersion strategy of $\text{C}_n\text{H}_{2n}\text{O}_2$ -coated silver NPs, as well as the obtained solid silver NPs, which provides a facile and scalable method to prepare conductive ink for flexible electronics.