Plasmon-enhanced nanosoldering of silver nanoparticles for high-conductive nanowires electrodes

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The silver nanowires (Ag NWs) electrodes, which consist of incompact Ag nanoparticles (NPs) formed by multi-photon photoreduction, usually have poor conductivities. An effective strategy for enhancing conductivity of the Ag NWs electrodes is plasmon-enhanced nanosoldering (PLNS) by laser irradiation. Here, plasmon-enhanced photothermal effect is used to locally solder Ag NPs and then aggregates of these NPs grow into large irregular particles in PLNS process. Finite element method (FEM) simulations indicate that the soldering process is triggered by localized surface plasmon-induced electric field enhancement at “hot-spots”. The effectiveness of PLNS for enhancing conductivity depends on laser power density and irradiation time. By optimizing the conditions of PLNS, the electrical conductivity of Ag NWs is significantly enhanced and the conductivity $\sigma$ is increased to $2.45 \times 10^7$ S/m, which is about 39% of the bulk Ag. This PLNS of Ag NWs provides an efficient and cost-effective technique to rapidly produce large-area metal nanowire electrodes and capacitors with high conductivity, excellent uniformity, and good flexibility.

Keywords: silver nanowires; silver nanoparticles; direct laser writing; laser nanosoldering; photothermal effect; conductivity


Introduction

Silver nanowire (Ag NWs) electrodes, with accurate controllable resistance $R$ via tuning geometry, have received much attention as the crucial components in various electronic devices, such as flexible circuits¹-⁴, organic solar cells⁵⁻⁷, and touch panels⁸⁻⁹. The common methods of patterning Ag NWs electrodes is photolithography, inkjet or printed technology¹⁰⁻¹³. In particular, femto-second laser direct writing (FsLDW), including multi-photon absorption induced photoreduction or photodynamic assembly of silver nanoparticles (Ag NPs), is used to build Ag NWs for engineered patterns in two and three dimensions with submicron resolution¹⁴⁻¹⁷. This method is widely used in the preparation of various optoelectronic devices¹⁴,¹⁶,¹⁸,¹⁹. However, the reported Ag NWs built by the FsLDW are all composed of aggregates.
of much smaller Ag NPs with void or polymer inclusions\textsuperscript{15,16}, which leads to poor conductivity. In our previous study, we have systematically fabricated the patterned Ag NWs electrodes with the designed resistance by FsLDW\textsuperscript{14,15}. The highest value of electrical conductivity $\sigma$ is $2.44 \times 10^{6}$ S/m, which is about 3.9\% of bulk Ag\textsuperscript{15}. To our knowledge, most of the resistance $R$ of Ag NWs comes from slight surface oxidation and particle-particle gaps of Ag NPs compared to bulk Ag. To enhance the conductivity $\sigma$, and reduce its resistance $R$, we must minimize the energy dissipation of conduction electrons in Ag NWs electrodes by reducing the gaps and increasing the contact areas among the NPs\textsuperscript{46}.

The widely applied methods to increase the contact areas of adjacent Ag NPs and enhance electrical conductivity of Ag NWs electrodes are thermal and laser annealing\textsuperscript{20–23}. Jahn et al. described the utilization of thermal treatment for ink-jetting Ag patterns on glass and flexible substrates, and the conductivity $\sigma$ is increased to 43\% and 18\% of bulk Ag, respectively\textsuperscript{44}. Nonetheless, a temperature of one hundred Celsius degrees is required during thermal annealing, leading to the unacceptable damage of the substrates\textsuperscript{25,26}. Laser annealing, as an alternative method, has been systematically investigated in recent years, benefiting from the efficient energy deposition and reduced heat affected zone, which would allow for more fragile or flexible substrates\textsuperscript{21,23,27–29}. Yang et al. demonstrated the rapid laser irradiation to anneal the printed Ag NPs film, and the conductivity $\sigma$ is 4\%-8.3\% of bulk Ag\textsuperscript{47}. Garnett et al. reported a light-induced plasmonic-nanowelding of Ag NWs technology, similar to laser annealing which significantly improves the conductivity of the connected Ag NWs networks\textsuperscript{31}. After the light illumination, the conductivity is roughly three orders of magnitude higher than the previous results. Considering the poor conductivity of Ag NWs electrodes consist of incompact NPs fabricated by FsLDW methods, the above laser annealing can be used to heat Ag NWs electrodes locally at the gaps of connected region to solder the incompact Ag NPs and improve its conductivity.

In this study, we propose an optical method for enhancing the electric conductivity of the Ag NWs by plasmon-enhanced laser nanosoldering (PLNS). PLNS of Ag NWs utilizes the plasmon-enhanced photothermal effect to realize the localized nanosoldering at room temperature. We have investigated the effects of two important parameters, including laser power density and nanosoldering time on the electric conductivity of Ag NWs. We found that the resistance of Ag NWs is reduced significantly through either increasing the laser power density or the nanosoldering time. After the plasmon-enhanced laser nanosoldering, the obtained Ag NWs have a maximal electric conductivity of $2.45 \times 10^{6}$ S/m at the proline concentration of 0.1 M, the laser power density of 9.55 MW/cm$^2$ and the nanosoldering time of 15 minutes. This study provides an efficient and cost-effective approach for enhancing electrical conductivity of Ag NWs in a controllable fashion, and promoting direct writing Ag NWs for further use as active SERS substrates, transparent electrode, capacitor, light-emitting diodes, thin-film solar cells, etc.

**Results and discussion**

**Experimental design for plasmon-enhanced laser nanosoldering of Ag NWs**

The schematic illustrations of the plasmon-enhanced laser nanosoldering system and the detailed optical experimental setup are presented in Fig. 1(a). Pulsed Nd:YAG laser (Spectra-Physics, Quanta-Ray) with a center wavelength of 532 nm, pulse width of 8 ns and repetition rate of 10 Hz, is used as a light source for laser nanosoldering. Ag NWs were fabricated by FsLDW and showed comparatively high absorption at this wavelength\textsuperscript{67}. The nanosecond(ns)-pulse laser beam passes through a pinhole to form a light spot with 5 mm-diameter, in order to shape the laser beam to produce a uniform radiation optical field. The attenuator is employed to adjust the laser power density, and a mechanical shutter is utilized to control the laser irradiation time as accurate as 1 ms, in order to investigate the influence of laser irradiation on the electric conductivity.

The Ag NWs with Ag NPs at an average size of ~30 nm were fabricated by FsLDW as shown in Fig. 1(b), based on the multi-photon absorption induced photoreduction of Ag ions\textsuperscript{57}. In our PLNS process, the absorption of ns-pulse lasers for Ag NPs induces rapid heating and melting at time scale of a few picoseconds\textsuperscript{31–34}. Thus, the adjacent Ag NPs are in contact and welded together after the laser irradiation. This photothermal effect can be strongly enhanced when several NPs aggregate together\textsuperscript{35–44}, arising from surface plasmon resonance (SPR) of Ag NPs. Thus, a low density of light concentrates at the gaps between two adjacent Ag NPs, and these areas are referred to as “hot-spots ”\textsuperscript{23,36–44}. 

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Interaction of light with Ag NPs is modeled using the previously reported method\textsuperscript{36,37}, and the numerical calculations of plasmon-enhanced electric field are shown in Fig. 1(c). The electric field among the particles is significantly enhanced when the polarization direction of the incident light is parallel to the interparticle axis instead of perpendicular to the interparticle axis. The heating values of Ag NPs are proportional to the local light field intensity\textsuperscript{34-36}. The enhanced light intensity is beneficial to increase the local nanosoldering temperature to the melting point in room temperature environment.

Figure 1(d) shows the schematic illustrations of the plasmon-enhanced laser nanosoldering process. Ag NWs electrodes consisting of Ag NPs are placed on a cover glass by the irradiation with a 532 nm laser. The aggregation of Ag NPs leads to the formation of Ag NWs. Thus, the fabricated Ag NWs electrodes are incompact, as shown in Fig. 1(d-i). Under the laser irradiation, Ag NWs have a strong optical absorption at 532 nm owing to SPR absorption. This photothermal effect can make the nanoparticles generate temperature enhancement through converting light energy into thermal energy. As the temperature rises, the melting or sintering occurs on the surface of nanoparticles, and is enhanced at the particle-particle gaps by plasmon-enhanced light field shown in Fig. 1(d-ii). As the nanosoldering time increases, sintering occurs by atoms migrating mainly along the particle surface\textsuperscript{42}. When two nanoparticles join together, they create a “neck”. The melting and sintering process of Ag nanoparticles begins with rapid “neck” formation followed by “neck” growth driven by surface diffusion\textsuperscript{42-44}. Finally, the recrystallization of Ag NPs leads to the formation of compact Ag NWs as shown in Fig. 1(d-iii).

Morphology characterization of Ag NWs electrodes
Firstly, we demonstrate the effect of PLNS process to modify the morphology of Ag NWs. We prepare the Ag NWs by the previously reported FsLDW\textsuperscript{14,15}. The surface topographies, such as shape and roughness, play important roles in the electrical properties of the Ag NWs electrodes. The average widths of Ag nanowires can be controlled within the range of 500 nm with the input laser power of 0.2 mW and the laser scanning speed of 6 μm/s as shown in Fig. 1(e). Before the laser nanosoldering, the Ag NWs consist of individual Ag NPs, and a large number of nano-intervals exist among the nano-particles as shown in Fig. 1(e-i). After the laser nanosoldering, the

![Diagram of experimental system for PLNS](https://doi.org/10.29026/oea.2021.200101)
melting of nanoparticles leads to the reduction of nano-intervals and the increase of particle size as shown in Fig. 1(e-ii). With the increase of nanosoldering time, the melting is more sufficient, and the nanoparticles are tightly connected as shown in Fig. 1(e-iii). The PLNS process can accelerate the accumulation and agglomeration of Ag NPs in the region exposed to sufficient laser power input, thus forming the relatively smooth and compact continuous NWs.

In order to further demonstrate the changes in the aggregation morphology of nanoparticles before and after the nanosoldering, we draw a comparison map about the transmission electron microscopy (TEM) of Ag NWs on carbon-coated copper grids with or without the ns-pulse laser irradiation. As shown in Fig. 2(f–2(h), Ag NPs are sintered and welded together to form neck between the particle-particle gaps in a programmed manner by irradiating laser pulses of 532 nm and 9.55 MW/cm$^2$ for 15 min, which are different from the isolated ones shown in Fig. 2(a–2(c)). Therefore, PLNS changes the aggregation morphology of the nanoparticles, but not the lattice distribution at the atomic level. Laser pulses were utilized to join, to hold closely, and to solder Ag NPs on TEM grids.

Further evidence of this mechanism comes from the magnified HRTEM images and the selected area electron diffraction (SAED) patterns of Ag NWs before and after the PLNS process [Fig. 2(d, i) and 2(e, g), respectively]. Lattice-resolved HRTEM images taken on the individual Ag NP [Fig. 2(d, i)] in single nanowire [Fig. 2(a, f)] confirmed that two typical crystal orientations [111] and [200] existed at the Ag NP and they were the polycrystalline whether or not being illuminated. Moreover, SAED patterns collected for representative Ag NPs before and after the nanosoldering process [Fig. 2(c) and 2(j), respectively] also prove that the basic constituent of Ag NP is polycrystalline. This comparison suggests that individual Ag NP does not completely melt to form a single crystal during the laser nanosoldering, but melt and recrystallize at the interface among adjacent Ag NPs after the illumination. PLNS process promotes the aggregation of small Ag NPs to form larger particles, and further makes the nanoparticles welded together to form dense nanowires.

**Electrical properties of Ag NWs electrodes**

Laser nanosoldering results in the appearance of large nanoparticles due to the laser-induced melting and coalescence. Meanwhile, laser nanosoldering enhances the neck growth between particles and therefore the electron diffusion coefficient correspondingly reduces with the decrease of the defect after photothermal sintering and welding$^{11,21,42}$. Therefore, laser nanosoldering

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**Fig. 2 |** TEM images of Ag NWs for overall (a), local (b) and magnified (c) topographies before the laser illumination. (d) Typical HRTEM images and (e) SAED patterns of Ag NPs before the laser illumination. TEM images of Ag NWs for overall (f), local (g) and magnified (h) topographies after the illumination. (i) Typical HRTEM images and (j) SAED pattern of Ag NPs after laser illumination for 15 min.
The electric resistivity of Ag NWs ($\rho_s$) can be written as follows:

$$\rho_s = R \cdot \frac{A}{L} = R \cdot \frac{dh}{2L},$$

where $A$, $R$, $d$, $h$ and $L$ represent the cross-sectional area, resistance, linewidth, height and length of Ag NWs, respectively. The electric conductivity $\sigma_s = 1/\rho_s$ has been enhanced corresponding to the resistance from $2.44 \times 10^6$ S/m to $24.51 \times 10^6$ S/m, which is up to $39\%$ of bulk Ag ($63 \times 10^6$ S/m).

The control of irradiation power and time is critical to achieve optimal nanosoldering. In our experiment, we have varied the average nanosoldering laser power ($P$) of 2, 5, 8, 11 and 15 mW, which is equivalent to the power density ($I_0$) of 1.27, 3.18, 5.10, 7.01 and 9.55 MW/cm². For $ns$-pulse laser, the power density ($I_0$) can be calculated by the formula $I_0 = P/(\pi \omega^2 \times \tau f)$, where $P$ is the average laser power, $\tau$ is pulse width, $f$ is repetition frequency and $\omega$ is radius of the beam. Figure 4(a) shows the experimental dependence of the resistance $R$ on laser power density $I_0$ for single Ag NWs electrode under the fixed nanosoldering time of 11 min. With the increasing of the laser power density $I_0$, the resistance $R$ decreases significantly. This is because the conductivity behavior relies on the aggregation degree and size of the Ag NPs. Furthermore, the dependency between the resistance $R$ and the laser nanosoldering time has also been

Fig. 3 | (a) Schematic of two-probe measurement method. (b) I-V curve of the fabricated Ag NWs before and after the laser nanosoldering. (c, f) Morphology of Ag NWs cut by focus ion beam. (d, g) AFM images and the height profile of the Ag NWs before and after the laser nanosoldering.
investigated as shown in Fig. 4(b). The resistance of Ag NWs is declined with the increasing of nanosoldering time when the concentration of proline is 0.10 M and the laser power density of 7.01 MW/cm². The resistance of Ag NWs declined from 445 Ω to 180 Ω after the laser nanosoldering. With 0.10 M or 0.15 M proline presents in the Ag precursor solutions, the resistance of Ag NWs exhibits similar variation tendency and similar resistance range due to the similar particle’s size distribution. As shown in Figs. 5(a) and S2, the average size of the Ag NPs is about 30 nm, 28 nm and 15 nm for different concentrations of prolines of 0.10 M, 0.15 M and 0.20 M, respectively. All of the Ag NWs fabricated in Ag ions solution with different concentrations of proline have a similar variation tendency between the resistance $R$ and laser power density as well as laser nanosoldering time, see the experimental results in Figs. S3 and S4. The increase in conductivity of Ag NWs approaches saturation state with the increasing of either laser power density or the nanosoldering time.

Mechanism analysis of PLNS for Ag nanowires

In PLNS process, Ag NP is considered to absorb many photons of pulsed lasers successively and reaches the temperature as high as the melting point$^{32,33}$. Thus, the adjacent Ag NPs are welded together after multiple pulses laser irradiation. This PLNS process increases the conductivity of Ag NWs containing Ag NPs. Currently, the heating behavior among individual NP has been well established$^{32-34}$. In the steady-state regime, the local temperature increasing $\Delta T$ (°C) around a single NP is described by the following equation:

$$\Delta T(r) = \frac{V_{NP} Q}{4\pi k_0 r},$$

$$Q = \frac{\omega E_0^2}{8\pi} \left| \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_{NP}} \right|^2 \text{Im}(\varepsilon_{NP}) (r \geq R_{NP}),$$

where $r$ is the distance from the center of a NP, $k_0$ is the thermal conductivity of the surrounding medium, and $V_{NP}$ is the NP volume. The temperature increment of all particles depends on the size of the particles and the laser pulse power$^{35}$. The above model only describes the nanosoldering behaviors for individual NP. However, Ag NWs structures with different aggregation morphologies are rarely considered in the studies of the nanosoldering behaviors. In our study, Ag NWs fabricated by FsLDW are composed of the aggregation of NPs. Laser nanosoldering for Ag NWs can be strongly enhanced because several NPs aggregate together form the “hot-spots”$^{36-43}$, as shown in Fig. 5(b). Whereas grain growth requires the temperature approaching the melting point ($T_m$) in bulk materials melting, however, it can occur at temperatures as low as ~0.2 $T_m$ (see Fig. S5) in Ag NPs aggregations$^{45}$. Thus, local melting can occur and form necks at the interfaces, enhancing electrical conductivity of Ag NWs structured by Ag NPs.

We have investigated the interaction between nanoparticles and light using commercially available finite element method (FEM) solver COMSOL Multiphysics. The surface plasmon resonances are usually dependent on the size, shape, and degree of particle-to-particle coupling$^{35-43}$. The spatial distribution of Ag NPs is irregular and random but the particle’s size meets the normal distribution in Fig. 5(a). In our simulation model, the aggregate states of several NPs are arranged via a statistical method according to the experimental results in Fig. 5(a). A random system of Ag NPs has “hot-spots” where
the electric field and heating intensity are greatly enhanced as shown in Fig. S6. The concentrated light field intensity at the hot-spots (the gaps between adjacent Ag NPs) has increased hundreds of times compared to the uniform incident light field shown in Figs. 5(d, e) and S6(c–f).

As we mentioned before, Ag NPs with different sizes have their corresponding heat generation $\Delta T$ and melting point $T_m$. We have calculated the temperature increase $\Delta T$ at the surface of Ag NPs as a function of Ag NPs size, considering the local light intensity increased 300 times. The black areas (hot-spots) present the simulation results of the temperature distributions when the enhanced light field intensity increases 10 (d) and 300 (e) times by using FEM method.

![Diagram](https://example.com/diagram.png)

**Fig. 5** (a) Size distribution of Ag NPs in the Ag NWs fabricated in the silver ion contained precursor solutions at different concentrations of surfactant. (b) Schematic of simulation setup, a planar configuration is taken as an example. (c) Calculated temperature increasing $\Delta T$ (°C) at the surface of Ag NPs as a function of Ag NPs size, considering the local light intensity increased 300 times. The black areas (hot-spots) present the simulation results of the temperature distributions when the enhanced light field intensity increases 10 (d) and 300 (e) times by using FEM method.

The smaller the particles size, the more particle-particle gaps, leading to the bigger resistance value. As shown in Fig. 4(a, b), the resistance value of Ag NWs fabricated from Ag ions with the proline concentration of 0.20 M (light blue area) is larger than that of 0.10 M.
and 0.15 M (light red area). Furthermore, the more particle-particle gaps, the easier chance to form hot-spots to improve the conductivity. Therefore, the resistance value of Ag NWs containing small NPs decrease rapidly with the increasing power density or nanosoldering time compared to that of large NPs. All of the resistance values gradually decrease as time increases, approaching the saturation state. This is because the soldering as well as melting become faster non-linearly with the power density or nanosoldering time increasing. In our strategy, laser induced soldering and melting of NPs could be locally controlled in a single Ag NW, in which local heating occurs in the vicinity of the NPs. In addition, a large number of Ag NWs can be treated simultaneously without the necessary for precise irradiation of the laser beam at an individual Ag NW the vicinity of the NPs. In addition, a large number of Ag NWs can be treated simultaneously without the necessity for precise irradiation of the laser beam at an individual Ag NW.

Conclusions

We have obtained the highly conductive silver nanowire electrodes by FsLDW with the assistance of the subsequent laser nanosoldering. Laser nanosoldering of Ag NPs was utilized to achieve the low temperature and localized nanosoldering based on surface plasmon resonance enhancement photothermal effect. The dependence of resistance on the nanosoldering time and power density of pulse laser has been investigated, which is of critical importance for improving the electric conductivity of Ag NWs. The plasmon-enhanced laser nanosoldering process has successfully enhanced the electric properties of Ag NWs corresponding to a conductivity of 24.51×10⁵ S/m, which is up to 39% of that of the bulk Ag. Furthermore, we propose the surface plasmon resonance assisted theory to illustrate the nanosoldering process, which is in good agreement with the experimental results. This plasmon-enhanced laser nanosoldering of Ag NWs can be achieved in a controlled manner to yield high-performance nano-electrode for the further applications in microelectronics field.

References


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Competing interests

The authors declare no competing financial interests.

Supplementary information

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