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# Precise assembly and joining of silver nanowires in three dimensions for highly conductive composite structures

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## Abstract

Three-dimensional (3D) electrically conductive micro/nanostructures are now a key component in a broad range of research and industry fields. In this work, a novel method is developed to realize metallic 3D micro/nanostructures with silver-thiol-acrylate composites via two-photon polymerization followed by femtosecond laser nanojoining. Complex 3D micro/nanoscale conductive structures have been successfully fabricated with  $\sim 200$  nm resolution. The loading of silver nanowires (AgNWs) and joining of junctions successfully enhance the electrical conductivity of the composites from insulating to  $92.9 \text{ S m}^{-1}$  at room temperature. Moreover, for the first time, a reversible switching to a higher conductivity is observed, up to  $\sim 10^5 \text{ S m}^{-1}$  at 523 K. The temperature-dependent conductivity of the composite is analyzed following the variable range hopping and thermal activation models. The nanomaterial assembly and joining method demonstrated in this study pave a way towards a wide range of device applications, including 3D electronics, sensors, memristors, micro/nanoelectromechanical systems, and biomedical devices, etc.

Supplementary material for this article is available [online](#)

Keywords: precise assembly, joining, silver nanowires, nanofabrication, three dimensional

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Over the last decade, micro/nanostructures have been receiving increasing attention due to their potential applications in modern

nanotechnology and emerging fields, such as microelectronics [1], flexible electrodes [2], micro/nanoelectromechanical systems (MEMS/NEMS) [3], photonics and optoelectronics [4], metamaterials [5], and energy storage [6]. As it becomes increasingly challenging for Moore's Law to continue to push the two-dimensional miniaturization limit toward the atomic level, research on the integration/assembly of functional micro/nanostructures in three-dimensional (3D) space for device applications is becoming increasingly important [7]. Direct laser writing by two-photon polymerization (TPP) has been established as one of the most promising methods for achieving 3D

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fabrication in micro/nanoscales, due to its ability to produce arbitrary and complex 3D structures with subwavelength resolution [8]. However, the lack of TPP-compatible and functional materials represents a significant barrier to realize the functionality of the fabricated devices, such as high electrical conductivity, high environmental sensitivity, high mechanical strength, etc [9].

Recently, several studies have demonstrated the use of TPP for the fabrication of electrical conductive microstructures, including selective plating [10], metallic inversion [4], *in situ* photoreduction with photopolymerization [11], and direct photopolymerization of composite resins [12]. Both selective plating and metallic inversion methods involve multiple, time- and cost-intensive synthetic steps. *In situ* photoreduction synthesis allows single-step fabrication of two-dimensional patterns of noble metallic NPs [11], discrete NP-doped polymer microstructures [11], and even bridge-like conductive elements [11]. However, this method is intrinsically difficult to simultaneously satisfy precise morphology and high electrical conductivity [13]. In our previous work, multiwalled carbon nanotubes (MWNTs) were employed for the fabrication of 3D conductive micro/nanostructures [12]. The composite photoresist showed significantly enhanced electrical conductivity (up to  $46.8 \text{ S m}^{-1}$  @ 0.2 wt% MWNTs), with strong anisotropic properties and high optical transmittance. Nevertheless, the composite conductivity is still limited by the intrinsic conductivity of MWNTs (roughly  $5 \times 10^3$  to  $5 \times 10^6 \text{ S m}^{-1}$ ) [14] and relatively high tube-to-tube contact resistance. Compared with carbon nanotubes, silver (Ag) is considered to be an ideal conductive material ( $6.3 \times 10^7 \text{ S m}^{-1}$ ). The small dimension and high aspect ratio of one-dimensional silver nanowires (AgNWs) could effectively transport electrical carriers along one controllable path [15], and moreover, interconnected nanowire networks can be realized by the wire-to-wire junction joining/welding [2, 16], thereby leading to increased electrical properties with a low nanofiller loading concentration. However, to the best of our knowledge, 3D AgNWs-based micro/nanostructures of high electrical conductivity and surface morphology have not been realized yet.

In this paper, we report a method for designing and preparing a TPP-compatible AgNW-thiol-acrylate (ATA) composite photoresist and simultaneously achieving reliable 3D micro/nanofabrication with high structuring accuracy and high electrical conductivity (figure 1(a)). Moreover, a femtosecond laser was used for the nanojoining of AgNW junctions inside a polymer matrix to further reduce the wire-to-wire junction resistance and thus increase the electric conductance of the overall 3D micro/nanostructure substantially. Finally, the temperature-dependent electrical conductivity and the resistance switching mechanism of the as-fabricated ATA bridge structures were investigated by employing the variable range hopping (VRH) model and thermal activation estimation. The as-fabricated bridge structures made of ATA composites showed a substantial three-step increase in electrical conductivity over ten-orders of magnitude with the AgNW addition, femtosecond laser nanojoining and resistive switching, respectively (figure 1(b)). These nanocomposites are distinct from the conventional view of the electrical properties

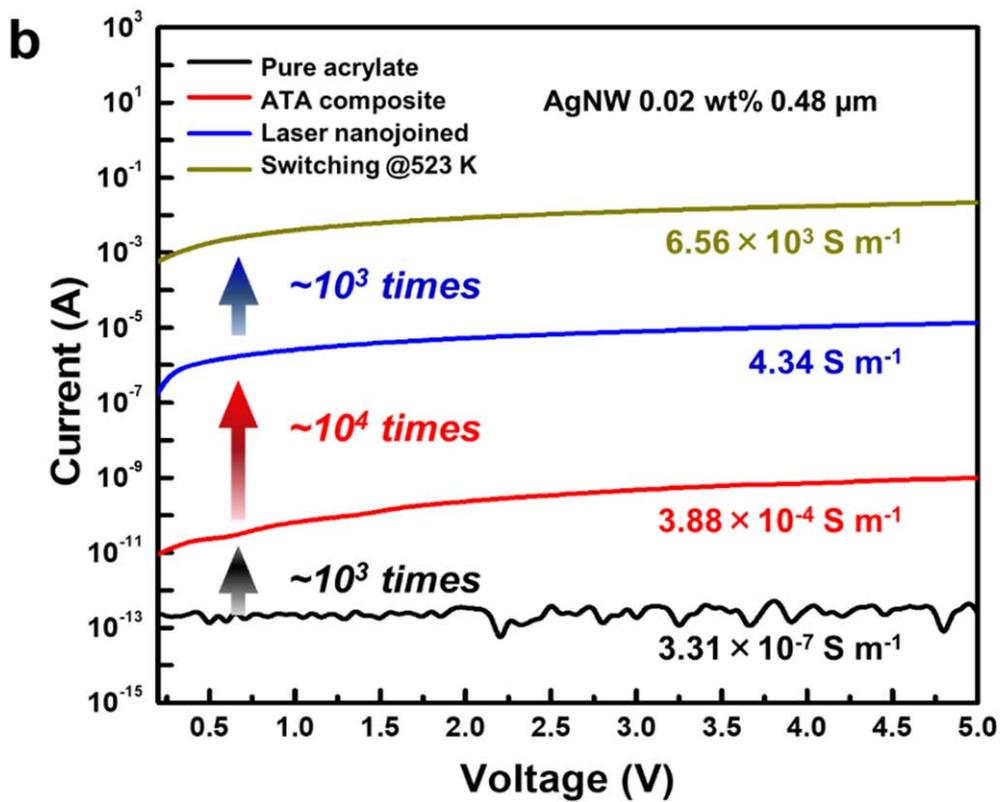
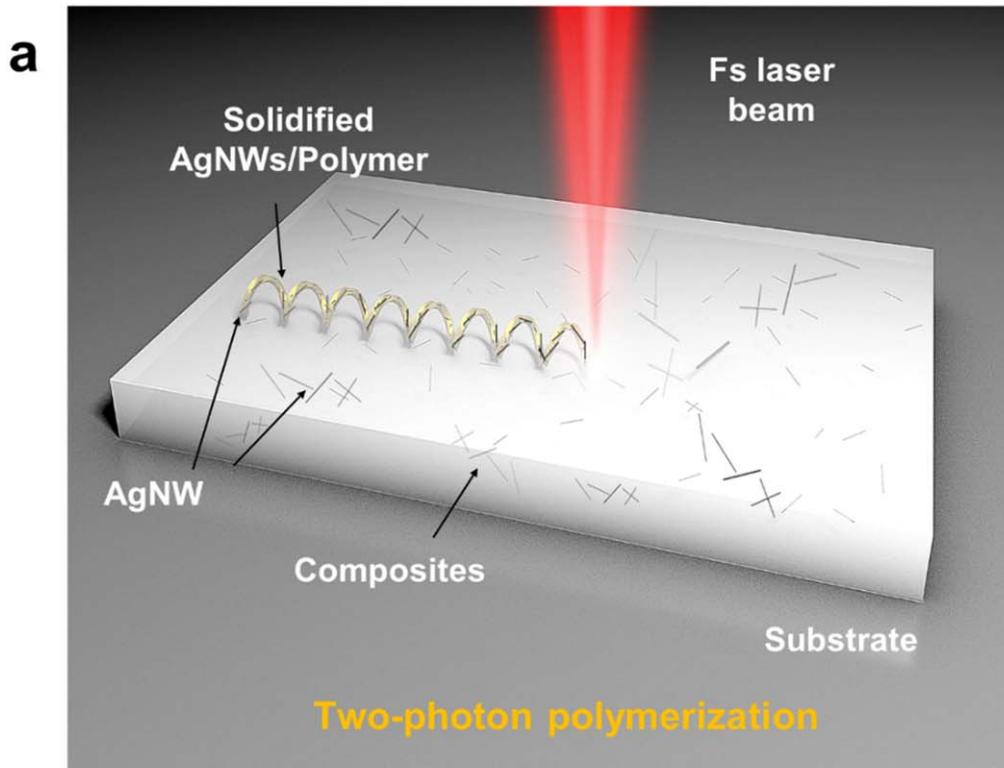
in polymer nanocomposites as either insulating or conducting below and above the percolation threshold, respectively. The fabrication method simultaneously realized the user-defined arbitrary 3D micro/nanostructuring, high spatial resolution, fine surface quality, and superior electrical conductivity, which makes it promising for various functional device applications, including 3D electronics, sensors, plasmonics, memristors, MEMS/NEMS, and biomedical devices, etc.

## 2. Result and discussion

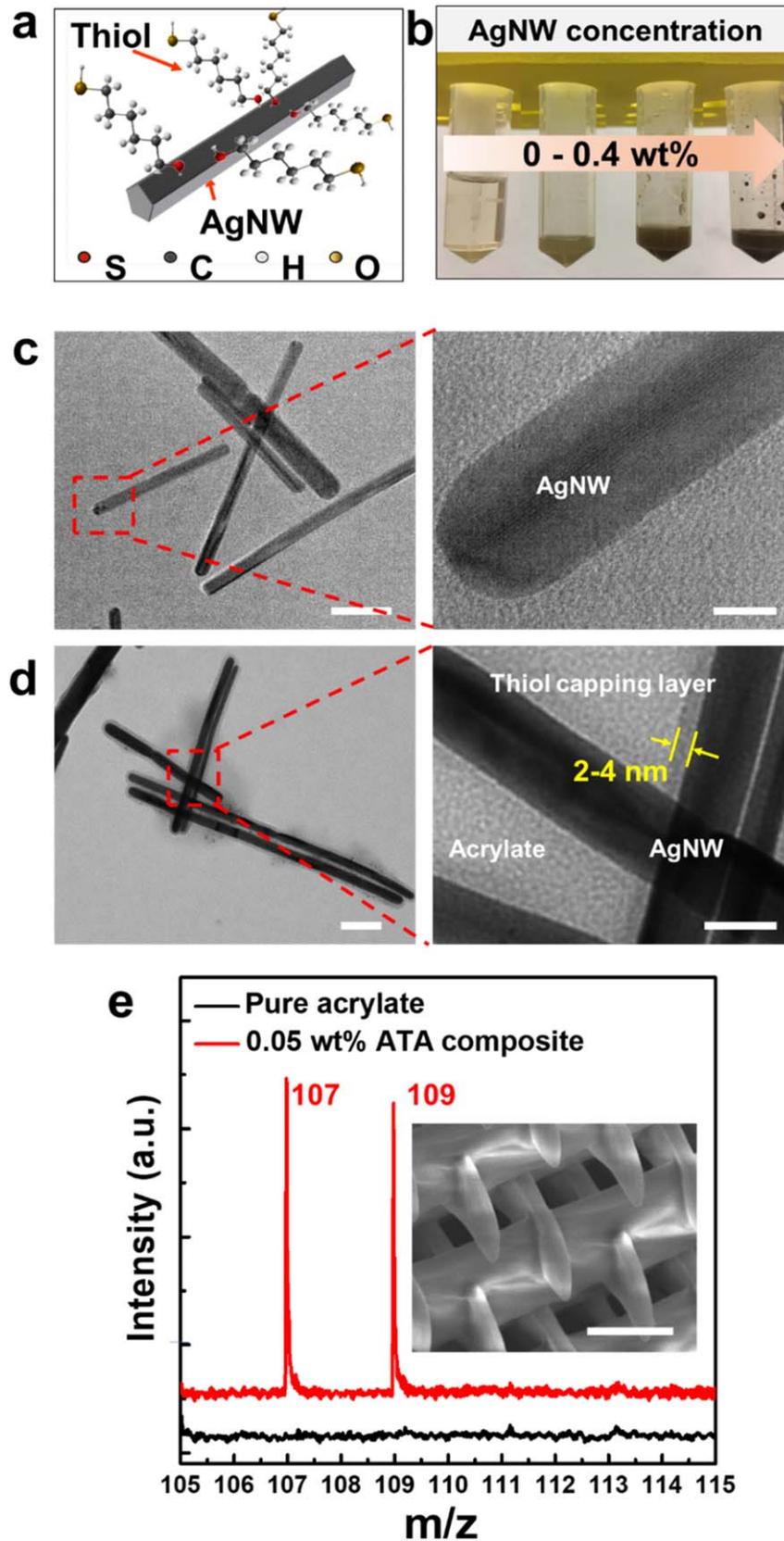
### 2.1. Preparation of ATA composite resin

The TPP-compatible ATA composite resins were prepared by directly mixing thiolated AgNWs with acrylate-based resin (table S1, supporting information available online at [stacks.iop.org/IJEM/1/025001/mmedia](https://stacks.iop.org/IJEM/1/025001/mmedia)) and characterized using transmission electron microscopy (TEM) and mass spectrometry. Silver nanowires were used in the composites with lengths ranging from 0.1 to  $4.15 \mu\text{m}$  and concentrations from 0.005 to 0.4 wt%. Nanowires with an average diameter of 40 nm and lengths from 0.48 to  $4.15 \mu\text{m}$  were prepared by breaking  $>30 \mu\text{m}$  long AgNWs using ultrasonic vibration (figures S1(a)–(e), supporting information). Using TPP processing to fabricate structures, the laser beam will be scattered by agglomerated nanowires at high concentration, which will distort the fabricated structures. Therefore, the maximum 0.4 wt% AgNW concentration was chosen to avoid agglomeration until changes in the electrical properties of the composites reaching a plateau value. Moreover, it is expected that shorter AgNWs could result in better dispersion and smoother composite structure surfaces compared with longer ones. However, a balance on AgNW length should be considered since it is easier to form a connecting network in polymers with the same effective concentration by using longer AgNWs. To obtain stable and homogeneous dispersion of AgNWs, thiol with a suitable length of carbon chains ( $\text{HOC}_n\text{H}_{2n+1}\text{SH}$ ,  $n = 6$ ) was used as the surfactant in the composite resins (figure 2(a)). The composite resins appeared to be stable under ambient conditions with a color transition from clear to gray as the AgNW concentration increased (figure 2(b)).

TEM images of the ATA composite (figure 2(d)) were captured by directly analyzing the thin film made by TPP with a thickness of  $\sim 1 \mu\text{m}$  on a copper grid. A shell (2–4 nm thickness) comprised of multiple, intertwined layers of thiol molecules formed on the surface of the AgNWs, as the thiol sulfur formed a strong chemical bond with Ag [17], leaving the other group (OH) miscible in the acrylate resin to undergo subsequent polymerization reactions [18] (magnified image in figure 2(d), figures S1(f) and (g), supporting information). The thiol layer allowed the individual AgNWs to maintain distance between each other, preventing them from aggregation and causing the resulting thiolated AgNWs to be well dispersed in the polymer matrix. In addition to TEM characterization, a KrF excimer laser (248 nm, 23 ns) was used to assist laser ablation in ambient mass spectrometry using a



**Figure 1.** (a) Schematic illustration of 3D micro/nanofabrication of functional ATA composites by TPP lithography. (b) *I*-*V* curves of bar-shaped channels fabricated using pure acrylate (black) and ATA composite (red), after laser nanojoining (blue), and thermally treated at 523 K (yellow). The AgNW concentration and length were 0.02 wt% and 0.48  $\mu\text{m}$ , respectively.



**Figure 2.** Thiol-capped AgNWs embedded in polymer matrix. (a) Illustration of AgNW thiol functionalization. (b) Optical image of the ATA composite resins with 0, 0.05, 0.2, and 0.4 wt% AgNW concentrations. The AgNW length was kept at  $0.48 \mu\text{m}$ . TEM micrographs of (c) AgNWs and (d) thiol-capped ATA composite thin film. (e) Mass spectra of micro-woodpile structures fabricated using pure acrylate and the ATA composite. Inset shows the SEM micrograph of the woodpile fabricated using the composite resin (0.05 wt% AgNW concentration,  $0.48 \mu\text{m}$  AgNW length). The laser power and scanning speed were  $17.5 \text{ mW}$  and  $50 \mu\text{m s}^{-1}$ , respectively. Scale bar: (c), (d) left  $100 \text{ nm}$ , right  $10 \text{ nm}$ ; (c) inset  $2 \mu\text{m}$ .

time-of-flight mass spectrometer (TOF-MS). Two prominent peaks were observed in the spectra of a micro-woodpile composite structure, at 107 and 109, which were ascribed to isotopes of  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , respectively (figure 2(e)) [19]. A clear change in contrast was observed in the scanning electron microscopy (SEM) image of the micro-woodpile (figure 2(e) inset), indicating a compositional difference of metallic phase inside the polymer matrix, revealing the existence of the AgNWs in the ATA composite [20]. The SEM and TEM results provide experimental evidence that the AgNWs within the polymer matrix distributed in a combined way of separate nanowires and connected networks. Therefore, TPP-compatible ATA composite resins, with thiolated AgNWs uniformly dispersed in the acrylate resins, were successfully prepared. Our approach also paves a way for dispersion and assembly of various functional nanomaterials into 3D polymer structures, including carbon nanotubes, metallic NPs, semiconductor NPs or magnetic NPs, for the fabrication of advanced micro/nano-devices with additional functional properties.

## 2.2. Fabrication of 3D metallic micro/nanostructures

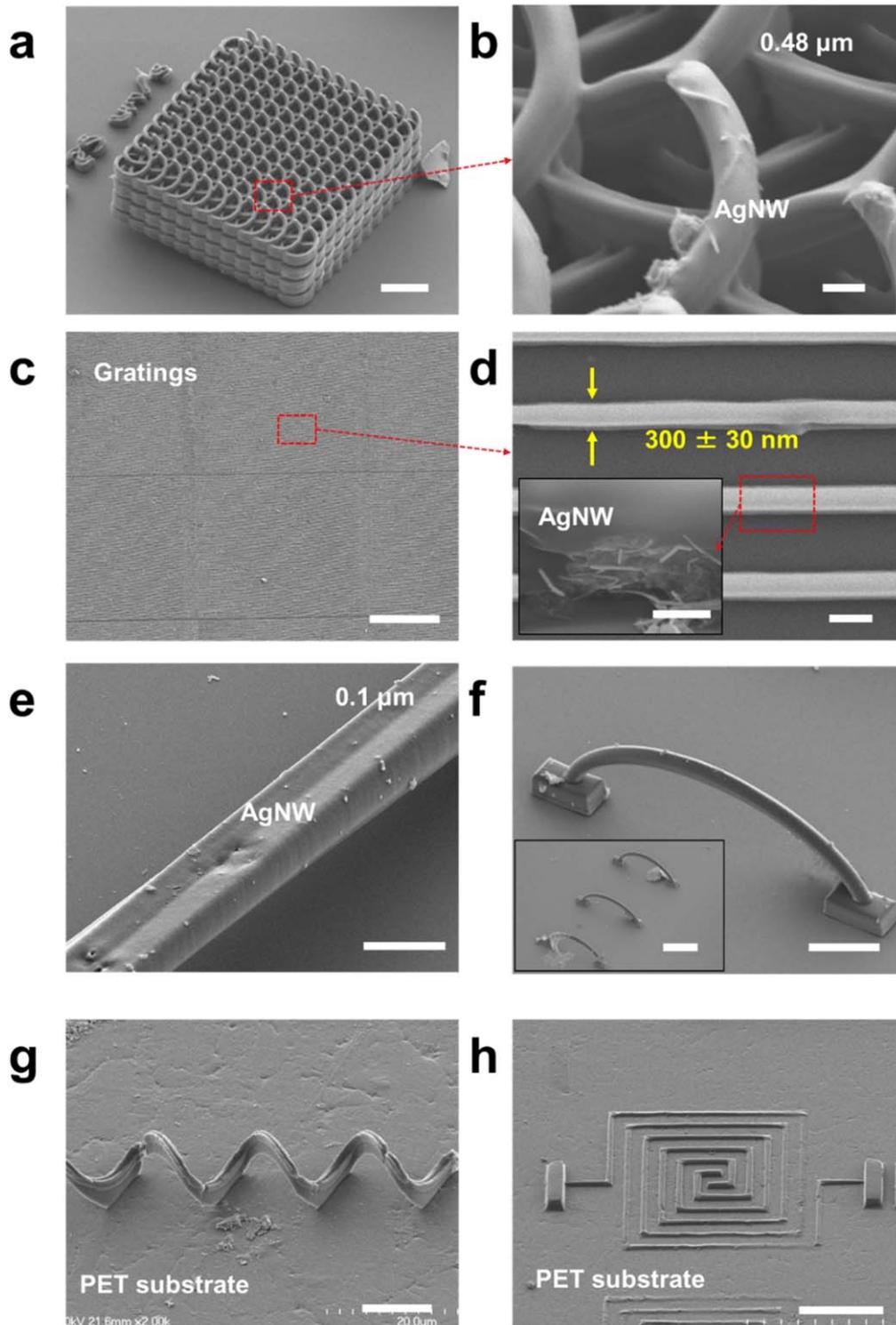
After identification and characterization of the composite resins, the ATA composites were employed to fabricate conductive 3D micro/nanostructures with high spatial resolution and fine surface quality. An integrated set of beam transport optics directed the laser output with circular polarization to a final focusing objective ( $63\times$ ,  $\text{NA} = 1.4$ ) that scanned in 3D according to the user-defined geometric designs and assemble AgNWs within the focal spot. After TPP lithography, the samples were developed. The unsolidified resin was rinsed away, leaving AgNWs embedded inside the solidified ATA composite structures on the substrates. Figures 3(a)–(h) shows examples of 3D microstructures made from the ATA composite resins with various AgNW lengths on both rigid and flexible substrates. A spiral-like photonic crystal and large-scale gratings were fabricated with  $0.48\ \mu\text{m}$  long AgNWs embedded and confined within the composite lines (figures 3(a)–(d)). A suspended microbar, arc-shaped wire bonding bridges, a microhelix, and a microcapacitor were fabricated using ATA composite with  $0.1\ \mu\text{m}$  long AgNWs (figures 3(e)–(h)). The TPP fabrication was independent of substrates, which can be conducted on either flexible polyethylene terephthalate (PET) or rigid substrates, such as silicon (Si) wafer and glass substrates.

To optimize the laser fabrication condition, the dependence of structural resolution on the laser power (figure 3(i)) was carefully evaluated. Large parallel cuboid supports were fabricated first, and then a series of lines were scanned across the supports. The suspended lines were fabricated using different laser powers and a fixed writing velocity of  $100\ \mu\text{m}\ \text{s}^{-1}$ . A minimum line width of  $202 \pm 18\ \text{nm}$  was observed at a polymerization threshold power of  $3\ \text{mW}$ . It was also found that the feature size of the fabricated woodpile structures decreased with the existence of AgNWs in the composite under the same processing conditions (figure S2, supporting information). The line width of the sample prepared with  $0.2\ \text{wt}\%$  AgNWs exhibited a  $\sim 15\%$  decrease

compared with that of pure acrylate structure, which can be attributed to absorption by AgNWs in the path of the laser beam prior to reaching the focal point [21].

The elliptically shaped cross-section was revealed by multi-photon ablation (MPA) on the solidified grating structures on a glass substrate (figure S3, supporting information). This ‘TPP + MPA’ method has been demonstrated to be an effective technique for the fabrication of microvoids and microfluidic structures [22]. Polarization of the laser beam has been reported to affect the intensity distribution and thermal gradients around the focal spot thus leading to different polymerization rates, which can, in certain cases, affect the feature size [23]. In our work, the circular polarization of incident light could ensure a more spherical voxel within the  $xy$ -plane [24] and avoid polarization-dependent linewidth.

The electrical conductivity of the composites was characterized by performing cyclic  $I$ – $V$  measurements of  $100\ \mu\text{m}$  long line and bar-shaped channel bridging two pairs of gold (Au) electrodes. A single line was fabricated using the ATA composite ( $0.05\ \text{wt}\%$  AgNW concentration,  $0.1\ \mu\text{m}$  long-AgNWs), and the resulting conductivity from  $I$ – $V$  measurement was calculated to be  $12.5\ \text{S}\ \text{m}^{-1}$  (figure S3(c), supporting information). Bar shape channels with a cross-section of  $5 \times 5\ \mu\text{m}^2$  were fabricated in the following experiments, due to the multilayer structure of the host polymer could provide sufficient charge carriers’ transport channels (i.e. connected AgNW junctions in 3D), and therefore avoid instability compared with single layer or line structures. Figure 3(j) shows the electrical conductivity of the ATA composites as a function of AgNW concentrations at a fixed AgNW length of  $0.1\ \mu\text{m}$ . The experimental results indicate that the AgNW loading plays a significant role in determining the conductivity of the composites. With only  $0.005\ \text{wt}\%$  AgNWs loaded into the acrylate resin, an approximate seven-orders of magnitude increase in the electrical conductivity was observed, which could be ascribed to the highly uniform distribution of short-length AgNWs. The conductivity of the composite polymers increased as the AgNW concentration increased and reached a maximum of  $32.51\ \text{S}\ \text{m}^{-1}$  at  $0.2\ \text{wt}\%$  AgNW concentration. Furthermore, the effect of AgNW length on conductivity is shown in figure 3(k). With a fixed  $0.02\ \text{wt}\%$  AgNW concentration, the conductivity increased from  $2.35 \times 10^{-4}$  to  $1.13 \times 10^{-3}\ \text{S}\ \text{m}^{-1}$  as the AgNW length increased from  $0.3$  to  $1.35\ \mu\text{m}$ , due to the reduced nanowire distance and sufficient conduction pathways established by the longer AgNWs. However, as the AgNW length exceeded  $1.35\ \mu\text{m}$ , the conductivity of the ATA composite dropped slightly. The  $4.15\ \mu\text{m}$  long AgNWs were prone to forming larger aggregates which were centrifuged out of the composite resin, thus the ATA composite would have a smaller ‘effective’ filler concentration. The same phenomenon was observed for the composite with  $0.1\ \mu\text{m}$  long AgNWs at a  $0.4\ \text{wt}\%$  loading concentration (figure 3(j)). Moreover, long AgNWs tended to produce a high number of networked AgNWs with a relatively large nanowire cross-junction resistance [25]. Consequently, the as-fabricated conductivity of the ATA composites with  $0.3$ – $4.15\ \mu\text{m}$  long AgNWs ( $10^{-4}$  to  $10^{-3}\ \text{S}\ \text{m}^{-1}$ ) was lower than  $0.1\ \mu\text{m}$  long AgNWs at the



**Figure 3.** SEM micrographs of various functional micro/nanostructures fabricated on (a)–(f) rigid Si/SiO<sub>2</sub> substrates and (g), (h) flexible PET substrates, including (a), (b) a spiral-like photonic crystal, (c), (d) large-scale gratings, (e) a suspended microbar, (f) arc-shaped wire bonding bridges, (g) a microhelix, and (h) a microcapacitor. The AgNW length was 0.48  $\mu\text{m}$  for (a)–(d) and 0.1  $\mu\text{m}$  for (e)–(h). The laser power and scanning speed used in the TPP fabrication were (a), (b), (g) 12.5 mW and 25  $\mu\text{m s}^{-1}$ , (c)–(e), (h) 25 mW and 1  $\text{mm s}^{-1}$ , and (f) 17 mW and 1  $\text{mm s}^{-1}$ , respectively. A thin layer of Ni was coated on the back of transparent PET substrate to generate sufficient refractive index difference with the composite resin. (i) Dependence of feature size on the laser power used for TPP lithography. The inset is a suspended line with a minimum line width of  $202 \pm 18$  nm fabricated using the ATA composite resin with a 0.2 wt% AgNW concentration and a 0.1  $\mu\text{m}$  AgNW length. (j) Electrical conductivity of the ATA composites with respect to the AgNW concentration. The AgNW length was kept at 0.1  $\mu\text{m}$ . The inset shows the SEM micrograph of a microbar-shaped channel. (k) Electrical conductivity of the ATA composites with respect to the AgNW length. The AgNW concentration was kept at 0.02 wt%. Scale bar: (a) 10  $\mu\text{m}$ ; (b) 1  $\mu\text{m}$ ; (c) 50  $\mu\text{m}$ ; (d) 500 nm; (e) 5  $\mu\text{m}$ ; (f) 20  $\mu\text{m}$ , inset: 50  $\mu\text{m}$ ; (g) 10  $\mu\text{m}$ ; (h) 50  $\mu\text{m}$ ; (j) inset: 20  $\mu\text{m}$ .

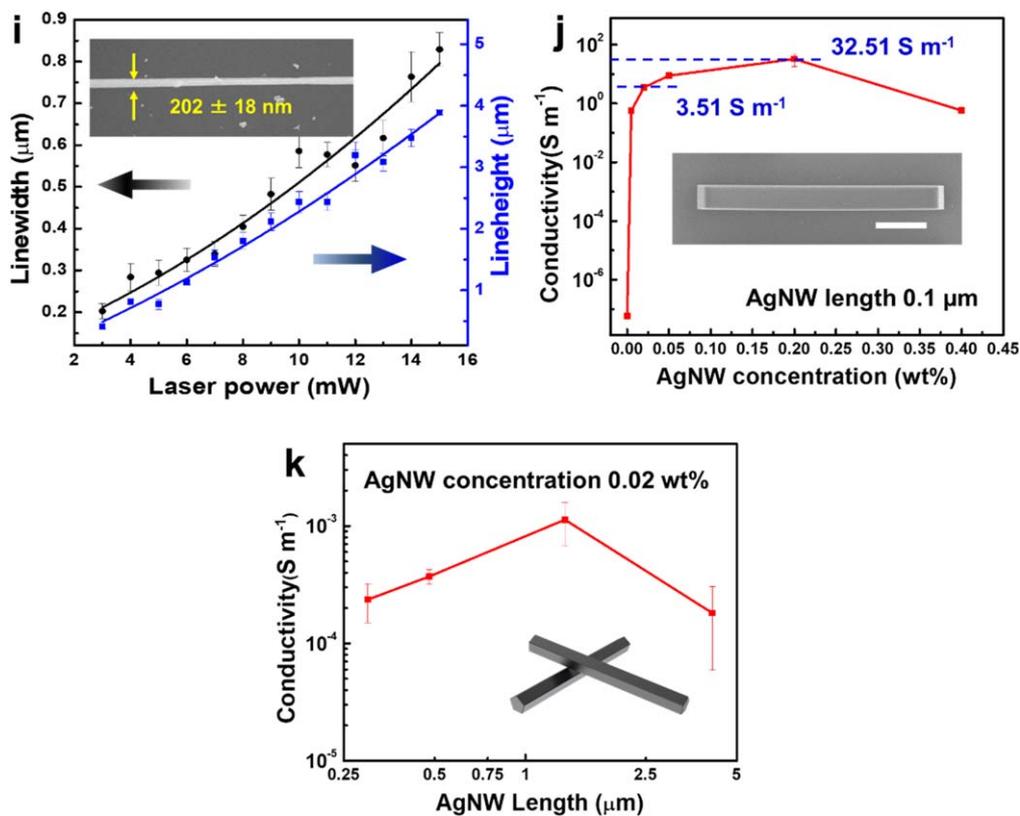


Figure 3. (Continued.)

same concentration ( $3.51 \text{ S m}^{-1}$ , figure 3(j)). Based on the ATA composites, the TPP technique offered arbitrary 3D structuring capability with relatively high electrical conductivity as well as submicron spatial resolution. However, in the ATA composites, although the thiol sheath layer significantly enhanced the disperse quality of the AgNWs in the polymer matrix, it also introduced conduction barriers between nanowires. Therefore, the authors needed to find a way to further enhance the electrical conductivity of the as-fabricated 3D micro/nanostructures.

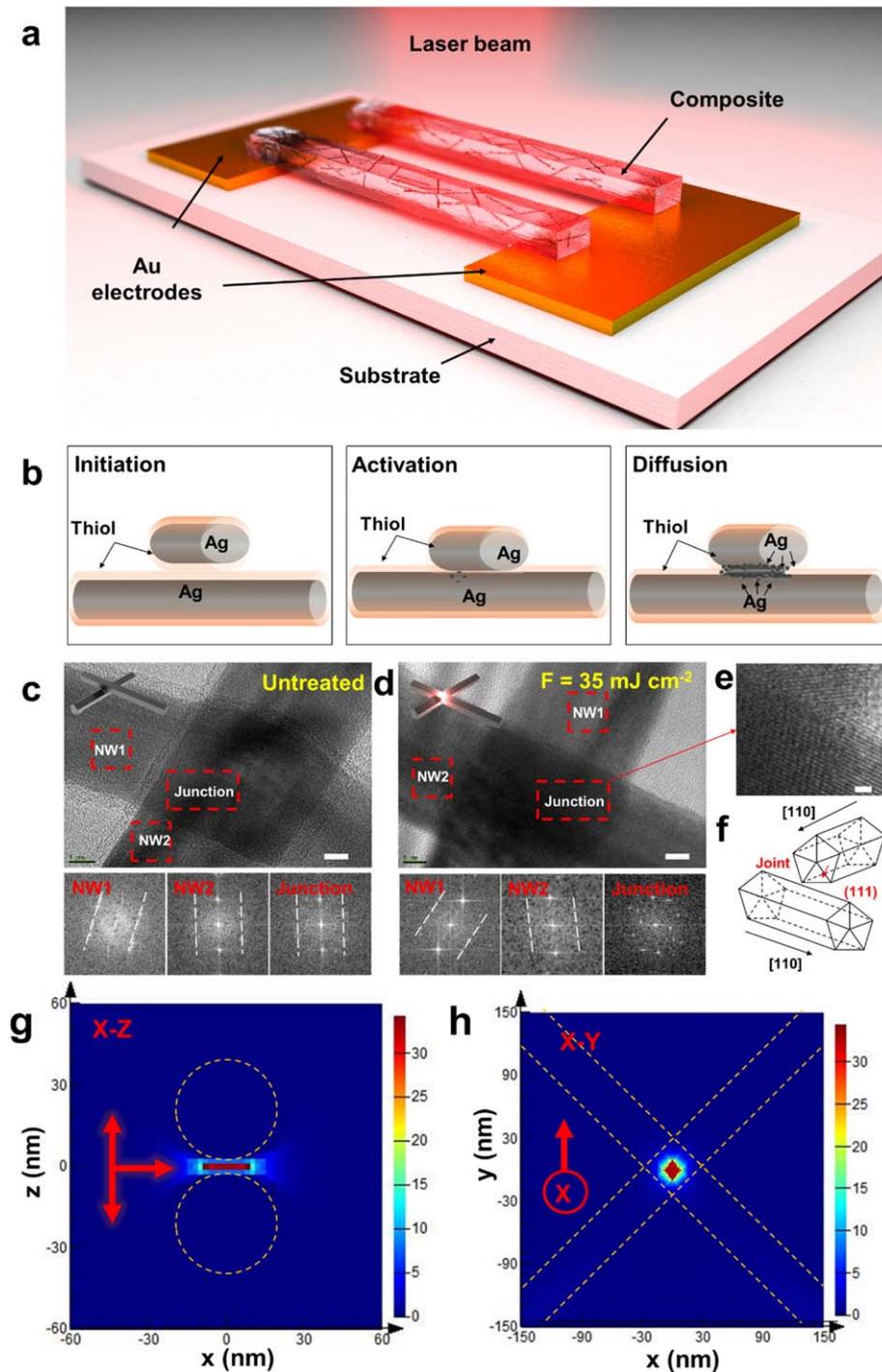
### 2.3. Laser joining of the AgNW junction

With an aim of optimizing the electrical conductivity of the ATA composites, a nanojoining process was developed using femtosecond laser pulses to further reduce the wire-to-wire junction resistance of AgNWs. A variety of attempts have been made to improve the junction contacts, including Joule heating [26], thermal annealing [27], mechanical pressing [28], and plasmonic welding [29]. However, the high surface-to-volume ratio of the AgNWs makes them vulnerable to traditional thermal treatments which cause the AgNWs to undergo a morphological instability and fragmentation into a chain of nanospheres, due to the Rayleigh instability (figure S4, supporting information) [30]. This instability presented a challenge to applying thermal annealing as a method of reducing the junction resistance of AgNWs. Femtosecond

laser-induced plasmonic joining appeared to be a good candidate in terms of noncontact processing and minimum thermal damage to the nanowires and the substrate [29]. It is known that femtosecond laser irradiation can deposit energy with a time scale shorter than the electron-phonon equilibrium time and constrain the heat generation within a well-defined hot spot region determined by the distribution of the localized electrical field between the gap of AgNWs [29, 31].

After TPP fabrication, a femtosecond laser (1 kHz amplified Ti:sapphire laser system, Legend F, Coherent Inc.) at 800 nm was used to join the junctions of AgNWs inside the composite structures (figure 4(a)). As shown in figure 4(b), the nanojoining process can be described in three stages: (1) high intensity laser field was concentrated at the AgNW junctions, which initiated the decomposition of the thiol layer and softened the lattice of the AgNWs [32]; (2) the Ag atoms at the junction were thermally excited, and some portion of the material was ejected in the form of NPs (supported by the formation of NPs after laser irradiation, figure S5, supporting information); and (3) these excited NPs possessed high mobility, which diffused to the AgNW junctions and enabled the AgNWs to be joined locally (figure 4(d), figure S6, supporting information).

In a first attempt, AgNW networks were irradiated with different laser energies to obtain optimized parameters (figure S6, supporting information). As the network was processed with a sufficient laser fluence ( $35 \text{ mJ cm}^{-2}$ ), the SEM images showed evidence of spheroidization, fusion, and significant



**Figure 4.** Femtosecond laser nanojoining of AgNW junctions within the ATA composites. (a) Schematic of the laser nanojoining process. (b) Illustration of joining process represented by cross-sectional views of the AgNW junctions (i) initiation, (ii) activation, and (iii) diffusion. TEM micrographs of AgNW junctions within the composite thin film (c) before and (d) after laser irradiation. Insets represent the FFT patterns of selected areas of NW 1, NW 2, and junction. Parallel lines in the insets show the crystal orientations in different areas. (e) Magnified HRTEM image of the joint area formed by laser nanojoining. (f) Scheme of AgNW joining by merging over (111) growing plane, where central axis of the AgNWs in the [110] direction. (g), (h) FDTD simulation of irradiance intensity distributions at the AgNW junction in XZ and XY planes. Dashed circles and lines indicate the AgNWs with the diameter of 40 nm and the length of 0.48  $\mu\text{m}$ . The gap distance was set to be 4 nm in the z direction. The electric field of the incident beam was in the YZ-plane (double arrow), and incident radiation propagated in the y direction (single arrow). (i)  $I$ - $V$  curves of a bar-shaped channel before and after femtosecond laser nanojoining. The AgNW concentration and length were 0.02 wt% and 0.48  $\mu\text{m}$ , respectively. (j) Electrical conductivity of the ATA composites before (black curve) and after laser nanojoining (red curve) with respect to the AgNW concentration. The AgNW length was kept at 0.1  $\mu\text{m}$ . (k) Electrical conductivity of the ATA composites before (black curve) and after laser nanojoining (red curve) with respect to the AgNW length. The AgNW concentration was kept at 0.02 wt%. Scale bar: (b) inset: 50  $\mu\text{m}$ ; (c), (d) 5 nm; (e) 1 nm.

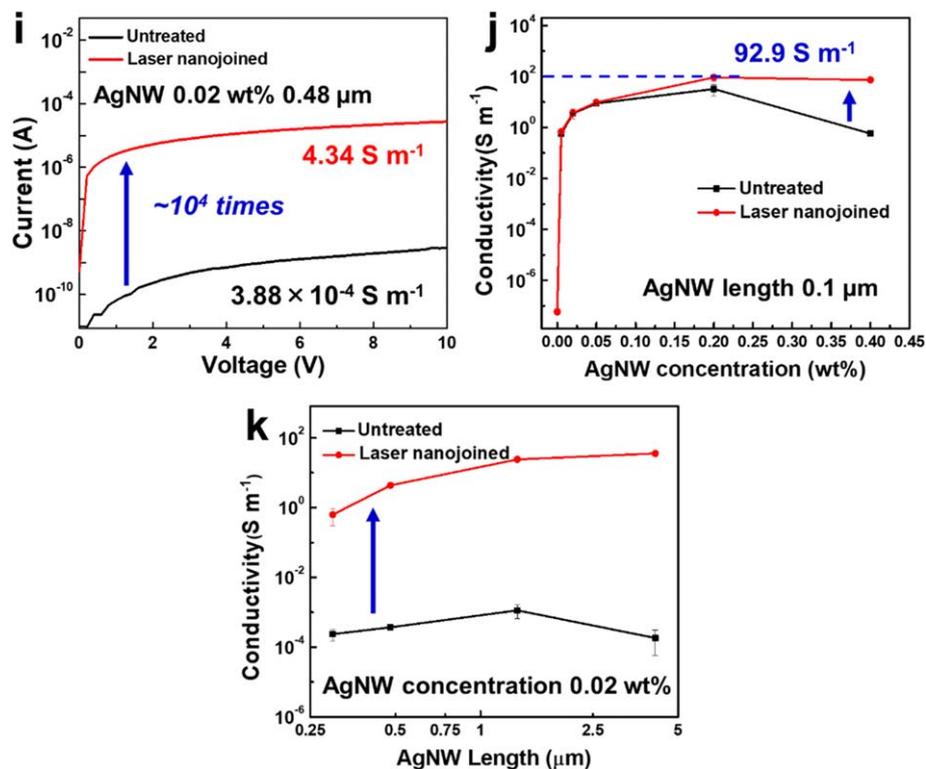
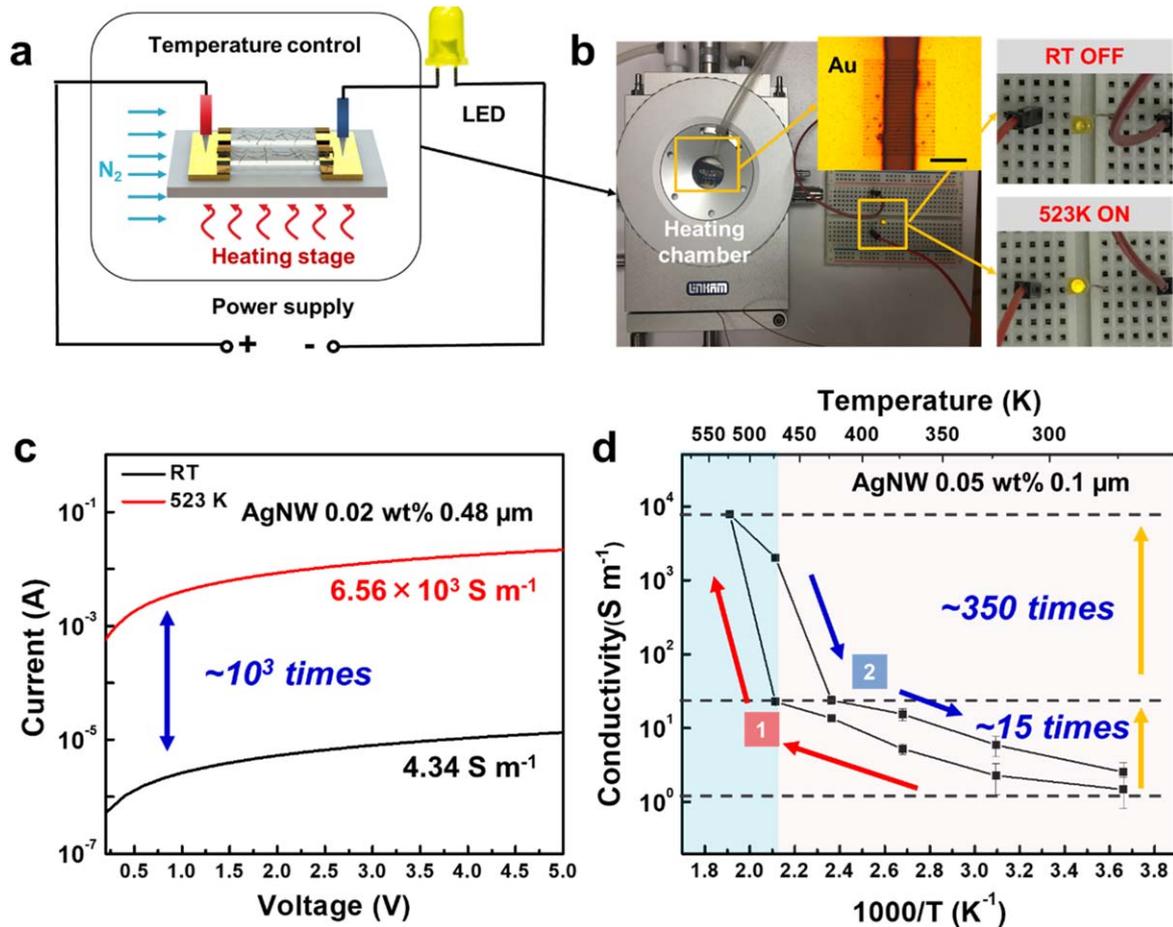


Figure 4. (Continued.)

local change in morphology at the junctions, while the rest of the AgNWs remained intact. A further increase in laser fluence induced photofragmentation and caused the breakup of the AgNWs [33]. Once the optimized irradiation conditions were obtained, laser nanojoining was carried out on the solidified ATA composites after the TPP process. The ATA composite films were highly transparent at 800 nm (figure S7, supporting information), thus enabling laser energy to be predominately absorbed by the AgNWs for proper nanojoining. High resolution TEM (HRTEM) images of the AgNW junctions before and after laser irradiation are shown in figures 4(c) and (d). Fourier spectra were obtained by fast-Fourier transform (FFT) from three different areas in each figure. Before laser irradiation, two AgNWs were laid on each other and separated by the thiol sheath. The diffraction patterns of the two nanowires were visible along two different directions, with roughly equal intensity and certain rotation symmetry ( $\sim 45^\circ$ ). These diffraction patterns represented the [110] growth direction of the AgNWs (the long axis of the nanowires). The junction showed diffraction spots primarily along a single direction, matching the diffraction pattern from the bottom nanowire. After laser illumination, the diffraction patterns and lattice structures at the contact junction were different from both of the individual nanowires (figures 4(d) and (e)). This revealed a localized laser-induced Ag atom diffusion and recrystallization following the (111) plane at the junction area during laser irradiation [34] (figure 4(f)). Moreover, it is important to point out that the original crystal orientation was intact in each NW at locations away from the junction.

A four-orders of magnitude increase in electrical conductivity, from  $\sim 3.88 \times 10^{-4}$  to  $4.34 \text{ S m}^{-1}$ , was observed in a bar-shaped channel structure fabricated using the ATA composite (0.02 wt% AgNW concentration,  $0.48 \mu\text{m}$  long-AgNWs) after laser illumination, indicating the successful nanojoining of AgNWs inside the composites (figure 4(i)). In addition, the laser nanojoining process was demonstrated to be more effective on composite resins with longer AgNWs (figures 4(j) and (k)). The enhanced electrical performance was gauged by the ratio of the conductivity with and without laser irradiation ( $\sigma_{\text{joined}}/\sigma_{\text{as-fabricated}}$ ). For the ATA composite with  $0.1 \mu\text{m}$  long AgNWs, the ratio increased from 1.18 to 126.89 as the AgNW concentration increased from 0.005 to 0.4 wt%. The conductivity reached a maximum of  $92.9 \text{ S m}^{-1}$  with 0.2 wt% AgNWs concentration (figure 4(j)). In the case of the composite with a longer AgNW length, the ratio increased from  $2.65 \times 10^3$  to  $1.97 \times 10^5$  with the increase in the AgNW length, due to the effective joining of an increased number of networked AgNWs in the composites (figure 4(k)).

To disclose how the AgNWs were locally joined together, finite-difference time-domain (FDTD) modeling of an individual AgNW and AgNW junction was conducted. The localized surface plasmon (SP) of a free-standing single AgNW (40 nm diameter,  $1.5 \mu\text{m}$  length) occurred at 364 nm, which was far away from the wavelength of the femtosecond laser. Therefore, the joining of AgNWs does not rely on the SP of individual AgNWs (figure S8, supporting information). With the 780 nm laser incident to the AgNW junction, the free electrons on the metal surface oscillated collectively, leading to a local electromagnetic field enhancement in the



**Figure 5.** (a) Demonstration of temperature-dependent electrical conductivity of the ATA composites as electrical conductor in an LED circuit. The composite sample was placed in a temperature controllable chamber. (b) Photograph of the ATA composite turning on an LED light when a DC current passes at 523 K. The inset shows the optical image of the bridge bar array. (c)  $I$ - $V$  curves of an as-fabricated bar-shaped channel and thermally treated at 523 K. The AgNW concentration and length were 0.02 wt% and 0.48  $\mu\text{m}$ , respectively. (d) Temperature-dependent electrical conductivity of the composite with a 0.1  $\mu\text{m}$  AgNW length and a 0.05 wt% AgNW concentration. Red arrows and (1) show the heating process. Blue arrows and (2) show the cooling process. Scale bar: (b) inset: 50  $\mu\text{m}$ .

near field. At the AgNW junction, resonance coupling of SP endowed an intense and durable near-field enhancement of approximately 35 times the incident light, which suggests the occurrence of the localized joining effects of the nanowires, matched with our experimental results (figures 4(g) and (h), figure S8, supporting information).

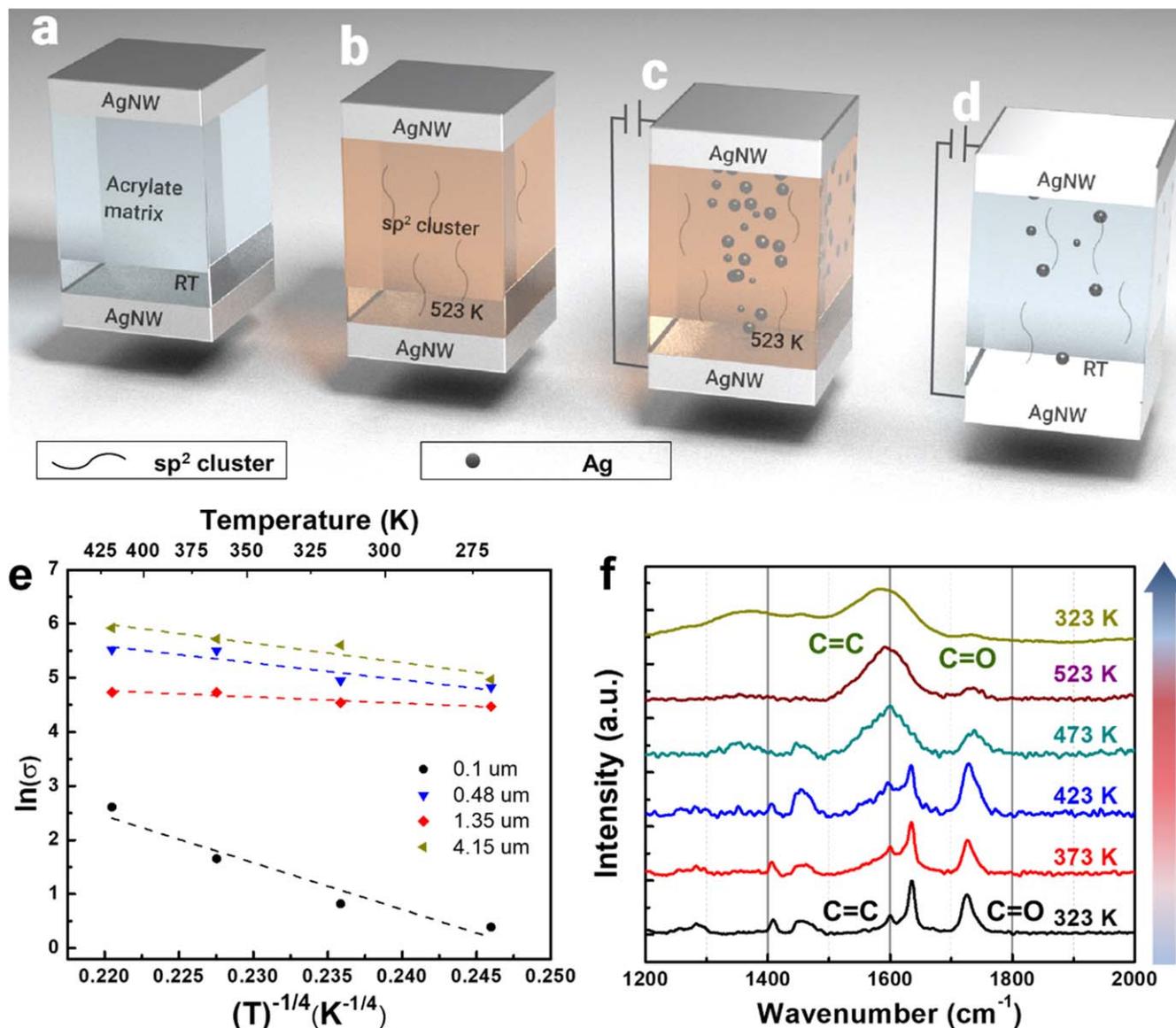
Therefore, both experimental and numerical simulation results confirmed that femtosecond laser irradiation provided a direct, efficient, and selective nanojoining of AgNW junctions in ATA composite, resulting in significantly improved electrical performance.

#### 2.4. Temperature-dependent electrical conductivity of ATA composite

To reveal the physical origin of the electrical charge transport in the composites and explore the potential device applications, temperature-dependent studies of the ATA composites were conducted. As a proof-of-principle demonstration for electronic devices, an array of bar-shaped channels ( $5 \times 5 \times 100 \mu\text{m}^3$   $W \times H \times L$ ) fabricated between two Au electrodes using the ATA composite (0.02 wt% AgNW

concentration, 0.48  $\mu\text{m}$  long-AgNWs) were connected in a simple circuit with a light-emitting diode (LED) (figure 5(a)). The sample was placed in a heating chamber with nitrogen gas protection to control the temperature. When the temperature increased from room temperature (RT) to 523 K, the LED was lit with a DC voltage of 10 V (figure 5(b)). The LED went off as the temperature decreased back to RT. The composite conductivity increased from 4.34  $\text{S m}^{-1}$  at RT to  $6.56 \times 10^3 \text{ S m}^{-1}$  at 523 K (figure 5(c)). This result is a clear demonstration of the temperature-dependent conductive ATA composites and their potential for temperature-dependent electronic devices.

Temperature-dependent  $I$ - $V$  curves were collected for composites with different AgNW lengths and a fixed concentration of 0.05 wt%. The temperature was controlled below 523 K to avoid spheroidization of the AgNWs and decomposition of the polymer matrix. Figure 5(d) depicts the two-stage conductivity increase of the ATA composite with 0.1  $\mu\text{m}$  long AgNWs. The conductivity first increased slowly by  $\sim 15$  times from 273 to 473 K and then increased abruptly by  $\sim 350$  times from 473 to 523 K. This temperature



**Figure 6.** Schematic concept of the resistive switching mechanisms for the ATA composites. (a) Junction structure, (b) formation of  $sp^2$  clusters of acrylate polymer by thermal treatment, (c) temperature- and field-induced Ag filament formation, and (d) recovery to high resistance at RT. (e) The conductivity ( $\ln(\sigma)$ ) data of the composites described by the VRH model for a 3D transport mechanism. The AgNW length was kept at 0.05 wt%. All data were linearly fitted. (f) Temperature-dependent Raman spectra of the ATA composites ranged from 298 to 523 K. The AgNW length and concentration were 0.48  $\mu\text{m}$  and 0.05 wt%, respectively. The average laser power used for Raman spectroscopy was 10 mW (wavelength 514.5 nm).

dependency of electrical conductivity was reversible and applicable for all composite samples. In Stage 1, from 273 to 473 K, charge carriers were activated by elevated temperature with a stable increase in conductivity, showing the semi-conducting behavior of the composites [35]. Using the slopes of an Arrhenius plot, the activation energy  $E_A$  was determined for quantitative analysis (figure S10(b), table S2, supporting information). In Stage 2, from 473 to 523 K, the composite exhibited a jump in electrical conductivity and reached a maximum of  $3.6 \times 10^5 \text{ S m}^{-1}$  at 523 K (0.05 wt% AgNW concentration, 0.48  $\mu\text{m}$  AgNW length). This jump in conductance was demonstrated to be a typical resistive switching phenomenon [36] and occurred by the combination of temperature and field-assisted excitation.

### 2.5. Reversible switching mechanism of electrical conductance

The  $I$ - $V$  measurement revealed that the temperature-dependent reversible switch of electrical conductance was reproducible in the ATA composites. This two-stage variation of electrical conductivity can be described by the VRH model [37] in Stage 1 (from 273 to 473 K) and reversible switching model in Stage 2 (from 473 to 523 K). The reversible switching was attributed to carbonaceous pathways that resulted from degradation of the organic polymer [38] (figures 6(a) and (b)) and metallic Ag filament formation across the polymer matrix (figures 6(c) and (d)).

In order to clarify the electrical conductance enhancement by the AgNW loading in Stage 1, a 3D Mott's variable hopping model, which is a model depicting the low

temperature conduction in strongly disordered systems with localized states, was used to calculate the variation of electrical conductivity with elevated temperature [39]:

$$\sigma(T) = \sigma^0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/4} \right] \quad (1)$$

where  $\sigma^0$  is the temperature-independent prefactor, which represents the limiting value of the conductivity at infinite temperature; and  $T_0$  is the characteristic temperature, which is inversely proportional to the localization length of the charge carriers, thus a small  $T_0$  implies a weak localization and increased conductivity [40]. In figure 6(e),  $\ln(\sigma)$  versus  $T^{-1/4}$  for the composite resins is plotted and fitted for the ATA composites with different AgNW lengths. The characteristic temperature  $T_0$  and linear quality factor  $R^2$  for each sample are summarized in table S2 (supporting information). The characteristic temperature  $T_0$  decreased from  $1.44 \times 10^9$  K (pure acrylate) to  $1.85 \times 10^4$  K (ATA composite, 1.35  $\mu\text{m}$  long AgNWs), indicating a reduced localization of the charge carriers and thus enhanced electrical conductivity [41]. In addition, a diminishing tendency of  $T_0$  and  $R^2$  as the AgNW length increased was observed. Since the metallic ohmic conductance and VRH conductance had the opposite temperature dependences [42], the decreased values of  $T_0$  and  $R^2$  implied that the number of metallic ohmic contacts in the composites increased as the length of the AgNWs got longer, which is consistent with the fact that laser nanojoining is more effective on composite resins with long AgNW lengths. However, in the case of the ATA composite with 4.15  $\mu\text{m}$  long AgNWs, the values of  $T_0$  slightly dropped due to the formation of large clusters that enlarged the hopping distance in the composite.

In Stage 2, the internal chemical reactions and structural phase transitions of the composites were studied by temperature-dependent Raman spectroscopy [43] (figure 6(f)). In the authors' composite system, the glassy transition temperature ( $T_g$ ) for acrylate monomer was found to be 286 K [44], which was unlikely to be the cause of the reversible switching at around 473 K. As shown in the Raman spectra, the transition occurred in a temperature range from 423 to 523 K, that resulted in three Raman peaks at  $\sim 1366$ ,  $\sim 1593$ , and  $1731 \text{ cm}^{-1}$ , which were ascribed to the D, G, and C=O bands. As the temperature increased, the G band intensity slowly increased from RT to 473 K and then increased abruptly until 523 K. The significantly increased  $\text{sp}^2$  bonding indicated the degradation of the acrylate matrix, which was promoted with the AgNWs serving as the catalyst [45], creating special  $\text{sp}^2$  cluster pathways with high electron mobility within the polymer medium (figure 6(b)). However, the G band intensity did not drop as the temperature decreased, indicating a permanent degradation of the polymer matrix.

At temperatures above 473 K, resistive switching behavior occurred with a threshold voltage of 10 V, ascribed to electromigration-induced Ag filament formation (figures S11(a)–(c), supporting information). When an electric field was applied, due to the increased Ag mobility at high temperatures, Ag

atoms dissociated from individual AgNWs to form bridging filaments among the closest AgNWs, bringing them together to form electrical contacts (supported by the nanoparticle formation around AgNW junctions, figure S11(d), supporting information). This Ag filament formation was demonstrated in a single AgNW junction [46] and AgNWs/polystyrene composites [47]. Furthermore, when the bias was removed, the filaments were ruptured, which can be attributed to the thermal motion of Ag atoms within the filaments. Finally, at temperatures below 473 K, the Ag mobility was limited; and the AgNWs were kinetically trapped, returning the ATA composite back to a high-resistance state (figure 6(d)).

The authors' findings demonstrated that the resistive switching of ATA composites can be explained by a combination of  $\text{sp}^2$  carbon cluster pathways and Ag filaments. It is promising that micro/nanostructures made of the ATA composite material can be engineered to exhibit prominent temperature- and electrical-field-dependent electrical behaviors.

### 3. Conclusions

In this work, a new strategy was presented for realizing metallic 3D micro/nanostructures with ATA composites via TPP followed by a femtosecond laser nanojoining process. By employing thiol functionalization, TPP-compatible ATA composite resins were obtained with AgNWs uniformly dispersed in a polymer matrix. Micro/nanoscale 3D conductive structures were successfully fabricated with  $\sim 200$  nm resolution. Moreover, a femtosecond laser irradiation process was conducted to further enhance the electrical conductivity of the solidified ATA composites by up to  $10^5$  times, resulting from the effective joining of AgNW junctions. A strong temperature dependence of the conductivity of the ATA composite was observed and analyzed, revealing the charge carriers' transport mechanism following the VRH and reversible switching models. The nanomaterial assembly and joining method demonstrated in this study represent a new opportunity for developing functional devices for a broad range of applications, such as 3D electronics, temperature sensors, memristors, MEMS/NEMS, and biomedical devices.

### 4. Experimental section

#### 4.1. Materials

Pentagonal AgNWs:  $0.1 \text{ mmol l}^{-1}$  monodispersed pentagonal-shaped AgNWs with a diameter of 40 nm and lengths varying from 0.1 to 0.3  $\mu\text{m}$  in isopropyl alcohol (IPA) solutions were purchased from Sciventions Inc. (supporting information, figure S1). Long AgNWs: 20  $\text{mg ml}^{-1}$  AgNWs dispersed in IPA solutions were purchased from ACS Material, LLC. The AgNWs had an average diameter of 40 nm and average lengths of  $>30 \mu\text{m}$  (figure S1, supporting information). Acrylate photorealist: di-trimethylolpropane tetraacrylate (Di-TMPPTA), benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (BDMP),

and 6-Mercapto-1-hexanol (6-MCH) were purchased from Sigma Aldrich.

#### 4.2. Photoresist preparation

Homemade ATA composite resins were prepared by direct mixing of thiol-functionalized AgNWs, acrylic monomer (Di-TMPTTA), and photoinitiator (BDMP). First, the AgNW aqueous solutions underwent ultrasonic agitation (agitation power: 60 W, SONIFIER<sup>®</sup> SLPe Energy and Branson Ultrasonics) from 30, 60, to 120 min to reduce the average length to 4.15, 1.35, and 0.48  $\mu\text{m}$ , respectively. The surface modification of AgNWs was then performed by mixing the liquid thiol 6-MCH with the aqueous AgNW solution at a concentration of 10  $\text{mmol l}^{-1}$ . The aqueous solution underwent a 120 min ultrasonic bath, resulting in the formation of thiol-capped AgNWs. Excess IPA solvent was removed from the solution obtained using high-speed centrifugation (10 min at 15000 rpm, bench top centrifuge Z230M, Hermle Labor-technik GmbH). After the centrifugation, the IPA was evaporated completely from the precipitation. The remnant thiol-capped AgNWs were dispersed in acrylic monomer with concentrations varying from 0.005, 0.02, 0.05, 0.2, to 0.4 wt%. Photoinitiator was added to the dispersion with a constant concentration of 1 wt% in all samples. The composite resins underwent ultrasonic agitation for 60 s followed by a magnetic stirring for 24 h at RT (VWR, standard hot plate stirrer). They were then purified using centrifugation (30 min at 6000 rpm, mini spin 5452, Eppendorf) to remove large AgNW aggregations from the resins. The as-prepared resins were stored in brown glass bottles and stirred continuously.

#### 4.3. Two-photon polymerization

TPP fabrication was performed on a 3D laser lithography system (Nanoscribe GmbH, Photonic Professional). A frequency-doubled, Er-fiber laser (center wavelength of 780 nm, pulse width of 100 fs, repetition rate of 80 MHz, and maximum power of 150 mW) was used as the irradiation source. An oil immersion objective lens (63 $\times$  and 1.4 NA) was used to focus the laser beam.

#### 4.4. Femtosecond laser nanojoining

A femtosecond Ti:sapphire laser with a regenerative amplification system (center wavelength of 800 nm, pulse width of 120 fs, repetition rate of 1 KHz) was employed in the laser nanojoining experiment. The laser beam was linearly polarized with a Gaussian energy distribution (M squared factor <1.2). A half-wave plate and a polarizer were used to adjust the laser pulse energy. A plano-convex lens with a focal length of 100 mm was used to focus the laser beam. The sample was stationed on an X–Y–Z stage, and the stage was vertically displaced 4 mm from the focal plane to have a defocused beam of 170  $\mu\text{m}$  spot size on the sample surface. The laser beam scanned the sample surface by moving the sample stage at a speed of 100  $\mu\text{m s}^{-1}$ .

#### 4.5. Scanning electron microscopy

A field-emission SEM (Hitachi, S4700) with an acceleration voltage of 5–10 kV was used for the observation and analysis of the TPP-fabricated structures and AgNW morphology. A chromium layer of 5 nm thick was deposited on the samples before the SEM characterization to prevent the electric charge effect.

#### 4.6. Tunneling electron microscopy

A HRTEM (FEI Tecnai Osiris) with a voltage of 200 kV was used for analyzing the AgNW distribution and femtosecond laser nanojoining. Pristine AgNW TEM samples were prepared by drop casting on copper grids with Formvar/carbon supporting film and 400 mesh. The AgNW-acrylic composite TEM samples were prepared by direct TPP writing of a single layer thin film on the same kind of copper grid.

#### 4.7. Laser ablation ambient mass spectrometry

The laser ablation ambient mass spectrometry system consists of three major modules: a KrF excimer laser (COMPexPro 205 F, wavelength = 248 nm, pulse duration = 23 ns, Coherent Inc.), a time-of-flight mass spectrometer (TOF-MS, JEOL, AccuTOF<sup>™</sup>, JEOL, USA Inc.), and a sample stage. The laser fluence was fixed at 8.75  $\text{J cm}^{-2}$ . The laser beam was focused at normal incidence on the samples with a spot size of 0.80  $\times$  1.60  $\text{mm}^2$ . The voltages of the outer and inner orifices of the TOF-MS were fixed at 30 and 5 V, respectively. The temperature of the skimmer cone was fixed at 100  $^{\circ}\text{C}$ . The accumulation time was 1 s for each measurement.

#### 4.8. Temperature-dependent electrical conductivity measurement

To characterize electrical conductivity, bar-shaped channels were fabricated between two Au electrodes with sputtering deposited on the desired regions through shadow masks (Kurt J Lesker, 99.99% purity Au target). The homemade electrical conductivity measurement system consisted of a semiconductor parameter analyzer (Agilent 4155 C), a heating chamber (Linkam Scientific Instruments (UK), 77–800 K, THMS600), a heating power/temperature controller, and a probe station (Cascade Microtech, MPS 150). A liquid nitrogen tank was used for providing a nitrogen environment. Before measurements, composite devices were loaded into the chamber and placed at the center of the heating stage. A purging process was then performed to ensure all of the air was purged out. After that, the heating stage began to ramp up the temperature from 273 to 523 K at a rate of 10  $\text{K min}^{-1}$  and then cooled down at the same rate. A current–voltage ( $I$ – $V$ ) sweep was then performed at an incremental temperature of 50 K.

#### 4.9. Temperature-dependent Raman microspectroscopy

Raman microspectroscopy was conducted using a Raman microscope (Renishaw, InVia™ H 18415). To conduct temperature-dependent Raman characterization, the samples were placed in the same heating chamber (Linkam Scientific Instruments (UK), 77-800 K, THMS600) used for electrical conductivity measurements. The excitation laser beam, with a wavelength of 514.5 nm, was focused onto the sample surface through the chamber window by an objective lens (50×, NA 0.75). Before each measurement, the purging process was performed. The heating stage ramped up the temperature from 273 to 523 K at a rate of 10 K min<sup>-1</sup>. The average laser power used to produce Raman spectra was 10 mW. Raman spectra were recorded with an accumulation time of 10 s each at an incremental temperature of 50 K.

#### 4.10. Optical characterization

The optical absorption was measured using an ultraviolet-visible spectrophotometer (Evolution 201, Thermo Scientific™). The samples were prepared by spin coating (1 min at 1500 rpm, WS-650MZ-23NPPb, Laurell) with a thickness of 13.5 μm.

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