

Supplementary Information for

Microwatt 3D printing metal nanostructures by photothermally-activated Coulombic potential

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Supplementary Note 1 | Optical diffraction limit in TPLP

Throughout the context, optical diffraction limit is evaluated by the full width of the ideal laser focus. In particular, focal intensity distribution $I_{focus}(x, y, z)$ is computed by evaluating the vectorial Debye integral⁴⁵

$$\mathbf{E}_{focus}(x, y, z) = \frac{i\lambda_0 f}{4\pi^2 \epsilon_r^{ink}} \text{FT} \left\{ \frac{\mathbf{E}_{pupil}(\theta, \varphi)}{\cos \theta} e^{ik_z z} \right\}$$
$$I_{focus}(x, y, z) = \mathbf{E}_{focus} \cdot \mathbf{E}_{focus}^*$$

in terms of Fourier transform of the electric field at the pupil plane $\mathbf{E}_{pupil}$, assuming that the monochromatic laser with free-space wavelength λ_0 is tightly focused by an objective with focal length f into a homogeneous immersion medium with relative permittivity $\epsilon_r^{ink} = n^{ink}$. Numerical implementation is achieved using chirped-z transform algorithm. For typical optical setup used in this work, the absolute values of optical diffraction limit are calculated and summarized in Supplementary Table S3.

In practice, to avoid undesired scattering by the as-printed parts, invert sample configuration is adapted and the laser beam is focused through the electrolyte solution (measured to be $\sim 100 \mu\text{m}$ for the sample configuration used in Methods) during printing (Fig. S3). Both the near-UV laser wavelength (405 nm) and in-depth focusing impose difficulties on complete aberration compensation for the present experimental condition, because of the large refractive index mismatch between the ink and the coverslip. Experimentally, the lateral and axial full widths of the focus were measured to be about 452 nm and 1346 nm, respectively. In spite of the approximately 19% and 38% broadenings along the lateral and axial directions, the measured values well match the simulations in which the influences of aberrations are taken into account (Fig. S3). Also, the intensity values I used for simulations are computed via dividing the absolute laser power values P by the focal area A that

$$I = \frac{P}{\pi FWHM^2}.$$

Supplementary Note 2 | Laser-induced optical and thermal effects of nanometals

The optical properties of metals dictate both the lossy nature and surface plasmon resonances of metal nanoparticles (NPs) in ultraviolet to visible range. Particularly, excitation of surface plasmons (SPs) near the resonant frequency ω and the following decay of SPs are the physical sources of electromagnetic (EM) field concentration and the parasitic photothermal heating in TPLP^{6,7}.

Throughout the context, if not mentioned, all the calculations are performed using silver as the paradigm metal.

1. Method for plasmonic effect simulations

In this work, boundary element method (BEM) is employed for fast calculation of plasmonic effects of the photoreduced NPs. In brief, (electric) scalar potential ϕ and (magnetic) vector potential $\mathbf{A}$ at arbitrary field point $\mathbf{r}$ are evaluated by^{46,47}:

$$\begin{aligned}\phi(\mathbf{r}) &= \phi_{inc}(\mathbf{r}) + \oint G(\mathbf{r}, \mathbf{s}) \sigma(\mathbf{s}) da \\ \mathbf{A}(\mathbf{r}) &= \mathbf{A}_{inc}(\mathbf{r}) + \oint G(\mathbf{r}, \mathbf{s}) \mathbf{h}(\mathbf{s}) da\end{aligned}\quad (S1)$$

where ϕ_{inc} and $\mathbf{A}_{inc}$ denote the potential perturbations imposed by the incident wave. The terms $\sigma(\mathbf{s})$ and $\mathbf{h}(\mathbf{s})$ are the so-called auxiliary surface charge and surface current at boundary surface point $\mathbf{s}$, respectively, and $G(\mathbf{r}, \mathbf{s})$ is the dyadic Green's function. The induced (scattered) fields can be computed through the relations:

$$\begin{aligned}\mathbf{E}_{sca}(\mathbf{r}) &= ik\mathbf{A}(\mathbf{r}) - \nabla\phi(\mathbf{r}) \\ \mathbf{H}_{sca}(\mathbf{r}) &= \nabla \times \mathbf{A}(\mathbf{r})\end{aligned}\quad (S2)$$

in which k is the wavenumber in the dielectric medium. Subsequently, the absorption and scattering cross sections, σ_{abs} and σ_{sca} , of the metal NPs can be determined simply by evaluating the normalized power flow P through an imaginary surface enclosing the NPs⁴⁸:

$$\begin{aligned}\sigma_{abs} &= \frac{P_{abs}}{|\mathbf{S}_{inc}|} = \frac{-\oint \mathbf{S}_{tot} da}{|\mathbf{E}_{inc} \times \mathbf{H}_{inc}^*|} \\ \sigma_{sca} &= \frac{P_{sca}}{|\mathbf{S}_{inc}|} = \frac{\oint \mathbf{S}_{sca} da}{|\mathbf{E}_{inc} \times \mathbf{H}_{inc}^*|}\end{aligned}\quad (S3)$$

where $\mathbf{S}$ is the time-averaged Poynting vector corresponding to the incident ($\mathbf{S}_{inc}$), scattered ($\mathbf{S}_{sca}$), or the total field ($\mathbf{S}_{tot}$).

2. *SP enhanced photothermal heating*

(a) *Calculation of steady-state temperature distribution*

Under continuous-wave illumination, the heat-dissipation power Q of a source NP can be calculated with the knowledge of absorption cross section at frequency ω :

$$Q \approx Q(\mathbf{r}_s) = \sigma_{abs}(\omega) I(\mathbf{r}_s, \omega), \quad (S4)$$

where $I(\mathbf{r}_s)$ is the intensity at the position $\mathbf{r}_s$ that the source NP locates. In steady state, the resulting temperature distribution due to the local heat source is governed by the heat equation:

$$-\nabla[\kappa \nabla T(\mathbf{r})] = \nabla Q(\mathbf{r}), \quad (S5)$$

with κ be the thermal conductivity of the media.

To solve Eq. (S5) for the experimental configuration, where complex source structures along with stratified media might be involved, the thermal Green's function method discussed by Baffou et.al is used²⁹. In brief, an arbitrary metal structure is first volumetrically meshed into N_{cell} cubic cells, to each of which an imaginary heat source is allocated. For source NP in ink solution, which is separated from the substrate by single, flat interface, the thermal Green's function $G(\mathbf{r})$ can be determined, using the method of image, to be:

$$G(\mathbf{r}, \mathbf{r}_i) = \frac{1}{4\pi\kappa^{(ink)}} \frac{1}{|\mathbf{r} - \mathbf{r}_i|} \quad (S6)$$

for printing in bulk solution with thermal conductivity $\kappa^{(ink)}$, and

$$G(\mathbf{r}, \mathbf{r}_i) = \frac{1}{4\pi\kappa^{(ink)}} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_i|} - \frac{\kappa^{(sub)} - \kappa^{(ink)}}{\kappa^{(sub)} + \kappa^{(ink)}} \frac{1}{|\mathbf{r} - \mathbf{r}_i^*|} \right) \quad (S7)$$

for printing near the substrate with thermal conductivity $\kappa^{(sub)}$. While $\mathbf{r}_i$ denotes the position vector of the i^{th} imaginary source, $\mathbf{r}_i^*$ is the position vector of the image of the i^{th} source in the substrate. Next, the inner temperature rise ΔT_0 is retrieved, by energy conservation and prescribed boundary conditions, with the help of an imaginary metal nanosphere that is assumed

to share identical heat dissipation power as the structure of interest. Precisely, ΔT_0 is obtained by:

$$\Delta T_0 = \frac{Q}{4\pi\kappa^{(ink)}R}. \quad (\text{S8})$$

The effective radii R of the imaginary metal nanosphere can be computed by:

$$R = \sum_{i=1}^{N_{cell}} \sum_{j=1}^{N_{cell}} (L^{-1})_{ij}. \quad (\text{S9})$$

The L matrix is determined simply based on the position vectors of the physical sources $\mathbf{r}_i$ and the image sources $\mathbf{r}_i^*$. The matrix elements L_{ij} reads:

$$L_{ij} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (\text{S10})$$

for in-solution printing and

$$L_{ij} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{\kappa^{(sub)} - \kappa^{(ink)}}{\kappa^{(sub)} + \kappa^{(ink)}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j^*|} \quad (\text{S11})$$

for near-interface printing with $i \neq j$, otherwise L_{ij} equals the inverse of half spatial sampling step dr . Using Eq. (S6) to Eq. (S11), the temperature distribution in exterior of the source structure can be calculated through:

$$\Delta T(\mathbf{r}) = \sum_{i=1}^N \left[G(\mathbf{r}, \mathbf{r}_i) \sum_{j=1}^N (L^{-1})_{ij} \Delta T_0 \right]. \quad (\text{S12})$$

Since the absorption cross sections of the source particles (on the order of 10^4 nm^2) are two order-of-magnitude larger than that of the feed NPs (on the order of 10^2 nm^2 , see Fig. S4), the contributions of heat dissipation by the feed NPs to total temperature distribution is not comparable to that by the source NPs unless the feed NP population reaches 10^3 scale in the focus (Fig. S7 and see discussions in the next section). Therefore, for the sake of simplicity, during temperature field calculations, only contributions from the source NPs are included. Also, it should be pointed out that the presence of a metallic feed NP at field point $\mathbf{r}$ leads to equalized temperature gradient for field points nearby. Specifically, from continuity requirement for the heat flux through the NP-ink interface one can easily find that the local temperature gradient suffices:

$$|\nabla T|_{|\mathbf{r}-\mathbf{r}_f|=R_f} \approx \frac{3\kappa^{(ink)}}{2\kappa^{(ink)} + \kappa^{(Ag)}} |\nabla T(\mathbf{r}_f)|,$$

where $\mathbf{r}_f$ represent the position vector directed from the focus to the mass center of the feed NP and R_f is the hydrodynamic radius of the feed NP. Because of the high thermal conductivity of silver (429 W/m/K), ‘flattened’ temperature gradient is expected near the surface of the feed NPs. As would be discussed in Supplementary Note S3.2, this property gives rise to suppressed osmotic diffusions of the feed NPs in our case.

(b) Validation of steady-state analysis for TPLP

On the one hand, from Eq. (1) in the main text (and Eq. (S35) below) the effectiveness of NP confinement in TPLP is dictated by the focal temperature gradient. Numerical simulations reveal that with the presence of single dominating source NP in the focus (Figs. S5 and S8), the maximum value of focal temperature gradient reaches as high as 3 K/nm. Approximately, a gradient value variation over 0.1 K/nm can be regarded significant to induce ‘considerable’ change on the CC field thereby the NP transport behaviors. The corresponding change in feature size of the NP structure is derived to be ~ 1 nm, based on calculations of feature-size dependent focal temperature gradient for a source NP in the laser focus (Fig. S8). Accordingly, the characteristic growth time τ_{grow} for inducing such ‘noticeable’ size change is estimated to be of 1-ms scale through evaluating the first-order derivative of the exposure-time dependent feature size curve shown in Fig. 2n.

On the other hand, the characteristic time τ for the typical system considered in TPLP to reach local equilibrium is calculated to be of 1- μ s scale (Fig. S6), by solving time-dependent heat equation:

$$\rho_m c_p \frac{\partial}{\partial t} T(\mathbf{r}, t) - \nabla \cdot [\kappa \nabla T(\mathbf{r}, t)] = \nabla Q(\mathbf{r}, t), \quad (\text{S13})$$

where ρ_m and c_p denotes mass density and specific heat capacity. Since τ appears to be three order-of-magnitude smaller than τ_{grow} , the change on focal temperature gradient distribution is considered to be negligible for $(i-1)\tau_{grow} \leq t \leq i\tau_{grow}$, with $i = 1, 2, 3, \dots$. The validity of steady-state analysis is thus held within one τ_{grow} interval. For the sake of clarity and simplicity, the discussions are restricted within one τ_{grow} interval throughout this work.

3. SP-assisted photoreduction

In TPLP, excitation of SPs of the metal NPs modifies the local (photonic) density of states and varies spontaneous transition rates of the dipole-like precursor ions. Herein, a semi-classical model is employed to describe the coupling between the plasmonic NPs and the precursor ions⁴⁷.

Assuming that the quantum yield of photoreduction (from metal ions to zero-valence atoms) following dipolar excitation is unity, the photoreduction rate is equivalently evaluated by the change on light absorption rate by the metal ions. Specifically, a two-level electric dipole with transition energy $\hbar\omega$ of 3.06 eV (equivalent to a transition wavelength of 405 nm) and dipole moment $\mathbf{p}$ (direction of which is averaged along the three main axes of Cartesian coordinate system) is assumed. The absorption rate of the dipole can be computed using⁴⁹:

$$\frac{\Gamma^{(abs)}}{\Gamma_0^{(abs)}} = \frac{6\pi\epsilon^{(ink)}}{|\mathbf{p}|^2} \frac{1}{k^3} \text{Im}\{\mathbf{p}^* \cdot \mathbf{E}_{sca}\}, \quad (\text{S14})$$

where $\epsilon^{(ink)}$ represents the electric permittivity of the ink solution at frequency ω and $\Gamma_0^{(abs)}$ is the free-space absorption rate. For an ideal two-level system, $\Gamma_0^{(abs)}$ equals

$$\Gamma_0^{(abs)} = \Gamma_0^{(rad)} = \frac{|\mathbf{p}|^2 k^3}{6\pi\epsilon^{(ink)}}. \quad (\text{S15})$$

Numerical evaluation of Eq. (S18) is achieved by sequentially placing the probe dipole at field points of interest, the transition rate of which is then recorded and normalized to $\Gamma_0^{(abs)}$.

4. SP-induced capping agent desorption

As has been shown in previous reports, photoinduced hot carriers are capable of triggering capping agent desorption from the NP surfaces^{50,51}. Considering the intense near-field enhancement (Fig. S14) and efficient hot carrier generation by SP damping in noble metals^{7,50}, desorption of capping agents (in our case the surfactant capping agents) from the feed NP surface could be induced as source-feed gap distance is small enough to excite the gap plasmon resonance.

Supplementary Note 3 | Thermal transport of the photoreduced NPs

Based on the experimentally measured feature size range (Fig. 2), the maximum focal temperature rise is calculated to remain mild, with $\Delta T < 60\text{K}$ (Figs. S5-S8). Consequently, for the present configurations thermal convection induced NP transport effects are neglected. The non-equilibrium thermal transports of the elemental feed NPs are ascribed to three mechanisms for TPLP: 1) randomizing Brownian motions, 2) thermo-osmosis driven by electric-double layer force, and 3) Coulombic confinement (CC) driven by thermoelectricity.

1. Randomizing Brownian motion:

In the TPLP ink, the random collisions between the solvent molecules and the feed NPs give rise to Brownian motion, which fundamentally persists for finite temperature values. Classically, the equation of motion of an unconstrained feed NP with radius R_f can be described by the Langevin equation³⁶:

$$m \frac{d^2 \mathbf{r}}{dt^2} + \gamma \frac{d\mathbf{r}}{dt} = \sqrt{2k_B T \gamma} \boldsymbol{\xi}(t), \quad (\text{S16})$$

where m is the mass of the feed NP and $\gamma = 6\pi\eta R_f$ is the Stokes friction coefficient with η the viscosity of the ink solution. The term $\sqrt{2k_B T \gamma} \boldsymbol{\xi}(t)$ on the right-hand side of Eq. (S16) is the Brownian force arising from random collisions, with $\boldsymbol{\xi}$ the random Gaussian vector. Solving Eq. (S16) in overdamping limit leads to an estimation on the mean squared displacement from the release point (set as the geometric focus for all simulations) for a time duration Δt :

$$\frac{1}{2} \langle \mathbf{r} \cdot \mathbf{r} \rangle = \frac{k_B T}{\gamma} \Delta t \quad (\text{S17}),$$

where the term $k_B T / \gamma$ is known as the mass diffusion coefficient D_m , i.e.,

$$D_m = \frac{k_B T}{\gamma}. \quad (\text{S18})$$

Using Eq. (S17), a rough estimation shows: for a 10-nm feed NP, released free to move in a heat bath at 323 K (equivalently, $\Delta T = 25\text{K}$) at $t = 0$, the average displacement $\langle \mathbf{r} \cdot \mathbf{r} \rangle^{1/2}$ becomes comparable to the optical diffraction limit (on the order of 100 nm) at times ca. 1 ms from the release. Comparable with typical unit exposure times in common 3D metal laser nanoprinting techniques (on the order of 1 to 10 ms), Brownian motion of the elemental feed NPs cannot be

ignored (Fig. 2e).

In the presence of a harmonic confining potential well, Eq. (S16) becomes:

$$m \frac{\partial^2 \mathbf{r}}{\partial t^2} + \gamma \frac{\partial \mathbf{r}}{\partial t} - \chi \mathbf{r} = \sqrt{2k_B T \gamma} \xi(t), \quad (\text{S19})$$

where χ is the stiffness of the potential well and connects with the potential energy ΔU via $\chi_i = \nabla_i^2 (\Delta U)$, $i = x, y, z$. Since the characteristic timescale for ‘noticeable’ system change in TPLP is on the order of 1 ms, which is 10 order-of-magnitude larger than the momentum relaxation time (of 10 ps scale) of the feed NPs, the second-order inertia term in Eq. (S18) is neglected during numerical evaluations. Thusly, Eq (18) can be rewritten as:

$$\gamma \frac{\partial \mathbf{r}}{\partial t} - k_r \mathbf{r} = \sqrt{2k_B T \gamma} \xi(t).$$

Using finite difference method, the position vector of the feed NP $\mathbf{r}_m$ at the m^{th} time step can be obtained:

$$\mathbf{r}_m = \mathbf{r}_{m-1} - \frac{1}{\gamma} \chi \cdot \mathbf{r}_{m-1} \Delta t + \sqrt{2D_m \Delta t} \xi. \quad (\text{S20})$$

Eq. (S20) is employed for numeric simulations on the motion trajectories of feed NPs with the presence or absence of the CC potential field (during which both the magnitude and distribution of the focal temperature is fixed for simplicity). Also, from Eq. (S20) it is straightforward that the existence of a confining potential well (which is ‘concave’ with positive χ_i) would lead to decreased mean displacement of the feed NPs during each time step and thus suppressed random NP diffusions.

2. Electric double layer driven thermo-osmosis:

In electrolyte solutions, a charged colloid could also electrostatically interact with the mobile ions thereof. In thermal equilibrium, a double-layer structure known as the electric double layer (EDL) is formed, screening the colloid⁴⁰. The distance over which the colloid is effectively screened can be characterized by the Debye screening length λ_D . Assuming that each ions species carries Z_i elemental charge e and has a bulk number density of $n_{0,i}$, λ_D reads:

$$\lambda_D = \left(4\pi\lambda_B \sum_i^N Z_i^2 n_{i,0} \right)^{-1/2}, \quad (\text{S21})$$

where $\lambda_B = e^2 / (4\pi\epsilon_\infty^{(ink)} k_B T)$ is the Bjerrum length (~ 0.6 nm) with $\epsilon_\infty^{(ink)}$ the static electric permittivity of the electrolyte ink and k_B the Boltzmann constant.

With finite temperature gradient values, the change of electric potential energy in the EDL causes slip flows tangent to the NP surface³³. In the spirit of boundary-layer approximation, the consequent NP drift velocity $\mathbf{u}$ can be expressed as the integral of force density $\mathbf{f}$ exerted on the NP subtracted by the gradient of osmotic pressure ∇P within the boundary layer^{34,36}:

$$\mathbf{u} = \frac{2}{3\eta} \int_0^{L_B} (\mathbf{f} - \nabla P) r dr, \quad (\text{S22})$$

where L_B the boundary layer thickness. Concerning solely the contribution from the temperature gradient to the osmotic pressure, it has been shown that for strong electrolyte solution (the concentrations of the solutes of which are well above 10 mmol/L) $\mathbf{u}$ equals:

$$\mathbf{u} = -\frac{\epsilon_\infty^{(ink)} \zeta^2}{3\eta} \frac{\nabla T}{T}, \quad (\text{S23})$$

where ζ denotes the surface potential of the NP with radii R and connects with the surface charges q_{NP} through⁵²:

$$q_{NP} \approx \frac{2eR^2}{\lambda_D \lambda_B} \sinh\left(\frac{e\zeta}{2k_B T}\right). \quad (\text{S24})$$

In Eq. (S23), the coefficient term on the right-hand side shows the dimension of m^2/s and is defined as the thermophoretic mobility D_T of the colloid by:

$$D_T^{(EDL)} = \frac{\epsilon_\infty^{(ink)} \zeta^2}{3\eta T}. \quad (\text{S25})$$

Eq. (S25) holds for charged colloids with radii R ranging from $R \gg \lambda_D$ to $R \sim \lambda_D$, and thus holds for both the charged feed NPs and ions in the TPLP ink³⁴. Together with Eq. (S23), thermophobic (i.e., hot-to-cold) migration is expected for the feed NPs and the ions, because of the quadratic dependence of surface potential, the non-negative electric permittivity and viscosity of the host ink solution. Utilizing Eq. (S23), the EDL force exerted on a probe feed NP can be evaluated by

$$\mathbf{F} = 6\pi\eta R_f \mathbf{u}. \quad (\text{S26})$$

The potential energy ΔU can then be equivalently evaluated through the reversible work done

by the EDL force by quasi-statically maneuvering the feed NP from $\mathbf{r}$ to infinity:

$$\Delta U_{EDL}(\mathbf{r}) = -\int_r^\infty \mathbf{F}(\mathbf{r}') d\mathbf{r}'. \quad (\text{S27})$$

Due to the flattening of local temperature gradient by the feed NP, the thermo-osmotic potential energy probed by single feed NP is weak with magnitude on the $10^{-3}k_B T$ scale (see Figs. 2a, S12). Thus, EDL-force driven thermo-osmosis is negligible in our case and is obscured by the randomizing Brownian diffusion of the feed NPs (Fig. S11).

In TPLP, micellization of the surfactant capping agents yields micellar ions with large charge numbers ($\sim 10^1$ scale) compared with the simple ions (unity for sodium and silver ions). From Eq. (S25), the resulted micellar ions share $D_T^{(EDL)}$ ($\sim 10^{-10} \text{ m}^2/\text{s}\cdot\text{K}$) that is about two-order higher than that of the simple counterions ($\sim 10^{-12} \text{ m}^2/\text{s}\cdot\text{K}$) and are expected to be more susceptible to thermo-osmosis³⁹. Using Eq. (S23), it can be found that the osmotic displacement of the micellar ions at a moderate temperature gradient value of 0.5 K/m is readily comparable with the diffraction limits for a time duration of ca. 2 μs , while both the osmotic displacements of the simple ions and feed NPs are negligible. Moreover, in accordance with Eqs. (S17) and (S18), the average displacement of the micellar ions by Brownian motion is evaluated to be about 1/3 of the simple ions. The above comparisons indicate that thermo-osmosis induced charge separation can be effectively established within thermal equilibrium timescale., which lays the basics of CC potential field formation.

3. Thermoelectricity induced Coulombic confinement

To quantify CC effect, explicit form of the induced electrostatic field is derived. Generally, the TPLP inks contain N mobile ion species, each of which carries charge $q_i = eZ_i$ and has a number density of n_i . Allowing the presence of non-zero temperature gradient ∇T and electric field $\mathbf{E}$ beyond ion density gradient ∇n , the ion flux $\mathbf{J}$ of the i^{th} mobile species can be written as:

$$\mathbf{J}_i = -\nabla n_i D_{m,i} - n_i D_{T,i}^{(EDL)} \nabla T + n_i D_{E,i} \mathbf{E}, \quad (\text{S28})$$

where $D_{m,i}$, $D_{T,i}^{(EDL)}$ and $D_{E,i}$ are respectively the mass diffusion coefficient, thermophoretic coefficient, and electrophoretic coefficient of the i^{th} species. The electrophoretic coefficient, under first-order approximation of the Poisson-Boltzmann equation, takes the form of

$$D_{E,i} = D_{m,i} \frac{eZ_i}{k_B T}.$$

In steady state, the ion flux vanishes for all species, that is, $\mathbf{J}_i = 0$. From Eq. (S28), one can find that in the absence of external field an induced electric field could still exist due to ion concentration and temperature gradients, as has been demonstrated in recent researches^{53,54}. Summing Eq. (S28) over all species and multiplying both sides of the equation with D_i / q_i , we obtain:

$$\sum_i^N \frac{q_i \mathbf{J}_i}{D_{m,i}} = -\sum_i^N q_i \nabla n_i + \sum_i^N \frac{q_i^2 n_i}{k_B T} \mathbf{E} - \sum_i^N q_i n_i \frac{D_{T,i}}{D_{m,i}} \nabla T = 0. \quad (\text{S29})$$

has been used. Assuming that the deviations on the local ion densities are small compared with the bulk values so that $n_i = n_{0,i} + \delta n_i \approx n_{0,i}$, Eq. (S29) can be simplified to be:

$$\nabla \rho - \frac{\varepsilon_{\infty}^{(ink)}}{\lambda_D^2} \mathbf{E} + \sum_i^N q_i n_{0,i} \frac{D_{T,i}}{D_{m,i}} \nabla T = 0, \quad (\text{S30})$$

where Eq. (S21) has been used. Because the charge density gradient is not necessarily vanishing, the use of Gauss's law $\varepsilon_{\infty}^{(ink)} \nabla \cdot \mathbf{E} = \rho$ leads to $\nabla \rho = \nabla \left(\varepsilon_{\infty}^{(ink)} \nabla \cdot \mathbf{E} \right)$. Neglecting permittivity change due to density variation of the ink solutions, Eq. (S30) becomes:

$$\left(\nabla^2 - \frac{1}{\lambda_D^2} \right) \mathbf{E} + S \nabla T = 0, \quad (\text{S31})$$

where S is defined as the thermoelectric (Seebeck) coefficient

$$S \equiv \frac{1}{\varepsilon_{\infty}^{(ink)}} \sum_i^N q_i n_{0,i} \frac{D_{T,i}}{D_{m,i}}. \quad (\text{S32})$$

The thermoelectric S coefficient reflects the strength of thermoelectric polarization by ion separation. The multiplication by the factor of $D_{T,i} / D_{m,i}$ modifies the neutrality condition ($\sum_i^N q_i n_{0,i} = 0$) and gives rise to non-vanishing S , which leads to a particular solution that links with the focal temperature gradient; meanwhile, the sign of S is explicitly determined by the ion species with high charge number, high thermophoretic mobility but low mass diffusion mobility. The larger the quotient difference (which is formally defined as Soret coefficient) between positive and negative ions is the larger the magnitude of S would be. Consequently, to effectively induce local electric polarization, the aforementioned surfactant ion (see the previous section) is employed.

From Eqs. (S21) and (S30), for radial symmetric system that are frequently involved for in-solution printing in TPLP, the temperature distribution simply follows Eq. (S8). The boundary conditions requires that the induced electric field must vanish for $r \rightarrow \infty$ but remains finite for $r = R_s$. Again, with Gauss's law the induced electric field satisfies:

$$\mathbf{E}(\mathbf{r} = R_s \hat{\mathbf{r}}) = \mathbf{E}_0 = \frac{\sigma}{\mathcal{E}_{\infty}^{(ink)}} \hat{\mathbf{r}}, \quad (\text{S33})$$

in which $\hat{\mathbf{r}}$ is the unit radial vector. Substituting Eq. (S8) into Eq. (S31) and taking use of the boundary conditions, the thermally-activated electric field, which we phrase as Coulombically-confining (CC) field, is solved to be:

$$\mathbf{E}_{CC}(\mathbf{r}) = \frac{\sigma}{\mathcal{E}_{\infty}^{(ink)}} \frac{\mathbf{R}_s}{r} \exp\left(-\frac{r-R_s}{\lambda_D}\right) + S \nabla T(\mathbf{r}) \left[1 - \exp\left(-\frac{r-R_s}{\lambda_D}\right)\right], \quad (\text{S34})$$

The first and the second terms in the right-hand side of Eq. (S34) account for the screened electric fields established due to the residual surface charges and thermally-induced charges, respectively. Because of the screening effect, for r well larger than λ_D (which is less than 1 nm for the strong electrolyte ink used in this work), the first term quickly vanishes, while the second term converges to $S \nabla T$ and predominates. Therefore, incomplete desorption of the ionic capping agents is considered to have little effect on the overall CC field strength. In the limit of zero surface charge, Eq. (S34) reduces to:

$$\mathbf{E}_{CC}(\mathbf{r}) = S \nabla T(\mathbf{r}) \left[1 - \exp\left(-\frac{r-r_0}{\lambda_D}\right)\right]. \quad (\text{S35})$$

In accordance with Eq. (S35), the spatial profile of the thermally-activated CC field is dictated by the temperature gradient distribution ∇T , which have not necessarily to be photoinduced and therefore offers an extra degree-of-freedom for CC field synthesis by ∇T devising. Besides, since the square bracket part in Eq. (S35) remains positive for $r > R_s$, given fixed ∇T the direction of the CC potential drop is determined by the S coefficient, the sign of which indicates whether positive or negative ions accumulate in the cold region (which in this work is the negative micellar ions ND-Sar⁻ and NH-Arg⁻). Forced transport of feed NPs towards the hot region can be initiated by charging the feed NPs with same sign as S . As mentioned in the main text, this is achieved by applying a high surfactant concentration (approx. 4-times of the critical micelle concentration of ND-Sar⁻ for the silver inks). Since the adsorption of the surfactant ions on the

colloidal nanoparticles is thermodynamically favourable⁴⁰, the surfactant ions tend to self-assemble into ionic shell on the feed NP surfaces and high concentration values guarantee sufficient supply of surfactant ions for such chemical charging process.

With Eq. (S35), the CC potential energy probed by a feed NP with charge q_{probe} can be evaluated, in a quasi-static manner, via

$$\Delta U_{CC}(\mathbf{r}) = -\int_r^\infty q_{probe} \mathbf{E}_{CC}(\mathbf{r}') d\mathbf{r}'. \quad (\text{S36})$$

The activation of CC field by single dominating source NP readily leads to effective capturing of surrounding feed NPs (Figs. 2f, 2g, and S9), which can further consolidate the dominance of the source NPs by continual feeding and SP-assisted photochemical joining. We also need to point out that without the central dominating NP(s) the feed NPs alone cannot effectively induce robust CC potential even for a large NP number up to 500 (Fig. S7).

Supplementary Note 4 | Size and charge number of the photoreduced NPs

As reported in previous publications^{11,13} and evidenced by Figs. 2h-j and 4c-4d, the sarcosinate surfactants could serve as growth inhibitor for photoreduced silver nanoparticles (NPs), circumventing over-agglomeration and effectively reducing the grain size of the printed structures. Supportively, a reference experiment is conducted for rough estimation on the average size of the feed NPs. In particular, the near-UV (405 nm) diode is replaced with a blue (470 nm) diode to ensure sufficient photoreduction efficiency but suppressed absorption by the source and feed NPs (Fig. S5). Using an objective with numerical aperture lower than that for common TPLP experiments (UPlanFLN 60×/0.90/0.13-0.21), silver microwires consisted of loosely-packed silver NPs are obtained at a exposure condition of 613 μW @ 600 nm/s (power requisite increased due to lowered photosensitivity of the ink and absorption cross section of the NPs at longer wavelength). Feature size statistics of NPs in the microwires shows a near-Gaussian distribution. The expectation value is fitted to be ca. 13 nm with a standard deviation of ~ 2 nm (Fig. S10). For this reason, the elemental feed NPs are presumed to be 10-nm spherical NPs throughout the context.

Also, since the typical concentration value of ND-Sar $^-\text{Na}^+$ used in this work is well-above the first critical micelle concentration³⁷, sufficient supply of surfactant ions for feed NP charging is expected. Taking common surface potential values (of 10 mV scale) of silver nanoparticles in electrolyte solutions^{55,56}, the charge number of the feed NPs is estimated to range between 20~80 using Eq. (S24). Assuming moderate charging of the feed NPs, a charge number of 50 is used for simulations.

Dictated by the length of the hydrophobic tail^{37,38}, the sarcosinate salt family shares aggregation numbers on the order of 10^1 , for which reason the charge number of the ND-Sar $^-\text{Na}^+$ micellar ions is chosen to be 10 for all simulations in this work.

For the gold and platinum inks, the capping agent NH-Arg $^-\text{Na}^+$ is moderate surfactant due to the shorter hydrophobic chain compared with ND-Sar $^-\text{Na}^+$. Though, in the light of previous reports^{57,58}, the presence of guanidinium group can facilitate self-assembly of the NH-Arg $^-\text{Na}^+$ molecules into macro-ions with large mass and charge number by the unique like-charge ion pairing property. Further reinforced by the experimental results (Figs. 3f-3g, S17-S18), we therefore apply similar theoretical treatment to the case of gold and platinum printings.

Supplementary Note 5 | Exclusion of optical trapping as dominant mechanism

On the one hand, a commercially-available silver NP suspension with optical density (OD) of 2 is employed as the alternative ink for conduction of reference optical trapping test with the same 3D nanoprinter used for TPLP. After 1-min irradiation at laser power up to 660 μW , which is 3-times larger than that used for 3D TPLP of silver structures, no significant refractive index contrast can be observed, indicating that silver structures cannot be formed by gradient-force directed particle assembly in our case (Fig. S13 and Supplementary Movie S4).

Second, the optical force probed by a 10-nm feed NP within the laser focus is computed using⁴⁸:

$$F_i = \sum_j \int_V \frac{\partial}{\partial x_j} T_{ij} d^3x. \quad (\text{S37})$$

The integration is taken within a sphere enclosing the NP, and T_{ij} is the Maxwell stress tensor that

$$T_{ij} = \varepsilon^{(ink)} \left[E_i E_j + c^2 B_i B_j - \frac{1}{2} (\mathbf{E} \cdot \mathbf{E} + c^2 \mathbf{B} \cdot \mathbf{B}) \delta_{ij} \right], \quad (\text{S38})$$

where $\mathbf{B}$, c , are the magnetic induction and the speed of light, respectively, and δ_{ij} refers to the Kronecker delta. The optical force computed using Eq. (S37) is found to be weak (on 1fN scale), and the corresponding potential energy ΔU_{OT} is evaluated to be far less than $k_b T$ (Fig. S13).

Putting together, consequently, optical trapping is considered to be insufficient to cause directional migration and assembly of the feed NPs, and optical trapping is excluded as the leading mechanism in TPLP.

Supplementary Note 6 | Nonlinear exposure dose accumulation in TPLP

To semi-quantitatively demonstrate the link between exposure dose accumulation and the potential fields, a simple classical model is introduced.

1. Exponential feed NP redistribution

At equilibrium, the feed NPs share identical temperature with the surroundings through heat conduction, thus the spatial variations in energy are dominated by the potential terms, i.e., the CC potential, thermo-osmotic potential, etc. (Figs. S9, S11 and S13). Applying mean-field approximation, the probability density $p(\mathbf{r})$ for a feed NP to settle at a field point $\mathbf{r}_j$ in the focus, viz., the field point $\mathbf{r}_j$ to be populated by the feed NP, at absolute temperature T follows³⁶:

$$p(\mathbf{r}_j) = \frac{p_0(\mathbf{r}_j) \exp \left[-\beta \sum_i \Delta U_i(\mathbf{r}_j) \right]}{\int_{focus} p_0(\mathbf{r}') \exp \left[-\beta \sum_i \Delta U_i(\mathbf{r}_j) \right] d\mathbf{r}'}, \quad (\text{S39})$$

where ΔU_i is the potential energy contributed from the i^{th} effect and β the thermodynamic beta that equals $1/(k_B T)$. $p_0(\mathbf{r})$ is the initial weight function that reflects the ‘likelihood’ of populating the field points through in-situ photoreduction and correlates with the focal intensity distribution to the first order via:

$$p_0(\mathbf{r}_j) = \frac{I(\mathbf{r}_j)}{\int_{focus} I(\mathbf{r}') d\mathbf{r}'}. \quad (\text{S40})$$

From Figs. S9, S11 and S12, with the presence of CC potential $\sum_i \Delta U_i$ becomes negative and monotonically increases in magnitude as source-feed interparticle distance decreases, indicating that confinement of feed NP towards the source NP is energetically preferable and thus leading to concentrated feed NP distribution in TPLP. Also, it should be noted during NP distribution simulations, the volume exclusion effect of the NPs along with short-range interactions between the NPs (e.g. van der Waals potential, which decays with $1/|\mathbf{r}_s - \mathbf{r}_f|^6$ and thus has little effect unless the interparticle distance is on the scale of Debye length) are neglected for the sake of simplicity.

2. Nonlinear feeding in TPLP

At equilibrium, the number density of the feed $n_f(\mathbf{r})$ can be computed with the help of Eq. (S39) so that:

$$n_f(\mathbf{r}) = Mp(\mathbf{r}). \quad (\text{S41})$$

The total number of feed NPs M generated within one τ_{grow} interval can be roughly estimated through:

$$M = \frac{\int_{focus} \tau_{grow} I(\mathbf{r}) d\mathbf{r}}{\int_{focus} \tau_{grow} I_{th} d\mathbf{r}}. \quad (\text{S42})$$

I_{th} denotes the intensity threshold, on exceeding which could feed NPs be photochemically generated. In regular experimental configurations discussed in this work, without the presence of CC field n_f roughly follows intensity distribution, i.e., $n_f = n_0 = Mp_0$ (Fig. 2b). However, the presence of CC potential with potential depth of $-6k_B T$ (for a feed NP with charge number of 50) modifies the potential energy distribution within the laser focus and reshapes feed NP distribution. According to Eq. (S39), the probability of ‘finding’ a feed NP in vicinity of the source NP can be increased by a factor of 10 (Figs. 2g, S16). The confining and subsequent joining of feed NPs to the source NP causes additive volume change and thus feature size change of the source structures. In radial symmetric systems, the number of available NPs m to feed the as-printed source structures at specific radial coordinate r (in one τ_{grow} interval) can be expressed as

$$m(r, I) = n_f(r, I) 4\pi r^2 dr \quad (\text{S43})$$

and satisfies $M = \int_{R_s}^{\infty} m(r) dr$. The feature size change ΔD can then be roughly estimated via

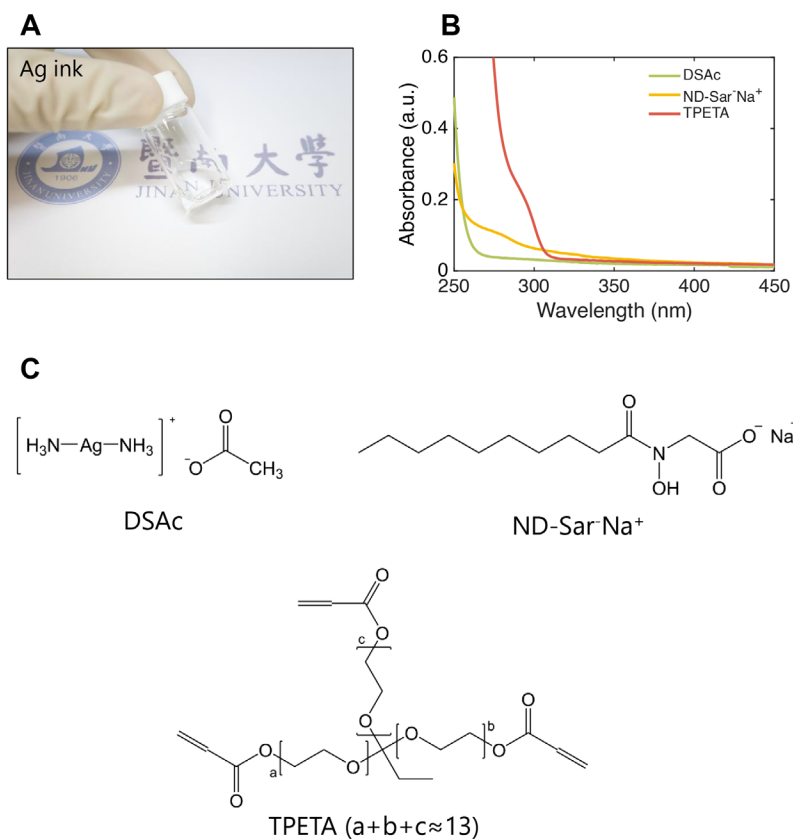
$$\Delta D = 2\Delta R_s = m(r, I) \frac{R_f^3}{3R_s^2} \quad (\text{S44})$$

The order of intensity dependency of the NP feeding can be evaluated by the logarithmic derivative as follows⁵:

$$slope = \frac{\partial \log(\Delta D)}{\partial \log(I)}. \quad (S45)$$

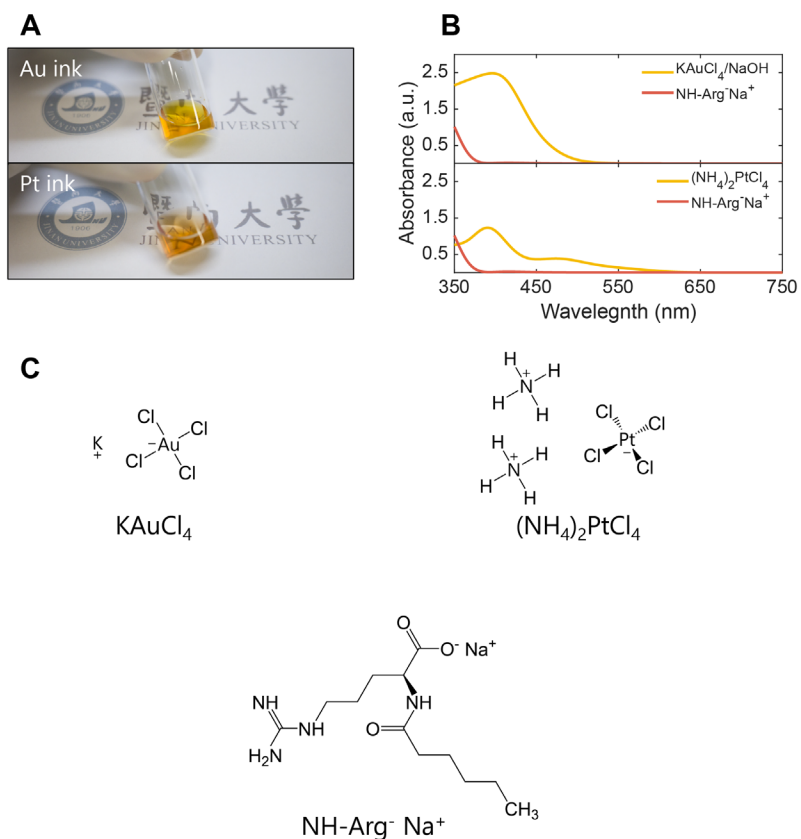
The nature of nonlinear NP feeding in TPLP is explicitly manifested by the exponentially scaling n_f . Notably, for CC potential field shown in Fig. 2f the nonlinear slope is derived to be about 2.2, which is in sharp contrast to the unity value for the case without CC field (Fig. 2k). Because of the nonuniform feed NP distribution, the nonlinear slope appears to be non-constant in the laser focus. The nonlinearity gradually decreases as the radial coordinate increases. The spatial inhomogeneity indicates that exposure dose accumulation is efficient only in proximity of the source NP surface (Fig. S16), at which both the feed NP density and photoreduction rate are high compared with the focal periphery. This property not only endows enhanced exposure dose confinement within the focus, but also attributes to the cleaner substrates in TPLP experiments compared with the control printing experiment group (since most feed NPs are fed to the source structures; also, the growth of the feed NPs themselves are limited due to the inhibitive surfactant shell and the low optical nonlinearity at positions far away from the source structure, see Figs. 2c-f, S15).

Supplementary Fig. S1 | Silver ink for TPLP



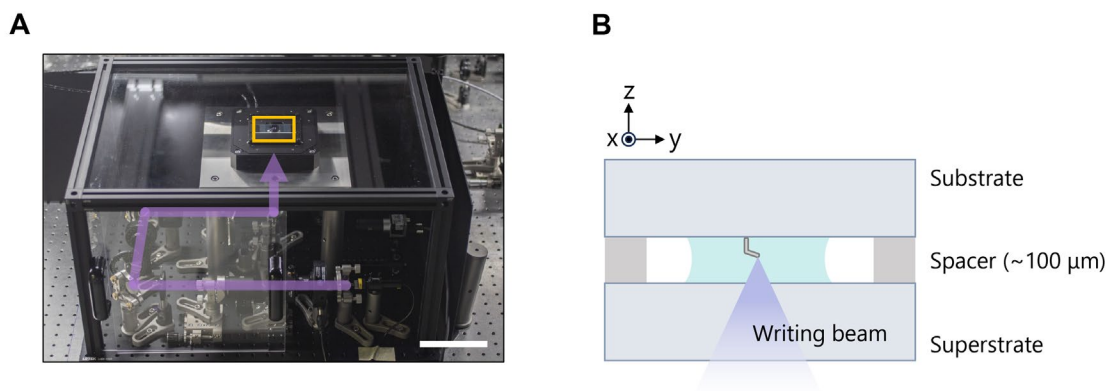
(A) Photograph of the as-prepared silver ink used for TPLP. (B) UV-Vis absorption spectra of the main ingredients of the ink. The concentrations of the solutions are the same as those in 3D printing. (C) Chemical structures of the metal precursor ion, the surfactant capping agent, and the organic reducing agent.

Supplementary Fig. S2 | Gold and platinum inks for TPLP



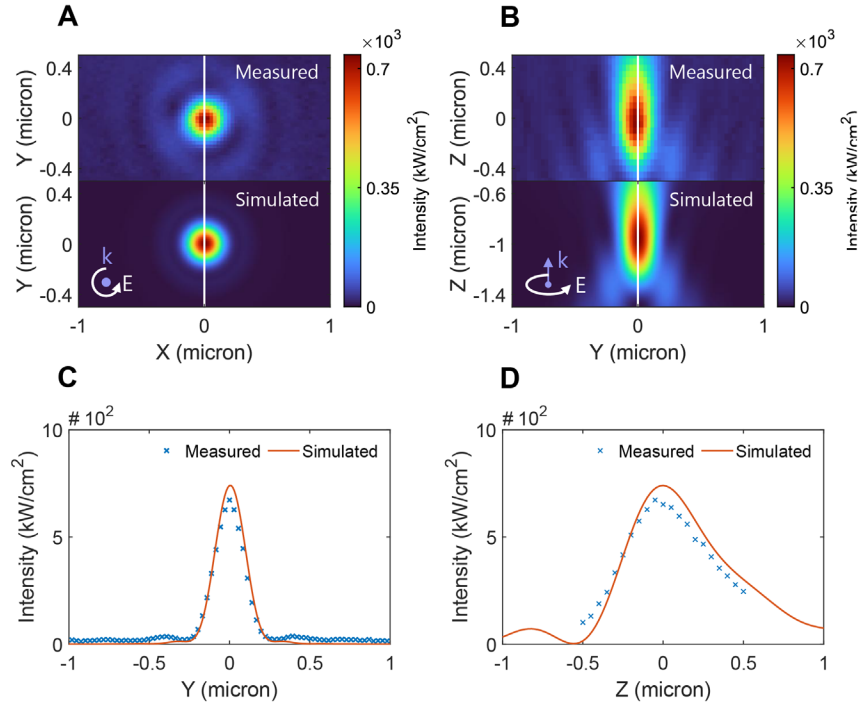
(A) Photograph of the as-prepared gold (upper panel) and platinum (lower panel) ink solutions used for TPLP. (B) UV-Vis absorption spectra of the precursor ion and capping agent solutions of the gold (upper panel) and platinum (lower panel) inks. The concentrations of the solutions are the same as those in 3D printing, except that the gold precursor is one-time diluted to prevent spectral saturation. (C) Chemical structures of the metal precursor ions and the capping agent used in gold and platinum ink formulations.

Supplementary Fig. S3 | Optical system and sample configurations



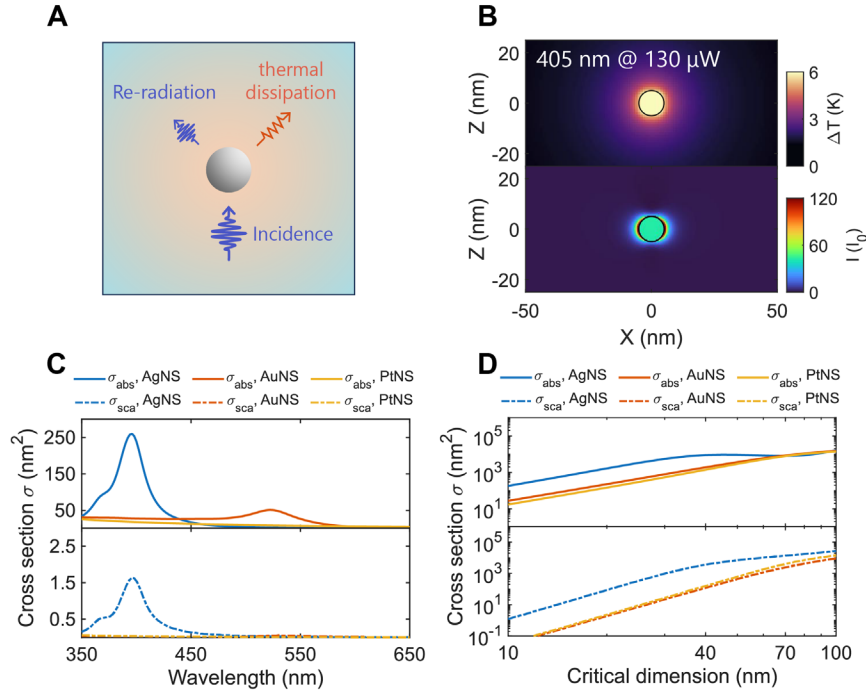
(A) Photograph of the compact 3D nanoprinter employed for TPLP. Scale bar: 100 mm. The purple line indicates the laser path while the yellow rectangle marks the as-prepared sample. (B) Schematic illustration of typical sample configuration used in TPLP.

Supplementary Fig. S4 | Focal intensity distribution in TPLP



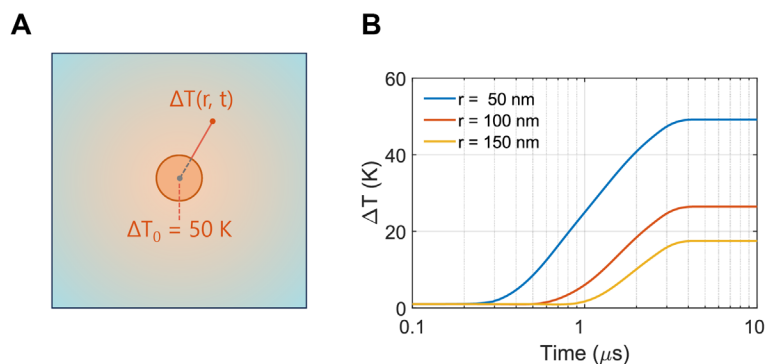
(A) Measured (upper panel) and simulated (lower panel) focal intensity distribution in the XOY plane. (B) Measured (upper panel) and simulated (lower panel) focal intensity distribution in the XOZ plane. The arrows in (A) and (B) mark the electric field polarizations (white) and the wavevectors (blue). Incident laser power: 1 mW. Effective penetration depth after correction is fitted to be 3 μm . (C) Lateral and (D) axial focal intensity profiles extracted along the white solid lines in (A) and (B). The full-width half maximum along Y and Z axes are measured to be 226 and 673 nm, respectively.

Supplementary Fig. S5 | Optical responses of nanosized metal particles



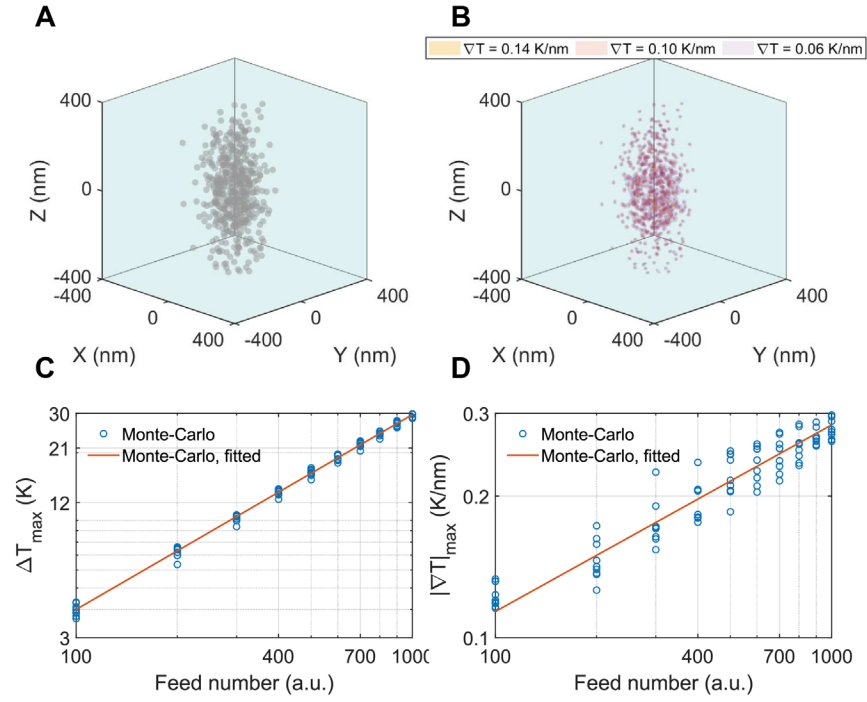
(A) Schematic illustration of optical responses of metal nanoparticles (NPs), the incident light is extinguished either non-radiatively by absorption, or, radiatively by scattering. The former could induce heating of both the NP and the surroundings, while the latter could lead to reshaped near-field intensity distribution. (B) Simulated (relative) temperature distribution (upper panel) and intensity distribution of a 10-nm silver feed NP. The feed NP is assumed to sit in bulk ink solution ($n = 1.33$, $\kappa = 0.598$ W/K/m) and illuminated by a 405-nm planewave at an absolute power of 130 μ W, or equivalently, an intensity of ~ 100 kW/cm². (C) Calculated absorption (solid line) and scattering (dashed line) spectra of 10-nm feed NPs made of silver (blue), gold (orange), and platinum (yellow). (D) Calculated size-dependent absorption and scattering cross sections of metal NPs made by the three metals at 405 nm.

Supplementary Fig. S6 | Thermal equilibrium timescale in TPLP



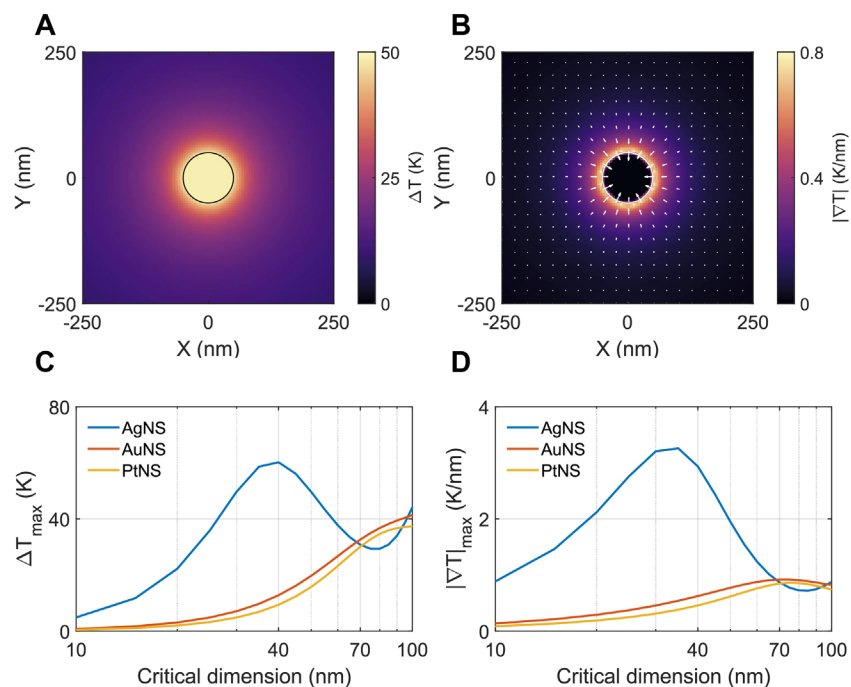
(A) Schematic illustration of the problem of interest: one source metal NP is heated up by ΔT_0 at $t = 0$ and then held at constant heat-dissipation power for $t > 0$. Thermal (indeed, local but not global) equilibrium between the NP and the surroundings causes a temperature rise of $\Delta T(\mathbf{r}, t)$ at position $\mathbf{r}$ and time t with respect to the initial temperature. Provided that the inner temperature of a 100-nm NP is raised by 50 K and then held at constant heat dissipation, (B) the time-dependent temperature variation for a field point located at different field points show an equilibrium time at around 4 μs .

Supplementary Fig. S7 | Focal temperature distribution without dominating source NPs



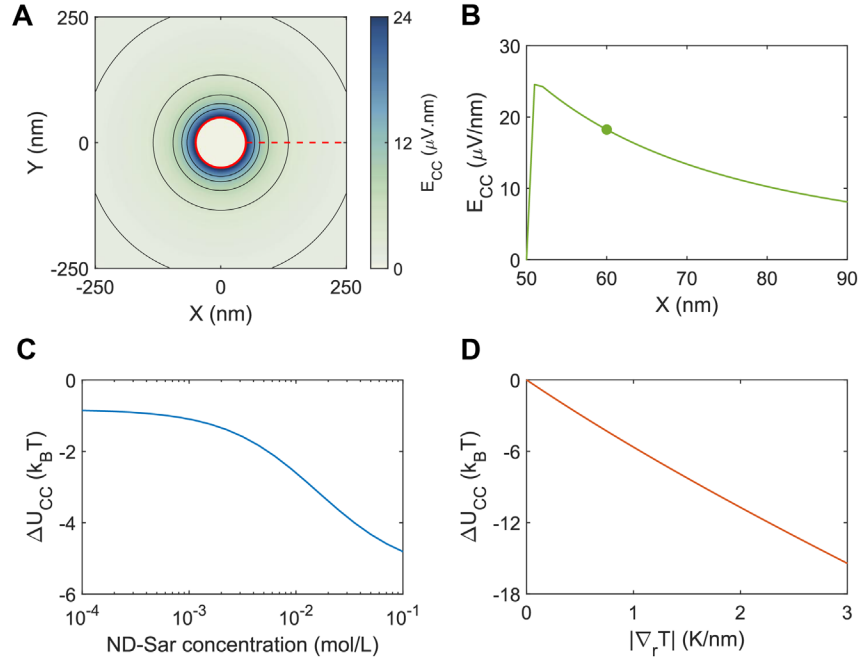
(A) Spatial distribution of a cluster of 10-nm feed NPs. The NPs are assumed to follow random normal distribution. The standard deviations of the distribution are set according to the FWHM of the laser focus. (B) iso-temperature-gradient distribution of the cluster shown in (A), provided that the cluster is illuminated by a 405-nm planewave at an intensity of 100 kW/cm². (C) Maximum focal temperature increment as a function of the feed NP population. (D) Maximum focal temperature gradient value as a function of feed NP population.

Supplementary Fig. S8 | Focal temperature distribution with dominating source NP



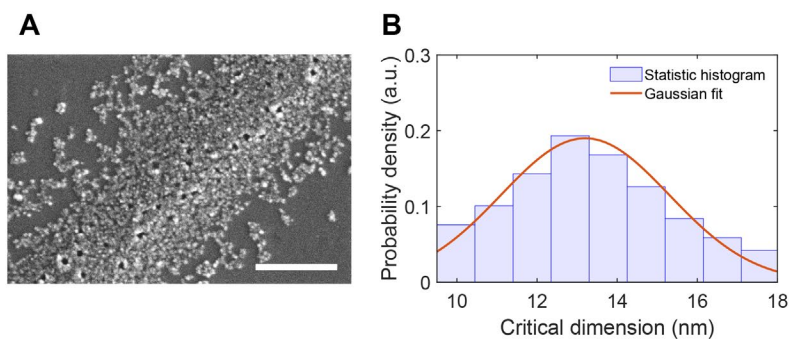
(A) Calculated temperature distribution of a 100-nm source NP, which is assumed to sit in homogeneous ink solution and illuminated by a 405-nm planewave at an intensity of 100 kW/cm²; (B) Corresponding temperature gradient distribution of (A). (C) Maximum focal temperature increment as a function of critical dimension of source NPs made of silver, gold, and platinum. (D) Maximum focal temperature gradient value as a function of critical dimension of source NPs made of the three metals. Note that contributions from the feed NPs are not taken into account in (C) and (D).

Supplementary Fig. S9 | Properties of the Coulombic-confining (CC) field



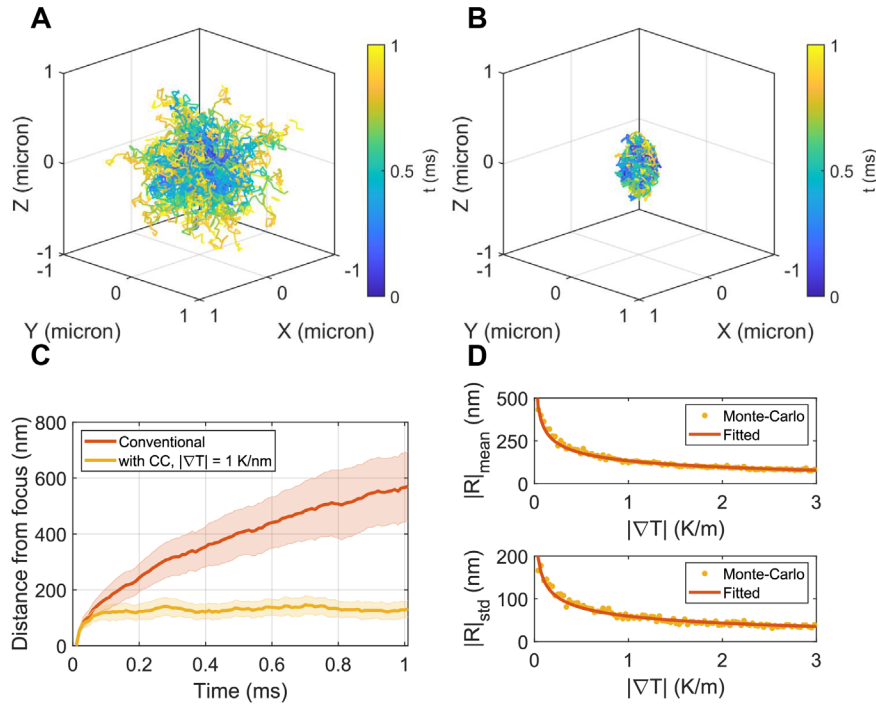
A two-body system, consisted of a 100-nm source NP coupled with a 10-nm feed NP in bulk TPLP ink, is considered. Concentration of ND-Sar and DSAC are set as 0.1 and 0.75 mol/L in accordance with the experimental conditions for 3D TPLP. And, the system is assumed to be heated under illumination of a 405-nm planewave at an intensity of 100 kW/cm². **(A)** Simulated CC field distribution. The red contour marks the NP boundary, while the black contours mark the iso-potential lines. **(B)** Profile of the CC field magnitude, extracted along the red dashed line in (A). The saw-like feature in the plot originates from the insufficient spatial sampling, which leads to failure in resolving of the fast-varying field in about one λ_D from the source NP surface. **(C)** CC potential energy probed by a charged, 10-nm feed NP as a function of ND-Sar concentration. **(D)** CC potential energy probed by the feed NP as a function of the maximum focal temperature gradient value. The CC potential energies in (C) and (D) are evaluated at the green solid dot (i.e., 10 nm away from the source NP surface) marked in (B).

Supplementary Fig. S10 | Feature size of the elemental feed NPs



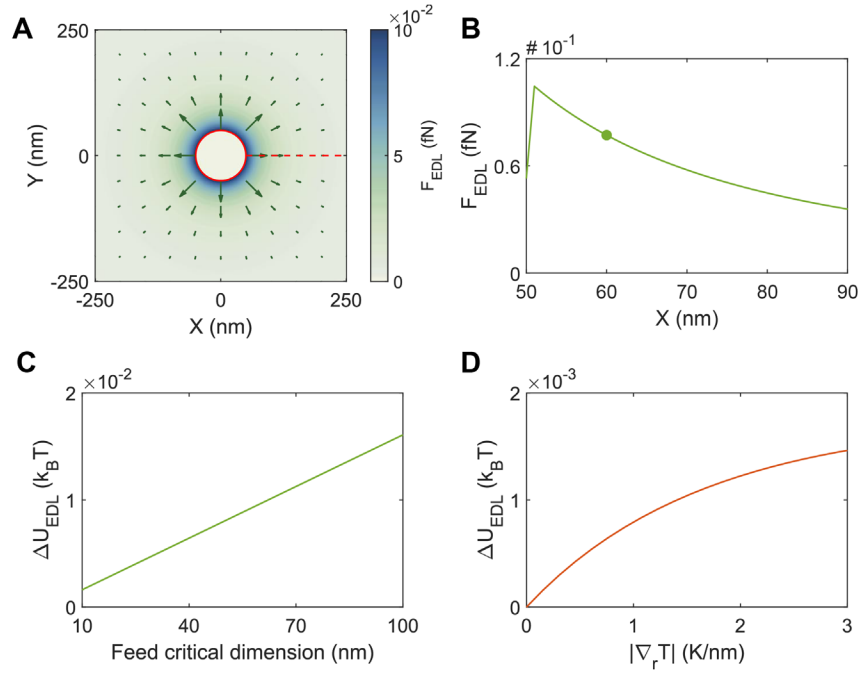
(A) High-magnification SEM micrograph of a segment of one of the loosely-packed silver microwires. The micro-wire is printed at 473 nm using a low-NA (0.90) objective, by which means the CC force is weakened due to the small temperature gradient value and allows close inspection of the feed NP morphologies. (B) Statistics on the size of 150 randomly-selected feed NPs in (A). The expectation value is measured to be 13.2 nm with a standard deviation of 2.4 nm.

Supplementary Fig. S11 | Brownian motion of feed NPs in the heated focus



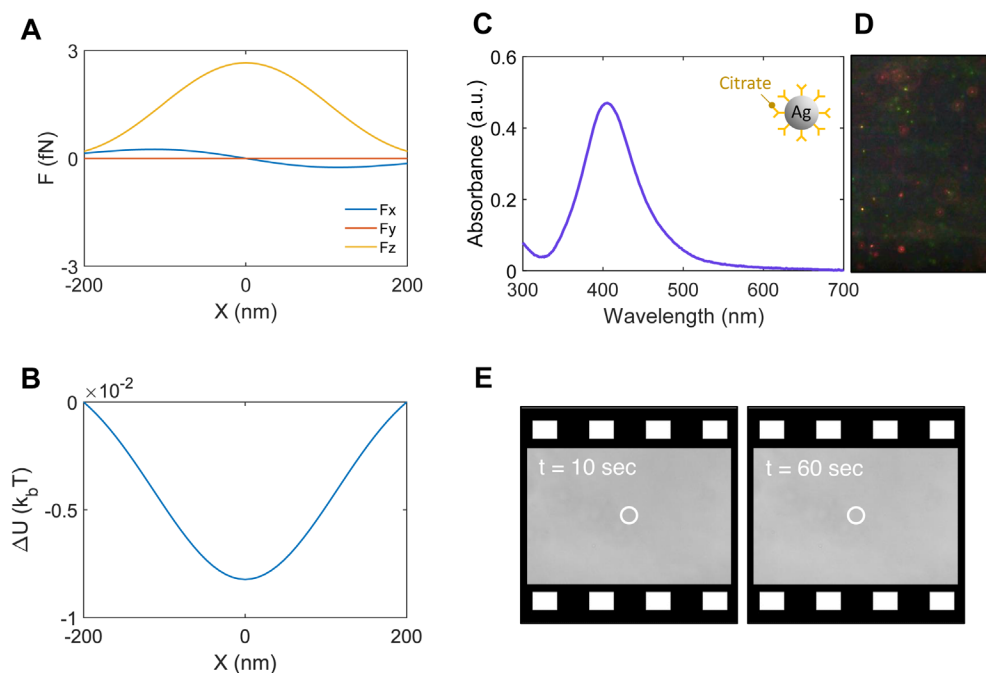
Time-traced trajectories of 100 feed NPs during a time duration Δt of 1 ms are simulated based on Monte-Carlo method, the particles are assumed to be non-interactive with each other and set free at the focal centre at $t = 0$. The absolute temperature at the focal centre is set as 318 K. **(A)** Trajectories of the feed NPs without the presence of confining potentials. **(B)** Trajectories of the feed NPs with the presence of CC potential field, the potential distribution is set according to Eqs. (S35) and (S36), with the potential depth set as $-6k_B T$. **(C)** Time-traced average NP displacement from the focal centre for conventional case as (A) and TPLP case as (B), the shaded areas mark the root mean square displacement at specific time. **(D)** Maximum average displacement (upper panel) and root mean square displacement (lower panel) as functions of maximum focal temperature gradient values.

Supplementary Fig. S12 | Properties of the thermo-osmotic potential field



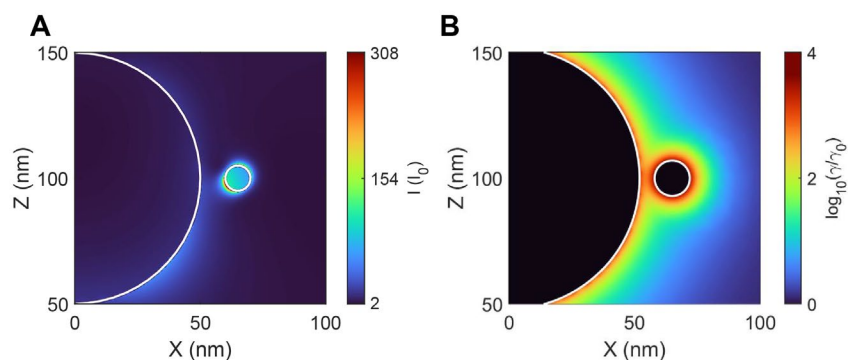
The coupled NP system in Fig.S9 is considered, but with the CC potential field disabled. the system is assumed to be heated under illumination of a 405-nm planewave at an intensity of 100 kW/cm². **(A)** Simulated EDL force map for feed NPs at different field points. The red contour marks the boundary of the source NP and the black arrows indicate the EDL force at specific locations. **(B)** Profile of EDL force magnitude, extracted along the red dashed line in (A). **(C)** Thermo-osmotic "potential" energy as a function of critical dimension of the feed NP probe (the surface potential of which is set as constant). **(D)** Thermo-osmotic potential energy probed by a 10-nm feed NP as a function of the maximum focal temperature gradient value. The thermo-osmotic potential energies variations in (C) and (D) are evaluated at the green solid dot (i.e., 10 nm away from the source NP surface) marked in (B).

Supplementary Fig. S13 | Exclusion of optical trapping effect in TPLP



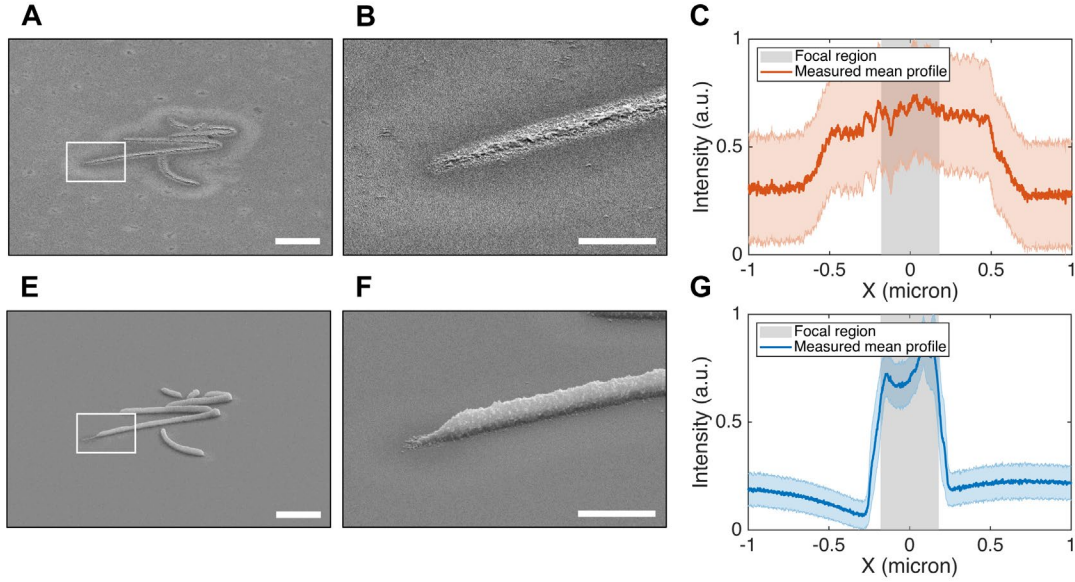
For optical force, a 10-nm feed NP is assumed to be free to move in the laser focus, with all heat-driven NP transport effects disabled. The absolute laser power is set as 200 μW . **(A)** Total optical force components as a function of NP position. The focal centre is set as the origin. **(B)** Computed potential energy contributed from the attractive gradient force (X and Y components) **(C)** Measured UV-Vis absorption spectrum of a commercially-available citrate-capped silver NP ($D = 25 \text{ nm}$) suspension, 30-times diluted. **(D)** Snapshot of dark-field micrograph of the diluted silver NP suspension employed for optical trapping test. **(E)** In-situ snapshots during trapping test at 10 seconds (left) and 60 seconds (right) after turning on the laser. The 405-nm laser (660 μW) is focused at the water-coverslip interface and the focus location is marked by the white circle (the laser spot cannot be seen due to the presence of laser-line filter before the CMOS camera).

Supplementary Fig. S14 | Plasmonic near-field concentrations in TPLP



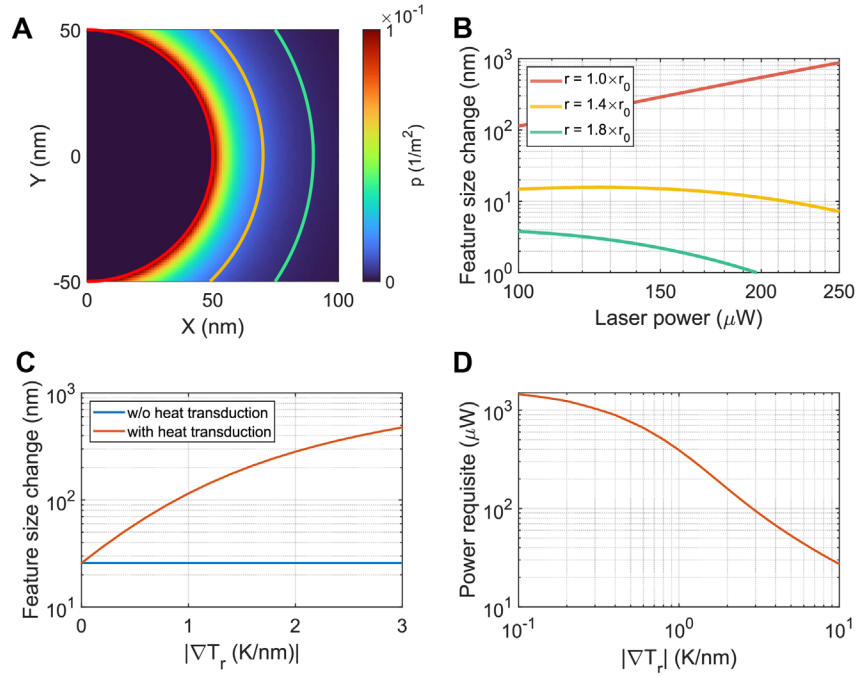
Again, the coupled NP system is considered. The surface-to-surface distance between the two NPs is set as 10 nm to activate near-field enhancement by gap surface-plasmon resonance. **(A)** XOZ slice of calculated near-field intensity distribution upon illumination by a 405-nm monochromatic planewave, the electric field polarization is directed along the X axis. **(B)** False-color map of photoreduction rate for a probe dipole with transition energy of 3.06 eV. The map is attained by consecutively placing the dipole at the field points in (A), during which the absorption rate at each location is recorded and normalized to the free-space value.

Supplementary Fig. S15 | Curvilinear printing with and without heat transduction



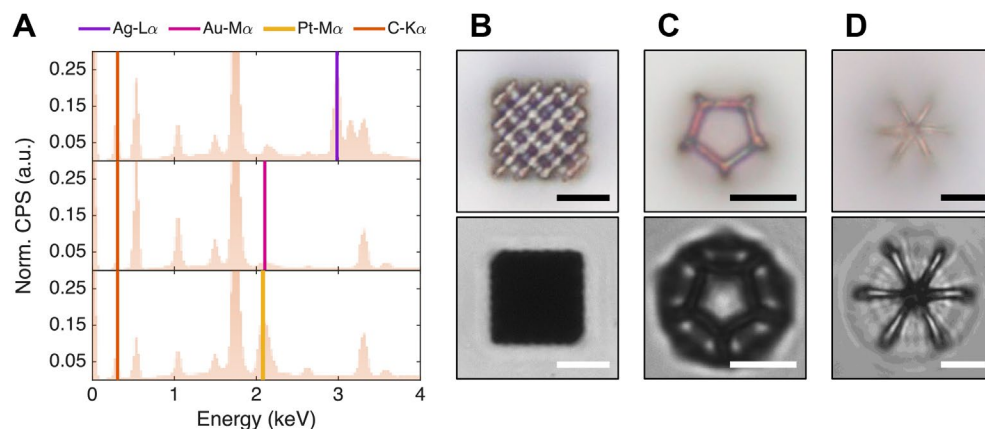
(**A**) Tilted SEM micrograph of the Chinese character ‘light’ shown in Fig. 2d. (**B**) Zoomed view of the rectangular area marked in (A). (**C**) Normalized secondary electron intensity from the wire elements in the (A), evaluated from the SEM micrograph and averaged over the whole pattern. The shaded orange area marks the standard deviation of the intensity, the gray area marks the focal region and spans the FWHM of the ideal laser focus. (**E**) Tilted SEM micrograph of the Chinese character ‘light’ shown in Fig. 2i. (**F**) Zoomed view of the rectangular area marked in (E). (**G**) Normalized secondary electron intensity from the wire elements in the (F), evaluated from the SEM micrograph and averaged over the whole pattern. The shaded blue area marks the standard deviation of the intensity, the gray area marks the focal region and spans the FWHM of the ideal laser focus. Scale bars: (A) and (E), 5 μm ; (B) and (F), 2 μm .

Supplementary Fig. S16 | Position and temperature dependent exposure dose accumulation



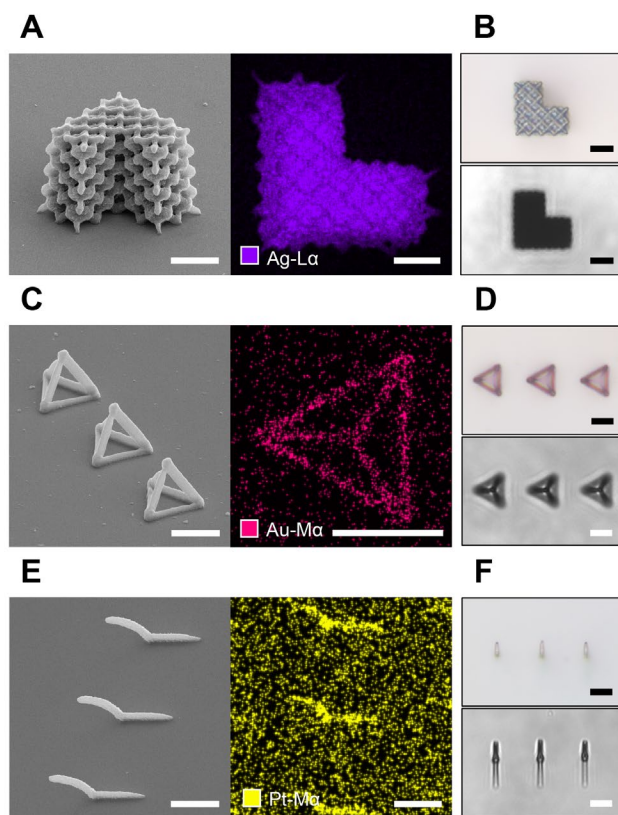
(A) Zoom-in view of the CC-potential reshaped probability density distribution that is demonstrated in Fig. 2g. (B) Simulated feature size changes on a primitive source NP structure as functions of laser power, extracted on the contours marked in (A). (C) Simulated feature size changes on a primitive source NP structure as functions of the maximum radial temperature gradient value in the focus, the absolute laser intensity is fixed at 100 kW/cm^2 . The introduction of heat transduction (orange curve) leads to nonlinearly increased exposure dose, which is in sharp contrast with the constant value for the case without heat transduction. (D) Simulated power requisite for reaching threshold exposure dose as a function of the maximum focal temperature gradient value. Decrease on power requisite by one order of magnitude is predicted provided that additional temperature gradient modulations are designed and introduced to further increase the focal temperature gradient value during printing.

Supplementary Fig. S17 | Extended data of Fig. 3a 3f and 3g



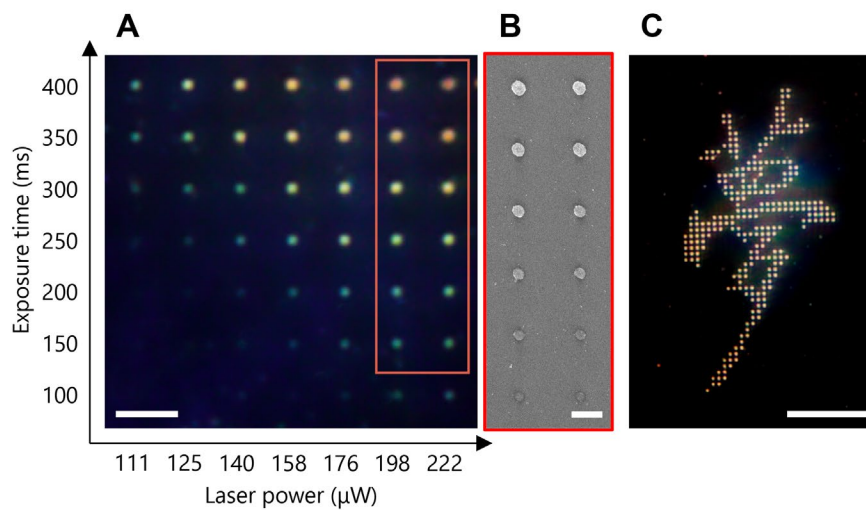
(A) from top to bottom: EDS spectra of the structures presented in Figs. 3a, 3f and 3g. (B)-(D) reflective bright-field micrographs (upper panel) and in-situ transmitting bright-field micrograph (lower panel) of the (B) diamond-structured silver lattice demonstrated in Fig. 3a, (C) dodecahedron structure demonstrated in Fig. 3f, and (D) nested hemi-ellipsoid cage structure demonstrated in Fig. 3g. Scale bars: 5 μm .

Supplementary Fig. S18 | Extended gallery of TPLP-printed 3D nanostructures



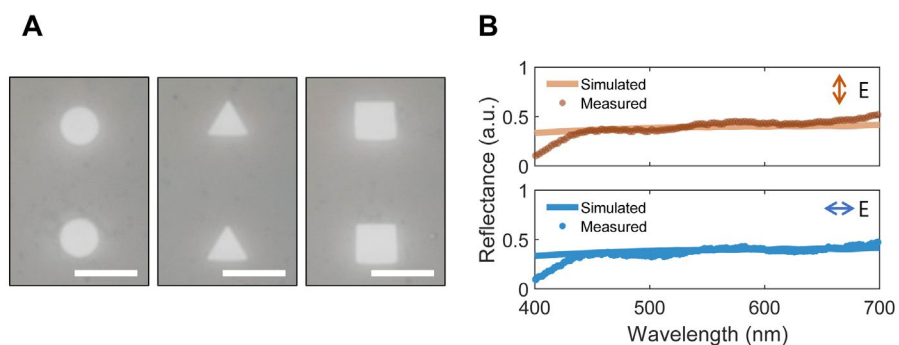
SEM micrographs (left panels), associated EDS maps, reflective bright-field optical micrographs (top right panels), and transmitting bright-field optical micrographs (bottom right panels) of (A) a cut fluorite-structured silver lattice structure, (B) an array of gold triangular cone structures, and (C) an array of platinum fly wire structures. Scale bars: 5 μm. Tilt angles: 60 degrees.

Supplementary Fig. S19 | Plasmonic laser colour printing by metallic exposure dose control



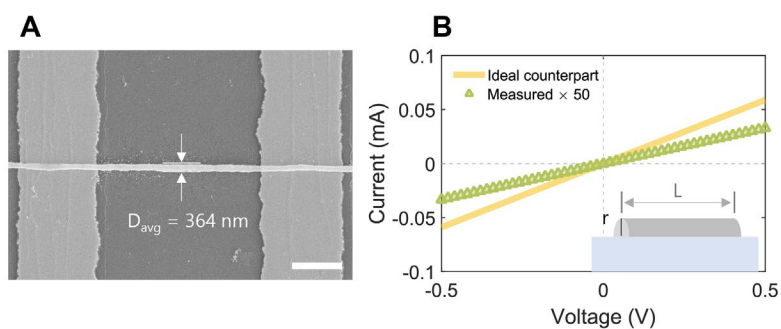
(A) Dark-field optical micrograph of a printed silver nanodot array, from which the elements with representative plasmonic colours are elected and displayed in Fig. 3a. (B) SEM image of the elements enclosed in the red rectangle in (A). (C) A pixelated pattern of the Chinese character ‘dream’, the exposure dose is fixed at $140 \mu\text{W}$ @ 400 ms . The pixel pitch is $1.5 \mu\text{m}$. Scale bar: (A), $3 \mu\text{m}$; (B), $1 \mu\text{m}$; (C), $20 \mu\text{m}$.

Supplementary Fig. S20 | Extended data about micromirrors printed by TPLP



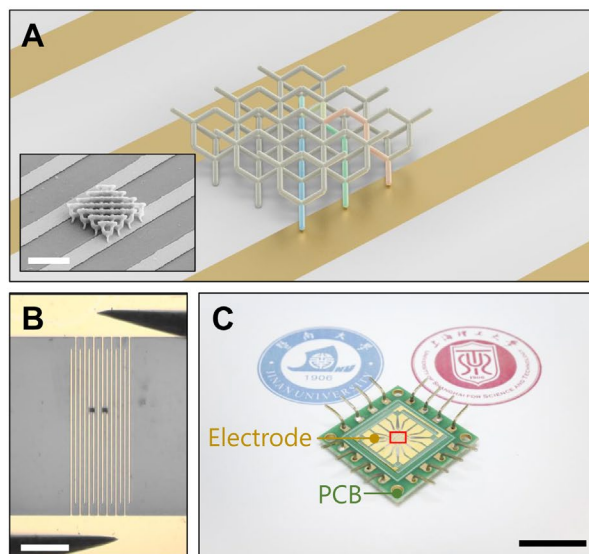
(A) Bright-field optical micrographs of as-printed micromirrors in three different shapes. Scale bar: 10 μm . **(B)** Comparisons between measured (dotted curve) and simulated (solid curve) polarized reflection spectra of the micromirrors, the spectral data are averaged from the mirrors presented in (A).

Supplementary Fig. S21 | Electrical properties of the elemental nanowires in TPLP



(A) SEM micrograph of one representative silver nanowire printed on gold interdigital electrodes. Scale bar: $3 \mu\text{m}$. **(B)** Measured U-I curve of the nanowire (line with triangle marks, averaged from three wires) and expected curve of an ideal counterpart made of pure silver (yellow solid line).

Supplementary Fig. S22 | Extended data about the 3D conductive network structures



(A) Schematics of a 3D silver network structure on gold interdigital electrodes, the colored rods mark the three of the possible 3D conducting routes during linear voltammetry measurements. Inset: zoomed SEM micrograph of the TPLP-printed structure. (B) In-situ BF optical micrograph of the test region during two-probe measurements. (C) Photograph showing the packaged sample on a circuit board. Scale bars: inset in (A), 10 μm ; (B), 200 μm ; (C) 20 mm.

Supplementary Table S1 | Summary on recipes of TPLP inks used in this work.

Recipes	Precursor^a	Capping agents^a	Reducing agents^b	Purposes
R1	DSAc (0.25 mol/L)	ND-Sar-Na ⁺ (0.10 mol/L)	TPETA (0.50 wt%)	For 2D TPLP experiments
R2	DSAc (0.25 mol/L)	Sodium citrate (0.03 mol/L)	TPETA (0.50 wt%)	For control experiment shown in Fig. 2c-e
R3	DSAc (0.75 mol/L)	ND-Sar-Na ⁺ (0.10 mol/L)	TPETA (1.25 wt%)	For 3D TPLP experiments
R4	KAuCl ₄ /NaOH (0.05 mol/L)	NH-Arg-Na ⁺ (0.10 mol/L)	TPETA (1.25 wt%)	For 3D TPLP experiments
R5	(NH ₄) ₂ PtCl ₂ (0.05 mol/L)	NH-Arg-Na ⁺ (0.10 mol/L)	TPETA (1.25 wt%)	For 3D TPLP experiments

Note:

^a: molar concentration in the final blend^b: mass concentration in the final blend

Supplementary Table S2 | Summary on exposure dose parameters used for the main-text figures.

Figures	Structure type	Laser power	Scanning velocity (exposure time)
Figure 2c, 2h	0D nanodot structures	ca. 130 μ W	200 ms
Figure 2d, 2i	2D curvilinear structures	ca. 200 μ W	4 μ m/s
Figure 2m	0D nanodot structure	ca.100~200 μ W	200 ms
Figure 2n	0D nanodot structure	ca. 120 μ W	100~400 ms
Figure 3a-3e	3D silver structures	180-220 μ W	4 μ m/s
Figure 3f	3D gold structures	ca. 280 μ W	2 μ m/s
Figure 3g	3D platinum structures	ca. 230 μ W	2 μ m/s
Figure 4a-4b	0D nanodot structure 2D pixelated pattern	ca. 110~220 μ W	200 ms
Figure 4c	2D planar structure	ca. 120 μ W	1 μ m/s
Figure 4e	3D network structure	ca. 180 μ W	4 μ m/s

Supplementary Table S3 | Summary on optical diffraction limits in TPLP

Directions	Absolute value (nm)	Relative value (λ)
X	380	0.47
Y	380	0.47
Z	972	2.40

Note:

Derived based on the nominal optical parameters, without inclusion of residual aberrations in the optical system. Laser wavelength, 405 nm; incident electric-field polarization: circularly polarized; NA, 1.20; index of immersion medium: 1.33

Supplementary Table S4 | Summary on optical sources required by different 3D metal printing techniques

Quantities	Descriptions	Typical (peak) power requisite ^a	Typical Footprint ^b	Typical apparatus cost ^b
Ultrafast lasers	Commonly used for multiphoton-absorption based techniques	$10^2 \sim 10^5$ W	$10^7 \sim 10^8$ mm ³	USD $10^4 \sim 10^5$ (CNY $10^5 \sim 10^6$)
High-power CW lasers	Commonly used for laser powder-fusion based techniques	$10^0 \sim 10^2$ W	$10^7 \sim 10^8$ mm ³	USD 10^5 (CNY 10^6)
Diode laser	Laser source required for implementation of TPLP	$\sim 10^{-4}$ W	10^2 m $\sim 10^6$ mm ³	USD $10^0 \sim 10^2$ (CNY $10^1 \sim 10^3$)

Note:

- Power requisite refers to the minimum source power output to support 3D printing in different methods, power loss caused by optical elements in the optical system are not included.
- Variation on costs and footprints usually relate to the specification of the package type, operating wavelength and the maximum power output.

Supplementary Movies.

Movie S1.

Movie of typical 2D printing experiment with TPLP configuration (with R1 in supplementary table S1). Exposure condition: 180 μW @ 4 $\mu\text{m/s}$. The movie is 2-times speeded up.

Movie S2.

Movie of typical 2D printing experiment with control group configuration (with R2 in supplementary table S1). Exposure condition: 180 μW @ 4 $\mu\text{m/s}$. The movie is 2-times speeded up.

Movie S3.

Movie of typical 3D printing experiment with TPLP configuration (with R3 in supplementary table S1). Exposure condition: 180 μW @ 4 $\mu\text{m/s}$. The movie is 3-times speeded up.

Movie S4.

Movie of optical trapping test using the same 3D nanoprinter for TPLP, with the focus area marked by the white circle. Exposure condition: 660 μW . The movie is 3-times speed-up.

Supplementary references

45. Lin, J., Rodríguez-Herrera, O. G., Kenny, F., Lara, D. & Dainty, J. C. Fast vectorial calculation of the volumetric focused field distribution by using a three-dimensional Fourier transform. *Opt. Express* **20**, 1060-1069, doi:10.1364/OE.20.001060 (2012).
46. García de Abajo, F. J. & Howie, A. Retarded field calculation of electron energy loss in inhomogeneous dielectrics. *Physical Review B* **65**, 115418, doi:10.1103/PhysRevB.65.115418 (2002).
47. Blanco, L. A. & García de Abajo, F. J. Spontaneous light emission in complex nanostructures. *Physical Review B* **69**, 205414, doi:10.1103/PhysRevB.69.205414 (2004).
48. Giannini, V., Fernández-Domínguez, A. I., Heck, S. C. & Maier, S. A. Plasmonic Nanoantennas: Fundamentals and Their Use in Controlling the Radiative Properties of Nanoemitters. *Chemical Reviews* **111**, 3888-3912, doi:10.1021/cr1002672 (2011).
49. Novotny, L. & Hecht, B. Principles of nano-optics. (Cambridge university press, 2012).
50. Linic, S., Aslam, U., Boerigter, C. & Morabito, M. Photochemical transformations on plasmonic metal nanoparticles. *Nature Materials* **14**, 567-576, doi:10.1038/nmat4281 (2015).
51. Cortés, E., Xie, W., Cambiasso, J., Jermyn, A. S., Sundararaman, R., Narang, P., Schlücker, S. & Maier, S. A. Plasmonic hot electron transport drives nano-localized chemistry. *Nature Communications* **8**, 14880, doi:10.1038/ncomms14880 (2017).
52. López-García, J. J., Aranda-Rascón, M. J. & Horno, J. Electrical double layer around a spherical colloid particle: The excluded volume effect. *Journal of Colloid and Interface Science* **316**, 196-201, doi:https://doi.org/10.1016/j.jcis.2007.07.054 (2007).
53. Majee, A. & Würger, A. Charging of Heated Colloidal Particles Using the Electrolyte Seebeck Effect. *Physical Review Letters* **108**, 118301, doi:10.1103/PhysRevLett.108.118301 (2012).
54. Lin, L., Wang, M., Peng, X., Lissek, E. N., Mao, Z., Scarabelli, L., Adkins, E., Coskun, S., Unalan, H. E., Korgel, B. A., Liz-Marzán, L. M., Florin, E.-L. & Zheng, Y. Opto-thermoelectric nanotweezers. *Nature Photonics* **12**, 195-201, doi:10.1038/s41566-018-0134-3 (2018).
55. Hedberg, J., Lundin, M., Lowe, T., Blomberg, E., Wold, S. & Wallinder, I. O. Interactions between surfactants and silver nanoparticles of varying charge. *Journal of Colloid and Interface Science* **369**, 193-201, doi:https://doi.org/10.1016/j.jcis.2011.12.004 (2012).
56. Badawy, A. M. E., Luxton, T. P., Silva, R. G., Scheckel, K. G., Suidan, M. T. & Tolaymat, T. M. Impact of Environmental Conditions (pH, Ionic Strength, and Electrolyte Type) on the Surface Charge and Aggregation of Silver Nanoparticles Suspensions. *Environmental Science & Technology* **44**, 1260-1266, doi:10.1021/es902240k (2010).
57. Vazdar, M. et al. Arginine “Magic”: Guanidinium Like-Charge Ion Pairing from Aqueous Salts to Cell Penetrating Peptides. *Accounts of Chemical Research* **51**, 1455-1464, doi:10.1021/acs.accounts.8b00098 (2018).
58. Vondrášek, J., Mason, P. E., Heyda, J., Collins, K. D. & Jungwirth, P. The Molecular Origin of Like-Charge Arginine–Arginine Pairing in Water. *The Journal of Physical Chemistry B* **113**, 9041-9045, doi:10.1021/jp902377q (2009).