Electronic Supplementary Material

Plasmon-directed polymerization: Regulating polymer growth with light

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Thermal calculation

The physical model of optical heating of plasmonic NPs can be simplified as electromagnetic energy conversion and subsequent thermal conduction.

As the particle size $a \ll \lambda$, we can use absorption cross-section to calculate the thermal input via

$$Q = I\sigma_{abs}$$
$$\sigma_{abs} = k \ln |\alpha|$$

where $\alpha = 4\pi\alpha^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$, a is the radius of Au NP and ε and ε_m are the dielectric constants of Au NPs (from Johnson Christy) and the surrounding medium (DVB), which has ε_m =2.4.

The temperature distribution around the Au NP can then be calculated using [1],

$$T(r) = T_\infty + \frac{Q}{4\pi kr}$$

where r is the distance from the center of Au NP ($r > a$).

The detailed settings for COMSOL simulations are:

Material	Thermal conductivity: k/W m^{-1} K^{-1}
DVB	0.16
Au	318
SiO_2/Si	9.864[a]

a) This thermal conductivity is experimentally determined with transient hot wire method.

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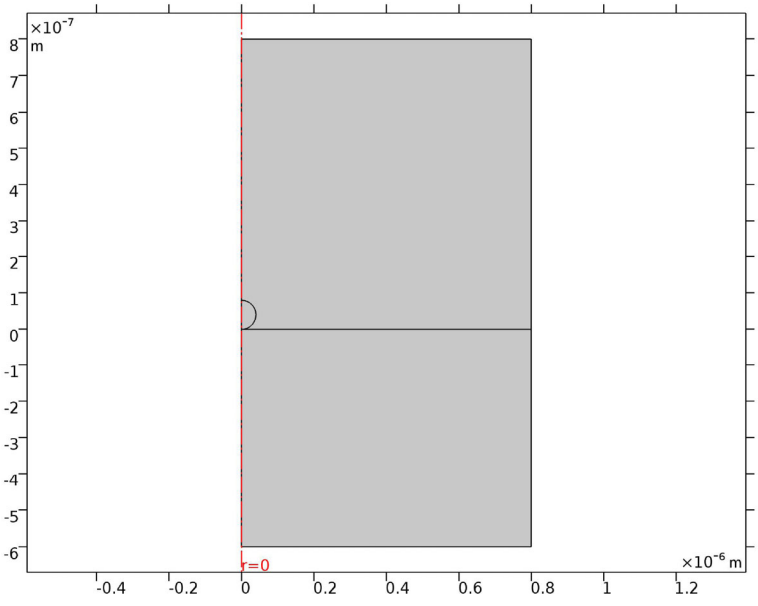
Geometry

We build the 3D model by rotating the cross-section plane around the z axis as shown below. The Au NP (r=40 nm) acts as the heating source, which is placed on a SiO_2 substrate surrounded by DVB monomer liquid.



Equations:

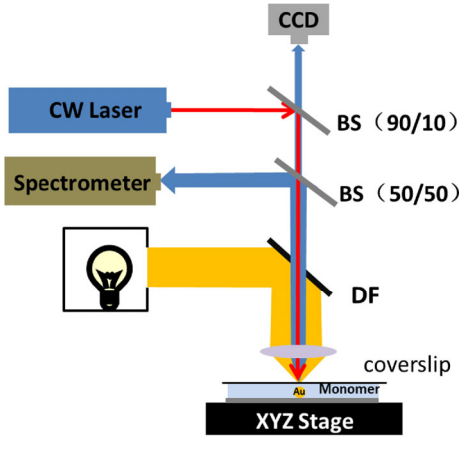
In this case, we use the steady-state temperature distribution $T(\vec{r},t)$, so the heat transfer equation can be simplified as the Poisson and Laplace forms :

$$k_{au}\nabla^2(x,y) = Q(x,y)$$
$$k_{sub}\nabla^2(x,y) = 0$$
$$k_{med}\nabla^2(x,y) = 0$$

with boundary condition T = T_0, and T_0 = 293K.

Meshing:

A triangular mesh of size 5 nm is used inside the Au sphere and 15 nm outside the Au sphere.



Scheme S1 Experimental setup for laser irradiation and dark field spectroscopy.

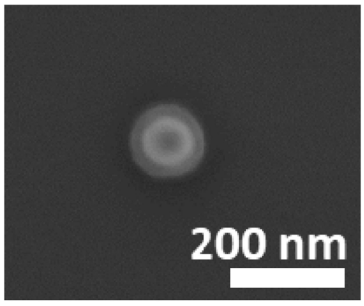


Figure S1 SEM image of Au@PDVB NPs after laser irradiation (2mW, 60s) in DVB. The Au NPs are plasma treated to remove organic ligands coating the Au NP that might potentially cause initiation.

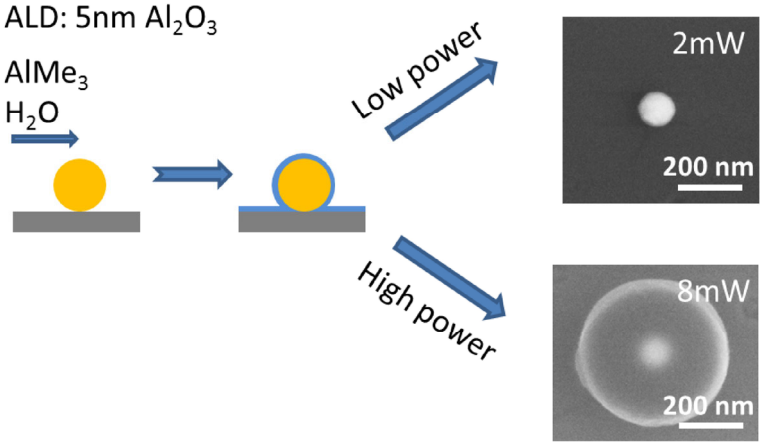


Figure S2 Irradiation on Al_2O_3 encapsulated Au NP with low (2mW) and high (8mW) power laser. At low power, no growth of PDVB is observed due to the blocking of hot electrons. At high power, initiation is mainly attributed to thermal effect, which grows into a much thicker PDVB shell.

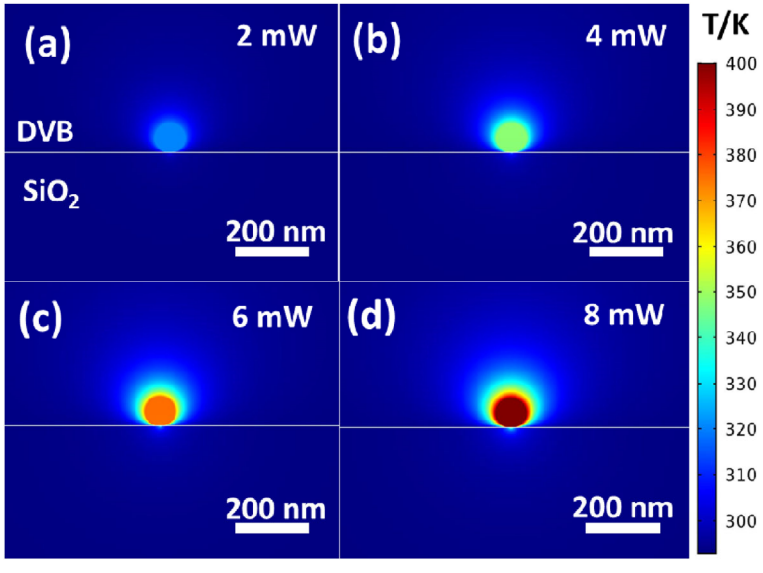


Figure S3 COMSOL simulations of the temperature distribution around Au NPs on SiO_2 substrate (immersed in DVB) at different laser powers. (a) 2 mW, (b) 4 mW, (c) 6 mW, (d) 8 mW. The scale bars are 200 nm.

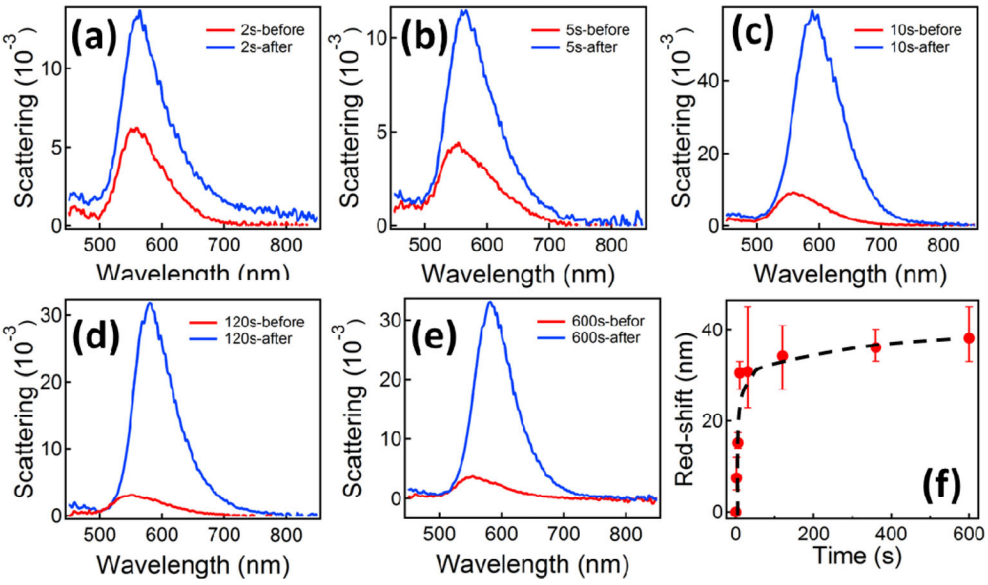


Figure S4 Scattering spectra of Au NPs before (red line) and after irradiation (blue line). (a) 2 s, (b) 5 s, (c) 10 s, (d) 120 s, (e) 600 s. (f) Change of plasmon red shift with irradiation time.

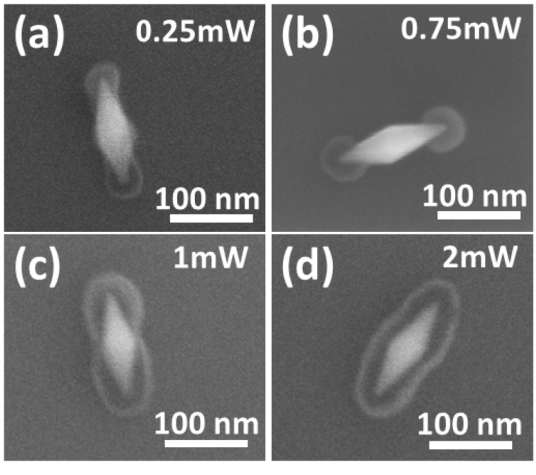


Figure S5 SEM images of AuBPN@PDVB formed at different irradiation powers for 30s. (a) 0.25 mW, (b) 0.75 mW, (c) 1 mW, (d) 2 mW.

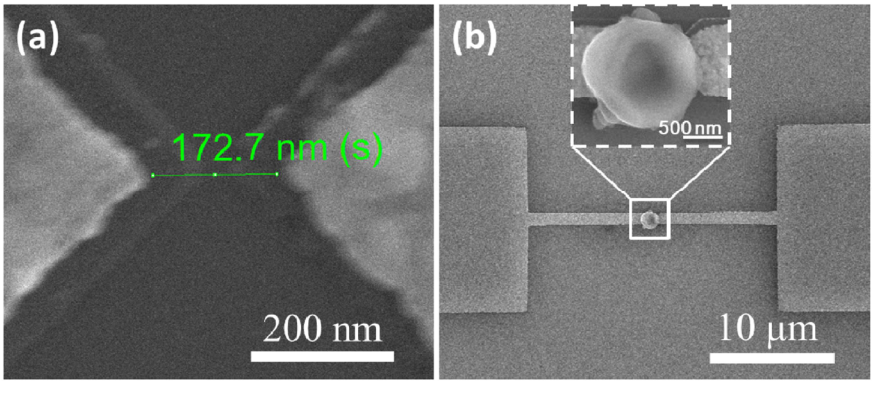


Figure S6 SEM images of Au bowtie-like nanoelectronic structures (a) before and (b) after laser irradiation (6mW, 60s). Inset in (b) shows a magnified view of PDVB in the nanogap.

Monomer mixtures. If a mixture of St and DVB monomers is used for polymerization, a more complicated growth scenario emerges due to elastic-driven phase separation (Fig. S7) [2,3]. With low DVB content (<10%), only a very thin polymer shell is formed (Fig. S7a,b) similar to the growth of pure PS (Fig. 1e,f). As the content of DVB increases from 20% to 50%, the polymer cross-linking increases as well as its thickness. Swelling of these polymer shells by the surrounding monomers leads to anisotropic protrusions wherever the elastic shell of cross-linked PS is weakest (Fig. S7c-d). These can puncture at lower DVB content (<40%). Further increasing the content of DVB to 80% results in near-spherical shells of much larger thickness (Fig. S7e). Since more DVB increases strongly the degree of cross-linking, the thicker shell resists internal swelling, maintaining a near-spherical shape. Further increases in DVB content lead to smaller polymer shells (Fig. S7f) as they almost completely resist any internal swelling. This size dependence of the polymer coating as a function of DVB content (Fig. S7g) shows specific domains where anisotropic growth occurs (20 to 80% of DVB). As the cross-linked shell becomes thinner (with more St), it suddenly becomes vulnerable to anisotropic stretching from the internal pressure which develops as monomers diffuse into the growing polymer, thus inflating it. The laser-induced plasmonic polymerization thus produces different sizes, geometries, and cross-linking from the different monomer mixtures, allowing considerable tuning of material properties (and not previously accessible for nanoscale particles).

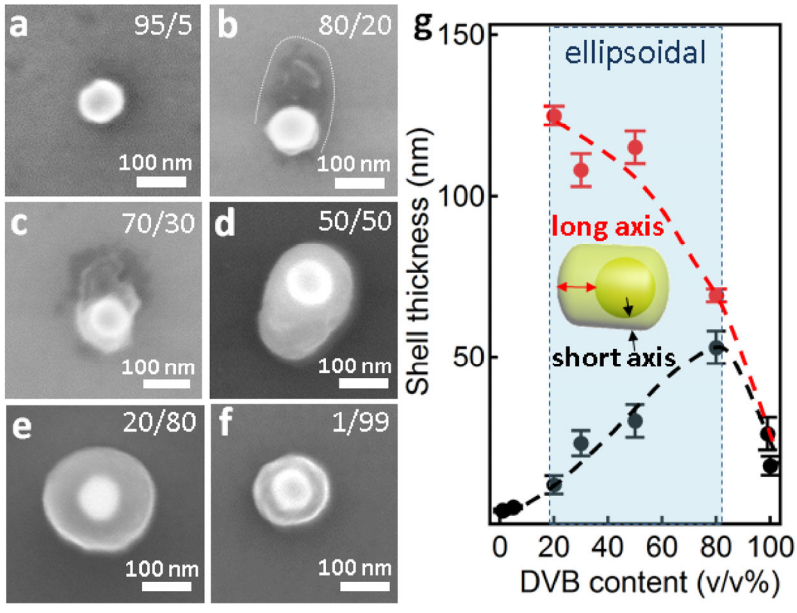


Figure S7 Hot-electron-induced polymerization from monomer mixtures. a-f, Monomer mixtures of different ratios of St/DVB under laser irradiation (2 mW, 100 s). g, Thickness of polymer shells (anisotropic in blue shaded region) with increasing DVB fraction.

References

[S1] K. Setoura, Y. Okada, D. Werner and S. Hashimoto, *ACS Nano*, **2013**, *7*, 7874–7885.

[S2] J.-W. Kim, R. J. Larsen and D. A. Weitz, *J Am Chem Soc*, **2006**, *128*, 14374–14377.

[S3] J. W. Kim, R. J. Larsen and D. A. Weitz, *Adv Mater*, **2007**, *19*, 2005–2009.