Supplementary information

Light-directed tuning of plasmon resonances via plasmon-induced polymerization

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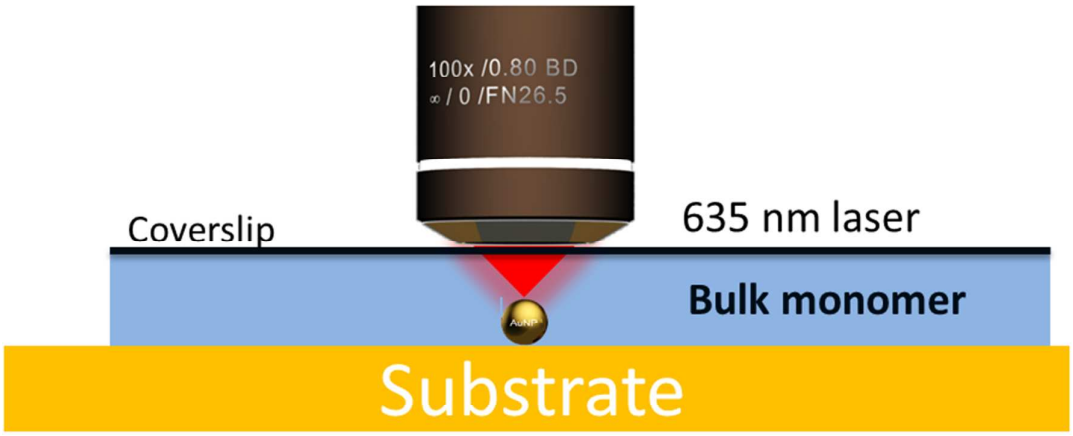
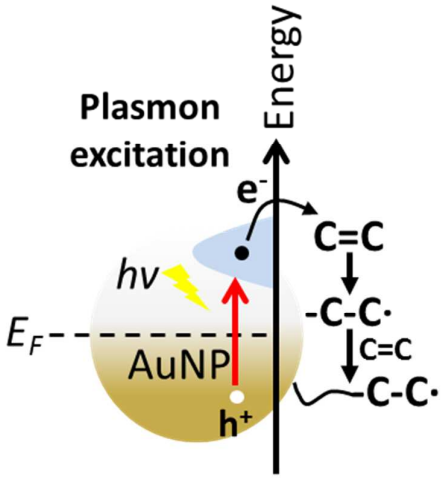


Scheme S1. Experimental setup for plasmon-induced polymerization using laser irradiation at 635 nm with power densities 0.1-1 mW/μm^2. Air NA 0.8 objective focusses through cover slip which traps bulk monomer to substrate surface.



Scheme S2. Reaction mechanism of hot-electron-induced polymerization.

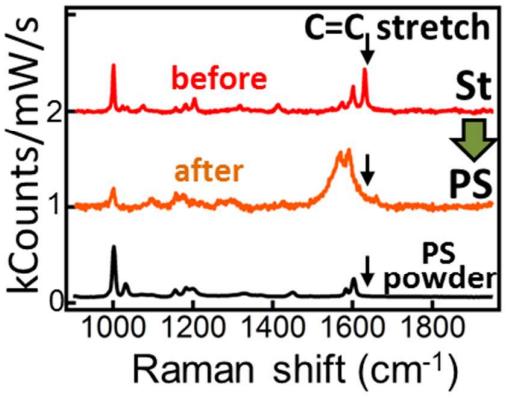


Figure S1. Raman signal of PS powder and SERS signal from Au NPoMs before/after irradiation. The strong 1630 cm^{-1} mode (black arrows) corresponding to C=C stretching in the styrene (St) (red line), disappears in the irradiated nanoparticles (orange line) due to polymerization.[1] This is further confirmed by its absence in the Raman fingerprint of PS powders, shown for comparison (black line, which of course averages over vast numbers of chains compared to the spectra above obtained from the few chains in the gap).

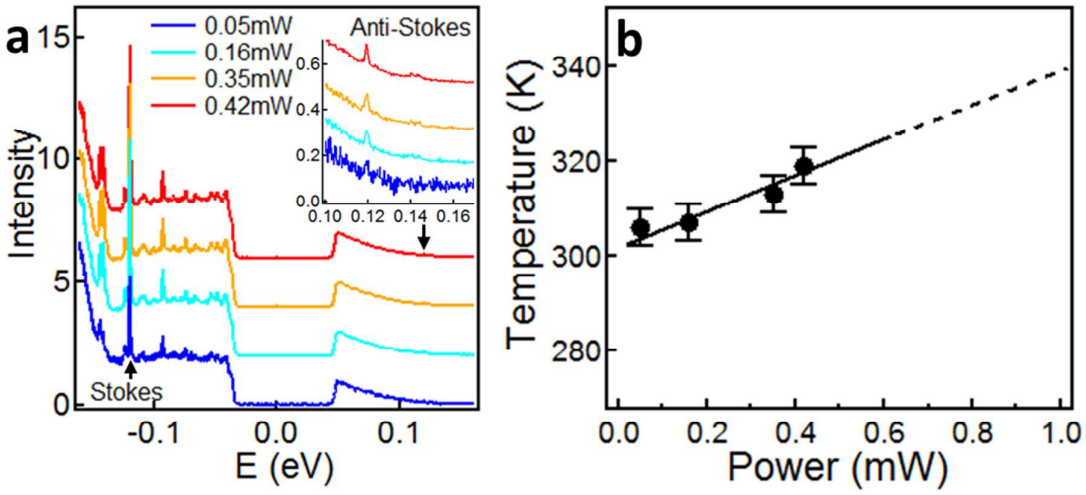


Figure S2. Stokes and anti-Stokes Raman spectra used to determine temperature of monomers in the gap of Au NPoM. (a) SERS of styrene monomer based on Au NPoM structures at different laser (633 nm) powers. (b) Exponential background on anti-Stokes side used with Boltzmann fit to give temperatures at different laser powers. Below 0.5mW heating in the gap is below 30K, excluding thermal polymerization. Above 3mW, temperature rises above 410K are possible in the nanogap region, thus supporting the auto-initiation mechanism.

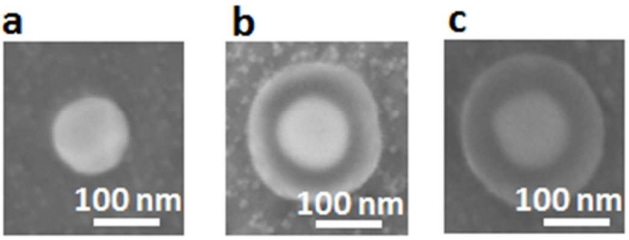


Figure S3. Light-induced polymerisation of P3HT under irradiation of AuNPs in monomer with 10 s of 635 nm laser at (a) 1mW, (b) 3mW, and (c) 4mW.

Reference

(1) Brun N, Youssef I, Chevrel MC, Chapron D, Schrauwen C, Hoppe S, Bourson P, Durand A. In situ monitoring of styrene polymerization using Raman spectroscopy: multi-scale approach of homogeneous and heterogeneous polymerization processes. *J Raman Spectrosc* 2013; **44:** 909-915.