## Supplementary Information for

## Active Strain Engineering of Soft Plasmene Nanosheets by Thermoresponsive Hydrogels

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Key words: 2D plasmene nanosheets, strain engineering, soft plasmonics, hydrogel, thermoresponsive.

## **Experimental Section**

*Materials:* chloride trihydrate Gold (III) (HAuCl<sub>4</sub>  $3H_2O_1$ ≥99.9%), hexadecyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH<sub>4</sub>), L-ascorbic acid (AA), silver nitrate (AgNO<sub>3</sub>), cetyltrimethylammonium chloride solution (CTAC, 25 wt % in H<sub>2</sub>O), polyvinylpyrrolidone (PVP, average M<sub>w</sub> ~55,000), 4-aminothiophenol (4-ATP, ≥97.0%), N,N'-Methylenebis(acrylamide) (MBAA, 99%), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-mthylpropiophenone (HHMP, 98%), N-isopropylacrylamide (NIPAm, 97%) and dimethyl sulfoxide (DMSO, ≥99.9%) were obtained from Sigma-Aldrich. Chloroform was purchased from Merck Millipore. Ethanol (EtOH, absolute) was purchased from Thermal fisher scientific (Ajax Finechem). Milli-Q (MQ) water was obtained from Milli-Q Advantage A 10 water purification System. All materials were used without any further purification.

Synthesis of gold@silver nanocubes (Au@Ag NCs): Au@Ag NCs were synthesised according to the method in literature with small modifications.<sup>1</sup> The CTAC-capped Au seeds were firstly synthesized by a two-step seed-mediated growth procedure. In the first step, 0.1 mL of 25 mM HAuCl<sub>4</sub>, 0.6 mL of 0.01M NaBH<sub>4</sub> and 10 mL of 0.1 M CTAB solutions were mixed in a 20mL glass vial by stirring for 30 s and then kept undisturbed in a 27-°C water bath for 3 hours to obtain the 3-nm Au seeds. In the following step, 6 mL of 0.5 mM HAuCl<sub>4</sub>, 6 mL of 0.2 M CTAC, 4.5 mL of 0.1 M AA and 0.3 mL of 3-nm Au seeds were added in a 20-mL glass vial and stirred at 1000 rpm for 1 hour in a 27-°C water bath. The CTAC-capped Au seeds were collected by centrifuging at 14500 rpm for 30 min and then washed with MQ water once and finally redispersed in 2.75 mL MQ water. 0.1 mL of the CTAC-capped Au seeds were mixed with 4.9 mL of 20 mM CTAC and heated in a 60-°C water bath for 20 min under stirring. In the following step, 5 mL of 2 mM AgNO<sub>3</sub> and 5 mL of the mixed 50mM AA and 40 mM CTAC was injected simultaneously into the pre-heated seed solution at a rate of 1 mL/min. After the injection, the mixture was kept in the 60-°C water bath for 4hrs under stirring. The Au@AgNCs solution was collected by centrifuge twice (10000 rpm for 15 min) and redispersing in 7.5 mL of 50 mM CTAB solution and kept undisturbed in a 30-°C water bath for 3 days. The purified Au@AgNCs was then collected by discarding the precipitation and redispersing in 7.5 mL of MQ water for further use.

Synthesis of gold nanorods (AuNRs): The AuNRs were synthesized according previously reported method.<sup>2</sup> Firstly, the gold seed solution was synthesized by adding 5 mL of 0.2 M CTAB, 0.1 mL of 25 mM HAuCl<sub>4</sub> and 0.6 mL of freshly prepared 0.01M NaBH<sub>4</sub> into a 20-mL glass vial with 4.9 mL of MQ water. The mixture was vigorously stirred for 2 minutes to obtain the seed solution. For the growth of AuNRs, 5 mL of 0.2 M CTAB, 5 mL of 1 mM HAuCl<sub>4</sub>, 0.6 mL of 4 mM AgNO<sub>3</sub>, 240  $\mu$ L of 80 mM AA and 12  $\mu$ L of above-prepared seed solution were mixed in sequence and then kept in a 30-°C water bath for 2 hrs. The final AuNRs were collected by centrifuging at 7000 rpm for 10 min and redispersing in 5 mL water for further use.

*Fabrication of plasmonic nanosheet on Si wafer:* 5 mL of as-synthesized Au@AgNCs aqueous suspension was diluted to 10 mL with MQ water, centrifuged at 11000 rpm for 10 min and then redispersed in a mixed solution with 5mL of 8 mg/mL PVP in EtOH and 100  $\mu$ L of 10 mM 4-ATP in EtOH. The solution was kept undisturbed overnight to obtain the PVP/4-ATP-capped

Au@AgNCs. The PVP/4-ATP-capped Au@AgNCs were then washed with EtOH once and finally concentrated to ~20  $\mu$ L by centrifugation (10500 rpm, 10 min). 10  $\mu$ L of chloroform was then added into the Au@AgNCs suspension. 600  $\mu$ L of MQ water was dropped on the surface of Si wafer to form the air-water interface. The concentrated Au@AgNCs suspension was then drop-casted on the interface. After evaporation of chloroform and EtOH, a layer of close-packed nanoparticles formed on the interface. The plasmene nanosheets sitting on Si wafer were then obtained after the evaporation of water at room temperature. For AuNR-based nanosheets, 3 mL of AuNRs suspension was used to fabricate nanosheets.

*Transfer nanosheet into PNIPAm hydrogel*: A typical pregel solution was firstly prepared by dissolving NIPAM (5 M), HHMP (1.5 mol% relative to NIPAm), MBA (2 mol% relative to NIPAm) into DMSO in a 20-ml vial wrapped with aluminium foil.<sup>3</sup> The mixture was ultrasonically agitated for 5mins in a room-temperature water bath. The glass slides were used to form a sandwiched mold for fabricating PNIPAm hydrogel. The as-assembled nanosheets on Si wafer was sandwiched between two glass slides with a spacing of ~1 mm. 0.5 mL of pregel solution was then injected into the mold. After the polymerization of pregel solution by irradiating with a UV light (Spectroliner XL-1000 UV cross-linker with wavelength of 365 nm) for 20 min, the nanosheets were embedded into the PNIPAm gel. After that, the nanosheets in PNIPAm gel were lift off from Si wafer into DI water, during which the DMSO was replaced by DI water, followed by immersing in MQ water to remove the unreacted monomers and solvent. The samples were then cut into a rectangular shape in size of ~1.5 cm × ~ 0.6 cm for further test.

*Discrete Au@AgNC in PNIPAm hydrogel*: 1 mL of the above-prepared PVP/4-ATP-capped Au@AgNCs in EtOH was centrifuged at 10500 rpm for 10 min and then redispersed in 1 mL of pregel solution and mixed thoroughly. The mixture was then used to fabricate the discrete Au@AgNC in PNIPAm hydrogel following the above-mentioned polymerization method.

*Deswelling properties of PNIPAm hydrogel:* The deswelling ratio of the hydrogels were measured by using gravimetric method. The hydrogels were soaked in MQ water at 23°C for equilibrium state, and then immersed in water bath with various temperatures (ranging from 23 to 43°C) for 1 min. The weights of the sample were measured after the immersion. Deswelling ratio (DS) was calculated by the following equation<sup>4</sup>:

$$\mathrm{DS} = \frac{W_T - W_0}{W_e - W_0}$$

where  $W_T$  is the weight of the hydrogel at temperature of T.  $W_e$  and  $W_0$  are the weight of the hydrogel at equilibrium and dry state respectively. The compressive strain induced by deswelling of PNIPAm hydrogel was estimated by the volume of water loss during heating.

*Characterization:* The morphology of plasmene nanosheets and nanoparticles was characterized by scanning electron microscope (SEM, FEI Nova NanoSEM 450 FEGSEM operating at voltage of 5 kV) and transmission electron microscope (TEM, FEI Tecnai G2 T20 TWIN LaB6 TEM operating at voltage of 200 kV). The cross-section SEM image of plasmene nanosheets in PNIPAm hydrogel was obtained by heating the sample in a 55°C water bath for 10 min and then dried in air at room temperature. An Agilent 8453 UV–vis spectrophotometer was used to record the extinction spectra. For the heated sample in aqueous solution, the CTAB-capped Au@AgNCs in aqueous solution was kept in 35°C and 55°C water bath for 10

min respectively to obtain the UV-vis spectra. For the samples in hydrogel, 5 random positions were checked each time. For the compressive state, the samples were heated in a 55-°C water bath for 10 min before recording their extinction spectra. For the strain engineering, the sample was incubated in the water bath with a certain temperature ranging from 21 to 43 °C for 1 min and then taken out to check its UV-vis spectrum. A Renishaw RM 2000 micro-Raman system with excitation laser wavelength of 633 nm, a laser spot size of ~ 1.5  $\mu$ m (50× objective) and a laser power of ~0.1mW was applied to record the Raman spectra. For nanosheets in hydrogel, 3 in-situ positions were checked for each sample at tensile and compressive states. For discrete Au@AgNCs in hydrogel, 5 random positions were checked. For the compressive state, the samples were heated at a 55-°C water bath for 10 min before recording their Raman spectra. The size of nanoparticles were analysed by Image J software.



**Figure S1**. (a)TEM images and (b) size distribution of Au@Ag NC for fabricating plasmene nanosheets. (Scale bar: 20 nm)



**Figure S2.** Extinction spectra of (a) discrete Au@AgNC in water (black curve), in ethanol (EtOH, blue curve) and in chloroform (CHCl<sub>3</sub>, red curve). Insert is the photo of Au@AgNC in water.



**Figure S3.** Extinction spectra of discrete CTAB-capped Au@Ag NC in water when at room temperature (RT, black curve), being heated to 35 °C (red curve) and 55 °C (blue curve).



**Figure S4**. SEM images of 4-ATP/PVP-capped Au@Ag NC nanosheet on Si wafer. (Scale bar: 100 nm)



Figure S5. Cross-section SEM image of the dried plasmene nanosheet embedded in PNIPAm

hydrogel. (Scale bar: 500 nm)



**Figure S6.** (a) Schematic illustration of temperature-enabled reversible strain engineering of discrete Au@AgNCs that has been evenly impregnated into PNIPAm hydrogel. The digital photos of the Au@AgNC-impregnated PNIPAm hydrogel at (b) tensile straining and (c) compressive straining states (scale bar: 0.5 cm).



**Figure S7.** Transmission optical microscope images of Au@AgNC-impregnated hydrogel at (a) tensile straining and (b) compressive straining states (scale bar: 100 μm).



**Figure S8.** Extinction spectra of the Au@AgNC-impregnated hydrogel at tensile straining (blue solid curve), compressive straining (red solid curve), recovered to tensile straining (green solid curve), discrete Au@AgNC in ethanol (black dashed curve).



**Figure S9.** Extinction spectra of 4-ATP/PVP-capped Au@AgNC nanosheet in PNIPAm hydrogel when heating from 23 °C to 43 °C.



**Figure S10.** De-swelling of Au@AgNC nanosheet in PNIPAm hydrogel (pink) and blank PNIPAm hydrogel (blue) at different temperatures.



**Figure S11.** Reversible SERS signal at 3 characterized peaks (a) 1074, (b) 1144, (c) 1579 cm<sup>-1</sup> of 4-ATP in the Au@AgNC nanosheet in hydrogel in 6 cycles of strain applying and releasing.



**Figure S12.** Representative SERS spectra of discrete Au@AgNC in hydrogel at a Raman shift range from 200 to 3200 cm<sup>-1</sup> at tensile (blue curve) and compressive (orange curve) state. The marked Raman peaks are from the PNIPAm molecules.



**Figure S13.** Schematic illustration of 4-ATP and PNIPAm polymeric chains in (a) plasmene nanosheet-based system and (b) discrete Au@AgNCs-impregnated 3D system. Note that strong SERS signal dominated in the nanosheets-based system under compressive straining state due to Raman "hot spot" effects. Such effects were not present in the impregnation system due to large interparticle spacing. Instead, collapsed polymeric chains densify around Au@AgNCs leading to dominant PNIPAm SERS signal.



Figure S14. Representative SERS spectra of blank hydrogel at tensile (blue curve) and compressive (orange curve) state.



**Figure S15.** Schematic illustration of nanoassemblies (dimers, trimers, or oligomers) within the plasmene nanosheet at tensile straining state. These oligomeric aggregates might form during self-assembly process on silicon surface, which couldn't be separated during hydrogel tensile straining process.



**Figure S16**. (a)TEM images, (b) length and (c) width distribution of AuNR for fabricating plasmene nanosheets. (Scale bar: 20 nm)



**Figure S17.** Extinction spectra of discrete AuNR in water (black curve), in ethanol (EtOH, blue curve) and in chloroform (CHCl<sub>3</sub>, red curve),insert is the photo of discrete AuNR in water.



**Figure S18**. SEM images of 4-ATP/PVP-capped Au NR nanosheets on Si wafer. (Scale bar: 100 nm)



**Figure S19.** (a, b) Digital photos (scale bar: 1 cm) and (c, d) optical microscope images (scale bar: 100  $\mu$ m) of AuNR nanosheet in PNIPAm hydrogel at (a,c) tensile and (b,d)compressive states.



**Figure S20.** Extinction spectra of 4-ATP/PVP-capped AuNR nanosheet in PNIPAm hydrogel when heating from 23 °C to 43 °C.



**Figure S21.** Summarized intensity at 830 nm in UV-vis spectra of 4-ATP/PVP-capped AuNR nanosheet in PNIPAm hydrogel when heating from 23 °C to 43 °C.

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