Supporting information

Dynamically Tunable Plasmonic Band for Reversible Colorimetric Sensors and SERS Effect with Good Sensitivity and Stability

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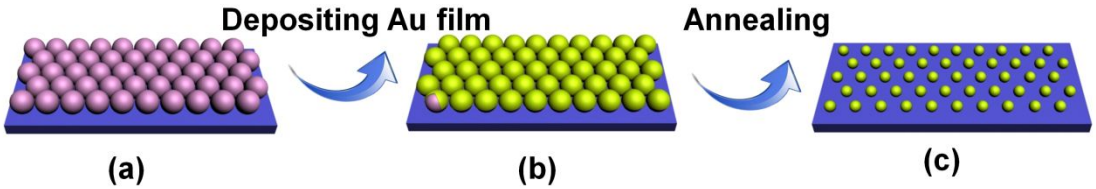
EXPERIMENTAL SECTION

Materials

Polystyrene (PS) microspheres (350 nm in diameter) suspension (2.5 wt% in water) were purchased from Alfa Aesar Corporation. The reagents including ethanol (≥99.7%), dimethyl sulfoxide (DMSO, ≥99.0%) and thiram (⩾97%) were purchased from Sinopharm Chemical Reagent Corporation. N, N'-methylenebisacrylamide (MBAAm, >98%) was obtained from Aladdin Industrial Corporation. 4-ATP (97%) was purchased from Sigma-Aldrich. 2-hydro-xy-1-[4-(2-hydroxyethoxy)-phenyl]-2-methyl-1-propanone (Irgacure 2959) was bought from Tianjin Heowns Biochemical Technology Corporation. In the experiment, the reagents were directly used without further purification. Water (18.2MΩ·cm) was obtained from an ultrafilter system (Direct Q 5 UV).

Preparation of the non-hexagonal close packed (NHCP) 2D Au NP arrays

2D Au NP arrays with a periodic length of 350 nm were prepared by using monolayer PS colloidal crystals as initial templates, followed by depositing Au thin film and annealing described elsewhere.[1] Briefly, a large-area (2 cm × 2 cm) monolayer PS colloidal crystals templates were first prepared on a clean quartz substrate via an air-water interfacial self-assembly method. Then a layer of Au film was deposited on the monolayer PS colloidal crystals by an ion-beam coater. Finally, the monolayer PS colloidal crystals coating with Au film were annealed at 1000 ℃ for 2 h to obtain 2D Au NP arrays with a HNCP structure. The preparation process in this study is shown in Scheme S1.

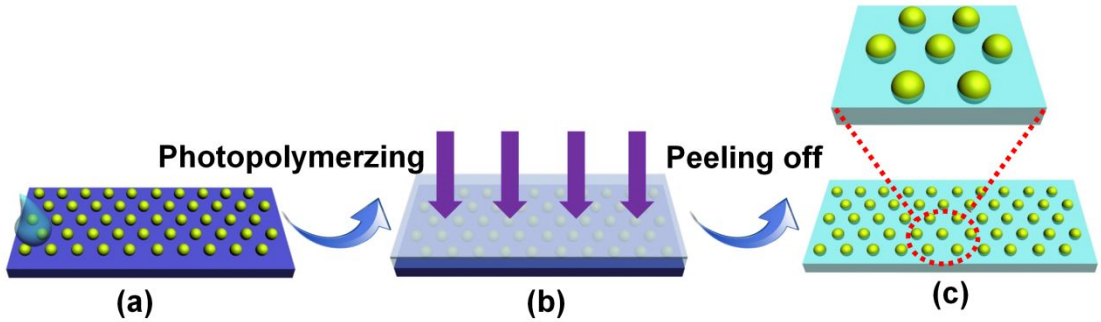


Scheme S1. A schematic diagram describing the synthesis of 2D Au NP arrays by using template method: (a) Monolayer PS colloidal crystals self-assembled on a quartz substrate with a HCP arrangement as a template. (b) Deposited Au film on the

PS colloidal crystals template. (c) Annealed at 1000 °C for 2 h to prepare Au NP arrays with a HNCP structure.

Preparation of the 2D Au NP arrays attached hydrogel composites

Transferring the 2D Au NP arrays onto the hydrogel films was performed by in-situ photopolymerization, as shown in Scheme S2. Firstly, 100 μL reaction solution prepared by mixing 1.000 g AAm, 0.018 g MBAAm and 100 μL Irgacure 2959 solution (0.330g Irgacure 2959 dissolved in 1mL DMSO) in 10 mL deionized water was dropped on the as-prepared 2D Au NP arrays, followed by photopolymerization. Then, a colored thin film of 2D Au NP arrays attached hydrogel composite was obtained when the substrate and cover glass were peeled off. The resulting composite was dialyzed with a lot of water for 3 days to remove unreacted materials. After that, the synthetic 2D Au NP arrays attached hydrogel composites were stored in water before further characterization and measurement.



Scheme S2. A schematic diagram describing the transferring the Au NP arrays from the substrate onto the hydrogel film by in-situ photopolymerization: (a) Poured the reaction solution on the as-prepared Au NP arrays. (b) Placed a cover glass on the surface of the reaction solution, followed by photopolymerization. (c) Peeled off the 2D Au NP arrays attached hydrogel composite from substrate and cover glass.

Water-response measurements. In order to measure the response to water content, the as-prepared Au NP arrays attached hydrogel composites were firstly put into water to become fully swollen, then were immersed in mixed solutions with different volume ratios of ethanol and water until reaching an equilibrium state. Subsequently, the extinction spectra and photos of the composites with different water contents were recorded.

SERS measurements. Before SERS measurements, the prepared 2D Au NP arrays attached hydrogel composites were immersed in 10 mL 4-ATP aqueous solutions and thiram with different concentrations. After that, the surface water of the hydrogel film was removed by filter paper and it was immersed in mixed solutions with different volume ratios of ethanol and water. After reaching an equilibrium state, these films were placed on clean silicon wafers and subsequently subjected to SERS measurements. The SERS measurements were conducted with a laser beam of 785 nm wavelength.

Characterization

The morphologies of all samples were observed by a field-emission scanning electron microscope (FESEM, SU8020). UV-vis-NIR extinction spectra were recorded by a microspectrometre system from Ideaoptics Corp. Raman spectra were monitored by a confocal microprobe Raman spectrometer (Renishaw inVia Reflex).

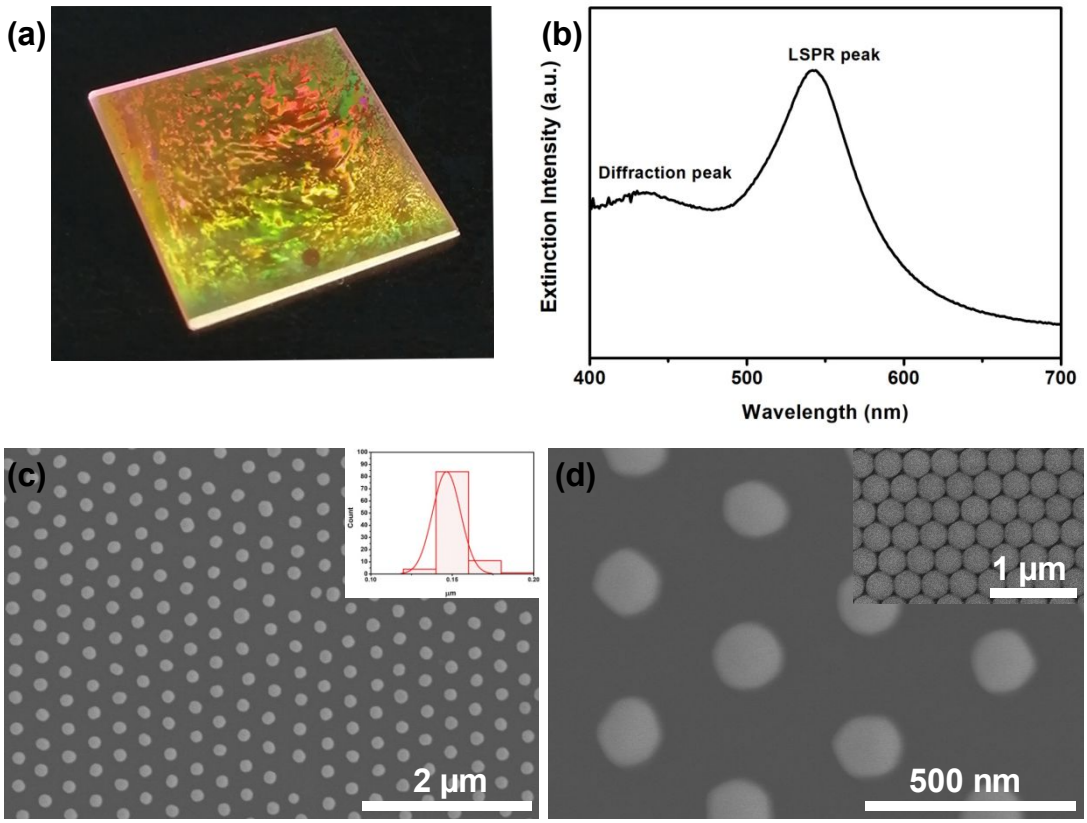


Figure S1. Characterization of the 2D Au NP arrays. Digital photograph (2 cm × 2 cm) (a), UV-Vis extinction spectrum (b) and SEM image (c,d) of the 2D Au NP arrays. The inset of (c) is diameter distribution map and the diameter of the Au NPs is ca.147 nm. The inset of (d) is SEM image of the PS colloidal crystal template.

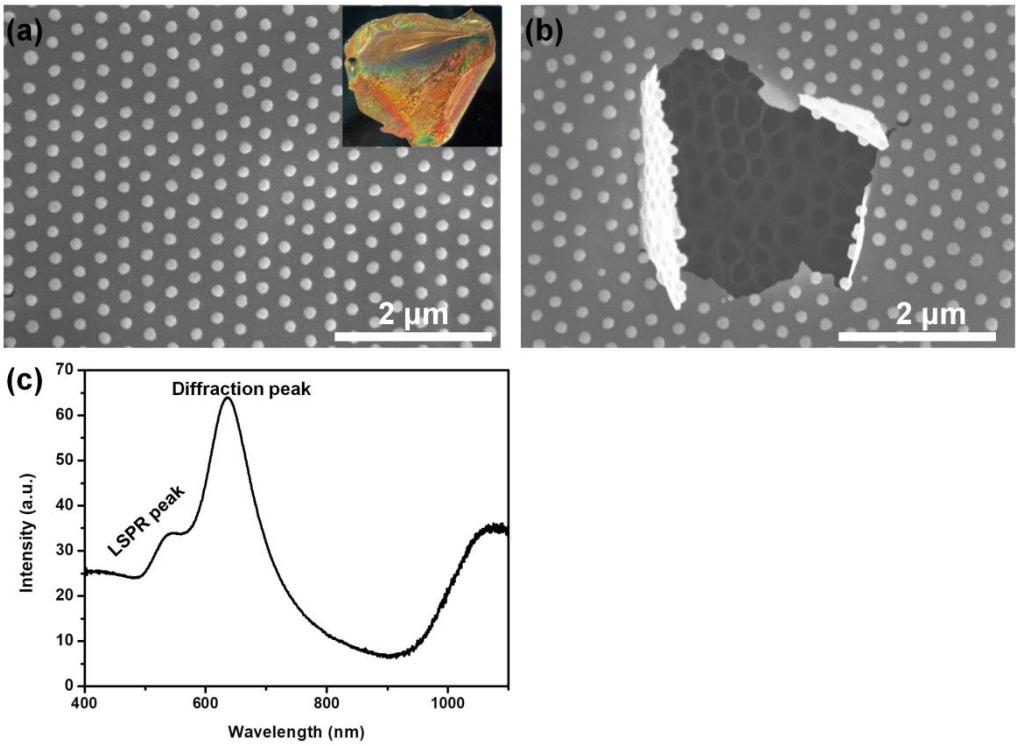


Figure S2. (a), (b) SEM images and (c) the UV-Vis extinction spectrum of the 2D Au NP arrays attached hydrogel composite. The inset of (a) is the digital photograph of the 2D Au NP arrays attached hydrogel composite in water.

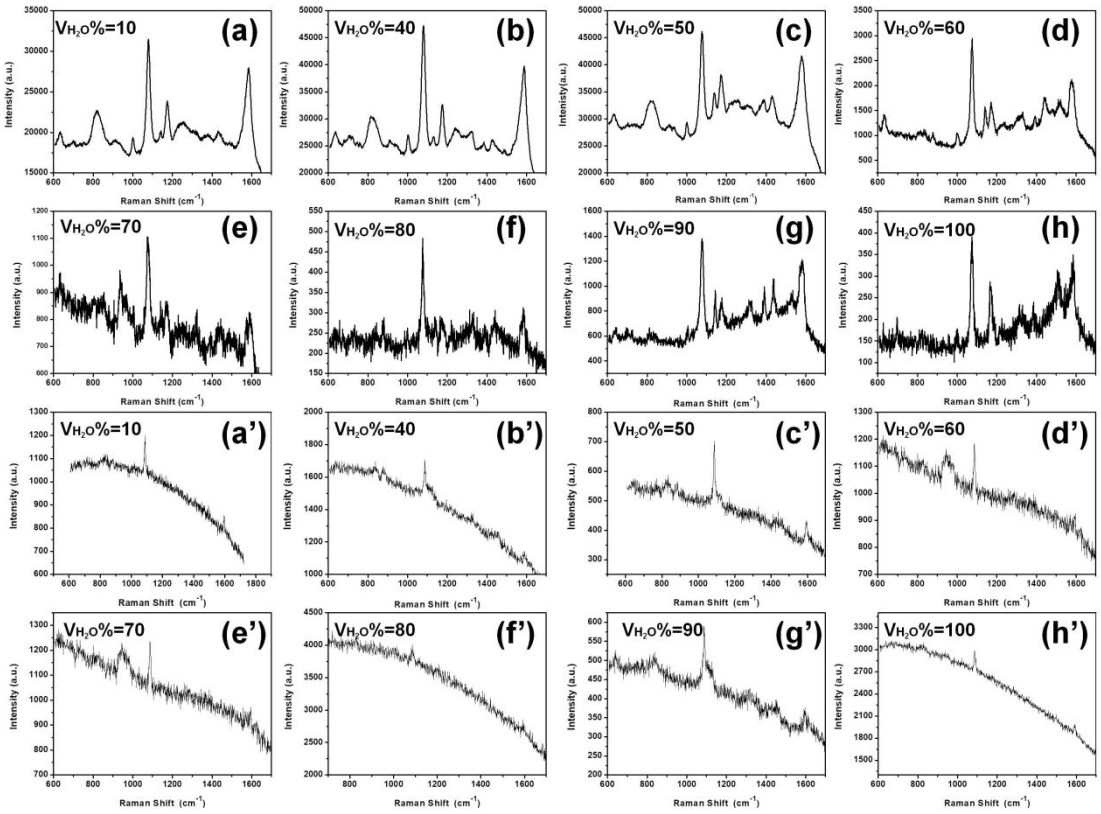


Figure S3. (a-h) SERS spectra of 4-ATP (10 μL, 10^{-6} M for a-f; 10^{-4} M for g-h) on the 2D Au NP arrays attached hydrogel composites in different water contents as substrates. (a'-h') Raman scattering spectra of 4-ATP (10 μL, 10^{-1} M) on the PAAM hydrogel composites in different water contents as substrates.

Table S1. EF of 2D Au NP arrays attached hydrogel composites at different water contents

V_{H_2O}%	10	40	50	60	70	80	90	100
EF	9.23×10^6	1.18×10^7	9.43×10^6	1.34×10^6	2.18×10^5	1.27×10^5	5.60×10^3	1.05×10^3

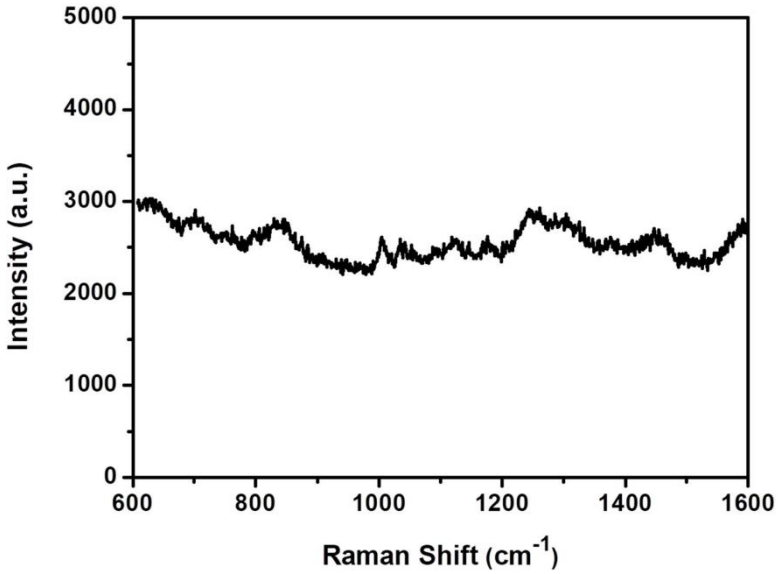


Figure S4. SERS signal of the 2D Au NP arrays attached hydrogel composite.

References:

[1] Men, D. D.; Zhou, F.; Hang, L. F.; Li, X. Y.; Duan, G. T.; Cai, W. P.; Li, Y. A Functional Hydrogel Film Attached with a 2D Au Nanosphere Array and Its Ultrahigh Optical Diffraction Intensity as a Visualized Sensor. *J. Mater. Chem. C* **2016**, *4*, 2117-2122.