Electronic Supporting Information

Gyroid-structured Au-Ag periodic bimetal materials for ultrasensitive SERS detection

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Experimental Section

Materials. All reagents and chemicals were purchased from commercial sources and immediately used without further purification. *Callophrys rubi* butterflies were obtained from Sichuan science and education insect Co., Ltd. Ethanol, nitric acid (NA, 67%), ethylenediamine (ED, 99%), chloroauric acid tetrahydrate (HAuCl₄·4H₂O), sodium borohydride (NaBH₄, 96%), ammonia solution (NH₃·H₂O, 26%), sodium chloride (NaCl), silver nitrate (AgNO₃) sodium potassium tartrate (NaKC₄H₄O₆) and diethanol amine were purchased from Sinopharm Chemical Reagent Co., Ltd. All of these are analytically pure and were used as received without further purification. The silica wafers were purchased from Zhejiang Lijing Silicon Material Co., Ltd.

Fabrication of GSPMMs@Au. The fabrication of GSPMMs@Au based on biotemplates includes four steps. (1) amination of the biotemplate: butterfly wings were first immersed in ethanol for 30 min to preliminarily clean the surface of the wings. Afterwards, the wings were aminated by immersion in dilute 8 vol% nitric acid for 2 h and then in an ethanol solution of ethanediamine (25 vol%) for 6 h. (2) Nanoseed growth: the aminated wings were immersed for 4 h in a mixed solution of HAuCl₄ (0.2 wt %), which was prepared by dissolving HAuCl₄ in equal weights of ethanol and deionized water. Afterwards, the wings were removed, rinsed with deionized water and immersed in a 0.1 M NaBH₄ aqueous solution for 2 min to form a homogeneous layer of Au nanoseeds on the activated biosurface by reducing the adsorbent AuCl₄⁻ on the aminated biosurface. (3) Ag deposition: The electroless deposition solution

consists of 0.5 g silver nitrate, 2.5 g potassium sodium tartrate, 50 mL deionized water and a certain amount of ammonium hydroxide to adjust the pH of the solution to be ~12. The GSPMMs was fabricated by immersing the Au-nanoseed-functionalized butterfly wings in this electroless deposition solution for a given time. All of these three steps were conducted at room temperature. (4) Galvanic replacement reaction:¹ decorating the external surface of GSPMMs with Au NPs. The fabricated GSPMMs were immersed into 0.1 wt% chloroauric acid aqueous solution for different time. The reaction temperature was controlled at ~70 °C. The samples were then taken out, naturally dried in air, and stored in moister buster cabinet for further measurement.

Characterizations of GSPMMs@Au. Scanning electron microscopy (SEM) was carried out using a field emission SEM instrument (Quanta 250 from FEI, 20 kV, Hillsboro, OR, USA). Transmission electron microscopy (TEM) images and TEM mapping of the cross-section of gyroid-structured scales are acquired from a Bio-TEM FEI Tecnai spirit Biotwin. X-ray diffraction (XRD) measurements were conducted using a D/max-2550 instrument (CuKa, Rigaku Corporation, Tokyo, Japan). The extinction spectrum of the GSPMMs@Au were achieved by Microscope Systems (ARM61) manufactured by Shanghai Ideaoptics Corporation, Shanghai, China.

TEM projection. Detailed fabrication process of the TEM cross-section samples was explained in our previous work.² The simulated TEM projections of different plane directions were modelled by MATLAB 2010 MathWorks Inc., Natick, MA, USA using the following equations:³

$$f(x, y, z) = \sin x \cos y + \sin y \cos z + \sin z \cos x = \mathbf{t} \quad (-1.5 \le \mathbf{t} \le 1.5)$$
Equation (1)

where x, y and z are equal to $2\pi X/a$, $2\pi Y/a$, $2\pi Z/a$, respectively; (X Y Z) is the coordinates of a specific point in a cubic unit cell; *a* determines the cubic unit cell size; **t** determines the VF of the gyroid.

SERS detection. SERS detection for CV, R6G, and DEHP was conducted under a Bruker Raman system operated with an Ar ion laser (532 nm). The laser had a power of 2 mW at the sample surface with the beam diameter of 1 μ m and an integration time of 10 s. SERS detection for *p*-MBA was conducted under a Renishaw inVia Qonto Raman system operated with an Ar ion laser (785 nm). The fabricated GSPMMs and GSPMMs@Au samples were tailed into pieces of 3 mm × 3 mm, and mounted onto 3 mm × 3 mm silica substrates. Then alcohol solution of target molecules with different concentration (25 μ L) was drop onto the surface of the samples and naturally dried in air for SERS detection.

Enhancement factor calculation. The enhancement factor (EF) is calculated by comparing the intensity of the SERS signal from single molecule based on the substrates and the silica wafer by the formula

$$EF = (I_{SERS}/N_{SERS})/(I_{Silica}/N_{Silica})$$
Equation (2)

Where I_{SERS} and I_{Silica} are intensities of the selected Raman shift bands in the SERS signals measured from the GSPMMs@Au system and the silica wafers, respectively. N_{SERS} and N_{Silica} are the number of probed molecules contributing to the SERS signals on substrates and silica wafer substrates, respectively. **Finite-difference time domain (FDTD) simulation.** For the FDTD simulations, the GSPMMs@Au model was built using a software FDTD solutions. The mesh size was chosen to achieve a balance between the required computer memory and the simulation time while ensuring convergence of the results. The refractive index of Ag is set to be 0.13+3.19i, and the refractive index of Au is set to be 0.46+2.42i. A plane-wave source with a wavelength of 532 nm (matching the laser source) was applied. The boundary condition in the light incidence direction was set to provide a perfectly matched layer, and the boundary condition in the horizontal direction was set to be periodic. Simulations in which the incident light showed both *s* polarization and *p* polarization were conducted. The diameter of Au NPs gradually increases from the 3 nm to 5 nm, and the amount increases until the surface of the Ag film is completely covered.

Supporting Figures



Fig. S1 Characterization of biotemplates. (a) Optical image of butterfly *C. rubi*. (b) Magnified optical images of gyroid scales piled-up on butterfly wings. (c-d) SEM images of the gyroid structure in biotemplates. (e) TEM image of the cross-section of gyroid scales. The right column is simulated TEM projections corresponding to the experiment results with the same VF.



Fig. S2 Top-view SEM images of GSPMMs with different deposition time of Au NPs: (a) 0 s, (b) 10 s, (c) 20 s, (d) 30 s, (e) 40 s, (f) 50 s, (g) 60 s, and (h) 70 s.



Fig. S3 (a) XRD spectra of GSPMMs with different deposition time of Au NPs: 0 s, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s, and 70 s from down to top. (b) Reflection spectra of GSPMMs with different deposition time of Au NPs: 10 s, 20 s, 30 s, 40 s, 50 s, 60 s, and 70 s from top to down. The inset is the partial enlarged view of GSPMMs with the deposition time of 70 s.



Fig. S4 Quantitative analysis of GSPMM@Au system. (a) TEM images of GSPMM@Au50. Inset is the HRTEM images of GSPMM@Au50. (b) Au/Ag atom ratio with deposition time increasing. Sample A-H is corresponding to the deposition time of 0 s, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s and 70 s, respectively.

The atom ratio of Au/Ag increases with the reaction time increasing. The Au nanoparticles grows slowly at first, and then grow with a constant speed.



Fig. S5 SERS signal of *p*-MBA detected on GSPMMs@Au50 (10^{-9} M) and on the silica wafer (10^{-2} M).

Take GSPMMs@Au50 as an example, according to the SERS measurements as shown in Fig. S5, the EF of the GSPMMs@Au50 is calculated to be 15.2×10^7 and 13.0×10^7 at the Raman shift of 1077 cm⁻¹ and 1589 cm⁻¹, respectively. The average EF of the GSPMMs@Au50 is 14.1×10^7 . The EF results of GSPMMs@Au system are summarized in Table S1.



Fig. S6 Reproductivity analysis of GSPMMs@Au50 as SERS substrate. (a, d, j) the Raman spectra of *p*-MBA on GSPMMs@Au50 randomly selected 20 points. The Raman intensity at (b, e, h) 1077 cm⁻¹ and (c, f, i)1589 cm⁻¹ of the 20 Raman spectra in (a, d, j), respectively.

The SERS spectra and RSD of the SERS intensities of GSPMMs@Au50 from other three batches are shown in Fig. S6 and Table S2, confirming good batch-to-batch reproducibility of SERS signal.



Fig. S7 Calibration curves where the peak intensity is plotted versus the logarithmic over solution concentration. A calibration curve where the SERS intensity of (a) GSPMMs and (b) GSPMMS@Au50 measured at 1364 cm⁻¹ is plotted versus the logarithmic concentration of R6G. A calibration curve where the SERS intensity of (c) GSPMMs and (d) GSPMMS@Au50 measured at 1383 cm⁻¹ is plotted versus the logarithmic concentration of DEHP.

The limit of detection (LOD) is an important index to evaluate SERS performance. LOD is defined as the concentration at which the signal-to-noise(S/N) ratio is equal to $3.^4$ The characteristic band of R6G (1364 cm⁻¹) and DEHP (1383 cm⁻¹) are picked out as the assessment standard of intensity. Establish orthogonal coordinate system with Intensity-Lg (concentration/M) and fit these data into a linear function. The results are shown in Fig. S7. Thus, the LOD (S/N = 3) results are shown in Table S3, indicating the high sensitivity.



Fig. S8 (a) SEM image of commercial SERS substrates Q-SERS. Inset is a magnified SEM image. Scale bar of the inset: 50 nm (b) SERS detection of R6G molecules based on Q-SERS.



Fig. S9 Time effect analysis of the GAPMMs. (a) Raman signals (*p*-MBA, 10⁻⁹ M) detected from a GSPMMs@Au50 substrate preserved for different time: fresh sample, 2 days, 4 days, 6 days, 8 days, 10 days, 12 days and 14 days from bottom to top. (b) Variation trend of the SERS intensity at peak wavelength 1589 cm⁻¹ in (a).

The stability of the GSPMMs@Au50 was systematically by SERS detection of *p*-MBA (10⁻⁹ M), using substrates preserved for different time in moister buster cabinet with a humidity of 1% at room temperature. As shown in Fig. S9, the SERS intensity went through a dramatic decrease in the first week, which can be explained by the inevitable losing of activity of Au/Ag nanoparticles on the external surface of samples when exposed to air. Then in the second week, the decrease slowed down as the Au/Ag nanoparticles gradually reached an equilibrium state.

Table S1 EF of GSPMMs@Au (*p*-MBA) compared with silica wafer calculated using Raman shift at 1589 cm⁻¹.

Sample A-H is corresponding to the deposition time of 0 s, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s and 70 s, respectively. $(C_{Silica} / C_{SERS} = 10^{-7})$

Sample	$I_{\rm SERS}/I_{\rm Silica}$ for 1077 cm ⁻¹	EF for 1077 cm ⁻¹	$I_{\rm SERS}/I_{\rm Silica}$ for 1589 cm ⁻¹	EF for 1589 cm ⁻¹	Average EF of for 1077 cm ⁻¹ and 1589 cm ⁻¹	
А	3.7	3.7×10 ⁷	4.4	4.4×10 ⁷	4.1×10 ⁷	
В	7.2	7.2×10 ⁷	5.9	5.9×10 ⁷	6.5×10 ⁷	
С	9.5	9.5×10 ⁷	7.4	7.4×10 ⁷	8.4×10 ⁷	
D	11.6	11.6×10 ⁷	9.5	9.5×10 ⁷	10.6×10 ⁷	
Е	12.8	12.8×10 ⁷	10.6	10.6×10 ⁷	11.7×10 ⁷	
F	15.2	15.2×10 ⁷	13.0	13.0×10 ⁷	14.1×10 ⁷	
G	12.6	12.6×10 ⁷	10.4	10.4×10 ⁷	11.5×10 ⁷	
Н	8.5	8.5×10 ⁷	7.9	7.9×10 ⁷	8.2×10 ⁷	

 Table S2 Average 1585 peak intensities of *p*-MBA SERS spectra collected from different batches.

Batch number	1	2	3	4
Raman Intensity of 1077 cm ⁻¹	8583±557	9095±540	7119±481	7746±549
$(aver. \pm std) (cps)$				
Raman Intensity of 1589 cm ⁻¹	9706±567	8980±546	7397±502	8679±715
(aver. ±std) (cps)				

Table S3 LOD of GSPMMs and GSPMMS@Au50 for R6G and DEHP.

Sample	GSPMMs	GSPMMS@Au50
LOD for R6G	9.7×10 ⁻¹⁴	9.5×10 ⁻¹⁶
LOD for DEHP	3.6×10 ⁻¹⁶	3.4×10 ⁻¹⁸

References

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