Supporting Information

TiO$_2$ Nanofoam-Nanotube Array for Surface-Enhanced Raman Scattering

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SI 1. Experimental Section

TiO₂ nanofoam-nanotube array preparation. TiO$_2$ nanotube array was prepared by a secondary anodic oxidation process. The anodization was carried out in a two electrode electrochemical cell. Titanium foil (99.9% purity, 0.25mm thickness) was used as the anode. Platinum electrode was used as the cathode. The electrolytic solution was NH$_4$F in ethylene glycol, the concentration of NH$_4$F was 0.25 wt% and the water content was 10 vol%. In the first anodization, a voltage of 10 V was used to oxidize the titanium foil for 30 min to grow the top layer of TiO$_2$ nanofoam-nanotube array. Then in the second oxidation process, the voltage was increased to 120 V, 100 V and 80 V respectively, to grow the bottom layer. Both anodization times for the two oxidation processes were 30 minutes. Finally, the synthesized samples were heated at 500 ℃ in the muffle furnace for 2 hours. We name those samples according to oxidation voltages and time, and shown in the Table S1.

Table S1. A list of synthesized TiO₂ nanofoam-nanotube array samples: "S", "T" and "R" represent TiO₂ samples discussed in the main text.

Sample	1ˢᵗ oxidation voltage(V)	1ˢᵗ oxidation time(min)	2ⁿᵈ oxidation voltage(V)	2ⁿᵈ oxidation time(min)
S10-80	10	30	80	30
S10-100	10	30	100	30
S10-120	10	30	120	30
S10-100-60	10	30	100	60
S10-100-90	10	30	100	90
S10-100-180	10	30	100	180
T60-10	60	30	10	30
T80-10	80	30	10	30
T100-10	100	30	10	30
R10-10	10	240	10	480
R10-20	10	240	20	480
R10-30	10	240	30	480
R10-40	10	240	40	480
R10-60	10	240	60	480
R10-80	10	240	80	480

Raman measurement. Methylene blue (MB) ethanol solutions were used as the analyte. 20 µL of MB solution was dropped and spread on the substrate (10 mm × 10 mm) which was subsequently dried in dark. Raman spectra were acquired at room temperature on a Horiba LabRAM HR-800 confocal Raman microscope (Horiba Scientific) coupled to an Argon ion laser (514 nm). The system is equipped with a 600 lines/mm grating. The sampling was carried out using a Leica (50×, NA = 0.75) optical microscope, which can produce a focused laser spot of about 1 μm^2. The Raman spectra were recorded for 10 s using the laser probe irradiance of 0.3 $mW/\mu m^2$. The laser irradiance was measured at the position of the sample using a portable radiometer positioned between the objective lens and the microscope stage. For the data reproducibility and statistics, Raman spectra were collected from five independent measurements, and we reported the averaged signal intensities in this work.

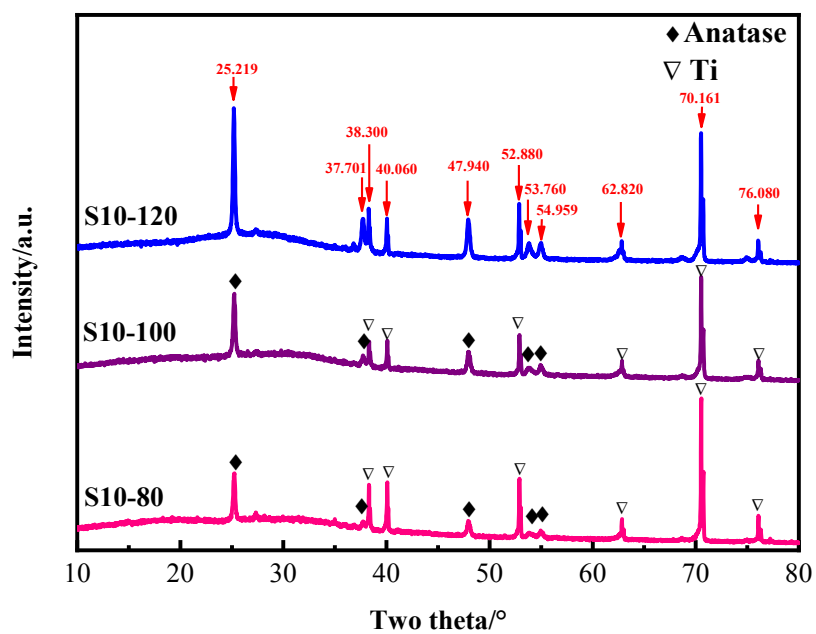**SI 2. TiO₂ nanofoam–nanotube array characterizations**

Figure S1. XRD patterns of TiO₂ nanotube array with (S10-100) or without the nanofoam layer (S10-80 and S10-120).
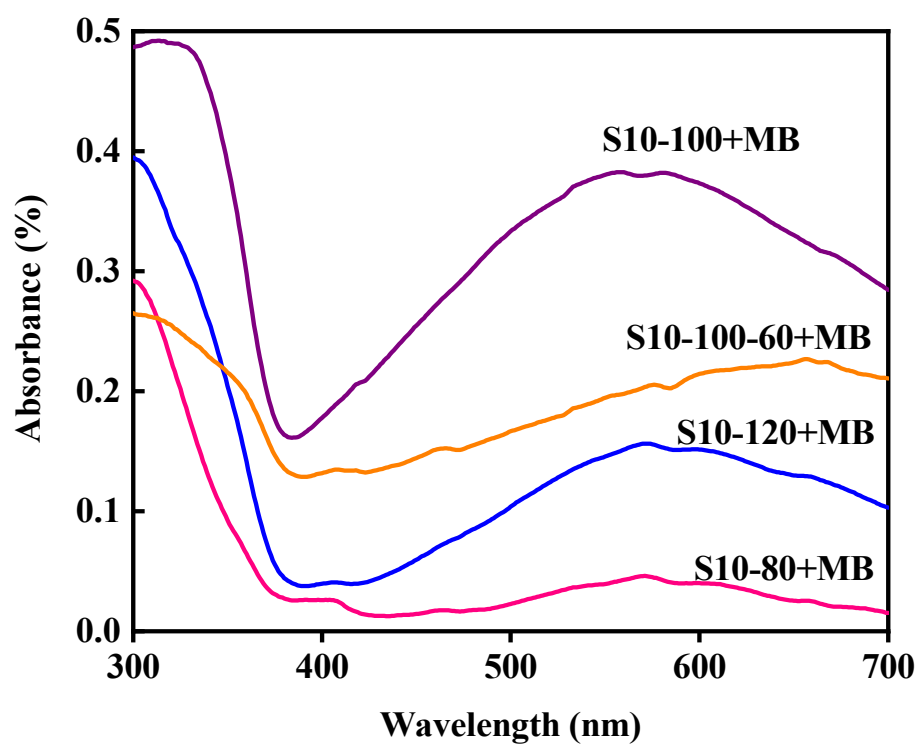
Figure S2. UV-vis absorption spectra of Methylene Blue (10^{-3}M) adsorbed on different samples.
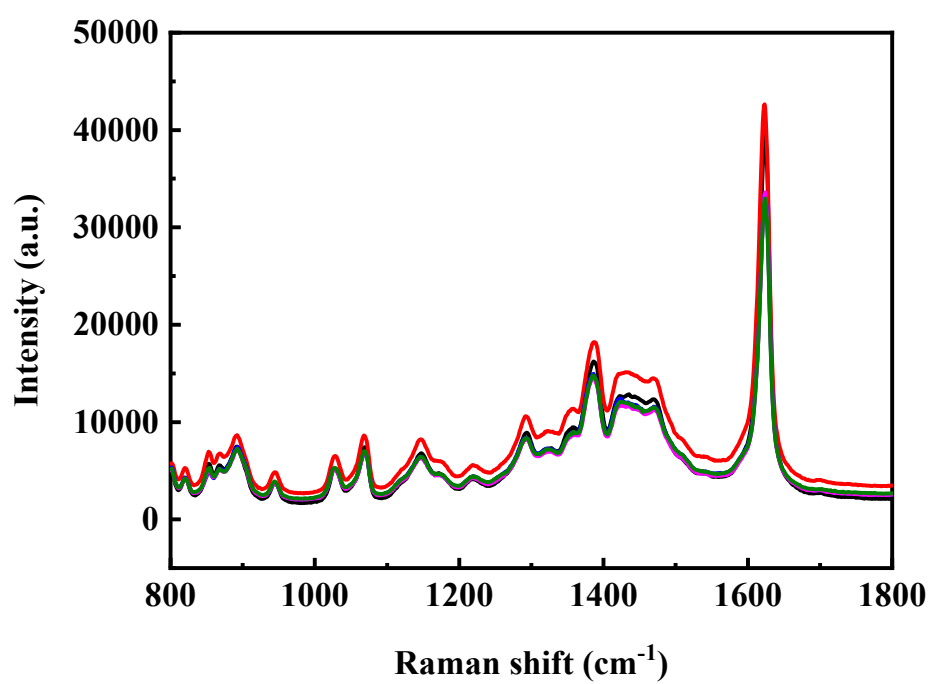
Figure S3. Measurement of Raman spectra of MB on sample S10-100 for five times to check SERS reproducibility.

SI 3. Enhancement factor (EF) calculation.

The Raman scattering enhancement is evaluated by calculating enhancement factor, EF:

$$EF = \frac{I_{SERS} / I_{bulk}}{N_{bulk} / N_{SERS}}$$

Where I_{SERS} is the Raman signal intensities at 1624 cm^{-1} from the 1.0×10^{-3} M Methylene blue (MB); I_{bulk} is the 1.0×10^{-3} M MB on the glass slide; N_{SERS} is the number of probe molecules on the TiO$_2$ sample; N_{bulk} is the number of probe molecules on the glass slide.

For the calculation, we assume that the low concentration probe molecules are forming monolayers on TiO$_2$ substrates. Therefore, the number of probe molecules can be estimated by:

$$N_{SERS} = \frac{N_A \times C \times V \times S_{laser}}{S_{sub}}$$

Where N_A is the Avogadro constant; C is the molar concentration of the solution, 1.0×10^{-3} M; V is the volume of the droplet, 20 µL; S_{sub} is dispersed area of the solution on TiO$_2$ substrate, 10 mm in diameter; S_{laser} is the size of the laser spot, 1 µm in diameter.

Also, the number of probe molecules in the solid sample is estimated by:

$$N_{bulk} = \frac{d \times \rho \times N_A \times S_{laser}}{M}$$

Where d is the penetration depth, about 2 µm; ρ is the density of solid MB, 0.98 g/cm^3; N_A is the Avogadro constant; S_{laser} is the size of the laser spot, 1 µm in diameter; M is the molar mass of MB, 373.9 g/mol.

According to those values, the calculated enhancement factor (EF) for 1.0×10^{-3} M Methylene blue on S10-100 sample is about 2.3×10^5.