

Supplementary information for:

Binary “Island” Shaped Arrays with High-Density Hot Spots for Surface-Enhanced Raman Scattering Substrates

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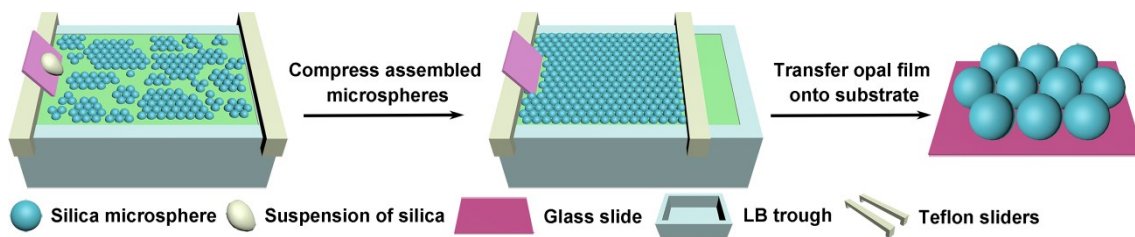


Fig. S1 Schematic illustration for fabrication of 2D SiO₂ opal structure.

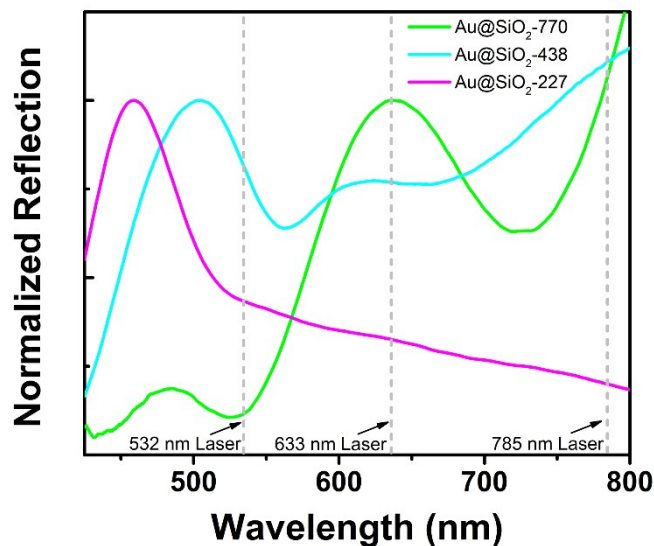


Fig. S2 The reflection spectra of the BISA based on 770 nm, 438 nm and 227 nm SiO₂ opal (denoted as Au@SiO₂-770, Au@SiO₂-438 and Au@SiO₂-227), respectively.

The constructed BISA is used as a 2D photonic crystal with photonic bandgap. It has previously been reported that photons at the corresponding frequency falling in the photonic bandgap are prohibited from propagating so that multiple-light scattering will be suppressed. However, light-matter interaction at the edge of the bandgap is enhanced by the slow light effect to achieve SERS enhancement.¹ The positions of the reflection peak in the Fig. S2 correspond to the photonic bandgaps of different substrates in the system. Obviously, the 785 nm excitation laser is far from bandgap of the system, so the 785nm laser is not considered. If the excitation laser with wavelength of 633 nm is chosen, it exactly falls into photonic bandgap for the Au@SiO₂-770, which is detrimental

to achieving optimal results. The use of a 532nm excitation laser, which happens to be on the edge of bandgaps for the system, will achieve maximum enhancement due to the slow light effect. Therefore, the 532nm excitation laser was selected throughout the all experiment.

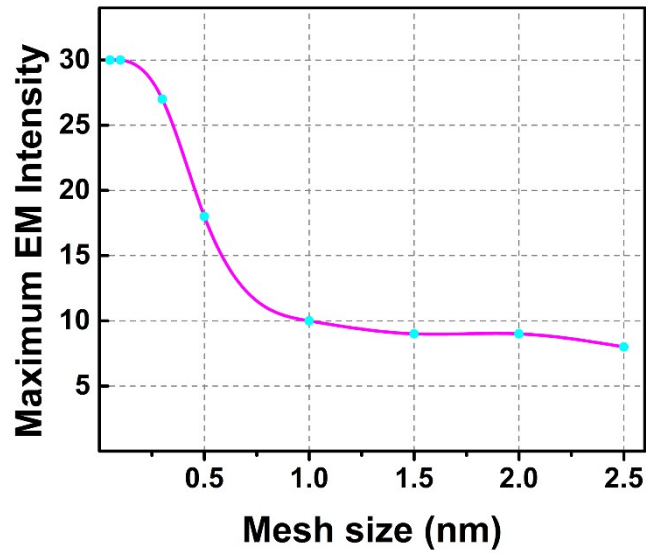


Fig. S3 A convergence test by altering the mesh size for FDTD simulation.

It can be found that the simulation result is considered to be convergent when the mesh size reduced to 0.1 nm, but a large amount of data was simultaneously generated, which brought difficulties for data processing. Therefore, we chose mesh size of 0.3 nm and considered the simulation results to be within an acceptable range.

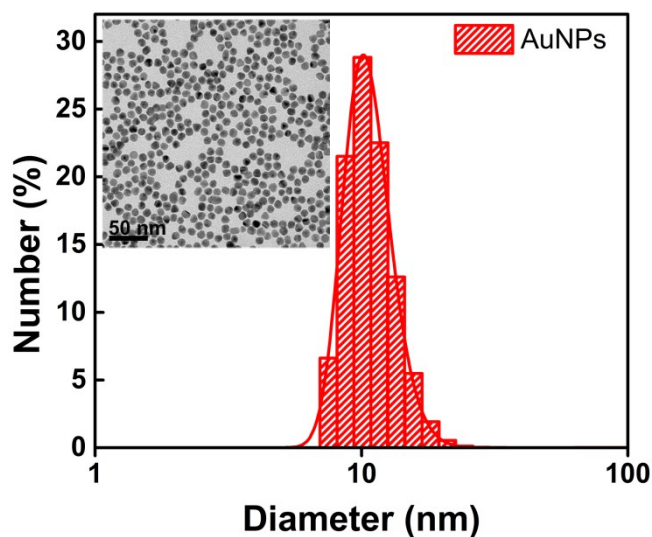


Fig. S4 Size distributions of AuNPs with fitted Gaussian distributions. The inset is TEM image of AuNPs.

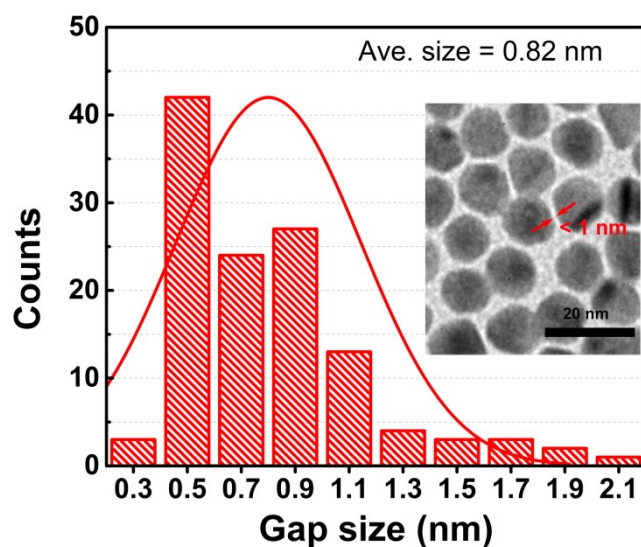


Fig. S5 Statistical histograms of nanogap distance between adjacent particles stabilized by TA. Statistical average size of nanogap is 0.82 nm. The inset shows TEM image of AuNPs assembled on copper grid.

Table S1 The Zeta potential of AuNPs stabilized by TA and citrate.

Stabilizer type	TA ^a	Citrate ^b
Zeta potential (mV)	29	36.27

^adata stems from experimental measurement. ^bdata stems from previous report.¹

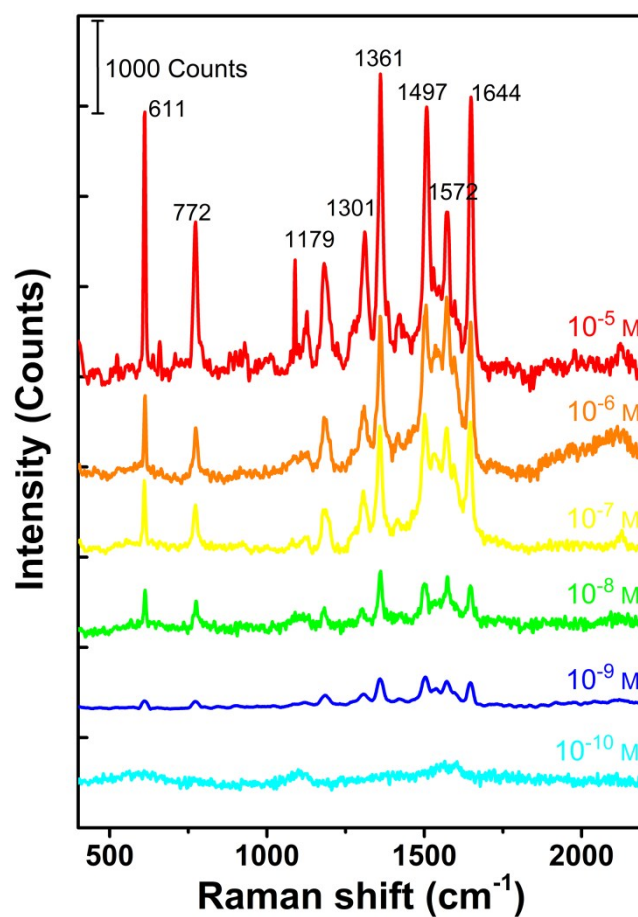


Fig. S6 Raman spectra of R6G with different concentrations from 10^{-5} M to 10^{-10} M acquired on Au@SiO₂-plane substrate.

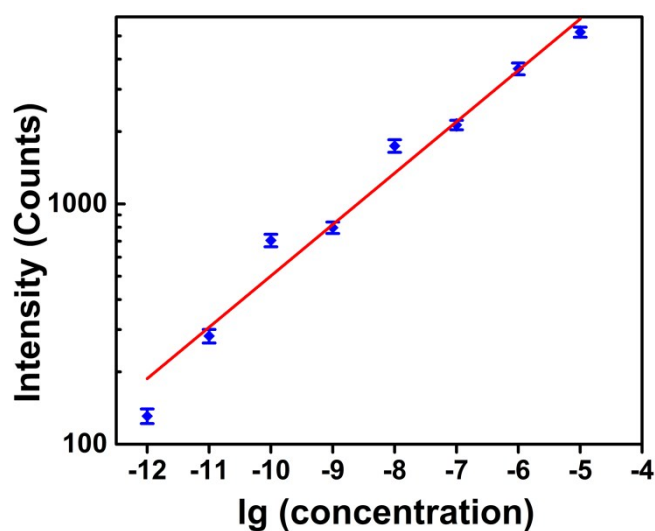


Fig. S7 The log–log plot of Raman intensity at 611 cm^{-1} versus R6G solution concentration with fitted line for Au@SiO₂-770 substrate.

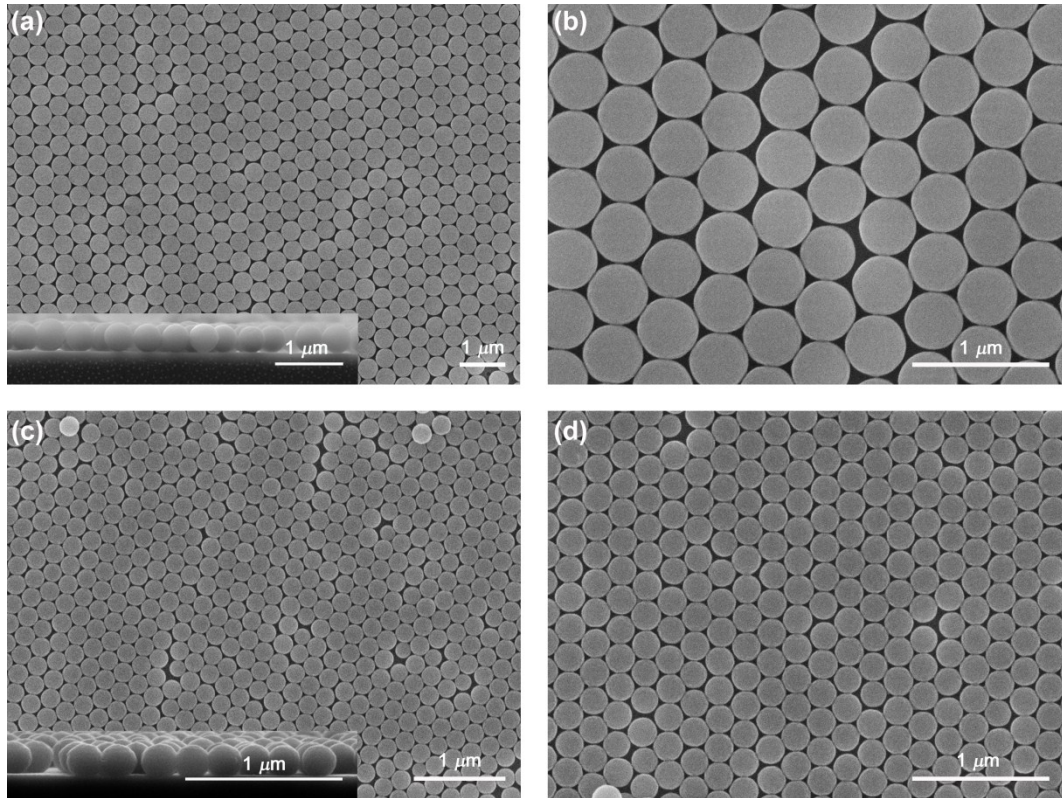


Fig. S8 SEM image of 2D SiO₂ opal structure with diameter of (a) 438 nm and (c) 227 nm and corresponding high-magnification SEM image (b, d). The bottom left inset in (a) and (c) is corresponding cross-sectional SEM image.

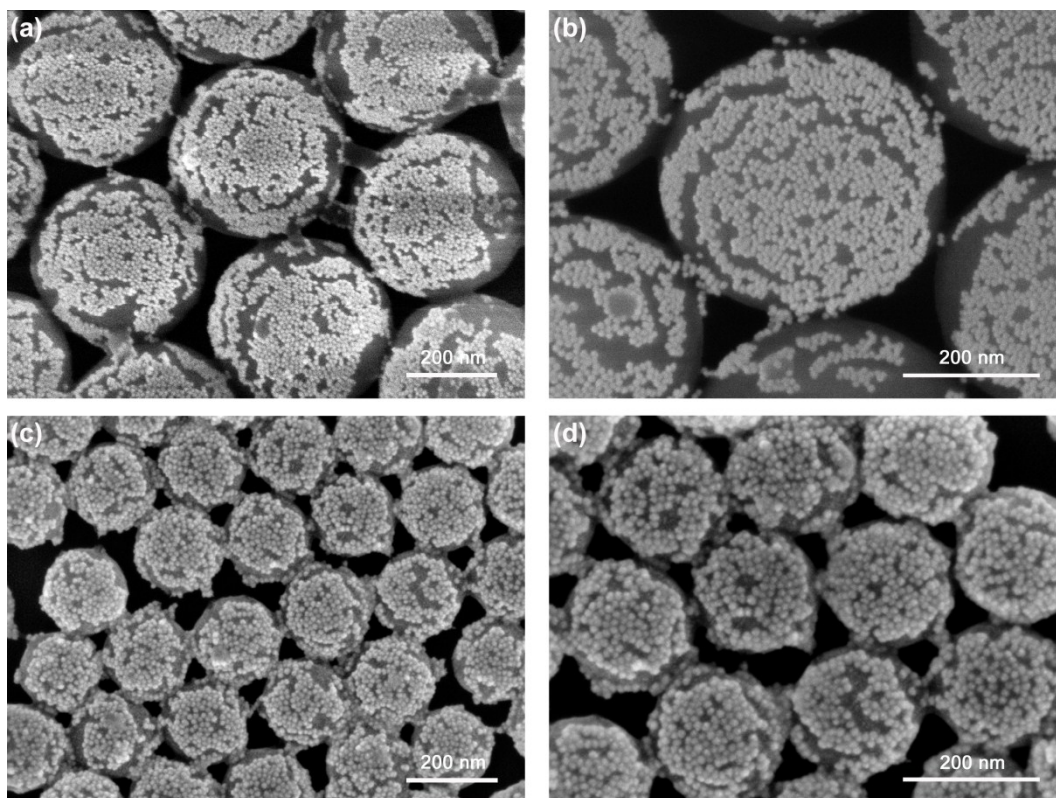


Fig. S9 Low-magnification (a) and high-magnification (b) SEM image of BISA based on 438 nm SiO₂ opal (denoted as Au@SiO₂-438). Low-magnification (c) and high-magnification (d) SEM image of BISA based on 227 nm SiO₂ opal (denoted as Au@SiO₂-227).

Calculation of the enhancement factor

The enhancement factor (EF) for four substrates was calculated based on the Raman specific peak of 611 cm⁻¹ by using the following formula:

$$EF = \frac{I_{SERS} \times C_0}{I_0 \times C_{SERS}}$$

C_0 and I_0 are the limit of detection and intensity of Raman peak for R6G solution acquired on quartz substrates (Fig. S10), respectively, and C_{SERS} and I_{SERS} represent the limit of detection and intensity of Raman peak for R6G solution on different SERS substrates.

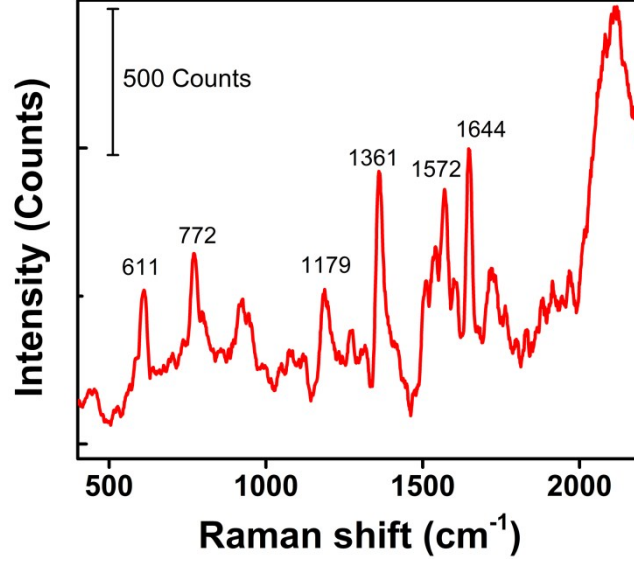


Fig. S10 Raman spectrum of R6G with concentrations of 10^{-1} M acquired on quartz (glass).

Calculation of the number of covered AuNPs on SiO_2 microsphere

The volume of spherical cap covered by AuNPs:

$$V_{\text{spherical cap} - \text{SiO}_2} = \pi h^2 \left(R - \frac{1}{3}h \right) \quad (1)$$

$$h = R(1 - \sin \theta) \quad (2)$$

$$\sin \theta = (1 - \cos^2 \theta)^{1/2} = \left[1 - \left(\frac{R}{R+r} \right)^2 \right]^{1/2} \quad (3)$$

where R and r are the radius of SiO_2 microsphere and AuNP, respectively. h is the height of spherical cap. θ represents an acute angle formed by the line OL and OO' ; point O is center of a SiO_2 microsphere; point O' is center of a AuNP; point L is contact point between two SiO_2 microspheres.

Therefore, the volume of spherical cap was shown as follow:

$$V_{\text{spherical cap} - \text{SiO}_2} = \frac{\pi}{3} R^3 \left\{ 2 + \left[1 - \left(\frac{R}{R+r} \right)^2 \right]^{1/2} \right\} \left\{ 1 - \left[1 - \left(\frac{R}{R+r} \right)^2 \right]^{1/2} \right\}^2 \quad (4)$$

We presume that the AuNPs closely covered on spherical cap of SiO₂ to form new spherical cap. The volume of spherical cap composed of SiO₂ spheres and AuNPs is

$$V_{\text{spherical cap - SiO}_2@Au} = \frac{\pi}{3}(R+r)^3 \left\{ 2 + \left[1 - \left(\frac{R}{R+r} \right)^2 \right]^{1/2} \right\} \left\{ 1 - \left[1 - \left(\frac{R}{R+r} \right)^2 \right]^{1/2} \right\}^2 \quad (5)$$

The volume of AuNP is considered as the volume of a positive six prism with edge length of $\frac{2\sqrt{3}}{3}r$ and height of $2r$ due to the close-packed structure. Therefore, the volume of AuNP is $V_{Au} = 4\sqrt{3}r^3$.

The number of AuNPs covered on SiO₂ microsphere is given by

$$N_{Au} = \frac{V_{\text{spherical cap - SiO}_2@Au} - V_{\text{spherical cap - SiO}_2}}{\frac{1}{2}V_{Au}} \quad (6)$$

In our report, r is a constant. When the irradiated area of the laser beam is 1 μm², the number of covered AuNPs on a bending substrate with different particle size was calculated by using above formula.

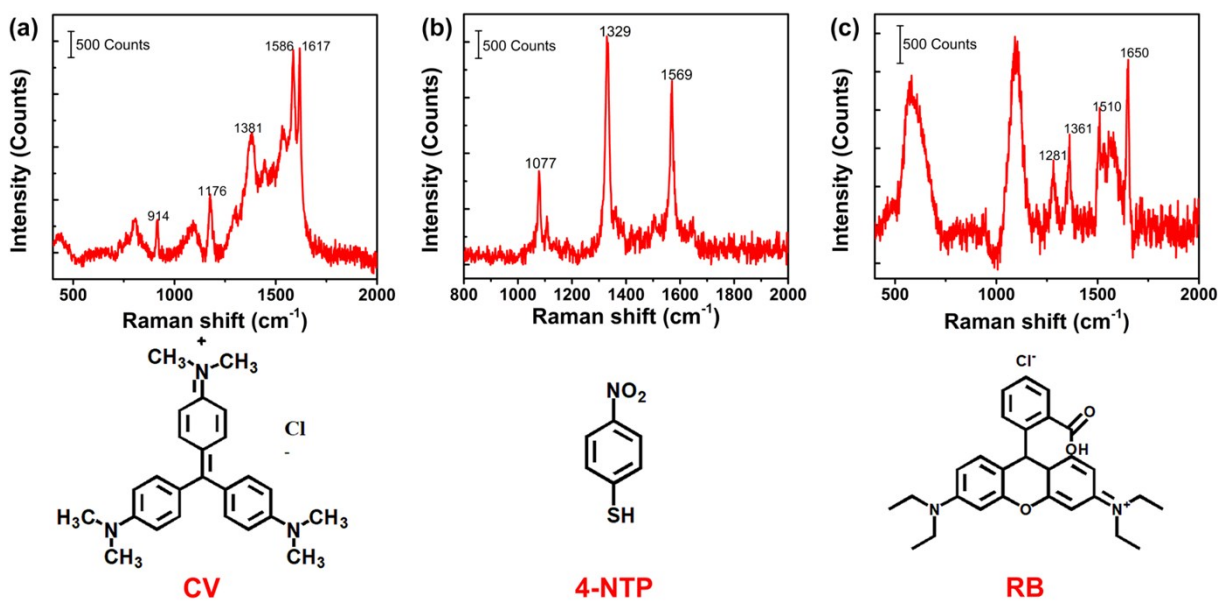


Fig. S11 Raman spectra of (a) crystal violet (CV), (b) 4-nitrothiophenol (4-NTP), and (c) rhodamine B (RB) acquired on Au@SiO₂-770 substrate with the concentration of 10⁻⁸ M, respectively.

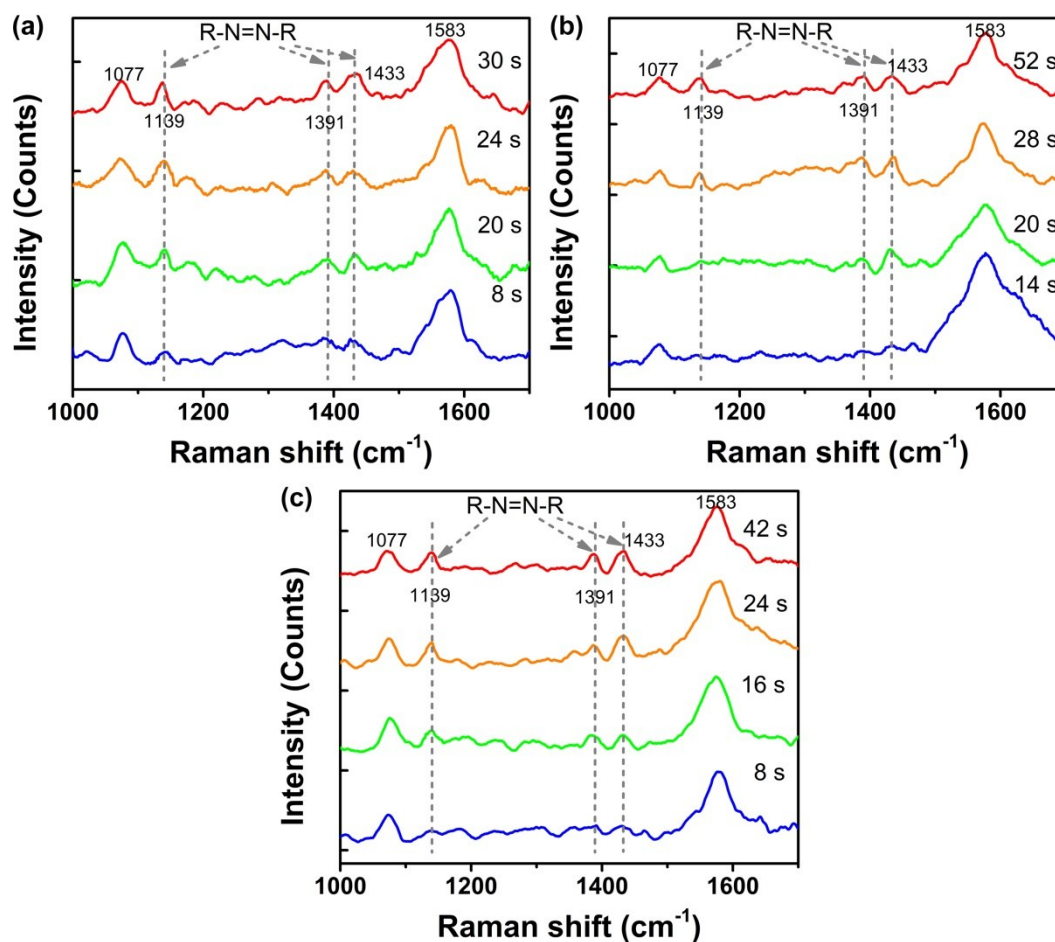


Fig. S12 Real-time monitoring Raman spectra acquired on the surface of (a) Au@SiO₂-438, (b) Au@SiO₂-227 and (c) Au@SiO₂-plane during the reaction of 4-ATP to 4,4'-DMAB.

Reference

1. D. Qi, L. Lu, L. Wang and J. Zhang, *J. Am. Chem. Soc.*, 2014, **136**, 9886-9889.
2. S. Si, W. Liang, Y. Sun, J. Huang, W. Ma, Z. Liang, Q. Bao and L. Jiang, *Adv. Funct. Mater.*, 2016, **26**, 8137-8145.