Coupling Au-loaded magnetic frameworks to photonic crystal for improvement of photothermal heating effect in SERS

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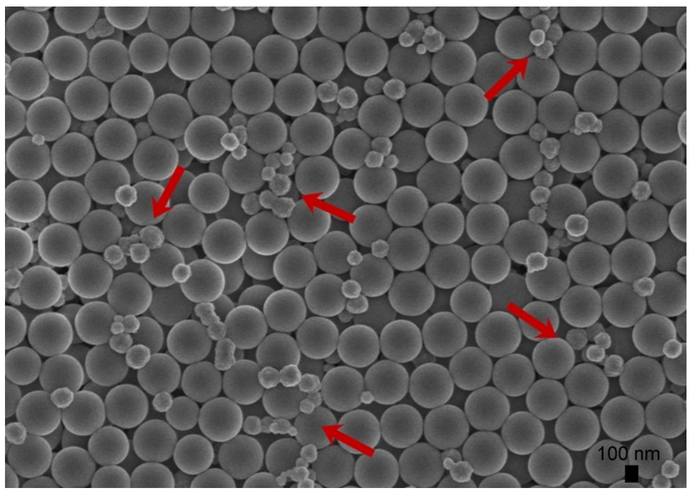

Fig. S1. SEM image of surface of Au-PC film (10 mL of Au solution).

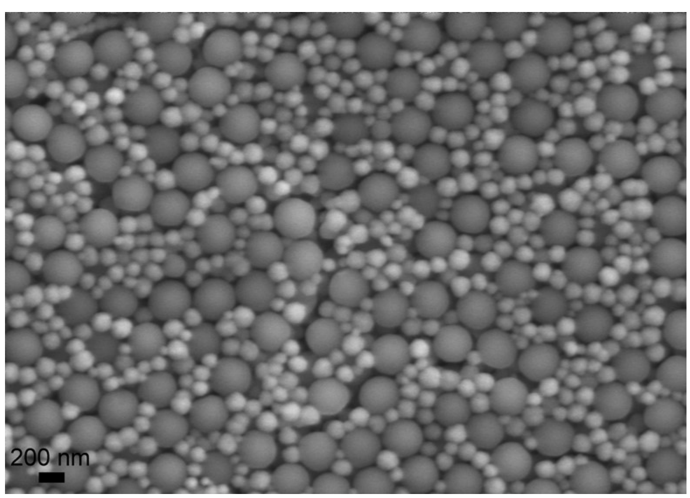

Fig. S2. SEM image of surface of Au-PC film (70 mL of Au solution).

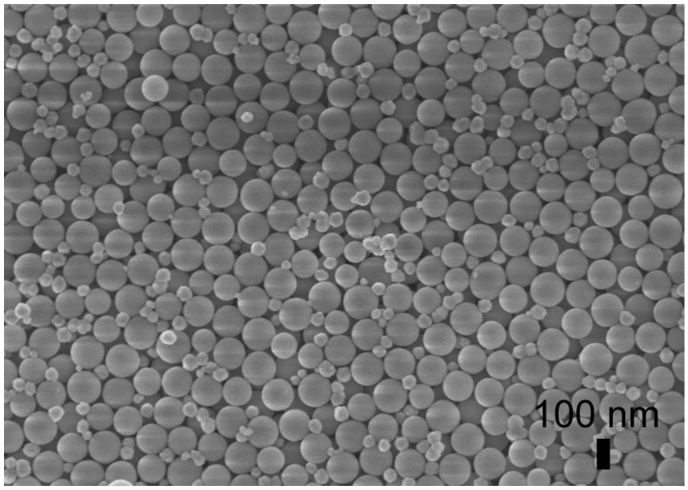

Fig. S3. SEM image of surface of Au-PC film (25 mL of Au solution).

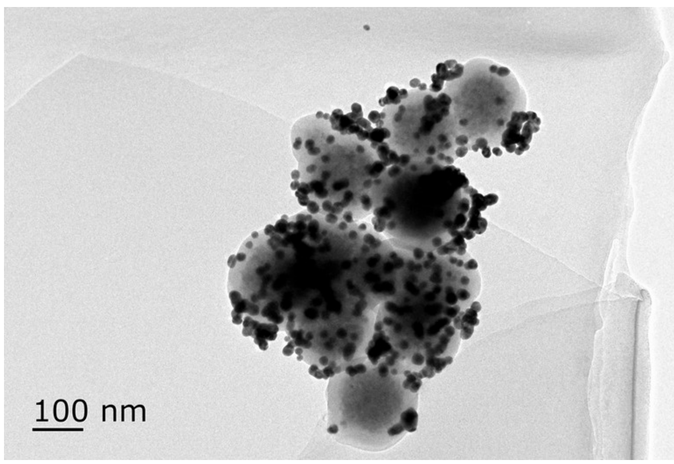

Fig. S4. TEM image of AuMF.

S1. Discussion of reflection peak positions of AuMF-PC films

The reflectance spectra of AuMF-PC with various amounts of AuMFs display different reflection peak positions, which are in accordance with Bragg-Snell law. The peak wavelength can be predicted as:

$$\lambda = 2\sqrt{2/3}D\sqrt{n_{eff}^2 - \sin^2\theta} \qquad \text{* MERGEFORMAT (S1)}$$

where D is the diameter of silica nanosphere, θ is the angle of the incident light (at normal incident θ=0°), and n_{eff} is the effective refractive index of the medium. According to the above equation, the following relation is obtained.

$$\frac{D}{\lambda} \propto \frac{1}{n_{eff}} \qquad \text{* MERGEFORMAT (S2)}$$

Generally, n_{eff} is calculated by:

$$n_{eff}^2 = fn_{material}^2 + (1-f)n_{void}^2 \qquad \text{* MERGEFORMAT (S3)}$$

where $n_{material}$ and n_{void} are refractive indices of the silica nanosphere and the interstitial void region, respectively. And f is the filling ratio. Hence, based on the above equations, the following relation can also be obtained.

$$\lambda \propto f \qquad \text{* MERGEFORMAT (S4)}$$

Therefore, there is no significant changes in filling ratio when AuMFs dope into the voids of PC, due to ordered opal PC structures show no obvious disruption (as shown in Fig. 4(a)-(c)). According to the relation (S4), the peak wavelength λ increases with the f. Therefore, the increasing amount of AuMFs may lead to a higher filling ratio, due to plenty of interstitial void region would be occupied.

S2. Calculation of enhancement factor of AuMF-PC substrate for SERS

Calculating the SERS EF value is a classical approach for evaluating the SERS performance of a substrate. The EF values can be estimated using the following standard equation:

$$EF = \frac{I_{SERS}}{I_{Bulk}} \times \frac{N_{Bulk}}{N_{SERS}} \qquad \text{* MERGEFORMAT (S5)}$$

Where I_{SERS} and I_{Bulk} are the integrated intensities of the adsorbed molecules of 10^{-6} M PATP solution (C_{SERS}) on the surfaces of the AuMF-PC substrate and solid PATP (C_{Bulk}) on the glass slide, respectively, and N_{SERS} and N_{Bulk} are the number of PATP molecules adsorbed on the AuMF-PC substrate surface and glass slide under the laser spot area, respectively. We have used the 50× microscopic lens (N_A =0.75) to measure SERS signal.

The diameter of the focused spot on the samples (D) and the exact transmission depth of the laser into the sample (h) are determined by the following equations (S6, S7), where λ_{laser} is the excitation wavelength (nm), n is the refractive index of solid PATP powder ($n \approx 1.6$), and N_A is the numerical aperture.

$$D = \frac{1.22\lambda_{laser}}{N_A} \qquad \text{* MERGEFORMAT (S6)}$$

$$h = \frac{2.2n\lambda_{laser}}{\pi N_A^2} \qquad \text{* MERGEFORMAT (S7)}$$

where n =1.6, and λ =633 nm. The value of D is calculated to be 1.03 μm and h is calculated to be 1.26 μm, respectively.

The illuminated volume (V) is determined by the penetration depth of the laser into the sample (h) and the illuminated area (A), is given by:

$$V = h \times A = h \times \pi \left(\frac{D}{2}\right)^2 \qquad \text{* MERGEFORMAT (S8)}$$

The value of V is calculated to be 1.05 μm^3, then the N_{Bulk} can be calculated by:

$$N_{Bulk} = N_A \times \frac{\rho V}{M_r}$$ * MERGEFORMAT (S9)

where ρ is the density of PATP (1.18 g/cm^3), The relative molecular mass M_r of PATP is about 125. The value of N_{Bulk} is calculated to be 7.43×10^{-15}. And the N_{SERS} is calculated by:

$$N_{SERS} = N_A \times \frac{AC_{SERS}V_1}{A_1}$$ * MERGEFORMAT (S10)

where V_1 is the volume of PATP solution (V_1 = 2 mL), A_1 is the SERS substrate area immersed in 2 mL of PATP solution (A_1 = 1 cm^2, due to the substrate sample of size 1 cm×1 cm was prepared). The value of N_{SERS} is calculated to be 1.25×10^{-17}. According to the measured SERS spectra, we can obtain the I_{SERS} and I_{Bulk} are 15879.32 (the mean value calculated by fifteen different spots for Fig. 7(c) in the main text) and 19.85 at 1077 cm^{-1}, respectively. Hence, the EF value of AuMF-PC substrate is calculated to be approximately 4.76×10^5.

Table S1. The compositions of three film samples.

Film	Composition	Element
Silica PC	SiO_2 nanospheres	Si O
Au-PC	SiO_2 nanospheres Au NPs	Si O Au
AuMF-PC	SiO_2 nanospheres Fe_3O_4@SiO_2 MNPs Au NPs	Si O Fe Au