

Supporting Information

Filtration-Assembling Colloidal Crystal Templates for Ordered Macroporous Nanoparticle Films

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1. Mesoporous copper hydroxide nanostrands layer

The SEM image of the copper hydroxide nanostrands (CHN) layer filtered on anodic alumina oxide membrane surface and TEM image of individual copper hydroxide nanostrands are shown in Fig. S1. Both SEM and TEM images clearly show that the nanostrands are in diameter of about 2.5 nm (subtracting the Pt layer sputtered for SEM observation). The nonwoven overlapped CHN generated tremendous mesopores. The surface of the CHN layer is very smooth and uniform.

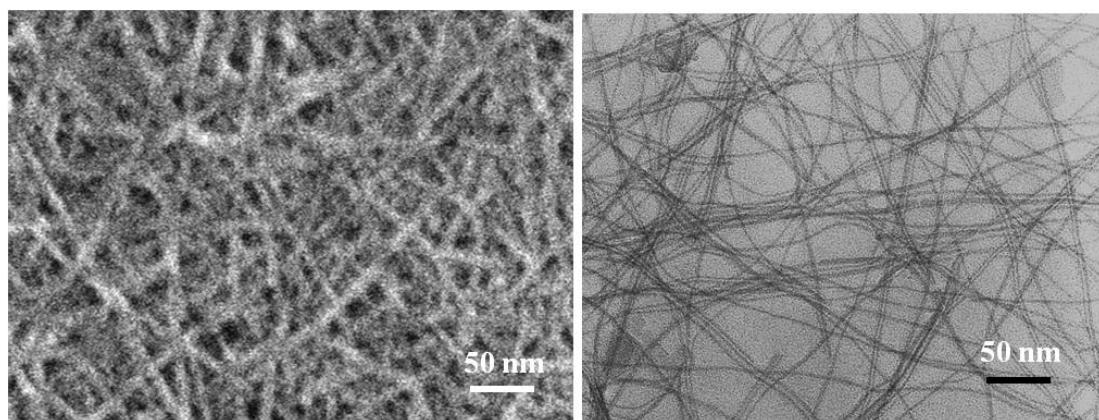


Figure S1 SEM and TEM imaged of copper hydroxide nanostrands.

2. Low magnification SEM images of the multilayer ordered polystyrene spheres

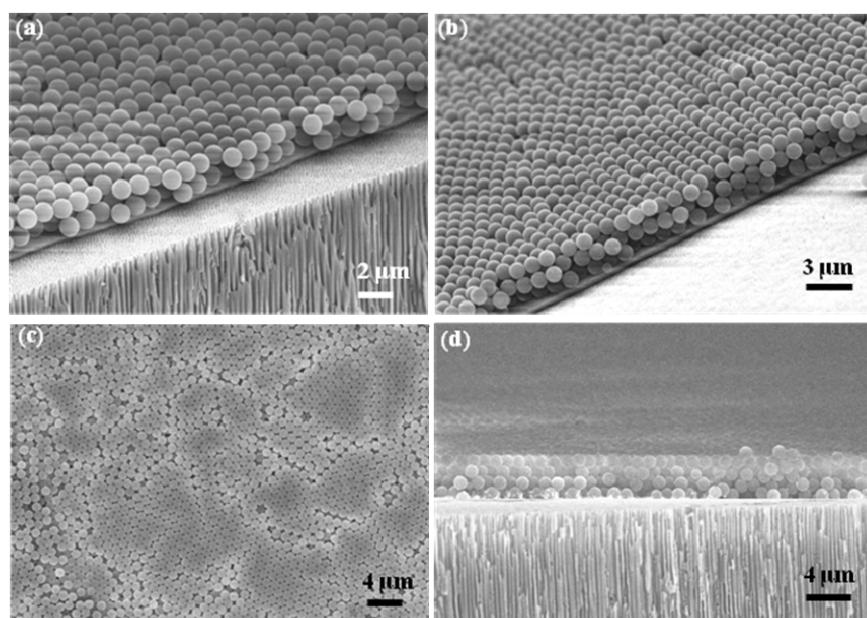


Figure S2 Low magnification SEM images of bi (a); tri (b); and tetra (c) and (d) -layers PS templates prepared from 1.09 μm PS, respectively.

3. Several examples of ordered macroporous gold nanoparticle film

Fig. S3 shows a bi-layer macroporous gold nanoparticle film prepared from 80 nm gold nanoparticles and bi-layer 0.62 μm PS templates. The gold nanoparticles are uniformly filled into all the voids of the PS templates from the bottom to the up. Fig. S3 c indicates that bi-layer ordered macroporous thin films are successfully formed after removing away the PS template.

Fig. S4, the SEM images of the film prepared from 20 nm gold nanoparticles and 0.62 μm PS monolayer templates. Due to the shortage of gold nanoparticles, the final macroporous structure is the two-dimensional replica of the PS template, not three-dimensional porous structures.

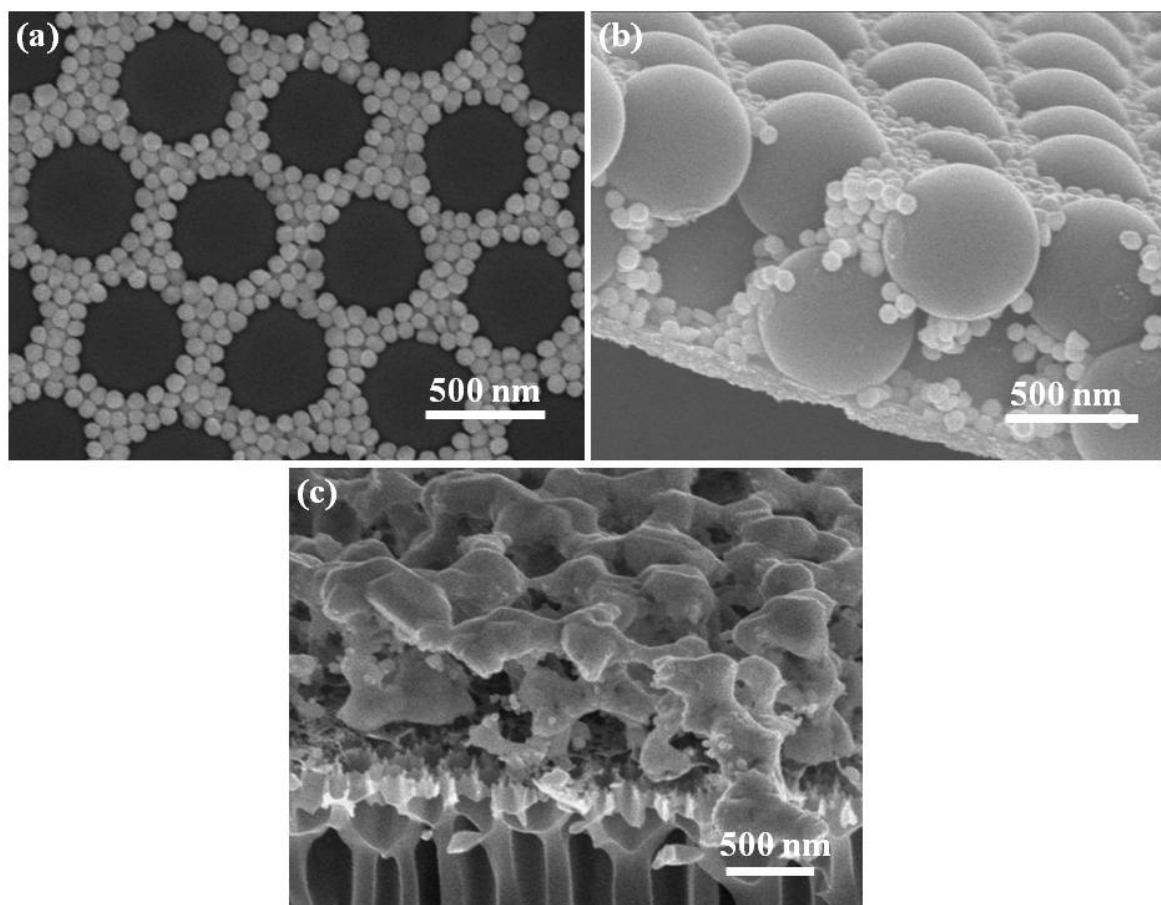


Figure S3 SEM images: (a) and (b) 80 nm gold nanoparticles filled into the interstitial voids of the bi-layer 0.62 μm PS template, (c) after removing PS and CHN layer, respectively.

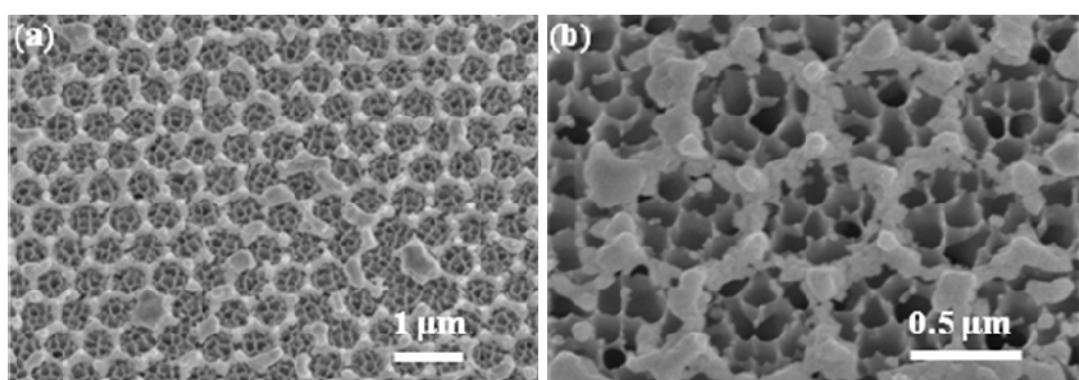


Figure S4 (a) and (b) SEM images of the sample prepared from 20 nm gold nanoparticle and 0.62 μm PS monolayer template after removing away PS and CHN, respectively.

3. SERS enhancement effect factor (EF) calculation

The representative SERS of the sample prepared from 100 nm gold nanoparticles and 1.09 μm PS monolayer template is shown in Fig. S5a. Rhodamine 6 G (R6G) molecules were used as probe molecules. The spectrum (Fig. S5b) is recorded from 1×10^{-4} M R6G solution as the normal Raman scattering reference. Laser excitation is 514.5 nm. From the spectra, it can be seen that the characteristic peaks of R6G are almost not observed from the solution. The Raman signal enhancements are significant by using the prepared continuous ordered macroporous gold nanoparticle films. The For the average enhancement effect factor (EF) calculation, the integration intensities of the corresponding characteristic peak position at 1363 cm^{-1} after subtracting the background were used. The SERS enhancement factor is calculated relative to the normal Raman scattering (NRS) by the following equation:¹⁻⁴

$$\text{EF} = (\text{I}_{\text{SERS}}/\text{N}_{\text{SERS}})/(\text{I}_{\text{NRS}}/\text{N}_{\text{NRS}}) \quad (1)$$

where I_{SERS} and I_{NRS} are the integration SERS and NRS intensities, respectively. The N_{SERS} and N_{NRS} are the number of the molecules on the surface of the most out layer of the macroporous gold nanoparticles film, which contributed major to the SERS. Supposing the surface of the gold nanoparticle film is fully covered by the R6G molecules (molecule size of 2.2 nm).¹⁻² The laser diameter is 2 μm . The surface porosity of the macroporous gold nanoparticles film is about 50%. Then, the N_{SERS} is calculated to be 0.71×10^6 . In solution, the detector distance was 70 μm ,^{3,4} the N_{NRS} is $1 \times 10^{-4} \text{ M/L} \times (\pi \times 2 \mu\text{m}^2)/4 \times 70 \mu\text{m} \times 6.02 \times 10^{23} = 7.7 \times 10^9$. Thus the average EF is 4.8×10^5 .

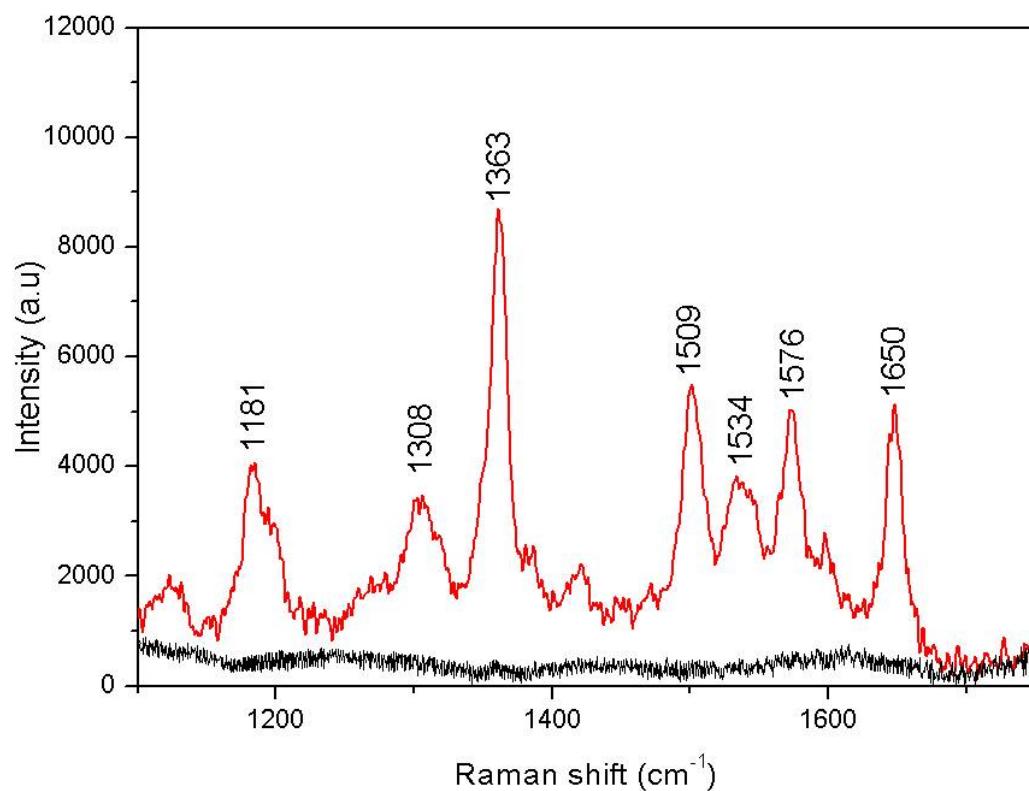


Figure S5 Raman spectra recorded from (a) the porous gold films prepared from 100 nm gold nanoparticles and 1.09 μm PS monolayer; (b) 1×10^{-4} M R6G solution.

4. Conductivity

Table S1 The sheet resistances of the prepared ordered macroporous gold nanoparticle films.

Gold nanoparticle size (Latex sphere size)	Resistance ($\Omega/\text{sq}r$)
150 nm (1.09 μm)	0.87 (Fig. 5e, f.)
100 nm (1.09 μm)	0.99 (Fig. 3a-b)
80 nm (1.09 μm)	1.25 (Fig. 4d)
20 nm (0.62 μm)	456.25 (Fig. S4)
80 nm (0.62 μm)	1.54 (Fig. S3 c)

5. Catalytic oxidation of CO

Table S1. Temperature effects of catalytic oxidation of CO over macroporous gold nanoparticle films prepared from 100 nm gold nanoparticles and 1.09 μm PS monolayer templates.

Temperature ($^{\circ}\text{C}$)	Catalytic efficiency $\times 10^{-5} \text{ mol}/(\text{g}_{\text{Au}} \cdot \text{s})$
50	8.1
100	43.1
150	38.9

6. XRD of ordered macroporous Fe_3O_4 nanoparticle films

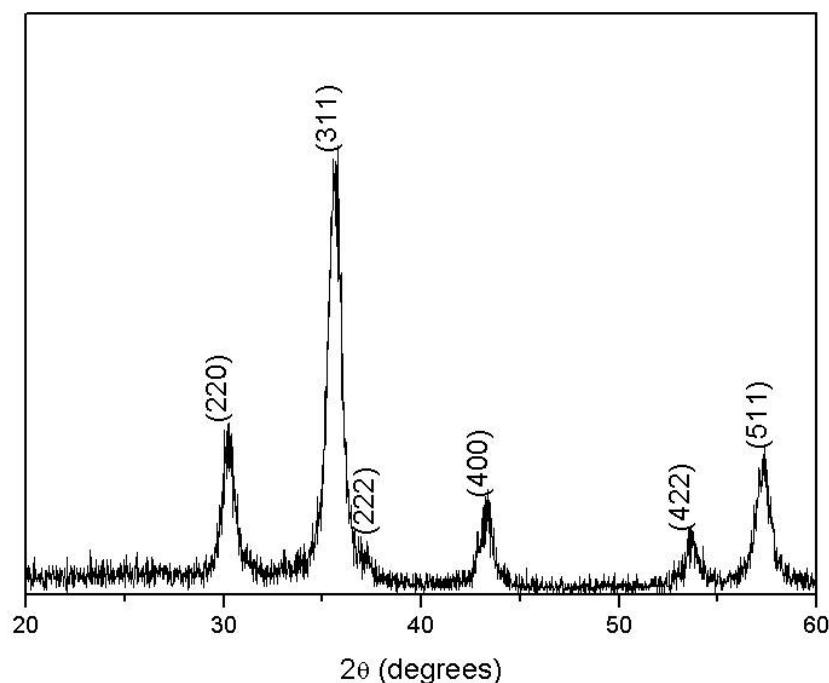


Figure S6 XRD pattern of ordered Fe_3O_4 macroporous structures after removing away PS and CHN.

Fig. S6 is the XRD pattern of the porous Fe_3O_4 strucutres prepared by using monolayer 1.09 μm PS templates after removing away PS and CHN layers. All the peaks are assigned to spinal Fe_3O_4 structure (JCPDF card 86-1354). From the XRD and Scherer's equation, it is calculated that the Fe_3O_4 nanopartcile size is close to 8 nm, in well agreement with the SEM observation and the size of the original Fe_3O_4 nanoparticle size.

References:

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