

Supplementary material (ESI) for *J. Mater. Chem.*

Supporting information for:

## Elevated Ag Nanohole Arrays for High Performance Plasmonic Sensors Based on Extraordinary Optical Transmission

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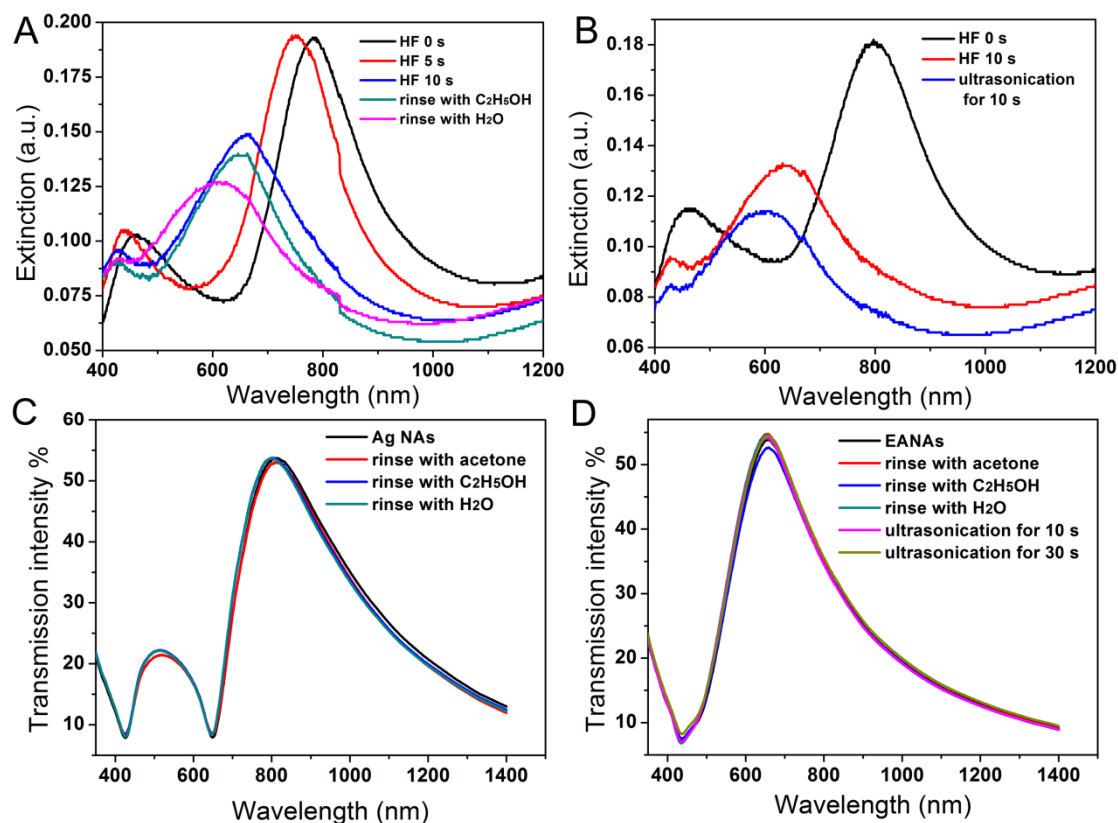
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Experimental:

**Fabrication of Ag Triangle Nanoparticles.** A hexagonally closed packed colloidal monolayer, used as mask, was assembled on a glass substrate by picking up PS particles (~450 nm) at the air/water interface. The mask is then mounted in a thermal evaporator to deposit 1.5 nm Cr and 20 nm Ag respectively in a line-of-sight fashion in the voids between the spheres. After that, colloidal masks are removed using adhesive tape, leading to a surface that is covered by Ag triangle nanoparticles.

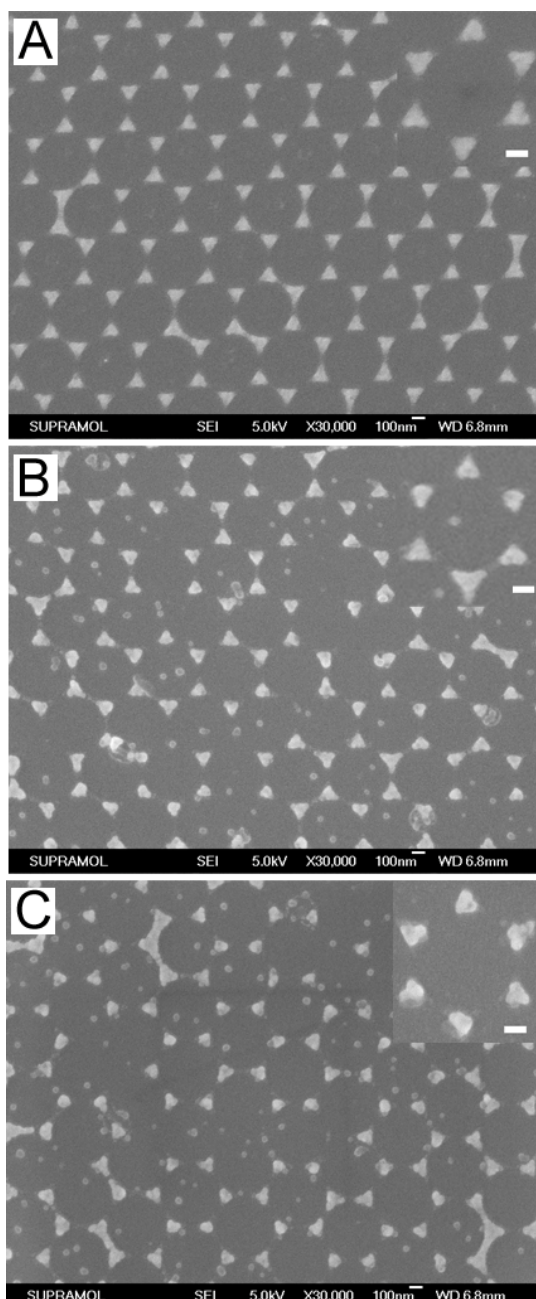
**Preparation of Suspended Ag Triangle Nanoparticles.** Suspended Ag triangle nanoparticles were fabricated by immersion of original samples in 0.3% HF solution for various durations, and then rinsed with H<sub>2</sub>O and dried with N<sub>2</sub>.

**Mechanical Stability Test.** The morphology and optical stability of EANAs and Ag triangle nanoparticles were investigated by thoroughly rinsing corresponding samples with different solvents and then dried in air, as well as by ultrasonication in water for various durations and then dried in air.



**Figure S1.** Optical spectra evolution of suspended Ag triangle nanoparticles (A and B) and Ag NAs (C and D) during the mechanical stability test.

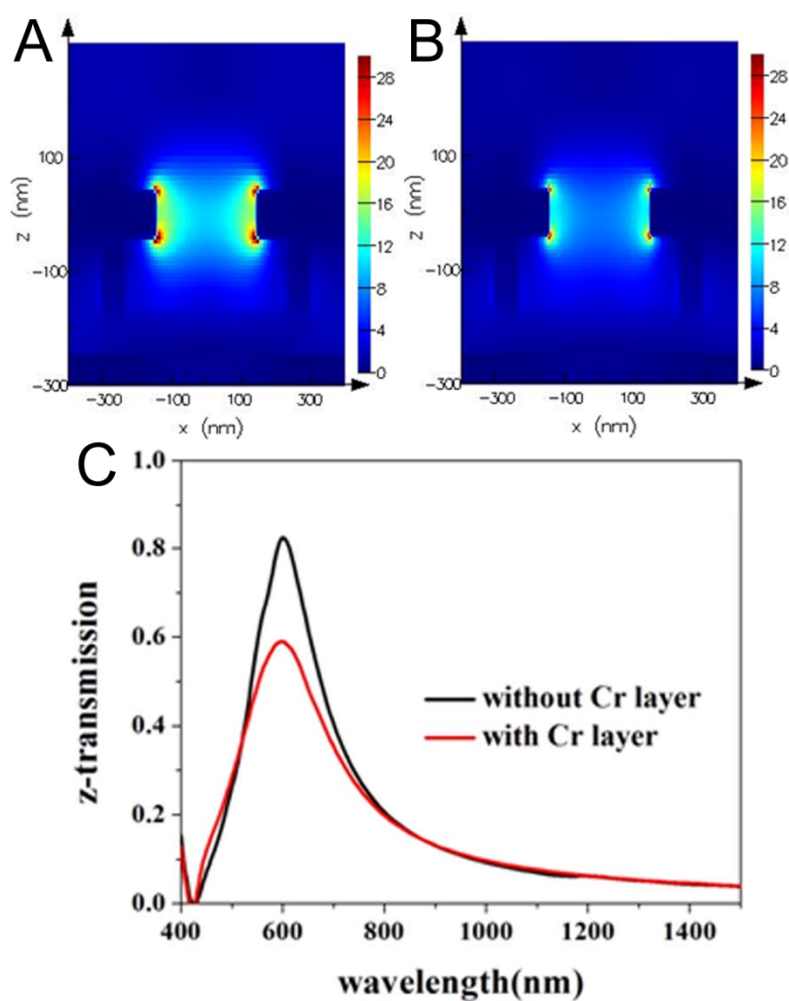
Figure S1A shows the extinction spectrum evolution of Ag nanotriangles upon dipping into 0.3% HF solution for various durations. After etched for 10 s, both blue shift of extinction peak and greatly decrease of the peak intensity are observed. The blue shift of extinction peak is partly induced by the decrease of refractive index around the nanoparticle, which is similar as the observations during the fabrication of EANAs. Besides, the solvent induced morphology remodeling of nanoparticles also plays a key role in this process. From figure S2A and S2B, it is evident that the three tips of Ag triangle nanoparticles become more rounded after HF etching process. According to the reports of Van Duyne and co-workers<sup>1</sup>, smoothen of triangle tips leads to obvious blue shift of extinction peak. The decrease of peak intensity is due to the detachment of Ag nanotriangles resulted by the etching of glass substrate (Figure S2B). Further rinsed the sample with ethanol and water leads to more and more nanoparticles detached; therefore, the decrease of peak intensity continues.



**Figure S2.** SEM image of Ag triangle nanoparticles directly attaching to a glass substrate (A), those treated with HF solution for 10 s (B) and further treated with ultrasonication in water for 10 s. insets are the magnified views, and scale bars represent 100 nm.

We also treated the suspended Ag nanotriangles with ultrasonication. After ultrasonication in water for 10 s (Figure S2C), ~20 % nanoparticles are detached from the substrate. Moreover the triangle nanoparticles become further rounded. As a result, blue shift of extinction peak and decrease of peak intensity can be observed (Figure S1B), implying the suspended Ag nanotriangles are not stable enough. For Ag NAs, the stability is greatly increased (Figure S1C and S1D). After rinsing in a series of solvent, for either NAs directly attaching to the glass substrate or EANAs, only a

small extent of blue shift is observed, indicating the nanohole structure has a good solvent resistance. This is because the nanohole structure is a thick and continuous integration, which is in agreement with previous reports.<sup>2</sup> Further ultrasonicated the EANAs in water for 30 s also has no evident effect on the transmission spectrum as shown in Figure S1D.



**Figure S3.** Near-field electric field profile of EANAs without a Cr layer (A) and with a 1.5 nm Cr layer (B). (C), calculated transmission spectra of EANAs without a Cr layer (the black line) and with a 1.5 nm Cr layer (the red line).

### References

- 1 C. L. Haynes and R. P. Van Duyne, *J. Phys. Chem. B* 2001, **105**, 5599.
- 2 Y. Luo, J. Ruff, R. Ray, Y. Gu, H. J. Ploehn and W. A. Scrivens, *Chem. Mater.* 2005, **17**, 5014.