Electronic Supplementary Information (ESI)

Experimental Section

The SERS substrates of Ag-nanosphere were synthesized as in literatures (Supplementary S1).

The morphologies of as-produced materials were observed by high resolution transmission electron microscopy (JEOL-2010). Metastable state and dry state film UV/Vis absorbance spectra were recorded by Solid spectrophotometers (3700DUV, Shimadzu). Raman, SERS and MSNERS measurements were carried out with a confocal microprobe Raman system (LabRam I from Dilor, France) using an Ar ion laser operating at 514.5 nm. The laser power (a beam diameter of ca. 20 μm) was approximately 1mW.

S1 Preparation of Ag-nanospheres

We synthesized Ag nanosperes with a diameter of about 36 nm according to our former study.[1] In a typical procedure to synthesize Ag nanospheres, 25 mL of a 5 mM aqueous deaerated solution of $H_4(SiW_{12}O_{40})$ was added into a test beaker along with 25 mL of 1 mM aqueous deaerated solution of $AgNO_3$ and 2 mL aliquot of isopropanol, the above solution was stirred for 2 h at room temperature. Finally, this mixture was irradiated by UV light (Pyrex filter, >280 nm, 450 W Hanovia mediumpressure lamp) for 1 h. The solution changed from colorless to gray gradually, indicating the formation of silver nanoparticles. Figure S1 gives the nanoparticles with a uniform size distribution.

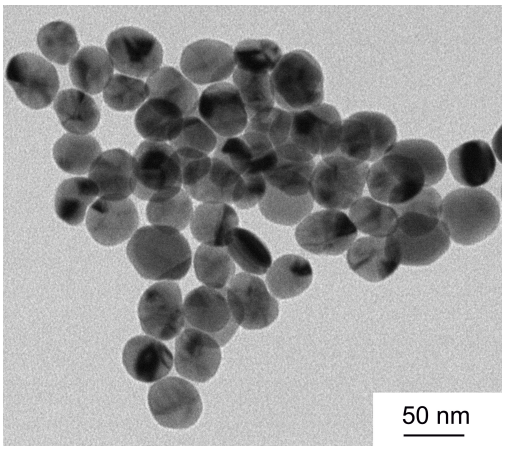

Figure S1 TEM of silver sphere nanoparticles

S2 Video of dynamic process

It is important to map out the experiment process, so that we can visually define the MSNERS scheme. The nanoparticles impacted each other, and it is possible to produce plenty of hot spots, which is beneficial to SERS enhancement effect. The movement may be reflected by the perspective of the following video. Please click the hyperlink to watch the dynamic process.

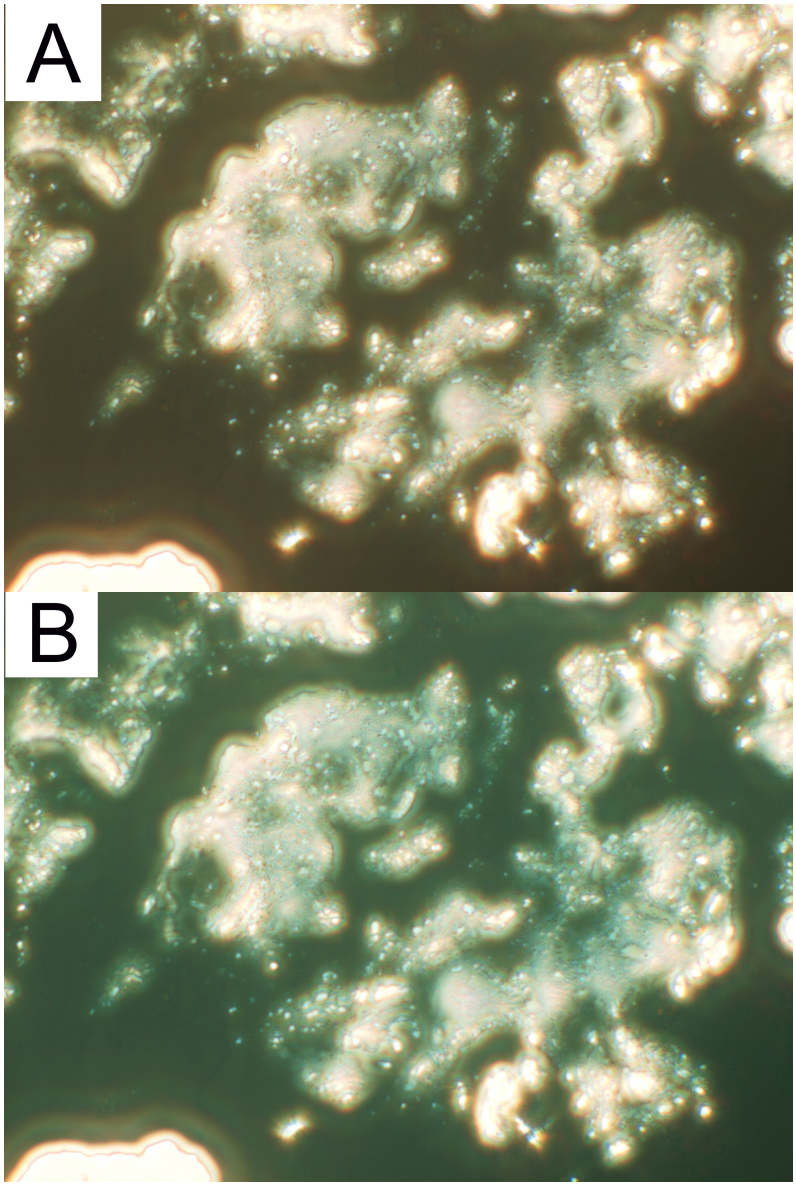

Figure S2. Dark-field images of silver nanoparticles on (A) dry film, (B) adding a drop of water on dry film. Plasmon band position is displayed in the color of the images. The doughnut shape of the images indicates that, on high permittivity surfaces, scattering is dominated by a vertically polarized mode.

1 L. B. Yang, Y. H. Shen, A. J. Xie, B. C. Zhang, *J. Phys. Chem. C*., **2007**, *111*, 5300-5308.