

## Electronic Supplementary Information (ESI)

### Experimental Section

Morphologies and structures of the samples were characterized with SEM (Philips XL 30 FEG). SERS and SNERS 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  $\mu\text{m}$ ) was approximately 1mW.

#### S1. Preparation of the silver nanorods array

Nanoporous alumina template with pore diameters about 50–70 nm were fabricated via a two-step anodization process as described previously<sup>1-2</sup>. Electrochemical deposition was performed in a three-electrode electrochemical cell by the use of a Model LK2005 electrochemistry workstation (LANLIKE, China). Briefly, one planar surface side of the alumina template was firstly deposited a thin layer of Au (about 25 nm), serving as working electrode. A Ag/AgCl electrode and a Pt plate were used as the reference electrode and the counter electrode, respectively. The template was immersed in the 10g/L AgNO<sub>3</sub>, and 10g/L H<sub>3</sub>BO<sub>3</sub> electrolyte. The Ag nanowire arrays were obtained by constant current electrodeposition in the pores of the alumina template at 0.5mA for 2400s at room temperature.

After deposition, the as-prepared samples were taken out from the electrolyte, and rinsed several times with ultrapure water, and then dried in air. The SERS substrate was fabricated as follows: The template sides coated with Au layer was potentiostatically electroplated at 4.0V, in the solution of 100g/l CuSO<sub>4</sub>, to protect the base of Ag array. After that, the array was dipped into 6% H<sub>3</sub>PO<sub>4</sub> at temperatures of 40 °C to remove the alumina template. Following that, the Ag array was rinsed several times with ultrapure water, and then dried in air.

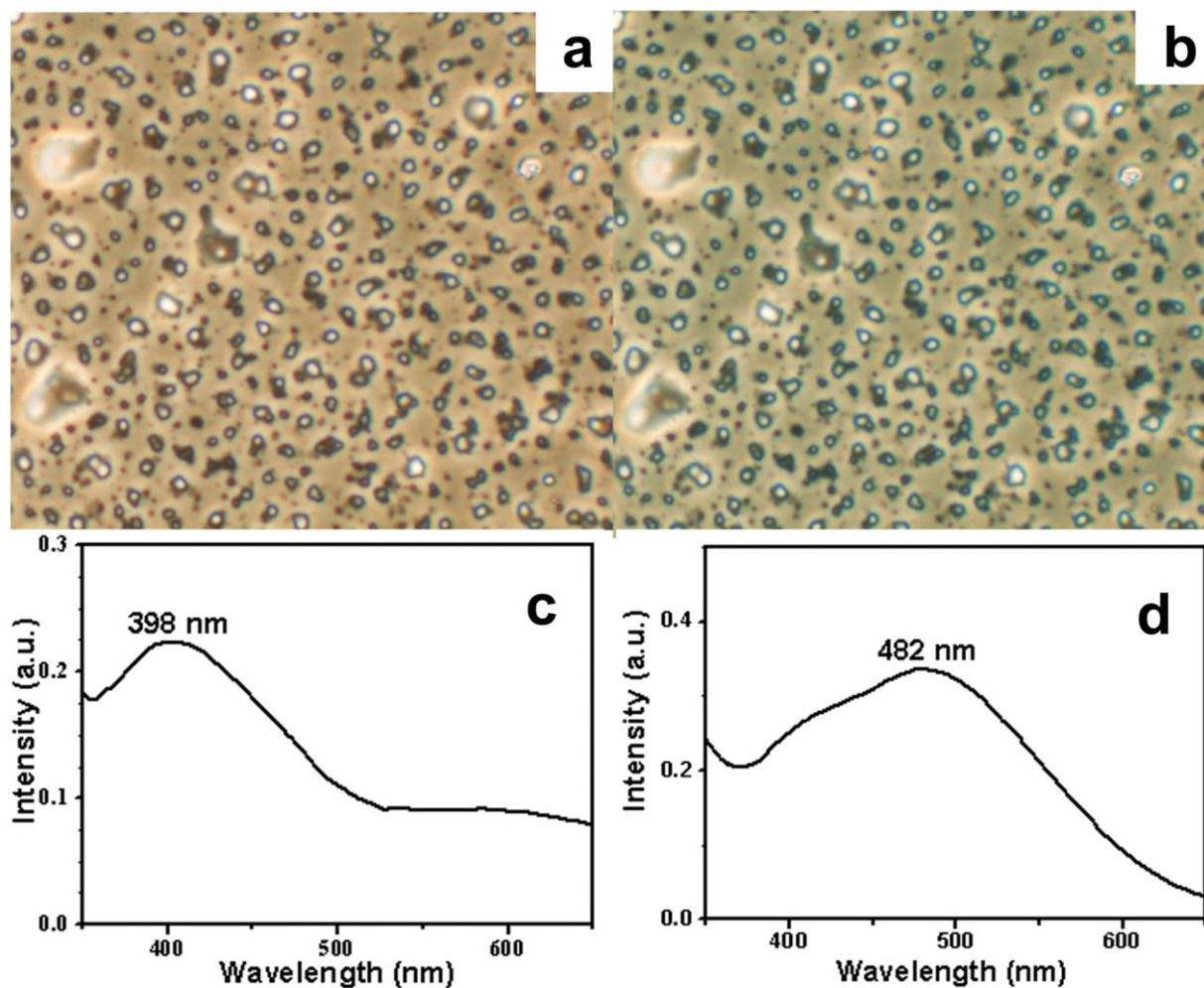


Figure S1 a-b: Dark-field images of silver nanorods array on (a) dry state, (b) adding a drop of water on dry substrate. Plasmon band position is displayed in the color of the images. The doughnut shape of the images indicates that, on high permittivity surfaces, scattering is dominated by a vertically polarized mode. c-d: UV-vis diffuse reflection absorption spectra of dry state film (c), adding water on the dry state film (d).

1 H. Masuda, and K. Fukuda, *Science* **1995**, *268*, 1466-1468.

2 X. Y. Sun, F. Q. Xu, Z. M. Li, and W. H. Zhang, *Mater. Chem. Phys.*, **2005**, *90*, 69-72.