

Electronic Supplementary Information

Ordered Arrays of Ag Nanodendrite Clusters as Effective Surface Enhanced-Raman Scattering Substrates

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The Supporting Information includes:

Part S1. Experimental Section

Part S2. Fig. S1 to S5

Part S3. Calculation of the average enhancement factor (EF).

Part S1. Experimental Section

Materials Silver nitrate (AgNO_3), citric acid, polyvinylpyrrolidone (PVP), hexadecyl trimethyl ammonium chloride (CTAC) and acetone were purchased from Sinopharm Chemical Reagent limited corporation. Zn plates were purchased from tianjin guangfu fine chemical research institute. Milli-Q deionized water (resistivity of $18.2/\text{M}\Omega \text{ cm}^{-1}$) was used for all preparations. All of the chemicals were used without further purification.

Preparation of Ag nanodendrite cluster arrays The Zn plates coated with micro-hole arrays were prepared via photolithography process. A nummular Zn plate (2 inches in diameter) was firstly ultrasonically cleaned in ultrapure water, ethanol, acetone for 15 minutes, respectively. Then the Zn plate was spin-coated with positive photoresist and soft-baked at 95°C for 15 min. After being exposed to UV light under a photomask, tetragonal micro-hole arrays pattern in photoresist will emerge on the Zn plate. Afterwards, immerse the Zn plate with micro-hole arrays into 10 mL mixed aqueous solution of AgNO_3 and citric acid (2 g/L AgNO_3 and 1 g/L citric acid). Then galvanic replacement will take place between Zn and Ag^+ rapidly and abundant Ag nanodendrite clusters will spread from inside to outside micro-holes. 1 minute later, the final product was taken out, cleaned with acetone several times to completely remove photoresist and dried in the air.

Characterization The morphology and composition of the as-prepared products was observed by field-emission scanning electron microscope (FESEM, Hitachi SU8020), transmission electron microscope (TEM, JEM-2010), energy dispersive X-ray

spectroscopy (EDS, Oxford). The X-ray diffraction (XRD) spectrum was characterized with a Philips X'pert-PRO diffractometer. The absorbance curve of the Ag nanodendrites films was observed by an Ultraviolet-Visible-Near-Infrared spectrophotometer (Shimadzu, UV3600).

SERS measurement Before SERS measurements, the as-prepared samples were cleaned by plasma for 15 minutes to eliminate residual contaminant on their surface. To evaluate their SERS performance, the Zn plates covered with Ag nanodendrite cluster arrays were immersed into 2 mL of Rhodamine 6G (R6G) or thiram solutions with different concentrations for 5 h and dried in the air. The Raman spectra were recorded using a confocal microprobe Raman spectrometer (Renishaw Invia Reflex) with a 532 nm argon ion laser line, where the effective power of the laser source was 1 mW. The laser spot focused on the sample surface was about 5 μm in diameter. The integration durations were maintained for 5 s. The effective power of the laser for testing the homogeneity of the SERS signals was 0.1 mW and the integration durations were maintained for 5 s. The Raman mapping was measured by the Renishaw StreamLine accessory with a step size of 1 μm and an exposure time of 0.1 s, the effective power of the laser source was 1 mW.

Part S2. Fig. S1 to S5

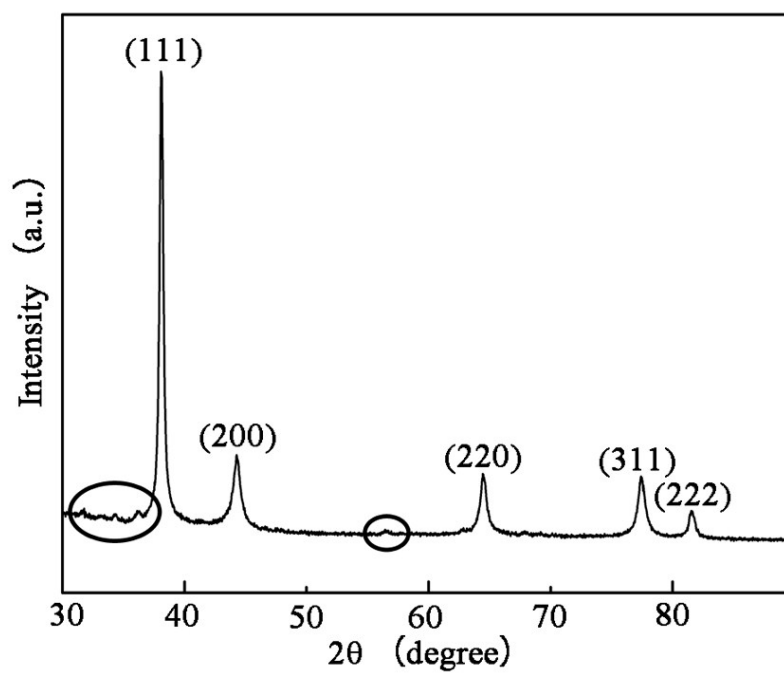


Fig. S1 XRD spectrum taken from the products shown in Fig. 2b.

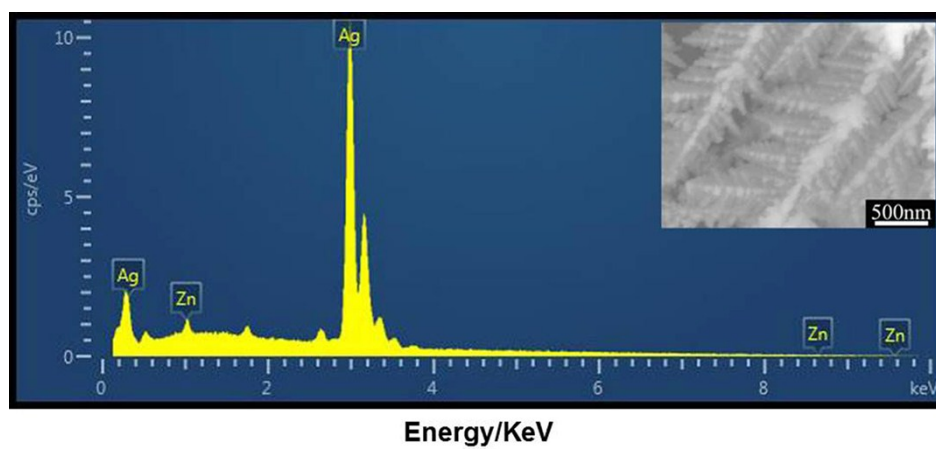


Fig. S2 EDS spectrum on the products.

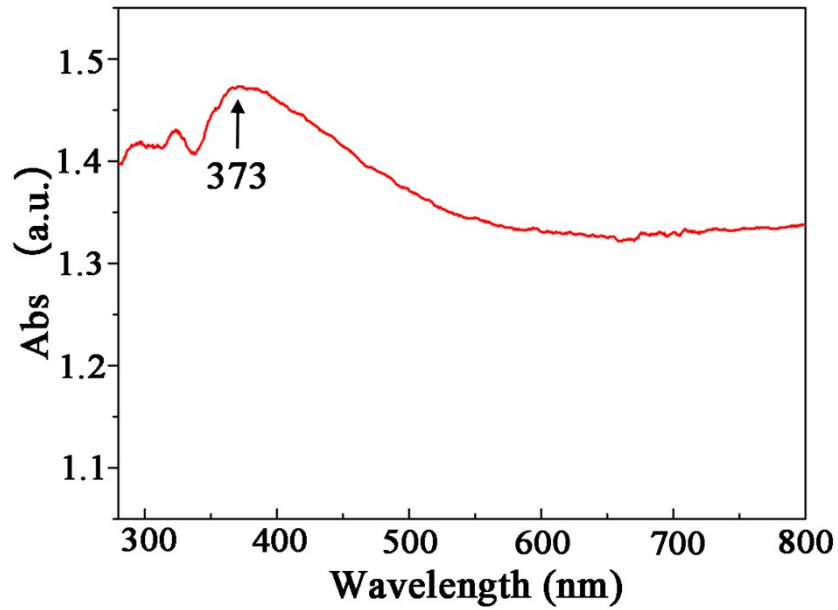


Fig. S3 The absorption spectrum of the Ag nanodendrites.

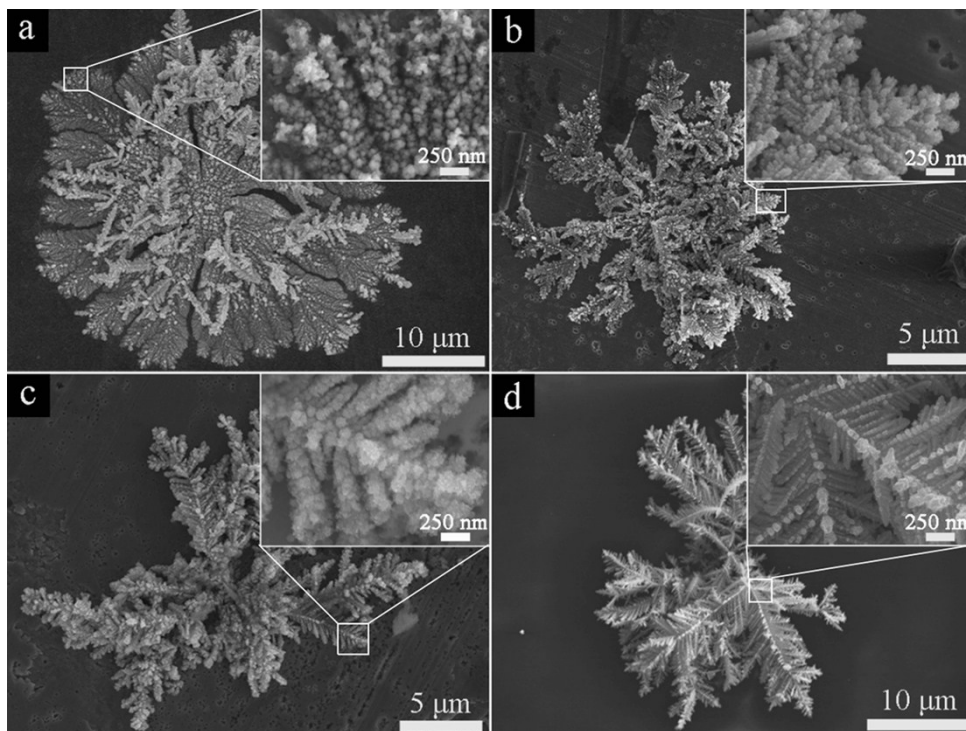


Fig. S4 SEM images of Ag nanodendrite cluster achieved on porous photoresist coated Zn substrates with the reaction solution contains (a) 2 g/L AgNO₃, (b) 2 g/L AgNO₃ and 1 g/L PVP, (c) 2 g/L AgNO₃ and 1 g/L CTAC and (d) 2 g/L AgNO₃ and 1 g/L citric acid, respectively. The insets are close-up views.

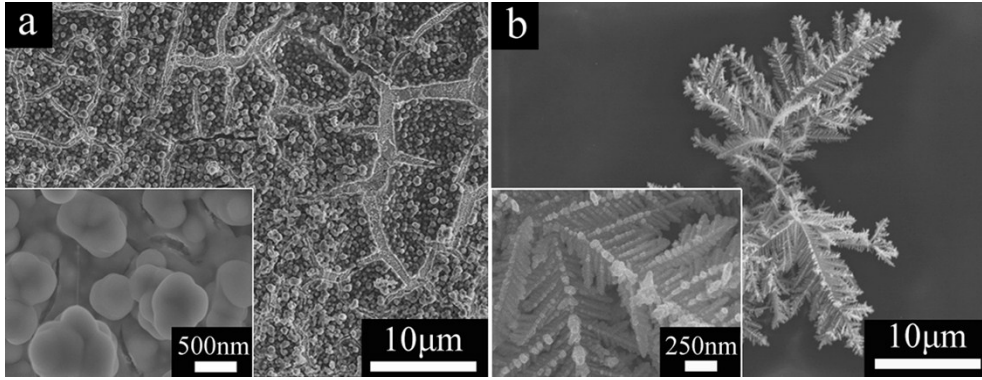


Fig. S5 SEM images of Ag nanostructures achieved on (a) a bare Zn plate; (b) a Zn plate coated with porous template. The insets are close-up views.

Part S3. Calculation of the average enhancement factor (EF).

The EF can be calculated by:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{RS} / N_{RS}}$$

Where I_{SERS} and I_{RS} represent the intensity of the 614 cm^{-1} band of R6G of SERS spectrum and Raman spectrum (non-SERS), under the same experimental conditions (laser wavelength, laser power, microscope objective/lenses, accumulation time), respectively. N_{SERS} and N_{RS} represent the corresponding number of molecules within the focused incident laser spot. Herein for SERS examination, a certain volume (V_{SERS}) R6G aqueous solution was dispersed to an area of S_{SERS} at a concentration of C_{SERS} on the Ag nanodendritic cluster arrays and a certain volume (V_{RS}) and concentration (C_{RS}) R6G solution was dispersed to an area of S_{RS} at a clean silicon wafer for Raman spectrum, similarly. Both the substrates were dried in the air. The preceding equation can be rewritten as:

$$EF = \frac{I_{SERS}}{I_{RS}} \cdot \frac{S_{SERS} V_{RS} C_{RS}}{S_{RS} V_{SERS} C_{SERS}}$$

In our experiment, 70 μL of 0.1 nM R6G aqueous solution was dispersed to an area of 25 mm^2 for the Ag nanodendritic cluster arrays substrate and 70 μL of 1 mM R6G aqueous solution was dispersed to an area of 25 mm^2 for the silicon wafer. Fig. S6 shows the Raman spectrum of R6G from the aforementioned substrates. For the band at 614 cm^{-1} , $I_{\text{SERS}}/I_{\text{RS}}$ was about 0.129. Hence the average enhancement factor for the band at 614 cm^{-1} is calculated to be 1.29×10^6 .

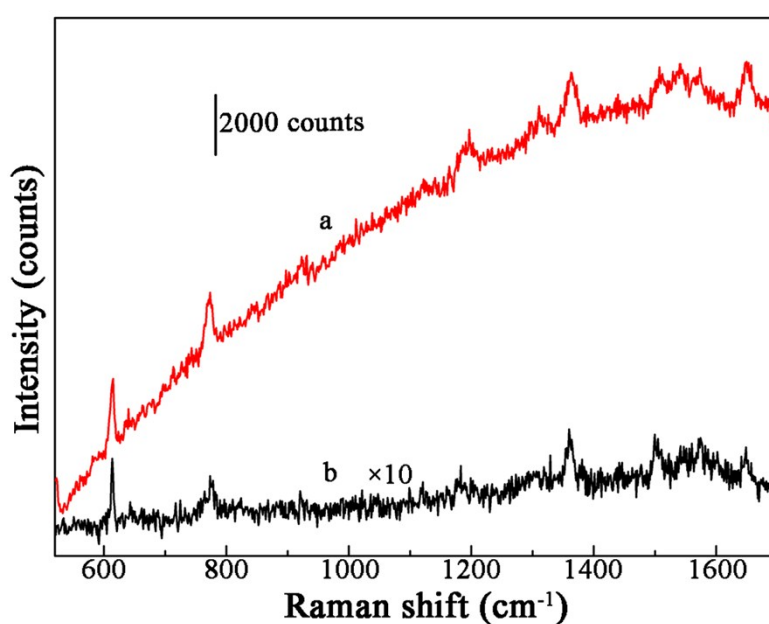


Fig. S6 (a) Raman spectra of 70 μL 1 mM R6G aqueous solution on 25 mm^2 silicon wafer. (b) SERS spectra of 70 μL 0.1 nM R6G aqueous solution on 25 mm^2 Ag nanodendritic cluster arrays. The spectra intensity has been multiplied by 10 for clarity.