Supporting information for

Seeded Growth of Silver Nanoplates with Rough Edges and Their Applications for SERS

Qiang Zhang,[ab] Li Long,[c] Gongguo Zhang,[a] Zhi-Yuan Li,[c] and Yiqun Zheng[a]*

[a]Department of Chemistry and Chemical Engineering, Jining University, Jining 237000, P. R. China

[b]Shanghai Key Laboratory of Regulatory Biology, School of Life Sciences, East China Normal University, Shanghai 200062, P. R. China

[c]School of Physics and Optoelectronics, South China University of Technology, Guangzhou 510640, P. R. China

*Corresponding author: Prof. Y. Zheng, whzyq@163.com

Experimental Details

Chemicals. Silver nitrate ($AgNO_3$ (99+%), poly(vinyl pyrrolidone) with molecular weights of 29000 and 55000 (PVP-29K and PVP-55K), ascorbic acid (AA, 99+%), 1,4-benzenedithiol (1,4-BDT, 99%), and ethanol (200 PROOF) were all obtained from Sigma-Aldrich and used as received. In all experiments, we used deionized water with a resistivity of 18.2 MΩ·cm, which was prepared using an ultrapure water system (Millipore, Billerica, MA).

Synthesis of 45-nm Ag nanoplate seeds. Typically, 10 mL of PVP-29K (1.0 mM) solution in ethanol was added in a Teflon liner, and then 0.3 mL of $AgNO_3$ (10.0 mM) solution in ethanol was added. The Teflon liner was sealed in a stainless vessel, and was heated in an oven at 80 °C for 4 h. After that, the vessel was water cooled to room temperature. The product was washed with deionized water three times via centrifugation (15000 rpm, 10 min), and then it was collected and re-dispersed in 5 mL of PVP-55K (1.0 mM) solution in ethanol for further use.

Synthesis of 95-nm Ag nanoplate seeds. Typically, $AgNO_3$ (10.0 mM, 0.3 mL) and PVP-29K (1.0 mM, 10 mL) in ethanol was mixed in a Teflon liner, followed by the addition of 1 mL of the as-prepared 45-nm Ag nanoplates as seeds. The Teflon liner was then sealed in a stainless vessel, heated in an oven at 80 °C for 4 h, and cooled down naturally. The product was washed with deionized water three times via centrifugation (15,000 rpm, 10 min), collected and re-dispersed in 5 mL of PVP-55K (1.0 mM) solution in ethanol for further characterization and use.

Synthesis of Ag nanoplates with rough edges. In a standard synthesis, 2.0 mL of PVP-55K (1 mM) and 0.5 mL of AA (10 mM) was mixed in a 23-mL glass vial, and then 0.25 mL of as-prepared Ag nanoplate seeds solution was added. After that, 1 mL of $AgNO_3$ (0.2 mM) in ethanol was injected into the reaction solution using a syringe pump at a rate of 0.3 mL/min at room temperature. The products were collected via centrifugation and washed with water for further use.

Characterizations. Transmission electron microscopy (TEM) images were taken using a H-7700 electron microscope (Hitachi, Japan) operated at 120 kV. High-resolution TEM image and selected-area electron diffraction were captured using a JEM-2100Plus electron microscope

(JEOL, Japan) operated at 200 kV. UV-vis extinction spectra were recorded using a Cary 60 UV−vis spectrometer (Agilent Technologies, Santa Clara, CA).

Raman measurements. The Raman measurements were conducted using a Renishaw inVia Raman spectrometer (Wotton-under-Edge, U.K.). Briefly, a small aliquot of the as-prepared Ag nanoplates with rough edges (3 μL in deionized water) was incubated with 30 μL of 1,4-BDT (1 mM in ethanol) for 1 h. The sample were then dropped on a Si substrate and dried naturally. Then the sample was rinsed with ethanol and dried naturally again. After that, the sample was immediately employed for SERS measurements by following a previously reported protocol. (*Nano Lett.,* 2007, *7*, 1013–1017).

Finite difference time domain (FDTD) Calculation. The E-field intensity distribution of the nanoplate was calculated using the FDTD, a numerical technique to solve boundary-value problem. This method provides a convenient and general approach for calculating the optical response of plasmonic nanostructures of arbitrary symmetry and geometry to an incident light wave. We constructed three models corresponding to Ag products as shown in Figure 2, A-C. Edge length was set to 50 nm and the thickness was set to 3 nm. Perfectly matched layer boundary conditions were used for all the simulations. To obtain accurate results in the simulations, the Yee cell size was set to 0.25 nm. The optical constant for Ag was taken from experimental report.[1] We aligned the TFSF source(x polarization) parallel to the normal to the nanoplates. And the light electric amplitude was chosen to be 1 V m^{-1}.

Reference

 [1] W Li, Human colorectal cancer (CRC) antigen CO17-1A/GA733 encoded by adenovirus inhibits growth of established CRC cells in mice. *J. Immunol.*, 1997, **159**, 763-769.

Note for Figure 4

The incident light intensity is set as 1. Under the 534 nm laser excitation the maximum local field intensity is 107 (NPRE-1), 138 (NPRE-2), and 168 (NPRE-3), respectively at X polarization, and 136 (NPRE-1), 149 (NPRE-2), and 308 (NPRE-3), respectively at Y polarization. The local field enhancement is much higher under the 785 nm laser excitation. The maximum local field intensity is 289 (NPRE-1), 1920 (NPRE-2), and 4120 (NPRE-3), respectively at X polarization, and 470 (NPRE-1), 3250 (NPRE-2), and 2340 (NPRE-3), respectively. These field enhancement features indicate that the Raman enhancement for NPRE-2 and NPRE-3 are much higher than NPRE-1, agreeing well with experiment.
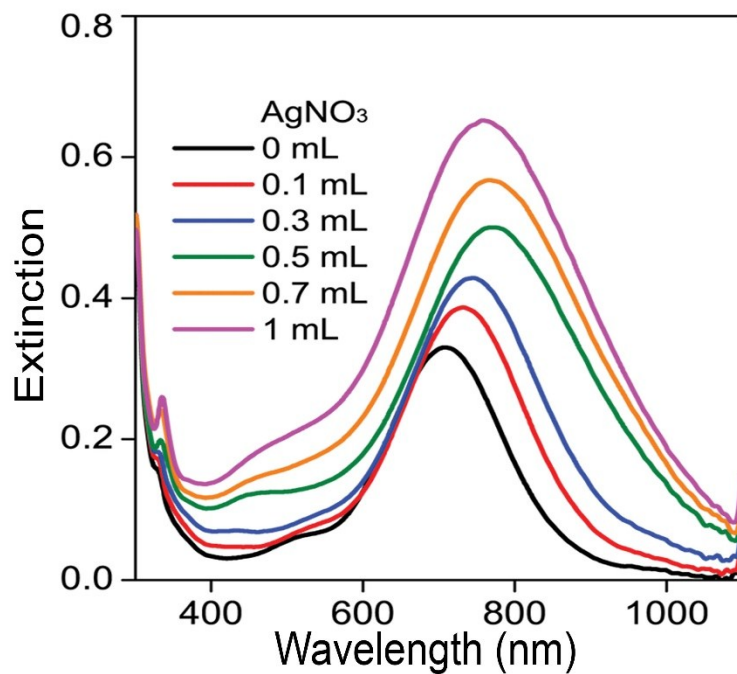
Figure S1. UV-vis extinction spectra of samples taken out during the standard synthesis of Ag nanoplates with rough edges as shown in Figure 1.
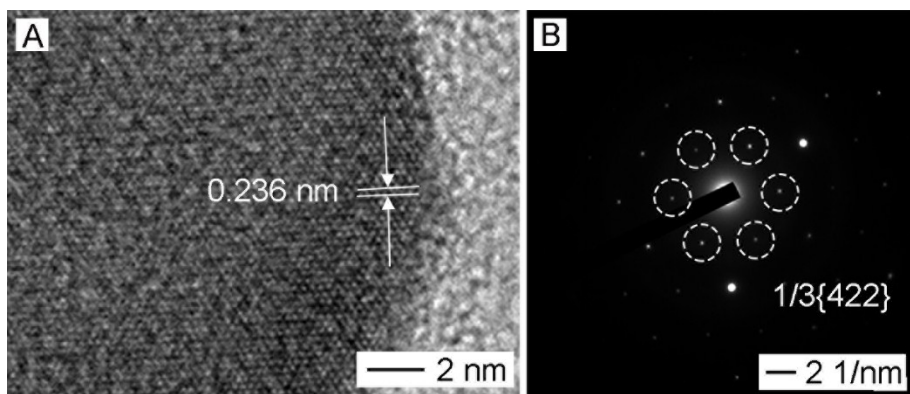
Figure S2. (A) High-resolution TEM image and (B) SAED pattern of edge part of an individual Ag nanoplate with rough edge.
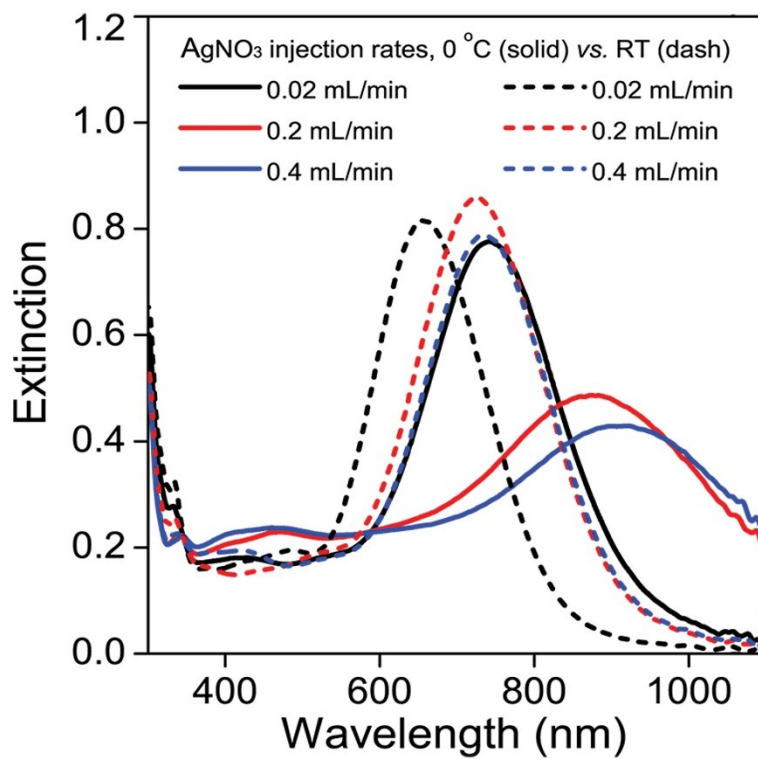
Figure S3. UV-vis extinction spectra of samples taken from aqueous suspensions of Ag products as displayed in Figure 2.
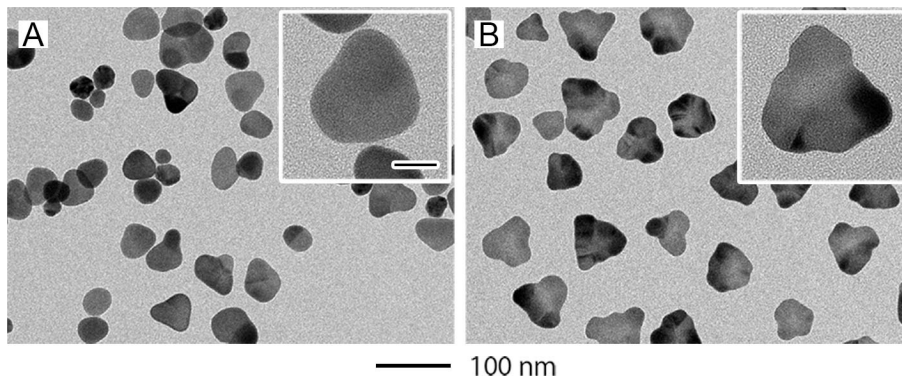
Figure S4. Effect of PVP amount on product morphology. TEM images of Ag nanoplates obtained via the standard procedure, except that the PVP amount was varied from 2 to (A) 0.02 and (B) 0.2 μmol, respectively. The scale bar in the inset of A is 25 nm and applies to inset of B.
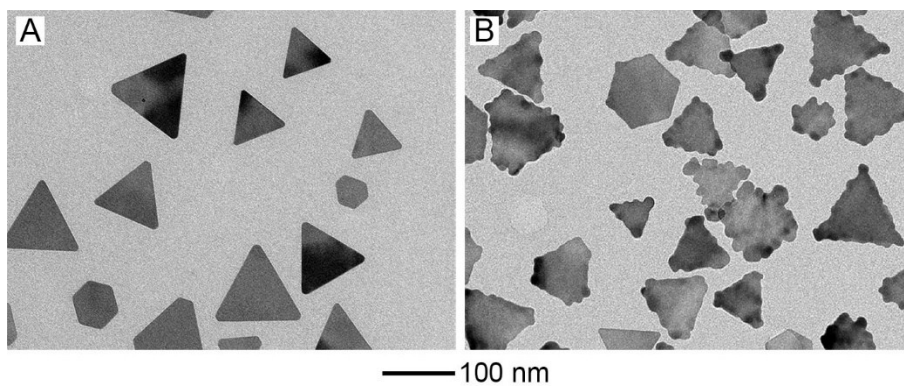
Figure S5. TEM images of (A) 95-nm Ag plate seeds and (B) Ag products obtained via the standard procedure, except that the 45-nm seeds were replaced by the 95-nm Ag nanoplates as shown in A.
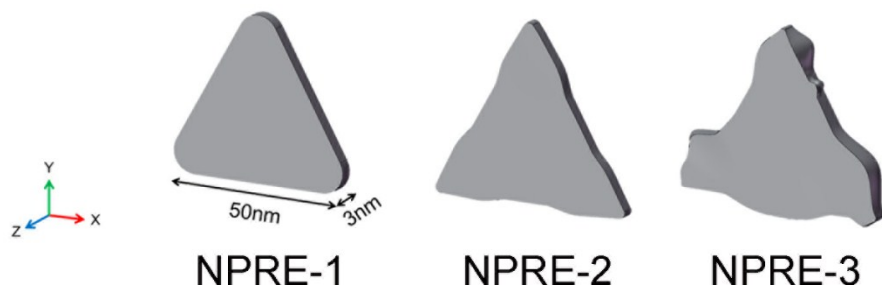
Figure S6. Models for E-field intensity distribution simulation.
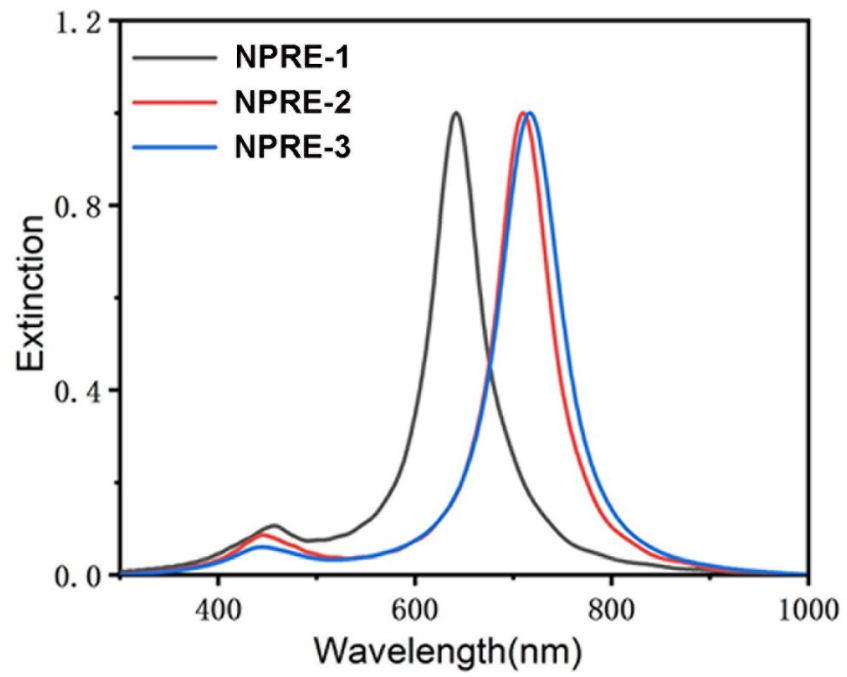
Figure S7. Simulated UV-vis extinction spectra of Ag nanoplates with different edge roughness.