

## Supporting Information

*for*

Real-time monitoring of oxidative etching on single Ag nanocube *via* light-scattering dark-field microscopic imaging

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### ***Experimental Section***

**Instrumentation.** Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the Ag nanocubes were taken using an S-4800 scanning electronic microscope (Hitachi Ltd., Japan) operated at 30 kV. Light-scattering dark-field images were captured by a BX51 optical microscope (Olympus, Japan) equipped with a DP72 single chip true-color charge coupled device (CCD) camera (Olympus, Japan). A dark-field condenser (U-DCW, 1.2-1.4) was used and the scattering light was collected by a 100× object lens. XPS spectra were taken using a Thermo ESCALAB 250Xi X-ray Photoelectron Spectrometer (Thermo Scientific, USA). The extinction spectrum of Ag nanocubes was measured by a UV-3600 UV-Visible-NIR spectrophotometer (Shimadzu, Japan). The software of Image-Pro Plus was used to analyze the data from optical imaging.

**Chemicals and materials.** Poly(vinyl pyrrolidone) (PVP,  $MW \approx 55\ 000$ ) was purchased from Sigma-Aldrich (St. Louis, USA). Silver trifluoroacetate ( $CF_3COOAg$ ), diethylene glycol (DEG), ethylene glycol (EG), and sodium hydrosulfide hydrate ( $NaHS \cdot xH_2O$ ) were all obtained from Aladdin Industrial Corporation (Shanghai, China). Silver nitrate ( $AgNO_3$ ) was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Potassium persulfate ( $K_2S_2O_8$ ), hydrogen peroxide ( $H_2O_2$ ), aqueous hydrochloric acid solution (HCl, 37%), and acetone were purchased from Chuandong Chemical Co., Ltd

(Chongqing, China). Deionized (DI) water with a resistivity of 18.2 M $\Omega$ ·cm was used throughout the experiment.

**Synthesis of Ag nanocubes.** The Ag nanocubes with edge length of ~45 nm were prepared by a two-step method. Firstly, single-crystal Ag seeds were synthesized in DEG.<sup>1</sup> In detail, 5 mL of DEG was added into a flask and heated under magnetic stirring in an oil bath (150 °C) for 30 min. Other reagents were separately dissolved in DEG and sequentially introduced into the flask using a pipet. Specifically, 0.06 mL of NaSH solution (3 mM) was added first. After 4 min, 0.5 mL of HCl (3 mM) was added, followed by 1.25 mL of PVP (20 mg/mL). After another 2 min, 0.4 mL of CF<sub>3</sub>COOAg solution (282 mM) was introduced. The synthesis was quenched by placing the flask in an ice-water bath after the major LSPR peak was located at ~405 nm, which could be monitored by a UV-vis spectrometer. Then, the products were collected by centrifugation, followed by washing with acetone and DI water to remove the remaining precursor, DEG, and excess PVP. The products were re-dispersed in 1 mL of EG.

Using the above Ag nanoparticles as seeds, Ag nanocubes could be obtained in EG through a seed-mediated growth method.<sup>2</sup> In detail, 20 mL of EG was added into a 100 mL flask and heated in an oil bath (150 °C) under magnetic stirring. After 30 min, 6 mL of PVP solution (20 mg/mL, in EG) was added using a pipet. After another 10 min, the above Ag seeds (dispersed in EG) were introduced, followed by the addition of 4 mL of AgNO<sub>3</sub> solution (282 mM, in EG). The synthesis was quenched by placing the flask in an ice-water bath after the major LSPR peak was located at ~440 nm, which could be monitored by a UV-vis spectrometer. The product was washed with acetone and DI water, and then re-dispersed in 1 mL of DI water for further use.

**Light-scattering dark-field imaging.** Dark-field scattering microscope was used to real-time monitoring of the oxidative etching of Ag nanocubes. We made a flow cell by the combination of a microslide and coverslips as the reaction zone.<sup>3</sup> Firstly, 10  $\mu$ L of Ag nanocubes were diluted by 0.5 mL of PVP solution (5 mg/mL), and 50  $\mu$ L of the diluted solution was dropped on the reaction zone. After 30 min, the flow cell was washed by DI water, and dried by N<sub>2</sub>. Then, the flow cell was placed under the microscope for light-scattering imaging. A representative area involving the deposited silver nanocubes with

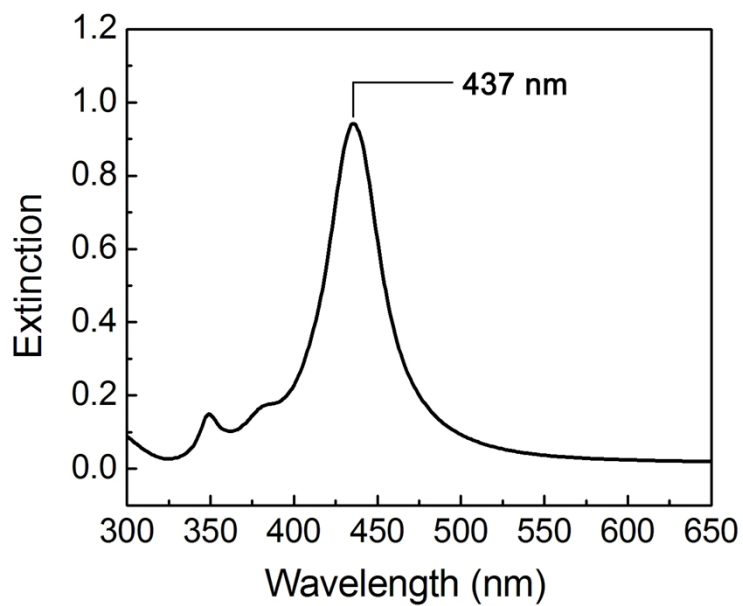
appropriate density was selected for real-time study. After taking the images of the initial Ag nanocubes, 100  $\mu\text{L}$  of etchant solution (100 mM of  $\text{K}_2\text{S}_2\text{O}_8$  or 50 mM of  $\text{H}_2\text{O}_2$ ) was added to the flow cell to initiate the oxidative etching. Immediately, a series of dark-field scattering images of the same region were recorded at different time points, as indicated in the text. We combined all the images orderly to describe the consecutive oxidative etching process of individual Ag nanocubes.

**FDTD simulation.** The simulations were performed using FDTD Solution 7.0, developed by Lumerical Solutions, Inc. In the simulations, a total-field scattered-field (TFSF) light source in the wavelength range from 300 to 600 nm was launched into a box containing the target nanoparticle to simulate a propagating wave interacting with the nanoparticle. The nanoparticle and its surrounding medium inside the box were divided into meshes of 1 nm in size. And the grid boundaries in the simulation space are perfectly matching layers (PML). The refractive index of the surrounding medium was set to be 1.33, which is the index of water. The dielectric functions in the simulations were formulated using Johnson and Christy data for Ag.<sup>4</sup>

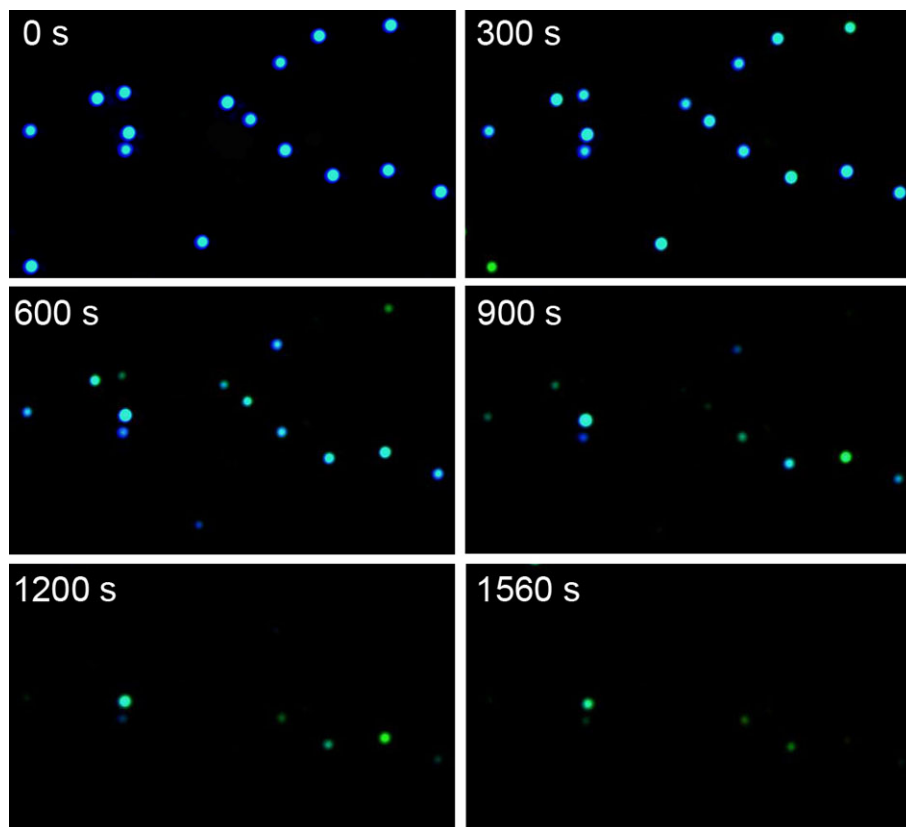
#### References:

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2. X. Xia, J. Zeng, L. K. Oetjen, Q. Li and Y. Xia, *J. Am. Chem. Soc.*, 2012, **134**, 1793.
3. Y. Liu and C. Z. Huang, *ACS Nano*, 2013, **7**, 11026.
4. J. M. Bennett, J. L. Stanford and E. J. Ashley, *J. Opt. Soc. Am.*, 1970, **60**, 224.

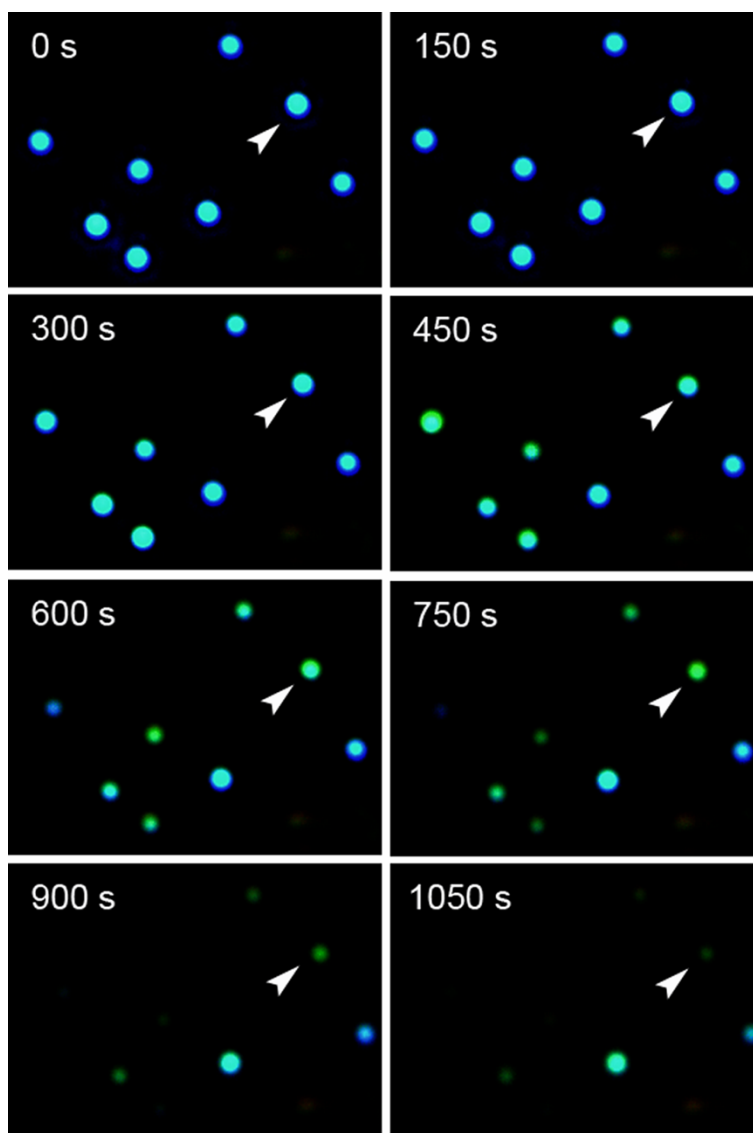
*Additional Figures*



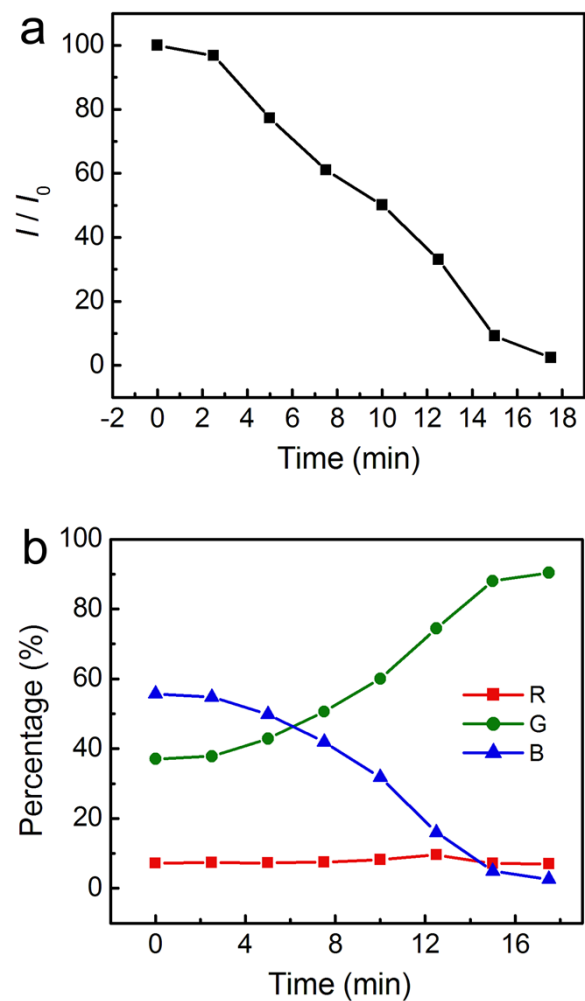
**Fig. S1** The extinction spectrum of Ag nanocubes with edge length of ~45 nm. The main LSPR peak is located at 437 nm.



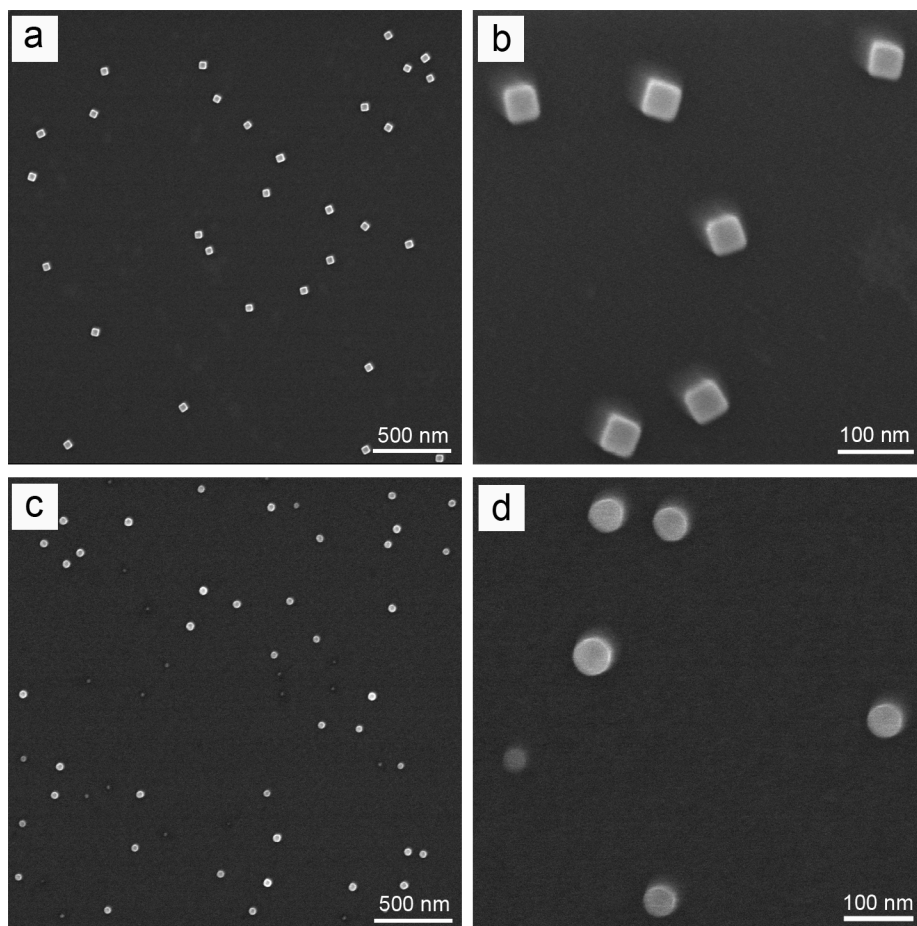
**Fig. S2** Time-dependent light-scattering dark-field images of AgNCs in the process of oxidative etching, using  $S_2O_8^{2-}$  as a typical etchant. The images were taken in the same region at different time points.



**Fig. S3** Time-dependent light-scattering dark-field images of AgNCs in the process of oxidative etching, using  $\text{H}_2\text{O}_2$  as an etchant. The images were taken in the same region at different time points. The white arrows marked in the images show the scattering light of a typical AgNP in the process of oxidative etching.



**Fig. S4** Time-dependent light-scattering intensity (a) and RGB (b) analysis of the typical AgNP (marked by white arrows, shown in Fig.S3) in the process of oxidative etching by H<sub>2</sub>O<sub>2</sub>.



**Fig. S5** SEM images showing the morphologies of AgNPs before (a, b) and after (c, d) the oxidative etching.