

Supplementary Information

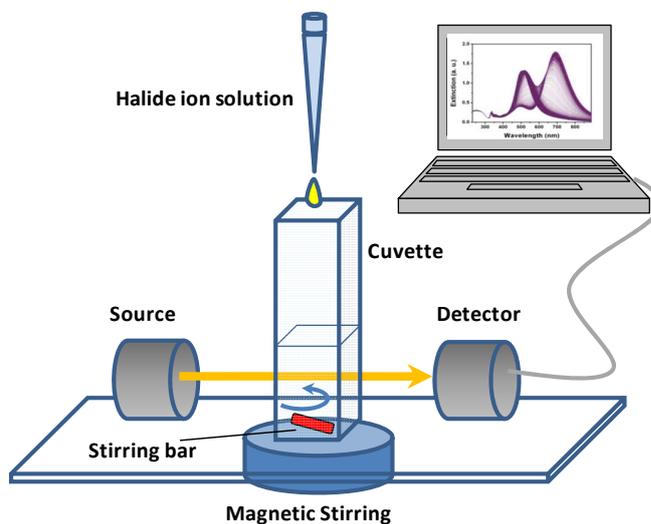
Kinetic Effects of Halide Ions on the Morphological Evolution of Silver Nanoplates

Bin Tang,^a Shuping Xu,^a Jing An,^a Bing Zhao,^a Weiqing Xu,^{*a} and John R. Lombardi^b

^a State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China. Fax: +86-431-85193421; Tel.: +86-431-85159383; E-mail: xuwq@jlu.edu.cn

^b Department of Chemistry, The City College of New York, New York, NY 10031, USA.

1. Schematic experimental setup of time-resolved extinction spectroscopy.



Scheme S1 Schematic experimental setup of time-resolved extinction spectroscopy.

2. Simulation of the extinction spectra of silver nanodisks by the discrete dipole approximation (DDA) method.

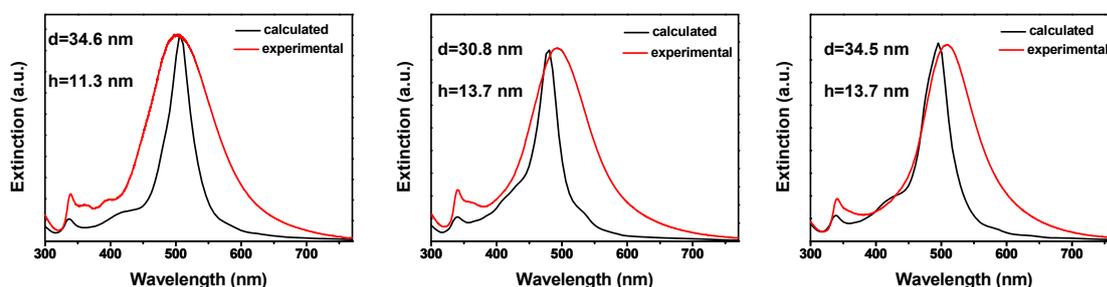


Fig. S1 Extinction spectra of the silver nanodisks with different diameter (d) and thickness (h): $d=34.6$ nm, $h=11.3$ nm; $d=30.8$ nm, $h=13.7$ and $d=34.5$ nm, $h=13.7$. Black curves are referred to the calculated spectra and the red curves are the experimental spectra.

The discrete dipole approximation (DDA) simulation enables us to learn the wavelength distribution of the absorption and scattering abilities of silver nanoparticles. Several studies have shown that the main optical features of silver nanoprisms by the DDA.¹⁻⁶ The extinction spectra of silver nanoprisms synthesized herein were consistent with the DDA results described previously. The peaks centered at 331 (weak), 500 (medium) and 699 nm (strong), correspond to the out-of-plane quadrupole, in-plane quadrupole and in-plane dipole plasmon resonance modes of silver nanoprisms, respectively. Nevertheless, there were a few reports involved in the DDA calculation about silver nanodisks.^{4,7} We did the simulation of the extinction spectra of different sized silver nanodisks. The calculated and experimental results are shown in Fig. S1. In accord with previous work, the strongest band at around 500 nm is assigned to the in-plane dipole resonance mode of silver nanodisks, and the 340-nm band is attributed to the out-of-plane quadrupole resonance mode. The in-plane dipole resonance peak of the silver nanodisks is strongly different from that of nanoprisms in position. The corresponding intensities of the in-plane dipole resonance peak of nanoprisms or nanodisks relate to the concentration of silver nanoplates. Therefore, the kinetics of the etching reaction of silver nanoplates can be discussed based on the intensity of the in-plane dipole resonance peak.

3. The effect of adsorbed halide ions on the SPR of nanodisks.

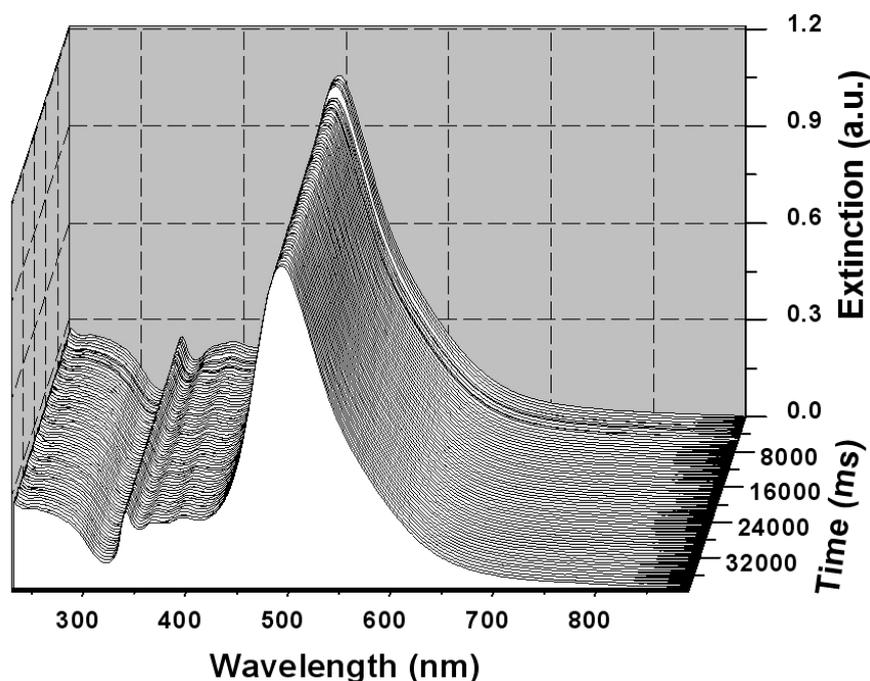


Fig. S2 Time-resolved spectra of silver nanodisks derived from a little chloride ions after more chloride ions were added. It contains 495 curves.

Influences of dielectric environment (adsorbed halide ions) on the SPR of the silver nanoplates have been considered. To investigate the effect of adsorbed halide ions on the SPR, the additional halide ions were employed to react with the produced silver nanodisks. The silver nanodisks (0.1 mM, 1.00 mL) were first obtained by the chloride ion etching shape conversion. Secondly, additional chloride ion solution (180 mM, 20 μ L) was added into the silver nanodisk solution. The evolution of the SPR of silver nanoplates was monitored by time-resolved extinction spectroscopy. As shown in Fig. S2, no significant variation was observed in the time-resolved extinction spectra of silver nanoplates with more chloride ions. The result indicates that the halide ions had little influence on the SPR properties of silver nanoparticles. Therefore, it is suggested that the variation on the extinction spectra of silver nanoplates after adding of halide ions were mainly caused by the change of their morphologies and concentration.

4. Time-resolved extinction spectra of silver nanoplates etched by different concentration of bromide and iodide ions at 298K.

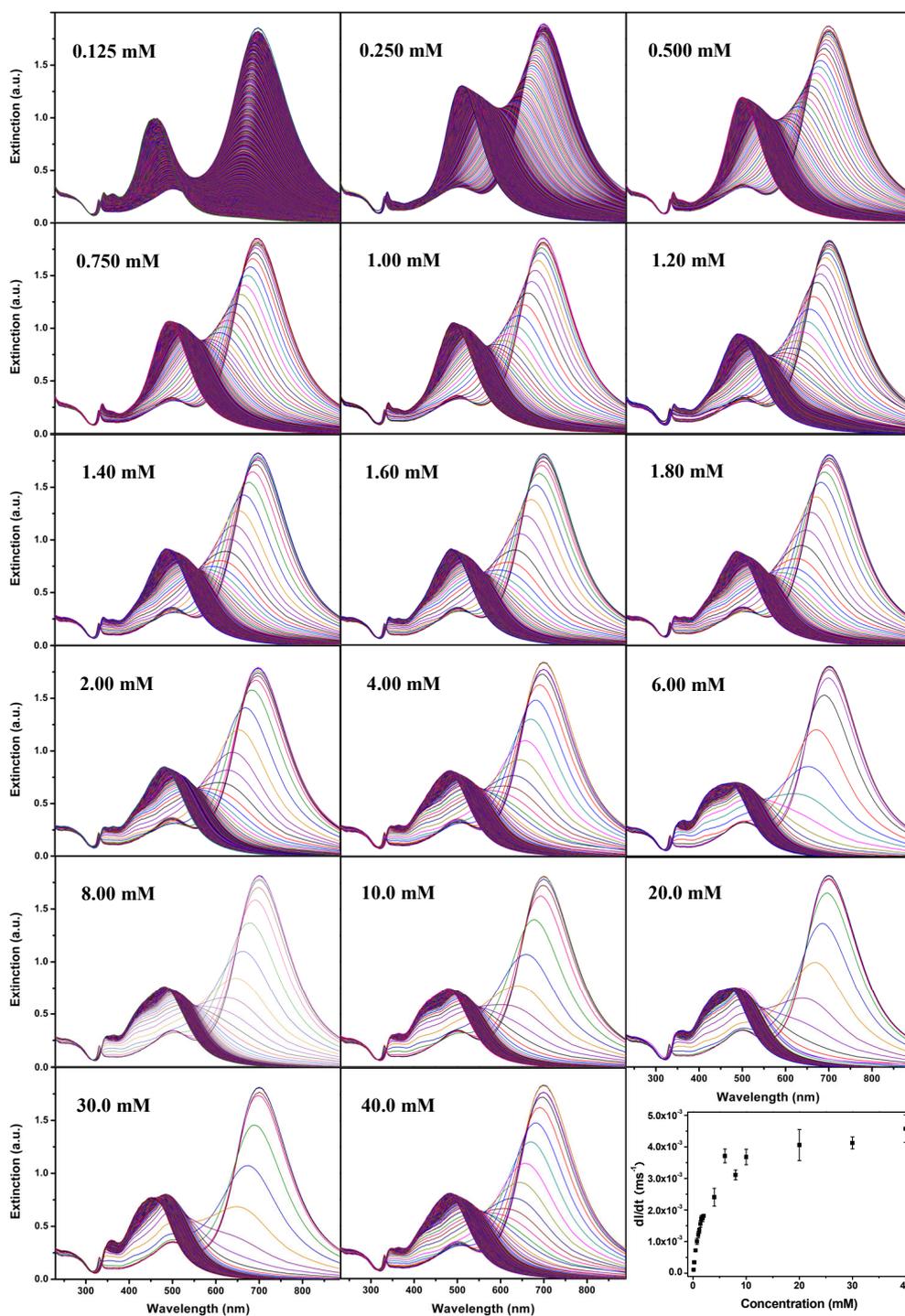


Fig. S3 Time-resolved extinction spectra of silver nanoplates etched by different concentration (0.125 ~ 40.0 mM) of bromide ions at 298 K. Lower right panel: plot of the etching rate (dl/dt) vs. concentration of the bromide ions at 298 K.

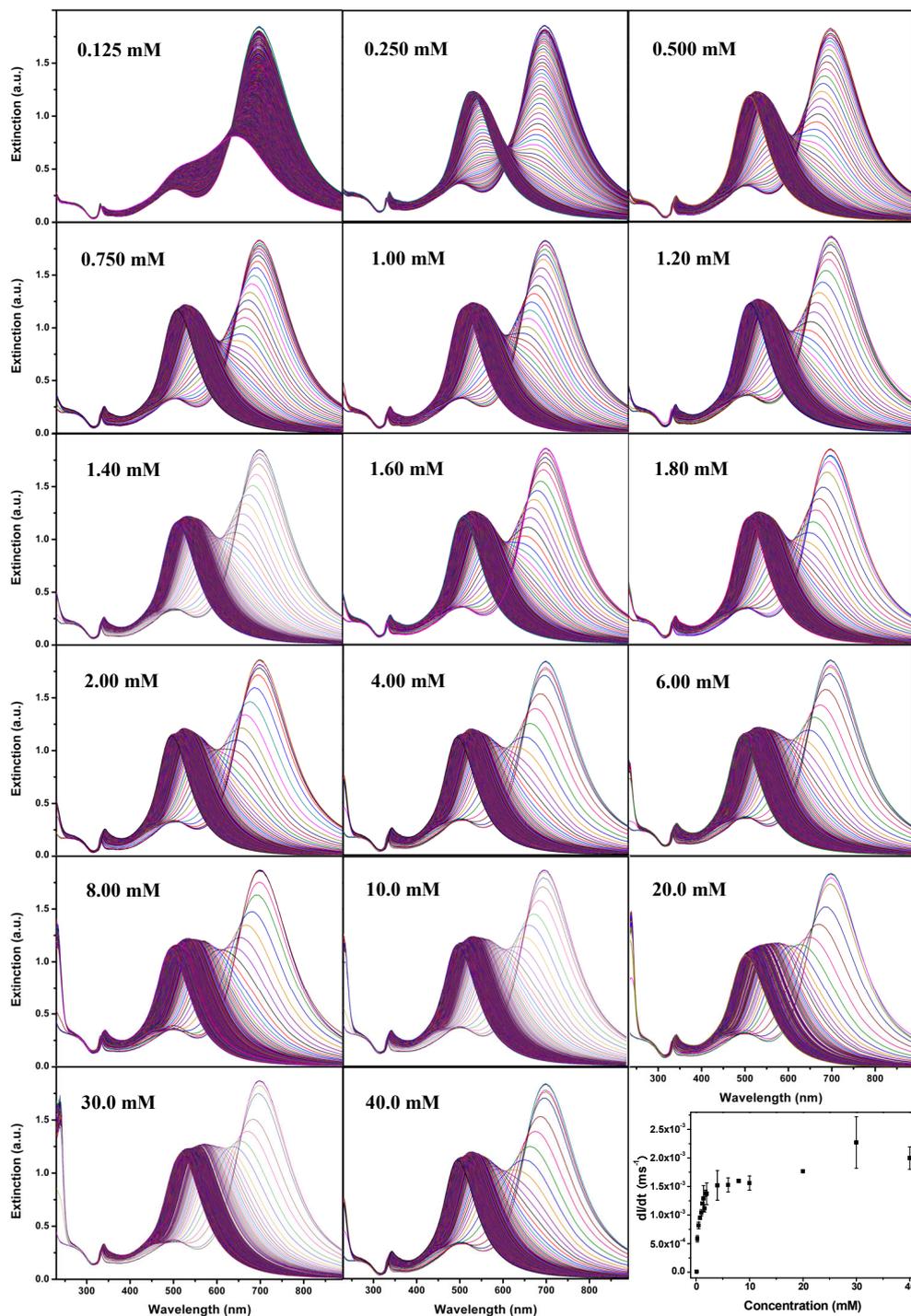


Fig. S4 Time-resolved extinction spectra of silver nanoplates etched by different concentration (0.125 ~ 40.0 mM) of iodide ions at 298 K. Lower right panel: plot of the etching rate (dI/dt) vs. concentration of the iodide ions at 298 K.

5. Time-resolved extinction spectra of silver nanoplates etched by different concentration of chloride, bromide and iodide ions at 273K.

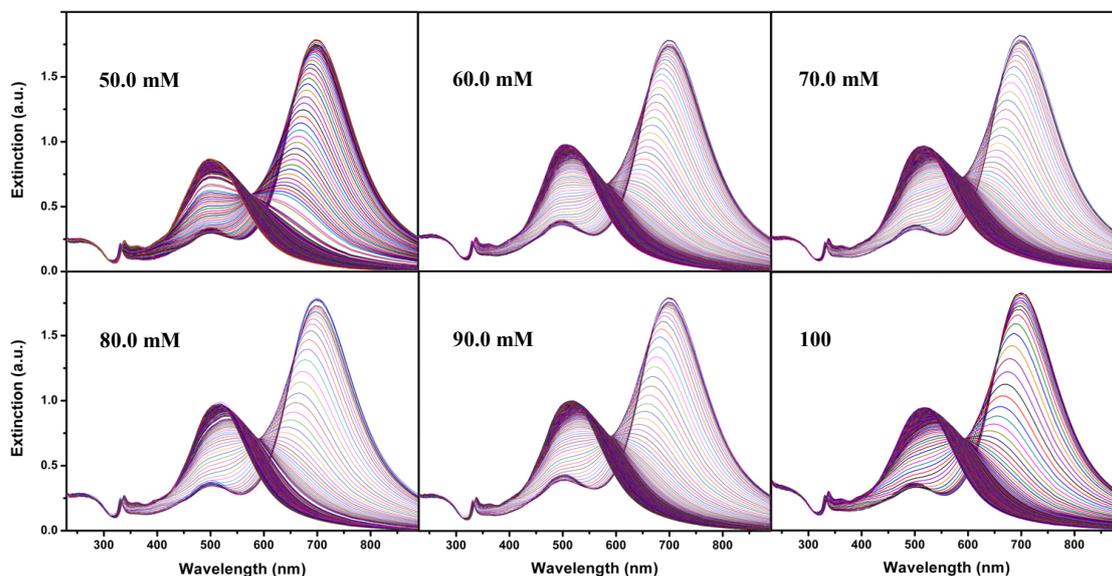


Fig. S5 Time-resolved extinction spectra of silver nanoplates etched by different concentration of chloride ion (50.0 ~ 100 mM) at 273K.

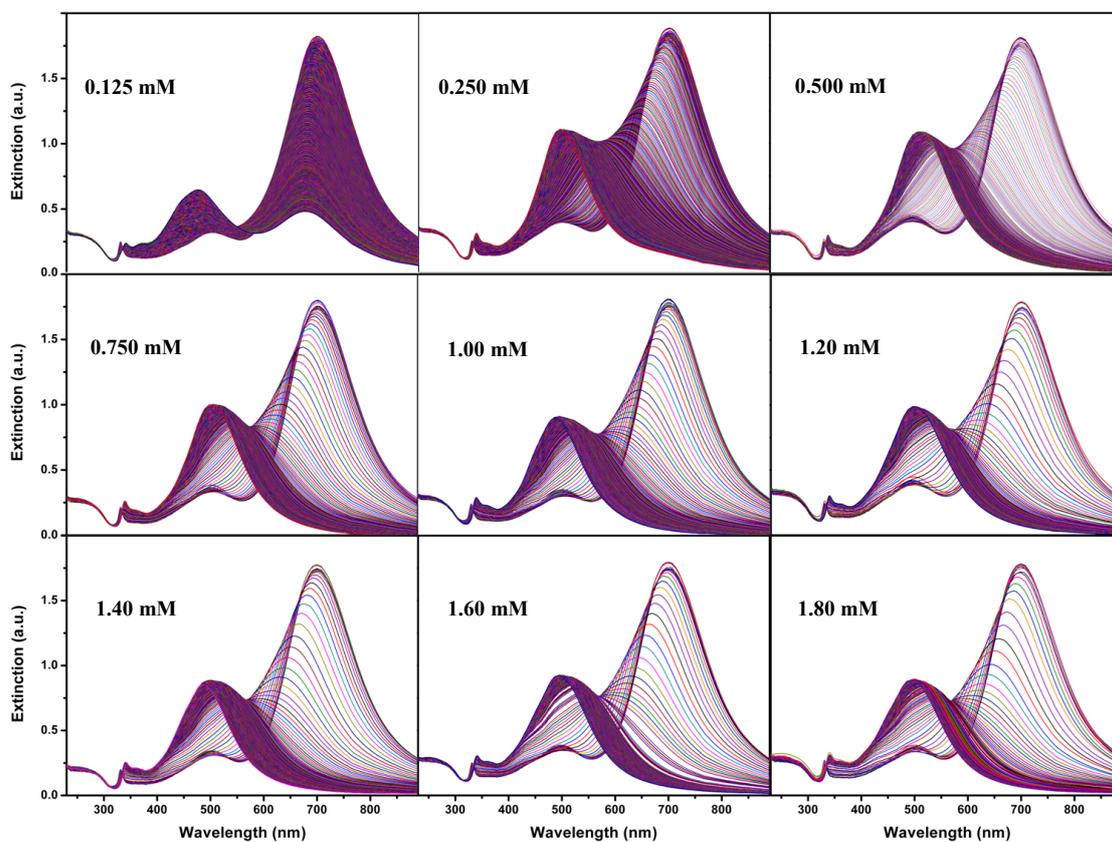


Fig. S6 Time-resolved extinction spectra of silver nanoplates etched by different concentration of bromide ions (0.125 ~ 1.80 mM) at 273 K.

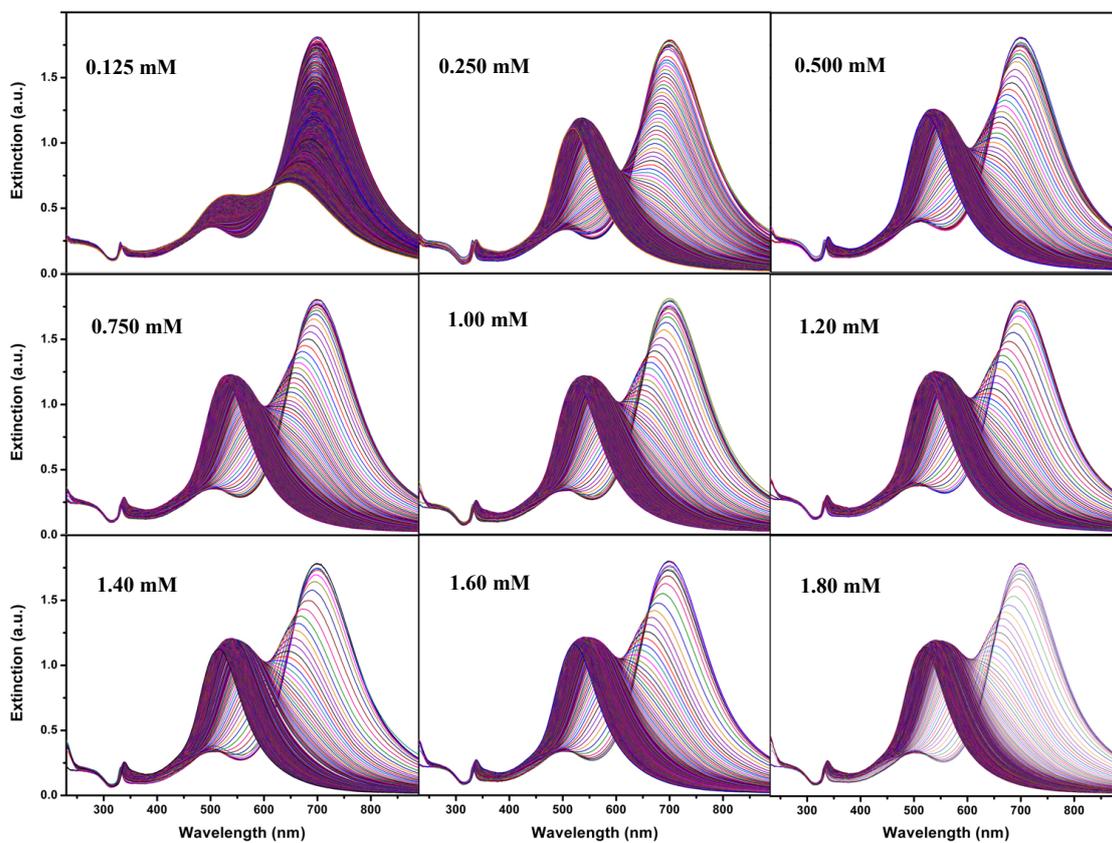


Fig. S7 Time-resolved extinction spectra of silver nanoplates etched by different concentration of iodide ions (0.125 ~ 1.80 mM).

6. Extinction spectra variation of silver nanoplates in the chloride ion reaction after deoxygenation and increasing oxygen.

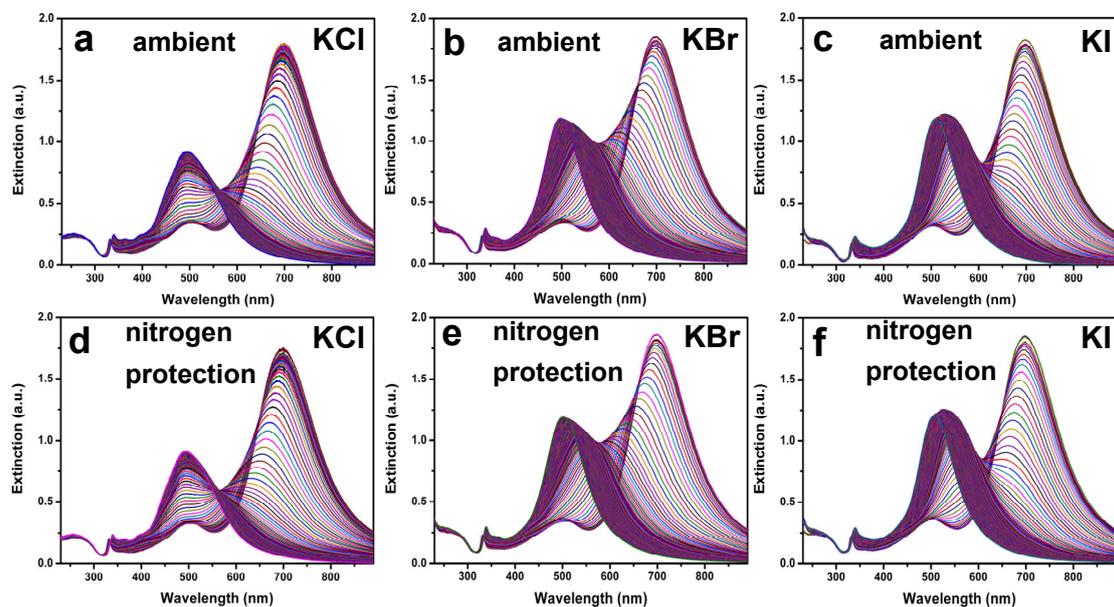


Fig. S8 Time-resolved extinction spectra of silver nanoplates etched by (a) chloride ions (50.0 mM), (b) bromide ions (0.50 mM) and (c) iodide ions (0.50 mM) under ambient condition, and (d), (e) and (f) corresponding time-resolved extinction spectra under full nitrogen protection condition.

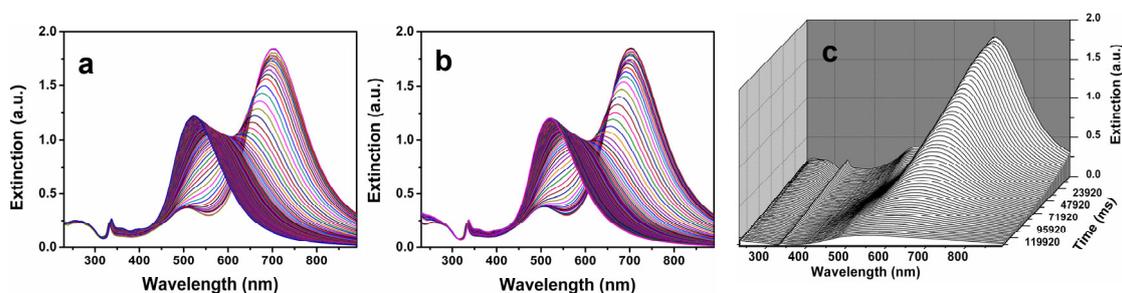


Fig. S9 Time-resolved extinction spectra of silver nanoplates etched by (a) chloride ions (50.0 mM), (b) mixtures of chloride ions and H₂O₂ (0.25%), and (c) H₂O₂ (0.25%).

To inspect whether the dissolved oxygen in the colloid solution assist the halide ion etching of the silver nanoplates, we obtained the time-resolved spectra of the etching process of all three types of halide ions under full nitrogen protection condition. Deoxygenating was implemented through a simple glove box by passing nitrogen. The reaction reagents were bubbled for twenty minutes by nitrogen after be put into

the glove box. Then the glove box was blow by nitrogen for thirty minutes before the halide ion etching reactions were performed. The time-resolved spectra recorded under full nitrogen protection were essentially identical with that under ambient condition without any protection for chloride, bromide and iodide ions (Fig. S8). The comparison of the spectra under two different conditions demonstrates that oxygen does not influence obviously the halide ion etching reaction.

Further, hydrogen peroxide mixing with the KCl solution was employed to observe the effect of the oxygen in the halide ion etching reaction. Fig. S9a the time-resolved extinction spectra of the silver nanoplates etched by the only chloride ions (50 mM, 20 μ L, Fig. S9a). The mixtures of chloride ions (50.0 mM) and H₂O₂ (0.25%) were used to test the role of oxygen in the halide ion etching reaction. Fig. S9b shows the time-resolved extinction spectra of the silver nanoplates obtained by the mixtures (20 μ L). It can be found that the evolution of the spectra in the both cases essentially identical, which implies the presence of the H₂O₂ does not bring obvious change in the etching reaction rate. The same experiments were repeated ten times in the different chloride ion concentrations and the effect of H₂O₂ on the halide ion etching reaction was almost unobserved in the recorded period. Fig. S9c presents the changes of the extinction spectra of the silver nanoplates after only H₂O₂ (0.25%, 20 μ L) was added, which indicated that the amount of the H₂O₂ in the mixtures (Cl⁻ and H₂O₂) was enough to oxidize the silver nanoplates. The results reveal that the influence of oxygen on the reaction rate is not obvious.

We believed that the oxygen might affect the etching rate in a certain extent. However it is difficult to determinate how serious of the oxygen in its effect. In the present study, all the halide ion etching experiments were performed under ambient condition without any protection. The role of chloride ion in the halide ion etching of silver nanoplates here might be different from that in the preparation process which has been discussed in Xia *et al.*'s works.⁸

7. The effect of fluoride ions on the silver nanoplates.

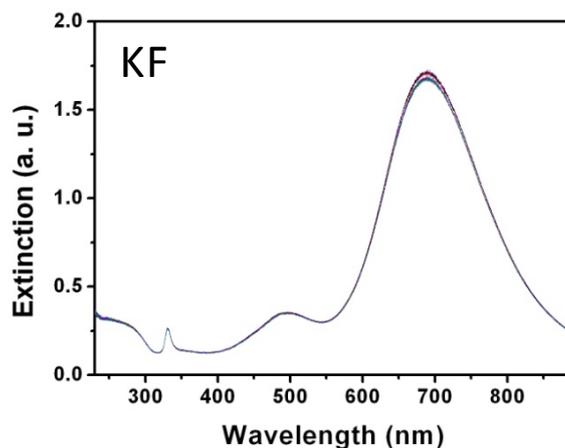


Fig. S10 Time-resolved extinction spectra of silver nanoplates involving fluoride ions (100 mM, 20 μ L) at 298 K. It contains 297 curves.

8. The effect of other inorganic ions on the silver nanoplates.

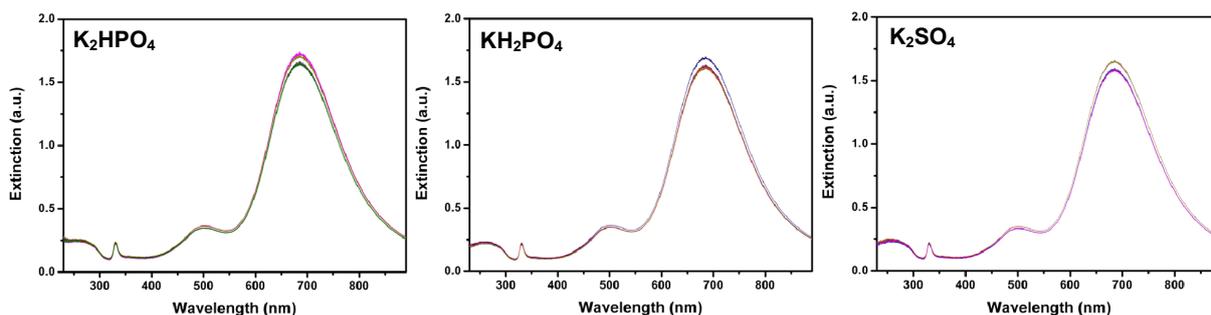


Fig. S11 Time-resolved extinction spectra of silver nanoplates involving K_2HPO_4 , KH_2PO_4 and K_2SO_4 (50.0 mM, 20 μ L) at 298 K. It contains 163, 165 and 241 curves respectively.

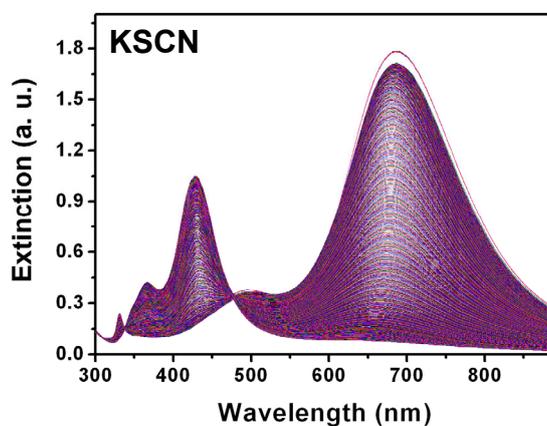


Fig. S12 Time-resolved extinction spectra of silver nanoplates involving thiocyanate ions (50.0 mM, 20 μ L) at 298 K.

The capture of time-resolved extinction spectra of silver colloid after addition of other inorganic ions is same as that of halide ions involved in the main text. The parameters of the time-resolved extinction spectra were also same, except for the interval changing to 500 ms.

References

- 1 R. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901–1903.
- 2 R. Jin, Y. C. Cao, E. Hao, G. S. Métraux, G. C. Schatz and C. A. Mirkin, *Nature*, 2003, **425**, 487–490.
- 3 L. J. Sherry, R. Jin, C. A. Mirkin, G. C. Schatz and R. P. Van Duyne, *Nano Lett.*, 2006, **6**, 2060–2065.
- 4 E. Hao, G. C. Schatz and J. T. Hupp, *J. Fluoresc.*, 2004, **14**, 331–341.
- 5 K. L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668–677.
- 6 A. Brioude, and M. P. Pileni, *J. Phys. Chem. B*, 2005, **109**, 23371–23377.
- 7 E. Hao, K. L. Kelly, J. T. Hupp and G. C. Schatz, *J. Am. Chem. Soc.*, 2002, **124**, 15182–15183.
- 8 B. Wiley, T. Herricks, Y. Sun and Y. Xia, *Nano Lett.*, 2004, **4**, 1733–1739.