Supplementary Materials

Understanding the Surface Oxidation of Ag Nanocrystals Under Different Environmental Conditions

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Received: 3 March 2026; Revised: 17 March 2026; Accepted: 20 March 2026; Published: 23 March 2026

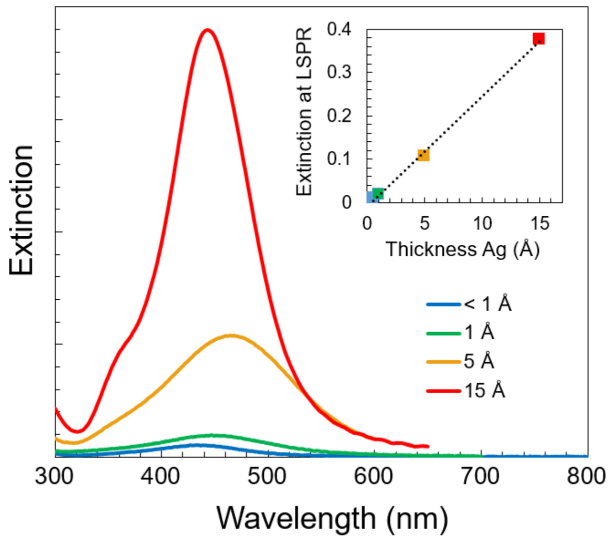
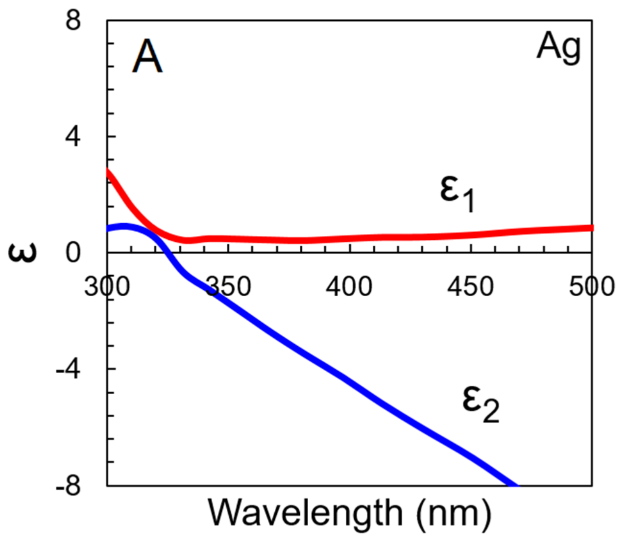


Figure S1. Extinction spectra of Ag nanocrystals derived from Ag films with effective thicknesses of <1, 1, 5, and 15 Å. The inset shows the LSPR peak intensity as a function of Ag film thickness, revealing a linear relationship.



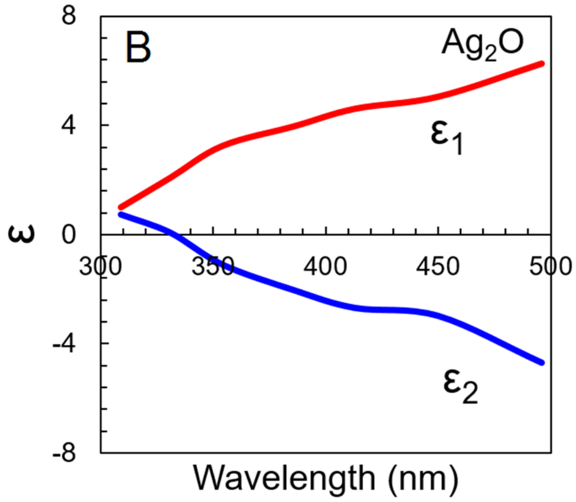


Figure S2. The dielectric constants of (**A**) Ag and (**B**) Ag_2O used for the DDA simulation. The dielectric functions (ε_1 and ε_2) of Ag and Ag_2O were obtained from literature reports [1,2] and used to generate the plots.

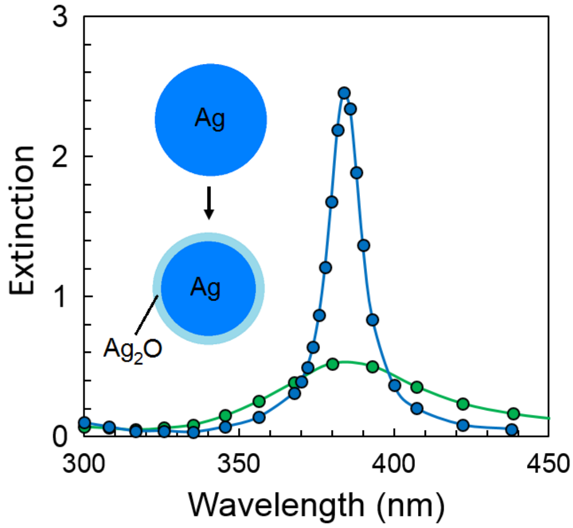


Figure S3. DDA simulation of the extinction spectra of a 4-nm Ag nanocrystal before oxidation (blue) and after formation of a 0.25-nm shell of Ag_2O (green). These results suggest that the high sensitivity of LSPR to surface oxidation is not unique to the hemispherical nanoparticles supported on a substrate. The simulation was carried out with a surrounding dielectric constant equal to that of water (ε_m = 1.78).

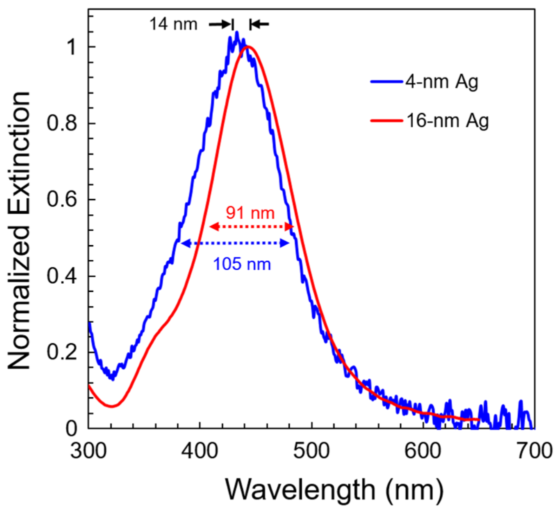


Figure S4. Normalized extinction spectra of the 4- and 16-nm Ag nanocrystals, showing that the FWHM of the LSPR was broader for the 4-nm sample.

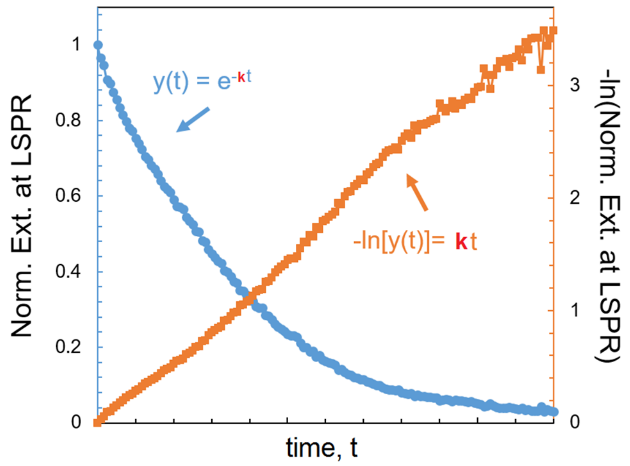


Figure S5. Plot of the LSPR peak intensity as a function of time (blue line), which is fitted with an exponential decay function with a rate constant of *k*. The rate constant can also be obtained from the slope of the linear plot of –ln(y) versus time (orange line).

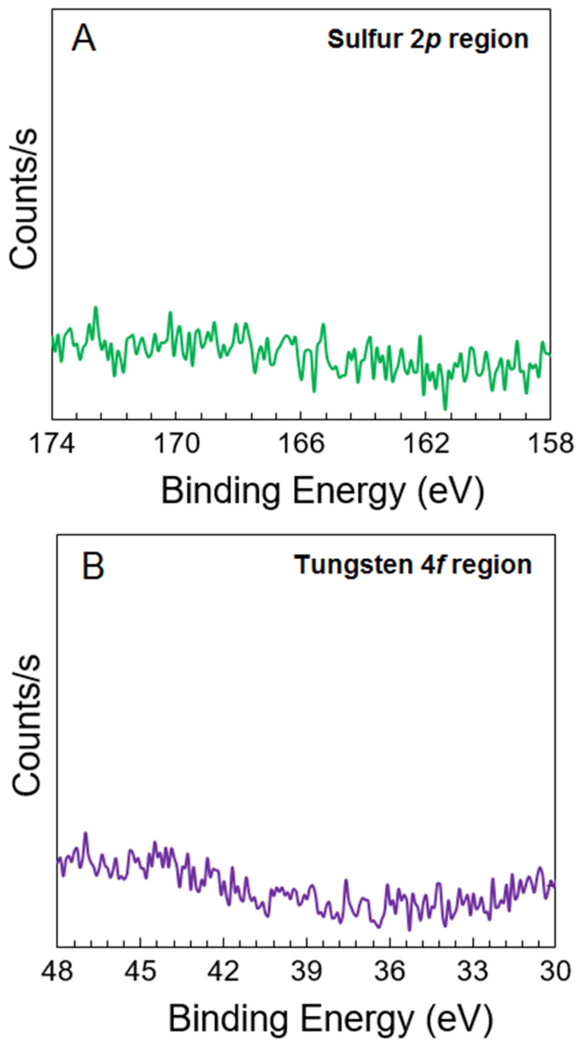


Figure S6. XPS spectra of the (**A**) sulfur 2p region and (**B**) tungsten 4f region measured from a typical Ag sample (derived from the 0.4-nm film), confirming the absence of sulfur- and tungsten-based contaminants.

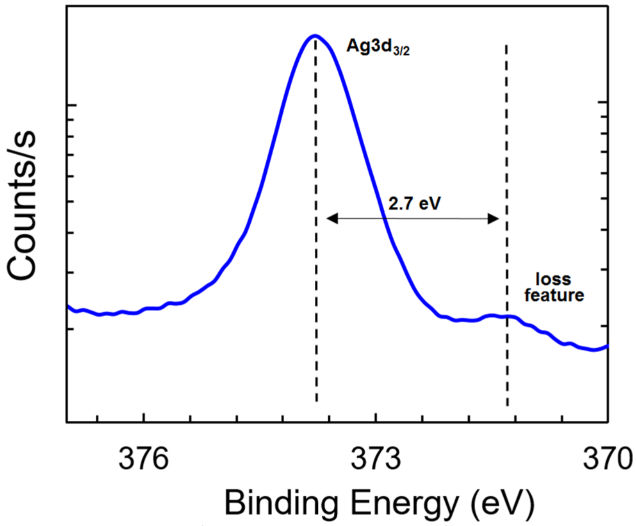


Figure S7. XPS spectrum of the Ag $3d_{3/2}$ region and associated loss feature, showing an energy separation of 2.7 eV.

References

1. Johnson, P.B.; Christy, R.W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, *6*, 4370–4379.
2. Gao, X.Y.; Wang, S.Y.; Li, J.; Zheng, Y.X.; Zhang, R.J.; Zhou, P.; Yang, Y.M.; Chen, L.Y. Study of Structure and Optical Properties of Silver Oxide Films by Ellipsometry, XRD and XPS Methods. *Thin Solid Films* **2004**, *455–456*, 438–442.