**Supporting Information**

# Controllable Tuning Plasmonic Coupling with Nanoscale Oxidation

*Tao Ding, Daniel Sigle, Liwu Zhang, Jan Mertens, Bart de Nijs and Jeremy Baumberg**

Nanophotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK

* Corresponding author email: jjb12@cam.ac.uk

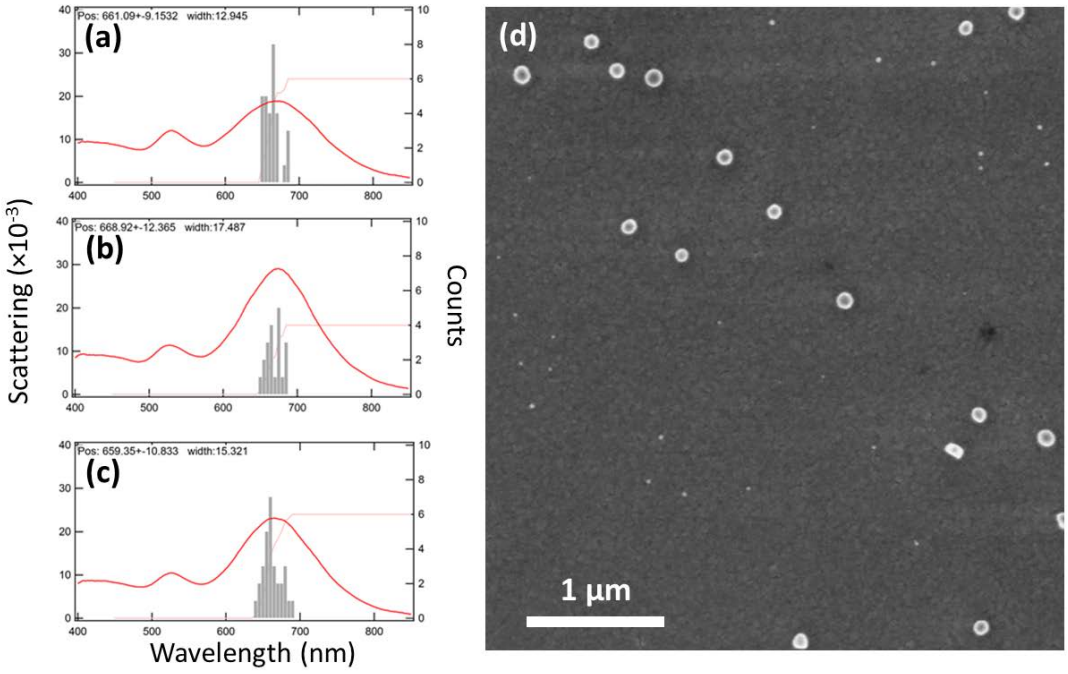


Figure S1. Scattering spectra of Au NPs on Al mirror with different thickness of Al films. (a) 20 nm, (b) 50 nm, (c) 100 nm. (d) is the typical SEM image of Au NPs on Al mirror. The spectra were averaged over ~20 Au NPs and the grey bars show the peak distribution. The light red line shows the total particle count as a function of wavelength.

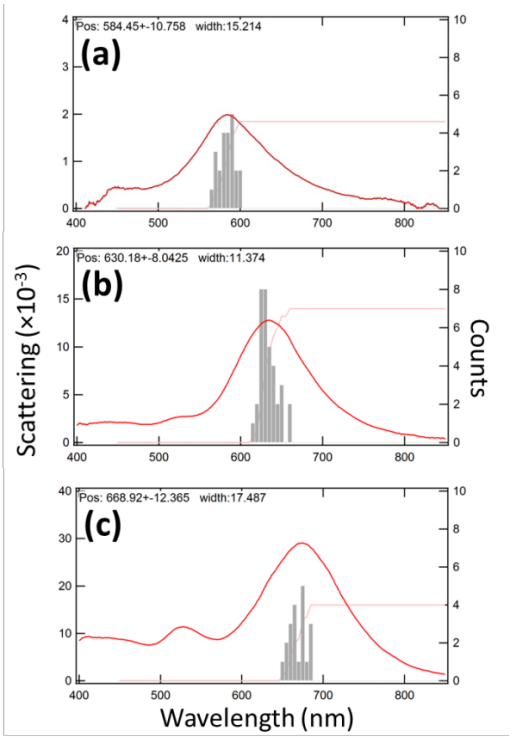


Figure S2. Scattering spectra of Au NPs on Al mirror with different sizes of Au NPs. (a) 60 nm, (b) 80 nm, (c) 100 nm. The spectra were averaged over ~20 Au NPs and the grey bars show the peak distribution. The light red line shows the total particle count as a function of wavelength.

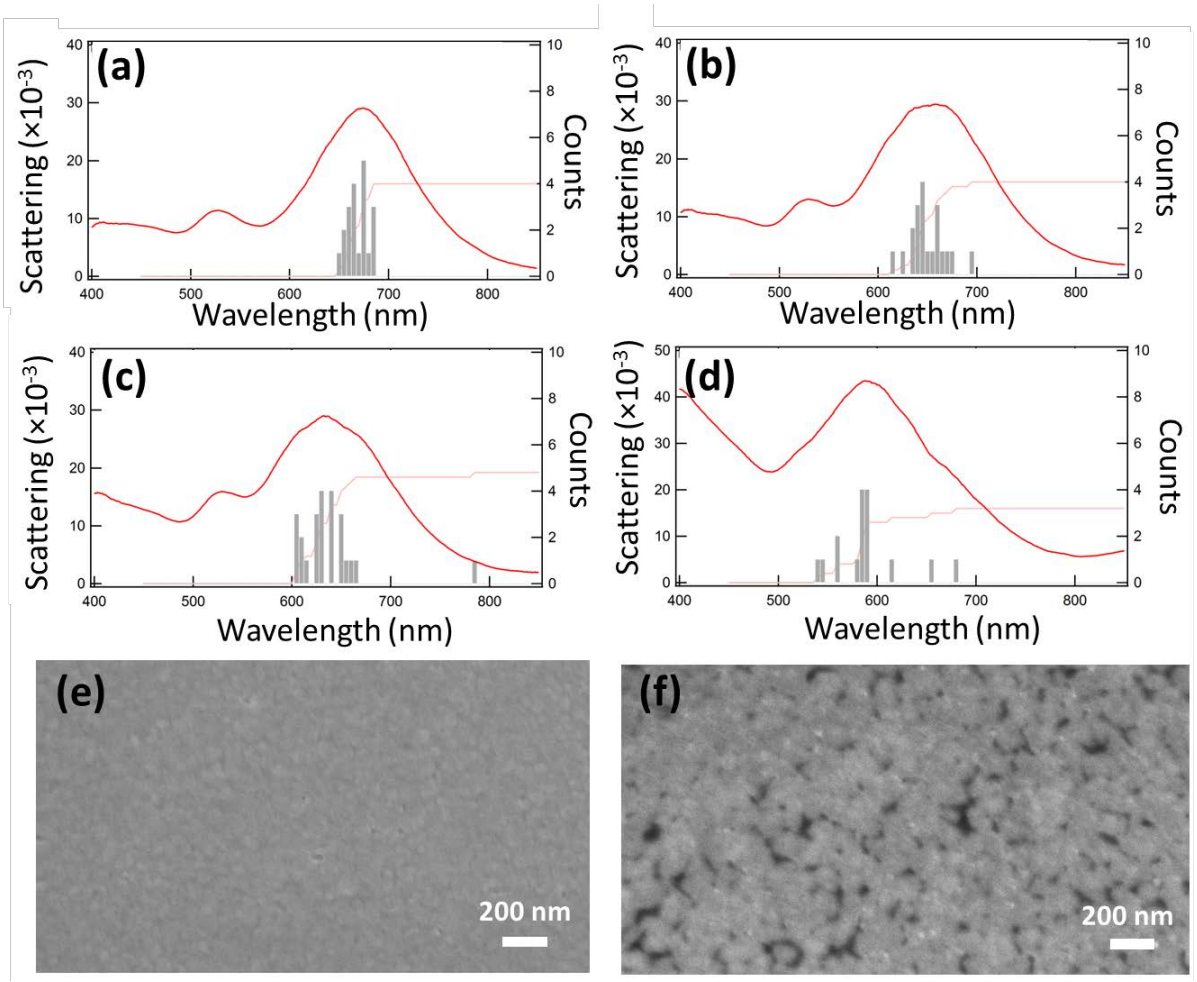


Figure S3. Scattering spectra of Au NPs on Al mirror with different annealing temperatures. (a) room temperature, (b) 450 $^{0}$C, (c) 500 $^{0}$C, (d) 550 $^{0}$C. The spectra were averaged over ~20 Au NPs and the grey bars show the peak distribution. The light red line shows the total particle count as a function of wavelength. (e) and (f) are the SEM images of Al films before and after annealing (550 $^{0}$C) showing roughened surface due to high temperature oxidation.

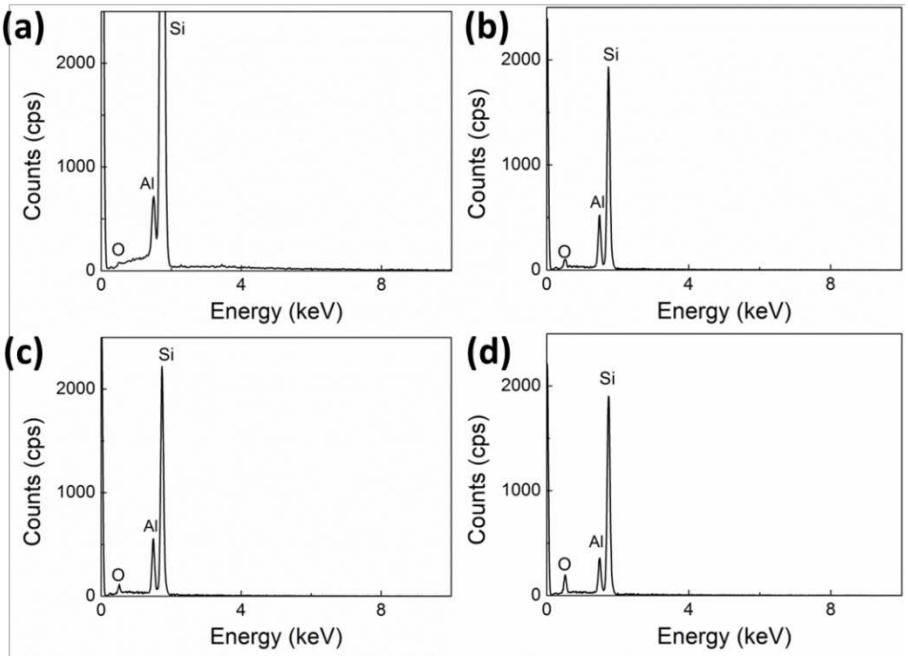


Figure S4. EDX elemental analysis of the Al films annealed at different temperatures. (a) Room temperature, (b) 450 $^{0}$C, (c) 500 $^{0}$C, (d) 550 $^{0}$C.

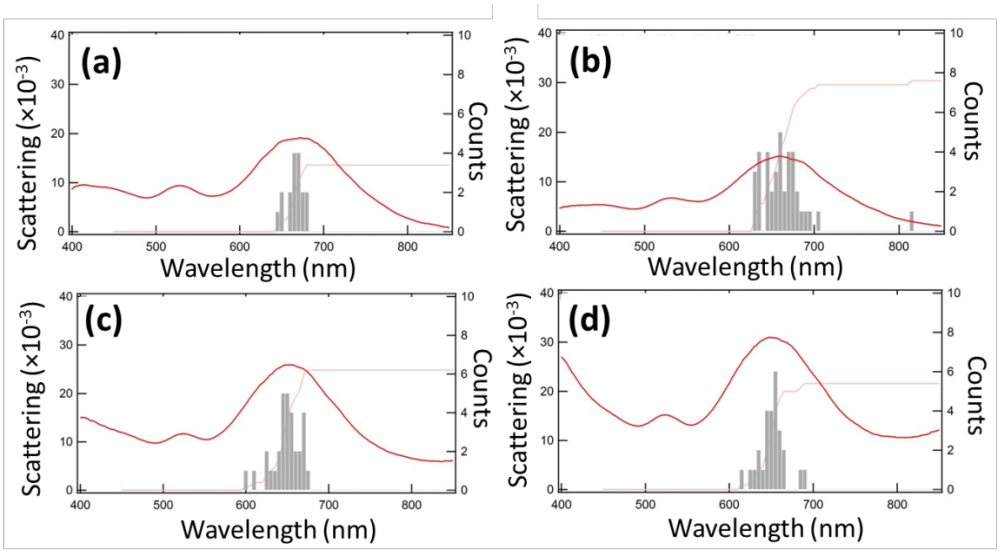


Figure S5. Scattering spectra of Au NPs on Al mirrors treated with different duration of oxygen plasma, (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min. The spectra were averaged over ~20 Au NPs and the grey bars show the peak distribution. The light red line shows the total particle count as a function of wavelength.

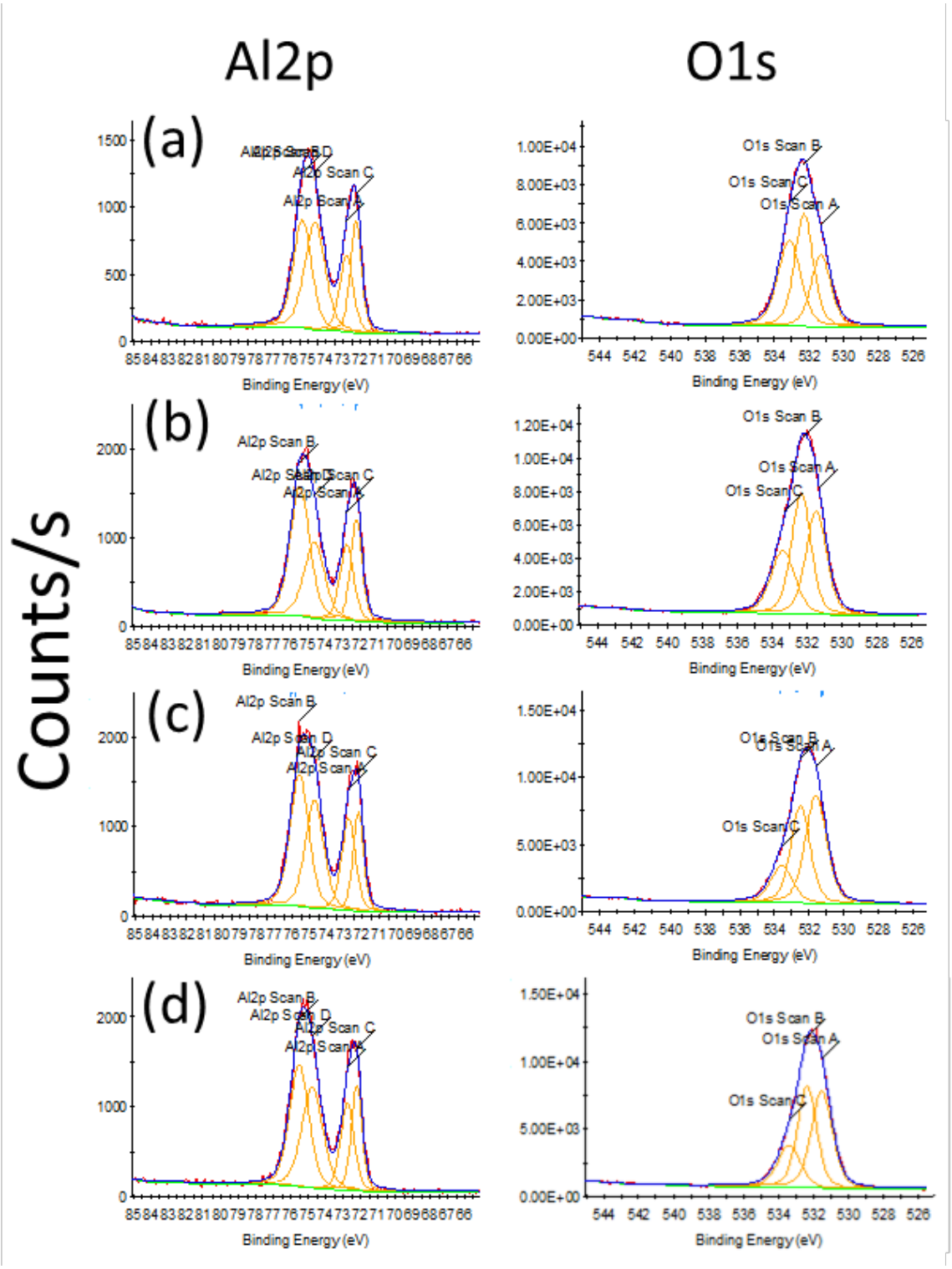


Figure S6: XPS of Al films before oxygen plasma treatment measured at different depths, (a) surface (b) 0.5 nm (c) 1 nm (d) 2 nm.

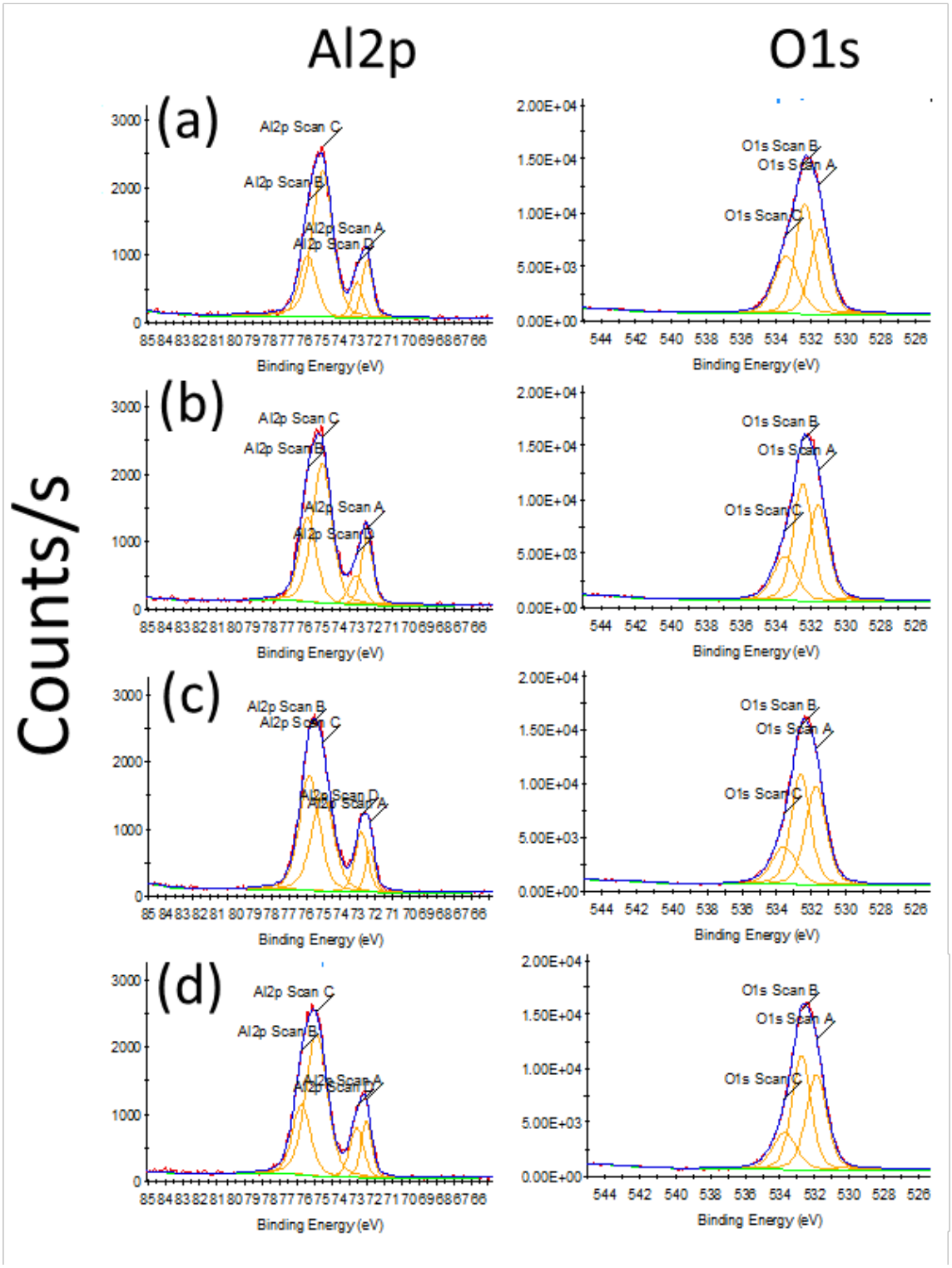


Figure S7: XPS of Al films (oxygen plasma 5 mins) measured at different depths, (a) surface (b) 1.5 nm (c) 2.5 nm (d) 3.5 nm.

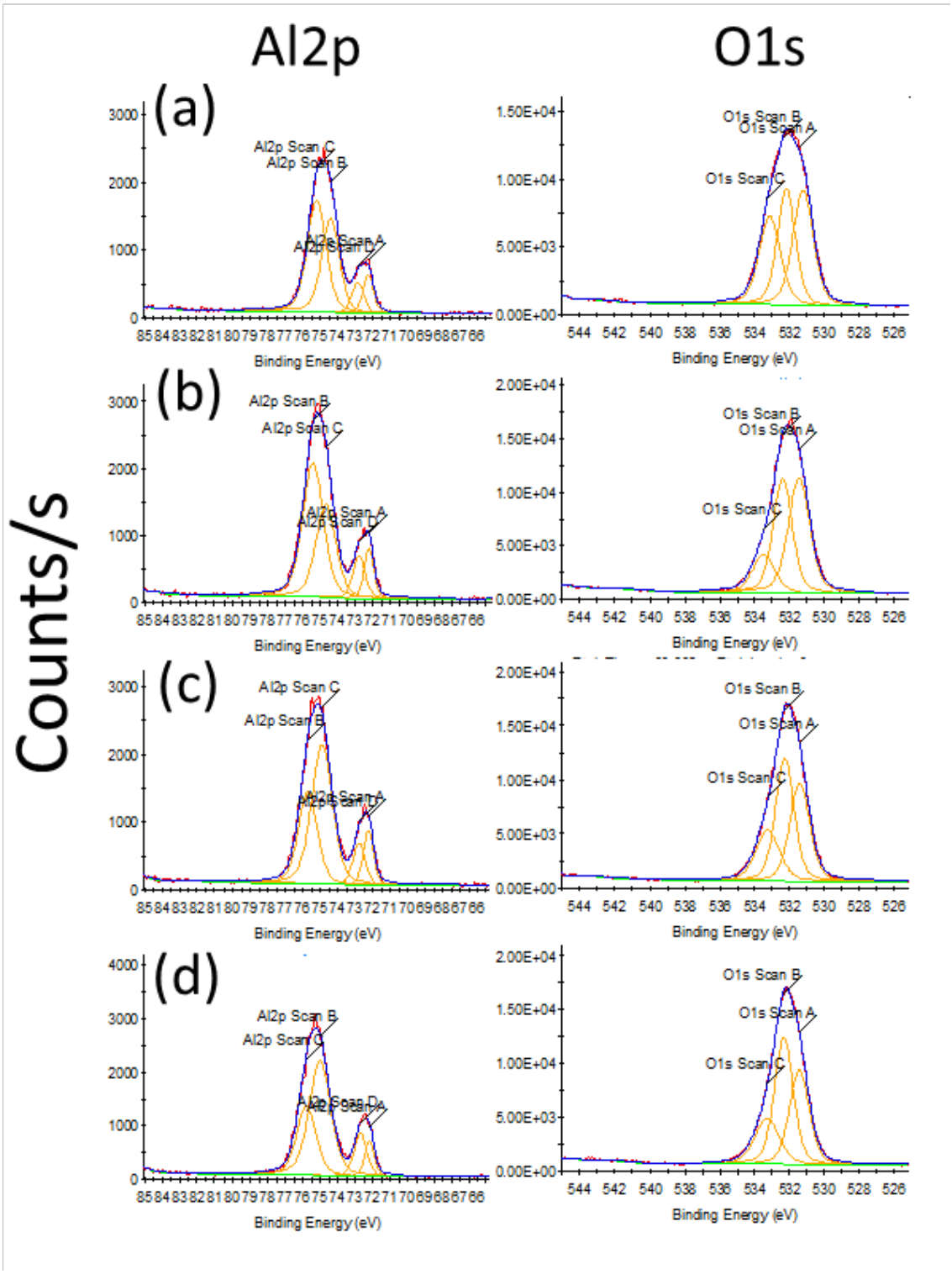


Figure S8: XPS of Al films (oxygen plasma 10 mins) measured at different depths, (a) surface (b) 1.5 nm (c) 2.5 nm (d) 3.5 nm.

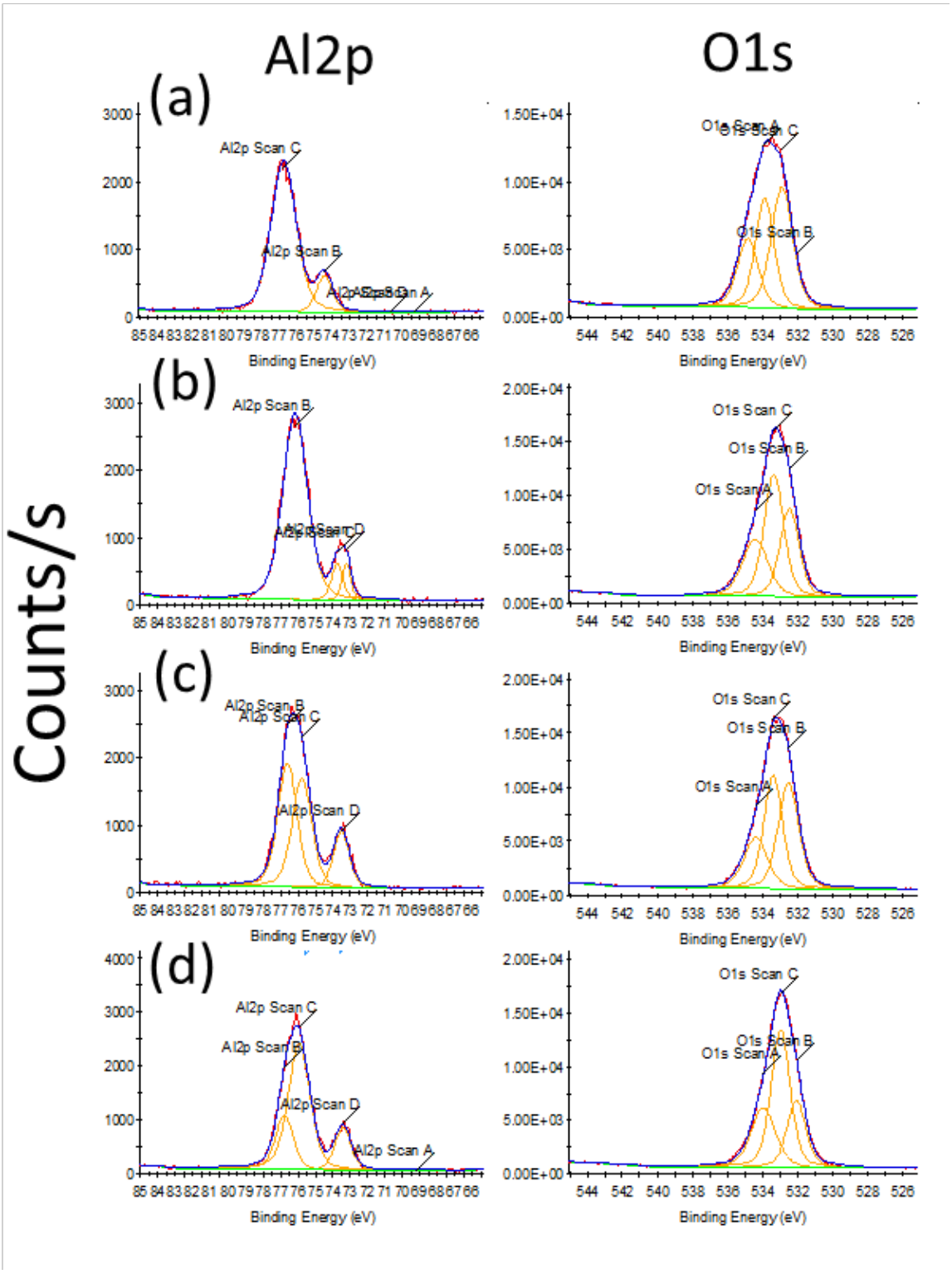


Figure S9: XPS of Al films (oxygen plasma 20 mins) measured at different depths, (a) surface (b) 1.5 nm (c) 2.5 nm (d) 3.5 nm.

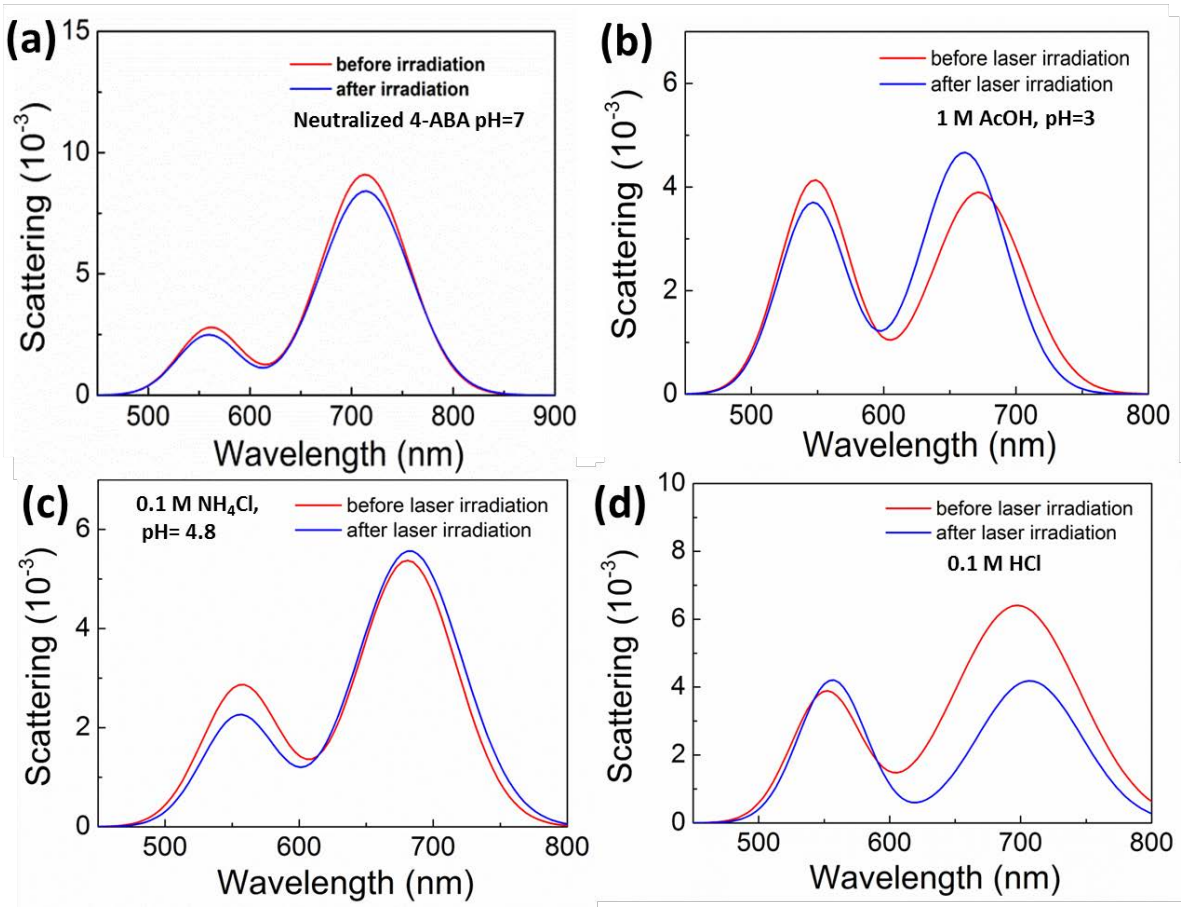


Figure S10. Scattering spectra of Au NPs on Al mirror, immersed in different etchants before and after laser irradiation (5 mW) for 15 min. (a) Neutralized 4-ABA solution, (b) AcOH solution, (c) $NH_4Cl$ solution, (d) HCl solution. Spectra were smoothed and fit to Gaussian resonances.

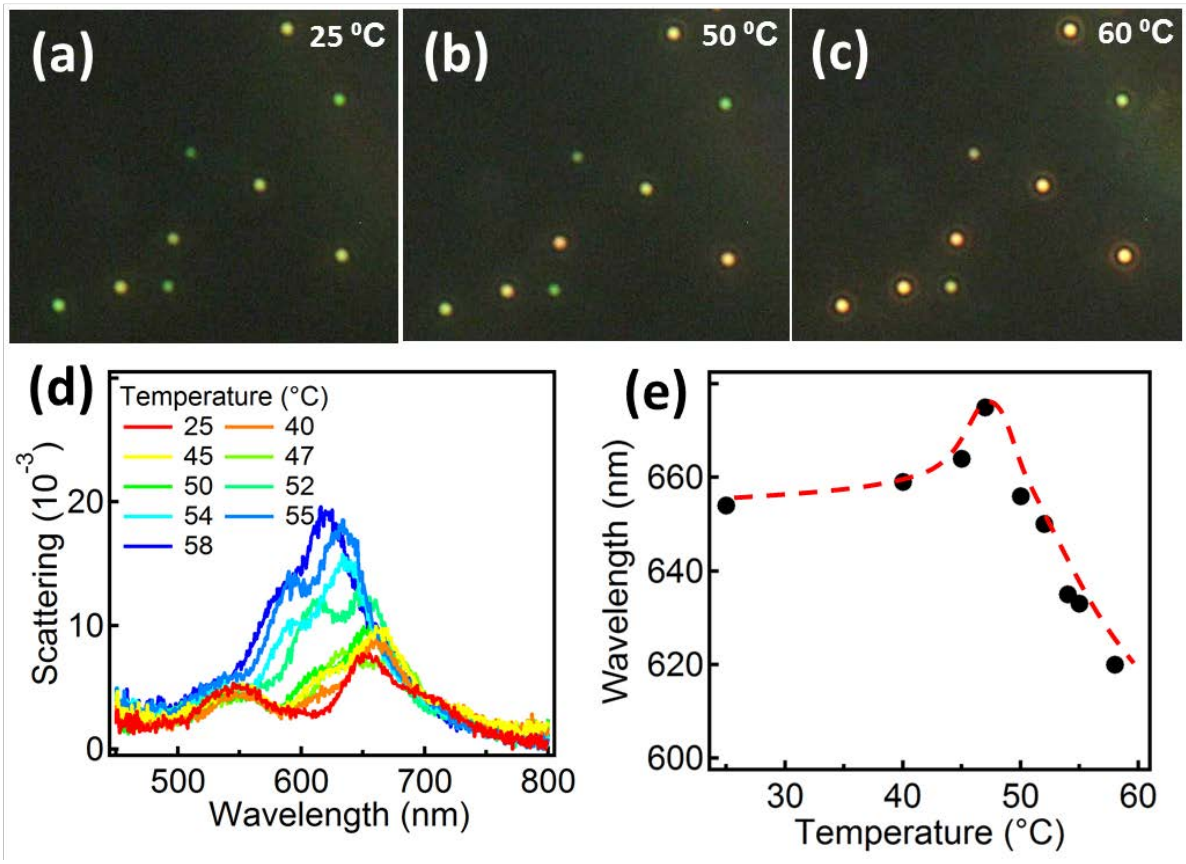


Figure S11. (a-c) Dark field images of Au NPo(Al)M in HCl (1 wt%) solution at different temperatures. (d) Scattering spectra of the same Au NPs (in HCl solution) at different temperatures with (e) extracted tuning of longitudinal plasmon mode vs temperature.

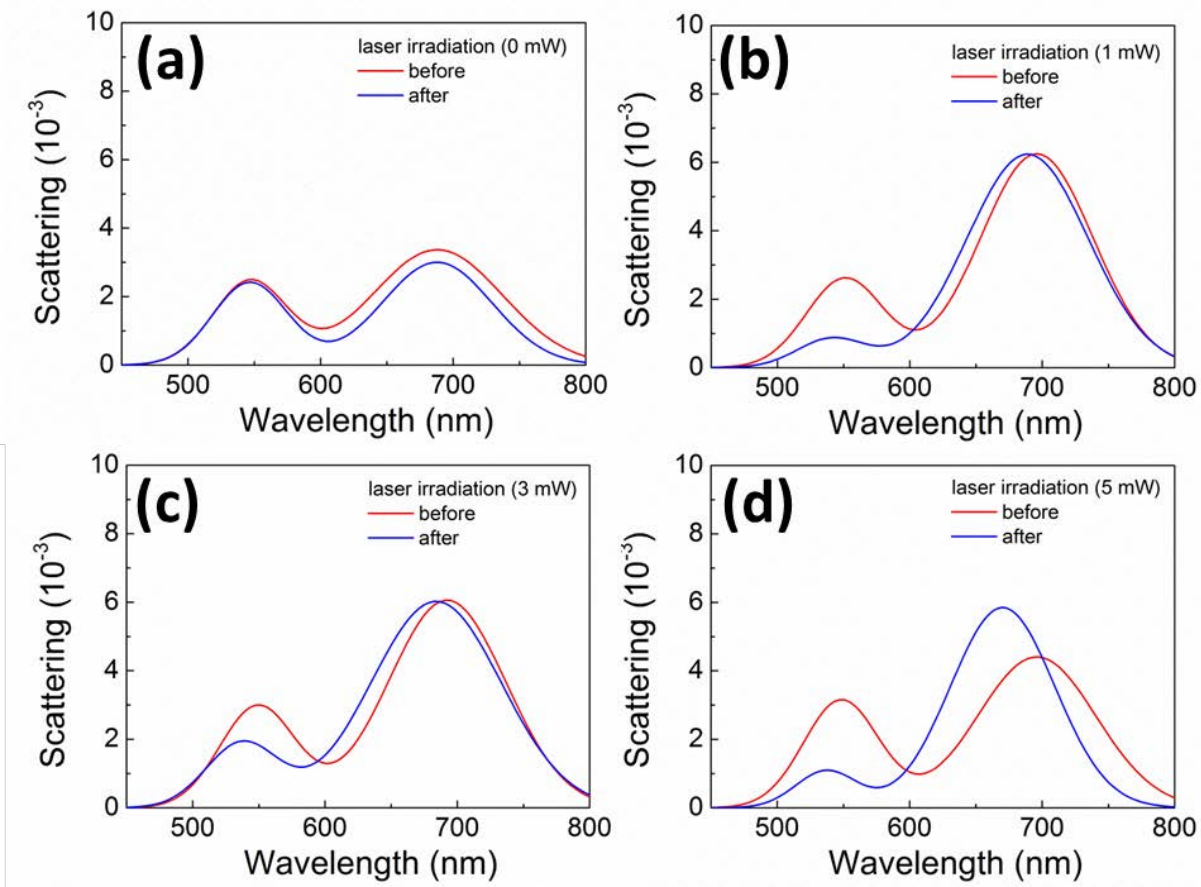


Figure S12. Scattering spectra of Au NP on Al mirror immersed in 4-ABA solution, irradiated with laser powers of (a) 0 mW, (b) 1mW, (c) 3 mW, and (d) 5 mW. Spectra were smoothed and fit to Gaussian resonances.

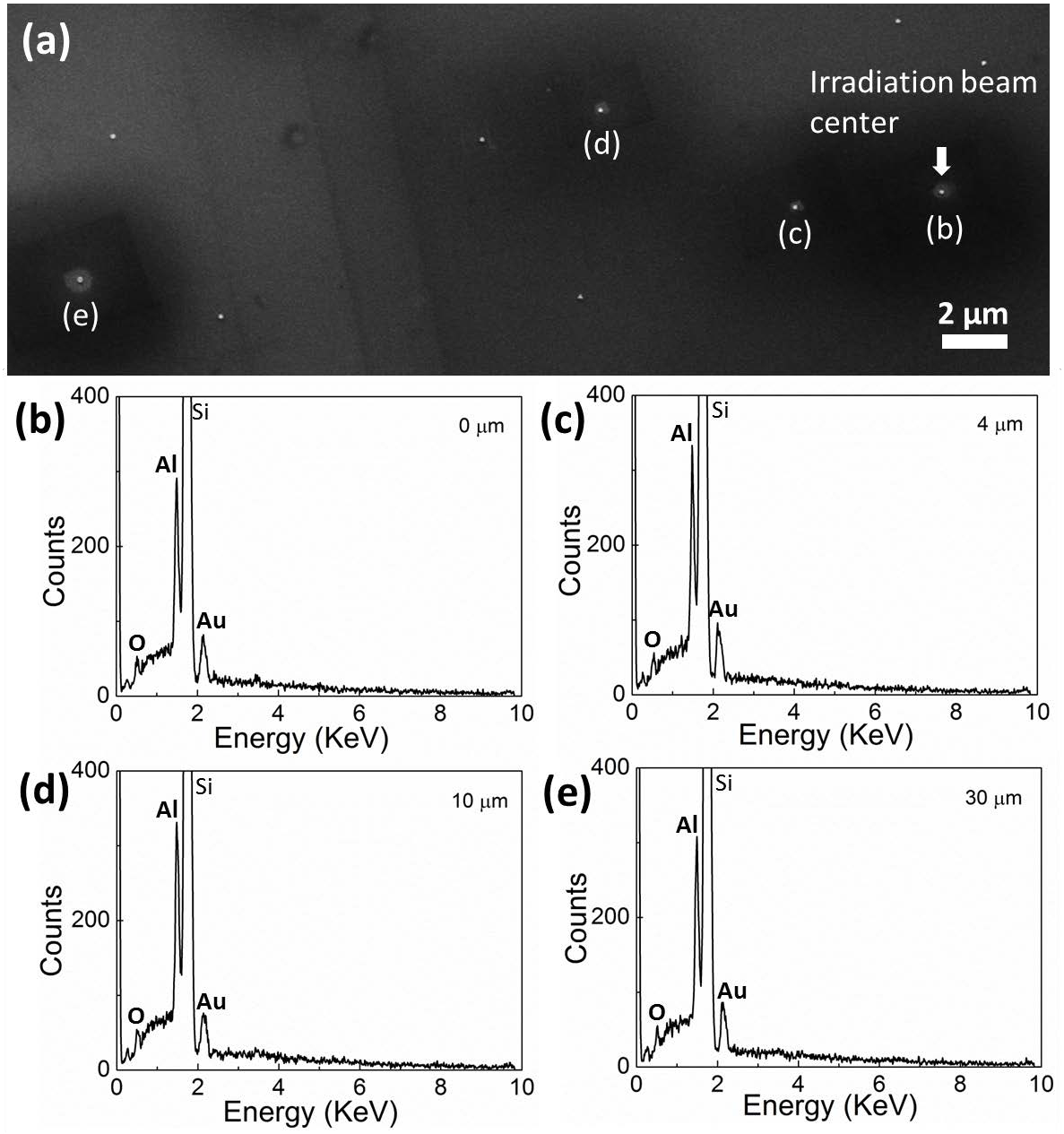


Figure S13. EDX analysis of the compositions at different locations away from laser beam center after irradiation. (a) SEM image of four typical points labelled with (b-e) and their EDX spectra, respectively in (b-e).

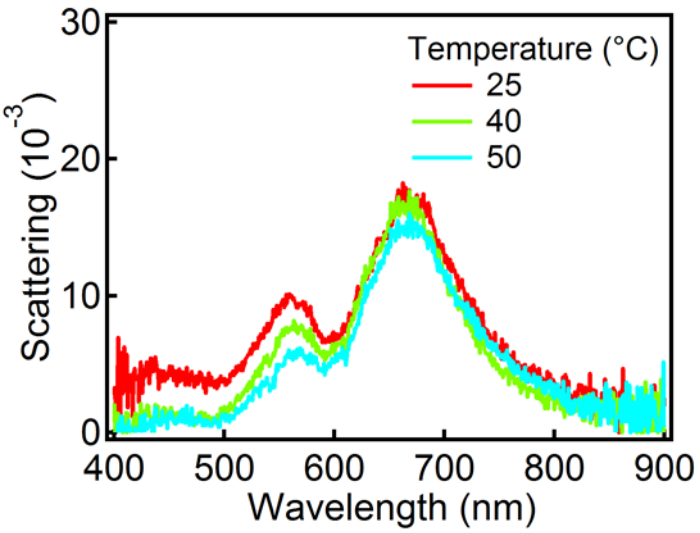


Figure S14. Scattering spectra of Au NPoM in ABA solution (0.1 M) at different temperatures. No blue shift is observed, which excludes plasmon-induced thermal oxidation.

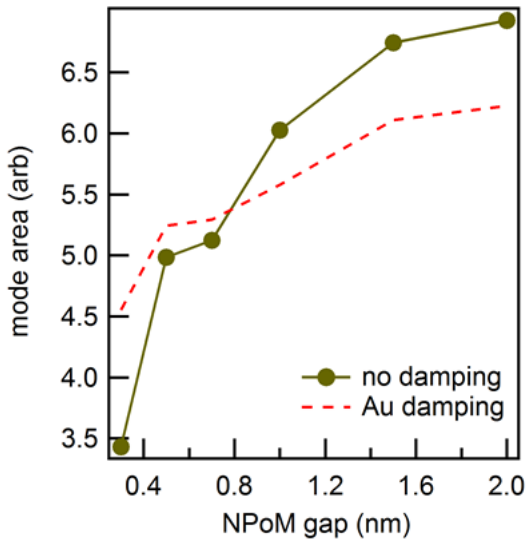


Figure S15. Simulations of scattering strength of the NPoM longitudinal mode as a function of the gap separation. Boundary Element Methods are used, which are fully converged, with 80nm diameter Au NPs on a uniform spacer layer of refractive index 1.8. Solid curve is when absorption of Au is removed, which dashed curve shows it included.