Supporting Information

Repeated Appearance and Disappearance of Localized Surface Plasmon Resonance in 1.2 nm Gold Clusters Induced by Adsorption and Desorption of Hydrogen Atoms

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1. Experimental

1.1. Synthesis

All chemicals were commercially available and used without further purification. Au:PVP clusters were prepared according to the reported protocol. PVP with an average molecular weight of ca. 40 kDa (555.5 mg, 100 equivalent moles of monomer unit to Au) was added to an aqueous solution of $HAuCl_4$ (1 mM, 50 mL), and the mixture was stirred for 30 min in an ice bath at 273 K. A cooled aqueous solution of $NaBH_4$ (0.1 M, 5 mL) was rapidly injected to the mixture while it was vigorously stirred. The reaction mixture was then further stirred for 1 h at 273 K. The resulting hydrosol of Au:PVP clusters was deionized with water using centrifugal ultrafiltration concentrators (Vivascience, Vivaspin20 (MWCO = 10 kDa)). The obtained clusters were lyophilized for storage with a lyophilizer (EYELA, FDU-2200).

1.2. Optical spectroscopy

The temporal evolution of the UV-vis absorption spectra of the Au:PVP cluster hydrosol was recorded with a spectrophotometer (Agilent Technologies, Agilent 8453) and a variable flow peristaltic pump (VWR, Variable Flow MINI-PUMP). All the measurements were performed with flowing solution that was cycled between a glass measurement cell and a vessel filled with the Au:PVP cluster hydrosol in an ice bath at273 K.

1.3. Transmission electron microscopy (TEM)

TEM images were recorded with an electron microscope (Hitachi, HF-2000) operating at 200 kV. Typically, images were taken at 200,000 magnification.

1.4. X-ray diffraction pattern (XRD)

XRD measurements were performed on a diffractometer (Rigaku, SmartLab 3) with Cu Kα radiation.

1.5. X-ray absorption fine structure (XAFS)

EXAFS spectra at Au L_3-edges were measured at room temperature in transmission mode at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute. Data analysis was carried out using the program REX2000 (Rigaku Co.).

2. Results

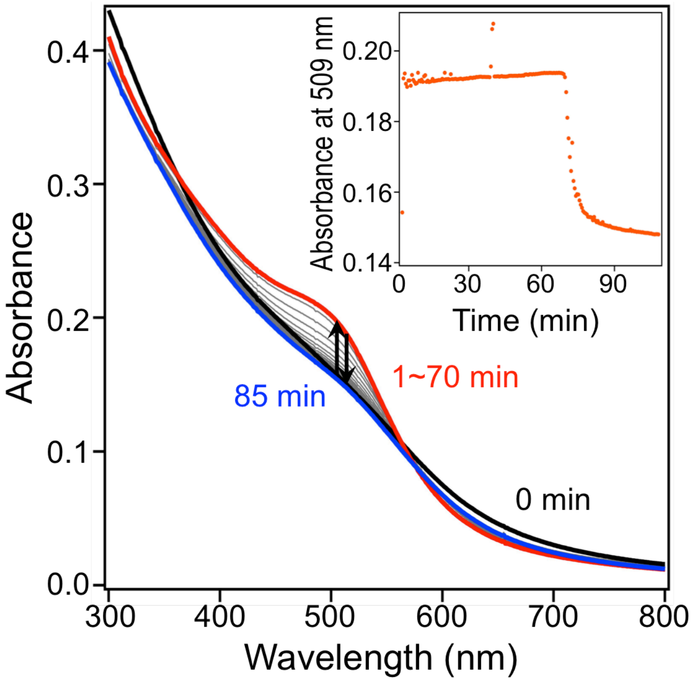

Figure S1. Changes in absorption spectra over time of the preformed Au:PVP clusters with an average diameter of 1.2 nm after the addition of $NaBH_4$. Inset shows the LSPR absorbance with time.

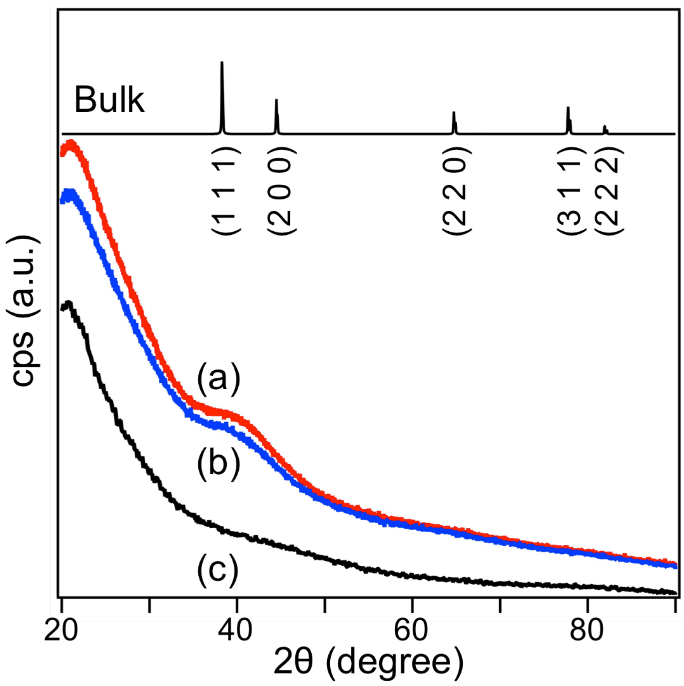

Figure S2. XRD patterns of Au:PVP before (a) and after (b) the reaction with $NaBH_4$ and of PVP (c).

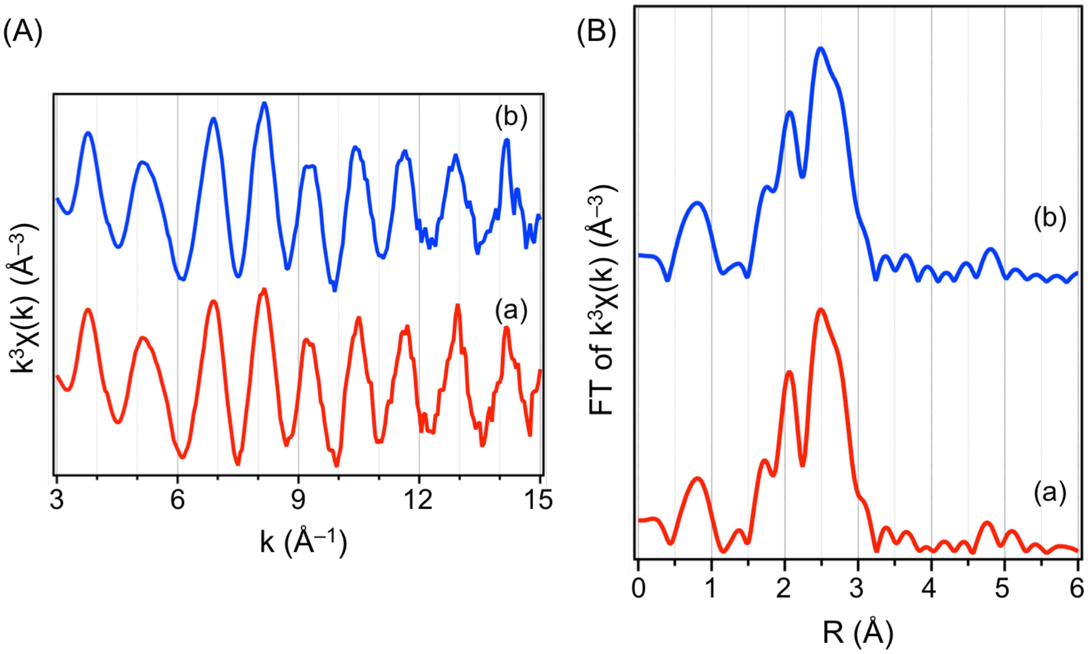

Figure S3. Au L_3-edge EXAFS oscillations (A) and Fourier transformed spectra (B) of Au:PVP before (a) and after (b) the reaction with $NaBH_4$.

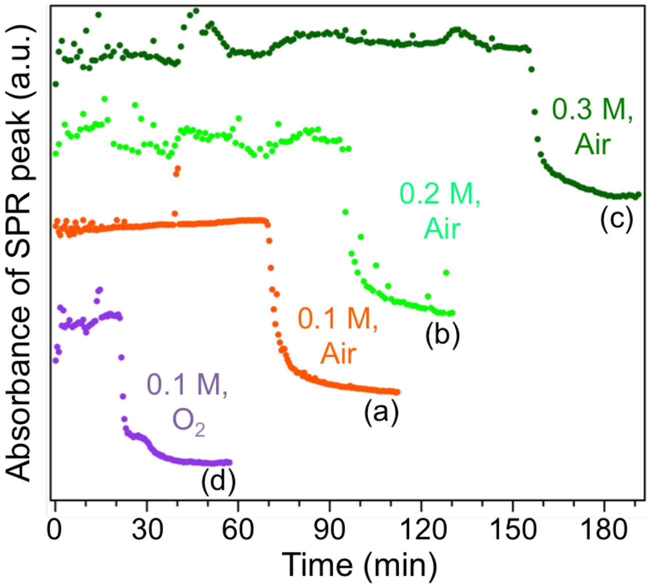

Figure S4. Changes in absorbance of the LSPR over time at different concentrations of $NaBH_4$ and under atmospheres: (a) [$NaBH_4$] = 0.1 M, air; (b) [$NaBH_4$] = 0.2 M, air; (c) [$NaBH_4$] = 0.3 M, air, (d) [$NaBH_4$] = 0.1 M, O_2.

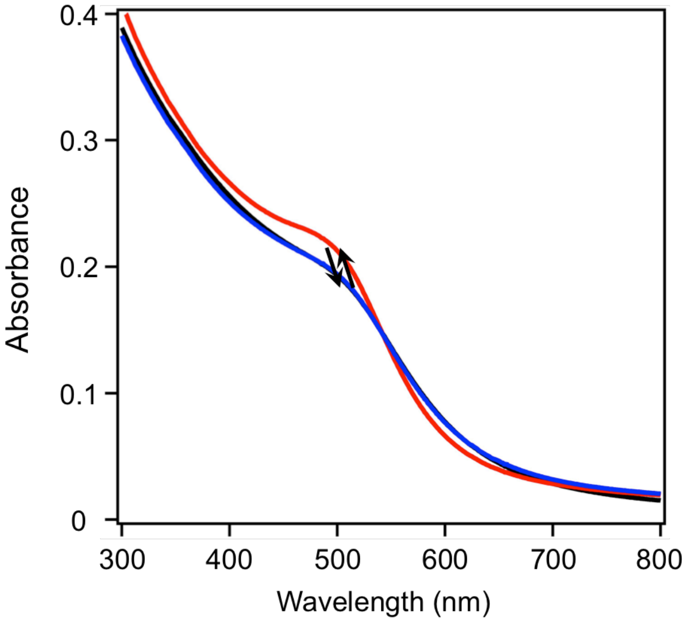

Figure S5. Absorption spectra of the preformed Au:PVP clusters with an average diameter of 1.8 ± 0.5 nm before (black), immediately after (red), and 70 min after the addition of $NaBH_4$ (blue). The blue line overlaps the black line The LSPR peak position was blue-shifted from 510 to 503 nm.