

## Supplementary information for

# Electrochemical Deposition of Gold Frame Structure on Silver Nanocubes

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## Experimental details

### Synthesis of Silver Nanocubes:

Ag nanocubes were prepared by previously reported polyol synthesis procedures with slight modification.<sup>12,13</sup> A 5.0 cm<sup>3</sup> aliquot of ethylene glycol (EG, Kishida Chemicals) was added to a 50 cm<sup>3</sup> sample vial and heated in an oil bath at 413 K for 1 h, followed by the addition of 1.0 cm<sup>3</sup> of 3.0 mmol/dm<sup>3</sup> HCl (Wako) EG solution. After 10 min, 3.0 cm<sup>3</sup> of 94 mmol/dm<sup>3</sup> AgNO<sub>3</sub> (Wako Chemicals) EG solution and 3.0 cm<sup>3</sup> of an EG solution containing polyvinylpyrrolidone (PVP, Mw ~ 40,000, Wako) (150 mmol/dm<sup>3</sup> in terms of the repeating unit) were simultaneously injected into the hot EG solution at a rate of 0.75 cm<sup>3</sup>/min, followed by stirring for more than 240 min at 413 K. The resulting suspension with a light brown color was centrifuged at 4,000 rpm for 10 min to isolate Ag nanocubes. The wet precipitates were washed with acetone and then with ultra-pure water (Milli-Q) to remove excess amount of PVP. Thus-obtained PVP-modified Ag nanocubes (PVP-Ag) were resuspended in water and then subjected to filtration with the use of a membrane filter of 5.0 μm in pore diameter. PVP-Ag nanocubes in the filtrate were isolated by centrifugation and then redispersed in ethanol with brief sonication.

### Surface Modification of Silver Nanocubes with 1-Octanethiol (OT):

A 3.0 cm<sup>3</sup> portion of the thus-obtained suspension of PVP-Ag nanocubes (4.8 mmol-Ag/dm<sup>3</sup>) was centrifuged at 4,000 rpm for 10 min. The precipitates were rinsed with acetone and ethanol and finally resuspended in ethanol (3.0 cm<sup>3</sup>). After the addition of 2.0 mmol/dm<sup>3</sup> OT (TCI, Japan) ethanol solution (3.0 cm<sup>3</sup>), the suspension was left standing for 1 h in the dark for surface modification. Thus-obtained OT-modified Ag nanocubes (OT-Ag) were washed with acetone and ultra-pure water and finally resuspended in EtOH.

### Electrochemical Deposition of Au:

A portion of the suspension containing PVP-Ag or OT-Ag was cast onto high-orientated pyrolytic graphite (HOPG, Veeco Instruments Inc.) to give an Ag atom density of  $0.075 \mu\text{mol}/\text{cm}^2$ , followed by drying. The resulting Ag nanocube-immobilized HOPG was used as a working electrode. The operative area of working electrode ( $0.28 \text{ cm}^2$ ) was restricted by an o-ring. Electrochemical deposition of Au onto PVP-Ag and OT-Ag nanocubes was performed in a three-electrode cell using a potentiostat (ALS-701C, BAS Inc.). An Ag/AgCl (saturated NaCl) electrode and a Pt wire served as a reference electrode and counter electrode, respectively. Electrochemical deposition of Au was performed with constant potential electrolysis at  $-0.50 \text{ V}$  vs. Ag/AgCl using the following procedures under Ar atmosphere. The Ag nanocube-immobilized working electrode was immersed in  $5.0 \text{ cm}^3$  of a phosphate buffer ( $0.10 \text{ mol}/\text{dm}^3$ , pH 6.8) and then potential was applied at  $-0.50 \text{ V}$  vs. Ag/AgCl. After 200 s, a  $380 \text{ mm}^3$  portion of  $20 \text{ mmol}/\text{dm}^3$   $\text{KAu}(\text{CN})_2$  phosphate buffer solution was injected into the cell, followed by stirring for several seconds to start the electrochemical deposition of Au. The potential was applied until the total deposition charge reached 10 mC or 50 mC.

### Chemical Etching of Ag:

The HOPG electrodes, on which Au-deposited Ag nanocubes were immobilized, were immersed in an  $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$  (30/70) mixed acid solution for 3 min, resulted in the oxidative dissolution of the Ag nanocubes used as a template. The thus-obtained HOPG electrodes were rinsed in pure water several times.

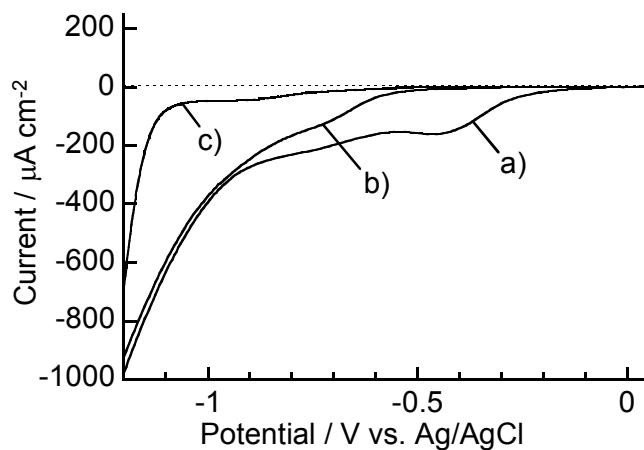
### Instrumentation:

Scanning electron microscope (SEM) images were captured with JSM-5600 (JEOL) and S-4300 (Hitachi) at an accelerating voltage of 20 keV. Energy-dispersive X-ray (EDX) spectroscopy was performed with JED-2200 attached to JSM-5600. FT-IR spectra were measured on an FTS6000 spectrophotometer (BIO-RAD).

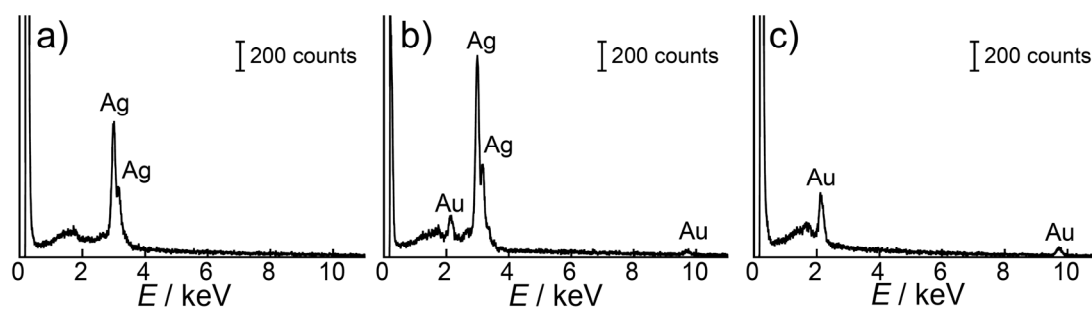
### TEM measurement:

A small amount of 2-propanol was dropped on the HOPG electrode on which Au nanoframes were prepared with the deposition charge of 10 mC, and then nanoframe particles were scratched off with a spatula to give a 2-propanol suspension. TEM samples were prepared by dropping the suspension onto a copper grid having an amorphous carbon overlayer, followed by

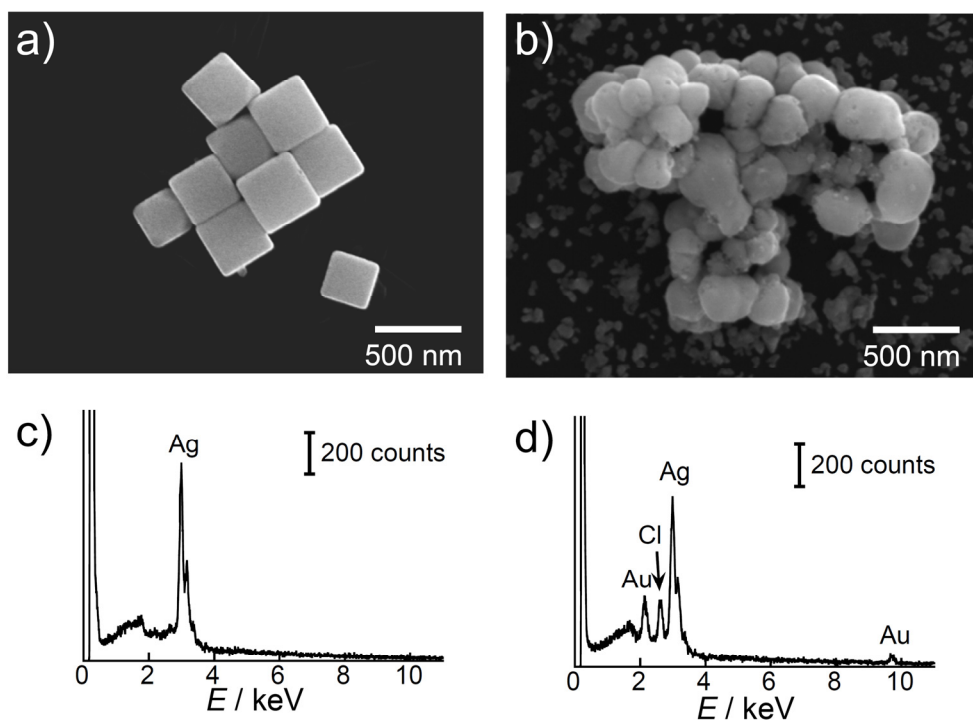
drying. TEM images and electron diffraction patterns were obtained using a JEOL 2010 transmission electron microscope operated at 200 kV acceleration voltage.



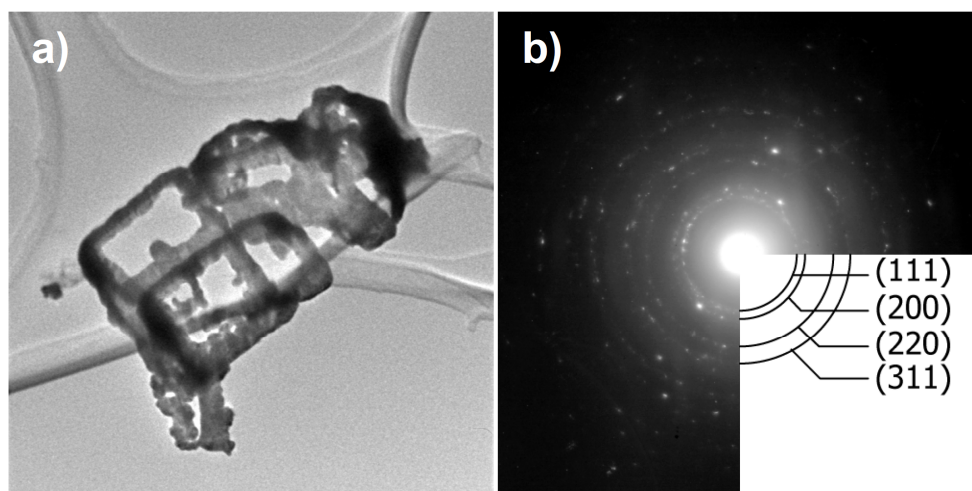
**Figure S1** Linear sweep voltammograms of the reduction of  $\text{KAu}(\text{CN})_2$  in  $0.10 \text{ mol/dm}^3$  phosphate buffer solution (pH 6.8). The working electrodes used were (a) Ag plate, (b) Au plate and (c) HOPG.



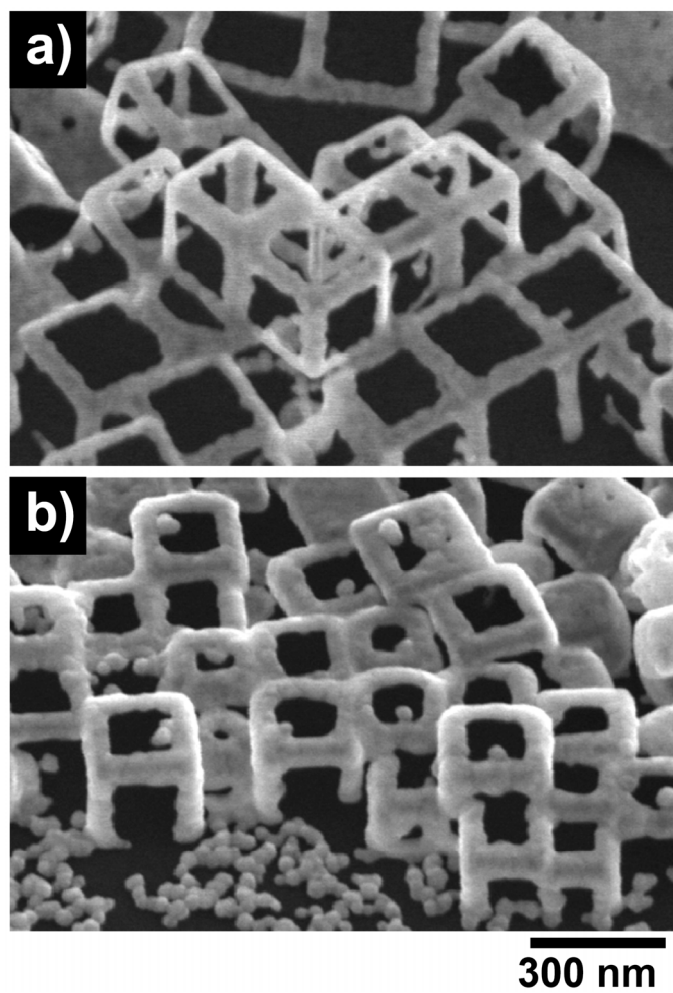
**Figure S2.** EDX analyses of Ag nanocubes (a), Au-deposited PVP-Ag (b) and Au nanoboxes (c) corresponding to SEM images of (a)-(c) in Fig. 1, respectively.



**Figure S3.** SEM images of PVP-Ag nanocubes immersed in  $2.0 \text{ mmol/dm}^3 \text{ KAu(CN)}_2$  (a) or  $\text{HAuCl}_4$  (b) aqueous solution for 3 h. EDX analyses corresponding to SEM images of (a) and (b) are shown in (c) and (d), respectively.

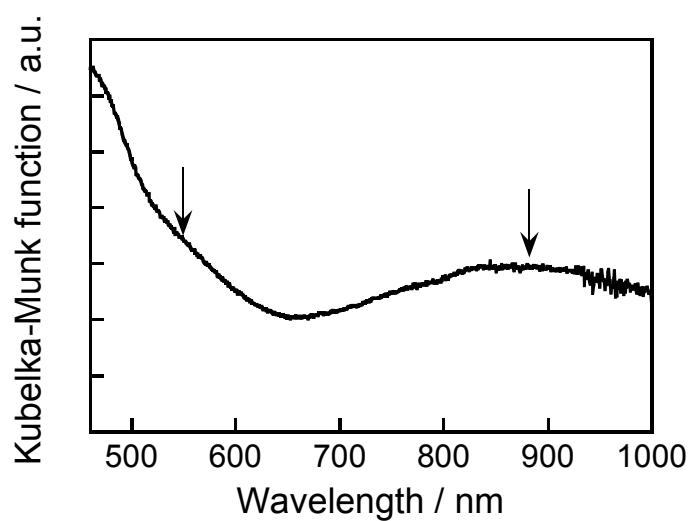


**Figure S4.** A typical TEM image (a) and the corresponding selected-area electron diffraction pattern (b) of Au nanoframes prepared with the deposition charge of 10 mC. The diffraction pattern is taken from the whole area of Au nanoframes in figure (a).



**Figure S5.** SEM images of Au nanoframes prepared with the deposition charge of 10 mC (a) and 50 mC (b).





**Figure S6.** Diffuse reflectance spectrum of the Au nanoframes immobilized on HOPG. Nanoframe structures were prepared with the deposition charge of 10 mC. The arrows show a peak at 880 nm and a shoulder at 550 nm.