A Distinct Platinum Growth Mode on Shaped Gold Nanocrystals

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Experimental Procedures

1. Coating gold nanocrystals on ITO glass

Shape-controlled gold nanocrystals dispersed in ethanol were synthesized as reported previously.[1] Gold nanocrystals in a 1,5-pentanediol solution were washed with ethanol (99.9%, Duksan) to remove excessive polyvinylpyrrolidone (PVP), which was used as a surface capping agent. Indium tin oxide (ITO) glass (<10 Ω/sq, Samsung Corning) was alternately cleaned by sonication with isopropyl alcohol (99.5%, Duksan) and DI water (18.3 MΩ) for 3 min. This washing process was repeated three times. The ITO glass was immersed in 10 vol% of 3-aminopropyltrimethoxysilane (APTMS, 97%, Aldrich) dissolved in methanol (99.8%, Duksan) for 1 day, which yielded an amine-terminated surface for easier assembly of the gold nanocrystals.[2] The gold nanocrystals were then immobilized onto the APTMS-modified ITO surface by immersing the APTMS-modified ITO in the gold nanocrystal dispersion. Formation of a uniform gold nanocrystal layer on the APTMS-ITO glass took approximately 4 hrs.

2. Electrochemical measurements

Cyclic voltammetry was performed using VersaSTAT3 (Princeton Applied Research) in a conventional three-electrode electrochemical cell. The ITO glass with the gold nanocrystals attached was used as the working electrode; a platinum wire was the counter electrode; and the KCl-saturated Ag/AgCl (K0260, Princeton Applied Research) was the reference electrode. All of the electrochemical measurements were recorded and reported versus the KCl-saturated Ag/AgCl reference electrode (+0.197 V vs. RHE).

3. Removal of PVP from the surface of the gold nanocrystals

The PVP on the surface of gold nanocrystals was removed using an O_2 plasma treatment (CUTE, FEMTO Science). The treatment time was varied depending on the sample, but it was typically approximately 4 min. Clean peaks from gold oxide formation were observed after O_2 plasma treatment following by imposition of high potentials using cyclic voltammetry (figure S1(a)). For the first sweep after the O_2 plasma treatment, a small oxidation peak was observed at 0.25 V (red line in figure S1), which indicates oxidation of cracked PVP species. The intensity of this peak decreased as the number of sweeping cycles increased, and it disappeared entirely after the tenth sweep. Gold oxide formation peaks and gold oxide reduction peaks became sharper and larger. After 10 cycles of cyclic voltammetry, the ITO glass with clean gold nanocrystals was removed from the electrochemical cell, washed thoroughly with DI water, and dried. This process yielded a clean gold surface on the shaped nanocrystals. A blue shift in the gold nanocrystals was observed by UV-vis spectra and even by the naked eye after the PVP removal, as shown in figure S1(b). The PVP layer not only blocked the electron flow but also affected the optical characteristics. SEM images of the clean shaped gold nanocrystals were shown in figure S1(c) and (d) after the PVP removal. Both shaped nanocrystals were well dispersed on the ITO glasses.

4. Platinum deposition on gold nanocrystals using UPD method

A platinum overlayer was formed on the gold nanocrystals through underpotential deposition (UPD) of copper and then by galvanic exchange of copper for platinum, which is typically referred to as the 'UPD method'.[3] The ITO glass with clean gold nanocrystals was immersed in a solution with 10 mM $CuSO_4$ (≥99.99%, Aldrich) + 0.1 M H_2SO_4 (95.0-98.0%, Aldrich), and a 0.05 V potential was applied to the gold nanocrystals for 120 sec to deposit a copper monolayer on the gold surface.

The potential used was slightly higher than the potential for bulk copper deposition, which begins at approximately 0 V. Figure S3(a) and (b) clearly demonstrates that copper UPD occurs at 0.31 V for cubic gold nanocrystals and 0.26 V & 0.07 V for octahedral gold nanocrystals (the lower portion of the black lines). The peak positions for Cu UPD had a positive dependence on the surface structure of the gold nanocrystals. The red lines in figure S3(a) and (b) show the linear scan voltammograms after copper UPD at a fixed potential of 0.05 V. The peaks from copper stripping are similar to the peaks from the cyclic voltammogram (the upper portion of the black lines), and there is no peak for stripping the deposited bulk copper. This agreement demonstrates that copper UPD performed at 0.05 V for 120 sec yields a copper monolayer with no bulk copper deposition.

After the copper UPD, the ITO glass with the copper-deposited gold nanocrystals was removed from the solution and directly immersed into a solution with N_2-purged 0.5 mM K_2PtCl_4 (98%, Aldrich) + 0.1 M $HClO_4$ (70%, Aldrich). The copper was exchanged with platinum because the standard reduction potential of platinum is much higher than copper. After 10 min of immersion, the ITO glass with platinum-deposited gold nanocrystals was removed from the solution, cleaned thoroughly with DI water, and dried in air. More platinum was deposited on the gold nanocrystals by repeating a cycle consisting of copper UPD and galvanic exchange of copper for platinum. When copper was deposited by UPD on the platinum surface, the potential for copper deposition was changed to 0.15 V (figure S3(c)).

5. CO stripping

The ITO glass with platinum-deposited gold nanocrystals was immersed in a CO-saturated 0.1 M H_2SO_4 solution and a -0.147 V potential was applied for 10 min. Then N_2 gas was purged for 30 min to remove all of the CO dissolved in the solution. After purging, linear sweep voltammetry was performed from -0.147 V to 1.0 V. The CO-stripping voltammograms were normalized by assuming that 420 μC is required to entirely oxidize a CO monolayer on a 1 cm^2 platinum surface.[4]

6. First-principles total-calculation method

The theoretical investigations were performed within the framework of the density functional theory (DFT)[5,6] as implemented in the Vienna ab-initio Simulation Package (VASP)[7,8] and based on the pseudo-potential plane-wave basis set total energy first-principles method. The electron-ion interactions were described by projector augmented-wave (PAW) potentials,[8,9] and the exchange-correlation terms were employed by using a generalized gradient approximation (GGA) proposed by Perdew and Wang.[10,11] The plane-wave energy cutoff was fixed at 500 eV. The Brillouin zone was sampled in the slab system with 9×9×1 and 10×10×1 special k-point meshes for the (111) and (100) surfaces, respectively. Spin-polarized calculations were performed for all of the systems.

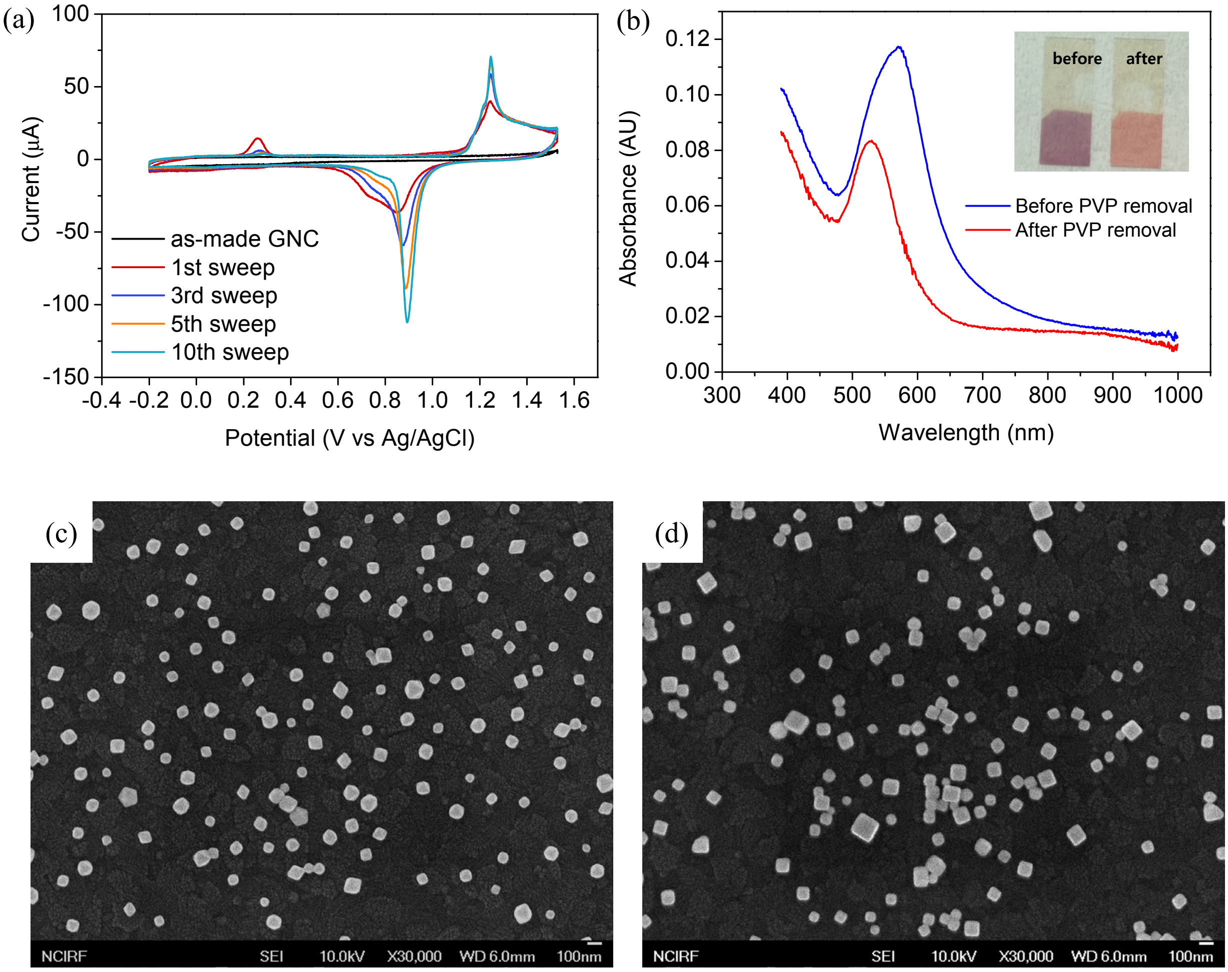

Fig. S1 (a) Cyclic voltammograms after O_2 plasma treatment. 10 cycles were conducted in 0.1 M H_2SO_4 solution with a scan rate of 50 mV/s. (b) Change in the color of gold nanocrystals before and after the PVP removal. SEM images of (c) octahedral and (d) cubic gold nanocrystals deposited on the ITO glasses after the PVP removal.

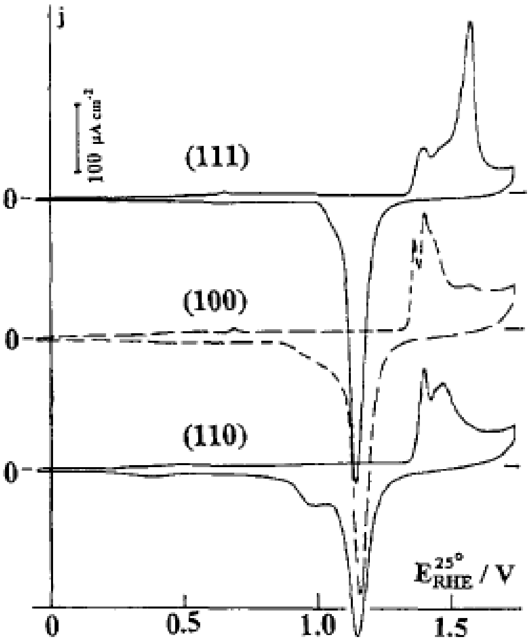

Fig. S2 Cyclic voltammograms for Au(111), Au(100), Au(110) in 0.01 M H_2SO_4, at 25±1℃ with a scan rate of 50 mV/s. (Journal of Electroanalytical Chemistry 407 (1996) 1-11, Figure 9)[12]

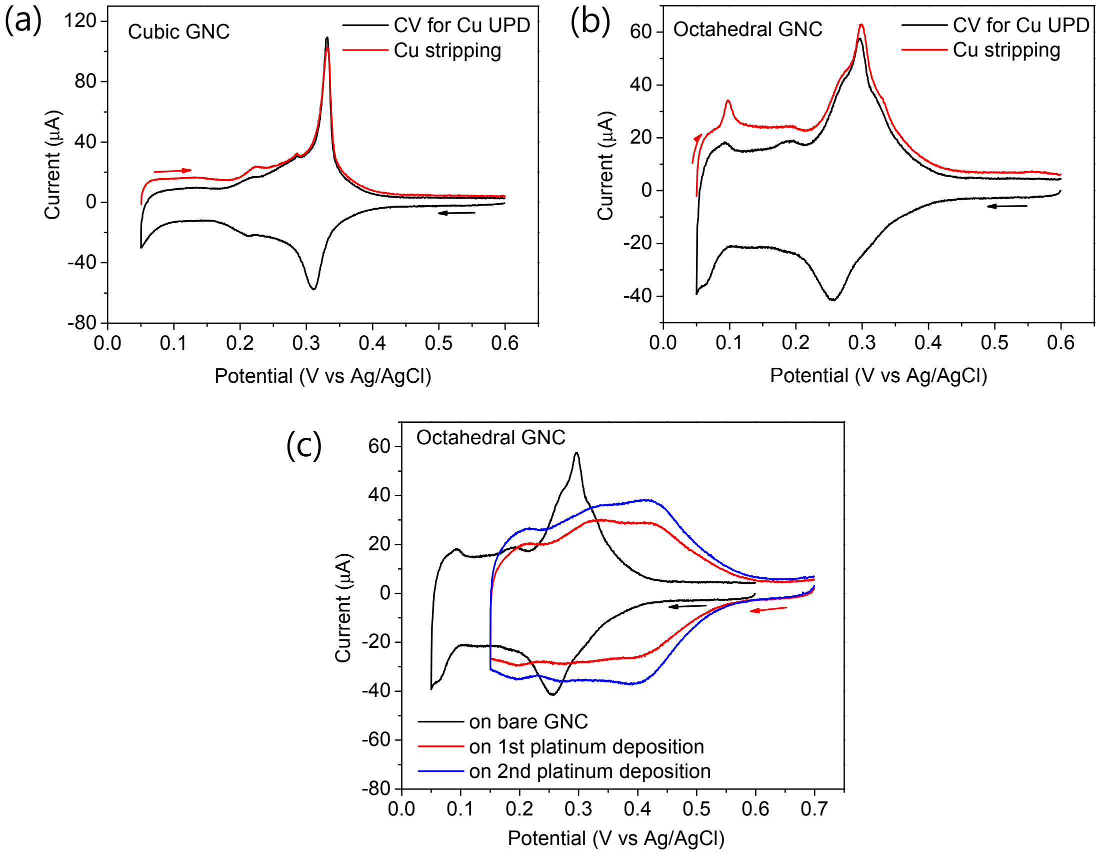

Fig. S3 Voltammograms in 10 mM $CuSO_4$ + 0.1 M H_2SO_4 solution with a scan rate of 50 mV/s on (a) cubic gold nanocrystals, and (b) octahedral gold nanocrystals. Black line shows a cyclic voltammogram (CV) of copper underpotential deposition (UPD), and red line shows a linear scan voltammogram after holding a potential at 0.05 V for 120 sec, which represents copper stripping. (c) CV of copper UPD on bare octahedral gold nanocrystals (black), octahedral gold nanocrystals with 1st platinum deposition (red), octahedral gold nanocrystals with 2nd platinum deposition (blue). Platinum deposition was performed by the copper UPD and subsequent galvanic exchange of copper into platinum. When copper UPD occurs on platinum surface, the potential for copper deposition was changed to 0.15V.

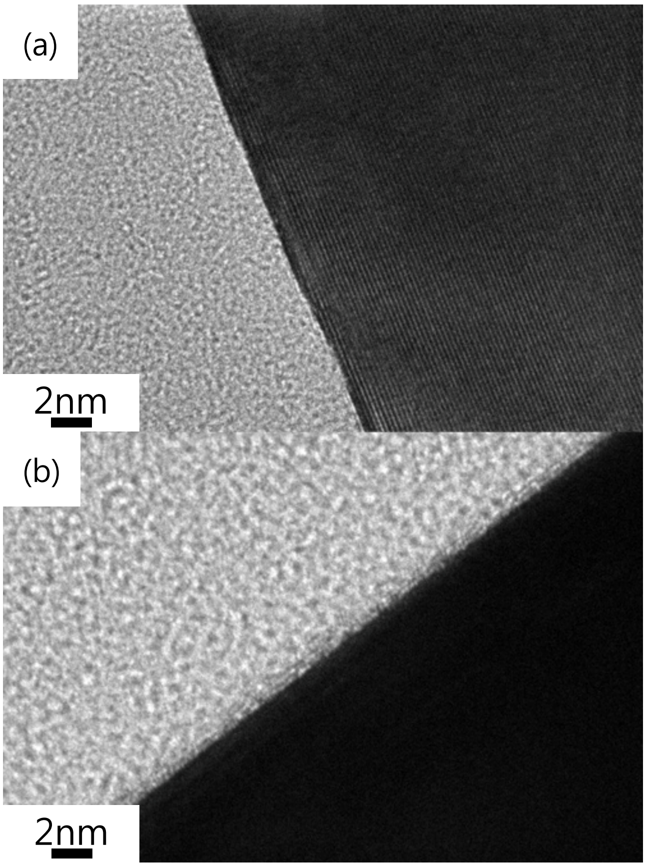

Fig. S4 High resolution TEM images for the surfaces of bare gold nanocrystals with (a) octahedral, and (b) cubic shapes.

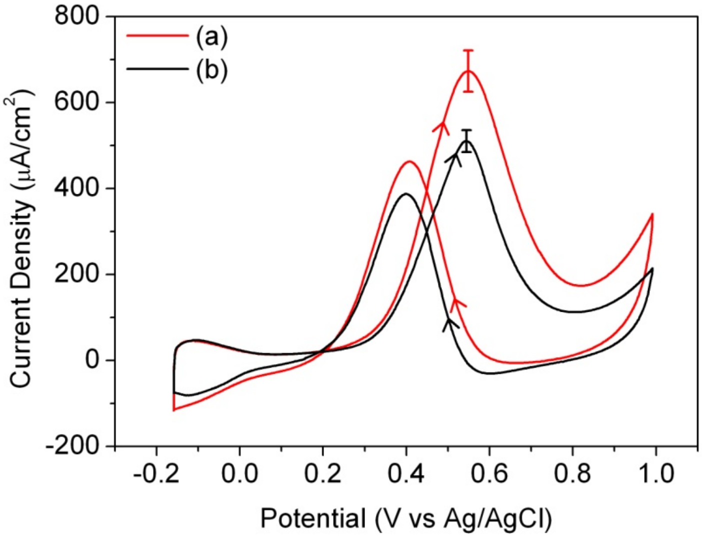

Fig. S5. Cyclic voltammograms in 0.1 M CH_3OH + 0.1 M H_2SO_4 with a scan rate of 50 mV/s for (a) octahedral and (b) cubic nanocrystals with three cycles of platinum deposition. The current density was normalized by electrochemically active platinum surface area measured from H adsorption and desorption.

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