Supporting Information

Synthesis of Concave Gold Nanocuboids with High-index Facets and Their Enhanced Catalytic Activity

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Experimentals

Chemicals and materials. Hydrogen tetrachloroaurate (III) hydrate (HAuCl4•4H2O, 99.9%), silver nitrate, (99.9%), sodium borohydride (98%), DDAB(98%), CTAB(98%), ascorbic acid (99%), and Nafion@ solution (5%, w/w) were obtained from Alfa-Aesar (Tianjin, China) and used without further purification. D-glucose (99.5%), 4-NTP, (98%), and 3-aminopropyltriethoxysilane (ATES, 98%) were purchased from J&K (Beijing, China). All other chemical reagents used were analytically pure and purchased from Beijing Chemical Works (Beijing, China). Deionized water was used in the experiments.

Synthesis of concave gold nanocuboids. To prepare the gold seed solution, 0.3644 g CTAB was dissolved in 5 mL deionized water and 5 mL HAuCl4 (1 mM) at 28°C. The Au seed solution was obtained by injecting fresh ice-cold NaBH4 solution (0.01 M, 635 μ L) into an aqueous mixture of CTAB and HAuCl4. To fabricate the concave Au NCs, 0.3 mL seed solution was injected into the growth solution containing DDAB (0.01 M, 5 mL), HAuCl4 (1 mM, 5 mL), AgNO3 (0.01 M, 100 μ L) and fresh ascorbic acid (0.1 M, 160 μ L). This solution was placed in a 30°C water bath overnight. The concave Au NCs were washed three times by centrifugation (10,000 rpm, 10 min), and dispersed in deionized water. For scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010F)

2

measurements, the solution of concave Au NCs was centrifuged twice at 5000 rpm for 10 min.

Electro-oxidation of glucose. Prior to use, the glassy carbon electrode (GCE) was immersed in piranha solution for 10 min, rinsed with copious amounts of water, and polished with 1.0, 0.3, and 0.05 μ m alumina slurries on polishing pads, consecutively. The GCE was then ultrasonically and electrochemically cleaned in 0.5 M H2SO4 until a typical CV curve was obtained. Afterward, the GCE was rinsed with deionized water and dried in N2. Next, 10 μ L of concave cuboid gold nanocrystals (approximately 0.5 mg/mL) was modified on the electrode and dried in air. The modified electrode was then coated with 5 μ L Nafion@ (0.25%). For the electro-oxidation of D-glucose, cyclic voltammograms were recorded at a sweep rate of 50 mV s-1 in a solution (25 mL) containing 0.1 M NaOH and 10 mM D-glucose between -0.8 V and 0.8 V.

Photo-catalytic reduction of 4-NTP under a laser. Polished Si wafers were cleaned in a piranha solution for 1 h, rinsed in deionized water and dried before being added to a solution of 10% (v/v) ATES. After aging overnight, the wafers were rinsed in ethanol. Then, 50 μ L of the concave Au NCs solution was added on the wafer to assemble on the Si surface. After being rinsed with water to remove unattached concave Au NCs, the wafers were immersed in a 1.0 × 10–4 M solution of 4-NTP in ethanol

for 4 h. The wafers were sequentially washed with ethanol and deionized water, and the Raman measurements were performed subsequently.

FIGURES:



Figure S1. SEM image of a monolayer of concave Au NCs showing a high-yield production.



Figure S2. Comparison of the theoretical and measured angles. Typical SEM images recorded from (a) the [001] zone axis with a measured angle of 11.49° and (b) the [100] zone axis with a measured angle of 11.58°. (c-d) Two-dimensional models of concave cuboid structures, which are consistent with the SEM images shown in Figures S2a-b.



Figure S3. (a-d) Typical TEM images from the [001], [100], [110] and [011] zone axes of a concave gold cuboid. (e-h) The SAED patterns recorded for the corresponding zone axes reveal the single crystalline nature of concave Au NCs.



Figure S4. UV-Vis spectra of the products at different times (3 h, 4.5 h and 6 h) showing the growth process of concave Au NCs.



Figure S5. SEM images of products formed during the control experiments using varying amounts of AA. (a) Typical icosahedrons were formed using 80 μ L AA, and (b) flower-like nanocrystals were formed using 200 μ L AA.



Figure S6. Typical TEM image of spherical gold nanoparticles synthesized by a previously reported method using sodium citrate as the reducing regent.¹



Figure S7. Cyclic voltammetry (CV) curves for catalytic Au NPs and concave Au nanocuboids modified on glassy carbon electrodes in 0.5 M H₂SO₄ at a scan rate of 50 mV·s⁻¹. The EASA of the Au NPs and concave Au NCs was estimated by EASA=Q₀/q₀, where Q₀ is the surface charge obtained from the reduced area of gold oxide under the CV trace and q₀ is the charge density accepted for the formation of one monolayer of gold oxide (q₀=386 μ C·cm⁻²). Based on the above calculation, the EASA for spherical Au NPs and concave Au NCs is 0.097 cm⁻² and 0.309 cm⁻², respectively.



Figure S8. The 10th and 100th cycle of CV curves for concave Au NC catalysts modified on a glassy carbon electrode in a 0.1 M NaOH solution of 10 mM glucose at a scan rate of 50 mV \cdot s⁻¹ using Ag/AgCl as the reference electrode. Peak values for CV curves that are greater than 95% indicate good stability of the electro-catalytic performance during the measurement, which is important for the application of concave Au nanocuboid catalysts in biofuel cells.



Figure S9. The SERS spectra of absorbed 4-NTP on regular gold nanoparticles recorded at various time points (0 s, 40 s, 80 s, 120 s, 160 s, and 200 s) under a 0.3 mW laser. As shown in this Figure, no peaks can be assigned to the formation of DMAB because the vibrational Raman bands at 1143, 1393, and 1439 cm⁻¹ are attributed to C-N symmetric stretching, N=N stretching, and C-H in-plane bending modes, respectively. This demonstrates that normal spherical gold nanoparticles exhibit no catalytic activity for the reduction of 4-NTP under a laser.



Figure S10. Raman spectra of 4-NTP absorbed on concave Au NCs and gold nanoparticles (Au NPs) under 4 mW laser for 2 s and 200 s, respectively. First, because similar quantities of concave Au NCs and Au NPs were used in this experiment, we can conclude that concave Au NCs have significantly higher SERS activity for 4-NTP. Second, the SERS spectrum of 4-NTP absorbed on concave Au NCs displays sharp peaks that can be assigned to the formation of DMAB from the reduction of 4-NTP. This demonstrates that concave Au NCs exhibit significantly enhanced catalytic activity for the reduction of 4-NTP. Additionally, the relative intensity is significantly higher (I₁₄₃₉/I₁₃₃₂=0.83) than at lower laser power (I₁₄₃₉/I₁₃₃₂=0.42 under a 0.3 mW laser) for a short period of time. Of note, no Raman band assigned to the intermediate DMHAB products at 1306 cm⁻¹ can be observed, because the reaction occurred too quickly.