Supporting Information

Shape-Dependent Electrocatalytic Activity of Monodispersed Gold Nanocrystals toward Glucose Oxidation

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1. Experimental Details

All chemicals were of analytical grade, and used as received without any further purification. 18 MΩ·cm deionized water refined by Millipore-Q Academic System was used as solvent.

Different shaped Au polyhedra were synthesized by seed-mediated growth method as described in our previous work.[1]

Glassy carbon electrode (3 mm in diameter) was polished before each experiment with alumina slurry (1.0, 0.3 and 0.05 μm) in sequence, and ultrasonically cleaned thoroughly with pure water between each polishing step. Subsequently, a 5.0 μL gold polyhedra solution was dropped onto the surface of a clean glassy carbon electrode. After drying, the electrode was modified further with a thin film of Nafion by dropping 3.0 μL 0.1% Nafion solution onto its surface. The electrode was then subjected to electrochemical treatment by potential cycling between -0.2 and 1.5 V at 50 $mV \cdot s^{-1}$ in 0.1 M H_2SO_4 until the stable voltammograms were obtained. The active surface area of the gold polyhedra modified electrode was determined by the charge

involved the peak of the reduction of gold oxide monolayer in the cyclic voltammogram (CV). The electrocatalytic activities of Au polyhedra toward glucose oxidation were examined by cyclic voltammetry in 0.1 M NaOH solution of 10 mM glucose at scanning rate 50 $mV \cdot s^{-1}$. All cyclic voltammetry data were collected after the cyclic voltammetry curves became stable.

Scanning electron microscopy (SEM) measurements were performed on a Hitachi S4800 scanning electron microscope at 10.0 kV. Electrochemical measurements were conducted with CHI660C electrochemical workstation (CHInstruments, USA) at room temperature in a conventional three-electrode cell, with Au polyhedra modified glassy carbon electrode as a working electrode, a platinum wire (φ = 0.5 mm) as a counter electrode and a Ag/AgCl electrode saturated with KCl as the reference electrode. All potentials used in this work were referenced to the Ag/AgCl electrode. Before each experiment, pure nitrogen gas was bubbled through the solution for at least 25 min to remove the dissolved oxygen in the solution.

2. XRD , SAED, HRTEM characterization of as-prepared different shaped Au nanocrystals

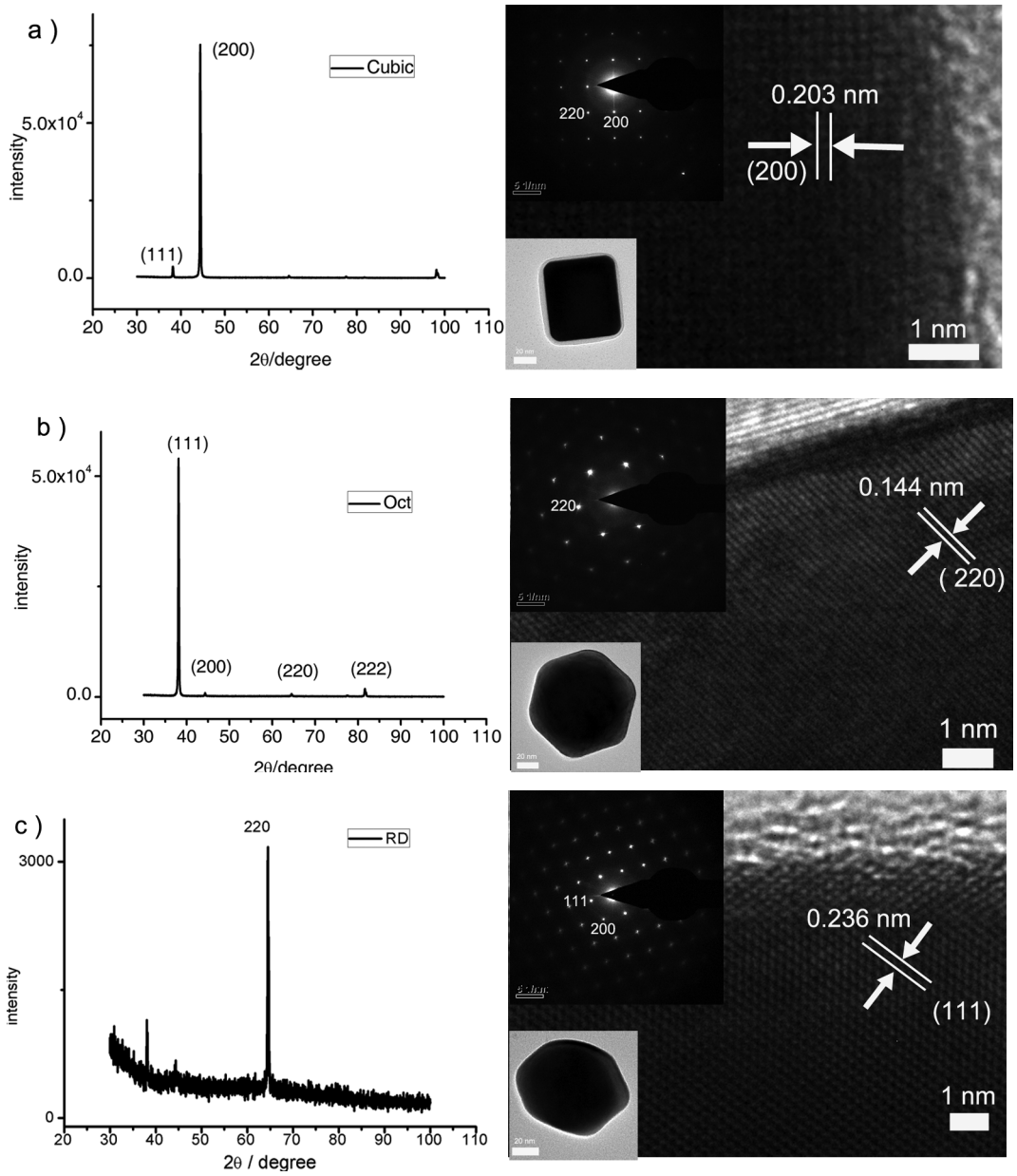

Figure S1. XRD patterns, STEM, SAED and HRTEM of Au polyhedra: (a) cubes, (b) octahedra, and (c) dodecahedra.

For Cubes， X-ray diffraction (XRD) pattern of the product shows an overwhelmingly intense peak from the (200) diffraction, indicating that the faces of these nanocrystals are primarily composed of {100} planes. The Au cubic nanocrystal was further confirmed by selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) measurements. The SAED pattern can be indexed to the [001] zone axis, indicating that the cubic

nanocrystal are single-crystalline and bound by {100} basal planes. The HRTEM image also demonstrates a *d*-spacing of 0.203nm for adjacent lattice planes corresponds to the {200} planes of fcc Au.

For octahedra，X-ray diffraction (XRD) pattern of the product shows an overwhelmingly intense peak from the (111) diffraction, indicating that the faces of these nanocrystals are primarily composed of {111} planes. Directing the electron beam perpendicular to the upper face of the flat lying octahedra nanocrystal show the typical SAED pattern of a gold crystal along the [111] zone axis, ndicating that the octahedra nanocrystal are single-crystalline and bound by {111} basal planes.

For dodecahedra，X-ray diffraction (XRD) pattern of the product shows a high intense peak from the (220) diffraction, indicating that the faces of these nanocrystals are primarily composed of {110} planes. Directing the electron beam perpendicular to the upper face of the flat lying RD nanocrystal produces the typical SAED pattern of a gold crystal along the [011] zone axis，indicating that the RD nanocrystal are single-crystalline and bound by {110} basal planes.

3. SEM images of gold nanopolyhedra after electrochemical treatment

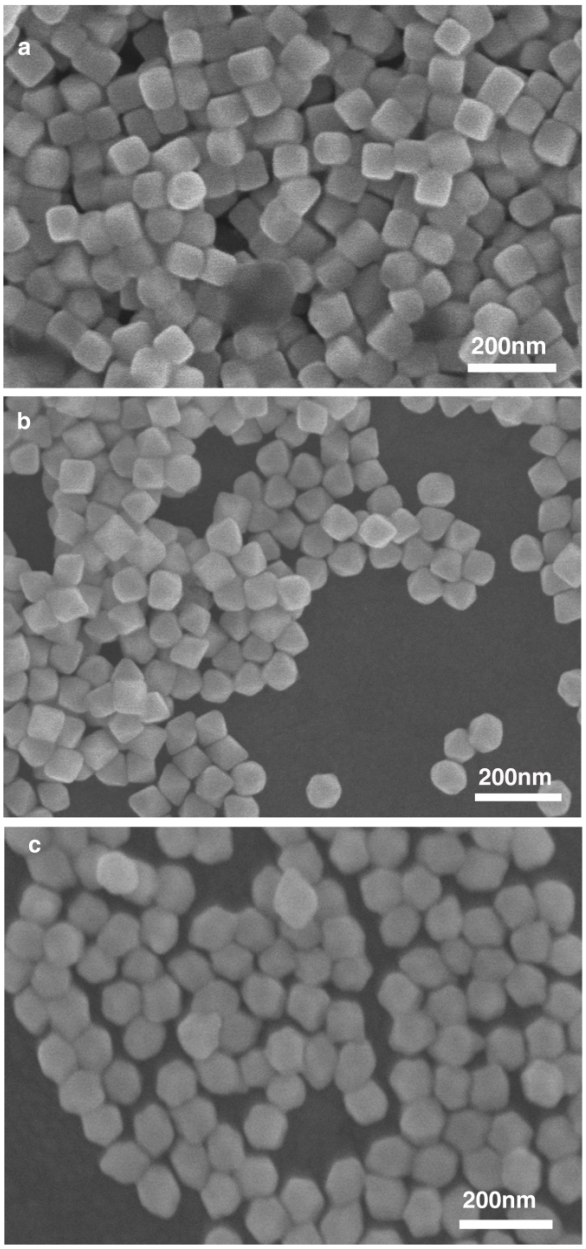

Figure S2. SEM images of Au polyhedra on the ITO surface after electrochemical treatment: (a) cubes, (b) octahedra, and (c) dodecahedra.

4. Calculation of current density

Current density is calculated using the following equation:

$$j = i/EASA$$

$$EASA = Q/Q_O^*$$

Where *j* is current density, *EASA* is electrochemical active surface area, *Q* is the charges needed to form an oxide monolayer on the gold Au surfaces.

The calibration factor, Q_O^*, of different single crystals was shown in Table S1 (Taken from ref. 1-2).

Table S1.Characteristics of different types of Au nanocrystals

Au NP shape	Surface facet	Q_O^*(μC·cm^{-2})
Rhombic dodecahedral	110	272
Octahedral	111	444
Cubic	100	384

5. Electrocatalytic stability of different shaped Au nanocrystals toward glucose oxidation

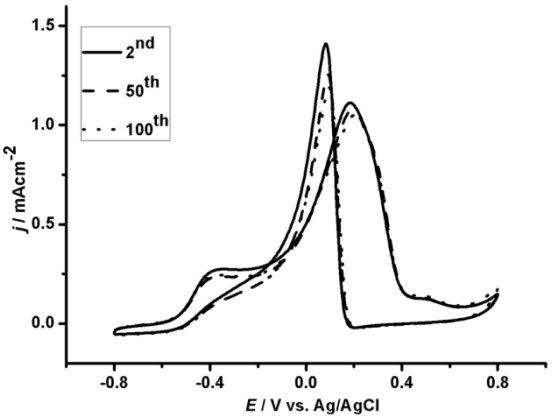

Figure S3. Cyclic voltammograms of Au cubes for glucose oxidation (2^{nd}, 50^{th}, 100^{th}) in 0.1 M NaOH with 10 mM glucose at a scan rate of 50 $mV \cdot s^{-1}$.

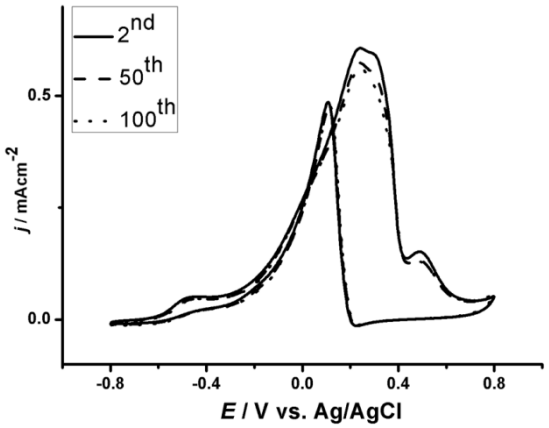

Figure S4. Cyclic voltammograms of Au rhombic dodecahedra for glucose oxidation (2^{nd}, 50^{th}, 100^{th}) in 0.1 M NaOH with 10 mM glucose at a scan rate of 50 $mV \cdot s^{-1}$.

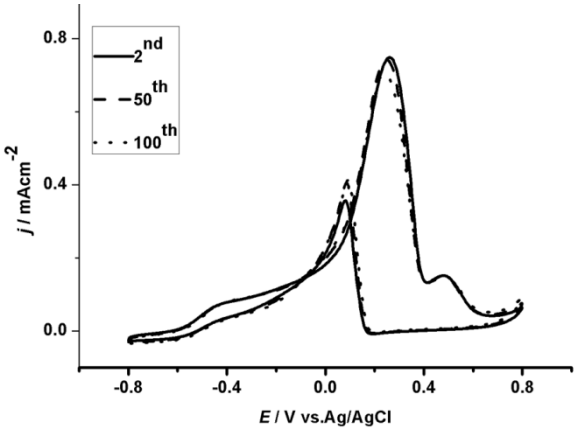

Figure S5. Cyclic voltammograms of Au octahedra for glucose oxidation (2^{nd}, 50^{th}, 100^{th}) in 0.1 M NaOH with 10 mM glucose at a scan rate of 50 $mV \cdot s^{-1}$.

6. Au polyhedra with larger sizes and electrocatalytic activity

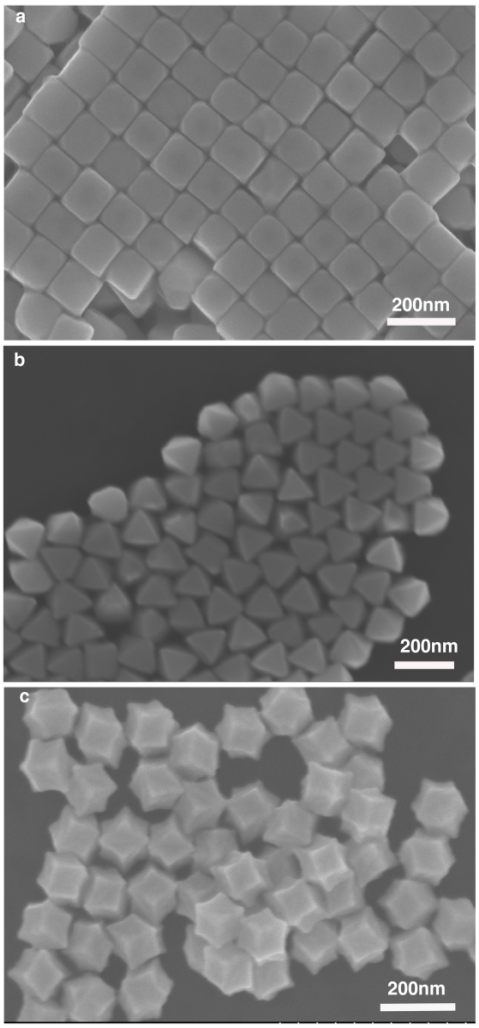

Figure S6. SEM images of different shaped Au polyhedra: (a) cubes, (b) octahedra, and (c) dodecahedra. The average edge length for all three types of Au nanocrystals is around at 100 nm.

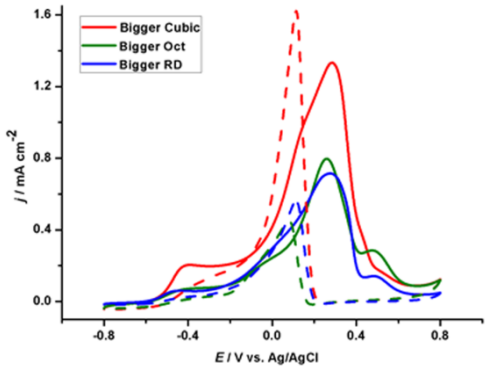

Figure S7. Cyclic voltammograms of the larger Au polyhedra on glassy carbon electrodes in 0.1 M NaOH solution of 10 mM glucose at a scan rate of 50 $mV \cdot s^{-1}$. Solid lines represent positive scanning and dotted lines represent negative scanning.

References:

1. W. X. Niu, S. L. Zheng, D. W. Wang, X. Q. Liu, H. J. Li, S. A. Han, J. Chen, Z. Y. Tang and G. B. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 697-703
2. S. Trasatti and O. A. Petrii, *Pure Appl. Chem.*, 1991, **63**, 711-734.
3. H. Angersteinkozlowska, B. E. Conway, A. Hamelin and L. Stoicoviciu, *Electrochim. Acta*, 1986, **31**, 1051-1061.