## **Electronic Supplementary Information**

## Morphology-controlled Au Nanostructures for Efficient and Selective Electrochemical CO<sub>2</sub> Reduction

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## **Experimental Methods**

Experimental procedures for the synthesis of Au nanostructures. A 160 nm-thick Au thin film with a 10 nm-thick titanium (Ti) adhesion layer was deposited onto a p-type (100) silicon (Si) wafer (Boron-doped, resistivity: 5-10  $\Omega$ ·cm) with an e-beam evaporator. The Au/Ti thin layers on the Si wafers were cut into pieces of about 0.5 cm<sup>2</sup> and then were sequentially rinsed by acetone and isopropyl alcohol (IPA) followed by deionized (DI) water. After cleaning the surface, a Cu wire was fixed onto an edge of the Au thin film with silver (Ag) paste to form an electrical connection. All edges of the Au electrode were then covered with Epoxy (Loctite 9460, Hysol) and dried for over 12 hours at 60 °C in an oven. For the reduced anodic (RA) treatment, anodization on the prepared Au electrode was performed by applying a constant anodic potential for various times in a 0.2 M KHCO<sub>3</sub> solution (pH 8.4, 99.7% purity of KHCO<sub>3</sub>, Sigma Aldrich) at room temperature. The surface of the as-anodized Au electrode was rinsed with DI water briefly, and galvanostatic electrochemical reduction was conducted until the potential transition and hydrogen evolution were observed in 0.2 M KHCO<sub>3</sub>. Ag/AgCl (in 3 M NaCl) and a Pt coil were used as the reference electrode (RE) and counter electrode (CE), respectively. In addition, all potentials are expressed as the reversible hydrogen electrode (RHE) by  $E_{RHE} = E_{WE} + (0.209 + 0.059 * pH) V$ unless otherwise stated.

**Characterization of the morphology, grain boundaries and surface state.** The morphology of the RA-treated Au samples was characterized with a field emission scanning electron microscopy (FE-SEM, Magellan400, FEI Co.). Bright-field transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) images were attained using the Libra200MC TEM (Carl Zeiss, Germany) at 200 kV with a spherical aberration corrector (CEOS GmBH) for the objective lenses. Surface chemical compositions of the as-deposited Au thin film, as-anodized Au thin film,

and RA-treated Au thin films were analyzed by X-ray photoelectron spectroscopy (XPS, Al Kalpha, Thermo VG Scientific). Grazing-incidence X-ray diffraction (GI-XRD) patterns of the asdeposited Au thin film and RA-treated Au thin films were collected by a thin-film X-ray diffractometer (XRD, Ultima IV, Rigaku) using Cu K-alpha ( $\lambda = 1.5405$  Å) radiation. An incidence angle of 2° was used for the GI-XRD.

Electrochemical surface area (ECSA) measurements. We carried out three different methods to obtain electrochemical surface area (ECSA) of our Au nanostructures, which are well established in the literature. First, cyclic voltammetry (CV) in N2-purged 0.05 M H2SO4 from 0 V to 1.5 V (vs. Ag/AgCl) was repeated until the trace converged by varying the scan rate: 25, 50, and 100 mV s<sup>-1</sup>. During the forward scan, chemisorbed oxygen is formed as a monolayer on the Au surface. This oxygen layer is reduced during the reverse scan. The area of the reduction peak at -0.85 V (vs. Ag/AgCl) was integrated. The integrated reduction charge obtained at each scan rate was averaged. The stripping charge of the monolayer of chemisorbed oxygen on the Au surface was reported to be 386 µC cm<sup>-2</sup>.<sup>1</sup> We also utilized the Cu and Pb underpotential deposition (UPD) techniques. Cu UPD was performed in N<sub>2</sub>-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> with 0.1 M CuSO<sub>4</sub> at a scan rate of 5 mV s<sup>-1</sup> in potential range of 0.11 - 0.60 V (vs. Ag/AgCl). The charge for anodic stripping of an underpotential deposited Cu monolayer was calculated by integrating the peak area centered at ~0.4 V. The ECSA of our Au electrodes was determined by normalizing the anodic stripping charge to that of polycrystalline Au foils reported in elsewhere (92.4 µC cm<sup>-2</sup>).<sup>2</sup> For Pb UPD, our Au electrodes were immersed in N<sub>2</sub>-purged 0.1 M NaOH including 1 mM Pb(NO<sub>3</sub>)<sub>2</sub> and CV was traced between -0.75 and 0.62 V (vs. Ag/AgCl) at a scan rate of 25 mV s<sup>-1</sup>. The stripping peaks are assigned to about -0.47 V and -0.35 V which are indicative the relative populations of (111) and (110) facets, respectively.<sup>3</sup> In this case, the stripping charge of 420  $\mu$ C cm<sup>-2</sup> of a

polycrystalline Au foil was used to determine the ECSA of Au electrode.<sup>4</sup> According to all methods, our bare Au shows the stripping charge values of 578, 114, and 680  $\mu$ C cm<sup>-2</sup> for chemisorbed oxygen, Cu and Pb monolayer, respectively, on Au surface. It indicates that the surface of our as-deposited Au has a 1.2 – 1.6 times higher surface area than a polycrystalline Au foil. Thus, in our experiments, we obtained RF values for all our prepared nanostructured Au on the basis of our bare Au thin film that is a mother substrate. To normalize current density, we representatively use the RF from the Cu UPD method, since the Pb UPD can cause the significant errors due to the fact that the atomic size of Pb is ~20% larger than that of Au.<sup>4</sup>

Electrochemical characterization for CO<sub>2</sub> reduction reaction. Electrochemical CO<sub>2</sub> reduction was performed with a single-compartment cell containing 0.2 M KHCO<sub>3</sub> (pH 8.4). The working electrode (WE) was directly used after fabricating the Au nanostructures by the RA-treatment. Ag/AgCl (in 3 M NaCl) and graphite were used as the RE and CE, respectively. Before the CO<sub>2</sub> reduction experiments, the electrolyte was purged with CO<sub>2</sub> gas (ultrapure, 99.999%) at a flow rate of 100 cc min<sup>-1</sup> for over 30 minutes until the pH was saturated at 6.8. All experiments were carried out with stirring of 400 rpm. Linear sweep voltammogram (LSV) was obtained at a scan rate of 50 mV s<sup>-1</sup>. Chronoamperometry for product analysis was performed under a gas-tight condition for 10-60 min. depending on the applied potentials. Gas products were quantified by gas chromatography (Micro-GC 3000, Inficon Co.). The gas chromatography was equipped with a Molsieve column and thermal conductivity detector (TCD). Ar gas was the carrier gas for the H<sub>2</sub> and CO detection. Electrocatalytic CO<sub>2</sub>RR analysis was performed three times with freshly prepared samples. For HCO<sub>3</sub><sup>-</sup> dependence investigation, the electrolysis was performed at -0.38 V for 30 minutes in KHCO<sub>3</sub> with various concentrations (from 0.1 to 1.0 M). KCl was added to maintain ionic strength.



**Fig. S1** XPS profile of (a) Au4f and (b) O1s for the as-deposited Au and as-anodized Au thin films as a function of the applied anodic potentials.



**Fig. S2** (a) Cross-sectional SEM images of the nanoporous  $Au(OH)_3$  anodized at 2.50 V for 10, 20, and 40 min. (b) The thickness of the nanoporous  $Au(OH)_3$  at 2.50 V as a function of the anodization time in 0.2 M KHCO<sub>3</sub>.



**Fig. S3** Cross-sectional SEM images of the (a) as-deposited Au and (b) as-anodized Au thin films at 2.15 V for 40 minutes. Note that the thickness of the as-anodized Au is nearly similar to that of the as-deposited Au (*i.e.*, ~160 nm). The insets for the plan-view SEM images of the corresponding Au films. As shown in the insets, the surface morphology seems to be slightly changed. The reason for this change might be because water (or OH<sup>-</sup> ions) is adsorbed, and a few nm-thick Au oxide layer is formed (as indicated in Fig. S1). The scale bar of the insets indicates 100 nm.



**Fig. S4** XPS profile of (a) Au4f and (b) O1s for the RA-Au-6.0, RA-Au-0.5, and Au(OH)<sub>3</sub> anodized at 2.50 V for 40 min. For comparison, the XPS profile of the as-deposited Au is also included.



**Fig. S5** TEM images at low-magnification and selected area electron diffraction (SAED) pattern of RA-Au-0.5 for (a) and (b), and RA-Au-6.0 for (c) and (d), respectively.



**Fig. S6** Additional HREM images of RA-Au-0.5. The while dotted lines designate the grain boundaries. All scale bar indicates 10 nm.



**Fig. S7** Additional HREM images of RA-Au-6.0. The white dotted lines designate grain boundaries. All scale bar indicates 10 nm.



**Fig. S8** (a) Grazing-incidence X-ray diffraction (GI-XRD) patterns for the as-deposited Au, RA-Au-0.5, and RA-Au-6.0, respectively. The peak observed at around  $2\theta = 55^{\circ}$  indicates Si (311) substrate. Williamson-Hall (W-H) plots extracted from the peak broadness in the GI-XRD patterns of (b) as-deposited Au, (c) RA-Au-0.5, and (d) RA-Au-6.0, respectively. To estimate the average grain size and microstrain, the following equation is adopted: Bcos $\theta = \varepsilon \cdot (4\sin\theta) + K\lambda/\langle D \rangle$ , where B is the integral breadth of peaks,  $\varepsilon$  is the microstrain, *K* is the Scherrer constant (assumed as 1 in this equation),  $\lambda$  is the wavelength used in the analysis of XRD, and  $\langle D \rangle$  is the average grain size. The above equation is considered as a linear relationship, so the slope of the straight line and the y intercept imply  $\varepsilon$  and  $\langle D \rangle$ , respectively. The error bars indicate one deviation obtained from three-independent W-H analysis.



**Fig. S9** Cross-sectional SEM images of the (a) RA-Au nanostructures after electroreduction of Au(OH)<sub>3</sub> formed at various anodic potentials,  $V_{anod}s$ , and (b) RA-Au nanostructures formed with various electroreduction rates for the Au(OH)<sub>3</sub>. In (a), anodization with various  $V_{anod}s$  (marked on each SEM image) was applied for 40 minutes, and a constant reduction current density,  $J_{red}$ , of - 3.0 mA cm<sup>-2</sup> was used. In (b), Au(OH)<sub>3</sub> is formed by a  $V_{anod}$  of 2.50 V for 40 minutes and subsequently reduced at different  $J_{red}s$  (marked on each SEM image). Notably, in (a), partial delamination of the RA-Au nanostructures is seen when the anodization was performed at a  $V_{anod}$  of 2.60 V for 40 minutes, and the corresponding SEM image of the RA-Au nanostructures was obtained from the remaining part of the sample. The inset shows the corresponding plan-view SEM images. Scale bars of the insets are 100 nm.



**Fig. S10** (a) Cross-sectional SEM image of the porous Au(OH)<sub>3</sub> layer by anodizing a Au thin film at 2.70 V for 40 minutes in 0.2 M KHCO<sub>3</sub>. When a high anodic potential (*e.g.*, 2.70 V) was applied, the unreacted Au/Ti film rarely existed between the Au(OH)<sub>3</sub> and Si substrate. (b) Chronopotentiometry curves by applying a constant  $J_{red}$  of -3.0 mA cm<sup>-2</sup> for the reduction of Au(OH)<sub>3</sub> formed at 2.60 and 2.70 V or for 40 minutes. Note that the potential fluctuates for both cases which can be attributed to the peeling off of the Au(OH)<sub>3</sub> and the exposure of the Si substrates. The insets show digital photographs showing the exposed Si substrate indicated by blue arrows and blue dotted circles.



**Fig. S11** Electrochemical characterization of Au electrode surfaces. (a) Cyclic voltammetric profiles in 0.05 M  $H_2SO_4$  with a scan rate of 25 mV s<sup>-1</sup>. (b) Cu underpotential deposition (UPD) profiles in 0.5 M  $H_2SO_4$  and 0.1 M CuSO<sub>4</sub> with a scan rate of 5 mV s<sup>-1</sup>. (c) Pb UPD profiles in 0.1 M NaOH and 1 mM Pb(NO<sub>3</sub>)<sub>2</sub> with a scan rate of 25 mV s<sup>-1</sup>. Note that Pb UPD reveals surface facet orientations of (111) and (110) at about -0.47 and -0.35 V, respectively.

**Table S1** Summary of roughness factors (RFs) obtained *via* the stripping charges of electrochemically chemisorbed oxygen, underpotential deposited Cu and Pb monolayer. The RFs of all nanostructured Au samples are normalized to that of our bare Au thin film.

Samples	Oxygen Chemisorption	Cu UPD	Pb UPD
RA-Au-0.5	8.6	8.3	4.1
RA-Au-1.0	9.0	8.4	4.3
RA-Au-2.0	6.8	6.7	N/A
RA-Au-3.0	7.7	6.5	2.9
RA-Au-6.0	7.7	5.6	2.8

Anodization time (min)	$ \begin{array}{c} \text{Total } \text{Q}_{\text{anod}}^{\text{a}} \\ \text{(C cm}^{-2}) \end{array} $	Q <sub>stripping</sub> <sup>b</sup> (C cm <sup>-2</sup> )	Faraday efficiency <sup>c</sup> (%)
10	6.56	0.072	1.10
20	11.97	0.13	1.09
40	16.42	0.19	1.16

**Table S2**  $Q_{anod}$  and  $Q_{stripping}$ , and Faraday efficiency of the Au(OH)<sub>3</sub> formation as a function of the anodization time.

[a] Total  $Q_{anod}$  and [b]  $Q_{stripping}$  stand for total passed charge density during anodization ( $V_{anod} = 2.50$  V) and the charge density used for reducing the Au(OH)<sub>3</sub> until the reduction of the Au(OH)<sub>3</sub> is completely terminated, respectively. [c] Faraday efficiency for the Au(OH)<sub>3</sub> formation is defined as  $Q_{stripping}/Q_{anod}$ .



**Fig. S12**  $10^{\circ}$ -tilted SEM images of the (a) pore-like RA-Au-0.5 and (c) pillar-like RA-Au-6.0, interrupted during the electrochemical reduction process, showing the growth interface during the reduction of the Au(OH)<sub>3</sub>. (b) and (d) are high magnification cross-sectional SEM images of (a) and (c), respectively. Note that the Au(OH)<sub>3</sub> layer was produced at 2.50 V for 40 minutes.



**Fig. S13** Cross-sectional SEM images of the RA-Au nanostructures produced by electrochemical reduction of the nanoporous Au(OH)<sub>3</sub> at  $J_{red}s$  of (a) -1.0, (b) -3.0, and (c) -6.0 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> and (d) a  $J_{red}$  of -6.0 mA cm<sup>-2</sup> in 2.0 M H<sub>2</sub>SO<sub>4</sub>. In (a) – (d), nanoporous Au(OH)<sub>3</sub> was formed by anodizing Au thin films at 2.50 V for 40 minutes in 0.2 M KHCO<sub>3</sub>.



**Fig. S14** Schematic illustration of the formation of RA-Au in an acidic media (*e.g.*,  $0.5 \text{ M H}_2\text{SO}_4$ ). Note that the nanoporous Au(OH)<sub>3</sub> was produced by the anodization of Au film in a mild base solution (*i.e.*,  $0.2 \text{ M KHCO}_3$ ).



Fig. S15 Cross-sectional SEM images of the nanoporous Au(OH)<sub>3</sub>, taken (a) before immersion in a 0.5 M H<sub>2</sub>SO<sub>4</sub> (*i.e.*, as-anodized form), and after immersion for (b) 5 min., and (c) 10 min. Note that the nanoporous Au(OH)<sub>3</sub> were produced from the anodization at  $V_{anod}$  of 2.50 V in 0.2 M KHCO<sub>3</sub> for 40 min.



**Fig. S16** Potential-dependent CO-producing partial current density  $j_{CO}$  and CO product selectivity of the as-deposited Au thin film in CO<sub>2</sub>-saturated 0.2 M KHCO<sub>3</sub>.



Fig. S17 Tafel plot for the as-deposited Au thin film (*i.e.*, bare Au) in CO<sub>2</sub>-saturated 0.2 M KHCO<sub>3</sub>.

Samples	The ratio of (110)/(111)	
Bare Au film	1.9	
RA-Au-0.5	1.2	
RA-Au-1.0	1.3	
RA-Au-3.0	1.3	
RA-Au-6.0	1.5	

Table S3 The surface facet orientation ratio of (110) to (111) estimated via the Pb UPD method.



**Fig. S18** HCO<sub>3</sub><sup>-</sup> concentration dependent  $j_{CO}$  at applied constant potential of -0.38 V for (a) RA-Au-0.5 and (b) RA-Au-6.0. The slope of plots (~1) means first-order dependence of HCO<sub>3</sub><sup>-</sup> concentration for RA-Au-0.5 and -6.0, and indicates that H<sup>+</sup> transfer by HCO<sub>3</sub><sup>-</sup> determines the rate of CO<sub>2</sub>RR.



Fig. S19  $H_2$  production partial current density  $j_{H_2}$  normalized by (a) geometric area and (b) electrochemical surface area (ECSA) estimated from the Cu UPD method. (c)  $H_2$  product selectivity of the RA-Au-0.5 and the RA-Au-6.0 at various potentials in CO<sub>2</sub>-saturated KHCO<sub>3</sub>.



Fig. S20 LSV of the bare Au, RA-Au-0.5, 1.0, 3.0, and 6.0 in CO<sub>2</sub>-saturated 0.2 M KHCO<sub>3</sub>.



Fig. S21 ECSA-normalized partial current density for CO production ( $j_{CO}$ ) of the nanostructured Au.



**Fig. S22** Total current density  $j_{tot}$  of RA-Au-0.5 and -6.0 normalized by (a) geometric area and (b) ECSA by Cu UPD as a function of applied potential in CO<sub>2</sub>-saturated 0.2 M KHCO<sub>3</sub>. Inset is an enlarged plot to display low potential regions.



Fig. S23 Cross-sectional SEM images of RA-Au-0.5 (a) before and (b) after  $CO_2RR$  at -0.79 V in Fig. 7.



Fig. S24 Comparison of the CO production selectivity of the RA-Au-0.5 and RA-Au-6.0 at -0.99 V in CO<sub>2</sub>-saturated 0.2 M K<sub>2</sub>HPO<sub>4</sub> (pH  $\sim$ 6.8) and 0.1 M KClO<sub>4</sub> (pH  $\sim$ 5.8).

## References

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