Electronic Supplementary Information

Facile decrease of the electron-transfer rate and surface roughness of gold by ultrasonic treatment

Kyungmin Jo,[a] Gorachand Dutta,[a] Jeong Won Kim[b] and Haesik Yang*[a]

[a]*Department of Chemistry and Chemistry Institute of Functional Materials, Pusan National University, Busan 609-735, Korea*
[b]*Korea Research Institute of Standards and Science, Daejeon 305-340, Korea*

Experimental Section

The electrochemical experiments were performed using a CHI405A potentiostat (CH Instruments, Austin, TX, USA). The electrochemical cell consisted of a Au working electrode, a platinum wire counter electrode, and an Ag/AgCl (3 M NaCl) reference electrode. Three types of Au were used as working electrode: Au disk working electrode (diameter = 2 mm, CH Instruments, Austin, TX, USA), Au plate (1,000 Å-thick Au and 50 Å-thick Cr on glass substrate; EMF Corp., Ithaca, NY, USA), and Au wire (diameter = 0.5 mm, Sigma). The surface of the Au disk and Au plate electrode was gently polished with 0.3 μm Al_2O_3 particles (Buehler, Lake Bluff, IL, USA) on a wet pad (Buehler, Lake Bluff, IL, USA) and rinsed thoroughly with water before use. The Au wire was treated with piranha solution (the piranha solution is a mixture of H_2SO_4 and 30% of H_2O_2 (3:1, v/v)) for 10 min at 70° C.

The ultrasonic treatment was performed using a bath-type ultrasonicator (JAC-1002; Kodo, Korea), from which consistent ultrasonic waves were generated by a BLT transducer. Treatment was carried out in 15-min intervals to minimize any temperature increase. Polished Au electrodes were dipped in about 4–5 mL of water in a 10 mL glass beaker, and later transferred to an ultrasonic bath containing about 1100–1200 mL of water for further sonochemical treatment. The ultrasonic power of 15 W was calorimetrically determined, and consistent with previous literature,[S1] although the input power of the ultrasonicator was 125 W. XPS data were obtained using an ESCALAB 250 instrument (VG Scientifics, England). AFM images were acquired using an XE-100 (Park System, Korea), operated in non-contact mode, using the XEI software. ICP-MS data were obtained using an ELAN DRC-e (PerkinElmer, Wellesley, MA, USA). UV-vis spectra were obtained using a UV-1650PC (Shimadzu, Japan).

Electrochemical Treatment (*via* Potential Cycling) of Au Disk Electrodes. Au disk

electrodes were mechanically polished and further electrochemically treated in 0.1 M H_2SO_4 by applying three potential cycles between −0.1 V and 1.4 V (vs. Ag/AgCl) at a scan rate of 0.1 V/s.[S2,S3] After three cycles, the anodic peak of Au oxidation and the cathodic peak of Au oxide reduction were reproducibly observed.

Sample Preparation for ICP-MS Measurement. Sample solutions were prepared by mixing 5 mL of aqua regia (formed by mixing concentrated HNO_3 (70%) and HCl (37%) in a volume ratio of 1:3) and 5 mL of water (where a mechanically polished Au disk electrode (3 mm in diameter) was dipped and ultrasonically treated for 1 h, while a blank solution was prepared with water). Sample solutions were further reacted for 1 h, and then diluted twice with water before ICP-MS measurement. During this sample preparation, initial sample solutions were diluted 4 times.

Ultrasonic Treatment with Horn-type Ultrasonicator. Electrochemically treated Au plates were vertically dipped in 30 mL deionized water in a Falcon tube. Ultrasonic Treatment was carried out using Sonosmasher (ULH-700S, Ulsso Hightech, Korea) with 15-min intervals for 1 h. To minimize temperature increase, used water was replaced with fresh water after each interval.

References

S1. T. Kimura, T. Sakamoto, J.-M. Leveque, H. Sohmiya, M. Fujita, S. Ikeda and T. Ando, *Ultrason. Sonochem.*, 1996, **3**, S157–S161.

S2. R. O. Córdova, M. E. Martins and A. J. Arvía, *J. Electrochem. Soc.*, 1980, **127**, 2628–2634.

S3. K. Jo, H. J. Kang and H. Yang, *B. Kor. Chem. Soc.*, 2011, **32**, 728–730.

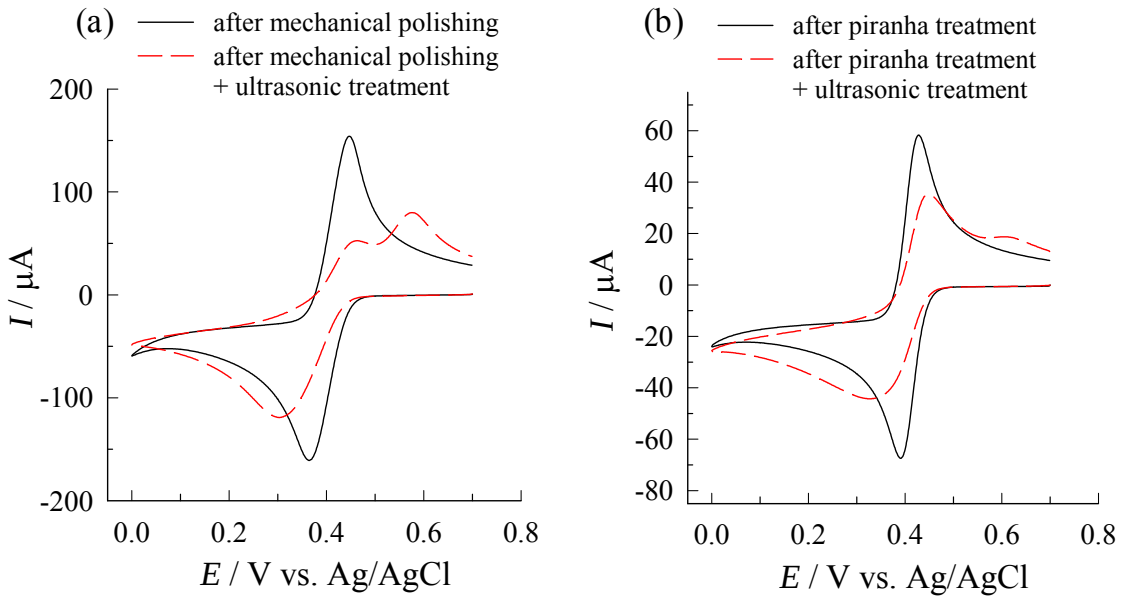


Fig. S1 Cyclic voltammograms (50 mV s^{-1}) obtained in a solution containing 1 mM *p*-benzoquinone, 0.1 M $HClO_4$, and 0.1 M $NaClO_4$ before and after 2 h ultrasonic treatment of (a) mechanically polished Au plate electrodes and (b) piranha-treated Au wire electrodes.

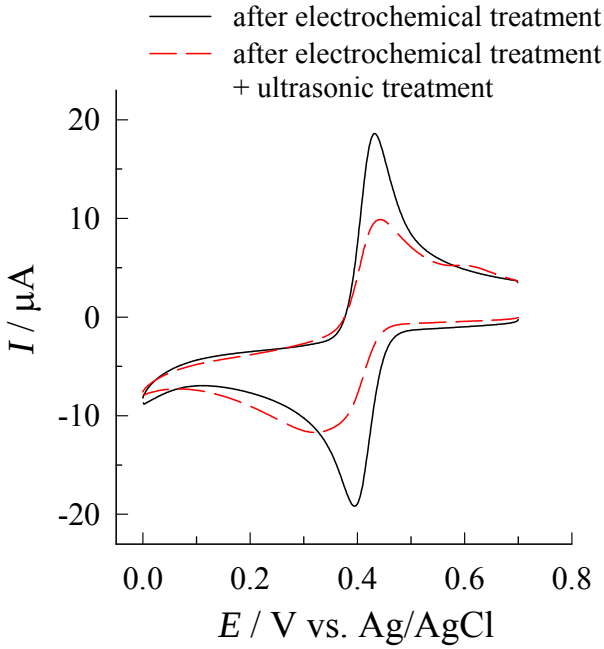


Fig. S2 Cyclic voltammograms (50 mV s^{-1}) obtained in a solution containing 1 mM *p*-benzoquinone, 0.1 M $HClO_4$, and 0.1 M $NaClO_4$ before and after 2-h ultrasonic treatment of electrochemically treated Au disk electrodes.

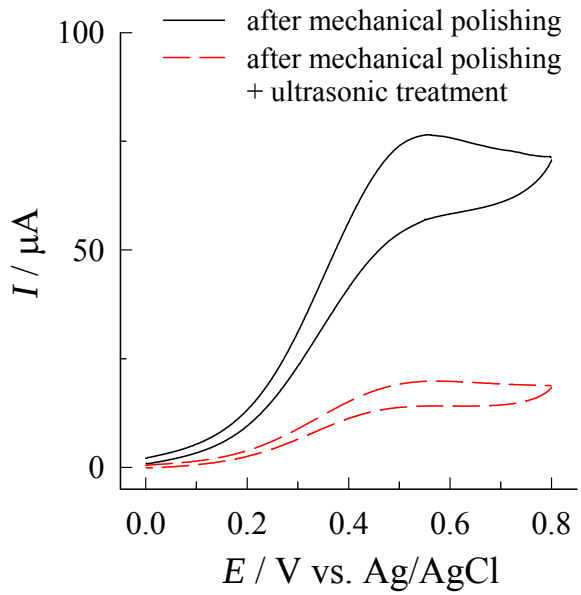


Fig. S3 Cyclic voltammograms for formic acid oxidation obtained in 0.5 M $NaHCO_3$ containing 0.25 M formic acid before and after 2-h ultrasonic treatment of mechanically polished Au disk electrodes.

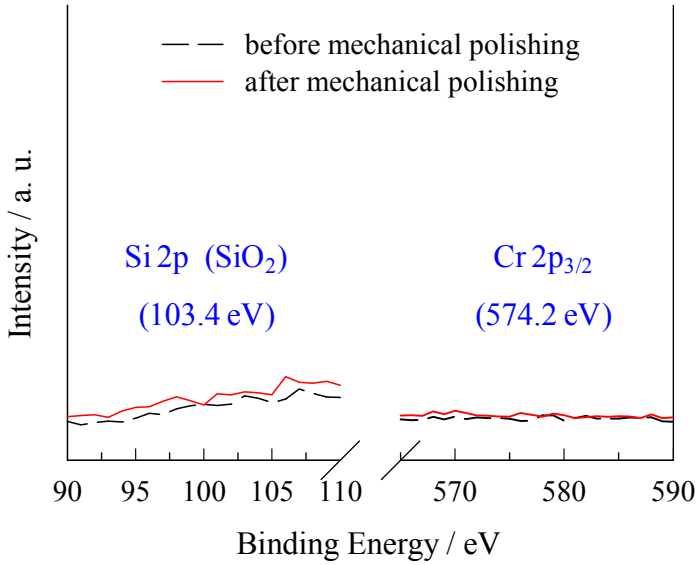
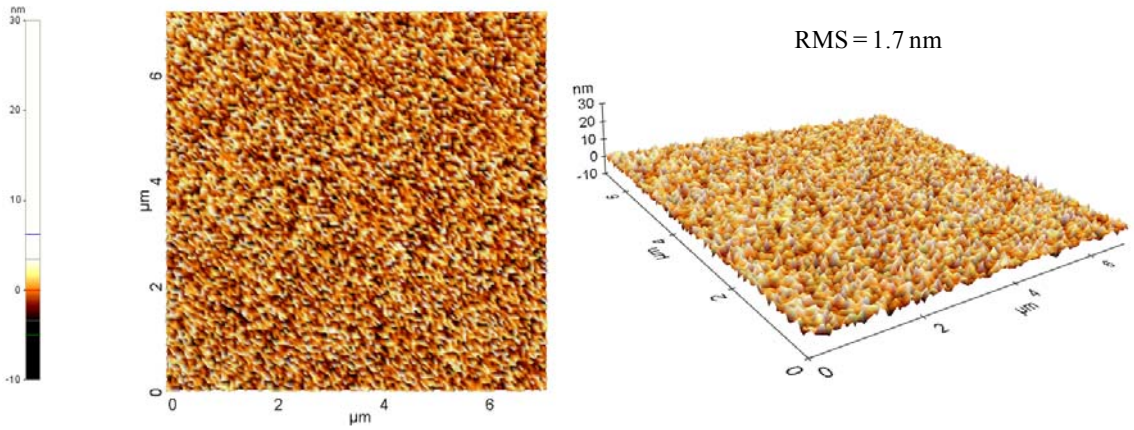
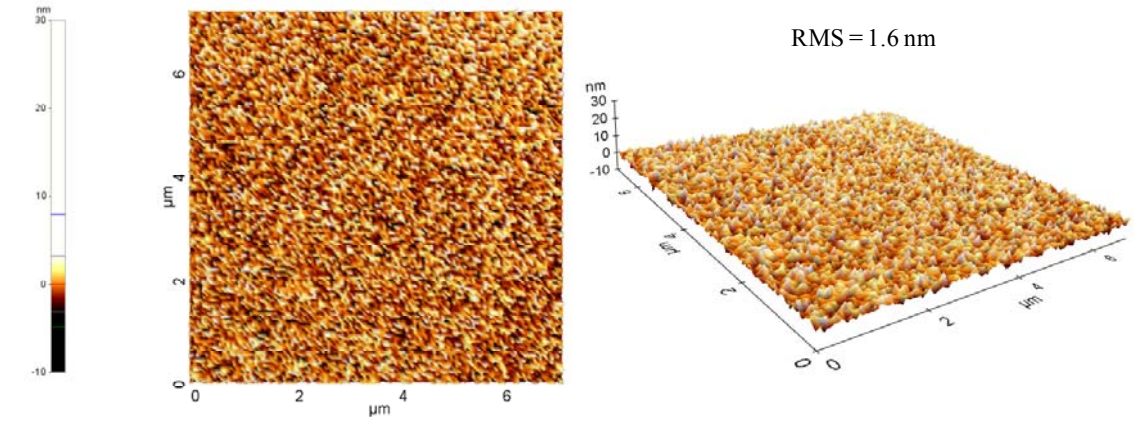


Fig. S4 XPS spectra for Si 2p (left) and Cr 2p (right) regions before and after mechanical polishing of Au plate electrodes.

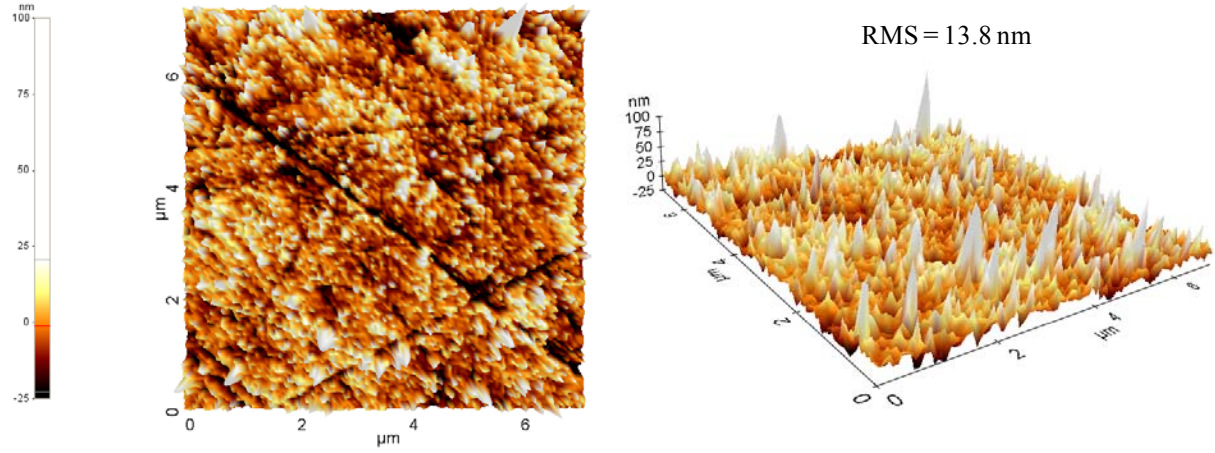
a)


RMS = 1.7 nm
nm
30
20
10
0
-10
µm
0
2
4
6

b)


RMS = 1.6 nm
nm
30
20
10
0
-10
µm
0
2
4
6

c)


RMS = 13.8 nm
nm
100
75
50
25
0
-25
µm
0
2
4
6

d)

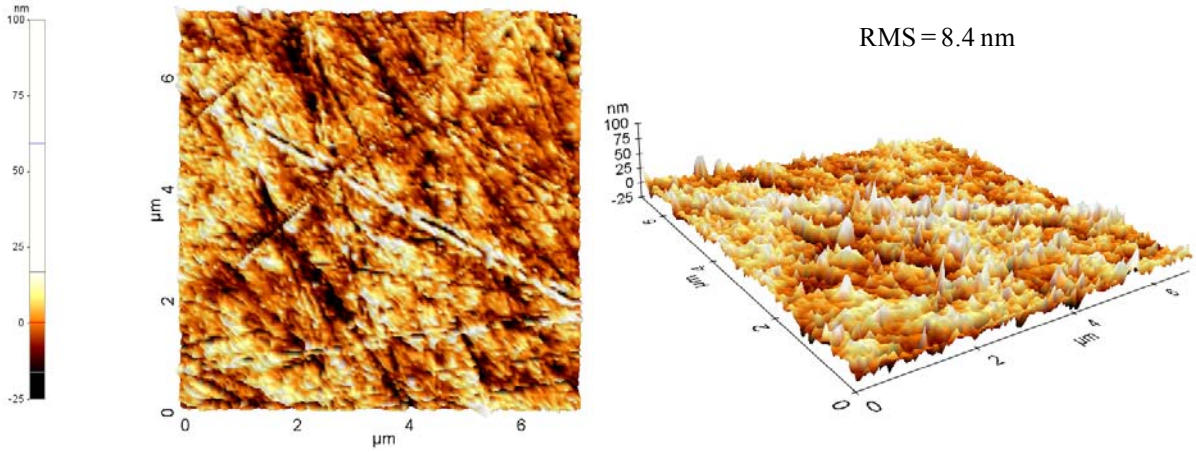


Fig. S5 AFM images of Au plate electrodes a) before any treatment, b) after 1 h ultrasonic treatment, c) after mechanical polishing, and d) after mechanical polishing followed by 1 h ultrasonic treatment.

Supporting Discussion

The amount of Au, which is possibly removed from the surface during ultrasonic treatment, is estimated by assuming that Au has face-centered cubic (fcc) unit cell. In each fcc unit cell, there are 8 atoms at the corners and 6 atoms at the faces. Therefore, one unit cell contains 4 atoms. Taking into account the unit cell edge of 4.0786 Å, a volume of 1 nm^3 contains 59 Au atoms. If we consider the removal of 1-nm height for the surface area of 1 mm^2, which is corresponding to the total volume of 10^{12} nm^3, the number of Au atoms removed during ultrasonic treatment can be estimated as 5.9×10^{13}. This number is then converted to molar concentration of 19.6 nM (the amount of liquid medium for ultrasonic treatment is 5 mL). Considering the atomic weight of Au (196.97 g/mol), this value corresponds to 3.86 ppb. In Table S1, noticeable changes were not observed for 3-time treatments.

Table S1. Amount of Au measured after ultrasonic treatment

Sample	Amounts of Au (blank subtracted, in ppb)[b]	Estimated change in height (nm)[c]
1st UT[a]	0.47 ± 0.01	0.07
2nd UT	0.41 ± 0.01	0.06
3rd UT	0.15 ± 0.01	0.04

[a] UT = Ultrasonic treatment. Each UT was carried out for 1 h. [b] 5-mL volume of water was used as liquid medium for UT with gold plate having surface area of 7.07 mm^2. [c] Estimations were performed, considering the surface area of 7.07 mm^2 and a dilution factor of 4 during ICP sample preparation.

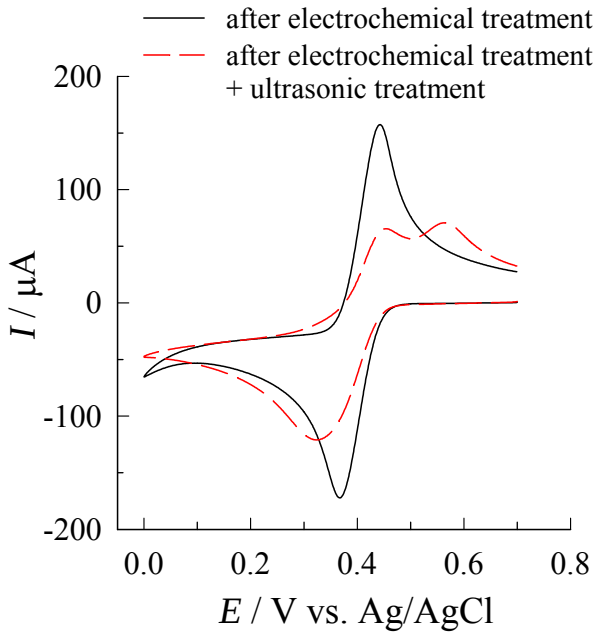


Fig S6 Cyclic voltammograms (50 mV s^{-1}) obtained in a solution containing 1 mM *p*-benzoquinone, 0.1 M $HClO_4$, and 0.1 M $NaClO_4$ before and after 1-h ultrasonic treatment (horn-type ultrasonicator) of electrochemically treated Au plate electrodes.