Electronic Supplementary Information

In situ Monitoring of Li–O_2 Electrochemical Reaction on Nanoporous Gold using Electrochemical AFM

Rui Wen[a, b] and Hye Ryung Byon[a]*

[a]*Byon Initiative Research Unit (IRU), RIKEN, Wako-shi, Saitama 351-0198, Japan*
[b]*Present address: Institut für Experimentelle und Angewandte Physik, Universität Kiel, Olshausenstr. 40, 24098 Kiel, Germany*

**E-mail: hrbyon@riken.jp*

Experimental Section

NPG preparation. The NPG electrodes were prepared by dealloying of a white gold leaf (Imaikinpaku Co., Ltd., Japan, Ag/Au ≈ 50/50, thickness: 0.7 μm) in a bath with a 70 vol.% nitric acid (Wako Chemicals) for 6 min at room temperature, followed by thoroughly washing with deionized water (R≈18.2 MΩ•cm) and acetone for several times. The acid-treated NPG electrodes were dried in a vacuum oven at 80 °C for 6 h then 150 °C overnight for the formation of a uniform and homogeneous nanoporous structure.[1]

Preparation of Li−O_2 model cell with bulk electrolyte for EC-AFM. All preparation works were done in an Ar gas-filled glove box (MTI-Korea, H_2O < 1 ppm). The Li−O_2 model cell was composed of the NPG (2 cm (*w*) × 2 cm (*d*)) as the working electrode, metallic Li wire (Acros Organics, 99+% purity) as the counter and reference electrodes, and Ar or O_2 gas-saturated tetraethylene glycol dimethyl ether (tetraglyme, UBE, < 5 ppm of H_2O measured by Karl Fischer titration) containing 0.5 M of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.7% purity, Kanto Chemical Co.) as the aprotic organic electrolyte. The as-prepared NPG electrode was put onto a HOPG substrate (SPI-II grade, SPI, USA) pre-heated at 60 °C for overnight under vacuum. After connecting the NPG with a gold-coated wire and being positioned on the Li−O_2 cell, 0.9 mL of tetraglyme electrolyte was added and dry O_2 (>99.999% purity, Tomoe Shokai Co., LTD) or Ar gas (99.9999% purity, Tomoe Shokai Co., LTD) was bubbled over 30 min. The metallic Li wire connecting with a platinum wire was then suspended along the inner wall of Li−O_2 cell and immersed into the electrolyte completely with a distance of ~4 mm from the NPG.

Electrochemical Performance and Image Scanning using EC–AFM. Electrochemical tests were conducted using a potentiostat coupled with the AFM (EC–AFM, Agilent 5500 AFM/SPM) in the Ar–filled glove box to avoid air and water contamination. All potentials were referred to Li^+/Li unless otherwise mentioned. CV curves were recorded at a sweep rate of 5 mV s^{-1} using EC–AFM. The potential was swept toward negative potential (from OCP to 2.0 V) for the reduction, and positive (2.0 to 4.5 V) for the oxidation reaction. The NPG surface was scanned by

EC–AFM with a contact mode using a triangular silicon nitride AFM tip (radius < 10 nm, Olympus) during electrochemical examination. More detailed information for the EC-AFM operation was described in the previous report.[2]

XPS Measurement. For the XPS analysis, potential sweepings toward negative potential at 2.4 and 2.0 V, and positive potential at 4.5 V using a battery cycler (WBCS3000, WonATech) at a sweeping rate of 1 mV s^{-1} were performed on the NPG electrodes (diameter ≈ 12 mm) in Li–O_2 cells (Tomcell®) separately. The NPG electrodes were disassembled from the Li–O_2 cells, washed out by anhydrous dimethyl carbonate (DMC, Wako Chemicals) for three times and dried in a vacuum chamber at 60 ^{o}C for 6 h without air exposure. The NPGs were then conveyed using a hermetic Ar–filled transfer vessel and directly transferred into a XPS vacuum chamber without air exposure. Synchrotron XPS experiments were performed at the beamline BL12 of the SAGA Light Source in Kyushu, Japan using a photon energy of 650 eV. Considering the escape depth of the photoelectron, the excitation energy was selected to measure surface sensitive spectra than those by using Al and Mg Kα sources (1486.5 and 1253.6 eV, respectively). In addition, this low photon energy allows us to obtain top thinner surface information on the NPG electrodes. The base pressure of the XPS chamber maintained less than 10^{-8} Pa. The XPS peaks were calibrated by Au $4f_{5/2}$ and Ag $3d_{3/2}$ and $3d_{5/2}$ peaks from the as-prepared NPG. The peak intensity was normalized as referring to the injection current (I_o) whilst different quantity of insulating Li–O_2 product on the NPG electrode can modulate the ejected sample current (I_s), which can affect the detected peak-intensity. The pass energy is 117.4 eV for survey and 23.5 eV for Li, O, and C 1s BE region. The scanning numbers are 100 times for Li 1s, 75 times for O 1s and 10 times for C 1s region with a time step of 50 ms. The reference powders, Li_2O_2 (99% purity, Kojundo Chemical Laboratory Co., Ltd), LiOH (98% purity, Sigma-Aldrich) and Li_2CO_3 (99% purity, Nacalai Tesque Inc.), were thinly pasted on a double-side carbon tape and the XPS data were calibrated by the carbon-related peak obtained from the tape.

References

1. Ding, Y.; Kim, Y. J.; Erlebacher, J. *Advanced Materials* 2004, *16*, 1897.

2. Wen, R.; Hong, M.; Byon, H. R. *J. Am. Chem. Soc.* 2013, *135*, 10870.

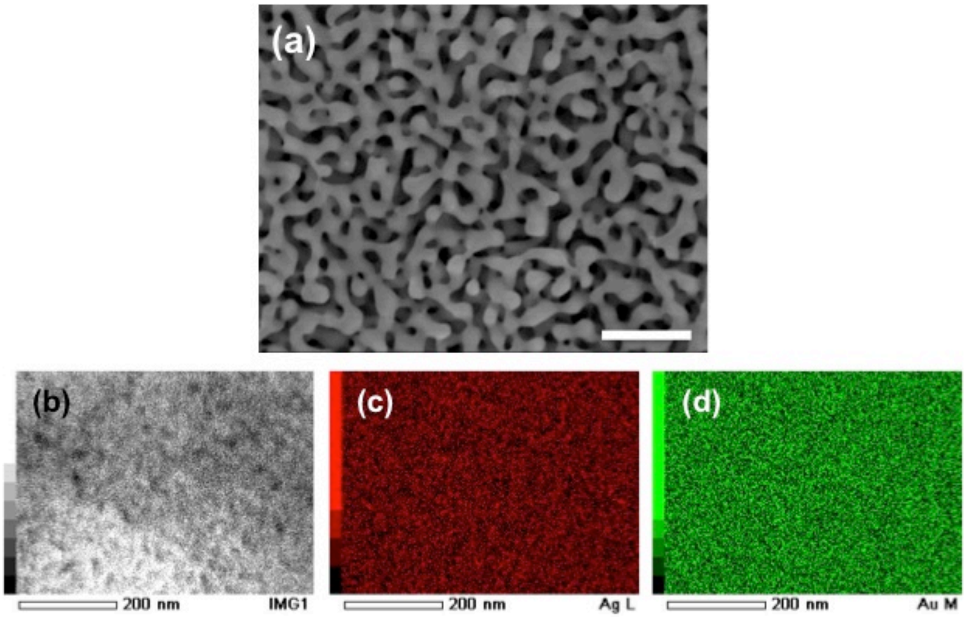

Figure S1. SEM and element mapping images of as-prepared NPG. (a) SEM image of NPG. The scale bar is 500 nm. (b) SEM and (c–d) the corresponding EDS mapping images of (c) Ag and (d) Au. The scale bars are 200 nm.

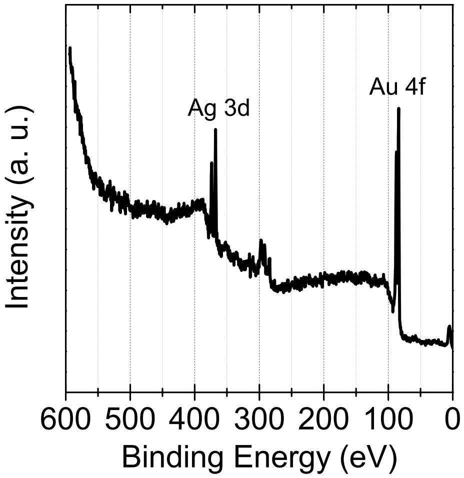

Figure S2. XPS survey of as-prepared NPG using synchrotron X-ray. The atomic % ratio of Ag/Au was around 30/70. Carbon impurity peak is also observed at around 285 eV.

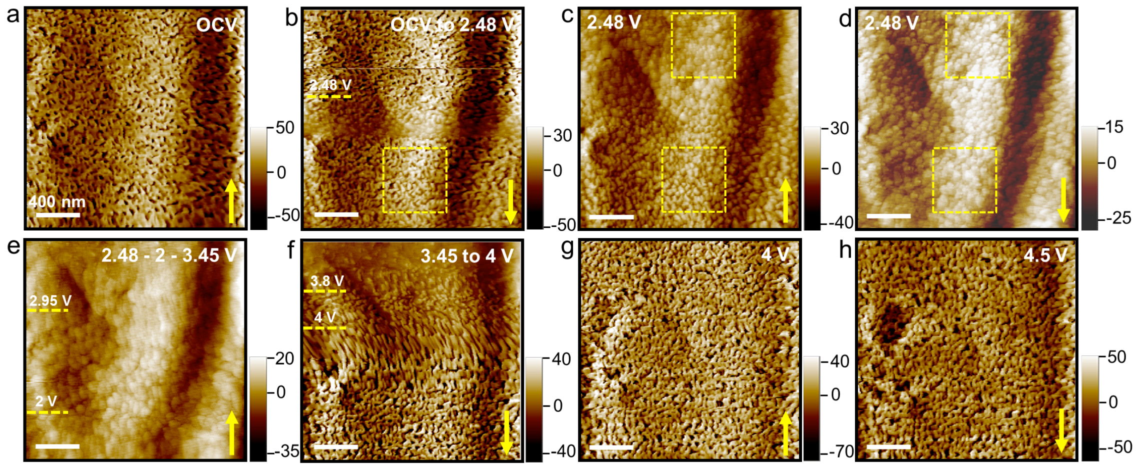

Figure S3. In situ AFM topography images of NPG electrode (same as Figure 2) with z-axis color scale bars (right side of each image, unit: nm). The z-axis is determined to show the clearest image of NPG and/or nanoparticle product morphology. The dashed boxes are zoomed in Figure 4 (b–f) with deflection mode.

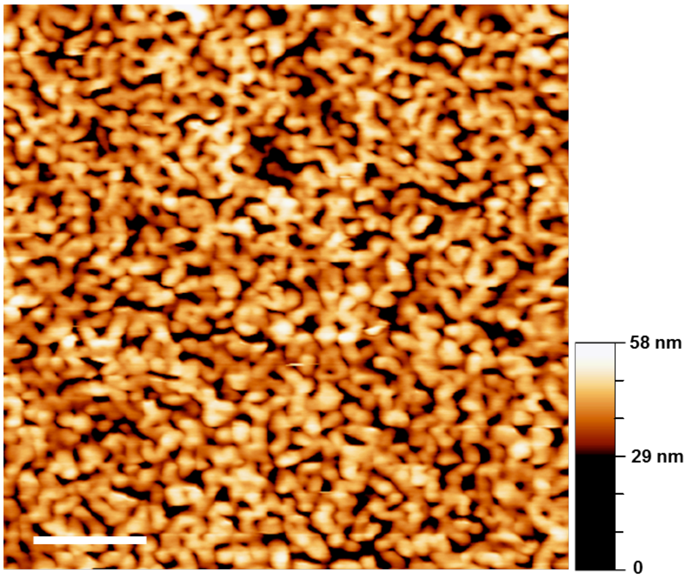

Figure S4. AFM topography image of NPG surface acquired after CV sweeping for ORR (2.0 V) and OER (up to 3.8 V) then 5 min holding at 3.8 V in O_2-saturated 0.1 M LiTFSI/tetraglyme. The scale bare is 600 nm. The right color bar indicates z-axis scale.

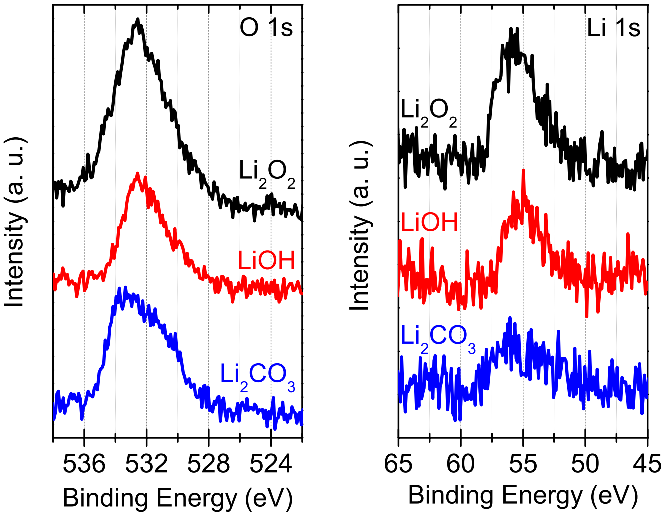

Figure S5. O 1s and Li 1s X-ray photoelectron spectra of reference Li_2O_2, LiOH and Li_2CO_3 using synchrotron X-ray with a photon energy of 650 eV. All reference powders were very thinly pasted on a double-side carbon tape. Large XPS peak shift, arising from charging effect in the insulating Li_2O_2, LiOH and Li_2CO_3, was corrected by the calibration as referring to carbon-related peak from the carbon tape positioned underneath the powders. The small ejected photoelectron current (I_s) from the insulating substances also resulted in low signal to noise ratio of spectra peaks despite with many scanning numbers; total 100 times of Li 1s and 75 times of O 1s for Li_2O_2, and 60 times of Li 1s and 45 times of O 1s for LiOH and Li_2CO_3. The reference O and Li 1s peaks are shown at 532.5/55.9 eV for Li_2O_2, 532.6/55.0 eV for LiOH, and 533.6/56.7 eV for Li_2CO_3. The Li_2O_2 and LiOH having similar peaks in the O 1s BE region can be identified in the Li 1s peaks. Unlike Li_2O_2 and LiOH, the Li_2CO_3 shows the asymmetric O 1s peak and broad Li 1s peak.

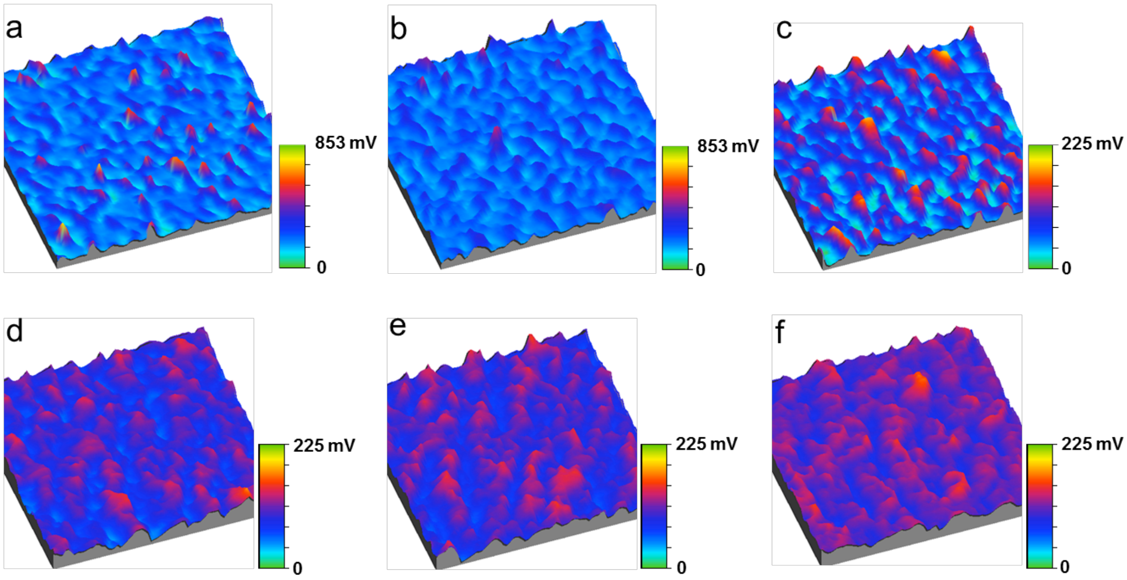

Figure S6. 3D AFM deflection images of NPG correlated with Figure 4 (a–f). The color bars on the right side of images indicate z-axis scale in deflection mode.