Supporting Information

Imaging Electrocatalytic Process on Single Gold Nanorods

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Experimental Section

Modification of Gold Nanoparticles. ITO slides were cut into small pieces (20 mm × 20 mm). The surfaces of ITO slides were cleaned in an ultrasonic bath with several steps. The slides were first ultrasonic treated in ethanol and acetone solutions to remove oily matter and then treated in water to remove water-soluble matter. The slides were cleaned in each solvent for more than 20 min. The cleaned ITO slides were dried under a stream of ultrapure nitrogen gas. Gold nanoparticles were modified on ITO slides via electrostatic adsorption by placing them in the diluted gold colloid solution (100 times) for 15 min. The GNP-functionalized ITO slides were rinsed with water to remove free nanoparticles on the surface and dried under a stream of ultrapure nitrogen prior to the dark-field measurements. The nanoparticles adsorbed on ITO slides were stable during the long-time electrochemical scanning as shown in Fig. S7 in the Supporting Information. The dark-field images showed no obvious difference before and after 100 circles of CV scanning from -0.10 V to 1.00 V.

Dark-Field Microscopy and Scattering Spectroscopy. The dark-field measurements were performed on an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser (0.8 < NA < 0.95) and an objective lens (40×, NA = 0.8). As shown in Fig. 1a, white light (100 W halogen lamp) was transferred through a light stop to form a ring-like light beam. After reflected by mirrors, the white light was irradiated on gold nanoparticles with an angle. As the side illumination of dark-field condenser, the incident light was transferred directly along with the incoming direction and could not be captured by objective lens. Therefore, the background is dark with very high signal to noise ratio. The excited plasmon resonance scattering light of GNPs was collected by objective lens. A true-color digital camera (Nikon DS-fi, Japan) was used to capture the dark-field color images as shown in Fig. 1c. The scattering light of gold nanoparticles was split by a monochromator (Acton SP2300i, Princeton Instruments, USA) which was equipped with a grating (grating density: 300 lines/mm; blazed wavelength: 500 nm) and recorded by a CCD (Pixis 400, Princeton Instruments, USA) to obtain the scattering spectra. The exposure time for every scattering spectrum and dark-field image were 5 s and 2 s, respectively. The scattering spectra from single gold nanorods were corrected by subtracting the background spectra taken from the adjacent regions.
SUPPLEMENTARY EXPERIMENTS

Figure S1 SEM images of mono-dispersed gold nanorods.

Figure S2 Peak intensity (a) and wavelength (b) change of plasmon resonance scattering spectra of a single GNR at open circuit.
Figure S3 Statistic averaged intensity change of entire gold nanoparticles in a dark-field image during CV scanning from -0.10 V to 1.0 V in 0.1 M KNO₃ solution, at scan rates of 10 mV/s, vs. Pt quasi-reference electrode.
Figure S4 Scattering spectra change of a single GNR under CV scanning from -0.10 V to 1.0 V in 0.1 M KNO$_3$ solution containing 1 mM H$_2$O$_2$, at scan rates of 5 mV/s (a), 10 mV/s (b) and 20 mV/s (c) vs. Pt quasi-reference electrode.
Figure S5 Statistic averaged intensity change of entire gold nanoparticles in a dark-field image during CV scanning from -0.10 V to 1.0 V in 0.1 M KNO$_3$ solution containing 1 mM H$_2$O$_2$, at scan rates of 10 mV/s, vs. Pt quasi-reference electrode.
Figure S6  Scattering spectral changes of four different nanoparticles (a-d) under CV scanning from -0.1 V to 1.0 V at scan rates of 10 mV/s, vs. Pt quasi-reference electrode. (1) Peak intensity (i) and wavelength (ii) changes of GNRs in 0.1 M KNO₃ solution without H₂O₂. (2) Peak intensity (i) and wavelength (ii) changes of GNRs in 0.1 M KNO₃ solution with 1 mM H₂O₂. (3) Differences of peak wavelength shift (i) and their differential results (ii) of GNRs in the absence and presence of 1 mM H₂O₂.
**Figure S7** Dark-field images of gold nanoparticles before (a) and after (b) CV scanning from 0.10 V to 1.0 V for 36 circles.

**Figure S8** Calculation procedure of the imaging results.