Electronic Supplementary Information

for

Single-Particle Spectroelectrochemistry: Electrochemical Tuning of Plasmonic Properties *via* Mercury Amalgamation in Mesoporous Silica Coated Gold Nanorods without Structural Deformation

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Experimental Section

Materials and Sample Preparation

HgCl₂ was purchased from Sigma-Aldrich (St. Louis, MO, USA). The AuNRs@mSiO₂ were obtained from Nanopartz (Loveland, CO, USA). The AuNR colloid solution was first diluted with 18.2-M Ω pure water to the appropriate concentration. The diluted solution was then sonicated for 15 min at room temperature. The samples were prepared by spin-casting the AuNR solution onto a pre-cleaned glass slide. Subsequently, a 22 mm × 22 mm no. 1.5 coverslip (Corning, NY) was placed on the glass slide.

Preparation of Spectroelectrochemical Cell

Spectroelectrochemical cell (SEC) was prepared using ITO glass (75 mm \times 25 mm \times 1.1 mm) as a working electrode. AuNRs@mSiO₂ were immobilized on an ITO glass by spin casting. Afterward, two adhesive imaging spacers (25 mm \times 25 mm \times 0.12 mm) with the hole size of 13 mm were placed on the ITO glass. Furthermore, two Pt wires with the diameter of 0.076 mm were placed between the imaging spacers as a counter electrode and reference electrode. Copper foil was placed on the external area of the ITO sample to connect working electrode to the instrument. The electrolyte was then dropped at the area of sample and a coverslip with the size of 22 mm \times 22 mm was placed on the top to make an isolated SEC.

Dark-Field Microscopy

DF microscopy imaging was performed under a Nikon inverted microscope (ECLIPSE Ti–U). In DF mode, the microscope utilized a Nikon Plan Fluor 100× 0.5-1.3 oil iris objective and a Nikon DF condenser. An Andor iXonEM+ CCD camera (iXon Ultra 897)

was used to record highly detailed DF scattering images of AuNRs@mSiO₂. The collected images were analyzed using ImageJ.

Single-Particle Scattering Spectroscopy

DF scattering spectra of AuNRs@mSiO₂ were acquired with an Andor spectrophotometer (SHAMROCK 303i, SR-303I-A) connected with an Andor CCD camera (Newton DU920P-OE). When obtaining a spectrum, the scanning stage moved the sample to the desired location so that only scattered light from the selected location was collected by the objective. The scattered light was directed to the entrance of the spectrophotometer, dispersed by a grating (300 l/mm), and detected by the Newton CCD camera. The background was measured at a region without any particles. The concentration of AuNRs@mSiO₂ deposited on the substrate was controlled to be approximately 1 μ m⁻² to facilitate single-particle characterization. Data analysis was performed with specially designed Matlab programs.

Spectroelectrochemical Measurements

Spectroelectrochemical experiments were performed using an Multichannel Potensiostat Wizmac series WIZECM-8100 Premium in a three-electrode system, whereby AuNR@mSiO₂ modified ITO-coated glass coverslips were used as the working electrode and Pt wires (50 µm in diameter) as counter and pseudoreference electrodes. A 0.1 M KCl solution at pH 6.5 was used as supporting electrolyte, to which various amounts of HgCl₂ were added for the nanorod amalgamation experiments in a custom-made electrochemical cell. For all linear sweep voltammetry measurements potentials were scanned at a rate of 10 mV/s. Single-particle spectra of randomly selected AuNRs@mSiO₂ were recorded before and

after the electrochemical step or in real time during the electrochemical step. The solution was then exchanged for 0.1 M KCl with added HgCl₂ at the concentrations of 5 μ M and 10 μ M. Again electrochemical measurements were performed with scattering spectra taken of the same selected AuNR@mSiO₂ before and after or real time during the electrochemical step. For background subtraction linear sweep voltammograms obtained in KCl only were subtracted from the respective data obtained in Hg²⁺- containing electrolyte.

Supplementary Figures



Fig. S1 SEM image to show many AuNRs@mSiO₂



Fig. S2 SEM image to show the shell thickness of single AuNRs@mSiO₂



AuNRs@mSiO₂ after LSV in 0.1M KCI, 10 μ M HgCl₂

Fig. S3 SEM image to show AuNRs@mSiO₂ after LSVs in 0.1-M KCl and 10-µM HgCl₂. No structural change was observed for AuNRs@mSiO₂ after LSV.



Fig. S4 A photograph to show the experimental setup for spectroelectrochemistry



Fig. S5 UV–Vis extinction spectrum of AuNRs@mSiO₂ (amalgamated) obtained after Hg amalgamation. The purple-dotted line indicates the position of the longitudinal LSPR peak.



Fig. S6 (A) A schematic depicting the electrochemical reduction on a AuNR@mSiO₂ in the presence of 0.1-M KCl and 5- μ M HgCl₂. (B) Linear sweep voltammograms obtained in 0.1-M KCl (red curve) and in the solution of 0.1-M KCl and 5- μ M HgCl₂ (black curve). (C) Histogram showing the change in LSPR wavelength of AuNRs@mSiO₂ before and after LSV in 0.1-M KCl and in 0.1-M KCl and 5- μ M HgCl₂. The reference electrode was a Pt wire.