Analysis of the Electron Transfer Property of Carbon Quantum

Dots on Gold Nanorods Surface via Plasmonic Resonance

Scattering Spectroscopy

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Experimental Section

1. Reagents and materials.

Gold nanorods (GNRs) with average dimensions of 68 nm in length and 40 nm in diameter were purchased from NanoSeedz (Hong Kong, China). The indium tin oxide (ITO) slides were purchased from the Wuhan Geao Chemical Technology Co. Ltd (Wuhan, China). Polydimethylsiloxane (PDMS) was purchased from Dow Corning (Wiesbaden, Germany) which was curing with a mix ratio 1:10 at 100 °C for 30 min. All other chemical reagents and materials are of analytical grade, and solvents were purified by standard procedures. All solutions were prepared by Milli-Qultrapure water with resistance of 18.2 M Ω cm at 25 °C (EMD Millipore, Billerica, USA) and were filtered with 0.02 mm Anotop filter (Whatman, Maidstone, UK). Two Pt electrodes, one is auxiliary electrode, the other one is reference electrode (Chenhua, Shanghai, China).

2. Experimental setup

The transmission electron microscopic (TEM) images were obtained on a JEM-2010 high-resolution transmission electron microscope (JEOL Ltd., Japan) equipped for analysis at an accelerating voltage of 200 kV. UV-vis spectra were obtained from Ocean Optic. Time-of-flight secondary ion mass spectrometry (ToF-SIMS V, IONTOF GmbH, Germany). The dark-field images were observed on an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser (0.8 <NA < 0.95) and a 40× objec-tive lens (NA = 0.8), and a white light source (100 W halogen lamp) was used to excite the plasmon resonance scattering light of GNPs. The scattered light was cap-tured through the objective lens and split by a monochromator (Acton SP2300i, PI) equipped with a grating (grating density = 300 lines/mm; wavelength = 500 nm), and finally recorded by a spectrometer CCD (PIXIS 400, Princeton Instruments, USA) to obtain the scattering spectra. One part of scattered light was collected by a true-color digital camera to obtain the dark-field color images. The other fraction of light was collected by a spectrometer to obtain single particle scattering spectra. All electrochemical measurements were conducted at an electrochemical workstation (CHI 660, CH Instruments, Chenhua, Shanghai, China).

3. Preparation of the carbon quantum dot.

The carbon nanodots were prepared with the modified procedures according to the previous publication^[1]. Briefly, a stable NaOH-saturated ethanol solution was used as

electrolyte and graphite rods as both the anode and cathode. When the constant potential of 5 V (a DC voltage) was added to the two electrodes for 3 h, the color of the electrolyte aqueous gradually changed from colorless to yellow. The excess NaOH precipitate was removed by centrifugation to afford homogeneous carbon nanodots solution.

4. Carbon covering the preparation of GNRs modification of ITO electrode.

Indium Tin oxide (ITO) slides were cleaned in an ultra-sonic bath. First, the slides were ultrasonic washed in ethanol and acetone for 1 h to remove oily matter and then sonicated in pure water for 1 h to remove water-soluble matter, allowing them to dry, and then placing them in a UV ozone cleaner (Jelight Co. model 342) for 25 min on each side. The clean ITO slides were silanized by incubating them in ethanol solution containing 6% (v/v) triethoxyoctylsilane for 4h, and then rinsed with ethanol several times before drying

them at 110°C for 1h. The silanized ITO slides were modified with diluted GNRs solution

 $(40\times)$ for 5 min. The ITO was modified with GNRs via electrostatic adsorption by placing them translocating of the GNRs. The GNRs-functionalized silanized ITO (GNRs/ITO) slide was rinsed with water, and dried with nitrogen condition. Then 0.1 mg/mL 100 µL aliquot of carbon quantum dot was drop-casted on GNRs-functionalized silanized ITO slide with a geometric area of 2 cm², which were further allowed to dry under room temperature, we have been given carbon covering of GNRs modification of ITO electrode (CQDs/GNR/ITO).

5. Electrochemical measurements.

All electrochemical measurements were conducted with an electrochemical workstation (CHI 660, CH Instruments). A conventional three-electrode configuration was employed in all experiments, which involved an ITO slide as working electrode, a platinum wire as auxiliary electrode and a platinum wire as reference electrode., Several successive electrochemical scanning cycles between -500 mV and 100 mV at a scan rate of 10 mV·s⁻¹ were obtained, and KNO₃ solution (400 mM) was employed as electrolyte in all the electrochemical experiments.

6. Single nanoparticle DFM imaging and scattering spectroscopy measurements.

The dark-field measurements were carried out on an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser (0.8 < NA < 0.95) and a $40 \times$ objective lens (NA=0.8) The GNPs functionalized ITO slides were immobilized on a platform, and a white light source (100 W halogen lamp) was used to excite GNPs and generate plasmon resonance scattering light. The scattered light was collected by a true-color digital camera (Nikon DS-fi, Japan) to generate the dark-field color images, and was also

split by a monochromator (Acton SP2300i, PI, USA) that was equipped with a grating (grating density: 300 lines/mm; blazed wavelength: 500 nm) and recorded by a spectrograph CCD (CASCADE 512B, Roper Scientific, PI, USA) to generate the scattering spectra. The scattering spectra from individual nanoparticle were corrected by subtracting the background spectra taken from the adjacent regions without GNPs and dividing with the calibrated response curve of the entire optical system. Additional details of the dark-field microscopy and spectroscopy setup have been reported in a previous work.^[2]



Figure S1. Typical TEM image of GNRs.



Figure S2. TEM image (left) and size distribution (right) of carbon quantum dots.



Figure S3. FTIR spectrum of carbon quantum dot.



Figure S4. Dark-field images of individual GNRs modified ITO electrode, before (A) and after (B) the modification of CQDs. (C) Typical scattering spectra of single GNRs, before (black solid line) and after (red solid line) the modification of CQDs. (D) The corresponding histogram of the scattering spectral peak shift for single GNRs, with the presence of CQDs film shell.



Figure S5. Fluorescence spectrum of CQDs on ITO/glass substrate, in the absence (black solid line) and presence (red solid line) of single GNRs.



Figure S6. Scattering spectra of single GNRs under the cyclic triangle wave scanning. Figure A-B and C-D show the scattering spectra of single GNR and CQDs/GNRs recorded every ten seconds in the 1st circle respectively, while the arrows show the scan directions. Cyclic voltammograms of GNRs modified ITO electrode were recoded in 400 mM KNO₃, scanning from -0.50 V to 1.0 V for 3 circles, at a scan rate of 10 mV.

References

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