†The Supplementary Data of

Optical Monitoring of Faradaic Reaction using Single Plasmon-Resonant Nanorods Functionalized with Graphene

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S-1 Experimental section

Chemicals, Materials and Instrumentations

Materials: Gold nanorods (GNRs) with average dimensions of 68 nm in length and 40 nm in diameter were purchased from NanoSeedz (Hong Kong, China). Nicotinamide adenine dinucleotide hydrogen (NADH) and 3-aminopropyltriethoxysilane (APTES) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were of analytical grade, and all chemicals were used without further purification. All solutions were prepared using 18 MΩ·cm deionized water obtained with a Mili-Q System (Billerica, MA, USA).

Synthesis of graphene oxide (GO): GO was prepared from graphite powder according to the modified Hummers method.[1] Briefly, graphite powder (5 g) was oxidized by adding to a hot solution (80 ºC) of concentrated H_2SO_4 (30 mL) containing $K_2S_2O_8$ (10 g) and P_2O_5 (10 g). The resultant dark blue mixture was thermally isolated and slowly cooled to room temperature over a period of 6 h. The mixture was diluted to 300 mL and then filtrated with a 0.22 μm filter membrane (Generay Biotech Co., Ltd., Shanghai, China). The filtered product was dried overnight at 60 ºC. The preoxidized graphite powder (4 g) was added to 82 mL cold H_2SO_4 (0 ºC), and 12 g $KMnO_4$ was gradually added under stirring in ice-bath. The resulted mixture was further stirred at 35 ºC for 2 h and distilled water (200 mL) was added. The reaction was stopped with the addition of a mixture of 560 mL distilled water and 10 mL 30% H_2O_2. For purification, the mixture was washed with 1:10 HCl and then with water. The GO product was resuspended in water to a brown dispersion, which was subjected to dialysis to remove residual metal ions and acids. The purified GO dispersion was sonicated for 1.5 h at 300 W to exfoliate GO, and unexfoliated GO was removed by centrifugation (3000 rpm, 5min).

Modification Procedure of GO/GNRs and erGO/GNRs: GO/GNRs was modified on the silanized ITO slides. The ITO slides were cleaned by rinsing the slides with methanol, allowing them to dry, and then placing them in a UV ozone cleaner (Jelight Co. model 342) for 25 min on each side. Slides were checked using water contact-angle measurements to determine cleanliness; a contact angle of 10° indicated that slides were sufficiently clean to produce uniform silane monolayer. The cleaned ITO slides were dipped in APTES (1% v/v) in ethanol for 8 h, rinsed with ethanol, and heated in an oven at 120 °C for 15 min. The silanized ITO slides were modified with diluted GNRs solution for 5 min. The GNRs-functionalized silanized ITO slide was rinsed with water, and dry under a stream of nitrogen. Then 50 μL aliquot of homogeneous suspension of GO was dropcasted on GNRs-functionalized silanized ITO slide with a geometric area of 2 cm^2, which were further allowed to dry under room temperature.

The erGO/GNRs/APTES/ITO electrode was prepared by immersing the GO/GNRs/APTES/ITO electrode into a phosphate buffer (PB, 0.1 M, pH 7.0) solution, followed by several successive electrochemical scanning cycles between 0 V and -0.8 V (*vs*. Ag/AgCl) at a scan rate of 0.1 $V \cdot s^{-1}$.

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× 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.

Electrochemical measurements: All electrochemical measurements were conducted at 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 auxiliary electrode and an Ag/AgCl wire electrode. Phosphate buffer (0.1 M, pH 7.0) was employed as electrolyte in all the electrochemical studies.

Reference

[1] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339-1339.

S-2. Figures S1-S9

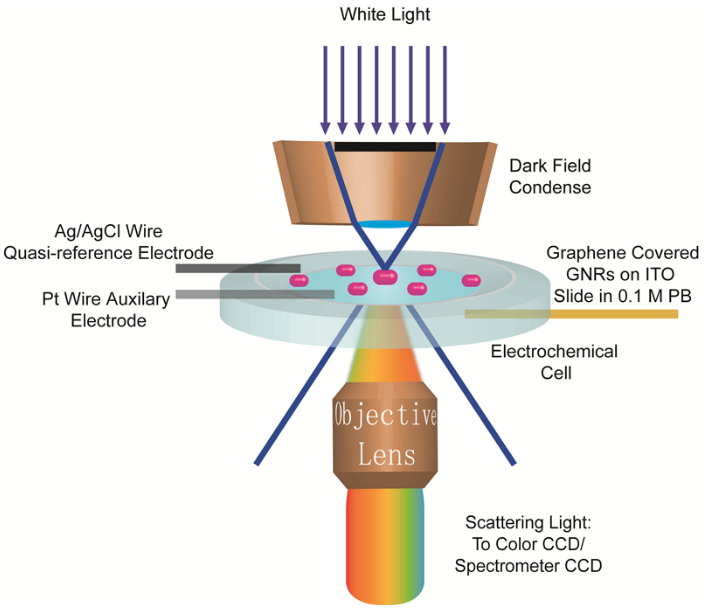

Fig. S1. Experimental configuration of the dark-field microscopy and plasmon resonance Rayleigh scattering spectroscopy, and the setup of the electrochemical cell.

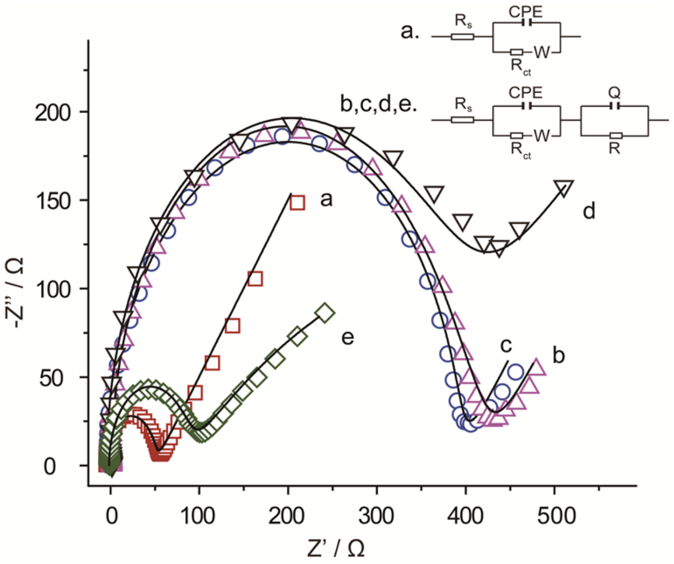

Fig. S2. Electrochemical impedance plots in the presence of 5 mM $Fe(CN)_6^{3-}$ and 5 mM $Fe(CN)_6^{4-}$ containing 0.1 M KCl on ITO electrodes: (a) bare ITO, (b) APTES/ITO, (c) GNRs/APTES/ITO, (d) GO/GNRs/APTES/ITO and (e) erGO/GNRs/APTES/ITO electrodes.

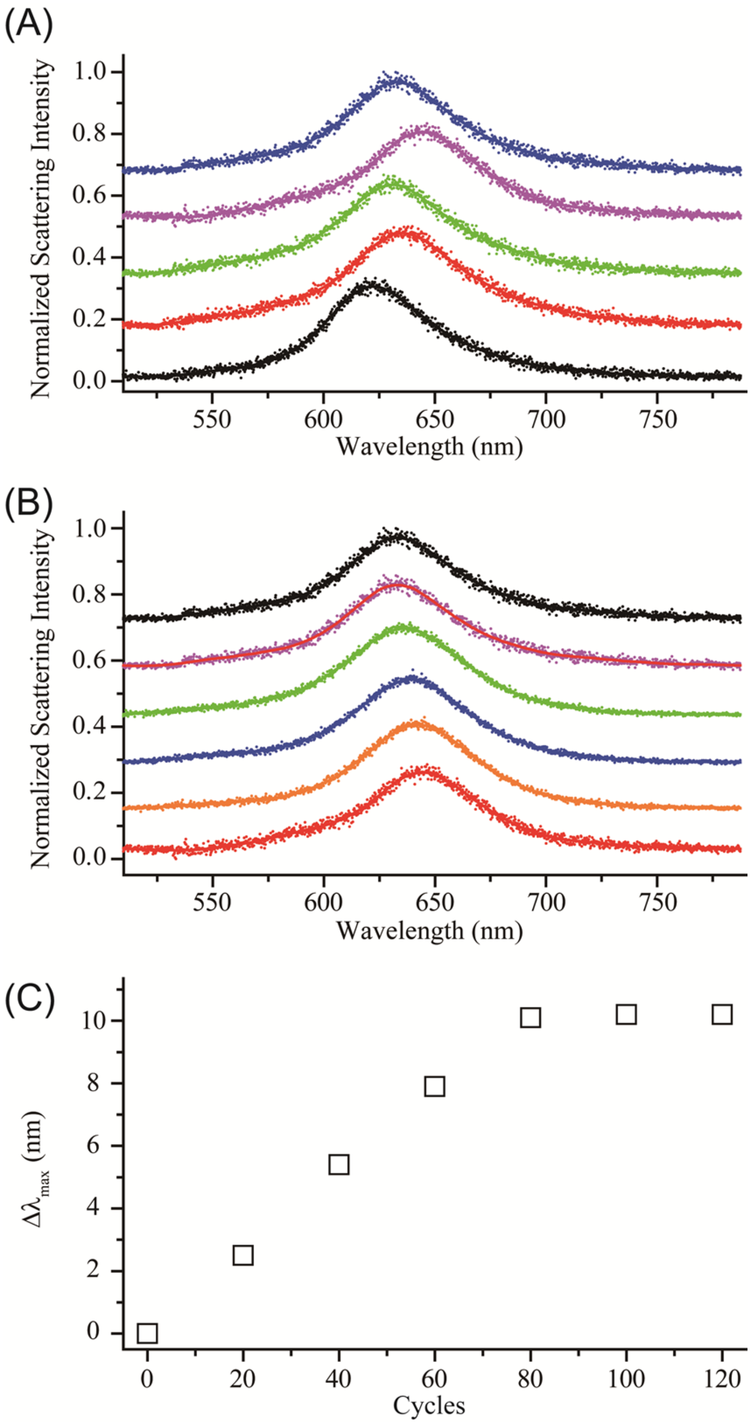

Fig. S3. (A) Plasmon resonance Rayleigh scattering spectra of single gold nanorods in PB solution (black curve), overcoated with 5 µg/cm^2 GO (red curve), 5 µg/cm^2 erGO (green curve), 10 µg/cm^2 GO (purple curve) and 10 µg/cm^2 erGO (blue curve). (B) Plasmon resonance Rayleigh scattering spectra of single gold nanorods depending on different scanning cycles (from bottom to top: 0, 20, 40, 60, 80 and 100). (C) Scattering spectral shift ($\Delta\lambda_{max}$) of single GNRs depending on different scan cycles.

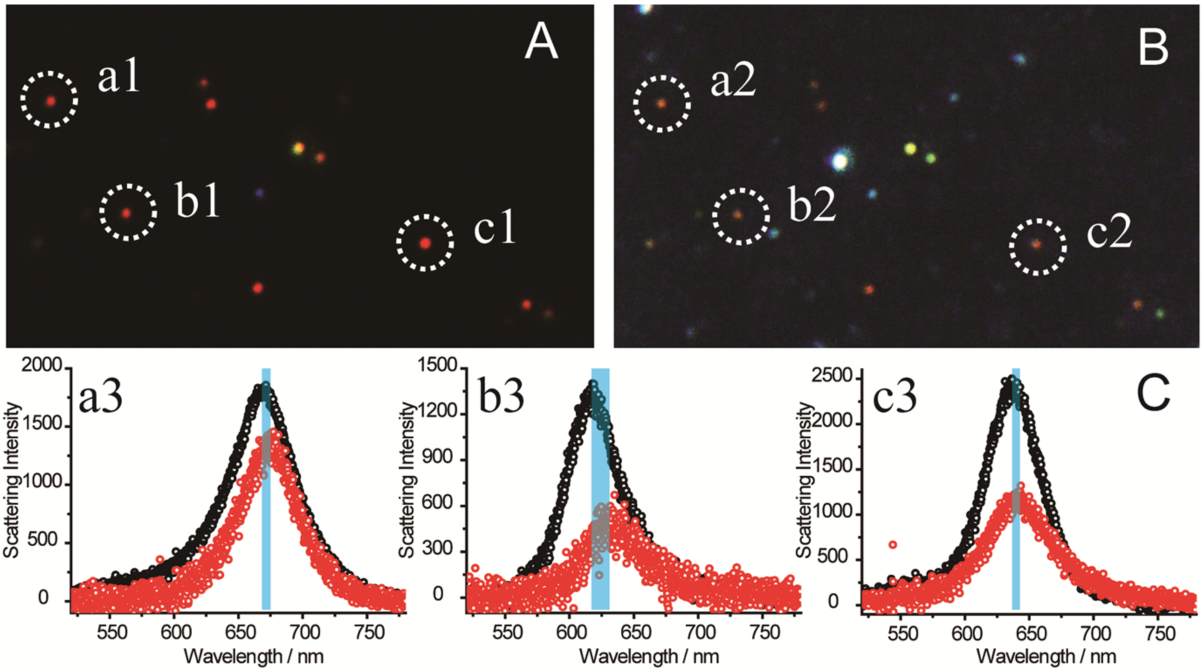

Fig. S4. Typical dark field microscopy images (A-B) and plasmon resonance Reyleigh scattering spectra (C) of single GNRs before and after the modification of graphene oxide. a1-c1: DFM of single GNRs on silanized ITO. a2-c2: DFM of GO covered single GNRs on silanized ITO. a3-c3: PRRS of bare (black) and GO covered (red) GNRs.

PRRS spectra peak ($\lambda_{\max}$) of three GNRs with varied sizes were monitored, with values of 618, 635 and 670 nm, respectivily. Upon the deposition of GO, the dielectric constant of local environment was changed, which redshift PRRS spectra of single GNRs to certain extend. When GNRs were covered by 10 μg/cm2 of GO, the red shift were observed to be 15, 7 and 6 nm, respectivily (As shown in Fig. S4, above). It seems that gold nanorods with lower aspect ratio and shorter scattering wavelength are more sensitive to GO deposition.

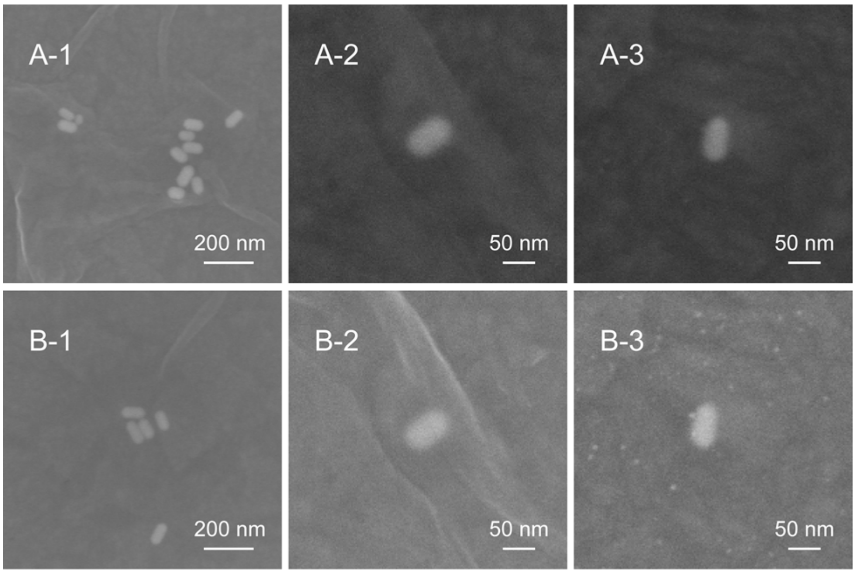

Fig. S5. Scanning electron microscope images of gold nanorods covered by (A) graphene oxide and (B) electrochemically reduced graphene oxide.

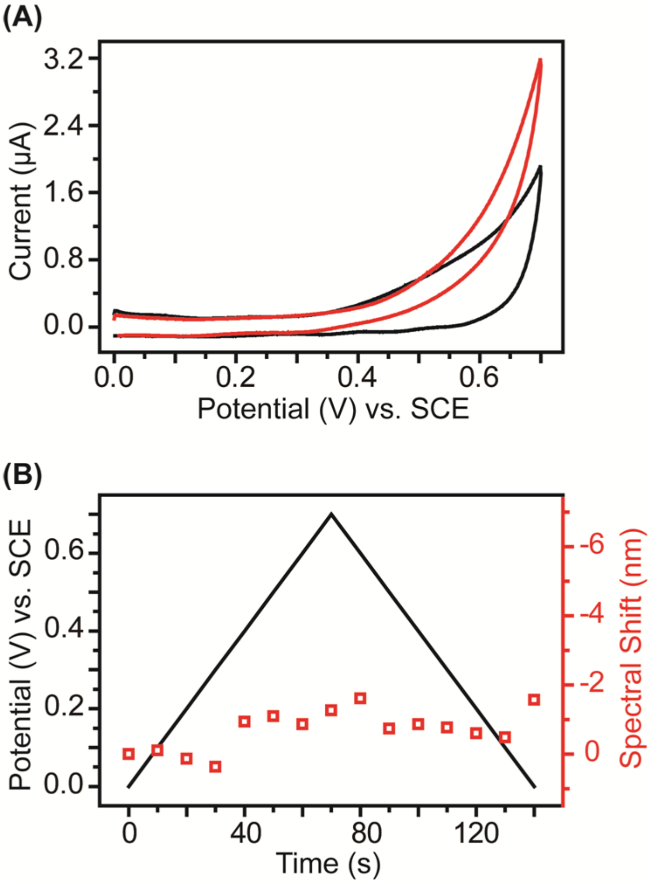

Fig. S6. Plasmonic shift of single gold nanorod synchronized with voltammetry on GNRs/APTES/ITO electrode. (A) Cyclic voltammograms recorded at 10 mV/s in the absence (black line) and presence (red line) of 3.0 mM NADH. (B) Faradaic current (black line) and spectral shift (red triangle) as a function of applied potential and time.

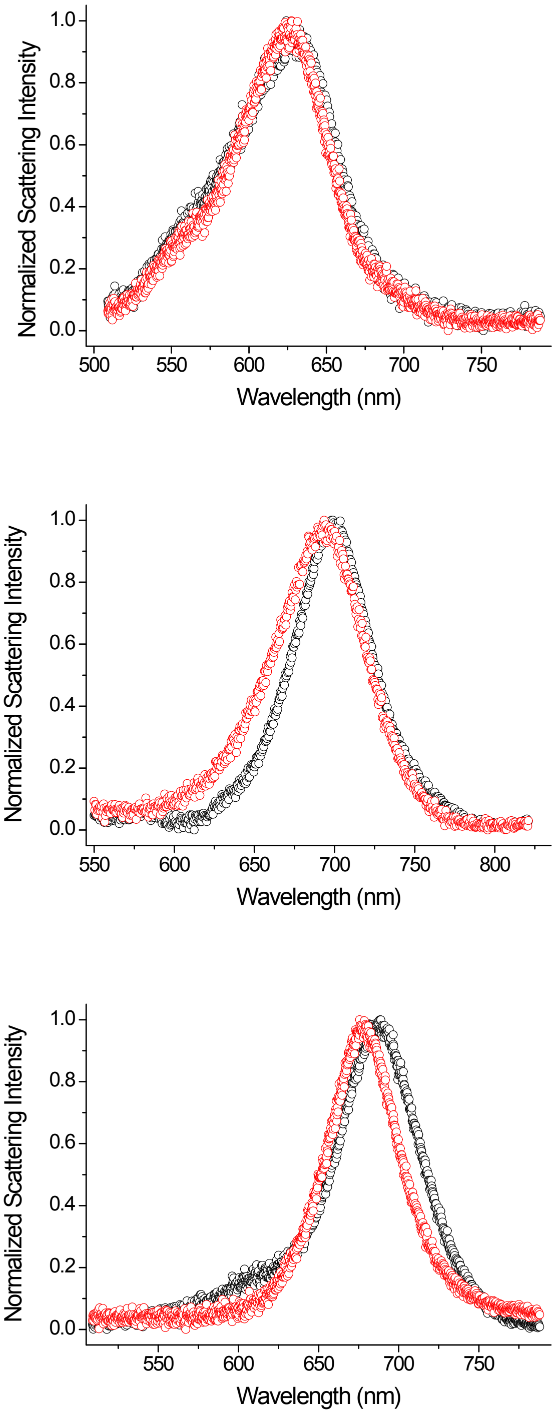

Fig. S7. The PRRS spectra of single GNRs overcoated with 10 μg/cm^2 GO (black) or erGO (red). The erGO were formed by scanning the GO covered GNRs/ITO from 0 to -0.8 V for 100 cycles, in phosphate buffer solution.

PRRS spectra of single GNRs were recorded at the GO/GNRs modified ITO electrode. After scanning cyclic voltammetry (CV) between 0 V and -0.8 V for 100 cycles, GO was thoroughly reduced, $\lambda_{\max}$ of single GNRs in GO-erGO hybrid material exhibit significant blue shift (As shown in Fig. S7, above). These results indicate that the observed modulations of the PRRS are attributed to the charge carrier density injected into the erGO through electrochemically reduction. For GNRs covered by graphene oxide, even the nanoparticles have similar initial scattering spectra and scattering maximum, they display different spectral shifts when the graphene oxide film was gradually reduced. In addition to the particle size distribution, the particle surface property, ITO conductivity and the graphene thickness (As shown in Fig. S8, below) difference at nanoscale may also have influence on the scattering peak shifts of nanoparticles.

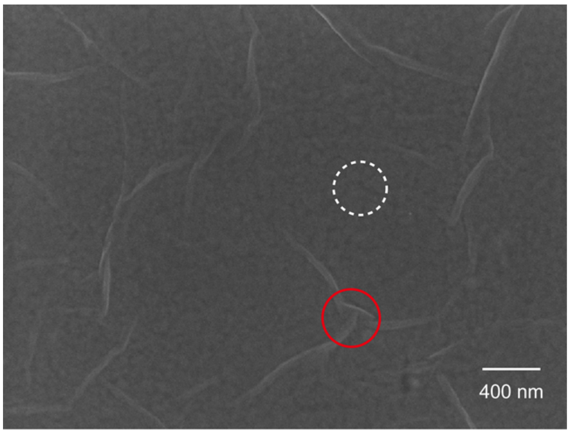

Fig. S8. Scanning electron microscope images of silanized ITO covered by graphene oxide. Red and white circles show nanoscale differnce of the grahene oxide film.

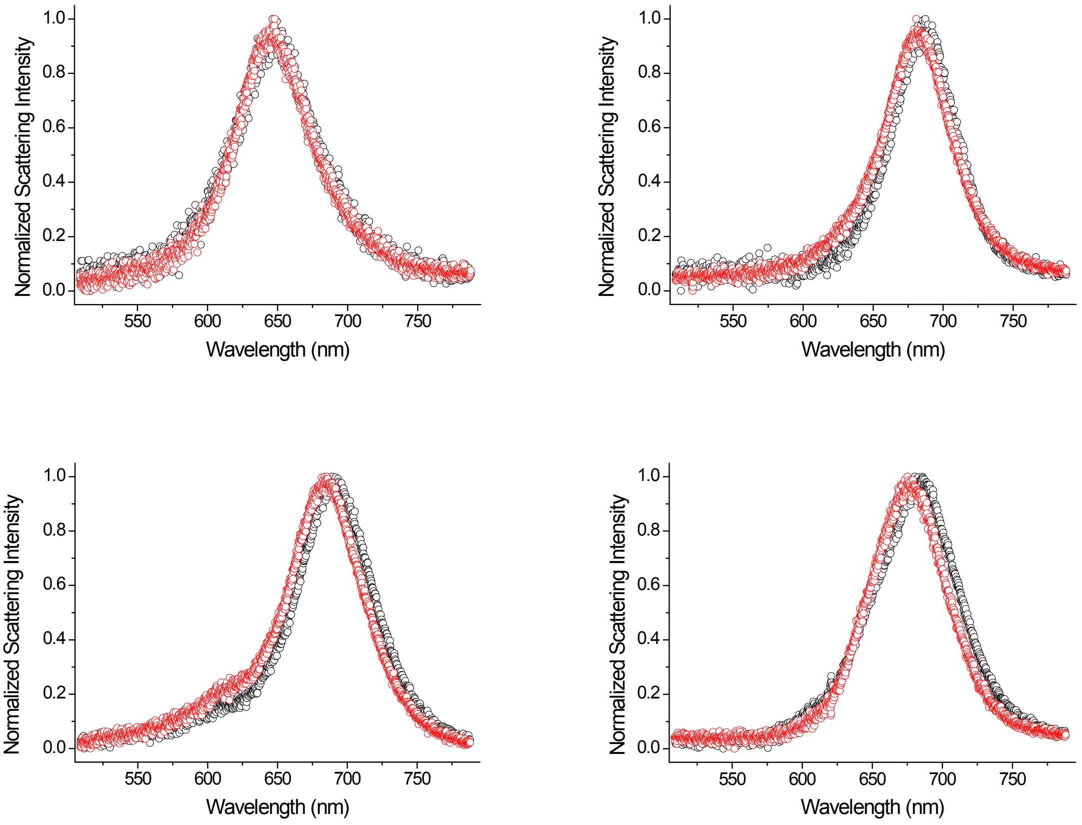

Fig. S9. Scattering spectra of different individual gold nanorods covered by GO with peak wavelength from 650 nm to 690 nm at potential of +0.6 V, in the presence (red) and absence (black) of 3.0 mM NADH.

Electron-transfer process was also investigated by using different individual gold nanorods. Potential of +0.6 V was applied to the GO/GNRs/APTES/ITO electrode before and after the addition of 3.0 mM NADH. It can be observed that NADH lead to different degrees of λ_{max} shift for varied GNRs. The λ_{max} value at the range of 3 nm and 10 nm were observed (As shown in Fig. S9, above). The nanorods with higher aspect ratio and larger scattering wavelength are more sensitive to surface electron density changes, similar with previous report (*Nat. Nanotech. 2008, 3, 598-602*). However, the size distribution isn't the only factor.

S-3 Scattering Spectral shift and Electron Density Calculation

To quantify the effects of electron injection on the PRRS spectra of single GNRs caused by NADH oxidation, the relationship between the surface plasmon resonance and the electron density is according to the follow equations:

$$\lambda_{\mathrm{p}} = \frac{2\pi \mathrm{c}}{\omega_{\mathrm{p}}} = \sqrt{\frac{4\pi^2 \mathrm{c}^2 \mathrm{m} \varepsilon_{\mathrm{o}}}{\mathrm{Ne}^2}}$$

(*Equation S1*)

$$\lambda = \lambda_{\mathrm{o}} \left(1 - \frac{\Delta \mathrm{N}}{2\mathrm{N}}\right)$$

(*Equation S2*)

$$\lambda_{\mathrm{o}} = \lambda_{\mathrm{p}} \sqrt{\varepsilon_{\infty} + \varepsilon_{\mathrm{m}} \left(\frac{1 - \mathrm{L}}{\mathrm{L}}\right)}$$

(*Equation S3*)

$$\Delta\lambda_{\mathrm{max}} = \lambda - \lambda_{\mathrm{o}} = -\frac{\Delta \mathrm{N}}{2\mathrm{N}} \lambda_{\mathrm{p}} \sqrt{\varepsilon_{\infty} + \varepsilon_{\mathrm{m}} \left(\frac{1 - \mathrm{L}}{\mathrm{L}}\right)}$$

(*Equation S4*)

Where λ_p is the bulk plasma wavelength, λ is the measured surface plasmon peak wavelength, λ_o is the plasmon peak position without electron injection and $\Delta\lambda_{max}$ is spectra shift. N is the electron density in the uncharged single GNRs, ΔN is the electron density injected to the single GNRs, ε_∞ is the high frequency contribution to the metal dielectric function, ε_m is the dielectric constant of the medium and L is the particle shape factor. For gold, λ_p is 131 nm and ε_∞ is 12.2. The full length and full width for the single GNRs by SEM characterization are 60 nm and 40 nm respectively. Based on one gold atom as 0.0170 nm^3, the number of gold atoms N in the single GNRs is calculated to be 4.04×10^6. In water the dielectric constant ε_m is 1.33^2=1.78. The PRRS spectra of the single GNR is 623 nm, thus L is calculated to be 0.146. The electron density injected to the single GNRs could be calculated according to equation S4.