Supporting Information for

Electrochemical impedance spectroscopy of single Au nanorods

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Materials and methods

1.1 Materials and instruments

Hexadecyltrimethylammonium bromide (CTAB, ⩾ 99%), L-Ascorbic acid (AA, 99%) and sodium borohydride ($NaBH_4$, 99%) were purchased from Sigma Aldrich. Hydrogen tetrachloroaurate (Ⅲ) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) and hydrochloric acid (HCl, 37 wt.% in water) were purchased from Sinoparm Chemical Reagent Co., Ltd in China. Sodium oleate (NaOL, > 97.0 %) and silver nitrate ($AgNO_3$, 99%) were purchased from Aladdin reagent Co., Ltd in China. Indium tin oxide (ITO) covered glass slides (8 ohms/square, 1.1 mm thick) were purchased from Wuhan Jinge-solar Energy Technology Co., Ltd. Ultrapure water with a resistivity of 18.2 MΩ cm^{-1}, which produced by a Milli-Q apparatus (Millipore), was used in all experiments. All chemicals were used as received without further purifications.

A Hitachi S-4800 field emission scan electron microscopy (SEM) was used to acquire the SEM images of AuNRs. And a UV-Vis spectrophotometer (G9821A, Agilent Technologies) was used to acquire the optical absorbance spectra of AuNRs.

1.2 The monochromatic dark-field imaging system building

The monochromatic dark-field imaging system (Figure 2a) was consisted of an inverted dark-field microscope (Eclipse Ti-U, Nikon) equipped with an oil immersion dark-field condenser (NA=1.20-1.43) and a water immersion objective lens (60x, NA=1.0). A supercontinuum white laser (EXR-15, NKT Photonics), which was equipped with an acousto-optical tunable filter (AOTF, SuperK SELECT VIS-NIR), was used as the excitation light source for single AuNRs. An AC modulation voltage, which was controlled by a potentiostat (Autolab PGSTAT302N, Metrohm AG) via an external function generator (33220A, Agilent), was applied to the electrochemical cell. A charged-coupled device (CCD, Pike F032B, Allied Vision Technologies) and a photon multiplier tube (PMTSS-A, Thorlabs) were used to acquire scattered light of single AuNRs. Here, an OptoMask (Cairn Research) was used to isolate the particle of interest from nearby particles. A data acquisition board (USB-6281, National Insrtruments) was used to synchronize recording the CCD TTL signal and electrochemical recordings from potentiostat. A lock-in amplifier (SR865, Stanford Research Systems) was used to synchronize recording the voltage-modulated optical signals of single AuNRs and electrochemical recordings.

1.3 Synthesis of AuNRs

The Au nanorods (AuNRs) were prepared by an improved seed-mediated approach.[1] Briefly, 0.6 mL of fresh and ice-cold 0.01 M $NaBH_4$ was diluted to 1 mL using water and was quickly added all at once to the 10 mL mixture consisting of 5 mL of 0.2 M CTAB and 5 mL of 0.5 mM $HAuCl_4$. This mixture was vigorous stirred for 2 min and aged at 30 °C for 30 min. To prepare the growth solution, 1.8 g of CTAB and 0.2345 g NaOL were dissolved in hot water (~ 50 °C). 590 μL of 10 mM $AgNO_3$ was then added to the 20 mL of CTAB-NaOL solution and this mixture was kept undisturbed for 15 min. 20 mL of 1 mM $HAuCl_4$ was added and was then stirred for 90 min. After that, 160 μL of concentrated HCl was injected into the reaction mixture. Another 15 min later, 70 μL of 0.01 M AA was added in, and the reaction mixture was vigorously stirred for 30 s. Finally, 10 μL of seed solution was injected into the growth solution and it was left undisturbed at 30 °C for overnight to complete the AuNRs growth.

1.4 Preparation of the electrochemical cell

The electrochemical cell was prepared with two cleaned ITO glass slides and polydimethylsiloxane (PDMS). First, the ITO glass slides were sequentially cleaned in an ultrasonic bath for 40 min with acetone, ethanol and ultrapure water. Here, the acetone and ethanol were used to remove oily matter, and the ultrapure water was used to remove water-soluble matter. And then, the ITO glass slides were dried with a stream of nitrogen. After that, 20 μL of 10000-fold diluted AuNRs colloids was dropped onto the surface of ITO glass slide surface, and then it was dried in vacuum for 1 h at 45 °C. The AuNRs-modified ITO glass slide was subsequently washed using ultrapure water and dried with a stream of nitrogen. Finally, the AuNRs-modified ITO glass slide and another ITO glass slide without AuNRs modification were mounted together using PDMS as spacer to build an electrochemical cell. Dissolved oxygen was removed from 0.1 M KCl solution by bubbling nitrogen in order to inhibit the reduction of oxygen. Oxygen-free solutions were used as the electrolyte solutions throughout the work.

1.5 Single AuNRs scattering spectra acquisition

The scattering spectra of single AuNRs (Figure 2c) were acquired using monochromatic dark-field microscopy. Note that the acquisition of scattering spectra of single AuNRs was performed in the absence of voltage modulation. AOTF was used to select a single wavelength from 670 nm to 860 nm with a typical bandwidth around 10 nm, and then CCD was used to record the scattering intensity of single AuNRs at each wavelength. Finally, the scattering intensity of single AuNRs at each wavelength as a function of wavelength was used to plot single AuNRs scattering spectra.

1.6 Impedance measurement of single AuNRs

Before measuring the EIS of single AuNRs, the open-circuit voltage of the system is determined to be + 52 mV. And then, the EIS of single AuNRs was performed with a sinusoidal AC modulation (peak-to-peak voltage amplitude: 1 V, offset: − 0.5 V, variable frequency ranged from 0.2 Hz and 30 kHz). The CCD was used to capture the dark-field scattering images of single AuNRs had a maximal acquisition rate of 953 frames per second (fps) at pixel resolution of 76 × 58. When CCD was used to measure the EIS of single AuNRs, a Fourier transform algorithm was applied to the dark-field images data captured by the CCD to generate amplitude information for single AuNRs. PMT was alternatively used to record the optical signals of single AuNRs by placing an OptoMask in front of the PMT. PMT was either connected with a digital acquisition device (DAQ) to record the original intensity curve, or connected with a lock-in amplifier to directly read the corresponding amplitude and phase information.

Results and Discussion

2.1 Characterization of synthesized AuNRs

As shown in Figure S1a, the synthesized AuNRs show a transverse plasmon resonance peak at 513 nm and a longitudinal plasmon resonance peak at 762 nm. As shown in Figure S1b, AuNRs are straight and very uniform in dimension with an average length of 85.4 ± 8.2 nm and an average width of 27.8 ± 2.8 nm.

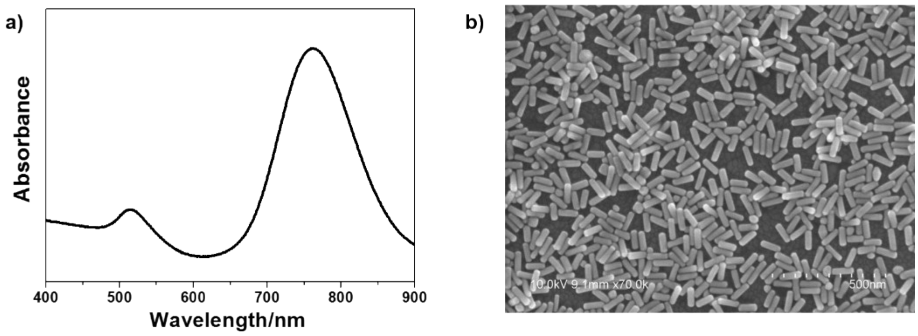

Figure S1. a) and b) UV-Vis absorbance spectrum and SEM image of the synthesized AuNRs, respectively.

2.2 The quantitative conversion from intensity fluctuation (at single wavelength) to spectral shift

Briefly, the electrochemical charging (from 0 V to – 1 V) of a single AuNR induces a blue shift of the LSPR band from λ_1 to λ_2 as shown in Figure S2. If a single wavelength illumination (λ=728 nm, see Figure 1) is applied all the time, an intensity increase from I_1 to I_2 is thus observed. If the spectral shift is sufficiently small (< 10 nm), a linear relationship between $\Delta\lambda$ and ΔI roughly holds. The conversion coefficient is the steepness (or slope) of the original spectrum, which clearly depends on the selection of illumination wavelength. However, similar slopes are often obtained if the wavelength is located in the range of 50%–80% maximal intensity, for instance, 720-740 nm. A calibration is performed to determine the conversion coefficient at the particular wavelength used in the experiment for each AuNRs (see Figure S11).

The conversion model remains valid even if a high frequency modulation (kHz) is applied. In this case, a lock-in amplifier reports the modulation amplitude (ΔI) of the PMT signal. Then, the same linear conversion is used to obtain the spectral shift $\Delta\lambda$.

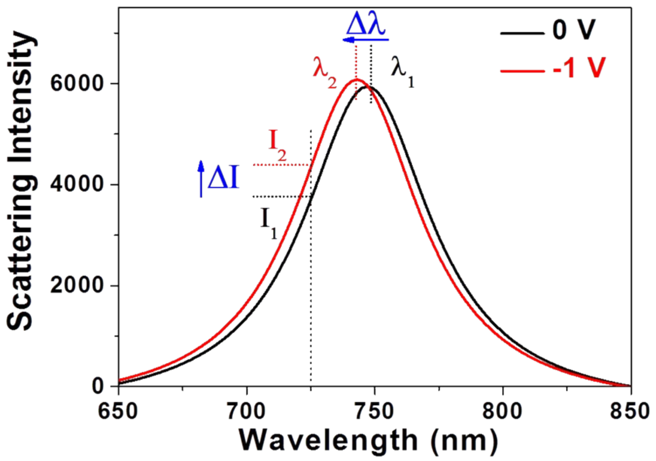

Figure S2. Full scattering spectra of a single AuNR under the voltages of 0 V (black) and −1 V (red), respectively.

2.3 Original intensity curves and the corresponding Fourier transform of a single AuNR

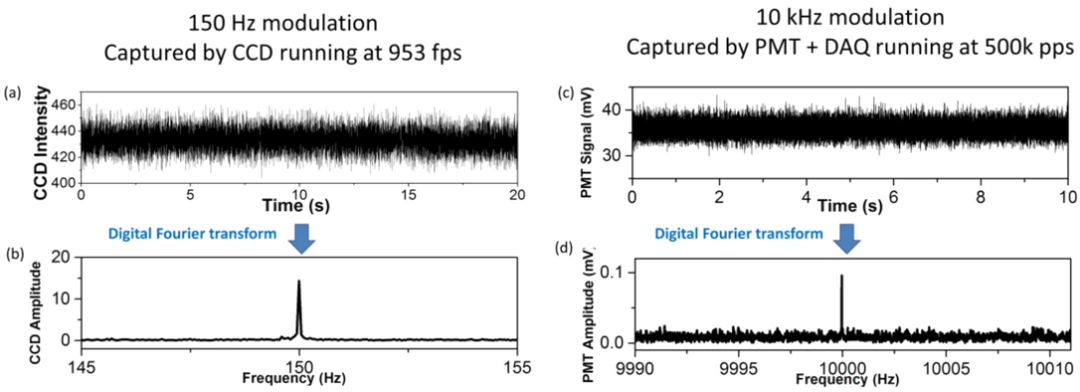

Figure S3. Original intensity curves (a, c) and the corresponding Fourier transform of a single AuNR under the potential modulation of 150 Hz (a, b, captured by CCD) and 10 kHz (c, d, captured by PMT and digital acquisition device, DAQ), respectively. Note the unit of CCD amplitude is Intensity Unit (IU) from gray-scaled camera image. That of PMT amplitude is the voltage (mV or μV) across a transistor when photocurrent passes through it.

2.4 Oxidation of a single AuNR under positive potentials

Irreversible oxidation of single AuNRs was observed (Figure S4) when applying positive potentials to the surface-bound AuNRs. That is the main reason that we focus on the reversible non-Faradaic charging process in the negative potential range. The oxidation of AuNRs led to gradual decrease in the scattering intensity due to the formation of non-plasmonic Au oxides. Reduced fluctuation amplitude was also observed under potential modulation.

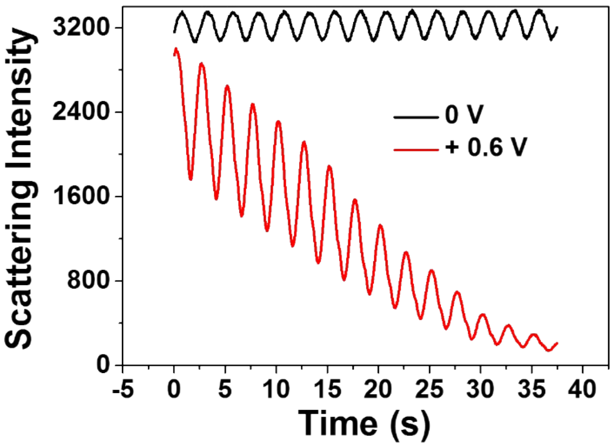

Figure S4. Both the scattering intensity and its fluctuation amplitude decreased when applying a positive potential to induce the oxidation of a single AuNR. A 0.4 Hz sine wave modulation with the peak-peak voltage of 1 V is applied. The offset is – 0.5 V (sweeping between – 1 V and 0 V) in black curve. It is + 0.1 V (sweeping between -0.4 V and + 0.6 V) in the red curve.

2.5 EIS spectrum of a single AuNR recorded by CCD and PMT

Comparison between CCD and PMT responses is important to demonstrate the consistency of different recording devices. Therefore, two EIS spectra of the same single AuNRs that were collected with CCD and PMT, respectively, are displayed in Figure S5. The two curves revealed similar trend in the frequency range below 400 Hz, which is close to the up-limit of CCD device with a maximal frame rate of 953 fps. Different intensity values were due to the slightly different detection areas (region-of-interest in CCD image vs. the optical mask in front of PMT). Representative original curves captured by CCD and PMT at the same frequency of 65 Hz are also provided in Figure S6.

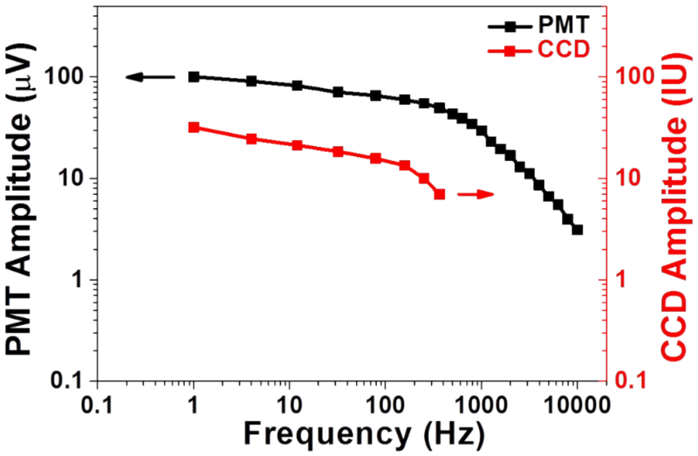

Figure S5. EIS spectrum of a single AuNR recorded by CCD (red curve) and PMT (black curve), respectively. Note the unit of CCD amplitude is Intensity Unit (IU) from gray-scaled camera image. That of PMT amplitude is the voltage (mV or μV) across a transistor when photocurrent passes through it.

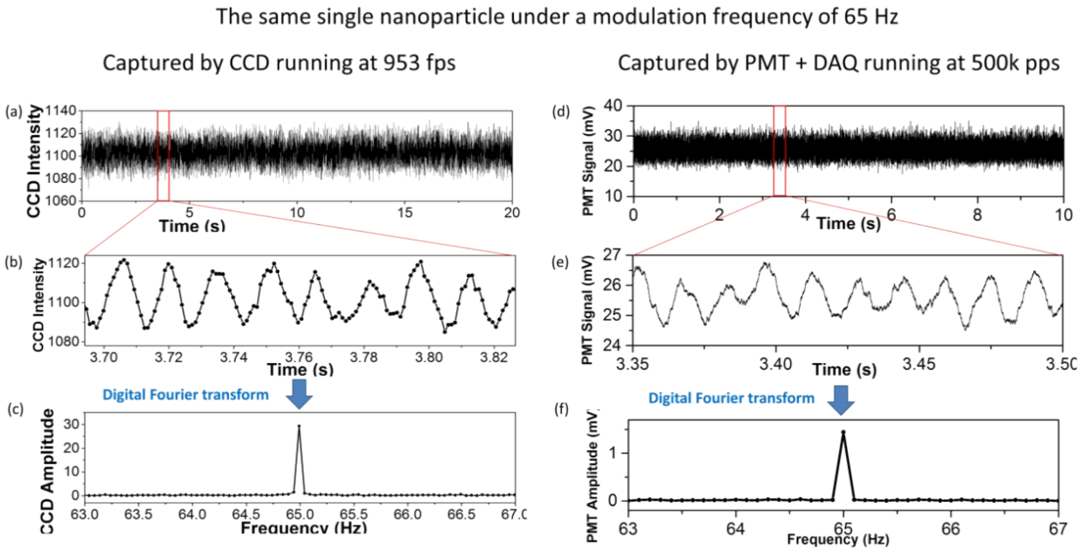

Figure S6. Original (a, d) intensity curves, zoom-in curves (b, e) and the corresponding Fourier transform results (c, f) of the same single AuNR under a modulation frequency of 65 Hz. Note the unit of CCD amplitude is Intensity Unit (IU) from gray-scaled camera image. That of PMT amplitude is the voltage (mV or μV) across a transistor when photocurrent passes through it.

2.6 The conventional EIS of the whole electrochemical cell current

As shown in Figure S7, We collected the conventional EIS of the electrochemical cell by analyzing the averaged current from the entire ITO electrode. A Randles equivalent circuit as illustrated in Figure 4c is used to analyze the amplitude and phase of electrode current. Based on this model, the amplitude of current ($I_{Amplitude}$) is given by

$$I_{Amplitude} = \left| \frac{U_{Applied}}{R_S + \left(R_P{}^{-1} + j\omega C_{DL}\right)^{-1}} \right| \quad (S1)$$

where $U_{Applied}$ is the applied voltage, R_S is electrolyte resistance, R_P is polarization resistance, C_{DL} is double layer capacitance, ω (= 2πf) is the angular frequency and f is the voltage modulation frequency. And also, the phase of current (I_{Phase}) is given by

$$I_{Phase} = \text{Angle}\left(\frac{U_{Applied}}{R_S + \left(R_P{}^{-1} + j\omega C_{DL}\right)^{-1}} \right) \quad (S2)$$

Therefore, using Eq. (1) and Eq. (S1), the relevant electrical parameters such as C_{DL}, R_S, and R_P could be provided, as shown in Table S1.

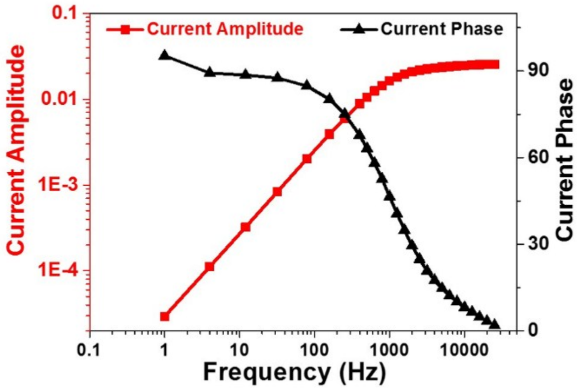

Figure S7. EIS of the whole electrochemical cell.

Table S1. The fitted electrical parameters using the EIS of ITO electrode and a single AuNR.

EIS types	C_{DL} (F)	R_S(Ω)	R_P (Ω)
ITO electrode	3.6×10^{-6}	40.1	4090.0
A single AuNR	8.1×10^{-6}	34.3	4370.0

2.7 Calculation of the double layer voltage

A Randles equivalent circuit shown in Figure S8 can be used to calculate the double layer voltage (U_{DL}). First, a polarization resistance (R_P) in parallel with double layer capacitance (C_{DL}) on the surface of ITO electrode can be served as a whole, it impedance is given by

$$Z' = \frac{1}{j2\pi f C_{DL} + (1/R_p)} \qquad \text{(S3)}$$

Thus, the impedance of electrochemical cell (Z) can be given by

$$Z = Z' + R_S \qquad \text{(S4)}$$

Finally, when a voltage ($U_{Applied}$) was applied to the electrochemical cell, the U_{DL} can be calculated by

$$U_{DL} = \frac{Z'}{Z' + R_S} \times U_{Applied} \qquad \text{(S5)}$$

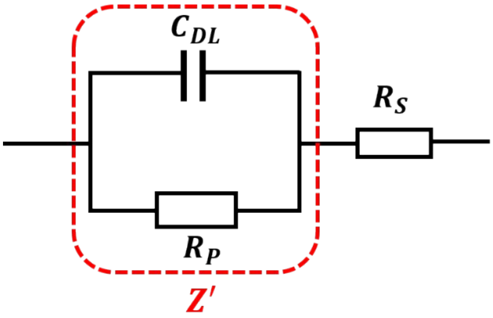

Figure S8. Randles equivalent circuit of the electrochemical cell.

2.8 The possibility of local heating effect

The typical output power of monochromatic illumination is ~ 5 mW. The illumination area is about 50 μm, leading to a power density less than 3×10^{-3} mW/μm^2 under an oblique-illumination configuration consisting of a common dark-field condenser. This power density is in the same level as the conventional halogen-lamp illumination. It is further supported by the fact that the CCD camera often runs at the same exposure time to record the colorful image (conventional mode, halogen-lamp illumination) and the monochromatic image (the present mode, AOTF coupled with white laser). Such a small power density should not induce strong local heating effect. For example, existing studies on the photo-thermal effect of AuNRs have shown that a temperature increase of 1 K was induced by the illumination density of 10 mW/μm^2,[2] which is several orders of magnitudes higher than the present illumination power density.

2.9 EIS spectrum of a single spherical Au nanoparticle

EIS spectrum of a single spherical Au nanoparticle can also be obtained by using the present setup. The major difference is that a much shorter illumination wavelength (520-580 nm) should be selected because spherical gold nanoparticles do not exhibit longitudinal LSPR band. Fluctuation amplitude of gold nanoparticle is also significantly smaller than that of AuNRs because the transverse mode of localized surface plasmon resonance is less sensitive to the electron density change. As a result, the amplitude is not detectable for spherical gold nanoparticles when the frequency is higher than 1000 Hz (Figure S9).

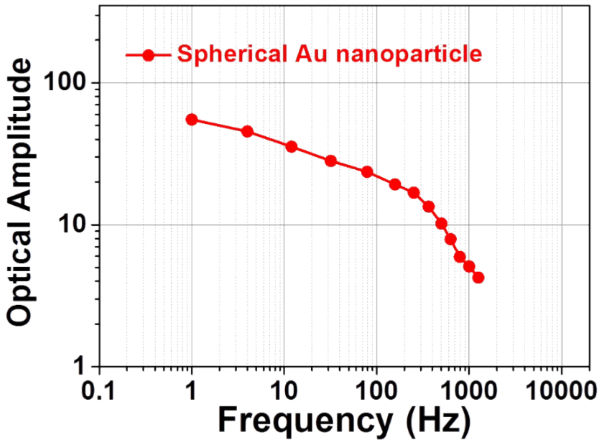

Figure S9. Representative EIS spectrum of a single spherical Au nanoparticle (diameter 70 nm).

2.10 Calculation of surface capacitance of the single AuNRs

As shown in Figure S10, the volume (V_{NP}) and the surface area (S_{NP}) of a single AuNR can be represented by

$$V_{NP} = \frac{4}{3}\pi r^3 + \pi h r^2 \quad \text{(S6)}$$

$$S_{NP} = 2\pi r h + 4\pi r^2 \quad \text{(S7)}$$

The volume of a gold atom is 0.0170 nm^3. Therefore, the number of gold atoms of a single AuNR is 2.72×10^6.

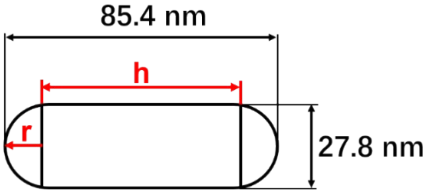

Figure S10. The length and width of the synthesized AuNRs.

According to the literature,[3-4] the relationship between LSPR peaks shifts of scattering spectra and electron charging could be determined by

$$\Delta\lambda = \lambda_2 - \lambda_1 = -\frac{\Delta N}{2N}\lambda_p\sqrt{\varepsilon_\infty + \left(\frac{1-L}{L}\right)\varepsilon_m} \qquad \text{(S8)}$$

where $\Delta\lambda$ is the blue shifts of LSPR peaks, λ_2 is the LSPR wavelength with electron injection, λ_1 is LSPR wavelength without electron injection, ε_∞ is the high-frequency contribution from interband transitions, N is the conduction electron concentration, ΔN is the number of electron injection, λ_P is the bulk gold plasma wavelength, L is the shape-dependent depolarization factor, and ε_m is the dielectric constant of the medium.

In our work, to calculate the surface capacitance of single AuNRs, we establish the relationship between optical intensity ratio $\left(= \frac{Optical\ intensity\ Amplitude}{Optical\ Intensity}\right)$ and blue shifts of LSPR peaks. Figure S11b shows a linear regression equation, Y = 0.06691X-0.04387 (Y is the optical intensity ratio and X is the blue shifts of LSPR peaks). Therefore, if we obtain an optical intensity ratio-based EIS of a single AuNR shown in Figure S11a, we can calculate the surface capacitance of a single AuNR. Here, the response at 100 Hz was typically selected to calculate the surface capacitance. Both Q_{NP} and U_{NP} are dependent on the frequency. The capacitance (Q_{NP}/U_{NP}), however, is less sensitive to the frequency as long as it is higher than 100 Hz in order to avoid the influence of ionic migration at low frequency. First, based on the obtained linear regression equation between optical intensity ratio and blue shifts of LSPR peaks, we can calculate the number of injected electrons ΔN using Eq. (S8), thus we can obtain the surface charge of a single AuNR (Q_{NP}). Finally, using Eq. (1) and Eq. (S7), the surface capacitance of a single AuNR (C_{NP}) can be represented by

$$C_{NP} = \frac{Q_{NP}}{S_{NP}U_{DL}} \qquad \text{(S9)}$$

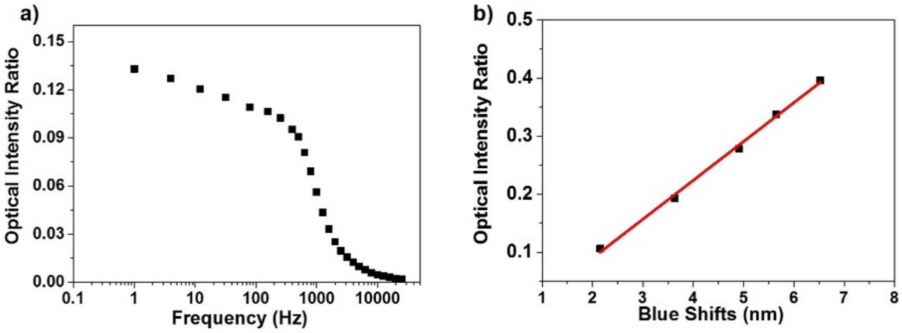

Figure S11. a) Changes of optical intensity ratio of a single AuNR under electrochemical charging and discharging. b) The linear relationship between the optical intensity ratio and the wavelength blue shifts.

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