Supporting Information for

Mapping Hot Electron Response of Individual Gold Nanocrystals on a TiO_2 Photoanode

Haifei Zhu, Hao Xie, Yi Yang, Kaiyu Wang, Fei Zhao, Weixiang Ye,* Weihai Ni*

Jiangsu Key Laboratory of Thin Films, School of Physical Science and Technology, Soochow University, Suzhou, Jiangsu, 215006, China.

Content

Materials

Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$), Sodium borohydride, Titanium isopropoxide (TIP), L-ascorbic acid, cetyltrimethylammonium chloride (CTAC), sodium sulfate (Na_2SO_4), and cetyltrimethylammonium bromide (CTAB) were obtained from Sigma-Aldrich. Nitric acid (HNO_3) was obtained from Sinopharm Chemical Reagent Co. Ltd. All of these reagents were used without any further purification. Solutions were prepared with deionized (DI) water (18.2 MΩ).

Characterization.

SEM analysis was performed on a Regulus8100 scanning electron microscope. Extinction spectra of AuNC solutions were acquired using an Agilent Technologies Cary 60 UV-vis spectrophotometer. X-ray diffraction patterns were obtained on D-MAX 2500 with a radiation source of Cu Kα at 40 kV, 150 mA, and scanning speed $2°min^{-1}$ at a step of 0.02°.

Preparation Thin Film of TiO2

The TiO_2 film was prepared according to the method reported previously [1] Solution I was prepared by diluting TIP (6.1 ml) with absolute ethanol (40.6 mL) under vigorous stirring for about 30 min. Solution II was prepared by mixing absolute ethanol (17 mL), deionized water (0.27 mL), and HNO_3 (68 wt%, 0.196 mL) as the acidic catalyst for the hydrolysis of TIP. The precursor solution was then prepared by adding solution II dropwise to solution I, followed by stirring for about 20 h at room temperature. The ITO glass substrate was cleaned by acetone, ethanol, and deionized water. The film was prepared by spin-coating the precursor solution onto

the ITO substrate at 5000 rpm for 35 s. The TiO_2/ITO substrate was then sintered at 500 ℃ for 2 h. The thickness of the TiO_2 film was measured to be 70 nm by X-section SEM.

Synthesis of AuNCs

AuNCs with average diameter of 54, 90, 120, 140, 177, and 240 nm were synthesized by the two-stage seed-mediated growth method and mild oxidation [2]. 24 nm AuNCs were firstly prepared. The seed solution was prepared by the addition of an aqueous $HAuCl_4$ solution (0.25 mL, 0.01 M) into an aqueous CTAB solution (9.75 mL, 0.1 M) in a glass vial. After the solution was mixed by inversion, a freshly prepared, ice-cold aqueous $NaBH_4$ solution (0.6 mL, 0.01 M) was injected into the Au(III)−CTAB solution under gentle stirring for 3 h at room temperature. 0.12 ml of the as-prepared seed solution was injected into a growth solution made of CTAB (0.1 M, 9.75 mL), water (190 mL), $HAuCl_4$ (0.01 M, 4 mL), and ascorbic acid (0.1 M, 15 mL). The reaction mixture was gently shaken and then left undisturbed overnight at room temperature. Au nanopolyhedrons with six sizes were grown by the seed-mediated method using the 24 nm AuNCs as seeds. Typically, a varying volume of the seed solution (0.03, 0.125, 0.25, 0.38, 1, and 4 mL) was added into a CTAC solution (0.025 M, 30 mL). For the seed solution at volumes less than 0.2 mL, the seed solution was diluted four times with water before use. After the sequential addition of ascorbic acid (0.1 M, 0.75 mL) and $HAuCl_4$ (0.01 M, 1.5 mL), the mixture solution was placed in an air-bath shaker (45 °C, 160 rpm) and kept for 3 h. The obtained Au nanopolyhedrons were centrifuged and redispersed in a CTAB solution (0.02 M, 30 mL). The Au nanopolyhedrons in CTAB solutions were mixed with a $HAuCl_4$ solution (0.01 M, 0.2 mL) for mildly oxidation. The resultant mixture solution was kept in the air bath shaker (45 °C, 160 revolutions per minute) for 2 h. The obtained AuNCs were centrifuged and

redispersed in water for storage.

Fabrication of The Photoelectrochemical Cell

The AuNC solution was drop-casted on the TiO_2/ITO substrate (2.5×2.5 cm) for the deposition of AuNCs. The surfactants on the AuNCs were removed by immersing the substrate in acetone for 12 h. Aqueous solution containing 0.1 M Na_2SO_4 was used as the electrolyte. The electrolyte was sandwiched between the TiO_2/ITO substrate and a cover glass slide. A Pt wire was inserted into the electrolyte. The photoelectrochemical cell was functional containing the AuNC-deposited TiO_2/ITO substrate as the working electrode and the counter electrode of Pt.

Single-Particle Dark Field Scatting Measurement

The dark field scattering measurements were performed on a home-made optical microscope (Olympus BX63F) system equipped with a monochromator (Acton, SpectraPro 2750i) and a charge-coupled device camera (Princeton Instruments, ProEM 1600^4+ EMCCD). The EMCCD was thermoelectrically cooled to -60 °C. The sample was illuminated by the white light from a 100 W quartz-halogen-tungsten lamp through an oil-immersion dark-field condenser (NA = 1.2-1.4). The scattered light from AuNCs was collected by a 60× water immersion objective (LUMFLN, NA = 1.1). The exposure time for collecting the scattering spectra was 5 sec. The alignment of the sample in DFM, SEM, and PCM measurements follows the procedure previously reported [3]. To be specific, a cross mark was firstly made on the ITO glass substrate, After the deposition of TiO_2 and AuNCs, the sample was taken under the dark field microscope for recording the scattering image of the AuNCs that includes their position patterns and orientations relative to the cross mark. With the help of the cross mark, the sample was coarsely

aligned to the same area, and SEM images were taken. By carefully comparing DFM images with those from SEM, each spot in the DFM image can be identified with its SEM structural details. The correlation of SEM and PCM measurements were therefore performed on exactly the same AuNCs.

Photocurrent Measurement on Individual AuNCs

The measurements were performed on the same dark field microscope (Olympus BX63F) system equipped with nanopositioning piezo stage from Physik Instruments and the digital source meter from Keithley. A 1064 to 532 nm frequency-doubled pulsed laser from IPG working at 27 mW, 90 ns, and 20 kHz and a 633 nm CW laser from Thorlabs working at 100 mW were used for the photocurrent measurements for the three cases of interface structures and the other dependences, respectively. The laser was focused on the AuNCs deposited on the surface of the TiO_2/ITO substrate through a 50× objective with NA = 0.5. The average power of the two lasers measured under the objective are the same at 4 mW. The piezo stage and the source meter were synchronized by a LabVIEW program. The PCM was measured in a region of 15 × 15 μm at a step of 0.5 μm with a dwell time 0.5 s at each pixel.

Simulations

FDTD Calculations. The FDTD method is an explicit time marching algorithm used to solve Maxwell's curl equations on a discretized spatial grid. A software package, FDTD Solutions, developed by Lumerical Solutions, Inc., was employed to perform the FDTD calculations on AuNCs. The Au dielectric function was represented using the Drude model, with parameters chosen to match the bulk gold dielectric data. FDTD calculations were carried out for AuNCs

on TiO_2 film with water (n = 1.33) as the surrounding medium. The refractive index of the standard anatase TiO_2 was taken for the TiO_2 film. The AuNC and its surrounding medium inside the simulation boundary were divided into the mesh of 1 nm in size.

Finite-element calculation of laser-Induced Heating of AuNCs. The local temperature of the AuNCs with different media (TiO_2 or water) were calculated by using the COMSOL Multiphysics' heat transfer module, following the method reported previously [4]. The local media were modeled as a half-sphere or sphere (with 200 μm diameter). In our calculation, the AuNCs were assigned as a heating source with certain thermal power, the transient solver was used to calculate the local temperature at the interface of AuNCs (at 1 s state and room temperature 293.15 K). We used the absorption cross-sections of AuNCs (determined by FDTD calculation) and the average power densities during PCM to calculate the thermal power. The thermal conductivity of Au (317 W/m/K), TiO_2 (1.15 W/m/K) and water (0.67 W/m/K) were used in our calculations [5]. The mesh sizes of AuNCs and local media were assigned as 1 and 5 nm (minimal) as well as 2 nm and 20 μm (maximum), respectively.

With the above setting, we calculated the local temperature of AuNCs with different sizes for 532 nm laser radiation (1.0 MW/cm^2). The AuNCs have a point contact with a TiO_2 half-sphere and surrounded by a water half sphere. In addition, we also calculated the local temperature of AuNC with 240 nm diameter for 633 nm laser radiation (650 kW/cm^2) in different interface structures (point contact, half-embedded and full-embedded with TiO_2). Specifically, (1) point contact with a TiO_2 half-sphere and surrounded by a water half-sphere; (2) half-embedded by a TiO_2 half-sphere and surrounded by a water half-sphere; (3) full-embedded by a TiO_2 sphere.

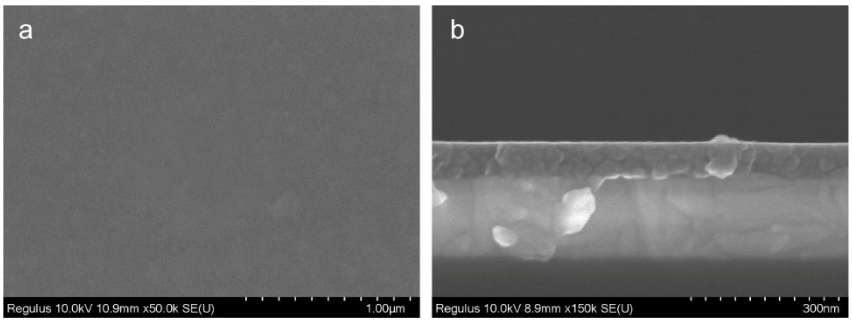

Figure S1. (a) SEM image of the as-prepared TiO_2 thin film after thermal treatment at 500 ℃. (b) SEM cross section image of the TiO_2 thin film on ITO substrate showing the thickness of TiO_2 film is about 70 nm.

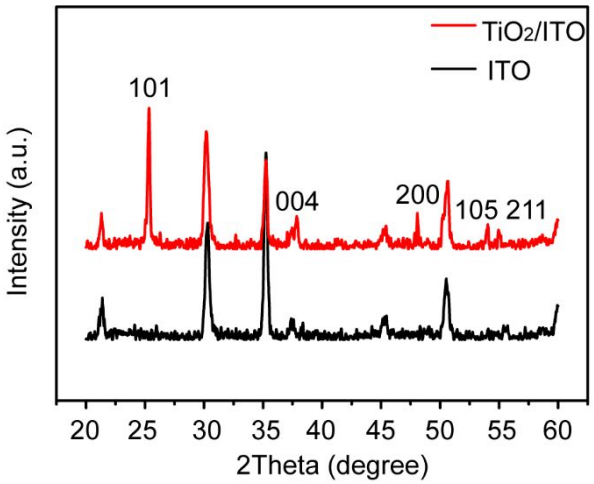

Figure S2. XRD patterns of the TiO_2 film on an ITO substrate and the bare ITO substrate. The TiO_2 film was thermally treated at 500 ℃. XRD peaks can be assigned to the lattice planes of the anatase phase of TiO_2, corresponding to JCPDS Patterns No. 21-1272.

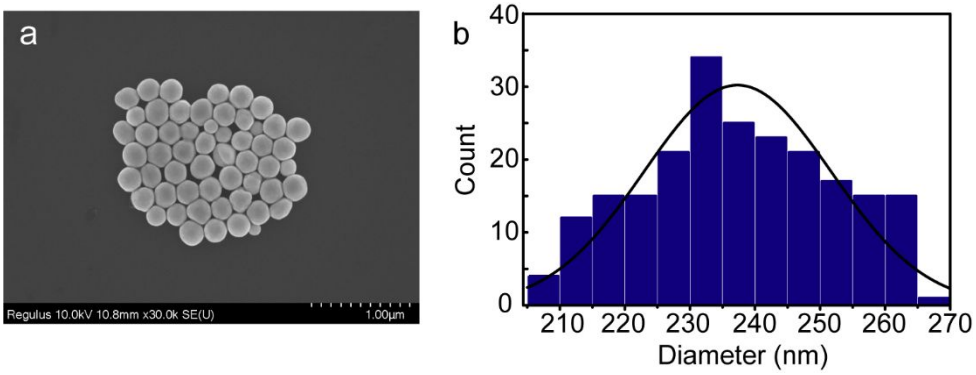

Figure S3. (a) SEM image of as-prepared AuNCs. (b) Statistics on the diameter of AuNCs. The diameter of AuNCs is 237±14 nm.

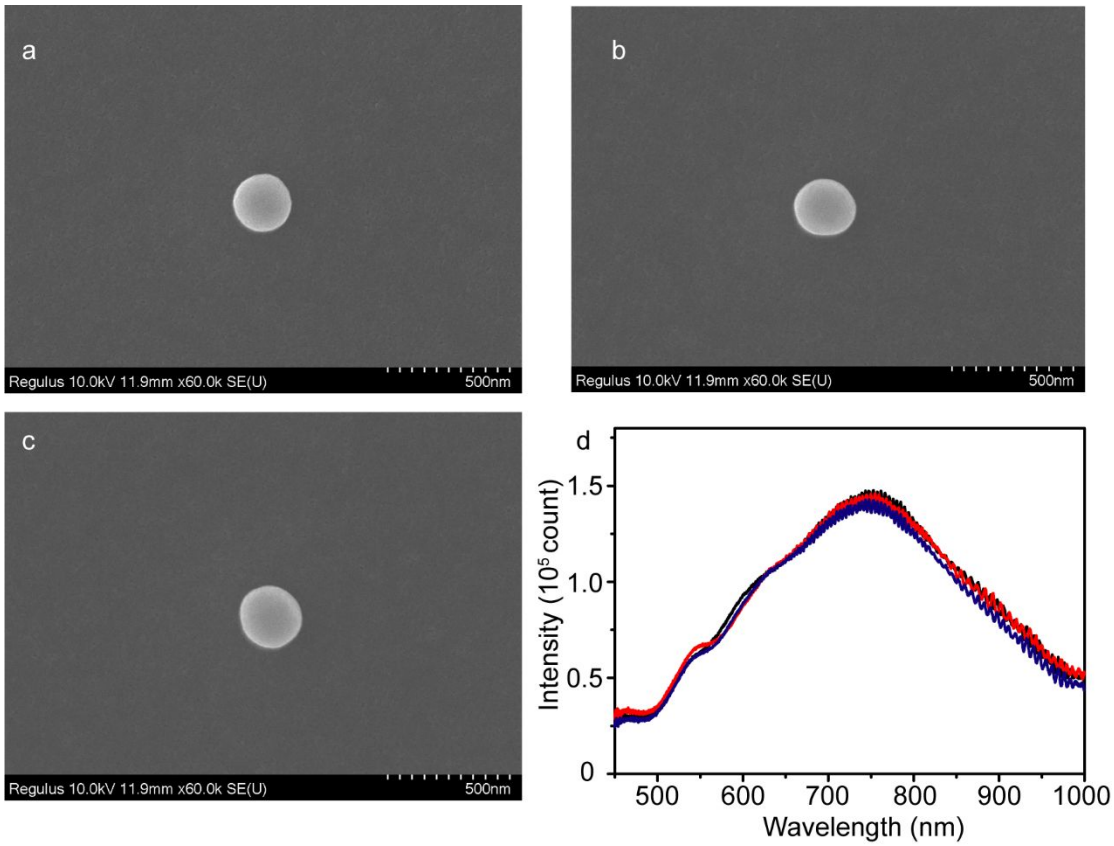

Figure S4. (a-c) SEM images of the other three AuNCs shown in Figure 1b. (d) Corresponding scatting spectra of the three AuNCs.

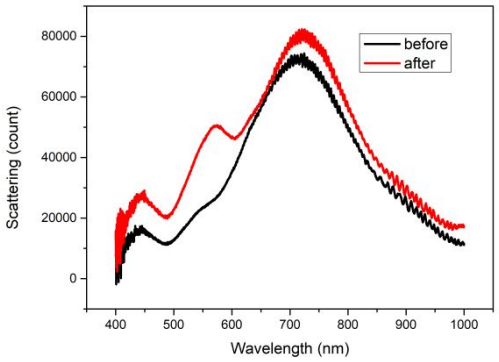

Figure S5. Scattering spectra from a typical 240 nm AuNC before and after the PCM measurement.

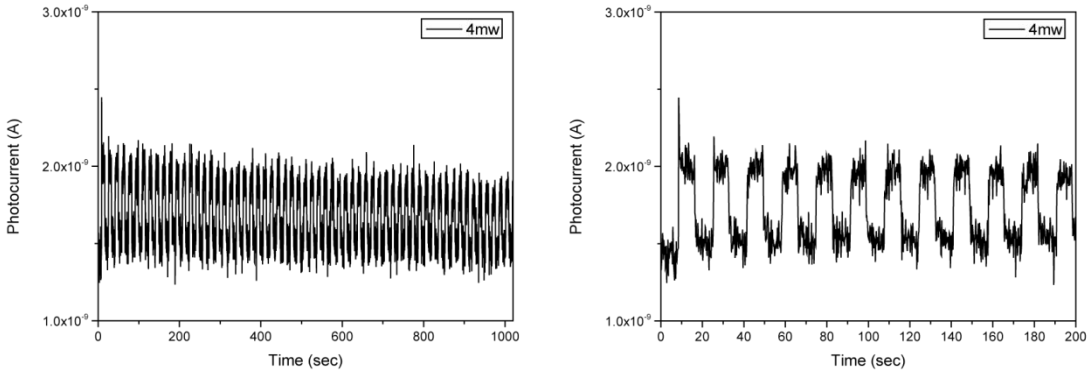

Figure S6. Photocurrent from an individual AuNC measured for 62 cycles.

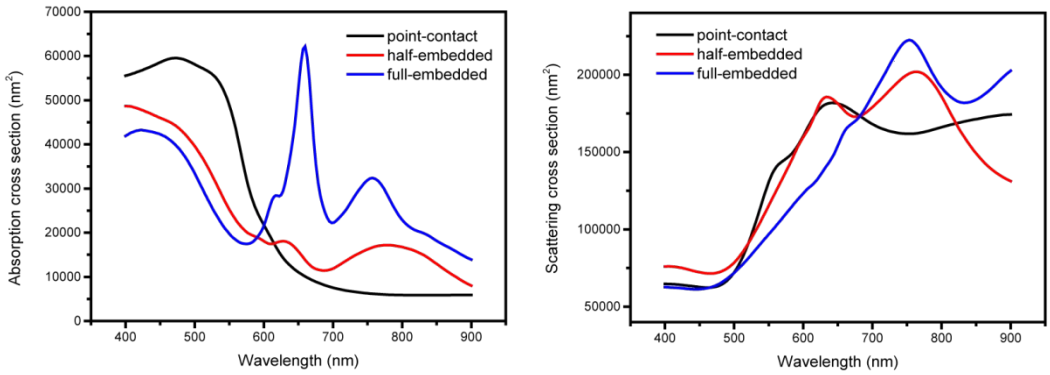

Figure S7. Absorption and scattering cross-sections of 240 nm AuNC in the point-contact, half-embedded, and full-embedded cases.

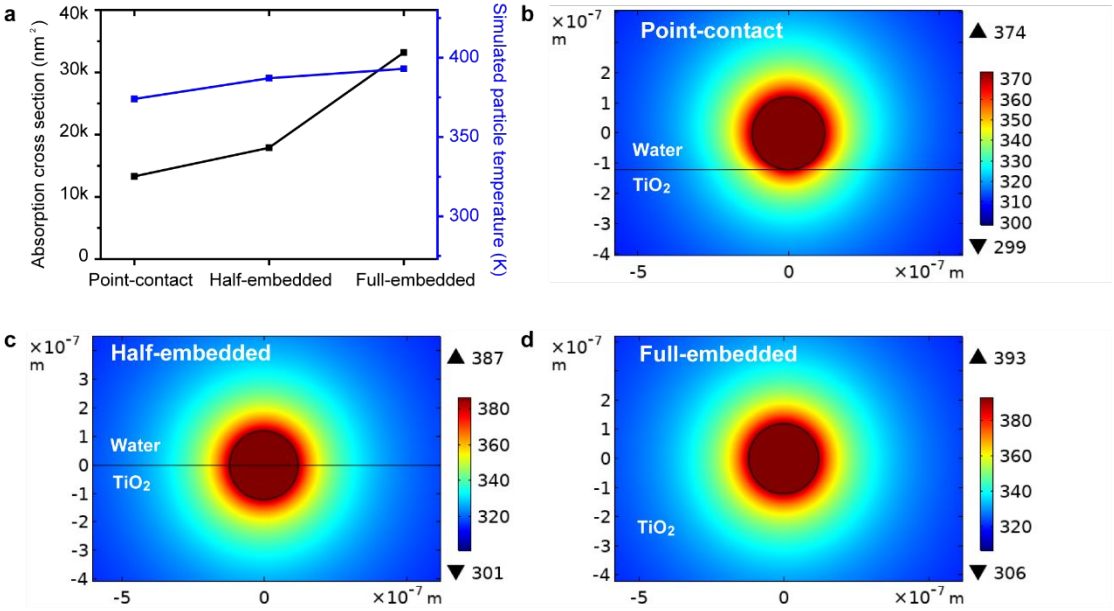

Figure S8. (a) Simulated absorption cross-section (black) and particle temperature (blue) of the 240 nm AuNC in the point-contact, half-embedded, and full-embedded cases. (b-d) X-section temperature profiles of the 240 nm AuNC in the three cases. The black lines are the interface between water and TiO_2.

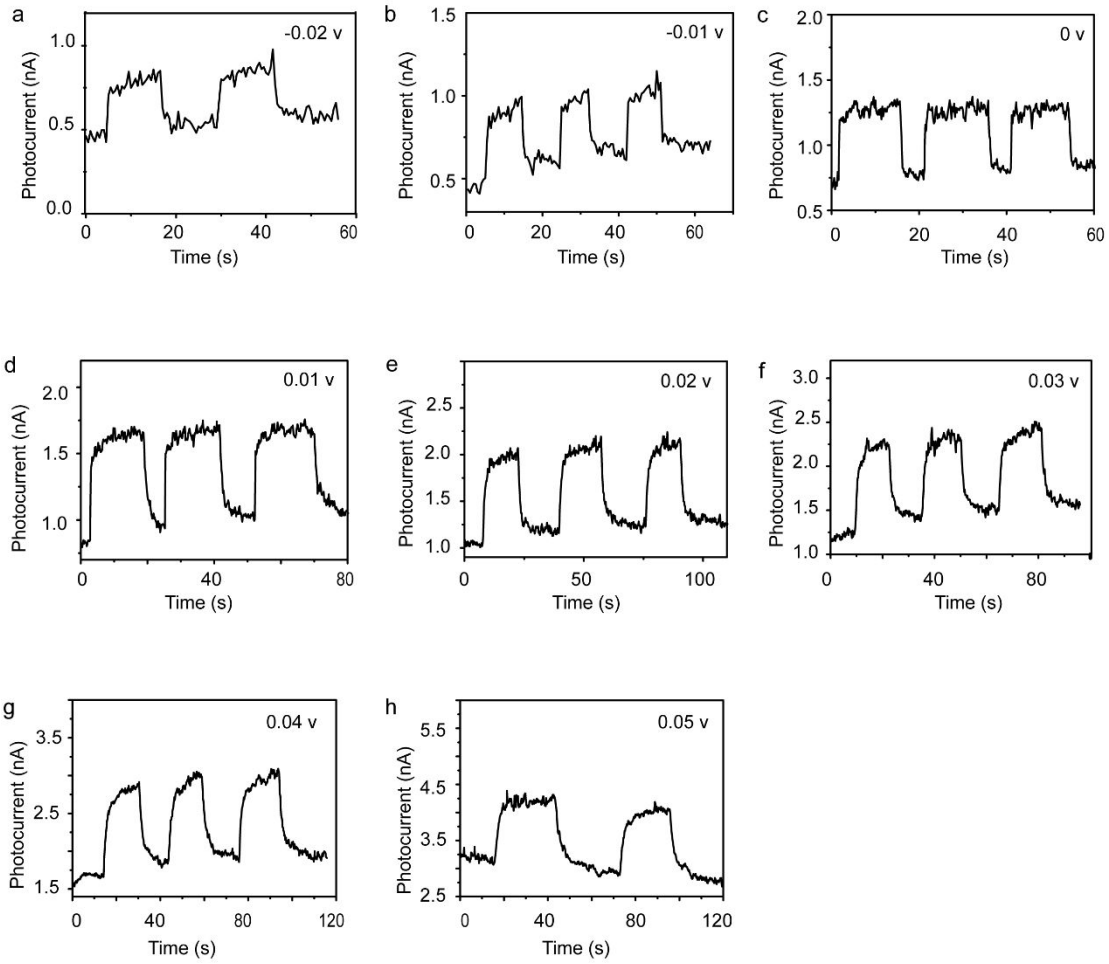

Figure S9. (a-h) Photocurrent measured on an AuNC at increasing applied bias from -0.02 to 0.05 V under chopped illumination.

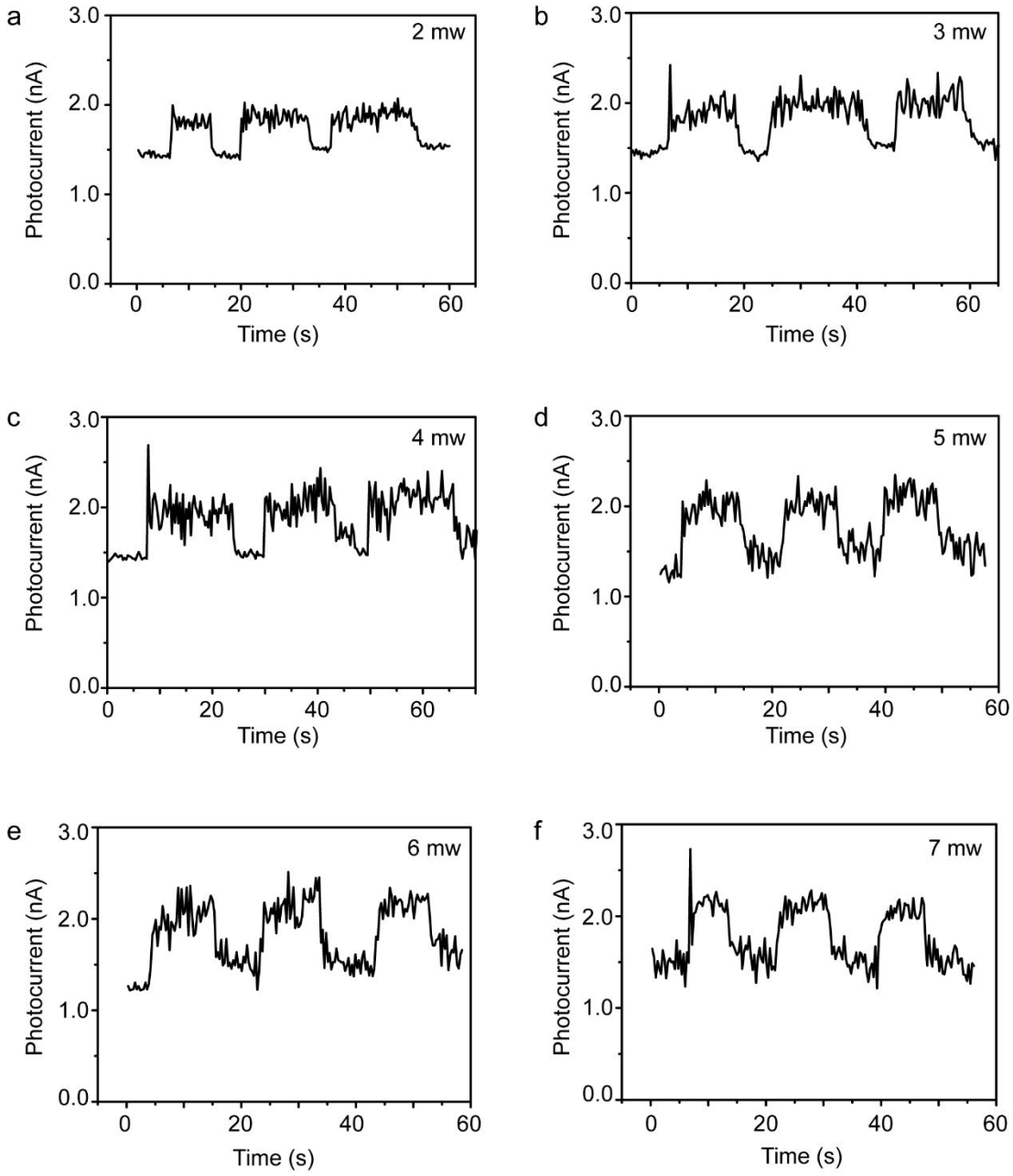

Figure S10. (a-f) Photocurrent measured on an AuNC at increasing power of the incident laser irradiation from -2 to 7 mW under chopped illumination.

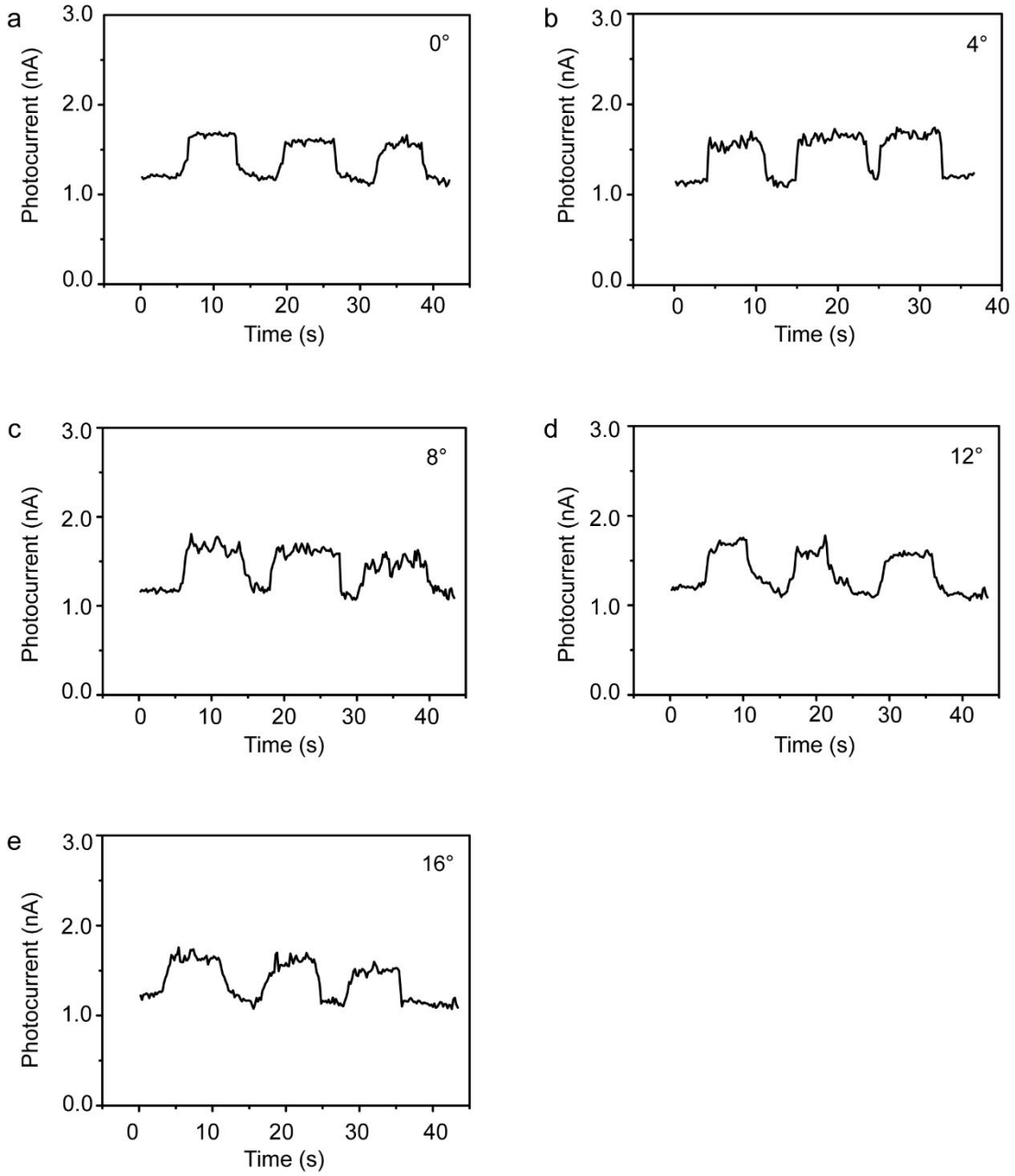

Figure S11. (a-e) Photocurrent measured on an AuNC at increasing incident angle from 0 to 16 degree under chopped illumination.

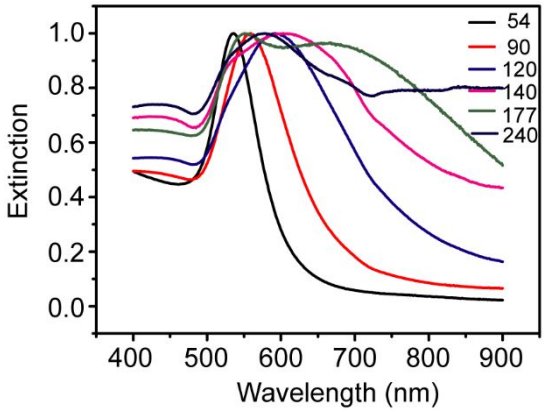

Figure S12. Normalized extinction spectra of AuNCs with average diameters increased from 54 to 90, 120, 140, 177, and 240 nm in aqueous solution.

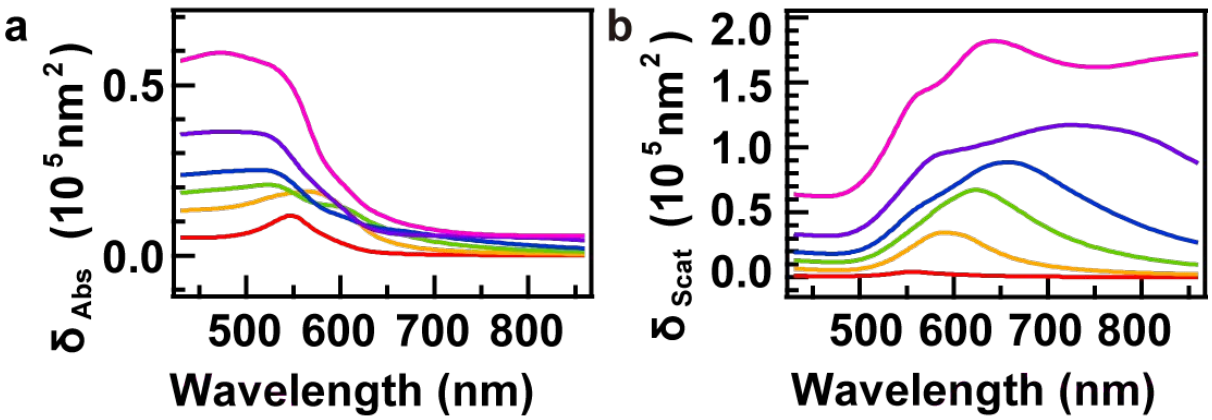

Figure S13. Simulated absorption and scattering cross-sections of AuNCs as a function of wavelength. The simulation was performed on AuNCs with different size (60, 95, 120, 141, 178, and 240 nm) according to the SEM measurement.

References

1. Que W , Uddin A , Hu X . Thin film TiO2 electrodes derived by sol–gel process for photovoltaic applications. *Journal of Power Sources*, **2006**, 159(1):353-356.

2. Ruan Q , Shao L , Shu Y , et al. Growth of Monodisperse Gold Nanospheres with Diameters from 20 nm to 220 nm and Their Core/Satellite Nanostructures. *Advanced Optical Materials*, **2014**, 2(1):65-73.

3. Lu, XX., Wu, J., Zhu, QN., Zhao JW., Wang QB., Zhan L., Ni, WH. Circular dichroism from single plasmonic nanostructures with extrinsic chirality. *Nanoscale*. **2014**, *6*,14244-14253

4. Ni, WH., Ba, HJ., Lutich, AA., Jackel, F., Feldmann, J. Enhancing Single-Nanoparticle Surface-Chemistry by Plasmonic Overheating in an Optical Trap. *Nano Lett*. **2012** *12*,4647-4650.

5. Mun, J., Kim, SW., Kato, R., Hatta, I., Lee, SH., Kang, KH. Measurement of the thermal conductivity of TiO2 thin films by using the thermo-reflectance method. *Thermochimica Acta*, **2007**, *455(1-2)*, 55-59.