Electronic Supplementary Information

Local Trapping of Energetic Holes at Gold Nanoparticles on TiO_2

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Characterization and spectral simulation

Extinction spectra were obtained by a Jasco V-670 spectrophotometer. Scanning electron microscopy (SEM) images were taken by using JEOL JSM-7500FA. Elemental analysis was performed on JEOL JSM-7800F equipped with an energy dispersive X-ray analyzer (JED-2300) for elemental mapping.

Spectral simulations were carried out by a finite-difference time-domain (FDTD) method using FDTD solutions (Lumerical Solutions). In the calculation model, a Au rounded cylinder (40 × 90 nm, radius of rounded end: 20 nm) or a Au rounded cube (80 × 80 × 80 nm, radius of rounded vertex: 10 nm) was placed on a TiO_2 (thickness: 60 nm)/SiO_2 substrate with 3-nm gap. Refractive index of the surrounding medium was set to 1.333. The entire simulation domain was 350 × 350 × 350 nm composed of 2 nm cubic cells and the region close to the Au NR or NC was further meshed in a three-dimensional box (200 × 200 × 200 nm) composed of 1 nm cubic cells. The light was incident normally from the SiO_2 side for excitation of transverse, longitudinal and proximal modes, while that was irradiated from the TiO_2 side for distal mode excitation. In the case of Au NR, electric filed distributions were monitored at the plane parallel to the substrate and passing through the center of the cylinder. The monitor for Au NC was parallel to the incident plane and passed through the NC center.

Electrode fabrication and PbO_2 deposition onto AuNSs, NRs, and NCs

An indium tin oxide (ITO)-coated glass substrate was further coated with a compact anatase TiO_2 (~60 nm thick) by a spray pyrolysis method and AuNSs synthesized by a malate reduction (~40 nm diameter)[S1] were deposited on the TiO_2 surface. The photoelectrode was immersed in aqueous $Pb(NO_3)_2$ (0.05 M, pH 4.5) and a bare ITO counter electrode connected electrically to the photoelectrode was soaked in aqueous $AgNO_3$ (0.05 M). These electrolytes were connected through a salt bridge. The photoelectrode was irradiated with 470–700 nm light (~58 mW cm^{-2}) to drive oxidation of Pb^{2+} to PbO_2 at the photoelectrode and reduction of Ag^+ to Ag at the counter electrode on the basis of PICS.

AuNRs (aspect ratio, ~2.9) and NCs (size, ~90 nm) were prepared by a seeded growth method according to literature[S2,S3] and deposited onto the TiO_2 electrode. The electrode was washed with hot methanol or ethanol by using a Soxhlet extractor to remove CTAB and heated at 150 ºC for 1 h under reduced pressure.[S4] 560-nm light (~17 mW cm^{-2}; full-width at half maximum (FWHM), 10 nm) and >700-nm light (~700 mW cm^{-2}) were exposed to the photoelectrode modified with AuNRs for 10-45 h to excite the transverse and longitudinal modes, respectively. The photoirradiation was carried

out in the same setup described above. For distal and proximal mode excitations, the photoelectrode modified with AuNCs was irradiated with 540-nm light (~17 mW cm^{-2}; FWHM, 10 nm, front incidence) and 660-nm light (~18 mW cm^{-2}; FWHM; 12 nm, back incidence) for ~45 and ~80 h, respectively.

References

S1. H. Nishi and S. Kobatake, *Dyes Pigm.*, 2012, **92**, 847–853.

S2. T. Ming, L. Zhao, Z. Yang, H. Chen, L. Sun, J. Wang and C. Yan, *Nano Lett.*, 2009, **9**, 3896−3903.

S3. M. Eguchi, D. Mitsui, H.-L. Wu, R. Sato and T. Teranishi, *Langmuir*, 2012, **28**, 9021–9026.

S4. H. Nishi and T. Tatsuma, *J. Phys. Chem. C*, 2018, **122**, 2330–2335.

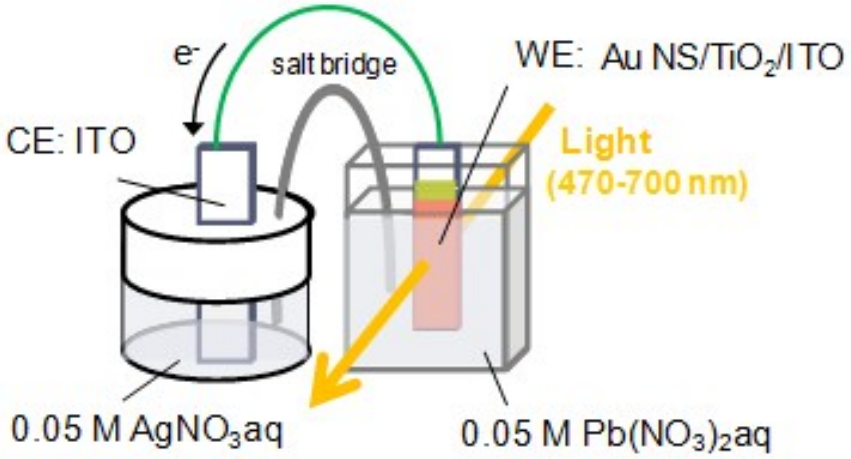

Fig. S1 Experimental setup for PbO_2 deposition on AuNSs by PICS.

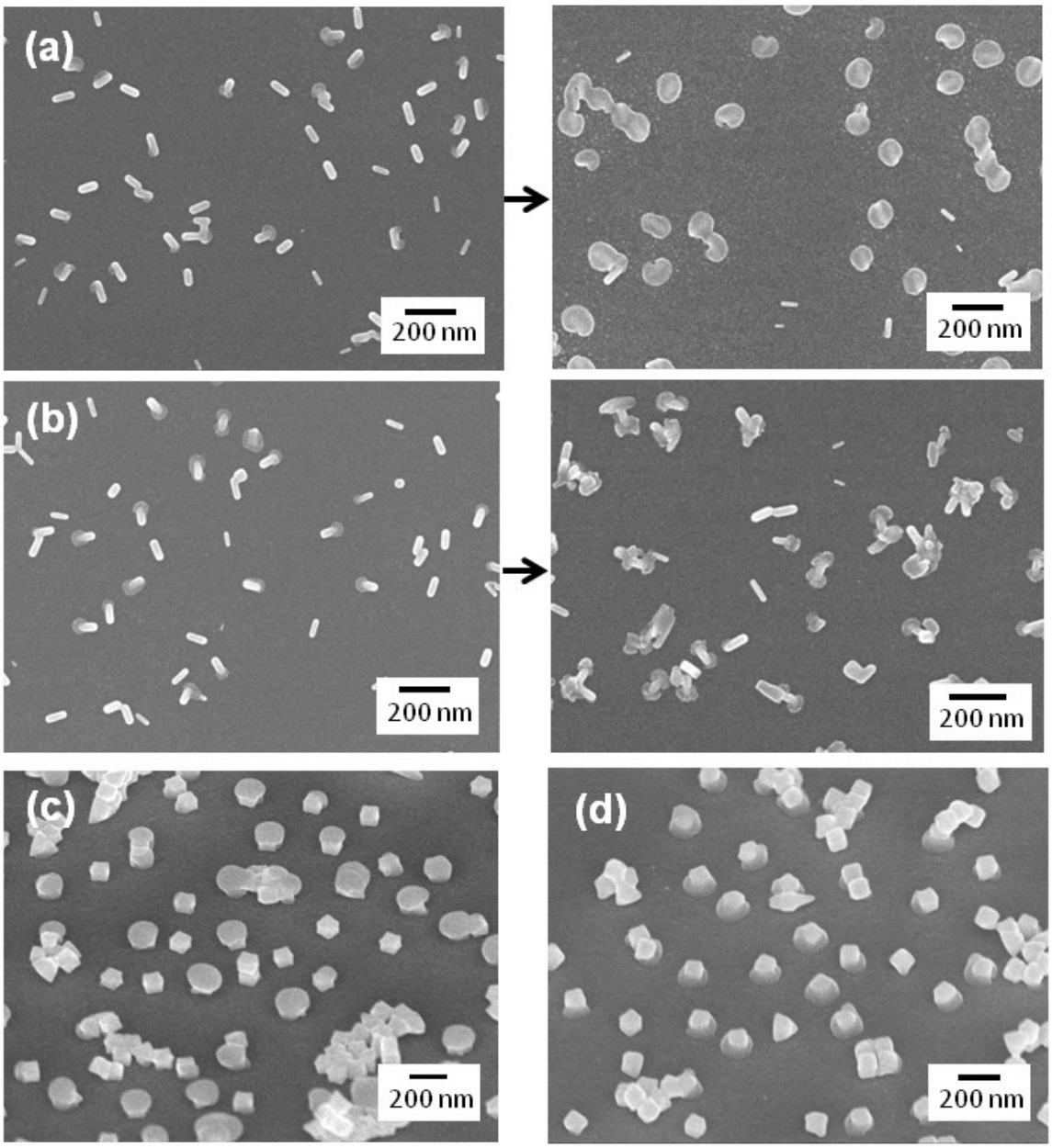

Fig. S2 Lower magnification SEM images for PbO_2-deposited (a, b) AuNRs and (c, d) NCs after excitation of (a) transverse, (b) longitudinal, (c) distal, and (d) proximal modes in the presence of Pb^{2+} ions.

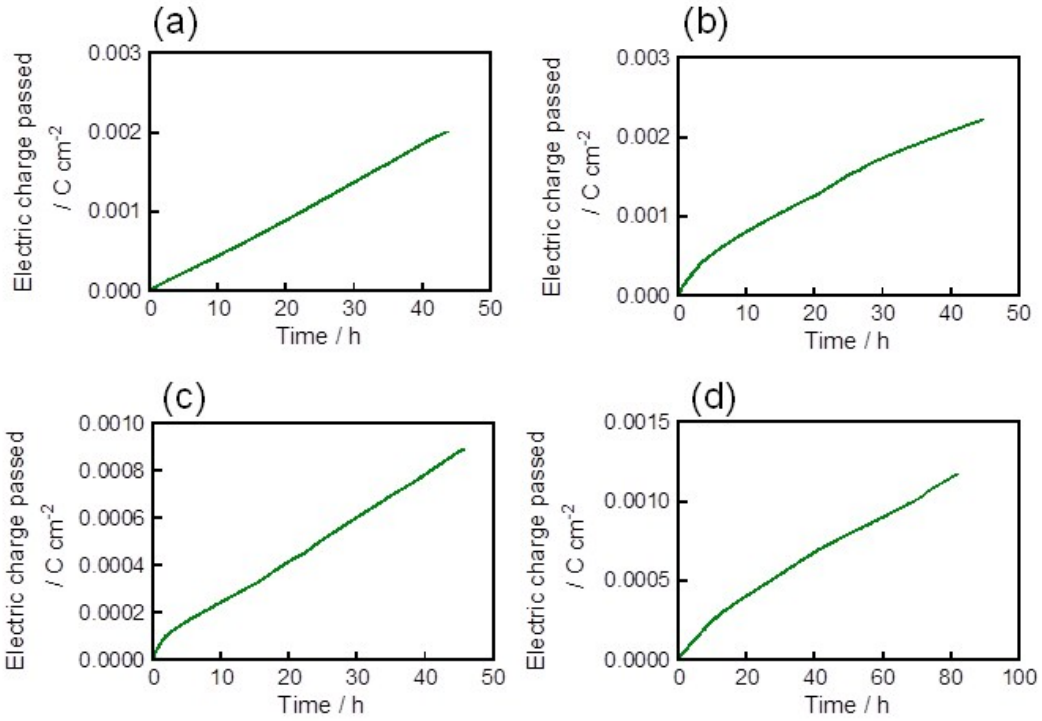

Fig. S3 Time courses of electric charge passed through the external circuit under excitation of (a) transverse, (b) longitudinal, (c) distal and (d) proximal modes.

Table S1 Experimental Conditions and Electric Charge Passed for the Experiments Using Au NRs and Au NCs

	Excited LSPR mode	Wavelength / nm	Light intensity / mW cm^{-2}	Irradiation time / h	Charge passed / C cm^{-2}
Au NR	Transverse	560	~17	~45	2.00
	Longitudinal	>700	~700	~45	2.22
Au NC	Distal	540	~17	~45	0.89
	Proximal	660	~18	~80	1.17