

Electronic Supplementary Information for Nanoscale

Dual plasmonic nanostructures for switching polarity of hot electrons induced photocurrent

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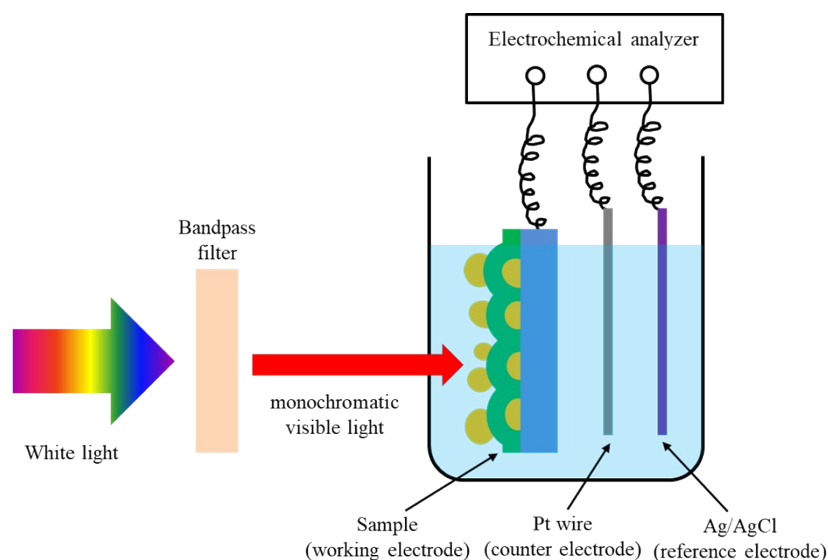


Fig. SI-1 Schematic view of the three-electrode photoelectrochemical measurement system. The sample, Pt wire and Ag/AgCl act as the working electrode, counter electrode, and reference electrode, respectively. White light passing through a 10-nm-bandwidth bandpass filter is used to simulate the semi-monochromatic visible illumination.

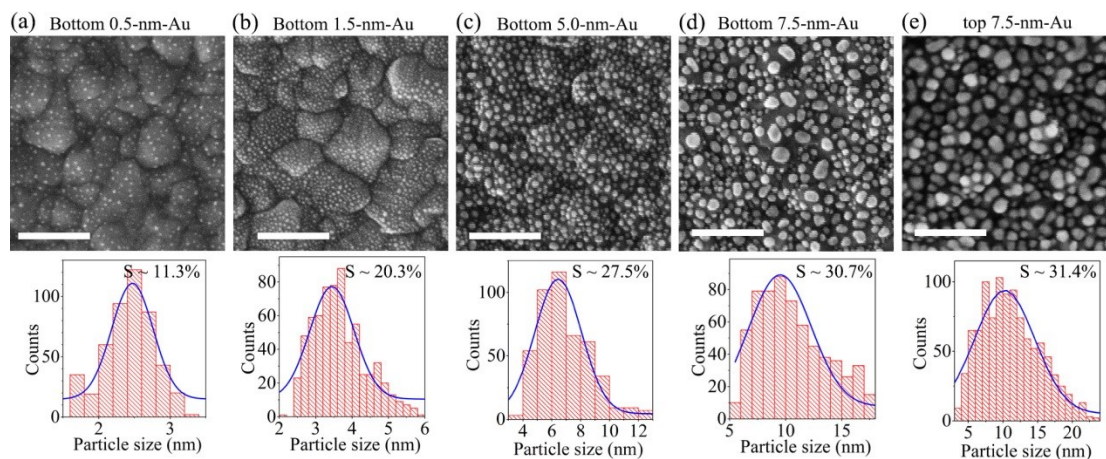


Fig. SI-2 Top-view SEM images and size distributions of the bottom layer of AuNPs formed from thin Au films with an initial thickness of 0.5 nm (a), 1.5 nm (b), 5.0 nm (c), 7.5 nm (d), and the top layer of AuNPs formed from a 7.5-nm-thick Au film (e). The analysis on these top-view SEM images shows that the sizes of AuNPs follow a Gaussian distribution, and the center size and the surface coverage of AuNPs increases with increasing the initial thickness of the Au film.

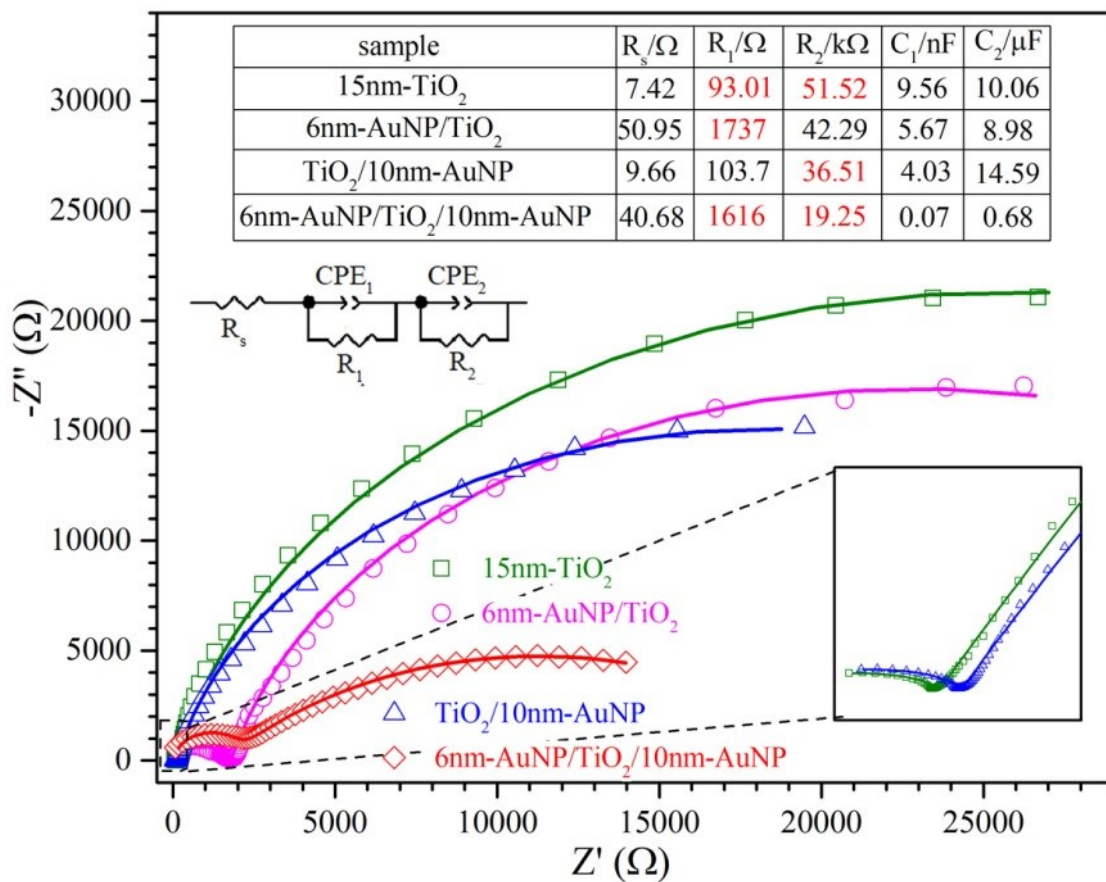


Fig. SI-3 Nyquist plots for the bare 15nm-thick TiO₂ film, 6nm-AuNP/TiO₂, TiO₂/10nm-AuNP, and 6nm-AuNP/TiO₂/10nm-AuNP measured under dark. Symbols represent real experimental data, and solid lines represent the fitting results. The right-bottom inset shows the enlarged high frequency region of the EIS spectra for the 15nm-thick TiO₂ film and TiO₂/10nm-AuNP samples. The middle inset shows the equivalent circuit model, which includes a series resistance (R_s) in series with two parallel arrangement of charge-transfer resistances (R_1 and R_2) and constant phase elements (CPE_1 and CPE_2). R_s represents the resistance of the whole circuit. R_1 and CPE_1 represent charge-transfer resistance and capacitance of the FTO/TiO₂ interface, respectively, which correspond to the first semicircle detected at high frequency. R_2 and CPE_2 represent charge-transfer resistance and capacitance of the TiO₂/electrolyte interface, respectively, which correspond to the second semicircle detected at low frequency. The top inset shows the best-fitting impedance parameters estimated from the impedance spectra and equivalent circuit.

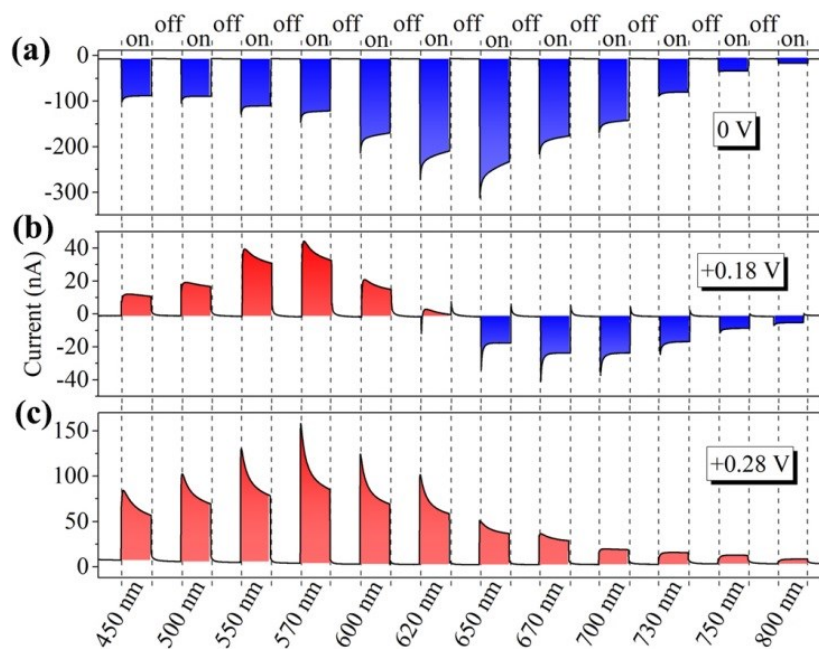


Fig. SI-4 Photocurrents in the 6nm-AuNP/TiO₂/10nm-AuNP nanostructure measured at a bias of 0 V (a), +0.18 V (b), and +0.28 V (c) when the illumination is turned on and off and swept in the wavelength range from 450 nm to 800 nm.