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Supplementary Information

Switching Direction of Plasmon-Induced Photocurrents by Cytochrome *c* at Au-TiO_2 Nanocomposites

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1. Experimental

Chemicals and Materials

Horse heart cytochrome c (cyt. *c*, oxidized state, MW 12, 384) and hydrogen tetrachloroaurate (III) tetrahydrate were purchased from Sigma–Aldrich. The reduced form of cyt. *c* on the modified electrode was generated by applying potentials of −0.18 V vs. Ag|AgCl on the surface–bound cyt. *c* for 200 s.[1] TiO_2 nanoneedles (FT–2000) was obtained from Ishihara Sangyo Kaisha. Gold nanoparticles (Au NPs) was prepared by the method previously reported.[2] Indium tin oxides (ITO)–coated glass plates with square resistance of ~10 Ω cm^{-2} were purchased from Shenzhen Nanbo Display Technology Co. Ltd. All other reagents were of analytical grade.

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Modification of electrodes

A high conductive TiO_2 nanoneedles film–coated ITO electrode was prepared from a TiO_2 nanoneedles sol by spin–coating, followed by sintering the electrode at 723 K for 1 h. And then the nanostructured TiO_2 film was immersed in the suspension of Au NPs for 12-15 h and rinsed with water to obtain Au NPs deposited on TiO_2 nanoneedles film (Au/TiO_2). The as–prepared Au/TiO_2 was adsorped in 25 mM phosphate buffer solution (PBS, pH 7.2) containing 0.2 mM cyt. *c* for about 30 min at 4 °C in refrigerator and then denoted as Au/TiO_2/cyt. *c*.

Apparatus and Measurements

SEM images of needle–TiO_2 and Au/TiO_2 nanoneedles film were taken by a Quanta 2000 FEG (FEI Company). All electrochemical and photoelectrochemical measurements were carried out in a home–made three–electrode cell using a KCl–saturated Ag|AgCl electrode as reference electrode and a platinum wire as counter electrode coupled with a computer–controlled CHI 660C electrochemical workstation (Shanghai, China). The working electrode was irradiated with a visible light ($\lambda > 450$ nm) from the back using a Xe lamp with an ultraviolet cutoff filter. Action spectrum for the photocurrent changes was collected by using a Xe lamp with an ultraviolet cutoff filter and an appropriate band–pass filter (fwhm 10nm). The supporting electrolyte was 25 mM PBS which was purged with N_2 for at least 30 min prior to experiments and a nitrogen atmosphere was kept over the solution in the cell.

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2. Spectroscopic Characterization for Bioactivity of Cyt. c Adsorped on Au/TiO_2 Film

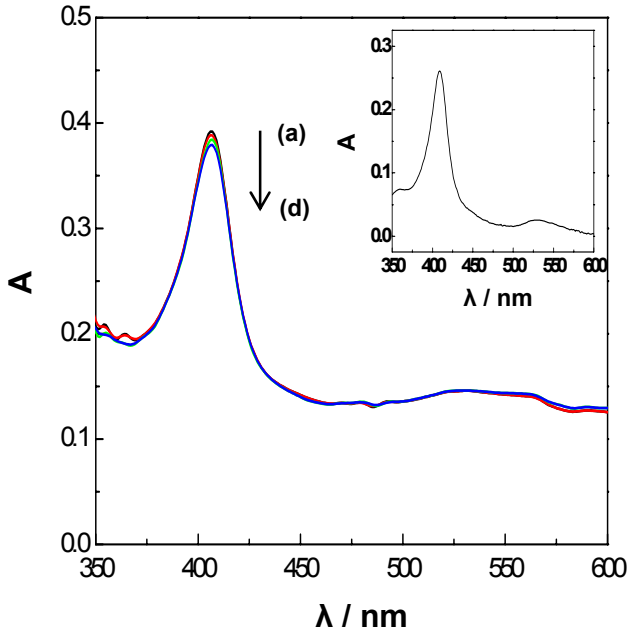

Figure S1. UV-vis absorption spectra of cyt. *c* adsorbed on the Au/TiO_2 film at variable time intervals of visible light irradiation: (a) 0 h, (b) 1 h, (c) 2h, (d) 3h. Inset: UV-vis absorption spectrum of 0.2 mM cyt. *c* solution.

Figure S1(a) depicts UV-vis absorption spectrum of cyt. *c* confined on the Au/TiO_2 film. The band for cyt. *c* adsorbed on the Au/TiO_2 film is located at 407 nm, just a 2 nm blue shift with that of native cyt. *c* solution (inset in Figure R1), suggesting that no obvious denaturation occurred after cyt. *c* adsorped on Au/TiO_2 film. Furthermore, no shift of the band for cyt. *c* adsorped on Au/TiO_2 film was observed under the continuous visible light ($\lambda > 420$ nm) irradiation up to 3 h (Figure S1, curve b-d). These results indicated that cyt. *c* adsorped on Au/TiO_2 film maintained its native bioactivity, even under plasmon excitation.

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References

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2. K. R. Brown, D. G. Walter, M. J. Natan, *Chem. Mater.,* 2000, **12**, 306.