

The Coupling of Localized Surface Plasmon Resonance-Based Photoelectrochemistry and Nanoparticle Size Effect: Towards Novel Plasmonic Photoelectrochemical Biosensing

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Experimental section

Materials.

Indium tin oxide (ITO) with type of N-STN-S1-10 was purchased from China Southern Glass Holding Co., Ltd. (Shenzhen, China), with coating thickness of $180\pm 20\text{nm}$ and sheet resistance of $8.1\pm 0.6\Omega\text{cm}^{-2}$. Glucose oxidase (GOx) was purchased from Sigma-Aldrich (Shanghai). $(\text{NH}_4)_2\text{TiF}_6$ and cetyltrimethylammonium chloride (CTAC) were obtained from Shanghai Jingchun Chemical Reagent Co., Ltd (China). H_3BO_3 was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (China). $\beta\text{-D}(+)\text{glucose}$ was obtained from Shanghai Bio Life Science & Technology Co., Ltd. $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$ and H_2O_2 were obtained from Nanjing Chemical Reagent Co., Ltd (China). Ascorbic acid (AA) was obtained from Sinopharm Chemical Reagent Co., Ltd (China). All other reagents were of analytical grade and used as received.

All aqueous solutions were prepared with ultrapure water ($18\text{M}\Omega\text{cm}^{-1}$) which was obtained from a Milli-Q water purification system. A 0.1 M phosphate buffer solution (PBS, pH 7.0) was prepared with NaH_2PO_4 and Na_2HPO_4 for 0.1 M AA solution.

Apparatus.

Photoelectrochemical (PEC) measurements were performed with a homemade PEC system. A 500 W Xe lamp equipped with monochromator was used as irradiation source to produce the monochromatic illuminating light on the front of the electrode. Photocurrent was measured on a

CHI 750a electrochemical workstation (Shanghai Chenhua Apparatus Co., China) with a three-electrode system: a modified ITO electrode with an area of 0.25 cm^2 as the working electrode, a Pt wire as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode. All the photocurrent measurements were performed at a constant potential of 0 V (versus Ag/AgCl). A 0.1 M PBS containing 0.1 M AA was used as the blank solution for photocurrent measurements, which was degassed by highly pure nitrogen for 15 min before PEC experiments and then kept over a N_2 atmosphere for the entire experimental process. Scanning electron microscopic (SEM) images were recorded by a Hitachi S4800 scanning electron microscope (Hitachi Co., Japan). Transmission electron microscopic images (TEM) were performed with a JEOL model 2000 instrument operating at 200 kV accelerating voltage. UV-vis absorption spectra were acquired with a Shimadzu UV-3600 UV/vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out on PHI5000 VersaProbe (ULVAC-PHI Co., Japan).

Fabrication of the electrode and plasmonic PEC biosensing.

The ITO slices were cleaned by immersion in 2 M boiling KOH solution solved in 2-propanol for 20 min, followed by washing copiously with water and dried at $120 \text{ }^\circ\text{C}$ for 2 h.

Liquid phase deposition (LPD) of TiO_2 was performed according to previous report¹ with slight modification. $(\text{NH}_4)_2\text{TiF}_6$ (3.9586 g) and H_3BO_3 (2.4732 g) were separately dissolved in deionized water (100 mL). 0.4 M H_3BO_3 solution was added to 0.2 M $(\text{NH}_4)_2\text{TiF}_6$ solution with the volume ratio of 1:1. Then the freshly cleaned ITO substrates were immersed vertically into the mixed solution immediately. After keeping the solution at room temperature for 65 h, the as obtained TiO_2 film was rinsed with distilled water and followed by annealing at $500 \text{ }^\circ\text{C}$ for 60 min in air atmosphere to transform the amorphous TiO_2 into anatase TiO_2 and finally naturally cooled down to room temperature.

The suspension of Au-NPs ($5 \pm 1 \text{ nm}$) was prepared according to the literature.² Then the ITO/ TiO_2 was immersed in the suspension for 12 h to optimize the surface coverage of Au NPs.³ After rinsing with distilled water, the Au/ TiO_2 film was allowed for incubation in the growth solutions of 0.01 M phosphate buffer (pH 7.0) containing $2.4 \times 10^{-4} \text{ M HAuCl}_4$, $2 \times 10^{-3} \text{ M CTAC}$ and with either variable concentrations of H_2O_2 or $\beta\text{-D (+) glucose}$ with $47 \text{ } \mu\text{g}\cdot\text{ml}^{-1} \text{ GOx}$. For the

detection of H_2O_2 and $\beta\text{-D (+)}$ glucose, the growth processes were performed at 30 °C for 5 min and 37 °C for 20 min, respectively. Thereafter, the electrodes were introduced for the respective absorbance or photoelectrochemical measurements.

References.

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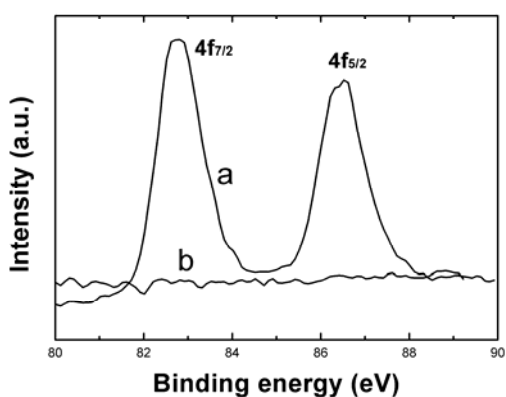


Figure S1. X-ray photoelectron spectra of the (a) Au NP seeds-LPD TiO_2 and (b) TiO_2 films.

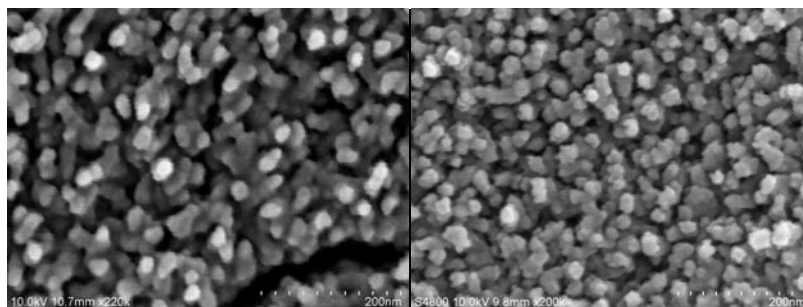


Figure S2. SEM images of Au NP seeds-LPD TiO_2 film before (left) and after (right) the enlargement process.