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±20nm and sheet resistance of 8.1±0.6Ωcm⁻². Glucose oxidase (GOx) was purchased from Sigma-Aldrich (Shanghai). (NH₄)₂TiF₆ and cetyltrimethylammonium chloride (CTAC) were obtained from Shanghai Jingchun Chemical Reagent Co., Ltd (China). H₃BO₃ was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (China). β-D(+) glucose was obtained from Shanghai Bio Life Science & Technology Co., Ltd. HAuCl₄·4 H₂O and H₂O₂ 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 (18MΩcm⁻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 NaH₂PO₄ and Na₂HPO₄ 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 cm² 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 N₂ 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 °C for 2 h.

Liquid phase deposition (LPD) of TiO₂ was performed according to previous report¹ with slight modification. (NH₄)₂TiF₆ (3.9586 g) and H₃BO₃ (2.4732 g) were separately dissolved in deionized water (100 mL). 0.4 M H₃BO₃ solution was added to 0.2 M (NH₄)₂TiF₆ 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 TiO₂ film was rinsed with distilled water and followed by annealing at 500 °C for 60 min in air atmosphere to transform the amorphous TiO₂ into anatase TiO₂ and finally naturally cooled down to room temperature.

The suspension of Au-NPs (5 ± 1 nm) was prepared according to the literature.² Then the ITO/TiO₂ was immersed in the suspension for 12 h to optimize the surface coverage of Au NPs.³ After rinsing with distilled water, the Au/TiO₂ film was allowed for incubation in the growth solutions of 0.01 M phosphate buffer (pH 7.0) containing 2.4×10⁻⁴ M HAuCl₄, 2×10⁻³ M CTAC and with either variable concentrations of H₂O₂ or β-D (+) glucose with 47 μg.ml⁻¹ GOx. For the
detection of \( \text{H}_2\text{O}_2 \) and \( \beta\text{-D (+)} \text{glucose} \), 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.**


**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.