

Supporting Online Material for  
**Photoelectrochemical Oxidation of Glucose for Biosensor and Fuel  
Cell Applications**

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**Experimental Section**

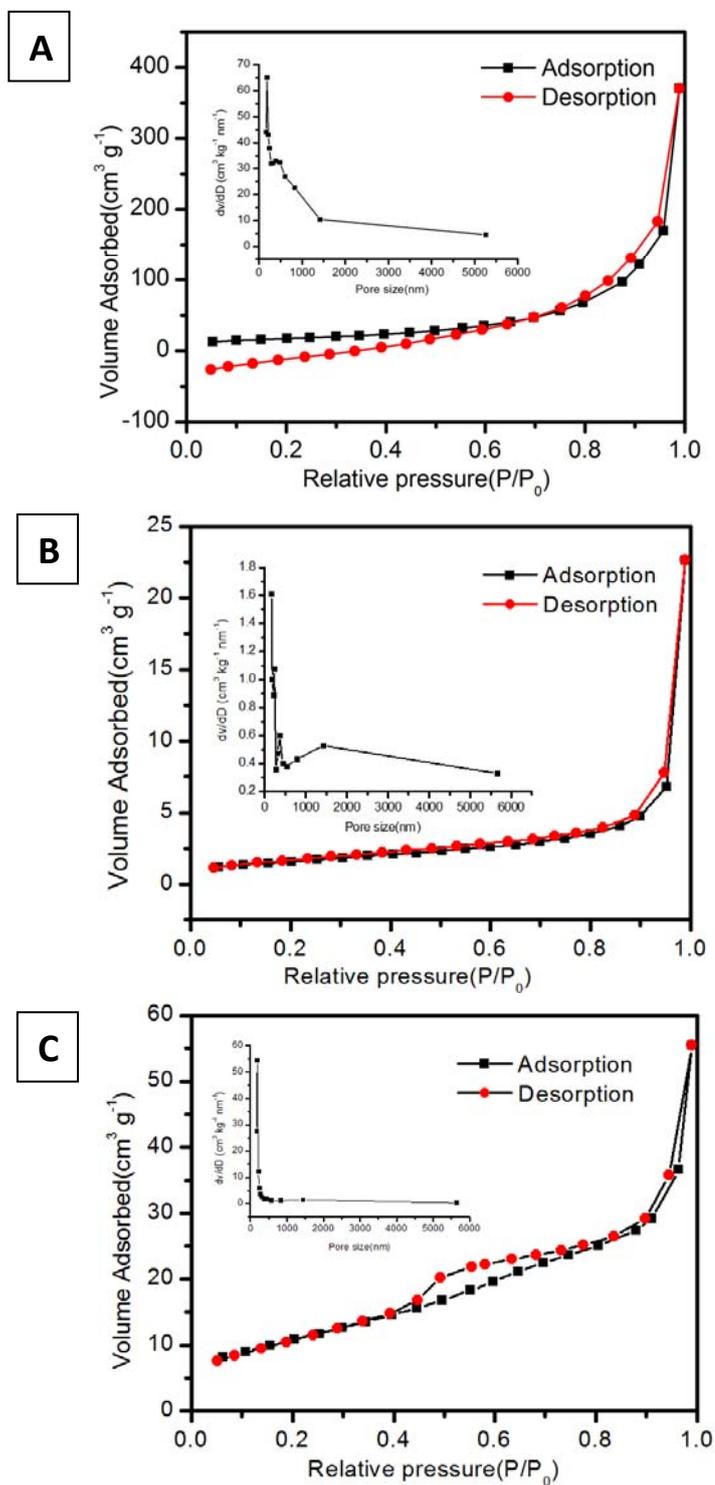
***TiO<sub>2</sub> Synthesis:*** Anatase TiO<sub>2</sub> was synthesized by a hydrothermal method. Typically, 10 mL of Triton X-100, 6 mL of n-hexanol, and 16 mL of cyclohexane were firstly mixed under magnetic stirring. Second, 3.4 mL of tetrabutyl titanate and 0.0682 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were dissolved in 4 mL of 5 M sulfuric acid solution, forming an aqueous phase. Then, the aqueous phase was added drop by drop to the oil phase, forming the clear microemulsion. All of the above steps were carried out at room temperature. The microemulsion was transferred into a 100-mL Teflon-inner-liner stainless-steel autoclave. The autoclave was kept for 13 h below 120 °C, and then, precipitate was collected at the bottom of the autoclave. The precipitate was washed repeatedly with ethanol and water to remove the oil, surfactant, cosurfactant, and acid, and then dried for 12 h in an infrared oven to obtain the final sample. Rutile TiO<sub>2</sub> was prepared with a traditional heat treatment of anatase TiO<sub>2</sub> at temperature of 1050°C with Ar atmosphere. The preparation of brookite TiO<sub>2</sub> was achieved by following the procedure proposed by Chen et al. Generally, 7.8 ml tetrabutyl titanate (TBOT) was directly hydrolyzed in a solution of 1.10 g sodium chloride (NaCl) and 68 ml aqueous ammonia (NH<sub>3</sub>H<sub>2</sub>O). The total volume of solution was 75 ml so that the concentration of NaCl was about 0.25 M. After stirring for a short time the resulting suspension was transferred to a teflon-lined auto-clave and heated to 180 °C for 24 h. The powders obtained were washed and dried at 80 °C for 12 h.

***Characterization:*** Morphology and size of the synthesized TiO<sub>2</sub> were observed using a field emission scanning electron microscope (FEI). The crystal structure of the TiO<sub>2</sub> was

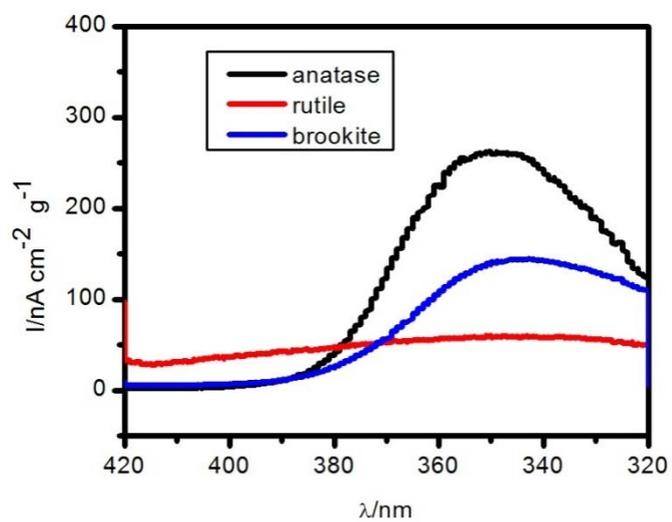
investigated using D/Max-2500 18 kW X-ray diffractometer (Rigaku, Co., Japan) equipped with nickel filter under scan speed of  $3^{\circ}/\text{min}$ , Cu K $\alpha$  radiation wavelength of 1.518Å. The specific surface areas of these samples were measured using the Brunauer Emmett Teller (BET) method (ASAP2010 Micromeritics).

**Photoelectrochemical Measurements:** Indium-tin oxide (ITO) slides (China glass Co., Ltd. China, sheet resistance  $42 \pm 0.6 \Omega \text{ cm}^{-2}$ ) were sonicated in soap water, acetone, ethanol, and water, for about 15min. respectively. Then, 1.0 mg of anatase, rutile, and brookite TiO<sub>2</sub> powder were dispersed in 0.5 mL ultra-pure water to obtain suspension. After that, 0.1mL of the suspension was carefully dipped onto the cleaned ITO slices with an active area of *ca.* 1.0 cm  $\times$  1.0 cm. The modified ITO electrodes were dried in 80°C for 30mins before use as working electrodes.

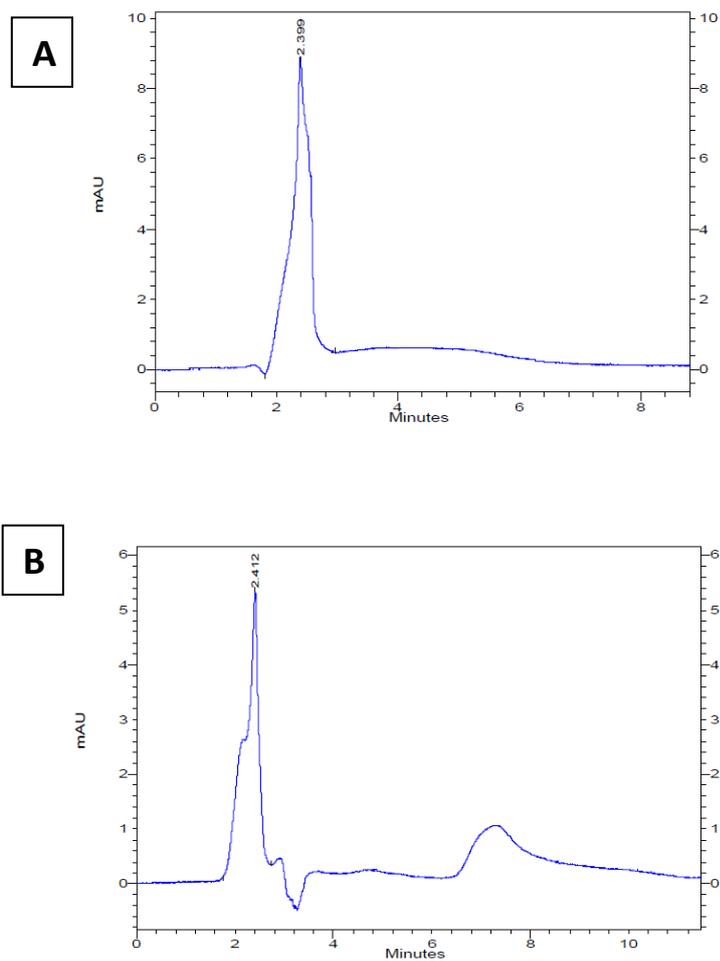
Photocurrent was collected by using an electrochemical testing instrument (CHI 660D, Chenhua, Shanghai, China) combining with a photo resource 500W Xe lamp with tunable cut-off filter (71SW30, Saifan, Beijing, China). The input power density of the light is  $0.5 \text{ mW cm}^{-2}$ . The measurements were performed in a 40 mL quartz cell containing 0.10 M Na<sub>2</sub>SO<sub>4</sub> as electrolyte solution, using TiO<sub>2</sub>/ITO as a working electrode, a saturated calomel electrode (SCE) as reference electrode, a Pt wire as counter electrode. All experiments were carried out at room temperature. A photoelectrochemical glucose fuel cell was constructed by using a two-compartment quartz cell with a Nafion membrane as separator. The anatase TiO<sub>2</sub> modified electrode was used as anode and a Pt wire was used as cathode, while a Nafion membrane was served as separator. The *V-I* polarization curves of the cell were measured with galvanostatic polarization technique. The power output profiles were obtained by plotting the power density ( $V \times j$ ) vs. the current (*I*).



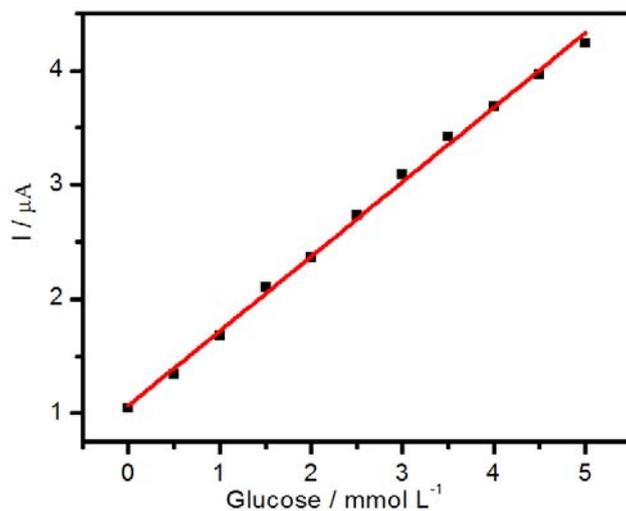
**Fig. S1**  $\text{N}_2$  adsorption-desorption isotherms of A) anatase, B) rutile, C) brookite  $\text{TiO}_2$ .



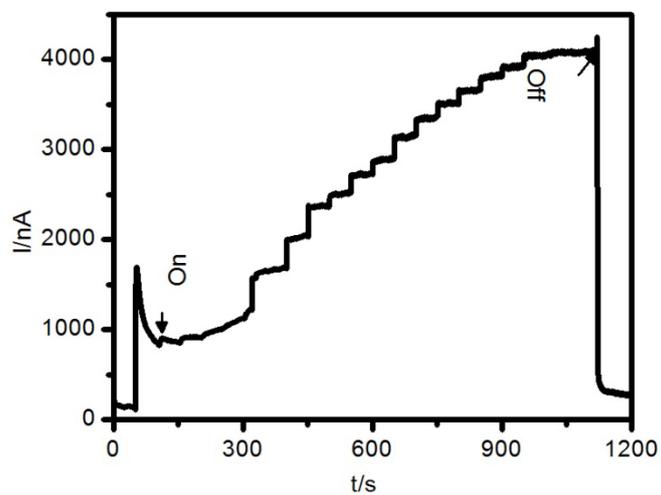
**Fig. S2** The normalized photocurrent obtained with anatase, rutile and brookite  $TiO_2$  according to their specific surface area.



**Fig. S3** HPLC chromatograms of the electrolyte containing 0.5 mM glucose before (A) and after (B) the photoelectrochemical measurement.



**Fig. S4** Calibration curve of the photoelectrochemical glucose sensor base on anatase TiO<sub>2</sub> modified electrode.



**Fig. S5** The recorded photocurrent towards the successive addition of glucose on anatase TiO<sub>2</sub> modified electrode in 0.1M Na<sub>2</sub>SO<sub>4</sub> (pH 5.9). The arrow indicates the “On” or “Off” state of the 380 nm irradiation.

**Table S1** The maximum photocurrent observed for five nanatase TiO<sub>2</sub> modified ITO electrodes in 0.1M Na<sub>2</sub>SO<sub>4</sub> (pH 5.9) in the presence of 3 mM glucose under 350 nm irradiation with a bias voltage of 0.4V vs. SCE.

	Electrode 1	Electrode 2	Electrode 3	Electrode 4	Electrode 5
Photocurrent	10.71 $\mu$ A	10.73 $\mu$ A	10.68 $\mu$ A	10.65 $\mu$ A	10.74 $\mu$ A