Electronic supplementary information

A biomimetic mussel-inspired photoelectrochemical biosensing chip for sensitive detection of CD146

Hongmin Ma, Tao Yan, Yong Zhang, Picheng Gao, Xuehui Pang, Bin Du and Qin Wei*

Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

*Corresponding author:

Tel.: +86 531 8276 7872.

E-mail address: sdjndxwq@163.com (Qin Wei)

Materials and Apparatus

CD146 (melanoma adhesion molecule antigen), and CD146 antibodies (Ab) were purchased from GuyanReagentCo.,Ltd.(Shanghai, China).Dopamine (DA)·HCl was used for preparing the polydopamine (PDA) film, which was purchased from ACROS Organics. Tetrabutylorthotitanate (TBOT), $CdCl_2 \cdot 2.5H_2O$, $Na_2S_2O_3$, EDTA, tris-(hydroxymethyl) aminomethane(Tris) and other reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, China. Phosphate buffer solution (PBS) (0.1 mol/L) was prepared by mixing stock solutions ofKH_2PO_4 and Na_2HPO_4 and used as the electrolyte in the PEC measurement.Indium-tin oxide (ITO) chip which purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd with the resistance of ≤ 10 Ohm/sq was used as the substrate electrode for the PEC experiment. Double distilled water (DDW) was used throughout theexperiment.

Electrodeposition experiments were performed on a CHI760E electrochemical workstation (Chenhua Instrument Shanghai Co., Ltd, China). Transmission electron microscopy (TEM) image was obtained from a JEOL JEM-2100F (Tokyo, Japan). Scanning electron microscopy (SEM) image and energy-dispersive X-ray spectroscopy (EDX) analysis were collected using a FEI QUANTA FEG250 coupled with INCA Energy X-MAX-50. XRD was performed with a D8 advance X-ray diffractometer (Bruker AXS, Germany). The size analysis of the nanoparticles was calculated by the software of the TEM image analysis (Nano Measurer System, 1.2). PEC and electrochemical impedance spectroscopy (EIS) analysis was performed with an IM6 electrochemical workstation (Zahner, Germany), coupling with a PP211 light source control system.

Experimental

Synthesis of TiO_2 NPs

In typical procedure, 0.02 mol TBOT was dissolved into 30 mL of ethanol, and then 10 mL DDW was added into the TBOT solution dropwisely under the magnetic stirring. After stirring for 2 h, the solution was transferred into Teflon-lined autoclave

and maintained at 200 °C for 10 h. The obtained white precipitates were collected and washed thoroughly with DDW and absolute ethanol for five cycles and then dried in vacuum at 80 °C for 12 h.

Preparation of TiO_2-ITO chip

Before fabrication of, ITO slices were cleaned thoroughly. Briefly, ITO slices (3 × 0.8 cm^2) were sonicated in acetone, ethanol and DDW consecutively for 30 min and dried under theN_2 stream.TiO_2-ITO chipwas fabricated by dropping 10 μL of 4 mg/mL TiO_2 aqueous solution on the ITO chip. After dried under anoven lamp, the electrode was placed in the muffle furnace and calcined at 450 ºC for 1 h.

Preparation of CdS/TiO_2-ITO chip

CdS/TiO_2-ITO chip was prepared by depositing CdS on the TiO_2-ITO chip through electrodeposition method, with a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and TiO_2-ITO chip as the working electrode. To be pointed out, the ITO without modification of TiO_2 was blocked by geoline to make sure CdS was deposited on the TiO_2 NPs. The electrodeposition electrolyte was composed of 15 mM Cd^{2+}, 8 mM $S_2O_3^{2-}$ and 8 mM EDTA. The deposition potential was -1.06 V and deposition time was 400 s.

Preparation of PDA/CdS/TiO_2-ITO chip

DA would self-polymerize in the alkalescentaqueous solution under the optimized condition. 5 mg DA was dissolved in 1 mL of 5 mmol/L Tris-HCl solution (pH 8.5), then CdS/TiO_2-chip was immersed in it and stored in the 4 ºC refrigerator for 2 h. Finally, the obtained PDA/CdS/TiO_2-ITO chip was washed by flow water and stored in the 4 ºC refrigerator for the following fabrication of immunosensor.

Fabrication of the immunosensor for the detection of CD146

Typically, 6 μL of 10 μg/mL Ab were dropped on the PDA/CdS/TiO_2-ITO chip and incubated for 1 h at 4 ºC. For the PDA has the stickiness property, the Ab could

be immobilized on the PDA surface without extra cross-linkers. After wash with water, 3 μL of 1% BSA was dropped on the electrode for blocking the non-specific active site and incubation at 4 ºC for another 1 h. Finally, 10 μL of CD146 solution was incubated on the chip for 1 h and used for quantitative analysis of CD146 after washed by water. So far, the PEC sensor for CD146 was fabricated successfully.

The PEC detection of CD146 was operated on an IM6 electrochemical workstation (Zahner, Germany), coupling with a PP211 light source control system. PBS (pH 4.98) was employed as the electrolyte.The conventionalthree-electrodesystem was employed for PEC measurement: A platinum wire electrode as the counter electrode, a saturated calomel electrode (SCE)as the reference electrode and a modified ITO electrode as the working electrode.In the PEC measurement, the applied potential was 0 V (*vs.*SCE), the wavelength of illumination light was 430 nmand the intensity was200 W/m^2.

Results and Discussion

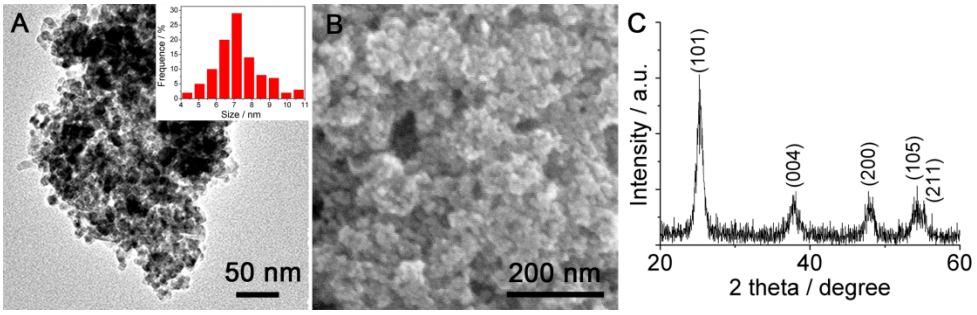

Fig. S1 TEM image (A), SEM image (B) and XRD pattern (C) of TiO_2 NPs. Inset of (A) displayed the size distribution column diagramof TiO_2 NPs.

The TEM image (Fig. S1A) showed that the synthesized nano-sized TiO_2 was particle morphology, with an average of 7 nm. The modified TiO_2 NPs were distributed on the surface of ITO chip closely (Fig. S1B), the huge superficial area provided abundant sites for the subsequent modification of CdS particles. Besides, XRD pattern exhibited the anatase crystal phase of TiO_2 NPs (Fig. S1C). All the diffraction peaks can be well indexed to the pure TiO_2 (JCPDS 73-1764).

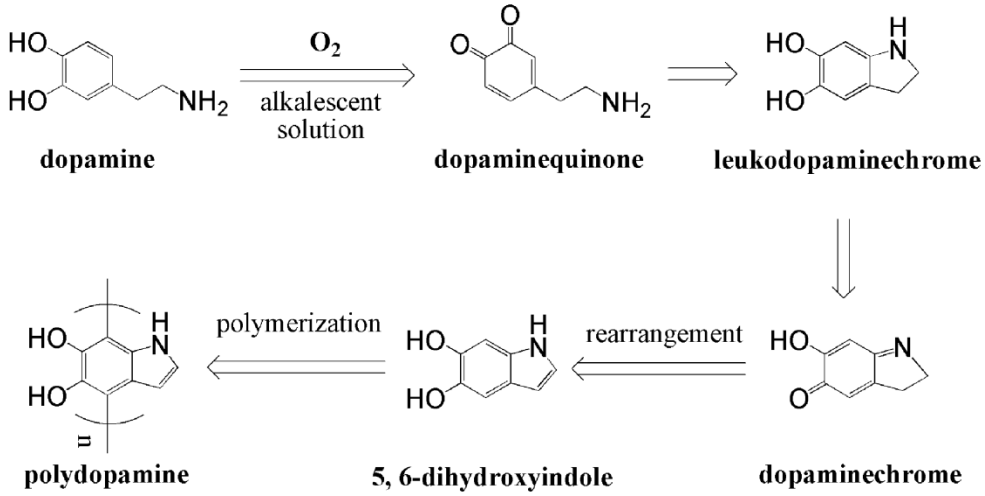

Fig. S2 The suggested formation mechanism of PDA.

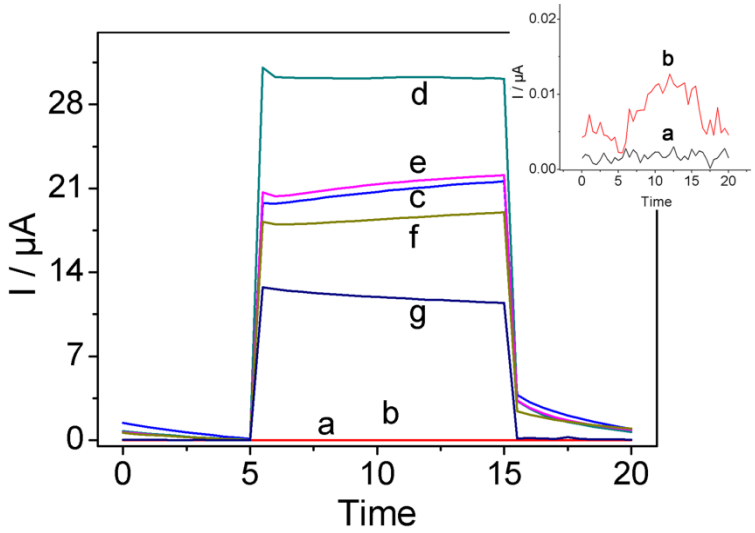

Fig. S3 Time-based photocurrent responses of (a) ITO, (b) TiO_2-ITO, (c) CdS/TiO_2-ITO, (d) PDA/CdS/TiO_2-ITO, (e) Ab/PDA/CdS/TiO_2-ITO, (f) BSA/Ab/PDA/CdS/TiO_2-ITO and (g) CD146BSA/Ab/PDA/CdS/TiO_2-ITO electrode.