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Recognition unit-free and self-cleaning photoelectrochemical sensing platform on TiO_2 nanotube photonic crystals for sensitive and selective detection of dopamine release from mouse brain

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ABSTRACT

For implementing sensitive and selective detection of biological molecules, the biosensors are been designed more and more complicated. The exploration of detection platform in a simple way without loss their sensitivity and selectivity is always a big challenge. Herein, a prototype of recognition biomolecule unit-free photoelectrochemical (PEC) sensing platform with self-cleaning activity is proposed with TiO_2 nanotube photonic crystal (TiO_2 NTPCs) materials as photoelectrode, and dopamine (DA) molecule as both sensitizer and target analyte. The unique adsorption between DA and TiO_2 NTPCs induces the formation of charge transfer complex, which not only expends the optical absorption of TiO_2 into visible light region, thus significantly boosts the PEC performance under illumination of visible light, but also implements the selective detection of DA on TiO_2 photoelectrode. This simple but efficient PEC analysis platform presents a low detection limit of 0.15 nm for detection of DA, which allows to realize the sensitive and selective determination of DA release from the mouse brain for its practical application after coupled with a microdialysis probe. The DA functionalized TiO_2 NTPCs PEC sensing platform opens up a new PEC detection model, without using extra-biomolecule auxiliary, just with target molecule naturally adsorbed on the electrode for sensitive and selective detection, and paves a new avenue for biosensors design with minimalism idea.

1. Introduction

Coupling photoelectrodes with biomolecule recognition units, the novel and promising photoelectrochemical (PEC) sensing platform is proposed and successfully implemented sensitive and selective detection of ions, small molecules, macromolecules, and even cells (Fan et al., 2014; Willner et al., 2001; Xin et al., 2015; Zhao et al., 2014; Zhao et al., 2015). The PEC sensing platform presents high sensitivity due to the photoelectrode's unique signal transducing modality of excitation energy sources of light and readout signal of electricity (Li et al., 2015a, 2015b; Tang et al., 2014), and achieves good selectivity through the contribution of recognition units, such as aptamers, enzymes, antibody, *etc.* (Haddour et al., 2006; Li et al., 2014; Sabir et al., 2015), however, the complex design process, harsh storage condition, and high cost of these recognition biomolecules limit the sustainable and practical applications of these PEC sensing platforms. Therefore, it is desirable to rationally design a recognition unit-free PEC sensing platform with both high sensitivity and selectivity.

There are two strategies for realizing recognition unit-free selective detection, one is the separation of target analytes from any other interferences, however, this method need complicated instruments, multiplex procedures, and sophisticated operation skills, and another one is the utilization of unique adsorption between analytes and photoelectrodes, that is, we hypothesize that the rationally selected photoelectrode materials present strong adsorption for special analytes, and the unique adsorption would result in significantly change of readout signal, photocurrent change in the PEC sensing case. Obviously, the latter strategy is much more convenient than the former one through a recognition unit-free PEC sensing process, and this concept, if proven right, will promise a significantly promotion for new design of PEC sensing platform in a minimalism style, and will circumambulate the disadvantages of conventional biomolecule recognition units, such as low stability, high cost, complicated operations. Therefore, in this work we are trying to explore a prototype of recognition unit-free PEC sensing platform, in addition, which will also own self-cleaning activity for repeatable applications.

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Titanium dioxide (TiO_2), with advantages of efficient separation of photo-generated charges that enables redox chemical reactions with attached molecules, and fantastic biocompatibility that opens up myriad possibilities for immunoassays, orthopedic implants, cancer treatment, and drug delivery, has been widely utilized in artificial photosynthesis, photovoltaic technology, and PEC sensing application (Chang et al., 2013; Chen et al., 2010; Dai et al., 2014; Jackman et al., 2014; Lu et al., 2008; Tachibana et al., 2012; Zhou et al., 2016). Dopamine (DA, $C_8H_{11}NO_2$) is an important neurotransmitter in the central nervous system that can control emotions and the balance of hormones in the human body (Li et al., 2016). Inspired from the unique adsorption between DA molecule and TiO_2, originate from the DA deprotonation and binding to the Ti atoms in a bridge bidentate mode (Dimitrijevic et al., 2005), the DA/TiO_2 complex is selected as a prototype for building a recognition unit-free PEC sensing platform. The Ti atoms of TiO_2 are hexacoordinated (octahedral) in the bulk and pentacoordinated (square pyramidal) at the surface, and the DA have a large affinity for these undercoordinated surface sites, restoring the Ti atoms to octahedral coordination and forming irreversible DA/TiO_2 charge transfer complexes (Finkelstein-Shapiro et al., 2010), under illumination, in which the excited electrons from DA molecules directly transfer to the conduction band of TiO_2, and generated holes localize on the DA molecules, which promotes spatial separation of photo-generated charges, and thus significantly enhanced the PEC performance (Urdaneta et al., 2014). In addition, the formation of DA/TiO_2 charge transfer complexes results in a red shift of the optical absorption edge compared to the pristine TiO_2 (Dimitrijevic et al., 2009; Wang et al., 2009). In this work, TiO_2 nanotube based photonic crystal (TiO_2 NTPCs) materials is employed as photoelectrode, thanks to its special light trapping ability in visible light region from its top photonic crystal layer and fast electron transfer property from its bottom vertical one-dimensional nanotubular layer (Zhang and Wu, 2014). After DA functionalization, the trapped visible light photons in TiO_2 NTPCs will be effectively converted, and thus boost the PEC performance for achieving a high sensitivity. In addition, the unique adsorption of DA on TiO_2 guarantees the high selectivity, and finally realize the sensitive and selective PEC sensing under illumination of visible light without any biomolecule auxiliary. Furthermore, the TiO_2 NTPCs photoelectrode presents self-cleaning ability, that is, the adsorbed DA molecules can be totally decomposed from the TiO_2 surface under illumination of full solar light (5% ultraviolet light) for recyclable utilization of the TiO_2 NTPCs photoelectrode. Finally, a prototype of recognition unit-free and self-cleaning PEC sensing platform of DA/TiO_2 NTPCs is proposed and is expected to open up a new PEC detection model.

2. Experimental section

2.1. Chemicals and materials

A 0.1 mm thick titanium foil (99.6%, Jinjia Metal, China) was cut into pieces of 40×10 mm^2. Ethylene glycol (EG), ammonia fluoride (NH_4F), hydrochloric (HCl), sodium chloride (NaCl), Potassium chlorate (KCl), anhydrous sodium hydrogen phosphate (Na_2HPO_4), monopotassium phosphate (KH_2PO_4), phosphate buffer saline (PBS, pH = 7.4), sodium sulfate (Na_2SO_4), dopamine, cysteine, glucose, glutathione, uric acid, ascorbic acid, catechol, resorcinol, hydroquinone, 3-Fluorocatechol, 4-tert-Butylcatechol, 1,2-dimethoxybenzene, Pyrocatechol violet, 3-Methylcatechol, 4-Bromocatechol, 4-Methylpyrocatechol were purchased from Macklin Chemical and used as received. All aqueous solutions were prepared using deionized water (DI) with a resistivity of 18.2 MΩ cm.

2.2. Preparation of TiO_2 NTPCs

The hierarchical TiO_2 NTPCs were fabricated by a two-step anodization process. Prior to anodization, the Ti foils were first degreased by sonicating in ethanol and DI water, followed by drying in pure nitrogen stream. The anodization was carried out using a conventional two-electrode system with the Ti foil as an anode and a Pt foil as a cathode respectively. All electrolytes consisted of 0.5 wt% NH_4F in EG solution with 2 vol% water. All the anodization was carried out at room temperature. In the first-step anodization, the Ti foil was anodized at 60 V for 30 min, and then the as-grown nanotube layer was ultrasonically removed in deionized water. The same Ti foil then underwent the second anodization sequentially at 20 V, 25 V, and 30 V for 30 min, respectively. After the two-step anodization, the prepared TiO_2 NTPCs samples were cleaned with DI water and dried off with nitrogen gas. The as-anodized TiO_2 NTPCs were annealed in air at 450 °C for 1 h with a heating rate of 5 °C min^{-1}.

2.3. Materials characterization

The morphologies of samples were characterized by scanning electron microscopy (SEM, S4800, Hitachi), and high resolution transmission electron microscopy (HR-TEM, JEOL JEM 2100). The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) (Bruker D8 Discover diffractometer, using Cu Kα radiation (1.540598 Å)). The diffuse reflectance UV–vis adsorption spectra were recorded on a spectrophotometer (Shimadazu, UV 3600), with fine $BaSO_4$ powder as reference. The chemical compositions and status were analyzed by X-ray Photoelectron Spectroscopy (XPS) with an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum ($< 10^{-8}$ Torr) and by using a monochromatic Al Kα X-ray source. The adventitious carbon 1s peak was calibrated at 285.0 eV and used as an internal standard to compensate for any charging effects. The Raman spectra were measured through DXR Raman Microscope (Thermo).

2.4. PEC detection of DA by TiO_2 NTPCs

Firstly, the TiO_2 NTPCs electrode was incubated DA of different concentrations at room temperature for 10 min in PBS (1 ×, pH = 7.4) solution, followed by cleaning with DI water. Then the photocurrent response of DA by TiO_2 NTPCs were conducted using a three-electrode configuration with the TiO_2 NTPCs, Ag/AgCl and Pt foil as working, reference and counter electrode, respectively. The supporting electrolyte used was PBS (1 ×, pH = 7.4) solution. The photocurrent was measured under an irradiation from a 300 W Xe lamp (PLS-SXE300, PE300BF) with 420 nm cutoff filter.

2.5. Microdialysis experiments

All procedures involving animals were conducted with the approval of the Ani-mal Ethics Committee in ECNU, China. Male Sprague–Dawley rats (weight ranges from 200 to 250 g) were purchased from Shanghai SLAC Laboratory animal Co. Ltd. and acclimatized for 4 days. Then the rats were anesthetized with chloral hydrate (initial dose of 300 mg/kg (i.p.) with additional doses of 50 mg/kg (i.p.) as needed to maintain anesthesia) and wrapped in a homeothermic blanket (Beijing Tide-Gene Biotechnology Development Center). The rats were placed in a stereotaxic frame (Beijing Tide-Gene Biotechnology Development Center) with the incisor bar set at 5 mm above the interaural line and appropriately placed holes were drilled through the skull. The microdialysis guide cannula (CMA/MD AB, Stockholm, Sweden) was implanted in the striatum at the site of 2.5 mm anterior to bregma, 2.5 mm lateral from midline,