



An enhanced photoelectrochemical immunosensing platform: Supramolecular donor–acceptor arrays by assembly of porphyrin and C₆₀

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ABSTRACT

A novel self-assemble approach was developed for constructing a linear bicontinuous donor–acceptor, (H₂BCPP)_n–C₆₀, arrays on indium–tin oxide electrode. Electronic absorption spectra, fluorescence spectra and atomic force microscopy were used as powerful tools to characterize H₂BCPP, (H₂BCPP)_n arrays and (H₂BCPP)_n–C₆₀ arrays. The (H₂BCPP)_n–C₆₀ arrays enhanced the photocurrent generation capability, and presented an efficient photoelectrochemical immunosensing platform for the ultrasensitive detection of carcinoembryonic antigen (CEA). The quantitative measurement of CEA was based on the decrease in the photocurrent intensity of the (H₂BCPP)_n–C₆₀ arrays, which was resulted from the competition between CEA and CEA–CdTe. A linear relationship between the photocurrent decrease and the CEA concentration was obtained in the wide range from 0.01 to 60 ng mL^{−1} with a detection limit of 3.4 pg mL^{−1}. The proposed sensor showed high sensitivity, stability and reproducibility, and provided a promising platform for other biomolecular detection.

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1. Introduction

As a newly developed analytical method for the detection of biomolecules, photoelectrochemical (PEC) immunosensing has become an attractive and promising analytical method (Zhang et al., 2014; Zeng et al., 2013). In the case of PEC detection process, light is used to excite active species on the electrode, and current is used as the detection signal, which is just the reverse process of electrochemiluminescence (Li et al., 2013; Zhao et al., 2014). Benefiting from the different forms of energy for excitation and detection, the sensitivity and specificity of PEC could potentially match that of the electrochemiluminescence. In addition, PEC immunosensing is simple, low-cost, and well-suited for rapid high-throughput biological assays (Wang et al., 2009). Thus, over the years this technique has been employed to analyze various biomolecules. However, PEC immunosensing is still in its infancy and the low phototocurrent conversion efficiency is still a big challenge. Therefore, it is essential to improve the photocurrent response efficiency.

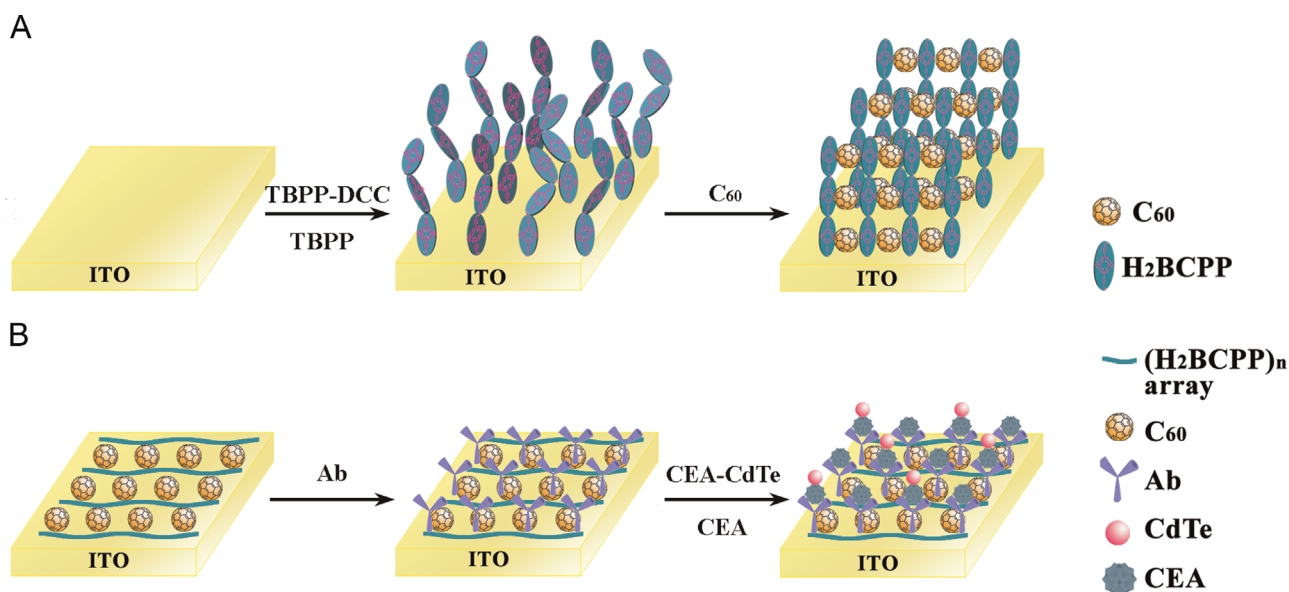
One way to approach high photoconductivity is to fabricate bicontinuous donor–acceptor (D–A) arrays in molecule level (Segura et al., 2005; Yamamoto et al., 2006). Such D–A arrays would yield efficient charge separation and transportation of separated

charges to their respective electrodes, which would lead to the enhancement of photocurrent. In particular, porphyrin–fullerene complexes have been proved as one of admirable building blocks for D–A arrays, because of the fast electron transfer and slow electron recombination (Choi et al., 2003a, 2003b). As yet, few nanostructures with porphyrin–fullerene arrays have been obtained by self-assembly (Schmidt-Mende et al., 2001; Hizume et al., 2010; Charvet et al., 2012). In addition, considering the fast electron transfer, the linear bicontinuous arrays were ideal. Many linear arrays of porphyrin have been fabricated, depending mainly on the π – π interaction in cooperation and/or competition with additional inter-molecular interactions, such as van der Waals, hydrogen bonding, hydrophilic/hydrophobic, electrostatic and metal–ligand coordination. However, it is still difficult to achieve the linear bicontinuous porphyrin–fullerene arrays on an electrode.

Herein, we report a novel approach for constructing a linear bicontinuous alignment of D–A arrays on ITO electrode for use as a PEC immunosensor (Scheme 1A). First, the self-assembly of 5,15-bis(4-carboxyphenyl)10,20-bis(mesityl) porphyrin (H₂BCPP) donor ensures the growth of porphyrin arrays on the ITO electrode using an ester bond between –COOH groups of H₂BCPP molecules and –OH groups of the hydrophilic pretreated ITO surface. Then, with this monolayer solid film of H₂BCPP as a template, H₂BCPP arrays were formed on it in situ through hydrogen bond between neighboring –COOH groups of porphyrin molecules. Fullerene

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Scheme 1. Schematic molecular structure of 5,15-bis(4-carboxyphenyl)10,20-bis(mesityl) porphyrin (H_2BCPP).

(C_{60}) acceptors were infiltrated into the porphyrin brush and resulted in porphyrin- C_{60} arrays using π - π interactions between the porphyrin and C_{60} moieties. In this paper, the $(H_2BCPP)_n-C_{60}$ arrays are first used to fabricate a novel competitive PEC immunosensor for carcinoembryonic antigen (CEA) detection with enhanced detection sensitivity (Scheme 1B). As a biomarker, rapid and accurate detection of CEA is crucial for the diagnosis, prognosis and treatment of cancer. Moreover, the results indicate that this novel $(H_2BCPP)_n-C_{60}$ arrays possesses great potential in the application of PEC immunosensors in the detection of other significant proteins.

2. Experiments

2.1. Reagents

Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200–300 mesh) with the indicated eluent. Mouse monoclonal capture CEA antibodies (Ab) and CEA standard solutions (0.5 mg mL^{-1}) were purchased from Shanghai Linc-Bio Science Co. Ltd. Blocking buffer for the residual reactive sites on the Ab immobilized ITO was phosphate buffer solution (PBS) containing 0.5% bovine serum albumin (BSA) and 0.5% casein. Tween-20 (0.05%) was spiked into 0.01 M PBS (pH 7.4) as a washing buffer to minimize unspecific adsorption. The aqueous solutions unless indicated were prepared with Milli-Q water (Millipore, USA). N-hydroxysuccin-imide (NHS, 98%) and N-(3-dimethyl-amino-propyl)-N-ethylcarbodiimide (EDC) were bought from Alfa Aesar China Ltd. All solvents were of reagent grade and used as received. The compound meso-(mesityl)dipyromethane was prepared according to the published procedures (Littler et al., 1999).

2.2. Apparatus

1H NMR spectrometry was recorded on a Bruker DPX 300 spectrometer (300 MHz) in DMSO- D_6 using the residual solvent resonance of DMSO at 2.5 ppm relative to $SiMe_4$ as internal reference. MALDI-TOF mass spectrometry was performed on a Bruker BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α -cyano-4-hydroxycinnamic acid as a matrix. Electronic absorption spectra were

obtained using a Hitachi U-4100 spectrophotometer. Scanning electron microscopic (SEM) images were obtained on a JEOL JSM-6700 F. For SEM imaging, carbon (1–2 nm) was sputtered onto these grids to prevent charging effects and to improve the image clarity. Electrochemical measurements for H_2BCPP solution were carried out with a CHI 660D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) with a three-electrode system. The cell comprised inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+ , which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced ex- or internally to the ferrocenium/ferrocene (Fc^+/Fc) couple [$E_{1/2}(Fc^+/Fc) = 501 \text{ mV vs. SCE}$]. Typically, a 0.1 mol L^{-1} solution of $[Bu_4N][ClO_4]$ in THF containing 0.5 mmol L^{-1} of sample was purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rate was 20 mV s^{-1} for CV. Photoelectrochemical measurements were carried out with a homemade photoelectrochemical system. A 500 W Xe lamp was used as the irradiation source with the light intensity about $400 \mu\text{W cm}^{-2}$ estimated with a radiometer (Photoelectric Instrument Factory of Beijing Normal University). The photocurrent was measured on a CHI 660D electrochemical workstation with a three-electrode system, where the modified indium tin oxide (ITO) electrode was employed as the working electrode, a Pt wire served as counter electrode, and a $Ag/AgCl$ electrode was used as reference electrode.

2.3. Preparation of 5,15-BIS(4-methylesterphenyl)10,20-BIS(mesityl) porphyrin complex

Meso-(mesityl)dipyromethane (132 mg, 0.5 mmol) and methyl-4-formylbenzoate (82 mg, 0.5 mmol) were dissolved in 50 mL of CH_2Cl_2 . Then, 66 μL of TFA (0.3 mmol) were slowly added and the mixture was stirred at room temperature under N_2 for 30 min. *p*-Chloranil (123 mg, 0.5 mmol) was added and the resultant solution was stirred for additional 1 h at room temperature. Then, the reaction mixture was chromatographed on an alumina column with CH_2Cl_2 as eluent, and further purified by silica-gel column chromatography. Recrystallization from $CHCl_3/n$ -hexane gave the target compound in the yield of 30% (60 mg). 1H NMR (DMSO- d_6 , 300 MHz, δ): 8.75 (d, 4H, pyrrole β H), 8.72 (d, 4H, pyrrole β H),

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