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TiO_2 nanoparticles embedded in borocarbonitrides nanosheets for sensitive and selective photoelectrochemical aptasensing of bisphenol A

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ABSTRACT

The establishment of ultrasensitive, highly selective and cost-effective photoelectrochemical (PEC) biosensing platforms is essential for biological assays. In this work, a novel visible-light driven PEC platform was developed for ultrasensitive detection of bisphenol A (BPA) based on TiO_2 nanoparticles embedded in borocarbonitrides nanosheets (TiO_2/BCN), which were fabricated through one-step thermal-treatment approach. The introduction of BCN not only extends photoresponding of TiO_2 to visible light area, but also effectively suppresses the recombination of photoinduced electron-hole pairs, and then presented enhanced PEC performances. The PEC sensing platform is constructed via a stepwise modification method with the aids of BPA aptamer, and characterized by PEC and electrochemical impedance spectroscopy (EIS). In the presence of BPA, the photocurrent can be greatly enhanced because BPA can inhibit the recombination of photogenerated electron-hole pairs and accelerate the interfacial charge transfer process. The results demonstrated that the photocurrent is highly linear over BPA concentrations ranging from 0.1 fM to 5 nM with a low detection limit of 0.03 fM (S/N = 3). Moreover, the as-fabricated PEC sensor exhibited high selectivity and low-cost, which could be successfully applied for the fast, sensitive, and selective determination of BPA in real water samples.

1. Introduction

Bisphenol A (BPA), as a noticeable industrial chemical, has been commonly utilized in the manufacture for food packing, epoxy resins, and flame retardants [1–3]. Considered as an endocrine-disrupting compound, various studies found that BPA can mimic the function of the 17-β estradiol hormone even at very low concentrations, and therefore disturb the estrogen-estrogen receptor binding process, resulting neurotoxicity, chronic diseases, and various types of cancer [3,4]. Hence, it is urgently to develop an ultrasensitive, selective, and reliable method for BPA detection to ensure food safety and human health. Till now, various analytical methods including high performance liquid chromatography [5], gas chromatography–mass spectrometry [6], chemiluminescence [7], fluorimetry [8], and electrochemical methods [2,4,9] have been reported for BPA quantification. Among them, electrochemical methods have been drawn extensive attention owing to its advantages of low cost, fast response, convenient instrument, simple operation and ease of miniaturization compared to those apparatus-approaches [4,9]. However, the major obstacle encountered in BPA detect by electrochemical methods is the high overpotential used for the BPA oxidation, which restricted the selectivity and reproducibility of the electrochemical sensors [4]. Therefore, it is still an urgent need to construct a novel methodology for BPA assay with high sensitivity, good selectivity and excellent reproducibility.

Photoelectrochemical (PEC) sensing is a novel and dynamically developed analytical technique, which has drawn mounting interests for its satisfactory analytical performances [10–16]. Since the complete separation of the excitation source and the detection signal, the PEC sensor possesses promising higher sensitivity than the traditional electrochemical methods [10,17]. Different from conventional electrochemical techniques, PEC sensing requires photoactive materials to generate photocurrent signal under photoirradiation. Various kinds of quantum dots (QDs) or semiconducting nanoparticles (NPs) based photoactive materials have shown great promise in PEC sensors [17]. Among them, TiO_2-based photoactive nanomaterials have been widely used in PEC sensing due to its superior photo-stability, low toxicity, abundance resource and chemical stability [18,19]. Especially, TiO_2 coupling with carbonaceous material could not only hamper the recombination rate of photoinduced electron-hole pairs, but also enhance

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the PEC performances of TiO_2 in the irradiation of visible light. For example, Niu's group [20] constructed TiO_2/C_3N_4 nanomaterials, which displayed a fabulous property in promoting transport and separation of photoinduced carriers, leading to an increased photocurrent under visible light.

Two-dimensional borocarbonitrides (BCN), as a novel kind of carbonaceous derived materials, has attracted recent interests in electrical conductors, gas storage/separation, energy storage and optical devices, owing to its good chemical and thermal stability, extremely fast electron mobility, improved electrical conductivity, high specific surface area and excellent optical performance [21,22]. Furthermore, theoretical calculations followed by experimental evidence have indicated that BCN have high charge carrier mobility, and it could improve the charge transport and improved light harvest [23,24]. For instance, Bharathidasan et al. [24] fabricated ZnO-containing BCN hybrids via solution combustion synthesis, and found that BCN could act as an important role in extending the photoresponse of ZnO in the visible region, inhibiting the recombination of photoinduced electron-hole pairs and promoting the interfacial charge transport process. Encouraged by these explorations, it is expected that the coupling of BCN and TiO_2 might have a high-performances in PEC sensing.

In this work, a novel PEC biosensor was developed for BPA assay based on TiO_2 nanoparticles embedded in BCN nanosheets (TiO_2/BCN) nanocomposites with the aids of BPA aptamer. As a high specific and affinity molecular recognition elements, aptamers have lots of advantages, such as easier artificial synthesis, better stability, smaller size, easy modification, and higher specificity, which are beneficial to the construction of PEC sensors. In addition, the as-prepared hybrid nanomaterials were considerably efficient for the transportation of photoinduced charge carriers, leading to increased PEC response compared with pure TiO_2. Furthermore, the introduction of BCN could extend the photoresponse of TiO_2 to visible light. Such sensor exhibited excellent performances including high stability, excellent selectivity, ultrasensitivity, and low cost. Moreover, we further explored the detailed sensing mechanisms by using electrochemical impedance spectroscopy (EIS) and Photoluminescence (PL) techniques. In addition, the as-prepared PEC sensor for determination of BPA in real water samples was studied.

2. Experimental section

2.1. Reagents

BPA, titanium nitrate ($Ti(NO_3)_4$), glycine, boron trioxide (B_2O_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. The BPA aptamer was synthesized and purified from Sangon Biotech Co., Ltd. with the sequence as follows: 5′-CCGGTGGGTGGTCAGGTGGGATAGC GTTCCGCGTATGGCCCAGCGCATCACGGGTTCGCACCA-3′.

For electrochemical impedance spectra (EIS) characterization, 5 mM $[Fe(CN)_6]^{3-/4-}$ solution with 0.1 M KCl was utilized as electrolyte. While for PEC measurement, phosphate buffered solution (PBS, 0.1 M) was employed as electrolyte.

2.2. Apparatus

The morphology was measured through transmission electron microscopy (TEM, JEOL JSM-6700) and scanning electron microscopy (SEM, Hitachi-S4800). Fourier transform infrared spectra (FTIR) were collected on Spectrometer (Nicolet Nexus 470). Powder X-ray diffraction measurements (XRD, Bruker D8 diffractometer) were characterized to detect the crystal structure of the samples. Raman spectra (Renishaw InVia Raman spectrometer) were conducted at 532 nm excitation wavelength. X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific ESCALAB 250 spectrometer) and UV–vis diffuse reflectance spectroscopy (UV-DRS, UV-2450 spectro-photometer) were measured the composition and the optical properties of the samples, respectively. PEC and electrochemical measurements were conducted on a CHI 660E electrochemical workstation (Chenhua) in ambient temperature, which was linked with three-electrode system comprising saturated calomel electrode (SCE) as the reference electrode, Pt wire as the auxiliary electrode, materials modified ITO electrode as working electrode. Xe lamp (CHF-XM35-500W, Beijing Changtuo) was used as the light source. The whole PEC tests were performed in 0.1 M PBS at 0.4 V potential and current-time (I-t) test was applied for the entire PEC measurements.

2.3. Preparation of samples

TiO_2/BCN nanocomposites were synthesized by a facile one-step thermal-treatment method. Firstly, 20 mg B_2O_3 and 40 mg Gly was dispersed in 4.5 mL double-distilled sterile water via several sonication minutes to obtain a transparent solution. After a certain amount of $TiO(NO_3)_2$ were added, the solution was sonicated for 1 h. Finally, the resulting solution was transferred into an alumina crucible and the temperature of the hybrid was gradually risen to 500 °C and then maintained for 2 h under argon atmosphere. Eventually, the resultant nanocomposites were gathered from the alumina crucible directly. The TiO_2/BCN nanocomposites with different TiO_2 amount were prepared by simply adjusting the amounts of $TiO(NO_3)_2$ (100 mg, 300 mg, 600 mg, 800 mg) during the synthesis process, which were labeled as TiO_2/BCN-1, TiO_2/BCN-2, TiO_2/BCN-3, and TiO_2/BCN-4, respectively. In addition, pure TiO_2 nanoparticles were synthesized by the same method except for the addition of B_2O_3 and Gly.

2.4. Fabrication of PEC sensor

Primarily, the ITO electrodes were cut into 1 cm × 2 cm and then washed by NaOH (1 M), deionized water and ethanol, respectively. After drying in ambient, 20 μL of the TiO_2/BCN suspension (2 mg mL^{-1}) was dropped on the surface of ITO, and the membrane was sintered at 400 °C for 2 h in atmosphere to improve the adhesion strength between substrate and the film. Next, the as-prepared TiO_2/BCN/ITO electrode was incubated with 1.5 μM BPA aptamer for several hours, and then rinsed with PBS (0.1 M, pH = 7.4) for removal of the physically absorbed aptamer. The aptamer was bonded on BCN through π–π stacking, hydrophobic interaction and van der Waals forces, which is similar to the interaction between graphene and DNA. Therefore, aptamer/TiO_2/BCN/ITO electrode was fabricated successfully. In contrast, the aptamer probes based on TiO_2 was obtained through the same method.

3. Results and discussion

3.1. Characterizations of the samples

The morphology and microstructure of the as-prepared TiO_2/BCN nanomaterials were characterized by TEM. Fig. 1A demonstrated that the BCN was two-dimensional structure with several hundreds of nanometers. Additionally, a great amount of TiO_2 nanoparticles were embedded in two-dimensional BCN nanosheets. It is also clearly uncovered that the average diameter of the TiO_2 nanoparticles is around 8 nm, such a small size of TiO_2 in the nanocomposites can be further ascribed to the strong coupling of TiO_2 and the detect sites on the BCN sheets [25]. The SEM image (Fig. S1) reveals that the as-prepared structure is composed of a large sheet like structure with holes. Fig. 1B presents the EDS elemental mapping of the as-prepared nanocomposites, clearly demonstrating that this TiO_2/BCN nanocomposites are comprised of B, C, N, Ti and O elements, which were consistent with reported BCN structures [24].

The XRD characterization was also employed to reveal the phase of the TiO_2 nanoparticles and effects of BCN incorporation on the crystal structure. We find that all the identified XRD peaks (Fig. 1C) are in