



One-pot hydrothermal route to fabricate nitrogen doped graphene/Ag-TiO₂: Efficient charge separation, and high-performance “on-off-on” switch system based photoelectrochemical biosensing

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ABSTRACT

Charge separation is crucial for increasing the performances of semiconductor-based materials in many photoactive applications. In this paper, we designed novel nanocomposites consisting of TiO₂ nanocrystals, Ag nanoparticles (NPs) and nitrogen doped graphene (NGR) via a facile one-pot hydrothermal route. The as-prepared ternary nanocomposites exhibited enhanced photoelectrochemical (PEC) performances owing to the introduction of Ag NPs and NGR, which increase the excitons' lifetime and improve the charge transfer. In particular, it is shown by means of the transient-state surface photocurrent responses that the photocurrent intensity of the as-fabricated composites exhibited 18.2 times higher than that of pristine TiO₂. Based on the robust photocurrent signal, a new kind of “on-off-on” PEC aptasensor was established with the assistance of Pb²⁺ aptamer, which integrates the advantages of low background signal and high sensitivity. Under optimal conditions, a wide linear response for Pb²⁺ detection was obtained from 1 pM to 5 nM as well as a detection limit down to 0.3 pM. With its simplicity, selectivity, and sensitivity, this proposed strategy shows great promise for Pb²⁺ detection in food and environment analysis.

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1. Introduction

Photoinduced electron-hole pairs in semiconductors allow for solar conversion into electrical or chemical energies (Yu et al., 1995; Lee et al., 2014). The total conversion efficiencies are highly dependent upon the separation of charge pairs because most photogenerated charge carriers get annihilated through recombination in the bulk or at interfaces, which adversely limits the total quantum efficiencies (Ingram and Lincic, 2011; Li et al., 2013; Dai et al., 2014a, 2014b). In order to increase charge separation efficiency, both enhancing the excitons' lifetime and ingeniously controlling the spatial charge transfer are essential (Lambright et al., 2014; Yoo et al., 2014; Chang et al., 2015). And the major method in practice is to rationally alter the components or design semiconductor-based composites at the nanoscale, which could inhibit the recombination of photo-generated

electron-hole pairs, resulting improved device/cell performance (Wu et al., 2015; Fan et al., 2015). Therefore, investigating and tailoring the component of the system at around the interfaces during light illumination is of significance in the fundamental understanding and application of photoactive fields.

Titanium dioxide (TiO₂) is a well-known photoactive material for photocatalytic and photoelectrochemistry in light of its chemical stability, abundance resource, low toxicity and superior photo-stability (Pu et al., 2013; Bian et al., 2014; Zhang et al., 2014). On its own, it shows a limited performance because most of the excitons cannot be involved in the surface reactions upon traveling in TiO₂ and the recombination of electron-hole pairs is fast (Pu et al., 2013; Yoo et al., 2014). In order to enhance the excitons' lifetime, asymmetric material systems have been suggested by inducing electrostatic anisotropy such as metal-semiconductor interfaces (Bian et al., 2014; Yoo et al., 2014). Metal nanoparticles (NPs)-decorated TiO₂ system is a well-established example where electrons can stay longer in the metal NPs upon charge transfer through the junction interfaces (Hirakawa et al., 2005; Murdoch et al., 2011). Meanwhile, such plasmonic nanostructures of metal NPs-decorated TiO₂ system are well-known to enhance the

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visible-light absorption via localized surface plasmon resonance characteristics because of the collective oscillation of surface electron cloud (Ingram and Linic, 2011). Notably, surface plasmons of Ag NPs can cause significant enhancement in the local electromagnetic field due to the intense surface plasmon resonance cross-section of silver (Brus, 2008; Zhao et al., 2012; Wang et al., 2013). However, there have been quite a few researches concerning with Ag-TiO₂ nanocomposites used as photoactive materials in many photoactive applications.

Carbonaceous materials such as carbon nanohorn (Dai et al., 2014a, 2014b), sulfonated graphene (Wang et al., 2014b), graphene quantum dots (Zhuo et al., 2012), have demonstrated to be important substrates by integration with TiO₂ to form multi-component photoelectrode system with the purpose of inhibition the photo-generated electron-hole pairs recombination. Recently, nitrogen doped graphene sheet (NGR), a novel kind of two-dimensional (2D) substrate material, has been widely applied in photocatalysis, energy storage and environmental treatment owing to its extremely fast electron mobility, good biocompatible C-N microenvironment, improved electrical conductivity and high chemically active sites (Wang et al., 2012; Wang et al., 2014a). Both theoretical and experimental studies have revealed that the doping of nitrogen in graphene networks is capable to facilitate charge transfer between neighboring carbon atoms, which enhanced light harvesting, prolonged life time of carriers, as well as higher photocurrent (Hou et al., 2013; Meng et al., 2013; He et al., 2014; Li et al., 2015). For example, He et al., (2014) successfully coupled NGR with nanocrystalline α -Fe₂O₃ through a common wet-chemical method, and found that the photogenerated charge separation of the resulting nanocomposite is greatly promoted. Chen's group (Hou et al., 2013) constructed 2D porous C₃N₄/NGR/MoS₂ composite, and disclosed that NGR have an important role in promoting separation and transfer of photogenerated carriers, leading to a high photocurrent. Inspired by these work, it can be expected that the coupling of NGR and Ag NPs with TiO₂ could might have a high-performances in photoactive applications.

Photoelectrochemical (PEC) sensing with semiconductor photoactive materials has received substantial attentions in a wide variety of research fields including DNA analysis, immunoassay, and cytosensing (Zhao et al., 2014; Zhao et al., 2015). The smart integration of photo-excitation and electrochemical analysis renders PEC sensing many potential advantages, such as simple instrumentation setup, short analytical time, and low cost (Zhao et al., 2015). Recently, (Wang et al., 2014b) reported a "signal-on" PEC sensor for global antioxidant capacity detection via a bi-component sulfonated graphene-TiO₂ nanohybrid. In our previous study, we fabricated a "signal-off" PEC sensor for chlorpyrifos assay based on BiPO₄-graphene (Qian et al., 2015a, 2015b). Despite their advantages, these "signal-on" or "signal-off" PEC sensors were restricted to the low sensitivity, which limits their application in analysis of real samples. Therefore, it is necessarily to fabricate "on-off-on" switch system based PEC sensing platform by coupling "signal-on" and "signal-off" strategies with merits of low background signal and high sensitivity. Obviously, the more highly the initial signal of the first "switch on" state enhanced, as well as the larger the quenching rate of the "switch off" state got, the more strongly the signal intensity of the second "switch on" state recovered. Thus, the design of the enhanced first "switch on" state may be one of the import key point in an "on-off-on" switch system construction.

Herein, NGR/Ag-TiO₂ nanocomposites were prepared via a one-pot hydrothermal route without employing toxic and harsh reducing agents, which is quite efficient for the charge separation, resulting in enhanced PEC response. In particular, the resulting NGR/Ag-TiO₂ exhibited 18.2 times the photocurrent intensity higher than the pristine TiO₂ under the light irradiation. Moreover,

a novel label-free PEC aptasensor based on the "on-off-on" switch system has been constructed for the sensitive and selective detection of Pb²⁺. The as-fabricated "on-off-on" pattern exhibits a good performance, opens new opportunities based novel switches for detecting a wide range of the analysts and significantly demonstrates a proof-of-concept for biosensing applications.

2. Experimental

2.1. Reagents and chemicals

Graphite was purchased from Qingdao Tianhe Graphite Co., Ltd. TiO(C₄H₉O)₄, AgNO₃, HNO₃, glycine (Gly) were purchased from Sinopharm Chemical Reagent Co., Ltd. GO was prepared using modified Hummers method from graphite powders (Gilje et al., 2007). TiO(NO₃)₂ was obtained by dissolving TiO(C₄H₉O)₄ in nitric acid. Aptamer was chosen according to the previously reported literature (Zang et al., 2014). The oligonucleotides used were synthesized and purified by Sangon Biological Engineering Technology & Co. Ltd. (Shanghai, China) with the following sequences:

Pb²⁺ aptamer: 5'-TTGGGTGGGTGGGTGGGT-3'.

The washing buffer was 0.1 M phosphate buffered saline (PBS) of pH 7.4 containing 0.1 M NaCl. Doubly distilled water was used throughout this work. All reagents used were commercially available and of analytical grade.

2.2. Apparatus

Characteristics were performed via transmission electron microscopy (TEM, Hitach H800, Japan), scanning electron microscopy (SEM, JEOL JSM-6700, Japan) equipped with an energy-dispersive spectroscopy (EDS, Oxford Inca Energy 400, UK), power X-ray diffraction spectra (XRD, Bruker D8 ADVANCE diffractometer, Germany) with Cu-K α radiation (λ =1.54 Å), Raman spectra (RM 2000 microscopic confocal Raman spectrometer, England), X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Japan), UV-vis diffuse reflectance spectroscopy (UV-DRS, UV-2450 spectrophotometer, Japan) utilizing BaSO₄ as the reference. Electrochemical impedance spectra (EIS) were conducted using ZENNIUM electrochemical workstation in 0.1 M KCl solution containing 5 mM Fe(CN)₆^{3-/4-} with the frequency range from 0.01 Hz to 10 kHz. Photoelectrochemical (PEC) currents measurements were performed by a CHI 660B electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) at room temperature, which was connected to a conventional three-electrode cell using samples modified ITO as a working electrode, saturated calomel electrode (SCE) as a reference electrode, and Pt wire as a counter electrode. All the PEC measurements were carried out in 0.1 M phosphate buffer solution (PBS) at 0 V and a 250 W Xe lamp (CHF-XM35-500W, Beijing Chang tuo) was utilized as the light source with an intensity of 100 mW cm⁻². Current-time (I-t) method was used for the whole PEC experiments.

2.3. Preparation of samples

The NGR/Ag-TiO₂ nanocomposites were prepared by a one-pot hydrothermal route. In a typical procedure, GO solution (2 mg mL⁻¹) was mixed with AgNO₃, TiO(NO₃)₂ and Gly at a certain mass ratio. After sonicated for two hours, the mixtures were then transferred to a Teflon lined autoclave of 25 mL capacity and subjected to heating at a temperature of 180 °C for 12 h, followed by natural cooling to room temperature. The precipitates were collected by centrifugation, and finally dried at 60 °C for 12 h. For comparison, pure TiO₂ was prepared using TiO(NO₃)₂ under the same process, NGR/TiO₂ nanocomposites were synthesized with

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