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Using silver nanocluster/graphene nanocomposite to enhance photoelectrochemical activity of CdS:Mn/TiO_2 for highly sensitive signal-on immunoassay

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ABSTRACT

A highly sensitive signal-on photoelectrochemical (PEC) immunosensor was fabricated here using CdS:Mn/TiO_2 as photoelectrochemical sensing platform, and silver nanoclusters and graphene naocomposites (AgNCs-GR) as signal amplification tags. The immunosensor was constructed based on the specific sandwich immunoreaction, and the photo-to-current conversion efficiency of the isolated protein modified CdS:Mn/TiO_2 matrix was improved based on the synergistic effect of AgNCs-GR. Under irradiation, the photogenerated electrons from the AgNCs at a higher conduction band edge level could be transport to the CdS:Mn/TiO_2 matrix with the assistance of highly conductive graphene nanosheets, as well as recycle the trapped excitons in the defects-rich CdS:Mn/TiO_2 interface. The electron transport and exciton recycle reduced the possibility of electron–hole recombination and greatly improved the photo-to-current conversion efficiency of the sensing matrix. Based on the signal enhancement, a signal-on PEC immunosensors was fabricated for the detection of carcinoembryonic antigen (CEA), a model analyte related to many malignant diseases. Under optimal conditions, the as-prepared immunosensor showed excellent analytical performance, with a wide linear range from 1.0 pg/mL to 100 ng/mL and a low limit of detection of 1.0 pg/mL. The signal-on mode provided 2.48 times higher sensitivity compared with signal-off mode. This strategy demonstrated good accuracy and high selectivity for practical sample analysis, thus may have great application prospective in the prediction and early diagnosis of diseases.

1. Introduction

As an important part of photoelectrochemical (PEC) analysis, PEC immunoassays have attracted considerable attentions in a wide range of application fields, such as clinical diagnosis, food safety, environmental monitor and national security (Zhao et al., 2015). Such immunoassay method not only inherits the unique advantages of PEC technique, including desirable low background, high sensitivity, and easily minimized instruments, but also possesses high selectivity originated from the specific immunoreaction (Haddour et al., 2006). Because of these attractive properties, since the pioneering work of Cosnier and co-workers (Haddour et al., 2006), a myriad of PEC immunosensors that integrate the advanced PEC nanomaterial, elegant interface assembly technique, and highly catalytic enzymatic reactions have been sequentially reported for the detection of different analytes (Fan et al., 2014a; Zhao et al., 2012a; Fan et al., 2015; Wang et al., 2009a, 2009b; Zhao et al., 2012b). Although great progresses have been made, compared to the traditional immunosensors, such as the electrochemistrical immunosensors (Wu et al., 2006), fluorescent immunosensors (Li et al., 2014a, 2014b), and electrochemiluminescent (ECL) immunosensors (Zhu et al., 2010; Zhu et al., 2012), the investigation on PEC immunoanalysis is still in the early stage. Especially, most of the reported PEC immunosensors belong to signal-off type, which means the signal decreases with the increase of target concentration. In comparison with its signal-on counterpart, the signal-off biosensors are not ideal for practical applications. Disadvantages include limitations in the signaling capacity (in which only a maximum of 100% signal suppression can be attained) and high possibility of false positives (Wang et al., 2009a, 2009b; Wu and Lai, 2014). To circumvent this problem, there would be merits in designing signal-on PEC immunosensors.

The main challenge in developing highly sensitive signal-on

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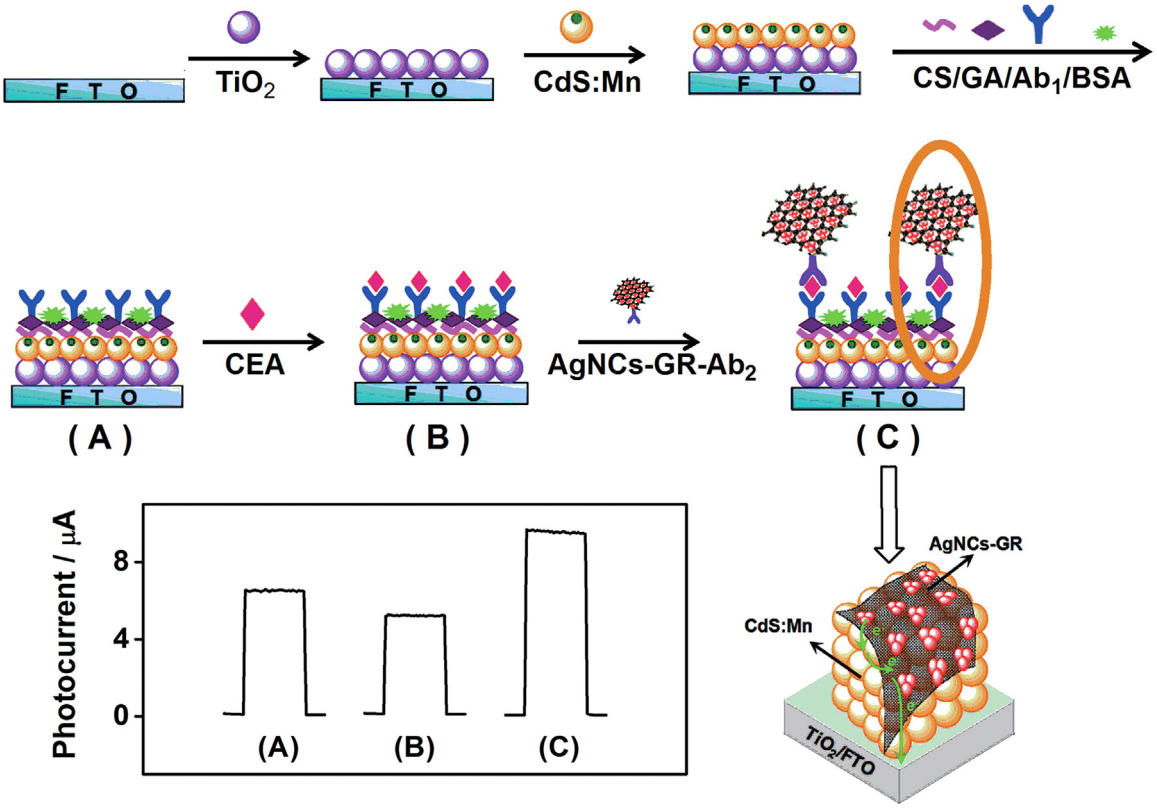
PEC immunosensors comes from the isolated protein multilayer formed on the sensing interface which severely impedes the interfacial electron transfer and reduces the photo-to-current conversion efficiency (Zhao et al., 2012a). To date, only a few signal-on PEC immunosensors have been developed by employing native enzymes, such as horseradish peroxidase (Tu et al., 2012; Zeng et al., 2014a), alkaline phosphatase (Zhao et al., 2012a; Sun et al., 2014), and glucose oxidase (Shu et al., 2015) as signal report labels. The labeled enzymes catalyze their substrates and in situ produce a large amount of electron donors (e.g., ascorbic acid) to suppress the e^-–h^+ recombination of photovoltaic materials, which could overcome the adverse effect arising from the isolated protein multilayers and lead to the formation of signal-on PEC immunosensors. However, because of the inherent nature of enzyme, those enzymes based PEC immunosensors have to suffer from several problems, such as poor stability, high cost, and poor reproducibility arising from the variable activity depending on batch, source, and detection conditions (Lin et al., 2015; Zhang et al., 2013a, 2013b). In addition, the sensitivity of those signal-on immunosensors is much lower than their signal-off counterparts since the labeled enzyme with poor conductivity would increase the steric hindrance on the PEC sensing interface and compete with the photovoltaic material to absorb irradiation light (Zhao et al., 2012a). Therefore, it is still of great importance to develop novel signal-on PEC immunosensors with improved analytical performances. One effective way is to design and synthesize novel labeling nanomaterials which could substitute enzyme and have the ability to improve the conductivity of isolated protein modified multilayers and to enhance the photo-to-current conversion efficiency of the PEC sensing matrix. However, to the best of our knowledge, this is still a blank area, but with great perspectives.

Herein, graphene and DNA stabilized silver nanoclusters (AgNCs-GR) is synthesized and applied as signal amplification tag for developing highly sensitive signal-on PEC immunosensors. The selection of graphene is because of its excellent conductivity, which could improve the electron transfer in the isolated protein layer modified electrode and enhance the photo-to-current conversion efficiency of PEC devices (Lightcap and Kamat, 2012; Zhao et al., 2012c; Kang et al., 2009). The selection of AgNCs to assemble with graphene is because they have stronger π–π stacking interaction with graphene and possess unique PEC properties, such as tunable bandgap/band-edge levels and high photo-to-current conversion efficiency (Liu, 2014; Li et al., 2014a, 2014b; Zhang et al., 2015). Using Mn^{2+} doped CdS QDs modified TiO_2 (CdS:Mn/TiO_2), a nanocomposite with high photo-to-current conversion efficiency as sensing matrix (Fan et al., 2014a; Fan et al., 2014b; Santra and Kama, 2012; Wu et al., 2015), a signal-on PEC immunosensor was fabricated for the highly sensitive detection of carcinoembryonic antigen (CEA). CEA is a tumor maker related with many malignant cancers, such as gastric carcinoma, pancreatic carcinoma, and lung carcinoma (Wu et al., 2006). Since its level in human serum can give information of the disease stage, the grade of metastasis and the recidivism of tumor, the determination of CEA is of great importance for clinical research and diagnosis. The detection process is illustrated in Scheme 1. At first, CEA is combined to the antibody and decreases the photocurrent (signal-off). Then, the antibody labeled AgNCs-GR is brought to the PEC sensing interface, which leads to a significant photocurrent enhancement (signal-on). Compared with signal-off mode, the detection sensitivity for CEA by introducing the AgNCs-GR dramatically increases 248%. The photocurrent enhancement could be ascribed to the synergistic interaction of AgNCs, graphene, and CdS:Mn/TiO_2 sensing matrix. In detail, graphene could improve the conductivity of the isolated protein multilayers and enhance the utilization of hot electrons/excitons trapped in the defects of QDs, while AgNCs could form a multilayered structure with the CdS:Mn/TiO_2 matrix with cascade conduction band edge potentials to ensure effective photoelectron injection to the PEC



Scheme 1. Fabrication process and detection mechanism of the PEC immunoassay method.