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Visible-light driven photoelectrochemical immunosensor for insulin detection based on MWCNTs@SnS_2@CdS nanocomposites

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A B S T R A C T

In this work, a label-free photoelectrochemical (PEC) immunosensor was developed for ultrasensitive detection of insulin based on MWCNTs@SnS_2@CdS nanocomposites. As graphene-like 2D nanomaterial, SnS_2 nanosheets loaded on the conducting framework of multi-walled carbon nanotubes (MWCNTs) were adopted for the construction of immunosensor for the first time, providing a favorable substrate for in-situ growth of CdS nanocrystal that had suitable band structure matching well with SnS_2. The well-matched band structure of these two metal sulfides effectively inhibited the recombination of photo-generated electron-hole pairs, thus improving the photo-to-current conversion efficiency. Besides, the introduction of MWCNTs facilitated electron transfer across the surface of electrodes, leading to a further increment of photocurrent. The as constructed label-free PEC immunosensor based on MWCNTs@SnS_2@CdS nanocomposites exhibited excellent PEC performance for the detection of insulin. The concentrations of insulin could be directly detected based on the decrement of photocurrent that was brought by the increased steric hindrances due to the formation of antigen-antibody immunocomplexes. Under the optimal conditions, the PEC immunosensor had a sensitive response to insulin in a linear range of 0.1 pg mL^{-1} to 5 ng mL^{-1} with a detection limit of 0.03 pg mL^{-1}. Meanwhile, good stability and selectivity were achieved as well. The design and fabrication of this PEC immunosensor based on MWCNTs@SnS_2@CdS nanocomposites not only provided an ideal platform for the detection of insulin, but also opened up a new avenue for the development of immunosensor for some other biomarkers analysis.

1. Introduction

Insulin, a polypeptide hormone secreted by pancreatic cells, plays a crucial physiological role in human metabolism. It promotes glucose transport, glycogenesis, protein synthesis of skeletal muscle and fat tissue via a tyrosine kinase receptor pathway, thus regulating glucose levels in blood within a narrow concentration range (Tomás et al., 2002). The dysfunction of insulin secretion can cause diabetes mellitus, and patients with persistent diabetes and hyperinsulinemia face increased risk factors for serious disorders including kidney failure, myocardial infarction, obesity, and neurodegenerative disease (Dikow et al., 2009; Schutte et al., 2015; Yagati et al., 2016). Therefore, sensitive detection of insulin is of great importance for early disease diagnosis and therapy monitoring, which will also undoubtedly promote the advances in improvement of disease stratification and assessment of treatment efficacy (Arruda et al., 2009; Swierczewska et al., 2012). There are already some methods developed for detection of insulin, such as enzyme-linked of immunosorbent assay (ELISA) (Heyduk et al., 2010), turbidimetry (Jasuja et al., 2012), chromatography (Chen et al., 2013) and high performance liquid chromatography (HPLC) (Mercolini et al., 2008). Even though high sensitivity has been achieved, these methods are time-consuming, cumbersome, expensive, and laborious, which make them difficult to meet convenient testing. Considering the above mentioned facts, the development of efficient detection methods which are sensitive and time-saving will be highly desired.

Among various detection procedures, PEC analysis, as dynamically developed technique, has attracted more and more attention (Shangguan et al., 2015; Shen et al., 2015; Zhao et al., 2015). Across the PEC detection process, light is adopted as the excitation source, with as-generated photocurrent acting as the detection signal. Due to different energy forms of excitation source

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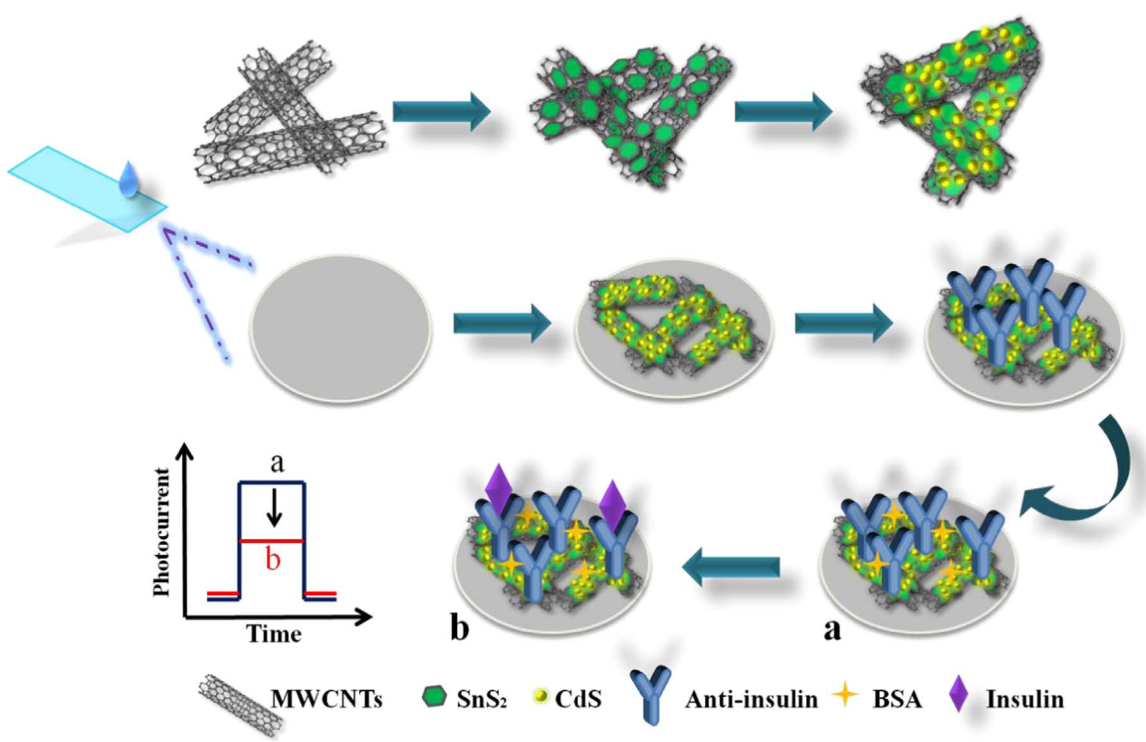
and detection signal, PEC analysis possesses potentially higher sensitivity than conventional electrochemical analysis benefiting from the reduced background signals (Tu et al., 2011). Additionally, compared with optical techniques which has high requirements on the experimental equipment, the application of electronic readout makes the PEC instrument simpler, cheaper, and easier to be miniaturized to appropriate scale (Zhao et al., 2014). Thus, given advantages mentioned above, tremendous studies combined with immunoassay have been reported addressing various targets using PEC technology, including DNA (Fan et al., 2014), proteins (Li et al., 2012b; Zhang et al., 2012) and small molecules (Li et al., 2012a), *etc*. Meanwhile, it is noteworthy that the adoption of appropriate photoactive species plays a significant role in analytical performance of the PEC immunosensor.

Tin disulfide (SnS_2), a typical n-type semiconductor, possesses a CdI_2-type layered structure with a bandgap of *ca.* 2.2 eV. Benefitting from wide distribution, low-price, good stability in acid and neutral conditions, and lower environmental toxicity, SnS_2 has been employed as a promising candidate in various fields, such as photocatalytic hydrogen generation (Yu et al., 2014), lithium-ion batteries (Wang et al., 2015), dye-sensitized solar cells (Cui et al., 2015), and photodegradation of organic pollutants (Liu and Bai, 2013; Zhang et al., 2013, 2015), *etc*. However, as for SnS_2 flakes with a smaller thickness, the weak photon absorption ability brought by the nanosheet structure obviously influenced the light-harvesting and excitation process, which limited the potential application in optoelectronic devices (Zang et al., 2016). Considering the facts mentioned above, a lot of efforts have been made to optimize the performance of SnS_2 for practical applications, including morphology control, doping with metal elements, or introduction of carbon materials (An et al., 2014; Yin et al., 2012; Zhang et al., 2011), etc. Furthermore, another effective way is to combine SnS_2 flakes with other semiconducting materials that acted as a sensitizer, such as CdS, of which the photogenerated charges can be transferred onto SnS_2. So, the construction of heterostructure based on SnS_2 and favorable semiconductor with well-matched band structure would be highly desired for the design of novel PEC immunsensor.

In addition to the photoabsorption ability, high electron conductivity is also desired for an advanced PEC immunsensor. Multi-walled carbon nanotubes (MWCNTs), as a well-known one-dimensional (1D) nanomaterial, have been widely applied as a perfect substrate in biosensing immunsensor ascribing to its extraordinary thermal, mechanical stability as well as high electronic conductivity (Chu et al., 2010; Du et al., 2008; Reddy et al., 2009). Across the whole process of PEC analysis, the adoption of MWCNTs as a conducting framework would promote the electron transfer upon light irradiation, leading to a much higher photocurrent. Thus, herein, in our work, MWCNTs were employed as conducting frameworks for loading of small-sized SnS_2 nanosheets, forming SnS_2/MWCNTs 2D/1D nanocomposites. The introduction of MWCNTs facilitated the electron transfer across the surface of electrodes, resulting improved PEC performance compared to the pure SnS_2. Meanwhile, CdS nanodots were also successfully produced on the as formed 2D/1D nanocomposites via the convenient refluxing reaction, which was probably due to the matching of lattice spacing between CdS and SnS_2. The well-matched overlapping band-structures of these two metal sulfides could effectively limit recombination rate of photogenerated charges, thus improving the photo-to-current conversion efficiency. Besides, the in-situ generation of CdS on SnS_2 could greatly broaden optical absorption in the visible region, which further improved the value in practical application.

Hence, based on as-synthesized MWCNTs@SnS_2@CdS nanocomposites, a novel label-free PEC immunosensor was constructed for ultrasensitive detection of insulin, as displayed in Scheme 1. Firstly, MWCNTs were employed as the conducting frameworks for loading of small-sized SnS_2 nanosheets through one-pot hydrothermal reaction, after which the CdS nanodots were in-situ formed on the surface of SnS_2 via a refluxing reaction. Then, the as-obtained MWCNTs@SnS_2@CdS nanocomposites were decorated on ITO electrodes as the photoactive materials for subsequent antibodies immobilization. To block the unbound active sites, bovine serum albumin (BSA) was dropped onto the surface of



Scheme 1. Schematic illustration of the assembly process of the PEC immunosensor.