Double-amplified photoelectrochemical response of hematin on carbon nanohorns superstructure support for ultrasensitive detection of roxarsone

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ABSTRACT

A new proposal for designing sensitive photoeletrochemical sensor with a ternary hybrid film developed by absorbing hematin on carbon nanohorns superstructures and poly-L-lysine complex support to achieve quantificational detection of 4-hydrox-3-nitrobenzenenearsonic acid (HNBAA) was offered. Here, hematin with easy acquirement, good biocompatibility and strong visible light harvesting capability, was introduced as photosensitizer for photoelectrochemical determination. Additionally, the complex support composed by fascicled superstructures of carbon nanohorns which possessed many superiors, such as excellent electronic conductivity, large specific area and adsorption etc., and poly-L-lysine which could form hydrogen bond with hematin performed excellent immobilization action of hematin. Due to the synergistic effect and surface enhancement effect, complex support provided a charge-transfer matrix to catch and transport excited electron from hematin rapidly, which was benefit to baffle photogenerated electron–hole recombination and improve photoelectrochemical signal in visible light region effectively. HNBAA, as a photogenerated hole scavenger, enhanced the photoelectrochemical response again. Furthermore, the excellent sensitivity and broad linear detection range to HNBAA of this sensor with good stability and high selectivity, satisfied reproducibility and acceptable accuracy was propitious to practical application of sample analysis, and the good biocompatibility of modified materials and low applied potential on this sensor laid a foundation for its promising application.

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1. Introduction

As a new developed technology, photoelectrochemical sensor achieves detection by transferring electrons which were excited from photoelectromaterials by light to electrode or detecting species, and producing current as detection signal. Benefiting from photo-excitation and electrochemical detection, photoelectrochemical sensor exhibits superiorities both of optical and electrochemical methods. Meanwhile, instead of complex and expensive optical devices, electronic readout makes apparatus cheaper, simpler and easier miniaturization. In addition, the separation of irradiation and detection, the sensitivity and specificity of photoelectrochemistry lay a foundation for detection of target. Contributing to so many advantages,

photoelectrochemial sensor attracted wide attention, and with development of photoelectrochemistry, various materials of photoelectronic properties were appeared [1], including semiconducting nanoparticles, quantum dots, small organic molecules, metal complex and so on. Thereinto, organic photosensitizer attracted much attention because of its advantages of lower cost, higher structure flexibility, easier preparation, environmental friendly etc. [2], however, the improvement of light harvesting and photo-to-electricity conversion efficiency was also a lager challenge of photoelectric device by using organic photosensitizer [3]. Porphyrin, metalloporphyrin and their derivatives play an important role among organic photoelectronic materials, because of its active electron of conjugated structure and broad photoresponse range in visible and near-infrared region [4]. Hematin (Hb), one of metalloporphyrin derivative, could be a promising photosensitizer. But it always served as sensitizer to enhance the photoelectric properties of semiconductor elements, instead of directly used as photosensitizer [5]. It could be account by some

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challenges of use of porphyrins as photosensitizer elements, such as efficient immobilizing strategies, improvement of photogenerated electron efficiency. It was also reported that time of the charge recombination between electron in highest occupied molecular orbital (HOMO) and hole of oxidized porphyrin had only several milliseconds [6], thus whether can excited electron be quick transferred to accepter is also a significant factor to boost the efficiency of the photoeletrochemical sensor based on porphyrin.

For structuring efficient electron-transport matrices, many materials were introduced into sensing interface, such as metal nanoparticles, conductive polymer and so on. Thereinto, carbon nanomaterials occupied a large proportion as electron conductor of matrix, for example, graphene and carbon nanotubes have been introduced on the electrode interface to accelerate the separation of photogenerated electron–hole pairs [7,8]. As a new carbon nanomaterial, carbon nanohorn (CNH) is a top sealed conical, and thousands of CNHs aggregated to form a nanometer super-structure (NSS) which is a spherical structure with conical tips in their outer sides like a dahlia or chestnut [9–11]. Due to the Van der Waals force between the two adjacent CNHs, this NSS of CNHs could form, and its size was dependent on the trade-off between the Van der Waals force between the two adjacent CNHs and the length of CNHs [10,11], resulting in the variable porosity. Thus, this NSS of CNHs performs much superiority, for example large specific surface area, porous, and especially excellent conductivity because of multi-tip effect, which could efficiently enhance the enrichment of photoelectrochemical material and prolong electron lifetime by decreasing recombination between excited electron and hole. Based on these charming characters, it has extensive applications as storage media of gases, carriers of drugs, catalyst support, supercapacitor etc. in various fields. Whereas, there is limited report of application of CNHs on photoelectrochemical sensing and the potential application of CNH is waiting for digging out. Herein, NSSs of CNHs were introduced to design a predominant photoelectrochemical support with poly(L-lysine) (PLL) formed organic–inorganic hybrid film. Thereinto, PLL could not only improve the dispersion of CNHs to increase their contact with Hb, but also as immobility reagent of Hb by forming hydrogen bond between amino of PLL and carboxyl of Hb.

To measure the properties of as-prepared photoelectrochemical sensor, 4-hydrox-3-nitrobenzenenearsonic acid (HNBAA) also named roxarsone, an electron donor, was used as target, which is one of organic arsenic compounds and often used as additive of feed for enhancing the rate of weight gain, improving feed efficiency, preventing and treating coccidial intestinal parasites [12]. Owing to easy bioaccumulation and largely excreted, it could cause potential harm to human health and environment, and its amount of allowable addition is from 25 to 50 mg/kg [13]. It is exigent and important to achieve rapid and sensitive detection of HNBAA. In this paper, a stable and sensitive photoelectrochemical sensor modified with NSSs of CNHs and PLL was built to achieve fast and quantificational detection of HNBAA. Here, Hb modified on electrode by adsorption and hydrogen bond, acted as a photosensitizer and was excited by visible light. The photoelectrochemical sensor was evaluated by analyzing collected electronic responses. Corresponding results performed the sensor had good conductivity and stability, fast electron transfer speed and long electron lifetime, wide linear response range and good selectivity. These prominent properties of photoelectrochemical sensing architecture proved that an excellent detection platform was structured for HNBAA and it has potential application in practical detection. Moreover, the good biocompatibility of modified materials and excited light at visible light range also laid a foundation for application in biosensor.

2. Experimental

2.1. Reagents

Hematin porcine and PLL were purchased from Sigma (St. Louis, MO, USA) and Lanzhou Weiri Bio-Engineering Co. Ltd. (China), respectively. Hematin was prepared by dissolving hematin power into 0.025 M NaOH, and PLL solution was prepared by dissolving PLL into water. 3 mg/mL CNH was obtained by dispersing CNHs into N,N-dimethylformamide with tempestuously shake and sonication. CNHs were obtained by synthesizing following our previous report [14], the details were performed in supporting information. HNBAA, ascorbic acid (AA) and others' reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The ultra-pure water utilized for the preparation of the solution was purified using a Water Purifier (Sichuan Water Purifier Water treatment Equipment Co., Ltd., China) purification system.

2.2. Apparatus

All photoelectrochemical processes were performed with a homemade photoelectrochemical system which is similar to our previous report [15]. And the electrochemical process was performed using a CHI760 Electrochemistry Workstation (Shanghai Chenghua Instrument Co., China) with a three electrode system concluding a platinum auxiliary electrode, Ag/AgCl reference electrode (sat. KCl) and a working electrode: a glassy carbon electrode (GCE, φ = 3 mm) or its modified electrode.

2.3. Preparation modified electrode

A clean GCE was obtained by polished on chamois leather with 0.3 μm alumina particles, then washed with ethanol and water in sequence and natural dry in air. 4 μL PLL solution, CNHs or CNHs-PLL mixture were dropped onto GCE, and then modified electrode was transferred under infrared lamp to dry to gain PLL/GCE, CNHs/GCE or CNHs-PLL/GCE, respectively. Subsequently, modified electrodes were immersed in 0.1 mM Hb solution for 20 min and rinsed by water for 1 min to remove redundant Hb, finally dried in air and gained Hb/GCE, Hb/PLL/GCE, Hb/CNHs/GCE, Hb/CNHs-PLL/GCE.

3. Results and discussion

3.1. Character of photoelectrochemical sensor

CNHs superstructures and PLL hybrid compounds served as support was firstly introduced to improve the separation efficiency of photoexcited electron–hole pairs, and its performance was monitored by various electrochemical and photoelectrochemical processes. The electrochemical performance of sensor with different modified layer was determined by cyclic voltammetry (CV) using Fe(CN)$_6^{3-/4-}$ as redox probe. As shown in Fig. 1A, a good reversible redox wave corresponding to Fe(CN)$_6^{3-/4-}$ was displayed, and with decoration of PLL on GCE surface, both oxidation and reduction currents had a little increase, because of good conductivity of PLL and decrease of interface resistance on the redox process. And current responses of CNHs/GCE enormously increased, indicating the increment of the electroactive probe on electrode interface, due to large surface area, good electrical conductivity and adsorption of NSS of CNHs. CNHs-PLL/GCE of Fig. 1A presented dramatically amplified current responses which are much larger than others, indicating achievement of the synergistic effects between CNHs and PLL as well as the surface enhancement effects of porous CNHs superstructures [16], and it benefits to good dispersion, large adsorption, increasing effective electrode area and electrochemical