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Fabrication and electrochemical properties of alizarin -aminophenylboronic acid ensembled with layered double hydroxide for glucose sensing selectivity

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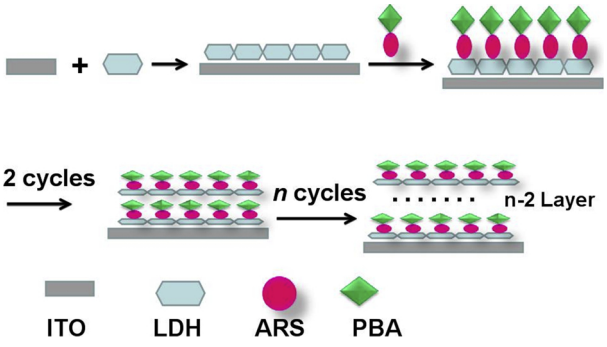
GRAPHICAL ABSTRACT



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ABSTRACT

The interaction of alizarin with aminophenylboronic acid (ARS-PBA) was used through a new strategy for electrochemical sensors of glucose. In the present work, ARS-PBA complex and the layered double hydroxide nanosheets (LDH nanosheets) were successfully assembled on indium tin oxide (ITO) electrodes via layer by layer technology method. The resulted electrode was characterized by UV–vis, X-ray diffraction (XRD), atomic force microscope (AFM) and scanning electron microscope (SEM) to achieve the morphological, structural and compositional information. Cyclic voltammetry and differential pulse voltammetry were conducted to investigate electrochemical properties of the modified electrode. Moreover, the modified electrode was used as a non-enzymatic sensor for glucose determination, exhibiting good electrochemical properties, fast response time and long-term stability. At the optimum conditions, the constructed electrode sensor shows a linear range of 0 ~ 1.00 μmol/L and a low detection limit of 4.0 nmol/L (S/N = 3) for glucose. On the basis of affinity between glucose and ARS-PBA complex, the functionalized electrode showed a high selectivity toward glucose over other concomitant biomolecues (dopamine, uric acid and ascorbic acid). Therefore, a simple and effective electrochemical method was developed and offers a complementary tool for the detection of glucose.

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1. Introduction

Nowadays, diabetes is a severe global health problem. Due to growing concern of this disease, accurate and rapid quantitative determination of glucose concentration is critically significant in physiology and clinic fields. Different analytical techniques have been used to detect glucose, such as spectrofluorimetry, electrochemistry, and chromatography [1–4]. Among these methods, the electrochemical approach based on enzymatic and non-enzymatic applications is very attractive because it is an easily scalable, cost effective method and allows glucose determination with fast response time, high sensitivity and low power requirement. Some inherent demerits including high cost of enzymes, poor reproducibility and chemical stability however still existed. Therefore, considerable research has been focused on the exploration of non-enzymatic glucose sensors by utilizing cost-effective hybrid nanomaterials [5–8].

Alizarin red S (ARS) is an anthraquinone derivative, and its complex with aminophenylboronic acid (PBA) has been recently selected as an electrochemical probe to research the biological molecular in the life sciences [9–11]. ARS-based sensors however encounter drawbacks such as aggregation or desquamation from the electrode surface, leading to the decrease of ARS electrochemical activity. Therefore, designing a host nanomaterial which supported ARS with high dispersion and enhanced activity is still a challenging goal. Recently, hydrotalcite-like layered double hydroxides (LDHs) have received growing attention due to their anion-exchange properties, good chemical stability, high adsorption capacity and biocompatibility [12–14]. More important, the monolayer LDHs nanosheets as building block can be prepared through an exfoliation strategy [15,16]. It is promising to incorporate ARS-PBA onto LDHs nanosheets by layer-by-layer assemble to achieve a new electrochemical sensor for glucose detection, which may offer the advantages as following: (1) The layered structure of LDH nanosheets can provide a stable environment for ARS-PBA complex, and also facilitate more dispersion of ARS which was favorable for the electron transfer; (2) The large superficial area of LDH nanosheets can ensure the more active sites and makes it approach to the targets with rapid response; (3) The immobilization of ARS-PBA onto LDH effectively ensure the stability of performance after cycle measurements.

In this work, a novel ultrathin films were conducted based on the layer-by-layer (LBL) assembly of ARS-PBA adduct and LDHs nanosheets (as shown in Scheme 1). The obtained $(ARS\text{-}PBA/LDH)_n$ ultrathin films (UTFs) show an ordered structure and ARS was highly dispersed. The electrochemical behaviors were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods in Tris-HCl buffer solution at pH 7.4. To highlight the role of PBA in electrochemical behaviors, a reference of sole ARS immobilized onto LDH nanosheets was prepared and its electrochemical properties were studied as control. The results indicated that the electrochemical sensor of ARS-PBA/LDH exhibited more improved analytical performance. In addition, the peak current of ARS-PBA/LDH correlated linearly to the concentration of glucose in the range of $0 \sim 1.00$ μmol/L. Thus, the ARS-PBA/LDH nanocomposite is useful as an electrode modifier for designing glucose sensor.

2. Experimental

2.1. Materials

Glucose, alizarin red S (ARS), dopamine, uric acid, ascorbic acid and 3-aminophenylboronic acid (PBA) were purchased from Sangon Biotech Ltd (Shanghai, China). All reagents including NaOH, $Co(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ were analytical grade and used as received.

2.2. Preparation of CoAl-LDH nanoparticles

A colloidal suspension of precursor LDH was synthesized according to the literature [17]. 120 mL solution containing 0.06 mol Co $(NO_3)_2{\cdot}6H_2O$, 0.03 mol $Al(NO_3)_3{\cdot}9H_2O$ and 120 mL NaOH solution (0.18 mol) were mixed into a colloid mill with a speed of 3000 rpm rotor. Then the obtained slurry of LDH was centrifuged, washed with water several times, and re-dispersed in 400 mL water. Transferring into a stainless autoclave, the suspension LDH was hydrothermal treated for 24 h (110 °C). A homogeneous and stable CoAl-LDH suspension can be obtained.

2.3. Construction of ARS-PBA/LDH ultrathin film modified electrode

The glass substrates of indium tin oxide (ITO) (1 cm × 3 cm) were pretreated in an ultrasonic bath in acetone, ethanol and water in turn for ten minutes respectively. Then the hydrophilic and negatively charged surfaces of the substrates were obtained. Quartz glass (1 cm × 3 cm) substrates were cleaned by immersing in a solution (H_2SO_4 : H_2O_2 (30%) = 3:1, v/v) for 40 min, rinsed thoroughly with deionized water and dried at 60 °C.

ARS-PBA adduct solution ($C_{ARS} = 1.0 \times 10^{-3}$ mol/L, $C_{PBA} = 1.0 \times 10^{-3}$ mol/L) was prepared in double distilled water, and pH = 7.4 controlled by Tris-HCl buffer (50 mol/L). The $(ARS\text{-}PBA/LDH)_n$ films were constructed on pretreated ITO glass electrode by alternate deposition of a LDH suspension (1.0 mg/mL) and ARS-PBA solution for n cycles.

The $(ARS/LDH)_n$ films were fabricated according to the same method.

2.4. Characterization

The UV–vis spectra were measured in the range of 200–700 nm on Shimadzu T-9201 spectrophotometer (slit width of 1.0 nm). Hitachi S-4700 scanning electron microscope (SEM) and a NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments were used to investigate the morphology of $(ARS\text{-}PBA/LDH)_n$ thin films. XRD patterns of $(ARS\text{-}PBA/LDH)_n$ were performed using a Rigaku XRD-6000 diffractometer under the condition of Cu K_α radiation ($\lambda = 0.154$ Å) and operated at 40 kV, 50 mA. The scanning rate is 2°/min, and the 2θ angle ranged from 0.5° to 70°.

All electrochemical measurements were conducted on a CHI 660B electrochemical analyzer. A three-electrode cell was employed in 0.5 mol/L aqueous Na_2SO_4 solution, which consists of the modified ITO glass as working electrode, $Hg|Hg_2Cl_2$ and platinum wire as the reference electrode and the counter electrode respectively. Electrochemical impedance spectral (EIS) measurements were performed by applying an alternating current voltage with 5 mV amplitude in a frequency range from 0.01 to 100 kHz.

3. Results and discussion

3.1. The assembling and monitoring of $(ARS\text{-}PBA/LDH)_n$ UTFs

The characterization of CoAl-LDH nanosheets precursor is shown in Fig. S1. By the help of SEM, the morphologies of CoAl-LDH nanoplatelets were determined and exhibited uniform hexagonal plate-like microcrystals (Fig.S1A and S1B). The X-ray diffraction (XRD) pattern of CoAl-LDH exhibits the high purity of LDH and no other crystalline phases were present (Fig. S1C). The well-dispersed colloidal suspension was observed by a clear Tyndall light scattering (Fig. S1D), and can be stable without precipitation under N_2 atmosphere for more than 20 days.

Then, the $(ARS\text{-}PBA/LDH)_n$ films were fabricated on ITO glass substrates by using CoAl-LDH nanosheets and ARS-PBA as building blocks through LBL assembly technology. The fabrication process of $(ARS\text{-}PBA/LDH)_n$ UTFs was monitored by UV–vis, EIS, CV and DPV (n varies from 2 to 12, Fig. 1). The inset in Fig. 1A displays the absorbance at 518 nm attributed to ARS increases linearly as a function of bilayer number n, indicating a stepwise and regular growth process for the LBL