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Study on Molecularly Imprinted Electrochemical Sensor for Bisphenol a Based on Nb_2O_5/GO/NiCo

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Abstract: *In this paper, a molecularly imprinted electrochemical sensor (miecs) for rapid and sensitive detection of bisphenol A (BPA) based on double-layer Nb_2O_5 / rGO loaded hollow nickel cobalt nanorod modified glassy carbon electrode (GCE) is proposed for the first time. The NiCo bimetallic nanorods (NiCo) were modified by double-layer Nb_2O_5 / rGO loaded hollow Ni Co nanorods, which expanded the active region and electronic transmission ability of the sensor signal. Molecular imprinted polymer (MIP) could further enhance the electrical signal. Then, MIP was polymerized by cyclic voltammetry (CV) with o-phenylenediamine as monomer and bisphenol A (BPS) as template, and BPA was detected by differential pulse voltammetry (DPV). At the same time, the factors affecting the response of the sensor were optimized, and the experimental conditions such as the molar ratio of monomer to template and pH were optimized. The results showed that miecs had good sensitivity, selectivity, reproducibility and stability to BPA when pH = 7.0 and the molar ratio of monomer to template was 4:1. The recoveries of actual samples (95.9% - 100.9%) and reasonable relative standard deviations (RSD) (3.2% - 4.8%) indicate that the sensor has strong practical potential, and has broad application prospects in the rapid determination of bisphenol A in samples such as metal cans and baby bottles.*

Keywords: *Nb_2O_5/rGO, Nickel cobalt nanorods, Molecularly imprinted polymer, Electrochemical sensor*

1. Introduction

Bisphenol A is called 2,2-bis (4-hydroxyphenyl) propane (BPA) for short. It is an organic compound with the chemical formula of $(CH_3)_2C(C_6H_4OH)_2$. It is a white crystal, melting point 156 ~ 158 ℃, insoluble in water and soluble in organic solvents. BPA is the main raw material for the production of polycarbonate (PC) and epoxy resin (EP). In terms of food packaging, the plastic added with BPA has the characteristics of colorless, transparent, durable, light and fall resistance. Coating on the inner wall of metal cans can prevent food from eroding the metal wall from the inside. The dissolution of BPA in food plastic packaging is a problem that can not be ignored. BPA and its epoxy derivatives can migrate in a variety of food packaging materials, be mixed into food or beverage, and then enter the human body. It has estrogen activity and interferes with normal hormone secretion in the human body, thus affecting reproductive function and leading to the production of malignant tumors. Even when the intake of BPA is very low, it will cause harm to human health[1-3]. Therefore, it is very important to develop a sensitive, efficient and stable method for the detection of BPA.

At present, the detection methods of BPA include: high performance liquid chromatography[4], gas chromatography-mass spectrometry[5], liquid chromatography-mass spectrometry[6], but the general analysis speed is slow, the sensitivity is low, and the operation is cumbersome[7]. Electrochemical analysis has the advantages of low cost, high sensitivity and easy operation. It can detect BPA well. However, the electrochemical response of BPA on the bare electrode is poor, and it is easy to cause electrode surface passivation. The electrode needs to be modified to improve the sensitivity and anti pollution ability.

Electrochemical sensing also has the advantages of simple design and manufacture, high sensitivity, low price and easy miniaturization[8-9]. The process is to copolymerize the target molecule to be separated with the crosslinking agent in the polymer monomer solution to prepare the granular medium, and then wash out the target molecule embedded in the medium to obtain the molecularly imprinted polymer (MIP) medium. Molecularly imprinted polymers have selective binding effect on template molecules, show the ability of molecular recognition. The identification principle is shown in Figure

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1[10-11].

Molecular imprinting technology (MIT) is widely used because it can provide specific recognition functions [12]. Among them, because the preparation is simple and the film thickness is controllable, molecularly imprinted polymers (MIPs) are usually prepared by electropolymerization. Functional monomers and template molecules can be electrochemically polymerized [13]. Recognition sites are introduced into the polymer membrane through the interaction between monomer and template [14]. Then the template molecules are extracted and the cavity matching the spatial structure of the template molecules is obtained. In electrochemical detection, the target molecules undergo electrochemical redox process, resulting in electron transfer, resulting in current enhancement and redox peak [15]. Molecularly imprinted electrochemical sensing system can combine the advantages of MIP and electrochemical methods.

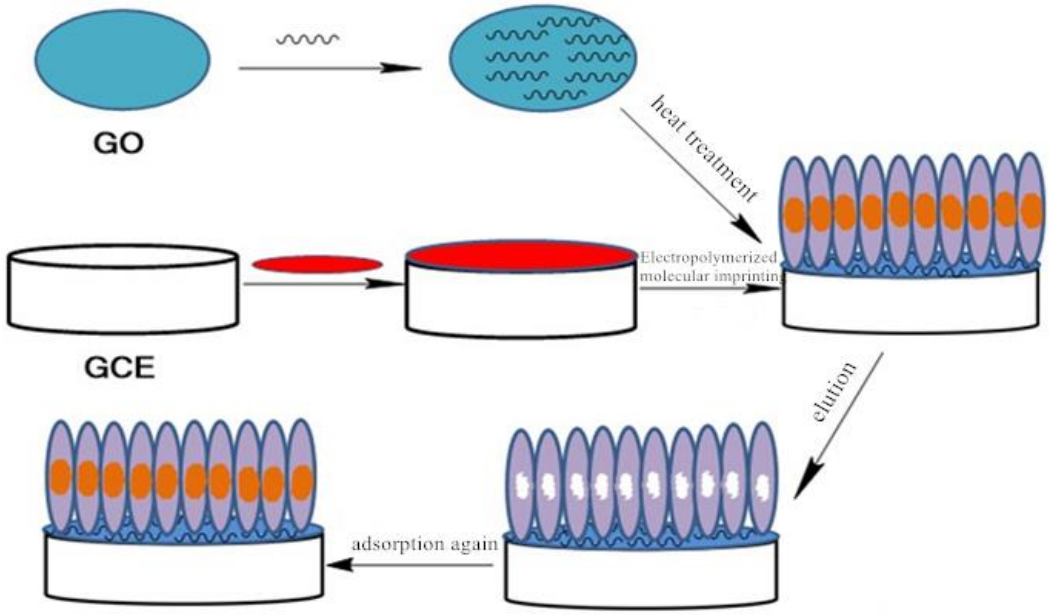

Figure 1: Schematic diagram for preparation of GO-Nb2O5-NiCo/MIP/GCE

2. Results and discussion

2.1 Instruments and reagents

Three electrode system: the working electrode is glassy carbon electrode (diameter 3mm); The reference electrode is Ag/AgCl (saturated KCl) electrode; The auxiliary electrodes are platinum wire electrode, tubular furnace (T1280A), ultrasonic cleaning instrument (sb-800DTD), timing and constant temperature magnetic stirrer (90-2), electronic analytical balance (BSA124S), High speed freezing centrifuge (HC-3018), constant temperature water bath, platinum electrode (PT), glassy carbon electrode (GCE), saturated calomel electrode (SCE), electronic balance, freezing centrifuge, chi660e electrochemical workstation, ultrasonic cleaning machine, freezing dryer, Scanning electron microscope (SEM), X-ray diffraction (XRD).

Natural graphite powder (C, ≥ 99.5%), bisphenol A (BPA, ≥ 99.5%), 4-vinyl pyridine (C_7H_7N, ≥ 99.5%), concentrated sulfuric acid (H_2SO_4, ≥ 99.5%), concentrated nitric acid (≥ 99.5%), concentrated hydrochloric acid (HCl, ≥ 99.5%), potassium persulfate ($K_2S_2O_8$ ≥ 99.5%), Niobium pentachloride ($NbCl_5$, ≥ 99.5%), potassium permanganate ($KMnO_4$, ≥ 99.5%), hydrogen peroxide (H_2O_2, 30%, ≥ 99.5%), Sodium hydroxide (NaOH, ≥ 99.5%), methanol (CH_3OH, ≥ 99.5%), ethylene glycol ($(CH_2OH)_2$, ≥ 99.5%), anhydrous ethanol (C_2H_5OH≥ 99.5%), Acetic acid (CH_3COOH, ≥ 99.5%), acetonitrile (C_2H_3N, ≥ 99.5%), nickel acetate ($Ni(CH_3COO)_2$, ≥ 99.5%), cobalt acetate ($C_4H_6CoO_4$, ≥ 99.5%).All the above reagents are purchased from Chengdu Kelong Chemical Reagent Factory.

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2.2 Experimental method

2.2.1 Synthesis of hollow nickel cobalt nanorod Composites

Synthesis of nickel hydrogen acetate: take PVP and a certain amount of nickel acetate and cobalt acetate, dissolve them in about 90 mL of ethanol, react at 80 ℃ and stir continuously. After the reaction, treat the mixture with a centrifuge, collect the precipitation, wash the precipitation with ethanol for 5 times, and put the obtained product into the oven, Bake in an oven at 60 ℃ for 5 hours to obtain Ni/CO precursors with different proportions while keeping the total amount of Ni+CO unchanged. Select precursors with Ni/CO ratios of 1:2, 2:1 and 1:2 for standby.Dissolve the above Ni/CO precursor in ethanol, and then disperse it with an ultrasonic instrument. Heat and stir the dispersed mixture at 80 ℃ for 2.5 h. After the reaction, collect the final product by centrifugation, remove impurities, and put all the products into a dry oven, Dry at 60 ℃ for 2 hours, select the most suitable sample and treat it at high temperature for 30 minutes under the condition of Ar gas. Check the effect of heat treatment and oer activity, remove oxides and hydroxides, take part of the obtained samples, treat them with sulfuric acid solution for 30 min, then wash them with ethanol and dry them in the sun [16-17].

2.2.2 Synthesis of double-layer niobium pentoxide

Add concentrated sulfuric acid to a 250 ml flask filled with graphite, then add $NaNO_3$ and $KClO_4$, and gradually add solid $KMnO_4$ while stirring in an ice bath. At the same time, keep the temperature of the mixture below 20℃ by using a contact thermometer and react at low temperature for 2 hours, Then raise the temperature to 30 ℃ (($t \leq 40$ ℃) for 24 hours, add excess distilled water to the mixture, raise the temperature to 80 ℃ for 30 minutes, and finally add 30% H_2O_2 until the color of the mixture turns bright yellow. Use the high-speed centrifuge to adjust the number of revolutions to 10000 rpm for centrifugation for 5 min. The obtained precipitate was washed with 5% hydrochloric acid aqueous solution for 5 times to remove metal ions in the precipitate, and then washed with distilled water for 3 times to remove acid. The obtained solid was vacuum dried at room temperature 25℃ for 16 h to obtain graphene oxide rGO.

Niobium chloride was dispersed in ethanol dissolved with rGO, refluxed overnight in 45 ℃ water bath, then centrifuged ($t \geq 40$ ℃) and washed with ethanol for three times ($t \geq 40$ ℃, preheated with water bath first). The obtained solid powder was dried overnight and burned in a horse boiling furnace for one hour. The temperature was controlled at 350 ℃ to obtain a double-layer Nb_2O_5 / rGO material.

2.2.3 Polymer molecular imprinting on composite surface

Bisphenol A and 4-vinylpyridine were added to 10 ml of acetonitrile to dissolve, the modified electrode was placed in it, the electrode system was switched on and connected with the instrument in the potential range of - 0.4-1.2V, and the modified electrode with polymer molecular imprinting on the surface of NiCo was obtained by scanning for 20 cycles at the scanning rate of 100 mV / s.

2.2.4 System construction and condition experiment

We constructed the detection system through the miecs of GCE modified by double-layer Nb_2O_5 / rGO loaded hollow nickel cobalt nanorods. Molar ratio of monomer to template: adjust the molar ratio of functional monomer to BPA, detect the response of the system, and select the optimal molar ratio of monomer to template. PH value: provide a series of different pH environments for the detection system of Molecularly Imprinted Electrochemical sensor. Each 1.0 pH is a unit from 2.0 to 9.0. Detect the response of Molecularly Imprinted Electrochemical sensor to BPA and detect the optimal pH value. Number of polymerization circles: use different number of polymerization circles to detect the response of Molecularly Imprinted Electrochemical sensor to BPA, and select the optimal number of polymerization circles. Incubation time: using different incubation time from 20min to 120min, every 20min as a unit, detect the response of Molecularly Imprinted Electrochemical sensor to BPA, and detect the optimal incubation time.

3. Results and discussion

3.1 Material characterization

It can be seen from Figure 2 that the XRD spectrum of the material is consistent with that of standard rGO, Nb_2O_5 and NiCo nano materials, indicating that rGO, Nb_2O_5 and NiCo nano materials with different proportions have been successfully synthesized.

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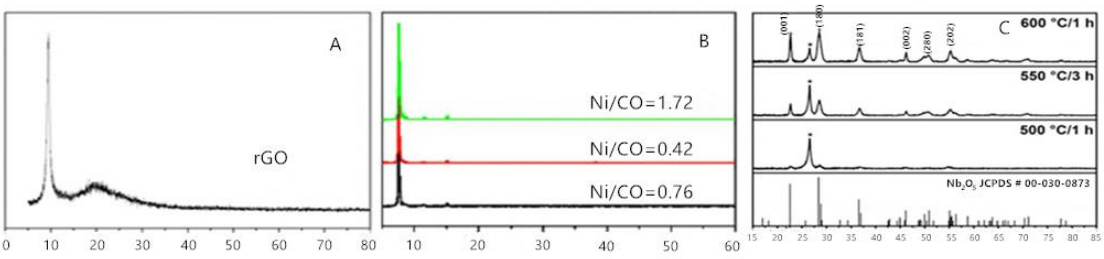

Figure 2: X-ray diffraction patterns (XRD) of rGO, Nb2O5 and NiCo nanomaterials with different Proportions

3.2 SEM characterization

The prepared rGO-Nb_2O_5-NiCo, BC/rGO-Nb_2O_5-NiCo and molecularly imprinted polymeric nanocomposites were characterized by scanning electron microscope(SEM) (Fig. 3). The characterization shows that the NiCo powder prepared by hydrothermal method has irregular nano rod structure and morphology (Fig. 3a). By observing the SEM images of BC/NiCo-Nb_2O_5 powder and BC/NiCo-Nb_2O_5 modified electrode (Fig. 3D), it can be seen that there is a folded irregular layer like spatial structure on the outer surface of BC. The interior of BC presents an irregular structure with different phase sizes and many spaces, which can provide a large effective surface area, so as to enhance the ability of the prepared imprinted polymerization membrane to capture template molecules.

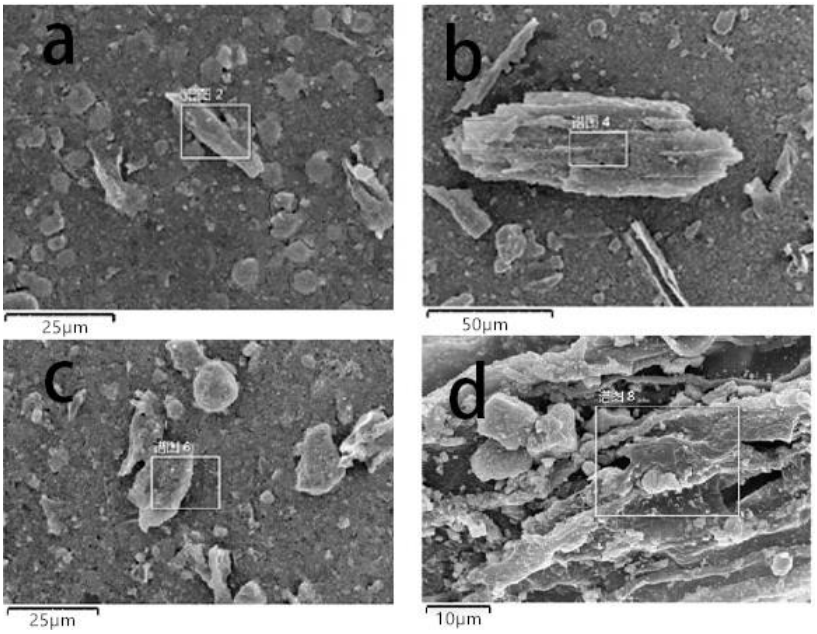

Figure 3: SEM image of BC/NiCo (a). The SEM images of BC/NiCo-Nb2O5 (b) and BC/rGO-Nb2O5-NiCo (c) were obtained. SEM images of BC/rGO-Nb2O5-NiCo/GC (d)

3.3 Properties of electrode materials

The bare electrode and modified electrode were electrochemically characterized in 5.0 mM $[Fe(CN)_6]^{3-/4-}$and 0.5 M KCl by cyclic voltammetry [30]. The potential range is -0.2 V to 0.6 V and the scanning rate is 50 mVs^{-1}. As shown in Figure 4, curve f shows a pair of obvious potassium ferricyanide redox peaks of bare GCE, with peak potentials of 0.18v and 0.31v respectively. When GCE is modified by rGO, the peak current of rGO/GCE is significantly increased (curve b), indicating that rGO has good conductivity. GCE was modified by rGO/Nb_2O_5/NiCo, and the peak current of rGO/Nb_2O_5/NiCo/GCE was also enhanced (curve C). This shows that the nanocomposite rGO/Nb_2O_5/NiCo plays an important role in improving the sensitivity. After electropolymerization of MIP, a dense film is formed on the surface of GCE electrode, which will hinder electron conduction. Therefore, the current response decreases significantly (curve a). When the template molecules were extracted with eluent, BPA imprinting cavity was formed on MIP membrane, which improved the

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electron transfer rate. The peak current (curve d) of rGO/Nb_2O_5/NiCo/MIP/GCE after elution was significantly greater than that of $CuCo_2O_4$/N-CNTs/MIP/GCE before elution (curve a). This shows that the molecularly imprinted membrane was successfully prepared and the detection of BPA was realized.

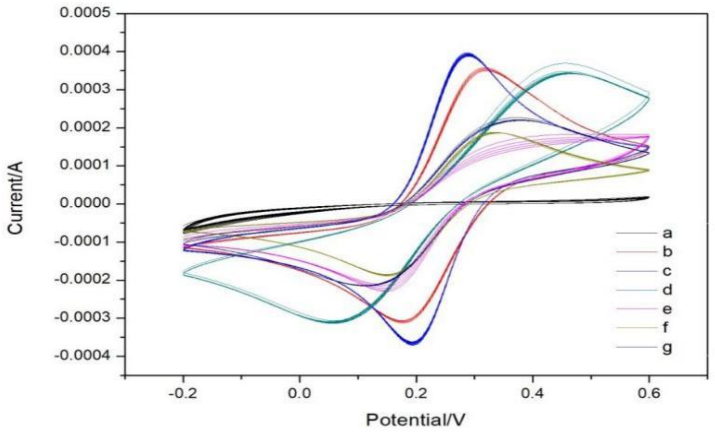

Figure 4: CV diagram of 0.5m KCl solution containing 5.0 mM [Fe (CN)6]3- / 4-(a) rGO/Nb2O5/NiCo/GCE/MIPs, (b) rGO/GCE, (c) rGO/Nb2O5/NiCo/GCE, (d) rGO/Nb2O5/NiCo/GCE/MIPS elution, (E) rGO/Nb2O5/NiCo/GCE reabsorption, (f) Bare GCE

3.4 Response of DPV under different concentrations of PBA

As shown in Figure 4, the effect of BPA concentration on peak current was studied in 0.1PBS (pH=7) by using DPV. The binding rate of different concentrations of BPA to molecularly imprinted cavity is different. With the concentration from 0.5 μM The electrochemical response increased gradually when m increased to 1 mM. This is because the binding strength between BPA and MIP recognition sites is different in different concentrations of BPA. The higher the concentration, the greater the binding probability between template molecule and MIP, resulting in the change of binding strength between template molecule and MIP. The response peak of the detected substance is between 0.3 and 0.5, which shows that the Molecularly Imprinted Electrochemical sensor (MIECS) constructed in this experiment has a good response effect on the detection of BPA.

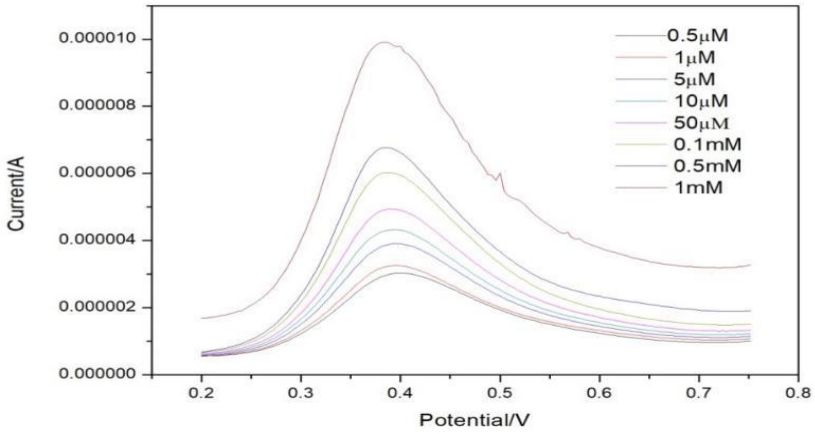

Figure 5: Response in DPV 0.1M PBS (pH=7.0) with different concentrations of BPA

4. Conclusion

In this study, a double-layer rGO/Nb_2O_5 loaded hollow nickel cobalt nanorod imprinted film

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electrochemical sensor was constructed for sensitive and selective detection of BPA. Coating composite nano materials on glassy carbon electrode (GCE) increases its conductivity and improves the sensitivity of the sensor. Subsequently, the template molecule BPA and the functional monomer o-phenylenediamine were electrochemically polymerized by cyclic voltammetry (CV) to form a molecularly imprinted polymer (MIP) film. The construction of rGO/Nb_2O_5/NiCo/MIPs/GCE complex significantly enhanced the electrochemical response of the sensor to BPA. The electrochemical performance of the sensor was evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The relationship between DPV current response and BPA concentration was obtained by optimizing the detection conditions. It provides a potential method for rapid determination of BPA in samples.

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