Research on Electrochemical Molecular Imprinting Sensor of P-Feco Nanoparticles

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Abstract. The electrochemical sensor is based on the principle of electrochemistry, which connects the concentration change of the tested component with the electrochemical signal. So as to provide real-time information of chemical components in the detected system. When electrochemical method is used to detect the tested object, it has the advantages of relatively simple detection process, fast detection speed, high sensitivity and low cost, so it has become a research hotspot in the field of analysis. In this paper, five preparation methods of MIPs are introduced, which have the characteristics of high affinity and stability. Then, the electrochemical sensor is constructed by molecularly imprinted technology combined with nanomaterials. It is a simple and convenient electrochemical sensor to detect the metal synthetic materials closely related to people's health in life. The surface current density of Nb2O5 / GO composite was increased by using FeCo nanoparticle material, and molecular imprinting technology was used. On the one hand, the carrier properties of composite materials are used. On the other hand, FeCo nanoparticles, which enhance the junction of molecularly imprinted and composite materials, are a kind of nanocomposites with many excellent properties. It has high activity of electrochemistry catalysis, high current density on the surface of electrode and long-term stability.

1. Introduction
Electrochemical sensor is a device that interacts with analyte and produces a specific electrical signal, and the change of electrical signal changes with the concentration of analyte [1]. Electrochemical sensors use different electrical analysis techniques, such as open circuit potential method, amper method, cyclic voltammetry, differential pulse voltammetry, differential pulse voltammetry. Impedance sensing. Various electrochemical technologies have been widely used in different research fields because of their relative maturity, simplicity and convenience. Molecular imprinting technology (MIT) combined with electrochemical sensor has the advantages of specific recognition ability, high sensitivity and fast reaction of electrochemical analysis method, so the electrochemical sensor based on molecularly imprinted polymer has a very large development space [2].

Bisphenol A, scientific name 2,2-bis (4-hydroxyphenyl) propane, referred to as bisphenol propane (BPA), is an organic compound, chemical formula is (CH3) 2C(c6h4oh) 2. It is a white crystal, melting point 156-158°C, insoluble in water, soluble in organic solvent. Bisphenol A is an important organic chemical raw material, an important derivative of phenol and acetone, with two phenolic hydroxyl groups. Bisphenol A is used to synthesize polycarbonate (PC) and epoxy resin in industry. Since the 1960s, it has been widely used in the manufacture of plastic (milk) bottles, suction cups for
children, and inner coating of food and beverage (milk powder) cans. Every year, about 27 million tons of BPA containing plastics are produced worldwide. But BPA can lead to endocrine disorders, which seriously threaten the health of fetus and children. Obesity caused by cancer and metabolic disorders is also thought to be related. The data show that bisphenol A is a low toxic chemical [3]. In animal experiments, bisphenol A was found to have the effect of simulating estrogen. Even at a very low dose, bisphenol A could make the animal produce premature puberty, decrease the number of sperm and increase the prostate gland. In addition, some data show that bisphenol A has certain embryotoxicity and teratogenicity, which can significantly increase the incidence of animal ovarian cancer, prostate cancer, leukemia and other cancers [4]. At the same time, studies have shown that BPA is associated with asthma in mice, and preliminary human experiments have shown that pregnant women affected by BPA in early pregnancy may lead to asthma infection in infants [5].

At present, the detection methods of bisphenol A are: high performance liquid chromatography, gas chromatography-mass spectrometry, liquid chromatography-mass spectrometry, etc., but the general analysis speed is slow, the sensitivity is low, and the operation is tedious [6]. Electrochemical analysis has the advantages of low cost, high sensitivity and easy operation, which can detect BPA well. However, the electrochemical response of BPA on bare electrode is poor, and it is easy to cause passivation on the electrode surface.

![Figure 1. Structure of bisphenol A.](image)

Molecularly imprinted electrochemical sensor is one of the electrochemical sensors. Molecularly imprinted is a new method developed in the later stage, which can provide people with molecular combination with desired structure and properties. Molecularly imprinting is the process of synthesizing polymers in the presence of template molecules and forming molecular recognition sites in polymers. In other words, when there are template molecules in the system, the functional monomers can be polymerized to immobilize the template molecules in a complementary way. After polymerization, the template molecules can be removed, so in this process, the changes of the system can be recorded by electrochemical signals. Thus, the obtained molecular assembly can specifically bond the template molecules and their analogues.

2. Preparation of E-MIPS
The complementary interaction between functional monomers and template molecules is maintained in spatial arrangement through polymerization process, and further stabilized through polymer crosslinking. The advantages of many molecularly imprinted polymers (MIPs) make more people interested in MIPS. More and more interested, their high affinity and selectivity are similar to those of natural receptors. If they are to be considered as real alternative receptors, this feature is essential; their stability is enhanced, superior to the stability of natural biomolecules; the preparation is simple, so that the receptors of interested analytes are much faster than those produced by antibody; the versatility of templates, MIPS It can recognize analyte, make antibody become a challenging target antigen, and it is easy to adapt to practical application of special analysis and sensor.

The fixing of MIPs film on the surface of signal converter is one of the important factors that affect the output electric signal and sensitivity of sensor. In order to ensure the good stability of the sensor during the test, MIPs film must be evenly and tightly attached to the transducer surface. Therefore,
According to the different combination mode between MIPS and transducers, the preparation methods of E-MIPS can be classified into the following five categories:

1. Surface coating method.
   Surface coating is an indirect film forming method. MIPS are dispersed in low boiling solvent, and MIPS suspension is fixed on the surface of transducer by drop coating, dip coating or spin coating. MIPS polymer film is formed after solvent volatilization. Although the E-MIPS prepared by this method have good specific recognition ability for the target, due to the tedious preparation process, time-consuming.

2. In situ initiated polymerization.
   Different from surface coating, in-situ polymerization is a direct film-forming method. It refers to coating the mixed droplets containing template molecules, functional monomers, initiators and porogens on the surface of the transducer, and directly forming MIPS film on the surface of the transducer through initiation polymerization. The initiation process can be divided into light or heat initiation. The preparation method is simple, and the imprinted film can be fixed on the surface of the transducer well and is not easy to fall off. As an initial method for the preparation of E-MIPS, the polymerization method has been greatly developed. However, due to the excessive reactants remaining in the polymer film during the polymerization process, the elution of template molecules is troubled and the quantitative test of template molecules is disturbed. Therefore, the development of this method is limited.

3. Electropolymerization
   Electropolymerization refers to the method that in the presence of target molecules, functional monomers, crosslinking agents and porogens, the surface of transducer is polymerized by cyclic voltammetry, potentiostatic method or galvanostatic method to form imprinted membrane, and then the target is eluted in a certain way to obtain E-MIPS. Electropolymerization is a relatively simple direct film-forming method, which can be realized only by using electrode potential at room temperature. The polymer film obtained by this method is uniformly and firmly attached to the surface of transducer, and the thickness of E-MIPS film can be accurately controlled by adjusting the polymerization parameters. The obtained membrane has stable structure and can be used in any medium, and the imprinted holes are not suitable for deformation and good reproducibility. By controlling the kinds of monomers in the polymerization process, multi-component copolymerization films can be formed. Therefore, electropolymerization is considered to be the most practical E-MIPS polymerization method.

4. Self assembly method
   The self-assembly technology refers to the process that the target molecule and the monomer spontaneously form the target monomer complex by intermolecular force (electrostatic force, van der Waals force, hydrogen bond, hydrophobic lipophilic force, etc.) and then get the polymer membrane by cross-linking polymerization. Different from the above methods, the self-assembly method uses compounds containing sulfur functional groups to carry out chemical adsorption on the surface of metals and metal oxides, which can form stable two-dimensional single-layer films.

3. Preparation of molecularly imprinted sensor

3.1. Preparation principle
   Graphene oxide is thinner and harder. Secondly, it can transfer electrons faster at room temperature, so its conductivity is better. In addition, niobium pentoxide also has a good conductivity. Therefore, the composite of niobium pentoxide and graphene oxide can not only conduct electricity well, but also make full use of the carrier performance of the composite, enhance the combination degree of molecular imprinting and the composite, so as to improve the detection performance and detection limit of bisphenol a.

   FeCo nanoparticle materials have a series of unique physical and chemical properties, which are widely used in sensitive materials, battery materials and other fields. The conductivity of FeCo
nanoparticles is significantly improved due to the synergistic effect of CO and Fe elements. Phosphorus doped FeCo nanoparticles have the advantages of high sensitivity, fast response and low detection limit. For this reason, FeCo nanoparticles have a good prospect in electrochemical research.

The difficulty of protein elution and diffusion can be effectively solved by Western blotting. It refers to the imprinting method that modifies the imprinting site on the surface of the substrate with certain bearing capacity, so as to overcome the steric hindrance caused by protein entering and leaving the polymer layer. Nano materials have the advantages of simple preparation, large specific surface area, good thermal stability and strong mechanical properties, which are applied in various fields. Therefore, MIPs based on simple and easy to get nanomaterials have the characteristics of large surface area, fast binding speed and high binding capacity.

![Figure 2. Western blotting principle of mimic antibody recognition site.](image)

### 3.2. Experimental reagents

(1) Natural graphite powder (AR), bisphenol A (AR), 4-vinyl pyridine (AR), concentrated sulfuric acid (AR), concentrated nitric acid (AR), concentrated hydrochloric acid (AR), potassium persulfate (AR), niobium pentachloride (AR), potassium permanganate (AR), hydrogen peroxide (30%).

### 3.3. Experimental equipment

Ultrasonic cleaner, magnetic stirrer, thermostatic water bath, analytical balance, suction filter, high-speed centrifuge, vacuum drying oven, infrared spectrometer, electrochemical workstation, X-ray diffractometer, scanning electron microscope

### 3.4. Preparation of P-FeCo nanomaterials

(1) Synthesis of FeCo nanoparticles: weigh a certain amount of cobalt chloride hexahydrate and ferric chloride hexahydrate and add them into 30ml ultra pure water. After ultrasonic treatment for 2h, the pH value of the solution was adjusted to 10 by NaOH, and then transferred to the autoclave. The product was collected by freeze-drying at 100℃ for 6h, and then transferred to the precursor FeCo nano material.

(2) Synthesis of phosphorus doped FeCo nanoparticles: take a certain amount of sodium dihydrogen hypophosphite, mix it evenly with the precursor FeCo nanomaterials, put it into a tubular furnace with nitrogen, keep it at 800℃ for 3 hours, and then obtain the phosphorus doped FeCo nanoparticle composite.

(3) Carry out structural features and element analysis.

### 3.5. Preparation of phosphorus doped FeCo nanoparticles supported on Nb2O5 / GO

(1) Synthesis of Nb2O5 / GO: niobium chloride was dispersed in ethanol with graphene oxide dissolved, refluxed overnight in a 45℃ water bath, then centrifuged (t ≥ 40℃) and washed with ethanol three times (t ≥ 40℃, preheated with water bath first). The obtained solid powder was dried overnight,
burned in a tubular furnace for one hour, and the temperature was controlled at 350°C to obtain Nb2O5 / GO material.

② Preparation of phosphorus doped FeCo nanoparticles loaded with Nb2O5 / GO: take a proper amount of Nb2O5 / GO and phosphorus doped FeCo nanoparticles, mix them in ultra pure water, stir for 24 hours, centrifugate them, wash them with ultra pure water several times, dry them in an oven, and obtain the composite of phosphorus doped FeCo nanoparticles loaded with Nb2O5 / GO.

3.6. Results and discussion

The samples were characterized by TEM, SEM and XRD. The specific surface area and pore structure of the composite were measured by the specific surface area analyzer, and the thermal stability of the composite was studied by thermogravimetry. Bisphenol A and 4-vinyl pyridine were added to 10ml acetonitrile for dissolution, the modified electrode was placed in it, the electrode system was connected with the instrument in the range of -0.4-1.2v potential, and the modified electrode was obtained by scanning 20 times at a scanning rate of 100mV/s.

The morphology of imprinted electrode and non imprinted motor was characterized by SEM. There are a lot of small particles on the surface of the non eluted imprinted electrode, but not on the eluted imprinted electrode, which may be caused by the adhesion of template molecules on the surface of the polypyrrole membrane. However, some specific shape structures are formed on the imprinted membrane, which provides a large adsorption area for the template molecules. There are a lot of small protuberances and globular particles on the surface of the non imprinted electrode, which may be that FeCo is coated on the imprinted polymer film; and some rod like structures on the surface of the non imprinted electrode are attributed to Nb2O5 / GO coated on the imprinted polymer.

![Figure 3](image)

**Figure 3.** Cyclic voltammogram of electropolymerization for preparation of non imprinted electrode and imprinted electrode.

The morphology and size of FeCo, P-FeCo and Nb2O5 / GO loaded phosphorus doped FeCo were characterized by SEM. The results are shown in the figure below.

![Figure 4](image)

**Figure 4.** (A) FeCo nanoparticles; (B) Phosphorus doped FeCo nanoparticles supported on Nb2O5 / GO; (C) P-FeCo nanoparticles.
FeCo nanoparticles are uniform regular dodecahedrons, and the effective specific surface area of P-FeCo nanoparticles is 0.52 cm$^2$. After high-temperature calcination, FeCo nanoparticles with Nb2O5 / GO loaded phosphorus doped were formed, which were porous nanospheres with a diameter of 500nm. These nanospheres are evenly and closely arranged on the surface, and the formation of porous nanospheres may be related to a large number of gases released during the calcination process. The effective specific surface area of Nb2O5 / GO integrated electrode increased to 0.87 cm$^2$, which was significantly larger than that of FeCo nanoparticles. The image shows that the surface of P-FeCo nanoparticles is covered by a film, which is formed by electrodeposition. After elution, the pores of template molecules were formed, so as to detect BPA. Due to the existence of molecularly imprinted membranes, the electron transport rate may be reduced, and the specific surface area of the membranes may be reduced to about 0.66 cm$^2$.

Cyclic voltammetry was used to characterize the template molecularly imprinted on the polymer membrane, as shown in the figure below. The cyclic voltammograms of electropolymerization with imprinted electrode and non imprinted electrode were prepared respectively, which was consistent with the experimental results reported previously. It can be seen from the figure that a very obvious oxidation peak is about 0.35V, which indicates that the template molecule has been successfully imprinted into the imprinted polymer.

4. Conclusion
In this paper, FeCo nanoparticle material was used to modify Nb2O5 / GO composite, which increased the current density of the electrode surface, and combined with molecular imprinting technology to make FeCo nanoparticle composite. It has the characteristics of large surface area, is conducive to the diffusion of objects and the combination of electrolyte, and successfully constructed a high-performance composite. A simple and convenient electrochemical sensor for the detection of metal synthetic materials which are closely related to people's health in our life has been constructed, which has great value in practice.

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