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Electrochemical sensor based on magnetic graphene oxide@gold nanoparticles-molecular imprinted polymers for determination of dibutyl phthalate



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ABSTRACT

A novel composite of magnetic graphene oxide @ gold nanoparticles-molecular imprinted polymers (MGO@AuNPs-MIPs) was synthesized and applied as a molecular recognition element to construct dibutyl phthalate (DBP) electrochemical sensor. The composite of MGO@AuNPs was first synthesized using coprecipitation and self-assembly technique. Then the template molecules (DBP) were absorbed at the MGO@AuNPs surface due to their excellent affinity, and subsequently, selective copolymerization of methacrylic acid and ethylene glycol dimethacrylate was further achieved at the MGO@AuNPs surface. Potential scanning was presented to extract DBP molecules from the imprinted polymers film rapidly and completely. As a consequence, an electrochemical sensor for highly sensitive and selective detection of DBP was successfully constructed as demonstration based on the synthesized MGO@AuNPs-MIPs composite. Under optimal experimental conditions, selective detection of DBP in a linear concentration range of 2.5×10^{-9} – 5.0×10^{-6} mol/L was obtained. The new DBP electrochemical sensor also exhibited excellent repeatability, which expressed as relative standard deviation (RSD) was about 2.50% for 30 repeated analyses of 2.0×10^{-6} mol/L DBP.

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1. Introduction

Phthalate esters, such as dibutyl phthalate (DBP), are widely used as additives in the manufacturing of poly (vinyl chloride) plastics to make them flexible in industry [1]. Extensive use of these chemicals results in their presence in various environmental matrices such as personal care products (e.g., perfumes, lotions, and cosmetics) [2], paints [3], industrial plastics [4], certain medical devices [5] and pharmaceuticals [6], including drinking water [7] and other environmental samples [8]. Due to the wide spread use in industry, they are considered as ubiquitous environmental pollutants [9]. They have adverse effects on human health, regarding as endocrine disrupting compounds by means of their carcinogenic action [10,11]. According to the previous report, these methods used for determination of DBP such as solid-phase extraction [12], liquid chromatography [13,14] always lead to high cost and low limit detection due to complex matrices in sample preparation procedures. Therefore, it is practically necessary to

establish a new method with high selectivity and sensitivity to determine DBP in the complex samples.

Graphene has enjoyed widespread attention owing to its unique electronic [15], thermal [16], and mechanical properties [17] since Geim and coworkers first isolated single layer samples from graphite in 2004 [18]. In recent years, unique electronic properties, mechanical properties and extremely large surface area endow graphene with more applications. For instance, graphene nanosheets could serve as the reinforcing element in a polymer matrix in fabricating new advanced materials [19–21]. Specifically, in nanocomposite materials, controlling of interfacial interaction between the graphene and the polymer, as well as homogeneous dispersion into polymer matrices are essential to achieve the required performance of the resulting hybrids [22]. Correspondingly, this combination between graphene and polymer offers an attractive route to introduce some novel properties. Some groups have already functionalized graphene with various polymers to assemble the composites with desired properties. The efforts were mainly made on the effective dispersibility of the composites [23], and improvement of the electrical conductivity [24], thermal stability and mechanical strength of the composites [21,25]. Whereas, the reports involved the preparation of composite based on graphene and high cross-linked polymers were seldom referred as the molecularly recognized element [26,27].

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Molecular imprinting technology is a newly developed technology, which has become a powerful tool for the preparation of polymeric materials with special recognition capacity [28]. The inherent advantages of molecularly imprinted polymers (MIPs) compared to biochemical recognition systems include robustness, storage endurance and lower costs [29]. Although the bulk MIPs prepared by conventional method exhibit high selectivity, certain drawbacks are still suffered, such as time-consuming and complicated preparation process, low binding capacity, poor site accessibility, and slow binding kinetics, etc. [30]. The attempts to solve these problems are generally required to optimize the structure of imprinted materials with suitable forms, which means that controlling templates to be situated at the surface or in the proximity of materials surface. The surface binding sites hold great promise as a means to achieve the excellent performances, such as the complete removal of templates, good accessibility to the target species, and low mass-transfer resistance, etc. Because nanostructured imprinted materials have a small dimension with extremely high surface-to-volume ratio, most of template molecules are situated at or approximate to the materials surface. Eventually, the nanosized imprinted materials are expected to possess several remarkable advantages over normal imprinted materials (e.g. easier removal of template molecules, higher binding capacity, faster binding kinetics, easier installing onto the surface of nanodevices, etc.) [31]. Some researchers have reported a surface monomer directing strategy for highly dense imprinting of molecules at the surface of some nanosized substrates, such as monodispersed silica nanoparticles [32], polystyrene core colloids [33], and polymer nanowires/nanotubes [31]. Graphene, with unique mechanical properties and extremely large area, would therefore propose to be an excellent candidate as a supported material for preparing imprinted materials. The prepared MIPs would be in possession of large surface area in case the polymerization occurring at the surface of graphene. The binding sites in the outer layer of the MIPs composite would provide complete removal of templates, improve the accessibility to target species, and also reduce the binding time.

During these decades, metal nanoparticles have been applied to the fabrication of nanocomposites. They have many excellent properties such as good electrical properties, strong adsorption ability, high surface reaction activity, small particle size and good surface properties [34]. Recently, magnetite nanoparticles (Fe_3O_4) and gold nanoparticles (AuNPs) have been widely used in many applications [35,36]. Fe_3O_4 are coated on MIPs, and the resulting polymer material is magnetically susceptible and therefore easily separated by external magnetic fields after adsorption and recognition. Meanwhile, AuNPs have good conductivity and electrocatalysis. Therefore, in this work, magnetite nanoparticles were applied to make the preparative nanocomposites easy to be separated, AuNPs were used to fabricate electrochemical sensor to improve the electrical conductivity of the sensor.

Herein, a novel composite of MGO@AuNPs and MIPs was prepared by using DBP as a template molecule. The MGO@AuNPs was used as the supported material in the MIPs matrix to prepare MGO@AuNPs-MIPs hybrids with molecular recognition capacity, then drop their suspensions onto a gold electrode surface. An electrochemical sensor fabricated by modifying the MGO@AuNPs-MIPs composite was successfully employed to detect the concentration of DBP.

2. Experimental

2.1. Materials

Graphite was purchased from Red Rock Chemical Reagent Factory (Tianjin, China). Nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric

acid (H_2SO_4) and acetic acid were purchased from Kant Chemical Co., LTD (Laiyang, China). Hydrogen peroxide (H_2O_2) and anhydrous alcohol were purchased from Fuyu Fine Chemical Co., LTD (Tianjin, China). Ferric chloride (FeCl_3), ferrous chloride (FeCl_2), chloroauric acid (HAuCl_4), trisodium citrate, methanol, toluene, ammonia and chitosan were obtained from the Chemical Reagent Third Company (Tianjin, China). Dibutyl phthalate (DBP), acetonitrile, 3-(trimethoxysilyl)propyl methacrylate (MPS), dimethylformamide (DMF), methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Aladdin Reagent Co., LTD (China). MAA and EGDMA were distilled under reduced pressure to remove inhibitors. Azodiisobutyronitrile (AIBN) was purchased from Chemical Plant (Beijing, China) and employed after twice recrystallization. All chemicals were of analytical grade and used as received except for special statements. All aqueous solutions were prepared with ultrapure water.

2.2. Apparatus

Nanocomposites were examined on a scanning electron microscopy (SEM, S-2500, Hitachi High-tech International Trading Co., LTD, Shanghai, China), a transmission electron microscope (TEM, JEM-1011, Can Treasure Technology Co., LTD, Xiamen, China) and X-ray diffraction (XRD, Philips, Germany) using $\text{Cu K}\alpha$ radiation (0.154178 nm). Electrochemical measurements were carried out on CHI832B electrochemical workstation (CH1760D, ChenHua Instruments Co., LTD, Shanghai, China). A three-electrode system (Gaosunion Technology Co., LTD, Wuhan, China) was used in the experiment with the bare and the modified gold electrodes (3 mm in diameter) as the working electrodes, respectively. An Ag/AgCl electrode (saturated KCl) and a Pt wire electrode were used as reference and counter electrode, respectively.

2.3. Synthesis of silanization modification of MGO

GO was synthesized from natural graphite by Hummers' method with little modification [37]. Magnetic graphene oxide (MGO) was synthesized by the modified in situ chemical coprecipitation of Fe^{2+} and Fe^{3+} in an alkaline solution at the presence of GO. Briefly, It was prepared by suspending 50.0 mg GO in 50.0 mL of solution containing 50.0 mg FeCl_3 and 35.0 mg FeCl_2 under N_2 atmosphere. After the solution was sonicated for 30 min, ammonia was added dropwise to precipitate the iron oxides while the mixture solution was under constant mechanical stirring at 90 °C. The pH of the final mixture should be 9.0 and the reaction was continued carrying out for about 60 min to promote the complete growth of the nanoparticle crystals. The obtained precipitate of MGO was isolated in the magnetic field, and the supernatant was separated from the precipitate by decantation. Then 100.0 mg of MGO were dispersed in 40.0 mL of toluene for 1.0 h with continuous stirring, and 3.0 mL of MPS was added. The solution was heated for 48 h under N_2 atmosphere and the resulting solid was washed with toluene for several times. Subsequently, the nanocomposite was dried under vacuum and finally silanization modification of MGO was obtained.

2.4. Synthesis of AuNPs and MGO@AuNPs

AuNPs were prepared by a trisodium citrate reduction method as reported before [38] with little modified. Briefly, 3.65 mL of 0.01 mol/L HAuCl_4 aqueous solutions was diluted with deionized water to 150.0 mL and then heated under vigorous stirring. While boiling, 3.0 mL of trisodium citrate aqueous solution (1 wt%) was added very quickly. When the solution turned to wine red, the heating was stopped but the stirring was kept until the solution was cooled to room temperature (RT). The final sol had good

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