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# Bifunctional polydopamine@$Fe_3O_4$ core–shell nanoparticles for electrochemical determination of lead(II) and cadmium(II)

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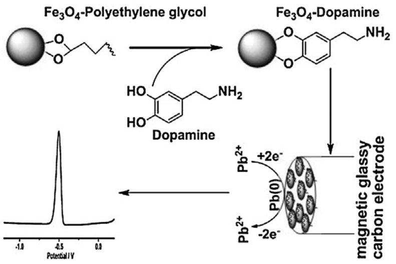
## HIGHLIGHTS

- The bifunctional nanocomposites were synthesized.
- A modified magnetic glassy carbon electrode was fabricated.
- The electrode was used for the selective detection of $Pb^{2+}$ and $Cd^{2+}$ ions.
- The proposed sensor features a wider linear range and higher sensitivity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The present paper has focused on the potential application of the bifunctional polydopamine@$Fe_3O_4$ core–shell nanoparticles for development of a simple, stable and highly selective electrochemical method for metal ions monitoring in real samples. The electrochemical method is based on electrochemical preconcentration/reduction of metal ions onto a polydopamine@$Fe_3O_4$ modified magnetic glassy carbon electrode at −1.1 V (versus SCE) in 0.1 M pH 5.0 acetate solution containing $Pb^{2+}$ and $Cd^{2+}$ during 160 s, followed by subsequent anodic stripping. The proposed method has been demonstrated highly selective and sensitive detection of $Pb^{2+}$ and $Cd^{2+}$, with the calculated detection limits of $1.4 \times 10^{-11}$ M and $9.2 \times 10^{-11}$ M. Under the optimized conditions, the square wave anodic stripping voltammetry response of the modified electrode to $Pb^{2+}$ (or $Cd^{2+}$) shows a linear concentration range of 5.0–600 nM (or 20–590 nM) with a correlation coefficient of 0.997 (or 0.994). Further, the proposed method has been performed to successfully detect $Pb^{2+}$ and $Cd^{2+}$ in aqueous effluent.

## 1. Introduction

The declining quality of drinking water primarily due to human activity has become a matter of grave concern [1]. The water contaminated with a trace amount of heavy metal ions, such as $Pb^{2+}$, $Cd^{2+}$, or $Hg^{2+}$, is colorless and tasteless yet poses dangerous health hazards [2,3], because these ions can be bioaccumulated through the food chain [4]. The U.S. Food and Drug Administration (FDA) set guidelines for the maximum amount of lead that can be leached out from ceramics, mugs, and flat dish plates to be between 0.5 and 30 $\mu g\,mL^{-1}$ (approximately 2.4–144.8 μM) [5]. Currently the amount of lead and heavy metal ions in solutions is mainly determined by atomic absorption or emission spectrometry methods, such as atomic adsorption spectroscopy (AAS) and inductively coupled plasma (ICP). However, due to the high costs for both the equipment and measurement, determining the heavy metal in solutions by using AAS or ICP is impractical in certain situations. Therefore, it is of great significance to develop simple and less expensive methods for sensitive and selective detection of heavy metal ions.

Anodic stripping voltammetry (ASV) is a powerful analytical technique for trace metal detection [6]. In the past few years, two conventional electrode systems, hanging mercury drop electrode

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and mercury film electrode, were mostly applied in those cases [7]. However, with a concern for sustainable development and the eco-design of instruments installed in the natural environment, the analytical methods involving toxic compounds must be banned, in particular mercury impregnation or films, even if the quantities used are relatively low [8]. Hence, mercury-free electrodes have become more attractive. To capture the metal ions in solution for improving the sensitivity of sensors, various nanoparticles (NPs) functionalized with species bearing terminal groups (e.g., —SH, —COOH, and —$NH_2$), which display high affinity for heavy metal ions, have been widely used for sensing of metal ions, as illustrated by the several recent review articles [9–11]. Among the different functionalized nanostructures, the magnetic NPs may be given preference. Because they can exhibit several features synergistically and deliver more than one function simultaneously, such multifunctional magnetic NPs could have unique advantages in analytical applications [12].

Recently, dopamine (DA) self-polymerization was discovered as a powerful approach to apply multifunctional coatings onto many surfaces, including noble metals, metal oxides, ceramics, and polymers, and served as an adhesion layer to immobilize biological molecules [13–15]. The previous reports have been demonstrated that catechol-derivative possesses irreversible binding affinity to iron oxide and then forms the multifunctional coatings onto magnetic NPs (e.g. polydopamine coated $Fe_3O_4$ NPs, denoted as PDA@$Fe_3O_4$ NPs), leading to ultrastable iron oxide NPs [16–20]. Because PDA@$Fe_3O_4$ has functional groups and unique magnetic property, the core–shell NPs can be used for separation. Ni et al. [21] described the synthesis of PDA@$Fe_3O_4$ NPs for *Gluconobacter oxydans* separation in situ. After optimization, 21.3 mg (wet cell weight) *Gluconobacter oxydans* per milligram of nanoparticle was aggregated and separated with a magnet. Sahin et al. [22] reported the comparative study of silica-coated $Fe_3O_4$ NPs and PDA@$Fe_3O_4$ NPs for magnetic bio-separation. In most cases, PDA@$Fe_3O_4$ NPs displayed a significantly higher adsorption capacity for proteins, such as IgG, fibrinogen, hemoglobin and myoglobin. However, to the best of our knowledge, to date there has been no report on enrichment of heavy metal ions by PDA@$Fe_3O_4$ NPs based on its high affinity of amine groups for heavy metal ions.

This contribution describes a simple and versatile electrochemical method using of a PDA@$Fe_3O_4$ modified magnetic glassy carbon (mGC) electrode to detect $Pb^{2+}$ and $Cd^{2+}$ with high sensitivity by square wave anodic stripping voltammetry (SWASV). Compared to the reported methods for electrochemical sensing toward heavy metal ions based on nanostructures, our method indeed possesses the desirable properties of electroanalysis and multifunctional magnetic NPs to improve the selectivity, sensitivity and stability. The concept how to get the most out of multifunctional materials should be very important for development of sensors with high performance.

## 2. Experimental

### 2.1. Apparatus and reagents

Dopamine hydrochloride (DA) and 2-amino-2-hydroxymethylpropane-1,3-diol (Tris) were from Acros Organics (New Jersey, USA). Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), sodium acetate (NaAc), ethylene glycol (EG), polyethylene glycol 4000 (PEG), were obtained from Aldrich. Other reagents were of analytical grade or better quality, which were purchased from J&K Chemical Ltd. (Shanghai, China). Stock solution of 10 mM Pb(II) was prepared by dissolving $Pb(NO_3)_2$ (99.9%, Aldrich) in 4% acetic acid (pH of about 2.3). 0.1 M acetate buffer solutions with various pH values were prepared by mixing the stock solutions of HAc and NaAc, and adjusted the pH with 0.1 M NaOH or HAc solution. Milli-Q ultrapure water (Millipore, $\geq$18.2 M$\Omega$ cm) was used throughout. Heavy metal compounds, such as Pb(II), Cd(II), and Hg(II), are known to be harmful (toxic to the nervous system) if inhaled and irritating to eyes and skin, so personal protective equipment, such as respirators, lab coat, chemical-resistant gloves, and safety goggles, should be worn to minimize the chances of exposure during handling. Solution mixing and handling were done in a ventilated fume hood, and all chemicals were stored in tightly closed containers when not in use.

The electrochemical experiments were performed on a CHI660C Electrochemical Analyzer (Chenhua Instruments, Shanghai, China). A three-electrode system was employed with an mGC electrode ($\phi$ = 3 mm, Tianjing Incole Union Technology Co., Ltd. www.incole.com) or modified electrode as the working electrode. A saturated calomel electrode (SCE) and a platinum wire served as the reference electrode and counter electrode, respectively. All electrochemical experiments were performed in solutions deaerated by pure nitrogen at room temperature. The size and morphology of the synthesized nanoparticles were measured using a JEOL-2010 transmission electron microscope (TEM) operated at 200 kV and an S-4800 field-emission scanning electron microscope (Hitachi, Japan) for obtaining the scanning electron microscopy (SEM) images. Powder X-ray diffraction (XRD) data were recorded by a Shimadzu XRD-6000 X-ray diffractometer (Shimadzu, Japan) based on Cu K$\alpha$ radiation ($\lambda$ = 0.15406 nm). The 2$\theta$ angle of the diffractometer was gradated from 5° to 70° at a scan rate of 0.02° $s^{-1}$. Fourier transform infrared (FTIR) spectra were taken on a FTIR-8400S Fourier transform infrared spectrophotometer after 20 scans within 4000–400 $cm^{-1}$ at a resolution of 8 $cm^{-1}$ by measuring the IR absorbance of a KBr disk that contented of 1–2 wt% of the sample.

### 2.2. Preparation of $Fe_3O_4$ NPs

$Fe_3O_4$ NPs were prepared as reported previously [23]. $FeCl_3{\cdot}6H_2O$ (1.35 g, 5 mmoL) was dissolved in ethylene glycol (40 mL) to form a clear solution followed by addition of NaAc (3.6 g) and polyethylene glycol 4000 (1.0 g). The mixture was stirred vigorously for 30 min and then sealed in a teflon-lined stainless-steel autoclave (60 mL, capacity). The autoclave was heated to maintain at 200 °C for 12 h and allowed to cool to room temperature. The as-prepared $Fe_3O_4$ NPs were washed several times with water and ethanol respectively. Finally the products were collected with a magnet and then dried at 60 °C for 6 h.

### 2.3. Synthesis of PDA@$Fe_3O_4$ NPs

The PDA@$Fe_3O_4$ NPs were synthesized according to references with slight modification [16–20]. Briefly, 100 mg dopamine hydrochloride and 50 mg $Fe_3O_4$ NPs were added into 10 mL deionized water (pH was approximately 6.0) and dispersed by 1 min sonication in water bath. This mixture was shaken for 1 h at room temperature. The DA@$Fe_3O_4$ NPs were collected with a magnet. To obtain the PDA@$Fe_3O_4$ NPs, 90 mL of 0.1 M Tris–HCl buffer (pH 8.5) was added into the above 10 mL mixture, and then the solution was incubated for 24 h at room temperature under shaking. Finally, the products were also collected with a magnet and then dried at 60 °C for 6 h.

### 2.4. Preparation of modified electrode

The fabrication of PDA@$Fe_3O_4$ NPs modified mGC (PDA@$Fe_3O_4$/mGC) electrodes was performed as follows: 20 mg PDA@$Fe_3O_4$ NPs were suspended by ultrasonic for 10 min in 2 mL