Synthesis of a novel electrode material containing phytic acid-polyaniline nanofibers for simultaneous determination of cadmium and lead ions

Hui Huang [a], Wencai Zhu [a], Xiaochun Gao [a], Xiuyu Liu [b], Houyi Ma [a, *]

[a] Key Laboratory for Colloid and Interface Chemistry of State Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, China
[b] Shandong Academy of Sciences, Jinan, 250114, China

HIGHLIGHTS

- One-dimensional phytic acid doped polyaniline nanofibers were prepared.
- Phytic acid based nanocomposite was used to detect metal ions for the first time.
- Detection limits for Cd and Pb using DPASV were 0.02 and 0.05 μg L^{-1}, respectively.
- Cd and Pb in real water samples were measured with satisfactory results.

GRAPHICAL ABSTRACT
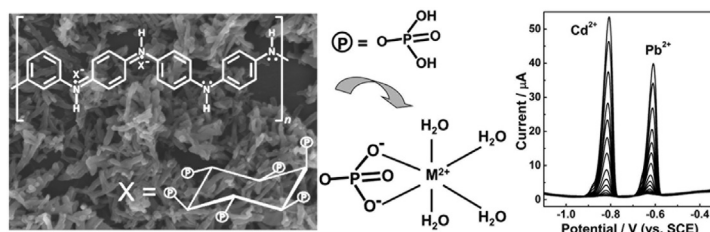
ABSTRACT

The development of nanostructured conducting polymers based materials for electrochemical applications has attracted intense attention due to their environmental stability, unique reversible redox properties, abundant electron active sites, rapid electron transfer and tunable conductivity. Here, a phytic acid doped polyaniline nanofibers based nanocomposite was synthesized using a simple and green method, the properties of the resulting nanomaterial was characterized by electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). A glassy carbon electrode modified by the nanocomposite was evaluated as a new platform for the simultaneous detection of trace amounts of Cd^{2+} and Pb^{2+} using differential pulse anodic stripping voltammetry (DPASV). The synergistic contribution from PANI nanofibers and phytic acid enhances the accumulation efficiency and the charge transfer rate of metal ions during the DPASV analysis. Under the optimal conditions, good linear relationships were obtained for Cd^{2+} in a range of 0.05–60 μg L^{-1}, with the detection limit ($S/N = 3$) of 0.02 μg L^{-1}, and for Pb^{2+} in a range of 0.1–60 μg L^{-1}, with the detection limit ($S/N = 3$) of 0.05 μg L^{-1}. The new electrode was successfully applied to real water samples for simultaneous detection of Cd^{2+} and Pb^{2+} with good recovery rates. Therefore, the new electrode material may be a capable candidate for the detection of trace levels of heavy metal ions.

1. Introduction

Heavy metals are the natural constituents of the earth and have

* Corresponding author.
  E-mail address: hyma@sdu.edu.cn (H. Ma).

been widely used in industry for a few decades [1]. However, the environmental pollution caused by the indiscriminating treatment of heavy metals has received global attention in recent years [2,3]. Among them, cadmium ions (Cd^{2+}) and lead ions (Pb^{2+}) are two highly toxic and persistent pollutants even at very low concentrations, since they have bioaccumulation effect and are hard to be degraded in human body [4–6]. Therefore, to assess and control the daily dietary intake for heavy metal ions, it is critically important to develop novel analytical materials and devices for sensitive, rapid and real-time detection of the trace levels of heavy metal ions.

Various sensitive methods, for instance, atomic absorption spectroscopy, plasma atomic emission spectroscopy, spectrophotometry, X-ray and nuclear methods, have been used for the detection of Cd^{2+} and Pb^{2+}, but they usually require expensive equipment and complicated sample preparation [7,8]. By comparison, electrochemical methods such as differential pulse anodic stripping voltammetry (DPASV) have intrinsic advantages of simple operation, low cost, less sample consumption, high sensitivity, portable instrumentation and simultaneous determination capability [9,10]. In anodic stripping voltammetric analysis, the working electrode performs a pivotal role since it undertakes the responsibility not only for the effective preconcentration of metal ions in a broad potential region but also for the adequate stripping ability. The previously employed mercury based electrodes provide high detection sensitivity owing to the liquid mercury's ability to form alloys with many metals, but they now become restricted for health considerations [4,11]. Alternatively, environmentally friendly electrodes like gold [12], bismuth [13], stannum film [14] etc. and chemically modified electrodes have shown great potential in substituting the mercury electrodes [15,16]. A variety of advanced materials have been employed to modify the electrodes including carbon nanotubes [17], graphene [10], organic polymers [18,19], and the corresponding nanocomposites by their flexible combinations [20,21]. The fundamental principle in designing these detection platforms is to i) enrich the electrostatic adsorption active sites by introducing specific binding groups, also ii) accelerate the electron transfer rate at the electrode surface by enhancing the conductivity of the modified materials, thus increasing the overall preconcentration efficiency.

Phytic acid, also known as inositol hexaphosphate, is a multivalent organic acid with six phosphoric acid groups ($-PO_3H_2$) attached to each carbon of a cyclohexane. The ionizable $-PO_3H_2$ can form complexes with heavy metal ions [22]. It was reported that phytic acid and its salts could be used to remove pollutants such as Cu^{2+}, Zn^{2+} and Cd^{2+} [23]. Besides, phytic acid is a green material mainly extracted from plants, and possesses various important properties, including nontoxicity, highly chelating ability, and low cost [24]. However, phytic acid based materials have seldom been reported for detecting heavy metal ions, since phytic acid is very soluble in water and cannot form stable and repeatable films on the commonly used electrodes, e.g. glassy carbon and gold electrodes.

To overcome this limitation, polyaniline (PANI) is employed as an immobilization matrix for phytic acid. PANI is one of the most promising conducting polymers and many studies have been focused on the nanostructured PANI due to its excellent properties such as inexpensiveness, easy synthetic procedures, environmental stability, reversible redox properties [25,26]. As an electrochemical sensor material, PANI provides abundant electron active sites for binding toxic chemicals, rapid electron transfer, and tunable conductivity by simple acid-base reactions with different dopants or by incorporating with other electro-conductive materials such as carbon nanotubes, graphene and metal nanoparticles [20,21,26,27]. Recently, versatile strategies have been explored to modify PANI for increasing the determination sensitivity of heavy metal ions. For example, Lee et al. reported a cyano group containing PANI derivative for simultaneous detection of Pb^{2+} and Cd^{2+} using DPASV, and low detection limits, 0.255 μg L^{-1} for Cd^{2+} and 0.165 μg L^{-1} for Pb^{2+}, were obtained [18]. Xie et al. employed a thiolated PANI-multiwalled carbon nanotubes nanocomposite for DPASV determination of Pb^{2+} and Cd^{2+}, with ultra low detection limits of 0.04 and 0.01 μg L^{-1}, respectively [28]. Another recent study reported by Djebbar et al., the humic acid-PANI composites modified cavity microelectrode was used to detect Ni^{2+} and Cd^{2+} via square wave voltammetry, and the limit of detection was 1.35 μg L^{-1} for Cd^{2+} [29]. More recently, Henry et al. developed a graphene-PANI nanocomposite electrode for simultaneous detection of Zn^{2+}, Cd^{2+} and Pb^{2+}, with limits of detection of 0.1 μg L^{-1} for both Cd^{2+} and Pb^{2+} in a linear range of 1–300 μg L^{-1} [20]. The progresses made in such sensors are due to on the one hand the increased strong chelating groups than the pure PANI, i.e. the cyano or thiol groups, or the large number of carboxyl and hydroxyl groups in humic acid and graphene, and on the other hand, the increased conductivity by using carbon nanotubes or graphene, but the cyano and thiol dopants employed are not environmental friendly.

In this study, a phytic acid incorporated PANI nanofibers nanocomposite was prepared by the "doping-dedoping-redoping" method and a glassy carbon electrode modified by the resulting nanocomposite was adopted for simultaneous detection of Cd^{2+} and Pb^{2+} using DPASV. The nanostructured PANI offers higher specific surface area, better conductivity, and more active sites for adsorbing metal ions than its traditional bulk counterpart. The $-PO_3H_2$ groups in phytic acid are expected to further enhance the accumulation efficiency of heavy metal ions. The stripping performance of the new electrode was compared with the H_2SO_4 doped PANI nanofibers modified electrode. In general, the synergistic contribution from PANI nanofibers and phytic acid makes the new material a capable candidate for the determination of trace levels of heavy metal ions.

2. Experimental

2.1. Reagents

Aniline (Aldrich) was freshly distilled over zinc dust to eliminate the oxidation impurities and stored in a refrigerator prior to use. Nafion (5 wt% in lower aliphatic alcohols, Sigma-Aldrich) was diluted to 0.1 wt% with ethanol before use. Phytic acid (50 wt% in water) was purchased from Aldrich. Standard stock solutions of Cd^{2+}, Pb^{2+} and Bi^{3+} ions purchased from Aladdin (Shanghai, China) were diluted as required. A 0.1 M HAc-NaAc buffer (pH 4.0) as the supporting electrolyte was prepared by mixing appropriate amounts of CH_3COONa and CH_3COOH. All other chemicals were analytical reagent grade or better. Ultrapure water (≥18 MΩ cm) was used throughout the experiments.

2.2. Apparatus

Differential pulse anodic stripping voltammetry (DPASV) and cyclic voltammetry (CV) measurements were performed with a CHI750D electrochemical workstation (CH Instruments, China) in a three-electrode quartz beaker, including a modified glassy carbon working electrode (GCE, 3 mm diameter), a platinum plate counter electrode, a KCl-saturated calomel reference electrode (SCE) and a magnetic stirrer. All potentials were measured toward the SCE. Electrochemical impedance spectroscopy (EIS) was carried out with an ACM Instruments (Gill AC 5A, UK) in the frequency range from 0.1 Hz to 100 kHz with a perturbation signal of 5 mV. A PHS-3B pH meter (Leici, China) was employed for measuring the solution pH. The physicochemical properties of the resulting nanomaterials