Analytica Chimica Acta 990 (2017) 67–77

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Hydrogels of polyaniline with graphene oxide for highly sensitive electrochemical determination of lead ions

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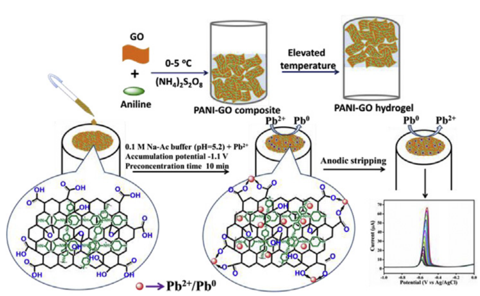
HIGHLIGHTS

- A novel polyaniline-graphene oxide hydrogel was explored for lead ions sensor..
- The detection limit obtained for this electrode is 0.04 nM with the longer linear concentration range.
- The electrode also showed an average of ~99.4% removal of Pb^{2+} ions with a relative standard deviation of 3.4%.
- The developed platform was successfully used for the analysis of real water samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 June 2017
Received in revised form
16 August 2017
Accepted 1 September 2017
Available online 13 September 2017

Keywords:
Polyaniline-graphene oxide hydrogel
Toxic heavy metal ions
Lead ions sensing
Square wave anodic stripping voltammetry
Water treatment

ABSTRACT

Conducting polymers with graphene/graphene oxide hydrogels represent a unique class of electrode materials for sensors and energy storage applications. In this article, we report a facile *in situ* method for the polymerisation of aniline resulting in the decoration of 1D conducting polyaniline (PANI) nanofibers onto the surface of 2D graphene oxide (GO) nanosheets followed by hydrogel formation at elevated temperature. The synthesized nanomaterial exhibits significant properties for the highly sensitive electrochemical determination as well as removal of environmentally harmful lead (Pb^{2+}) ions. The square wave anodic stripping voltammetry (SWASV) determination of Pb^{2+} ions showed good electroanalytical performance with two linear ranges in 0.2–250 nM (correlation coefficient = 0.996) and 250–3500 nM (correlation coefficient = 0.998). The developed protocol has shown a limit of detection (LOD) of about 0.04 nM, which is much lower than that of the World Health Organization (WHO) threshold limits. The prepared electrode showed an average of ~99.4% removal of Pb^{2+} ions with a relative standard deviation (RSD) of 3.4%. Selectivity of the electrode towards Pb^{2+} ions were tested in presence of potential interferences such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+} and Fe^{3+} of similar and higher concentrations. The sensor showed good repeatability and reproducibility. The

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http://dx.doi.org/10.1016/j.aca.2017.09.008

developed protocol was used to analyse samples from industrial effluents and natural water samples. The results obtained were correlated with atomic absorption spectroscopy (AAS).

1. Introduction

The release and accumulation of toxic heavy metals, derived from anthropogenic activities such as mining, burning of fossil fuels, disposal of heavy industrial and agricultural wastes into the environment causes serious health issues to both humans and aquatic life, depending on the concentration level and chemical nature of the heavy metals [1,2]. Particularly, lead (Pb) is widely recognized as highly toxic and non-degradable substance, most commonly found in environmental water due to its substantial use in industrial applications [2–4]. The trace level accumulation of these ions in biological processes may cause several health risks such as nerves, liver, and kidney damage, lung disease, stroke, high blood pressure, weight loss, etc. [4,5]. WHO has recommended the concentration of Pb^{2+} ions in drinking water should be below 10 nM [6]. Therefore, a simple, sensitive and selective determination of Pb^{2+} ions has received a great attention for the regular monitoring in both drinking and environmental water. Several types of analytical methods have been developed for the determination of Pb^{2+} ions including electrochemical techniques [7], spectrophotometry [8], spectroflurometry [9], atomic absorption spectrometry [10], inductively coupled plasma mass spectrometry (ICP-MS) [11], etc. Amongst the methods mentioned, electrochemical methods are more advantageous as they are simple, sensitive, selective, rapid and economically viable for the detection of toxic heavy metal ions. At present, graphene oxide/reduced graphene oxide (GO/rGO) composites with noble metals [12], bismuth [13], metal oxides [14,15], metal oxyhydroxides [16,17], chemically functionalized organic molecules [18], ionic liquid [19], conducting polymers [20–22] and enzymes [23] composite modified electrodes have been reported for the determination of toxic metal ions in aqueous electrolytes.

Hydrogels are also referred as soft or intelligent materials and are distinct from solid materials. They are obtained by cross linking of hydrophilic polymer network either through covalent linkage or non-covalent interactions such as hydrogen bonding, hydrophobic association, electrostatic interaction and π-π stacking [24–28]. They exhibit reversible phase transition based on external stimuli such as solvent composition, solutes, pH, temperature, pressure, light, electric and magnetic field [29,30]. Due to their excellent stimuli-responsive properties and biocompatibility, polymer hydrogels are widely used in biosensors, drug delivery vehicles, wound dressings, scaffolds for cell cultures, antifouling materials, wastewater treatment, microdevices, tissue engineering scaffolds, energy storage materials, artificial muscles etc. [31–33]. However, the conventional polymers prepared from organic cross-linker have shown slow response due to poor mechanical and water absorption retention properties [34,35]. To overcome these limitations and outspreading their practical applications, several types of hydrogels including double network, topological crosslinking, binary and ternary nanocomposites are explored [36].

Graphene oxide (GO) obtained from the oxidation of natural graphite, has received a great attention as nanofillers for polymer reinforcement due to its large theoretical surface area and good chemical compatibility [31,37]. GO can also greatly enhances the mechanical, thermal, and water absorption/retention properties of the polymeric materials [35,38,39]. Various strategies have been developed for the synthesis of PANI-GO and PANI-rGO nanocomposites [40,41]. However, there are only few reports on PANI-GO/(rGO) hydrogels, Tai et al. reported *in situ* polymerization of aniline on the surface of graphene nanosheets hydrogel in two steps. In this method require longer time for the synthesis [42]. Moussa et al. reported the synthesis of PANI-graphene hydrogel, by mixing of GO and polyaniline-poly (2-acrylamido-2-methyl-1-propanesulfonic acid) [43]. Here, additional copolymer has been used as a gelating agent. Chen et al. have reported graphene/polyaniline composite hydrogel by *in situ* polymerization of aniline on the surface of GO followed by hydrothermal heating of reaction mixture at 180 ^{O}C for 12 h [44]. The above discussed method requires higher temperature and pressure for the formation of hydrogels.

Herein, we present a simple single step synthesis of PANI-GO hydrogel by *in situ* polymerization of aniline in the presence of GO dispersion. The obtained PANI-GO hydrogel was used for ultrasensitive electrochemical detection and separation of Pb^{2+} ions. The synthesized materials have been characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and by cyclic voltammetry. The surface morphology was studied by scanning electron microscopy (SEM) and elemental analysis was performed using EDS. The selective determination and removal of Pb^{2+} ions was achieved using the PANI-GO hydrogel composite electrode by anodic deposition at −1.1 V vs Ag/AgCl for 10 min and stripping of the metal as its ions was achieved using SWASV. The SWASV shows two linear ranges between 0.2 and 250 nM (correlation coefficient = 0.996) and 250–3500 nM (correlation coefficient = 0.998). The detection limit obtained for this sensor was 0.04 nM. To the best of our knowledge, this is the first report using PANI-GO hydrogel based electrode for the ultra-sensitive environmentally hazardous Pb^{2+} sensor. The obtained detection limit is much lower and has a larger linear range compared to previously reported results based on graphene–PANI nanocomposites and other composites of PANI. The PANI-GO hydrogel electrode showed an average removal of Pb^{2+} ions is about 99.4% with the RSD of 3.4%. The developed protocol was employed for the detection of Pb^{2+} ions from industrial and environmental water samples.

2. Experimental

2.1. Materials and reagents

All the chemical reagents were used without any further purification. Deionised water was used in the experiments. Graphite powder (<20 μm diameter) was purchased from Aldrich chemicals. Potassium permanganate (99%) Laboratory reagent (LR) grade and Aniline (99.5%) was purchased from SD Fine chemicals. Ammonium persulfate (≥98%), sodium nitrate (≥98%), hydrogen peroxide (≥30%), lead nitrate (≥98%), sodium acetate anhydrous (≥99%), acetic acid glacial (99–100%), hydrochloric acid (≥35%) and sulphuric acid (95–98%) were analytical grade reagents (AR) purchased from Merck.

2.2. Synthesis of graphene oxide

Graphite oxide was synthesized from oxidation of graphite