

# Nanomaterial/Ionophore-Based Electrode for Anodic Stripping Voltammetric Determination of Lead: An Electrochemical Sensing Platform toward Heavy Metals

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A novel nanomaterial/ionophore-modified glassy carbon electrode for anodic stripping analysis of lead ( $\text{Pb}^{2+}$ ) is described. Nanosized hydroxyapatite (NHAP) with width of 20–25 nm and length of 50–100 nm has been prepared and used to improve the sensitivity for detection of  $\text{Pb}^{2+}$  because it provides unique three-dimensional network structure and has strong adsorption ability toward  $\text{Pb}^{2+}$ . An ionophore, usually used in ion-selective electrodes, is utilized here for its excellent selectivity toward  $\text{Pb}^{2+}$ . Nafion, a cation-exchange polymer, is employed as the conductive matrix in which NHAP and the ionophore can be tightly attached to the electrode surface. Such a designed NHAP/ionophore/Nafion-modified electrode shows remarkably improved sensitivity and selectivity to  $\text{Pb}^{2+}$ . The electrode has a linear range of 5.0 nM to 0.8  $\mu\text{M}$  with a 10 min accumulation time at open-circuit potential. The sensitivity and detection limit of the proposed sensor are 13  $\mu\text{A}/\mu\text{M}$  and 1.0 nM, respectively. Interference from other heavy metal ions such as  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  associated with lead analysis can be effectively diminished. The practical application of the proposed sensor has been carried out for determination of trace levels of  $\text{Pb}^{2+}$  in real water samples.

The contamination of natural waters by heavy metals is increasingly becoming a serious environmental problem throughout the world since heavy metals can cause many disorders in the plant and animal kingdoms and tend to accumulate in the food chains.<sup>1,2</sup> The determination of toxic heavy metals in the environment is of great importance from the ecotoxicological point of view.<sup>3,4</sup> Among a variety of new analytical tools under development, stripping voltammetry has been recognized as one of the

most sensitive methods for trace analysis of heavy metals. Compared to its spectroscopic competitors such as atomic absorption and atomic emission spectroscopy, stripping voltammetry has great potential for on-site environmental monitoring due to its favorable portability, suitability for automation, short analysis time, low power consumption, and inexpensive equipment.<sup>5</sup> Many electrode materials such as gold, platinum, silver, mercury, or their alloys have been investigated for stripping voltammetry.<sup>6–10</sup> Among them, mercury has been mostly used for its superior electroanalytical performance in terms of high sensitivity, sound reproducibility, and wide cathodic potential range. Unfortunately, the toxicity of mercury and its difficulties in handling, storage, and disposal may severely restrict its use as an electrode material.<sup>11,12</sup> Recently, a bismuth electrode as a favorable replacement for a mercury electrode has been introduced, because of behavior similar to the mercury electrode and the environmentally friendly nature of bismuth. However, it has been found that bismuth as an electrode material has a relatively narrow potential window (below the oxidation potential of bismuth) and can be easily oxidized upon contact with air, causing relatively low chemical stability.<sup>13</sup> Thus, new alternative electrode materials for stripping analysis are still highly desired to meet the growing demands for on-site environmental monitoring of trace heavy metal ions.

In recent years, nanotechnology has become one of the most active areas in analytical chemistry. Nanomaterials of various shapes, sizes, and compositions have found broad applications in many kinds of analytical methods.<sup>14</sup> These materials often exhibit unique chemical, physical, and electronic properties that cannot

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be achieved by their bulk counterparts. Such characteristics make nanomaterials suitable for construction of electrochemical sensors and biosensors. With manipulated composition and surface modification, nanomaterials such as carbon nanotubes,<sup>15–17</sup> metal nanotubes,<sup>18</sup> magnetic particles,<sup>19</sup> and metal nanoparticles<sup>20–22</sup> have been used in fabrication of novel electrodes for stripping analysis of heavy metals. Such nanomaterial-modified electrodes show dramatically increased sensitivity due to their large specific surface area and high surface free energy. However, it should be noted that these sensors like many other well-established electrodes for stripping voltammetry are still subject to interference from other heavy metal ions, such as the formation of intermetallic compounds and peak overlapping problems, which are specific and relate to the nature of the stripping measurement.<sup>23</sup>

Ionophores, also known as ion carriers, are typically macrocyclic molecules with a well-defined cavity and have the capability of selective extraction of specific ions from an aqueous solution into a hydrophobic membrane phase, where the ions typically would not be soluble.<sup>24</sup> Ionophores have been widely used in ion-selective polymeric membrane sensors which show near-Nernstian responses to the primary ions. The potentiometric selectivity of these sensors among different ions is dictated largely by the complexation specificity of the carrier molecules involved, and the relation between the dimensions of the ion and the ligand site.<sup>25</sup> Although ionophores exhibit elevated selectivity to certain metal ions, the use of them in volt-amperometric analysis other than potentiometric analysis has received little attention, probably because of their nonconductive property.

The aim of this paper is to combine the unique properties of nanomaterials (i.e., enlarged active surface area and strong adsorptive capability) with the specific complexing ability of ionophores to fabricate an electrochemical sensing platform toward heavy metal ions with high sensitivity and excellent selectivity for stripping analysis. Nanosized hydroxyapatite (NHAP),  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , a bioceramic analogous to the mineral component, has been used to provide unique three-dimensional

network structure and particular multiadsorbing sites.<sup>26–28</sup> Lead ( $\text{Pb}^{2+}$ ) has been chosen as a model of heavy metals because of the high toxicity of its compounds and accumulation in various organisms.<sup>29–31</sup> To sustain the neutral circumstance for cation extraction and supply the stability of the modifying layer, Nafion, a sulfonated cation-exchange polymer, has been utilized as the conductive membrane matrix. It will be shown that such a designed NHAP/ionophore/Nafion-modified electrode can offer remarkably improved sensitivity and selectivity for stripping measurement of  $\text{Pb}^{2+}$ .

## EXPERIMENTAL SECTION

**Reagents.** Lead ionophore (IV), 4-*tert*-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide), was purchased from Fluka. Nafion (5% w/w solution in a mixture of lower aliphatic alcohols and water) was obtained from Aldrich. Stock solution of 0.01 M  $\text{Pb}^{2+}$  was prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  (Shanghai Reagent Corporation, China) in deionized water and then diluted to various concentrations of working solutions. Unless otherwise stated, 0.2 M HAc-NaAc buffer solutions (pH 4.4) were used as the supporting electrolyte for  $\text{Pb}^{2+}$  determination. All other chemicals were analytical reagents and used without further purification. Deionized water (18.2 M $\Omega$  cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

**Instrumentation.** All electrochemical experiments were carried out in a conventional three-electrode cell controlled by CHI 660C Electrochemical Workstation (CH Instruments, Inc.). A modified glassy carbon (GC) disk working electrode (3 mm in diameter) was used as working electrode. A platinum foil was applied as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. All potential values given below refer to SCE. Experiments were carried out at room temperature.

The TEM micrograph was recorded using a JEOL-3010 transmission electron microscope (operating at 300 kV). A drop of the prepared NHAP solutions was placed on carbon-coated copper grids and dried under ambient conditions. The NHAP adduct was pressed into a KBr pellet for FTIR investigation (FTIR-8400S spectrometer, Shimadzu, Japan). The micrographs of the modified electrodes were investigated by scanning electron microscopy (SEM, JSM 5600 LV, operating at 20 kV). Atomic absorption spectrometric (AAS) measurements were conducted with an AA6300 atomic absorption spectrophotometer (Shimadzu, Japan). Natural organic matter in the real samples was destroyed by UV-irradiation using a 1000 W UV lamp (LT-UV Company, China).

**Preparation of NHAP.** NHAP was prepared easily and effectively by sonication synthesis. Briefly, 15 mL of 0.1 M  $(\text{NH}_4)_2\text{HPO}_4$  aqueous solution was added dropwise at a rate of 2–4 mL/min into 25 mL of 0.1 M  $\text{Ca}(\text{NO}_3)_2$  solution with continuous sonication. As a result, the total molar ratio of Ca and P was equal to 1.67. The pH of the above solution was controlled at about 10–12 using ammonia during the course of  $(\text{NH}_4)_2\text{HPO}_4$  addition. The mixture solution was then kept in continuous sonication for 1 h. The resulting liquid crystalline

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mixture was centrifuged, washed with water, and dried at 100 °C in an oven.

**Preparation of NHAP/Ionophore/Nafion-Modified Electrode.** The procedure for preparation of the NHAP/ionophore/Nafion-modified electrode is as follows: (1) GC electrode was polished with 0.3 and 0.05  $\mu\text{m}$  alumina slurries, washed with deionized water and acetone thoroughly, and then sonicated in deionized water for 1 min. The electrode was then transferred to the electrochemical cell for the activation by cycling between  $-0.15$  and  $1.3$  V in  $0.5$  M  $\text{H}_2\text{SO}_4$  solution, until a stable profile was obtained. (2) Original 5% w/w Nafion solution was diluted to 1% w/w solution with *N,N*-dimethylformamide (DMF). Then 1 mL of the above solution was used to dissolve 2 mM lead ionophore(IV) to get clear and pale yellow solution. Finally, 10 mg of NHAP was added into the mixture and sonicated for 20–30 min to get a homogeneous NHAP/ionophore/Nafion suspension. (3) A 5  $\mu\text{L}$  amount of the NHAP/ionophore/Nafion DMF suspension was added on the surface of GC electrode and dried under an infrared lamp. For comparison, Nafion-, NHAP/Nafion-, and ionophore/Nafion-modified GC electrodes were prepared in the same manner.

**Analytical Procedure.** The analysis of  $\text{Pb}^{2+}$  has three main steps including accumulation, electrochemical reduction, and stripping out. Accumulation of  $\text{Pb}^{2+}$  on NHAP/ionophore/Nafion-modified GC electrode at open-circuit potential was performed by immersing the electrode into the stirred  $\text{Pb}(\text{NO}_3)_2$  solution (300 rpm) for 10 min. Then the NHAP/ionophore/Nafion/ $\text{Pb}^{2+}$  electrode was rinsed thoroughly with deionized water and dried with a soft tissue. The resulting electrode was then transferred to a separate voltammetric cell containing a lead-free fresh supporting electrolyte (0.2 M acetate buffer of pH 4.4). The solution was deaerated by bubbling nitrogen through it while a potential of  $-1.1$  V was applied to the electrode for about 30 s in order to electrochemically reduce  $\text{Pb}^{2+}$ . Quantitative determinations of  $\text{Pb}^{2+}$  were performed with differential pulse anodic stripping voltammetry. The optimal conditions were as follows: amplitude of 0.05 V; pulse width of 0.01 s; sampling width of 0.005 s; pulse period of 0.2 s; quiet time of 15 s. After each measurement, the NHAP/ionophore/Nafion-modified electrode was regenerated in fresh stirred supporting electrolyte by electrolysis at  $+0.3$  V for 120 s to remove the previous residual lead from the electrode surface. For comparison, the electroaccumulation of  $\text{Pb}^{2+}$  was carried out by applying the electrode potential at  $-1.1$  V for 10 min.

## RESULTS AND DISCUSSION

**Characterization of NHAP.** Conventionally, HAP powders are synthesized by various methods including solid-state reaction, precipitation, and hydrolysis of calcium phosphates and sol–gel.<sup>32,33</sup> In this work, one easy and effective method to prepare NHAP was introduced by the aid of ultrasonication.<sup>34</sup> The formation of NHAP was identified by analyzing its FTIR spectrum and TEM image. The bands at 564, 602, and 962  $\text{cm}^{-1}$  in the FTIR spectrum

are attributed to the stretching modes of the phosphate group.<sup>35</sup> The split bands, mainly at 1027 and 1094  $\text{cm}^{-1}$ , seem to coincide with the formation of a well-crystallized apatite.<sup>36</sup> Carbonate bands were detected at 1389  $\text{cm}^{-1}$ . The presence of a hydroxyl group in NHAP gives rise to characteristic bands at 1637 and 3428  $\text{cm}^{-1}$ . The spectrum of NHAP from our experiment coincides with the standard HAP FTIR spectrum.<sup>36</sup> On the other hand, NHAP is a quite uniform spindle-like structure with width of 20–25 nm and length of 50–100 nm.<sup>34</sup>

**Electrochemical Behavior of  $\text{Pb}^{2+}$  at NHAP/Ionophore/Nafion-Modified Electrode.** In principle, the combination of accumulation and reduction prior to the actual stripping detection process can enhance both the sensitivity and the selectivity of the analysis of metal ions.<sup>37</sup> For the present work, lead ions can form complexes with the ionophore molecules on the electrode surface after open-circuit accumulation in  $\text{Pb}(\text{NO}_3)_2$  solution for 10 min. The complexes are further reduced and deposited on the electrode under cathodic potentiostatic conditions ( $-1.1$  V) for a defined time period (30 s). Finally, the accumulated lead ions are stripped off the electrode and the stripping current can be measured. The diagrammed illustration is presented in Figure 1a. The typical voltammetric behavior of 10  $\mu\text{M}$   $\text{Pb}^{2+}$  at the NHAP/ionophore/Nafion-modified electrode is shown in Figure 1b. Compared with the cyclic voltammogram of the electrode in pure supporting electrolyte (dotted line), a large anodic peak at  $-0.55$  V attributed to oxidation of metallic lead can be obtained after accumulation of lead ions from the sample solution to the electrode membrane surface (solid line). Additionally, the oxidation peak was found to vary linearly with the scan rate ranging from 50 to 400  $\text{mV s}^{-1}$  (inset in Figure 1b). This reveals that the electrochemical behavior of lead on the surface of the NHAP/ionophore/Nafion-modified GC electrode shows a surface-confined redox process.

To clarify the function of each component in the electrode coating matrix, the differential pulse voltammograms recorded from  $-0.90$  to  $-0.40$  V for stripping analysis of lead with various electrodes are shown in Figure 2. A very small stripping peak was obtained for 0.5  $\mu\text{M}$   $\text{Pb}^{2+}$  at bare GC electrode after accumulation at open-circuit potential for 10 min (Figure 2a). Under the same conditions, a slightly larger stripping peak for Nafion-modified electrode was observed (Figure 2b), which is probably due to the ion-exchange property of Nafion film. Larger stripping peaks at  $-0.62$  and  $-0.66$  V was found for NHAP/Nafion and ionophore/Nafion-modified electrodes, respectively (Figure 2c and 2d). NHAP and the ionophore both have particular multiadsorbing sites for  $\text{Pb}^{2+}$  which can attract  $\text{Pb}^{2+}$  from bulk solution to electrode surface, thus increasing the stripping peak currents. The highest peak at  $-0.63$  V occurred at NHAP/ionophore/Nafion-modified electrode (Figure 2e). The stripping peak currents of  $\text{Pb}^{2+}$  at bare GC, Nafion, ionophore/Nafion, NHAP/Nafion, and NHAP/ionophore/Nafion-modified electrodes are 0.14, 0.33, 0.90, 1.2, 6.3  $\mu\text{A}$ , respectively, indicating that the current response obtained with the NHAP/ionophore/Nafion-modified GC electrode is increased by nearly 45-fold

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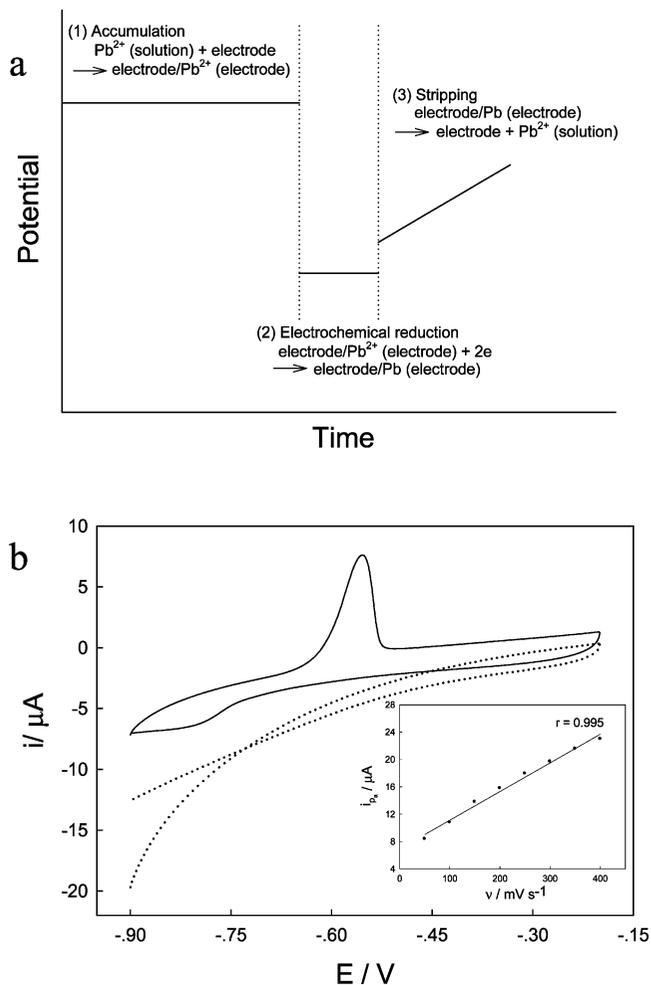
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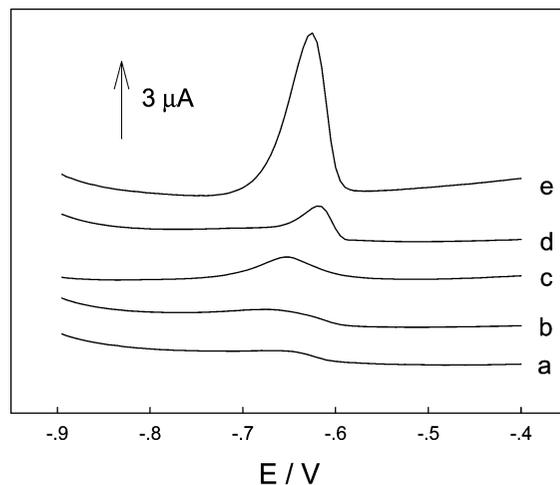
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**Figure 1.** (a) Schematic diagram of the potential–time profile for stripping analysis of  $\text{Pb}^{2+}$  and (b) typical cyclic voltammograms of the GC/NHAP/ionophore/Nafion electrode in 0.2 M pH 4.4 HAc-NaAc buffer solution with (solid line) and without (dotted line) open-circuit 10-min accumulation. Accumulation solution: buffer solution containing  $10 \mu\text{M}$   $\text{Pb}^{2+}$ . Scan rate:  $50 \text{ mV s}^{-1}$ . Reduction potential:  $-1.1 \text{ V}$ . Deposition time: 30 s.

as compared to that with bare GC electrode. To explain the above effects, the following synergy hypothesis could be formulated. The calixarene ionophore is capable of forming a strong complex with  $\text{Pb}^{2+}$  ions. Nafion, as a cation-exchange polymer, provides both a favorable conductive membrane matrix and anion sites in the ion-selective membrane for stabilizing the surface-extracted  $\text{Pb}^{2+}$  ions. The introduction of NHAP into the ionophore/Nafion film could improve the accumulation capacity of the ion-selective membrane because the NHAP nanoparticles provide a unique three-dimensional network structure which has a larger surface area with more active sites for  $\text{Pb}^{2+}$  accumulation on the NHAP/ionophore/Nafion-modified membrane layer. Accordingly, the enhanced accumulation of  $\text{Pb}^{2+}$  ions from the sample solution on the ion-selective membrane leads to the significant increase of the current response for stripping analysis. In our preliminary studies, such a synergistic effect on the sensor's sensitivity was also observed by using other nanomaterials such as carbon nanotubes and nanosized iron oxides. In this paper, we focus on the use of NHAP because it has strong adsorption for  $\text{Pb}^{2+}$  and is environmentally friendly.



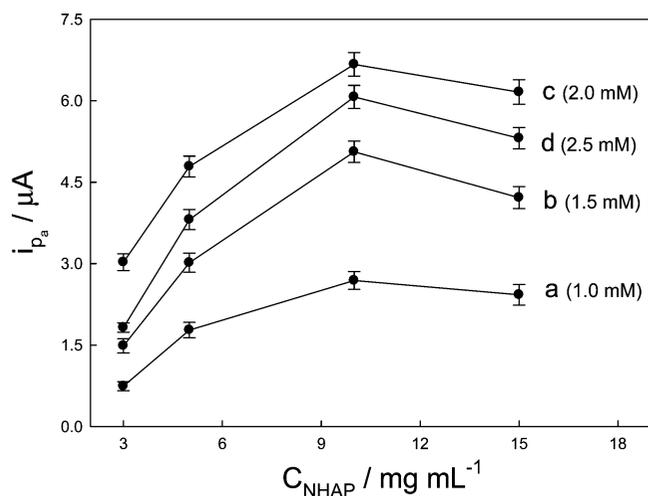
**Figure 2.** Anodic stripping differential pulse voltammograms of (a) bare GC, (b) Nafion-modified, (c) ionophore/Nafion-modified, (d) NHAP/Nafion-modified, and (e) NHAP/ionophore/Nafion-modified GC electrodes in 0.2 M HAc-NaAc buffer (pH 4.4) containing  $0.5 \mu\text{M}$   $\text{Pb}^{2+}$ . Amplitude of 0.05 V; pulse width of 0.01 s; sampling width of 0.005 s; pulse period of 0.2 s; quiet time of 15 s. Other conditions are as in Figure 1.

The morphologies of the ionophore/Nafion and NHAP/ionophore/Nafion film on the GC electrode were characterized using scanning electron microscopy (Figure S-1, Supporting Information). It can be seen that the ionophore/Nafion layer shows a flat and homogeneous film across the whole section (Figure S-1a). However, when the electrode is modified with NHAP/ionophore/Nafion, many NHAP particles are decorated across the whole surface, forming a three-dimensional, porous, and compact structure on the GC electrode (Figure S-1b). The unique NHAP/ionophore/Nafion membrane layer has high specific surface areas and multiadsorbing sites, which endow the nanomaterial/ionophore-modified electrode with the capability to effectively adsorb target ions on the electrode surface and hence improve the sensitivity for stripping measurement.

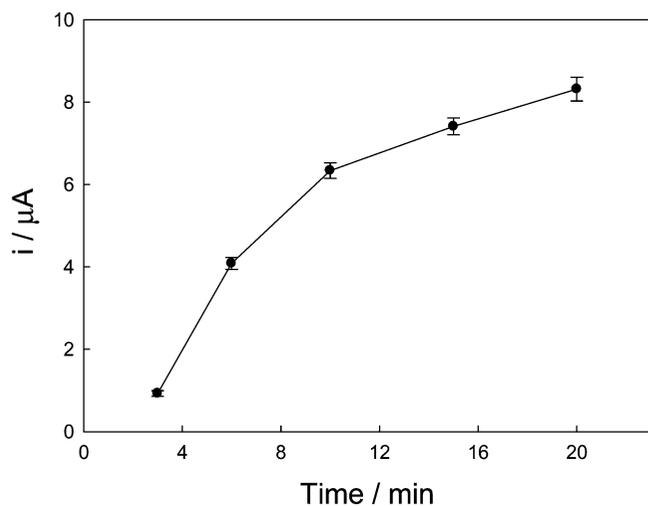
**Optimization for Measurement of  $\text{Pb}^{2+}$  at the NHAP/Ionophore/Nafion-Modified Electrode.** Since the nanomaterial and ionophore play important roles in the performance of the modified electrode, the effect of the amounts of NHAP and ionophore added to the composite membrane was investigated, and the results are shown in Figure 3. It can be seen that the response current increases with an increase of the concentrations of both NHAP and ionophore because of the excellent adsorption capabilities of NHAP and ionophore for  $\text{Pb}^{2+}$  ions and the enlarged active surface area provided by NHAP. However, maximum values of the response currents can be obtained when the concentrations reach  $10 \text{ mg mL}^{-1}$  for NHAP and 2 mM for ionophore, respectively. Indeed, at higher loadings of NHAP and ionophore, the Nafion film can be disrupted by the excrescent NHAP and nonconductive ionophore, in which the transport of ions may become difficult with the complexation taking place largely at the electrode/solution boundary and the electrochemical processes being available at the glassy carbon/coating boundary.<sup>38</sup>

The sensitivity of the proposed method for detection of  $\text{Pb}^{2+}$  can be increased with increase of the accumulation time

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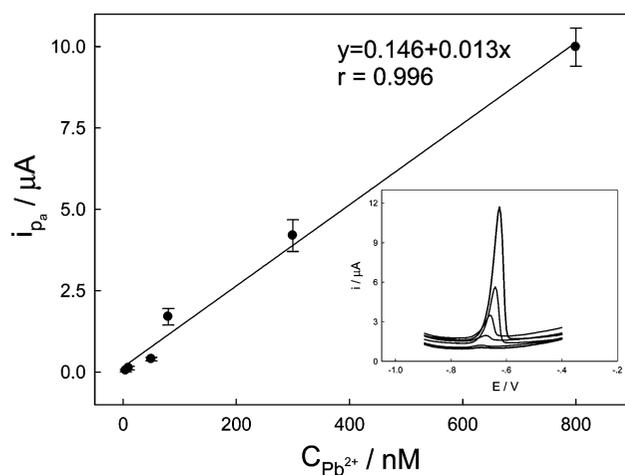
**Figure 3.** Effect of the amounts of NHAP and ionophore in the Nafion membrane on the current response to  $0.5 \mu\text{M Pb}^{2+}$ . The concentrations of ionophore are (a) 1.0, (b) 1.5, (c) 2.0, and (d) 2.5 mM, respectively. Error bars represent one standard deviation for three measurements. Other conditions are as in Figure 1 and Figure 2.



**Figure 4.** Effect of the accumulation time at open-circuit potential on the stripping peak current of the GC/NHAP/ionophore/Nafion electrode to  $0.5 \mu\text{M Pb}^{2+}$ . Other conditions are as in Figure 1 and Figure 2.

because of the increased amount of  $\text{Pb}^{2+}$  on the NHAP/ionophore/Nafion-modified GC electrode. Figure 4 shows that the response of the modified electrode to  $0.5 \mu\text{M Pb}^{2+}$  increases rapidly with accumulation time up to 10 min and then tends to increase gradually because of the limited active sites. Although increasing the accumulation time improves the sensitivity, it also lowers the upper detection limit due to the rapid surface saturation at high Pb concentrations. Therefore, to achieve lower detection limit and wider response range, 10 min was chosen as the accumulation time for subsequent experiments.

**Performance of the NHAP/Ionophore/Nafion-Modified Electrode.** The calibration curve of the proposed  $\text{Pb}^{2+}$  sensor was derived from the differential pulse stripping voltammetry curves obtained at the NHAP/ionophore/Nafion-modified with an open-circuit accumulation period of 10 min (Figure 5). The stripping peak current ( $i_{\text{pa}}$ ) is proportional to the concentration of  $\text{Pb}^{2+}$  from 5 nM to  $0.8 \mu\text{M}$  ( $i_{\text{pa}} = 0.146 + 0.013C$ ,  $r = 0.995$ ,



**Figure 5.** Calibration plots of Pb stripping peak current with  $\text{Pb}^{2+}$  solution concentration. Error bars represent one standard deviation for three measurements. Inset shows anodic stripping differential pulse voltammograms obtained at GC/NHAP/ionophore/Nafion electrode in acetate buffer solution (pH 4.4) containing 5, 10, 50, 80, 300, and 800 nM  $\text{Pb}^{2+}$  (from bottom to top). Other conditions are as in Figure 1 and Figure 2.

$i_{\text{pa}}$  in  $\mu\text{A}$ ,  $C$  in nM). The sensitivity of the modified electrode to  $\text{Pb}^{2+}$  is  $13 \mu\text{A}/\mu\text{M}$ . The detection limit is given by the equation  $C_L = 3s_{\text{bl}}/S$ , where  $s_{\text{bl}}$  is the standard deviation of the blank measurements and  $S$  is the sensitivity of the calibration graph. The detection limit of  $\text{Pb}^{2+}$  for 10 min of open-circuit accumulation was calculated to be 1 nM. The proposed electrode has a wider linear dynamic range, lower detection limit, and larger sensitivity than most of the other mercury-free electrodes for determination of  $\text{Pb}^{2+}$ .<sup>26,39–53</sup> For example, the sensitivity of the NHAP/ionophore/Nafion-modified electrode is almost 48 times that of the HAP-modified platinum electrode, which has an open-circuit accumulation of 30 min.<sup>26</sup> The linear range of the proposed sensor is superior to those using open-circuit accumulation,<sup>26,48–50</sup> and wider than those using electroaccumulation.<sup>51–53</sup> It should be noted that the detection limit can be further reduced to 0.3 nM by using electroaccumulation (see below), which is superior to those of most of the current anodic stripping methods for determination of lead. Recent improvements

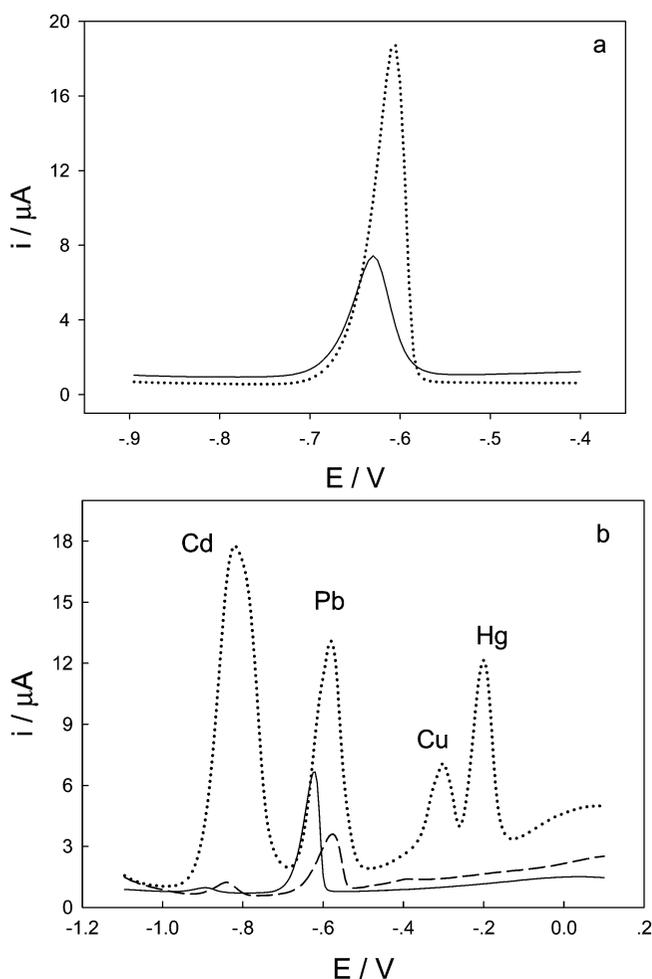
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in the detection limits of polymeric membrane ion-selective electrodes yield potentiometric sensors for the direct measurement of ions down to the subnanomolar concentration range. However, ion-selective electrodes are normally incapable of reaching the same detection limits for samples with high levels of electrolyte (salt) background.<sup>54</sup> For the proposed electrode, the detection limit of 1 nM can be achieved with 0.2 M acetate buffer solution.

The NHAP/ionophore/Nafion-modified GC electrode has a good repeatability, reproducibility and stability for  $\text{Pb}^{2+}$  detection. For 30 nM  $\text{Pb}^{2+}$ , the relative standard deviation (RSD %) was found to be 6.3% for one electrode with six measurements and 8.2% for six electrodes prepared with identical procedures. The stability of the NHAP/ionophore/Nafion-modified electrode stored at room temperature was studied, and the results showed that at least 85% response current could be retained after a period of 15 days.

**Interference Study.** The stripping analysis of  $\text{Pb}^{2+}$  can be affected by interferences from other heavy metal ions. In this work, three metal ions including  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  were chosen as interfering ions for investigation of the sensor's selectivity. For stripping analysis of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  can occupy available deposition and/or coordination sites on the electrode surface and thus decrease the peak current of  $\text{Pb}^{2+}$ .  $\text{Cu}^{2+}$  has been found to suppress the peak current probably because of formation of the intermetallic compound between copper and lead deposited on the electrode.  $\text{Hg}^{2+}$  heavily interferes with the measurement of  $\text{Pb}^{2+}$  because of the formation of mercury film at the modified electrode surface, which causes  $\text{Pb}^{2+}$  to be reduced more easily and increases the stripping peak current because of formation of amalgam consequently. Although the effects of this interference may be simply compensated for by standard additions, the presence of higher concentrations ( $>0.1 \mu\text{M}$ ) of interfering ions can generate large errors by the standard addition method.<sup>23</sup>

Figure 6 shows the differential pulse stripping voltammograms obtained at the NHAP/ionophore/Nafion-modified electrode using open-circuit accumulation or electroaccumulation for  $\text{Pb}^{2+}$ , which is alone (Figure 6a) or present with  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at the same concentration (Figure 6b). A large stripping peak at  $-0.61 \text{ V}$  can be obtained at the modified electrode using electroaccumulation in buffer solution containing only  $\text{Pb}^{2+}$  (dotted line in Figure 6a). When 10-min electroaccumulation is applied for the mixture of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  (with the same concentration), four peaks appear at  $-0.82$ ,  $-0.58$ ,  $-0.30$ , and  $-0.20 \text{ V}$  (dotted line in Figure 6b), which are ascribed to the oxidation of Cd, Pb, Cu, and Hg, respectively. The current response of  $\text{Pb}^{2+}$  is decreased by about 40% (from  $18 \mu\text{A}$  to  $11 \mu\text{A}$ ) because of the presence of the interfering ions, while the oxidation peak current of Cd is even larger than that of target lead ion. This implies that the interfering metal ions can be electrodeposited together with the target ion on the NHAP/ionophore/Nafion-modified electrode during the electroaccumulation procedure, which is probably because of forced ion extraction under the influence of a strongly polarizing applied potential, thus causing a poor selectivity for stripping analysis of the target ion.



**Figure 6.** Anodic stripping differential pulse voltammograms obtained at GC/NHAP/ionophore/Nafion electrode in 0.2 M HAC-NaAc buffer (pH 4.4) containing (a)  $0.5 \mu\text{M}$   $\text{Pb}^{2+}$  or (b)  $0.5 \mu\text{M}$   $\text{Pb}^{2+}$  +  $0.5 \mu\text{M}$   $\text{Cd}^{2+}$  +  $0.5 \mu\text{M}$   $\text{Cu}^{2+}$  +  $0.5 \mu\text{M}$   $\text{Hg}^{2+}$ . Solid line: open-circuit 10-min accumulation. Dotted line: electroaccumulation at  $-1.1 \text{ V}$  for 10 min. Dashed line: GC/NHAP/Nafion electrode for open-circuit 10-min accumulation. Other conditions are as in Figure 1 and Figure 2.

For measurement of the sample containing  $\text{Pb}^{2+}$  alone, the current response of  $\text{Pb}^{2+}$  obtained at the NHAP/ionophore/Nafion-modified electrode by open-circuit accumulation (solid line in Figure 6a) is ca. 30% of that at the same electrode by electroaccumulation (dotted line in Figure 6a). This is probably due to the adsorption of less target ions during the 10-min open-circuit accumulation (see Figure 4) and/or the incomplete reduction of absorbed target ion on electrode surface during 30 s electrodeposition. Interestingly, for measurement of the mixture sample solution, the NHAP/ionophore/Nafion-modified electrode with 10 min of the open-circuit accumulation shows the oxidation peak signal of  $\text{Pb}^{2+}$  at  $-0.62 \text{ V}$  along with a much smaller oxidation peak of  $\text{Cd}^{2+}$  at  $-0.90$ , while the oxidation peaks of Cu and Hg cannot be observed (solid line in Figure 6b). The current responses to  $\text{Pb}^{2+}$  in the sample solutions with and without interfering ions are almost the same (compare solid lines in Figure 6), indicating an excellent antiinterference ability of the NHAP/ionophore/Nafion-modified electrode by the use of open-circuit accumulation. This may be attributed to the selective transportation of  $\text{Pb}^{2+}$  ions from the sample solution to the ion selective membrane via the specific complexation with the

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ionophore. A similar situation also occurs at the NHAP/Nafion-modified electrode. Only the oxidation peaks of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  can be observed at  $-0.58$  and  $-0.84$  V, respectively (dashed line in Figure 6b). These results may be due to the adsorption capabilities of NHAP to  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  being much stronger than those to  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  under the open-circuit accumulation conditions. However, it should be noted that the presence of the ionophore can further inhibit the accumulation of  $\text{Cd}^{2+}$  and accelerate the enrichment of  $\text{Pb}^{2+}$  on the electrode surface, thus increasing the current response of  $\text{Pb}^{2+}$  by 2.0 times and decreasing the response of  $\text{Cd}^{2+}$  by 3.3 times (compare solid and dashed lines in Figure 6b). These results imply that the selectivity of the sensor can be remarkably improved by using the NHAP/ionophore/Nafion-modified electrode and open-circuit accumulation procedure. Under such conditions, a 200-fold excess of  $\text{Cd}^{2+}$ , 50-fold  $\text{Cu}^{2+}$ , or 100-fold  $\text{Hg}^{2+}$  could not have any influence on the stripping signal of  $0.1 \mu\text{M}$   $\text{Pb}^{2+}$ . A satisfactory selectivity of the proposed electrode is therefore evident.

**Practical Application.** The NHAP/ionophore/Nafion-modified electrode exhibits high sensitivity and good selectivity for the determination of  $\text{Pb}^{2+}$  under the optimum experimental conditions. In order to illustrate its accuracy in practical analysis, the comparison between the proposed electrode and atomic absorption spectrometry for detection of lead in real samples was carried out. Several lake water and tap water samples were filtered through a standard  $0.45 \mu\text{m}$  filter, treated with UV digestion for release of the trace  $\text{Pb}^{2+}$  from the lead-organic complexes, and analyzed by the standard addition method. The results are shown in Table 1. It can be seen that the NHAP/ionophore/Nafion-modified electrode has a great potential for real sample analysis with a high accuracy and good reliability.

## CONCLUSIONS

A novel chemically modified glassy carbon electrode for stripping analysis of  $\text{Pb}^{2+}$  has been described, based on the combination of the unique properties of the nanomaterial (i.e., enlarged active surface area and strong adsorptive capability) and the specific complexing ability of the ionophore. The

**Table 1. Comparison of the Results Obtained by the NHAP/Ionophore/Nafion-Modified Electrode and AAS for Determination of  $\text{Pb}^{2+}$  in Real Water Samples**

samples	AAS (nM) <sup>a</sup>	present electrode (nM) <sup>a</sup>
lake water 1	$61.8 \pm 1.7$	$64.1 \pm 2.7$
lake water 2	$37.8 \pm 0.9$	$39.9 \pm 2.0$
lake water 3	$38.5 \pm 1.3$	$39.7 \pm 2.1$
tap water 1	$50.6 \pm 0.8$	$53.0 \pm 1.0$
tap water 2	$55.5 \pm 0.7$	$58.4 \pm 1.1$

<sup>a</sup> Average value of three determinations  $\pm$  standard deviation.

proposed sensor has shown remarkably improved sensitivity and selectivity for  $\text{Pb}^{2+}$  detection. Since many nanomaterials and ionophores have been exploited in analytical chemistry and some of them are even commercially available, such a sensing scheme can provide an excellent platform for electroanalysis and has promising potential for fabrication of chemical sensors for various heavy metals. This aspect is now under study in our laboratory.

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## SUPPORTING INFORMATION AVAILABLE

Experimental details. SEM images of the ionophore/Nafion and NHAP/ionophore/Nafion modified GC electrodes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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