



Proceeding Paper Chromium-Modified Lanthanum-Based Metal–Organic Framework: Novel Electrochemical Sensing Platform for Pb(II) Ions [†]

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Abstract: Heavy metal ions (HMIs) in drinking water result from industrialization and can cause a nuisance to the environment. Due to their toxicity and carcinogenic tendencies toward humans, determining HMIs remains challenging. This study focuses on creating a cutting-edge electrochemical sensor with unprecedented sensitivity to lead (Pb(II)). In the present investigation, we have hydrothermally produced lanthanum porous coordination polymer (La-TMA), which was further modified with chromium (Cr) nanoparticles, characterized with structural, morphological, electrochemical, and spectroscopic techniques, and used as a sensing material. The differential pulse voltammogram pattern of the chromium-modified lanthanum porous coordination polymer (Cr@La-TMA) sensor indicates an affinity for Pb(II). Sensing parameters such as sensitivity, selectivity, and linearity have been investigated. The Cr@La-TMA sensor shows selectivity towards Pb(II), which is also validated by the interference study for various analytes such as Cd(II), Hg(II), Cu(II), Cr(II), and Fe(II). The sensor exhibited excellent linearity for the concentration range of 1 nM to 10 nM with a limit of detection of 1 nM, which is below the maximum contamination level (MCL) suggested by the United States Environmental Protection Agency (US-EPA) and World Health Organization (WHO). The proposed sensor would be incredibly useful for the real-time monitoring of heavy metal ions.

Keywords: electrochemical sensors; heavy metal ions; pollution; metal–organic frameworks; lanthanum porous coordination polymer

1. Introduction

Heavy metal ions (HMIs), such as lead (Pb(II)), are a significant environmental concern due to their toxic nature and potential adverse effects on human health and ecosystems [1]. Consequently, the development of sensitive and selective methods for the detection of HMIs has gained substantial attention. For the detection of heavy HMIs, some adaptive techniques have been utilized by various groups. However, electrochemical detection has several advantages over other techniques such as ICPMS [2], AAS, colorimetry [3], chromatography [4], and spectroscopy for HMI detection, including sensitivity, selectivity, speed, cost-effectiveness, non-destructiveness, and versatility [5]. These advantages of electrochemical detection make it a promising technique for HMI detection, particularly for applications that require rapid, sensitive, and selective analysis [6–8].

In recent years, metal–organic frameworks (MOFs) have garnered significant interest as versatile materials in the field of sensor development [9,10]. MOFs are three-dimensional structures composed of metal nodes and organic linkers, resulting in exceptional porosity



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and tunability. MOFs are usually insulators due to their porous organic–metal structure, which hinders the formation of charge carriers due to pores which prevents the continuous pathways from transferring a charge. Insulating behavior leads to an adverse effect on sensing properties. To further enhance their sensing capabilities, researchers have explored modifications of MOFs with transition metals, such as chromium, iron, copper, etc., to tailor their properties and create a platform for efficient HMI detection [11,12]. Among these, lanthanum trimesic acid (La-TMA) MOFs have demonstrated remarkable potential in adsorption and separation applications due to their unique structural characteristics [13].

This study focuses on the electrochemical detection of Pb(II) ions using chromiummodified lanthanum trimesic acid (Cr@ La-TMA) MOF. The rationale behind this research lies in the enhanced adsorption capacity and electrochemical activity offered by the combination of Cr^{3+} with the La-TMA. The resulting modified La-TMA not only retains the inherent porosity of the parent MOF but also gains the ability to selectively capture Pb(II) ions through tailored binding sites. The interaction between Pb(II) ions and the modified MOF leads to changes in electrochemical behavior, enabling the quantification of Pb(II) ions in solution.

In this context, the developed sensor demonstrates an unprecedented limit of detection (LOD) of 1 nM for Pb(II), making it exceptionally suitable for detecting trace levels of this toxic metal ion in diverse samples. The remarkable sensitivity is complemented by excellent repeatability, ensuring consistent and reproducible results across multiple measurements. Moreover, the sensor's linear response over a wide concentration range further underscores its utility for both qualitative and quantitative analysis of Pb(II). The proposed electrochemical sensor holds promise for applications in environmental monitoring, industrial quality control, and public health protection by providing a reliable and efficient tool for the rapid assessment of Pb(II) contamination levels in diverse samples.

2. Experimental

2.1. Chemicals and Reagents

Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) and chromium nitrate hexahydrate (Cr(NO₃)₃·6H₂O) were purchased from Sigma Aldrich, Darmstadt, Germany. Trimesic acid (C₆H₃-1,3,5-(COOH)₃) and N,N-dimethylformamide (HCON(CH₃)₂) were purchased from Alfa Aesar, Waltham, Massachusetts, US. Deionized water (DI) was utilized as a solvent. Buffer solutions were prepared using sodium dihydro phosphate (NaH₂PO₄), potassium ferricyanide (K₃[Fe(CN)₆]), sodium acetate (CH₃-COO-Na), acetic acid (CH₃COOH), and sodium phosphate dibasic (Na₂HPO₄). All heavy metal ion solutions (Hg²⁺, Cd²⁺, Pb²⁺, Cu²⁺, Zn²⁺, Fe²⁺, etc.) were prepared by dissolving heavy metal chloride salts in DI water.

2.2. Synthesis of La-TMA and Cr@La-TMA

La(NO₃)₃·6H₂O (1.91 g, 0.5 mM), C₆H₃1,3,5-(COOH)₃ (0.53 g, 0.25 mmol), DMF (40 mL), and DI (40 mL) were sealed in an autoclave. A pure, colorless precipitate of La-TMA was created after 24 h of heating at 115 °C, and it was subsequently cleaned three times with DI and ethanol using a vacuum filter. Further, La-TMA was modified by chromium. Cr(NO₃)₃·6H₂O was taken in a one-fourth gram proportion of La-TMA. The mixtures were added in a 20 mL volume of DMF and annealed at 60 °C for 5 h. The dark green precipitate was further cleaned and dried overnight.

2.3. Characterization Techniques

To perform X-ray diffraction (XRD) measurements, a Bruker (D8-Advance), Karlsruhe, Germany, was used at 40.0 mA and 40.0 kV with a monochromatic CuK radiation source ($\lambda = 1.54$). Using a non-contact mode and a scan area of 3 μ m \times 3 μ m, the AFM (Park XE-7, Suwon, Republic of Korea) atomic force microscopic pictures were taken. Utilizing Bruker's Alpha model in the ECO-ATR mode, Fourier-transform infrared (FT-IR) measurements

were taken. A CHI electrochemical workstation (CHI-660C, Austin, TX, USA) was used to perform electrochemical characterizations.

3. Results and Discussion

3.1. Structural, Spectroscopic and Morphological Characterization

X-ray Diffraction Pattern and Fourier-Transform Infrared Spectroscopy

The XRD patterns for Pristine La-TMA and Cr@La-TMA composites are shown in Figure 1a. The XRD pattern for La-TMA matches completely with the preceding literature [14]. After the incorporation of Cr into Pristine La-TMA, additional peaks were observed with several deformations of La-TMA phases. Intensive peaks were observed at 2θ angles (21.64° , 28.63° , 37.71° , and 64.13°) confirming the existence of Cr in La-TMA [15]. The blue shifting of the 2θ angle (9.84°) after Cr modifications suggested crystal size decrement. Figure 1b shows the FTIR spectra of La-TMA and Cr@La-TMA. The appearance of a wide band at 3500 cm^{-1} to 4000 cm^{-1} suggests the presence of O-H functional groups in both materials. Similarly, common bands for both materials were observed at 1370 cm^{-1} and 1650 cm^{-1} attributed to C-H stretching and C=O bending vibrations, respectively. The band observed for La-TMA at 2800 cm^{-1} was attributed to C-H bending vibrations. Non-appearance of this band for Cr@TMA confirmed the role of the C-H functional group in Cr modifications. Furthermore, the band observed for Cr@TMA at 700 cm^{-1} was attributed to the Cr-O bond, which suggested a strong interaction between O and Cr.



Figure 1. (a) XRD patterns of La-TMA and Cr@La-TMA, (b) FTIR spectra of La-TMA and Cr@La-TMA.

3.2. Electrochemical Characterizations Cyclic Voltammetry

The CV curves depicted in Figure 2 provide critical insights into the electrochemical behavior of three distinct entities: the Glassy Carbon Electrode (GCE), La-TMA, and Cr@La-TMA. In the CV curve corresponding to the GCE, a baseline response was observed, characteristic of the bare electrode's electrochemical activity. The CV curve associated with the La-TMA showcases the introduction of redox peaks. These peaks indicated a reversible electrochemical process, suggesting the presence of redox-active species within the La-TMA structure. The appearance of these peaks could be attributed to specific coordination sites on La-TMA's surface, enabling electron transfer processes during the voltametric scan. The most intriguing observation, however, arises from the CV curve of the Cr@La-TMA MOF. The presence of well-defined and intensified redox peaks in the CV curve of Cr@La-TMA is indicative of its enhanced electrochemical activity. This could be instrumental in its role as an electrochemical sensor, as the modified La-TMA's increased reactivity may contribute to improved selectivity and sensitivity toward the target analyte, Pb(II) [16].



Figure 2. Cyclic voltammograms of Bare GCE, La-TMA, and Cr@La-TMA.

3.3. Electrochemical Sensing Response

3.3.1. Selectivity Measurements

The glassy carbon electrode (GCE) was pre-treated via polishing with 0.3 and 0.05-micron alumina slurry, sonicated in deionized water and ethanol for 2 min, and then dried at room temperature. Later, 10 μ L of each material (i.e., La-TMA, Cr@LA-TMA) was drop cast over GCE and utilized for electrochemical sensing. For the selectivity measurement, we have added a 5 nM concentration of each heavy metal ion (Cd(II), Hg(II), Cu(II), Cr(II), Fe(II) and Pb(II)) into the acetate buffer electrolyte. We have set potential window, keeping in mind that the redox potentials of all aforementioned heavy metal ions lie in the wide potential window, i.e., -1 V to 1 V. The DPV response analysis of La-TMA- and Cr@La-TMA-modified electrodes (Figure 3) provided evidence of the selective behavior of the Cr@La-TMA-modified electrode towards Pb(II) ions. The absence of a notable response for other HMIs further underscored the potential of the Cr@La-TMA-modified electrode as a selective electrochemical sensor for Pb(II) detection.



Figure 3. Differential pulse response of La-TMA and Cr@La-TMA for 5 nM concentration of Pb(II),Cd(II), Hg(II), Cu(II), Cr(II), and Fe(II).

3.3.2. Differential Pulse Voltametric Response of Cr@La-TMA for Pb(II)

The DPV response obtained from Cr@La-TMA for different concentrations of Pb(II) ions is shown in Figure 4a. The plot showcased the electrochemical response of Cr@La-TMA when exposed to varying concentrations of Pb(II) ions, spanning from 1 nM to 10 nM. The DPV response curve exhibited a distinct and proportional increase in peak current as the Pb(II) concentration increased.



Figure 4. (a) Differential pulse voltammogram of Cr@La-TMA for detection of Pb(II) concentrations ranging from 1 nM to 10 nM and (b) linear calibration plot for DPV responses of Cr@La-TMA, I = 0.013 mA + 0.073 mA/nM, $R^2 = 0.90$.

Notably, the LOD achieved of 1 nM underscored the sensor's remarkable capability to reliably detect low concentrations of Pb(II). Figure 4b represents a linear calibration plot, which showcases a good linear response ($R^2 = 0.90$) with a sensitivity of 0.073 mA/nM.

4. Conclusions

In this study, Cr@La-TMA demonstrated exceptional promise in electrochemical sensing. While La-TMA exhibited a limited response, Cr@La-TMA showed selective and sensitive detection of Pb(II) ions, evidenced by distinct redox peaks. This heightened response extended from 1 nM to 10 nM Pb(II) concentrations, with an impressive LOD of 1 nM. The electrode's capacity to discriminate Pb(II) from interfering ions (Cd(II), Hg(II), Cu(II), Cr(II), and Fe(II)) enhances its practical applicability. These findings position Cr@La-TMA as a valuable tool for trace Pb(II) detection, holding great potential for environmental and health-monitoring endeavors.

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