

Chromium Modified Lanthanum Based MOF: Novel Electrochemical Sensing Platform for Pb(II) Ions[†]

Shubham S. Patil ¹, Vijaykiran N. Narwade ¹, Tibor Hianik ² and Mahendra D. Shirsat ^{1,2,*}

¹ RUSA Center for Advanced Sensor Technology, Department of Physics, Dr Babasaheb Ambedkar Marathwada University, Aurangabad (MS) - 431 004, India shubhampatil10297@gmail.com (S.S.P.); vkiran-physics@gmail.com (V.N.N.); mdshirsat.phy@bamu.ac.in (M.D.S.)

² Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, 842 48 Bratislava, Slovak Republic; tibor.hianik@fmph.uniba.sk (T.H.)

* Correspondence: mdshirsat.phy@bamu.ac.in; Tel.: +91 9422291987

† Presented at the 2nd E-Conference on Chemical Sensors and Analytical Chemistry (CSAC2023), 16-30 September 2023; Available online: <https://CSAC2023.sciforum.net/>.

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 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- Environment 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

Citation: Patil, S.S.; Narwade, V.N.; Hianik, T.; Shirsat, M.D. Chromium Modified Lanthanum Based MOF: Novel Electrochemical Sensing Platform for Pb(II) Ions. *2023*, *4*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor(s):

Received: date

Accepted: date

Published: date

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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 were 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-effective, non-destructiveness and versatility [5]. These advantages of electrochemical detection make it a promising technique for HMIs 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 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 to transfer 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) MOF has 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 chromium-modified 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 Cr³⁺ 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 the 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 1nM 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), 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 by, 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 hours 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 one-fourth gram proportion of La-TMA. mixtures were added in 20 ml volume of DMF and annealed at 60°C for 5 hr. 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 (λ= 1.54). Using a non-contact mode and a scan area of 3 μm × 3 μm, the AFM (Park XE-7, Suwon, South 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. CHI-electrochemical workstation (CHI-660C, Austin,US) was used to perform electrochemical characterizations.

3. Results and Discussion

3.1. Structural, Spectroscopic and Morphological Characterization

3.1.1. X-ray Diffraction Pattern and Fourier Transform Infrared Spectroscopy

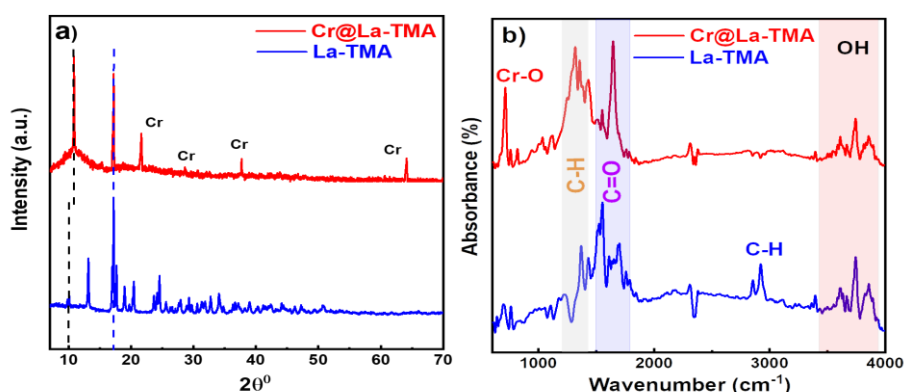


Figure 1. a) XRD patterns of La-TMA and Cr@La-TMA, b) FTIR spectra of La-TMA and Cr@La-TMA.

The XRD patterns for Pristine La-TMA and Cr@La-TMA composites are shown in Fig. 1. a). 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]. Blue shifting of 2θ angle (9.84°) after Cr modifications, suggested crystal size decrement. Fig. 1. b) 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} attributed to the Cr-O bond which suggested a strong interaction between O and Cr.

3.2. Electrochemical Characterizations

3.2.1. Cyclic Voltammetry

The CV curves depicted in Fig. 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 voltammetric scan. The most intriguing observations, 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].

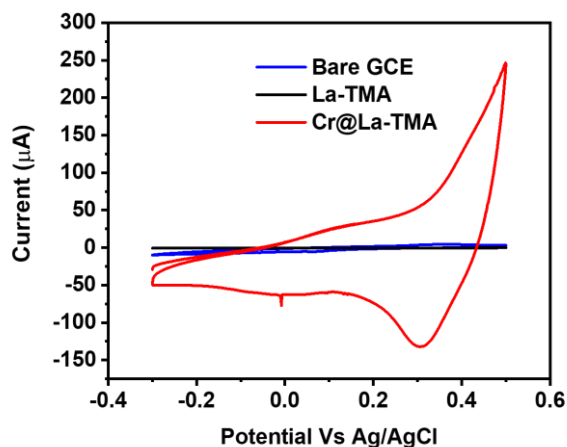


Figure 2. Cyclic Voltammograms of Bare GCE, La-TMA, and Cr@La-TMA.

3.3. Electrochemical Sensing Response

3.3.1. Selectivity Measurements

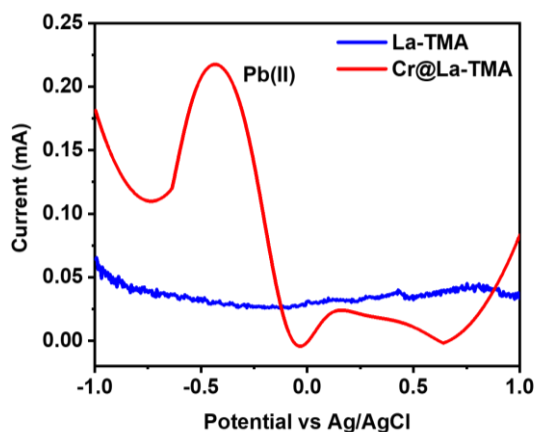


Figure 3. Differential pulse response of La-TMA and Cr@La-TMA for 5nM concentration of Pb(II), Cd(II), Hg(II), Cu(II), Cr(II), and Fe(II).

The glassy carbon electrode (GCE) was pre-treated by polishing it with 0.3 and 0.05-micron alumina slurry and sonicated in deionized water and ethanol for 2 min. and 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 5 nM concentration of each heavy metal ions (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 redox potentials of all aforementioned heavy metal ions lies in the wide potential window, i.e, -1v to 1 V. The DPV response analysis of La-TMA and Cr@La-TMA modified electrodes (Fig. 3) provided evidence of the selective electrochemical response 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.

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

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

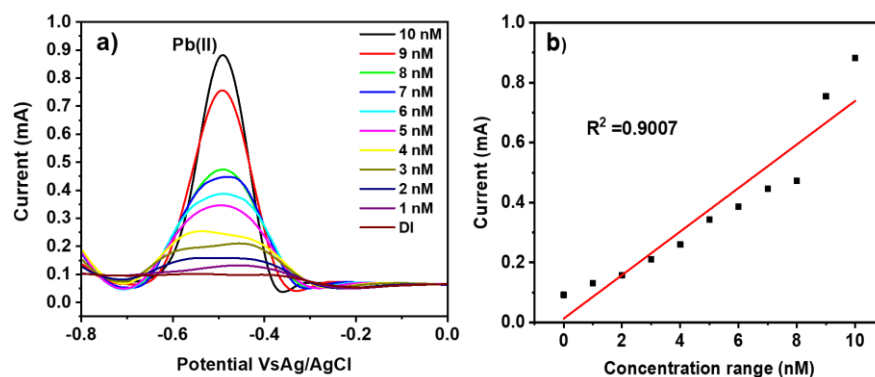


Figure 4. a) Differential pulse voltammogram of Cr@La-TMA for detection of Pb(II) concentrations ranging from 1 nM to 10 nM and b) linear calibration plot for DPV responses of Cr@La-TMA, $I = 0.013 \text{ mA} + 0.073 \text{ mA/nM}$, $R^2 = 0.90$.

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

5. Conclusions

In this study, Cr@La-TMA demonstrated exceptional promise in electrochemical sensing. While La-TMA exhibited 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), 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.

Author Contributions: Conceptualization, S.S.P. and M.D.S.; formal analysis, S.S.P., V.V.N, T.H. and M.D.S; investigation, S.S.P.; writing—original draft preparation, S.S.P. and M.D.S.; writing—review and editing, S.S.P., V.V.N, T.H and M.D.S.; supervision, M.D.S.; project administration, M.D.S.; funding acquisition, M.D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Inter-University Accelerator Center (IUAC), New Delhi, India (UFR no. 69330), University Grants Commission – Department of Atomic Energy (UGC–DAE) CSR, Indore (Project No. CRS/2021-22/ 01/456 dated March 30, 2022), Department of Science and Technology, Govt of India (DST–SERB), New Delhi (Project No. EEQ/2017/000645), University Grants Commission (UGC-SAP Programme) (F.530/16/DRS-I/2016 (SAP-II) Dt.16-04-2016), Department of Science and Technology, Govt of India (DST-FIST) (Project No. SR/FST/PSI-210/2016(c) dtd. 16/12/2016), and Rashtriya Uchchatar Shiksha Abhiyan (RUSA), Government of Maharashtra

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable

Acknowledgments: Mahendra D, Shirsat gratefully acknowledges the Slovak Academic Information Agency (SAIA) and Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovak Republic, for the sanction of scholarship under the framework of National Scholarship Program (NSP) of Slovak Republic

Conflicts of Interest: The authors declare no conflicts of interests.

References

1. Bodkhe, G.A.; Hedau, B.S.; Deshmukh, M.A.; Patil, H.K.; Shirsat, S.M.; Phase, D.M.; Pandey, K.K.; Shirsat, M.D. Detection of Pb (II): Au Nanoparticle Incorporated CuBTC MOFs. *Front. Chem.* **2020**, *8*, 803. <https://doi.org/10.3389/fchem.2020.00803>

2. Gao, Y.; Xu, M.; Sturgeon, R.E.; Mester, Z.; Shi, Z.; Galea, R.; Saull, P.; Yang, L. Metal ion-assisted photochemical vapor generation for the determination of lead in environmental samples by multicollector-ICPMS. *Anal. Chem.* **2015**, *87*, 4495-4502. <https://doi.org/10.3390/sym15030752>
3. Matica, O.-T.; Musina, C.; Brotea, A.G.; Ungureanu, E.-M.; Cristea, M.; Isopescu, R.; Buica, G.-O.; Razus, A.C. Electrochemistry of Rhodanine Derivatives as Model for New Colorimetric and Electrochemical Azulene Sensors for the Detection of Heavy Metal Ions. *Symmetry* **2023**, *15*, 752. <https://doi.org/10.3390/sym15030752>
4. Rahmalan, A.; Abdullah, M.Z.; Sanagi, M.M.; Rashid, M. Determination of heavy metals in air particulate matter by ion chromatography. *J. Chromatogr. A* **1996**, *739*, 233-239. [https://doi.org/10.1016/0021-9673\(96\)00025-8](https://doi.org/10.1016/0021-9673(96)00025-8)
5. Falina, S.; Syamsul, M.; Rhaffor, N.A.; Sal Hamid, S.; Mohamed Zain, K.A.; Abd Manaf, A.; Kawarada, H. Ten years progress of electrical detection of heavy metal ions (hmis) using various field-effect transistor (fet) nanosensors: A review. *Biosensors* **2021**, *11*, 478. <https://doi.org/10.3390/bios11120478>
6. Bodkhe, G.A.; Hedau, B.S.; Deshmukh, M.A.; Patil, H.K.; Shirsat, S.M.; Phase, D.M.; Pandey, K.K.; Shirsat, M.D. Selective and sensitive detection of lead Pb (II) ions: Au/SWNT nanocomposite-embedded MOF-199. *J. Mater. Sci.* **2021**, *56*, 474-487. <https://doi.org/10.1007/s10853-020-05285-z>
7. Guo, J.; Xue, X.; Yu, H.; Duan, Y.; Li, F.; Lian, Y.; Liu, Y.; Zhao, M. Metal-organic frameworks based on infinite secondary building units: recent progress and future outlooks. *J. Mater. Chem. A* **2022**, *10*, 19320-19347. DOI <https://doi.org/10.1039/D2TA03159K>
8. Guo, J.; Wan, Y.; Zhu, Y.; Zhao, M.; Tang, Z. Advanced photocatalysts based on metal nanoparticle/metal-organic framework composites. *Nano Res.* **2021**, *14*, 2037-2052. <https://doi.org/10.1007/s12274-020-3182-1>
9. Patil, S.S.; Deore, K.B.; Narwade, V.N.; Peng, W.P.; Hianik, T.; Shirsat, M.D. Ultrasensitive and Selective Electrochemical Sensor Based on Yttrium Benzenetricarboxylate Porous Coordination Polymer (Y-BTC) for Detection of Pb²⁺ from Bio-Analytes. *ECS J. Solid State Sci. Technol.* **2023**, *12*, 057002. DOI: 10.1149/2162-8777/acd1af
10. Deore, K.B.; Narwade, V.N.; Patil, S.S.; Rondiya, S.R.; Bogle, K.A.; Tsai, M.-L.; Hianik, T.; Shirsat, M.D. Fabrication of 3D bi-functional binder-free electrode by hydrothermal growth of MIL-101 (Fe) framework on nickel foam: A supersensitive electrochemical sensor and highly stable supercapacitor. *J. Alloys Compd.* **2023**, *958*, 170412. <https://doi.org/10.1016/j.jallcom.2023.170412>
11. Karimi, S.; Gholinejad, M.; Khezri, R.; Sansano, J.M.; Nájera, C.; Yus, M. Gold and palladium supported on an ionic liquid modified Fe-based metal-organic framework (MOF) as highly efficient catalysts for the reduction of nitrophenols, dyes and Sonogashira-Hagihara reactions. *RSC Adv.* **2023**, *13*, 8101-8113. <https://doi.org/10.1039/D3RA00283G>
12. Wang, Y.; Wang, L.; Huang, W.; Zhang, T.; Hu, X.; Perman, J.A.; Ma, S. A metal-organic framework and conducting polymer based electrochemical sensor for high performance cadmium ion detection. *J. Mater. Chem. A* **2017**, *5*, 8385-8393. <https://doi.org/10.1007/s12274-020-3182-1>
13. Prabhu, S.M.; Imamura, S.; Sasaki, K. Mono-, di-, and tricarboxylic acid facilitated lanthanum-based organic frameworks: insights into the structural stability and mechanistic approach for superior adsorption of arsenate from water. *ACS Sustain. Chem. Eng.* **2019**, *7*, 6917-6928. <https://doi.org/10.1021/acssuschemeng.8b06489>
14. Yang, W.; Feng, J.; Zhang, H. Facile and rapid fabrication of nanostructured lanthanide coordination polymers as selective luminescent probes in aqueous solution. *J. Mater. Chem.* **2012**, *22*, 6819-6823. <https://doi.org/10.1039/C2JM16344F>
15. Quan, C.; He, Y. Properties of nanocrystalline Cr coatings prepared by cathode plasma electrolytic deposition from trivalent chromium electrolyte. *Surf. Coat. Technol.* **2015**, *269*, 319-323. <https://doi.org/10.1016/j.surfcoat.2015.02.001>
16. Tran, L.T.; Dang, H.T.; Tran, H.V.; Hoang, G.T.; Huynh, C.D. MIL-88B (Fe)-NH₂: an amine-functionalized metal-organic framework for application in a sensitive electrochemical sensor for Cd²⁺, Pb²⁺, and Cu²⁺ ion detection. *RSC Adv.* **2023**, *13*, 21861-21872. <https://doi.org/10.1039/D3RA02828C>