A highly sensitive electrochemical sensor for the detection of lead(II) ions utilizing rice-shaped bimetallic MOFs incorporated reduced graphene oxide

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+Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

Supporting Information

S1. Experimental

Optimization of electrode preparation condition

The fabrication conditions of rGO/FeMg-BDC electrodes were carefully optimized. The Fe/Mg ratio was varied in three different ratios: 1/1, 1/2, and 1/4. The concentration of bimetallic MOF was tested at four different levels: 0.25, 0.5, 0.75, and 1.00 mg/mL. The GO concentration was also adjusted, with four different values: 0.01%, 0.02%, 0.03%, and 0.04%. The optimal conditions were determined based on the peak current obtained from square wave anodic stripping voltammetry (SWASV) measurements in a 0.1 M KCl-HCl solution (pH = 3) containing 1 μ g/L Pb²⁺, with an accumulation potential of -0.8 V for 120 seconds.

Optimization of analysis conditions

The analytical conditions were optimized by investigating several factors. The electrolyte solution was varied among NaNO₃–HNO₃, KCl-HCl, PBS, and ABS. The pH of the electrolyte solution was tested at four different levels: 2.5, 3.0, 3.5, and 4.0. The enrichment electrolysis potential was also adjusted, with values of 0.7 V, 0.8 V, 0.9 V, and 1.0 V. SWASV measurements were performed in the electrolyte solution containing 1 μ g/L Pb²⁺, with an accumulation time of 120 seconds. The optimal conditions were then determined based on the peak current of the electrochemical signal.

Pb²⁺ adsorption experiment

A series of beakers containing 20 mL of KCI-HCI solution (pH = 3) with 5 ppm Pb²⁺ were each mixed with a certain amount of MOF at a concentration of 1 mg/mL and stirred at 300 rpm. After specific adsorption times ranging from 5 to 60 minutes, 2 mL of the solution was collected by centrifugation at 4000 rpm. The concentrations of Pb(II) in the filtrates (C_{filtrate}) were then determined by ICP-MS to assess the adsorption efficiency of the MOF materials.

Adsorption efficiency was calculated using the following formula:

$$\frac{C_{ads}}{C_0}(\%) = \frac{(C_0 - C_{filtrate}) * 100}{C_0}$$

S2. Result and discussion



Fig. S1 (a) EDS spectrum of (a) FeMg-BDC (1/2), (b) EDX mapping analysis of FeMg-BDC (1/2), (c) Zeta potential distribution of the FeMg-BDC (1/2), (d) FT-IR spectra of various samples

The FTIR spectra of the bimetallic and monometallic MOF were shown in Figure S1d. The two characteristic bands around 1580 and 1387 cm⁻¹ are assigned to the symmetric and asymmetric stretching vibrations O-C=O of the organic ligands¹. In addition, the small band around 1504 cm⁻¹ was assigned to the C=C vibrational mode of the benzene ring; while the bands at 745, 820, and 878 cm⁻¹ corresponded to the C-H vibrational modes of the benzene ring². Meanwhile, the band at around 555 cm⁻¹ could be attributed to the Fe-O and Mg-O bending vibrations in the bimetallic and monometallic MOFs¹. The above-mentioned functional groups indicated the successful coordination of the carboxylate groups of the BDC bond with the metal ions.



Fig. S2 (a) TEM image of GO dispersed in water, (b) FTIR spectra, (c) XRD patterns, (d) zeta potential distribution of the GO.

The transmission electron microscopy (TEM) image of the graphene sample, dispersed in water, is presented in Fig. S2a. Notably, the graphene oxide (GO) is observed to exist as delicate, well-dispersed thin films in the aqueous medium, avoiding agglomeration into clusters. The specific properties of synthesized graphene oxide were systematically investigated, and the results are presented in Fig. S2b, c, d. The FT-IR spectrum of graphene oxide (Fig S2b) reveals the presence of oxygen-containing functional groups on the graphene surface. The broad peak at 3420 cm⁻¹ corresponds to the –OH group, while the absorption peak at 1720 cm⁻¹ arises from the stretching vibration of the C=O group. Additionally, the peak at 1180 cm⁻¹ corresponds to the stretching vibration of the epoxy C-O group. Furthermore, the X-ray diffraction (XRD) pattern (Fig S2c) exhibits a shift in the (001) peak position from $2\theta = 26.3^{\circ}$ (graphite) to $2\theta = 11^{\circ}$ (graphene oxide, reaffirming the successful synthesis of graphene oxide. Moreover, the zeta potential analysis (Fig S2d) reveals a sharp peak, with an average potential of approximately -38 mV for graphene oxide. This data underscores the remarkable stability of graphene oxide in aqueous environments, attributed to the abundant negative charges of COO⁻ groups formed to the oxidized graphene film, which effectively repel adjacent graphene oxide layers.



Fig. S3 a) CVs of Fe-BDC, FeMg-BDC, GO/FeMg-BDC and rGO/FeMg-BDC in KCI-HCI 0.1M, (b) CVs of rGO/FeMg-BDC electrode at different scan rates, and (c) the linear plot for the redox current response versus the square root of the scan rates.



Fig. S4 a) CV current curves for rGO/FeMg-BDC electrodes, b) FT-IR spectra of GO and rGO.

The electrochemical reduction curve of the GO/FeMg-BDC electrode was recorded (Fig. S4a). Notably, at the first scan, three reduction peaks at -0.5, -0.8, and -1 V were observed on the voltammogram of the electrode. The presence of reduction peaks at -0.8 and -1 V can be ascribed to the electrochemical reduction of epoxy and carbonyl groups present in the GO. These results corresponded to the reduction of the D/G ratio in the Raman spectrum of GO.

In addition, the results of the functional group survey on the surface of GO before and after electrochemical reduction are presented in Fig S4b. It is readily observable that the intensity and number of absorption peaks of rGO have significantly decreased compared to GO. Specifically, the strong absorption band in the region of 2800-3600 cm⁻¹ due to the stretching vibrations of O-H groups on GO has disappeared, replaced by a much weaker absorption band in the region of 3000-3300 cm⁻¹. The absorption peak intensity at 1740 cm⁻¹, characteristic of the stretching vibrations of C=O groups, also considerably diminished after reduction. This result also indicates that electrochemical reduction removes a large amount of oxygen-containing functional groups on GO during the reduction process.



Fig. S5. A proposed mechanism for the adsorption of Pb²⁺ onto the FeMg-BDC surface.



Fig. S6. A proposed mechanism for the electrochemical detection of Pb²⁺



Fig. S7. Adsorption efficiency of Fe-Mg-BDC (1/1), Fe-Mg-BDC (1/2), Fe-Mg-BDC (1/4), and other two monometallic MOFs for Pb^{2+}



Fig. S8 (a, b) Reproducibility and (c, d) durability over time of the rGO/FeMg-BDC electrode. All of these experiments were performed in 0.1 M of KCl - HCl solution pH = 3 containing 1 μ g/L Pb²⁺ with accumulation potential at -0.8V during 120 s.



Fig. S9 (a, b) Durability over time of the rGO/FeMg-BDC electrode. All of these experiments were performed in 0.1 M of KCl - HCl solution pH = 3 containing $1 \mu g/L Pb^{2+}$ with accumulation potential at -0.8V during 120 s



Fig. S10 Influence of (a) inorganic and (b) organic interfering substances



Fig. S11 (a, c, e) SWASV voltammograms of rGO/FeMg-BDC electrode at various concentrations of Pb^{2+} in Ha Long seawater, Red River water, West Lake water sample, and (b, d, f) the corresponding linear plot for the oxidation peak currents versus different concentrations of Pb^{2+} in the real samples, respectively

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