Research Article

Metal-Organic Framework MIL-53(Fe): Synthesis, Electrochemical Characterization, and Application in Development of a Novel and Sensitive Electrochemical Sensor for Detection of Cadmium Ions in Aqueous Solutions

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A metal-organic framework MIL-53(Fe) was successfully synthesized by a simple hydrothermal method. A synthesized MIL-53(Fe) sample was characterized, and results indicated that the formed MIL-53(Fe) was a single phase with small particle size of 0.8 μm and homogeneous particle size distribution was obtained. The synthesized MIL-53(Fe) has been used to modify a glassy carbon electrode (GCE) by a drop-casting technique. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements of the MIL-53(Fe)-modified GCE showed that the MIL-53(Fe) was successfully immobilized onto the GCE electrode surface and the electrochemical behavior of the GCE/MIL-53(Fe) electrode was stable. In addition, several electrochemical parameters of MIL-53(Fe)-modified GCE (GCE/MIL-53(Fe)) including the heterogeneous standard rate constant (k^0) and the electrochemically effective surface area (A) were calculated. Obtained results demonstrated that the synthesized MIL-53(Fe) with the small particle size, highly homogeneous particle size, and high electrochemically effective surface area was able to significantly enhance the electrochemical response signal of the working electrode. Therefore, the GCE/MIL-53(Fe) electrode has been used as a highly sensitive electrochemical sensor for cadmium ion (Cd(II)) monitoring in aqueous solution using differential pulse voltammetry (DPV) technique. The response signal of the electrochemical sensor increased linearly in the Cd(II) ion concentration range from 150 nM to 450 nM with the limit of detection (LOD) of 16 nM.

1. Introduction

The pollution of water sources caused by heavy metal ions, inorganic substances, organic matters, and bacteria from different agricultural, industrial, and medical waste sources has seriously affected people's lives and the ecosystems and organisms in the aquatic environment [1–3]. Determining the concentration of pollutants is an important step in environmental monitoring and supervision and is a basis for offering solutions to protect the environment. Chromatography and its associated techniques such as atomic emission spectroscopy (AES), atomic fluorescence spectroscopy

(AFS), atomic absorption spectroscopy, and inductively coupled plasma mass spectrometry are common and effective methods for identifying environmental contaminants [3, 4]. However, the above techniques showed many disadvantages such as long testing times, expensive equipment, and complex measurement processes [3, 5]. Therefore, development of new techniques, which possess the advantages of high sensitivity, quick detection, and ease of use, is needed for the on-site, real-time, and continuous monitoring of environmental pollutants [6–11].

In which, electrochemical sensors can offer advantages of low detection limits, wide linear response ranges, and good

stability and reproducibility. Moreover, electrochemical sensors can be easily prepared from many advanced materials to improve sensitivity and selectivity. In general, an electrochemical sensor is configured from two main parts, which are named a sensing element and a transducer. When the sensing element interacts with an analyte, the transducer can convert the sensed information into an electrical signal [10, 12–14]. The important characteristics of the sensor include sensitivity, stability, selectivity, response time, cost, and reusability [9]. To improve the sensitivity of electrochemical sensors, advanced materials have been applied to modified electrodes, including nanostructured conducting polymers [12, 15], metal and metal oxide nanoparticles [16–18], nanostructured carbon materials (such as porous carbon, carbon nanotube, and graphene/graphene oxide) [17–19], and metal-organic frameworks (MOFs) [6, 9, 20–24]. Among them, MOF materials which are constructed by metal ions or clusters and organic ligands via coordination bonds have unique properties including their structural diversity, flexible framework functionality, large metal cluster density, high stability, abundant adsorption sites, and a large surface area exceeding that of activated carbons and zeolites which are traditional porous materials [9, 21, 23–26]. Moreover, the physical and chemical characteristics of MOFs can be customized and precisely designed, depending on how they are synthesized [27]. The development of MOF material-based electrochemical sensors for determining pollutants in water has practical significance and high potential in the field of the environment [9, 28]. Therefore, a number of MOFs have been used in electrochemical sensors to detect organic substances, inorganic ions, antibiotics, and heavy metals in aqueous solutions [9, 20–24, 26, 29, 30].

MIL-53(Fe) (MIL: Materials of Institute Lavoisier), a class of MOFs generated by a combination between iron(III) cations and 1,4-dicarboxylic acid, consists of three-dimensional networks or secondary building units which contain FeO_6 hexagonal chains and dicarboxylate anions [31]. The emergent features of MIL-53(Fe) compared with other MOFs are chemically stable and have lower toxic metal centers and green, sustainable pathways for fabrication [31]. However, only few works have been dedicated to the development of an electrochemical sensor based on MIL-53 for detection of heavy metal ions in aqueous solutions (MIL-53(Al) [10]). Therefore, in this work, an effective hydrothermal method was carried out to synthesize a metal-organic framework MIL-53(Fe), which was then used to modify the glassy carbon electrode (GCE) for sensitive electrochemical determination of Cd(II) ion concentration in aqueous solutions. In addition, the specific characteristics of the synthesized MIL-53(Fe) were also carefully analyzed by various chemical-physical techniques.

2. Experimental

2.1. Chemicals and Instrumentations

2.1.1. Chemicals. Iron(III) chloride hexahydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%wt.), terephthalic acid $\text{C}_6\text{H}_4\text{-1,4-(COOH)}_2$ (TPA) (98%wt.), methanol CH_3OH (MeOH) (anhydrous, 99.8% v/v),

sodium acetate CH_3COONa (99%wt.), and cadmium nitrate tetrahydrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%wt.) were purchased from Sigma-Aldrich. Dimethylformamide $\text{C}_3\text{H}_7\text{NO}$ (DMF) (99.94%) was purchased from Fisher Chemical. Polyethylene glycol 2000 ($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, PEG 2000) was purchased from Alfa Aesar. Chitosan (CS, MW = 400,000 g mol^{-1} , degree of acetylation (DA) = 70%) was prepared by deacetylation of chitin in our laboratory [32, 33]. Acetate buffer solution 0.1 M (ABS) with pH 5.0 was prepared by using the appropriate amounts of sodium acetate and acetic acid.

2.1.2. Instrumentations. A PGSTAT302N AutoLab electrochemical workstation (Netherlands) was used to perform electrochemical measurements. X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advance diffractometer equipped with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electron microscope (SEM) images of MIL-53(Fe) were investigated using a Hitachi S4800 scanning electron microscope. The structure of MIL-53(Fe) was examined using Fourier transform infrared spectroscopy (FT-IR) spectra measured with a Nicolet 6700 FT-IR spectrometer. Transmission electron microscope (TEM) images were taken using a TECNAI F20-G2 high-resolution transmission electron microscope.

2.2. Synthesis of MIL-53(Fe). 0.623 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.383 g of TPA were mixed in 50 mL of DMF solvent using an IKA magnetic stirrer with a stirring rate of 200 rpm for 10 minutes to get a solution. Then, the solution was added in an autoclave, and the hydrothermal synthesis was performed at 150°C for 12 hours. The product obtained after the hydrothermal process was filtrated, washed with 150 mL of MeOH and distilled water, and then dispersed in distilled water and stirred on the IKA magnetic stirrer with a stirring rate of 200 rpm for 15 hours. After that, the product was vacuum-dried at 170°C for 12 hours. Finally, the synthesized product was finely ground and stored in a desiccator.

2.3. Electrochemical Characterizations of MIL-53(Fe) and Detection of Cd(II) Ions Using MOF-Based Electrochemical Sensors

2.3.1. Fabrication of MIL-53(Fe)-Modified Electrodes. GCE was polished using 0.3 and 0.05 μm alumina slurries on a polishing cloth; then, it was cleaned carefully by deionized water and dried under an infrared lamp. A slurry of MIL-53(Fe) was prepared by dispersing 6.0 mg of MIL-53(Fe) into a 2 mL mixture of CS solution (10 mg mL^{-1} in acetic acid 3% v/v) and 1.0 mg of PEG-2000 using ultrasonic processing for 5 minutes. Finally, 6 μL of the MOFs/CS/PEG mixture was drop-casted onto the surface of GCE, and it was dried in the air under an infrared lamp. The MIL-53(Fe)-modified GCE (GCE/MIL-53(Fe)) was obtained.

2.3.2. Electrochemical Measurements. A three-electrode configuration consisted of the GCE/MIL-53(Fe) as a working electrode (WE), a Pt electrode as a counter electrode (CE), and a Ag/AgCl electrode as a reference electrode (RE). CV and EIS measurements of the GCE/bare and GCE/MIL-

FIGURE 1: (a) XRD patterns of the fabricated MIL-53(Fe) samples when the hydrothermal time was (A) 8 h, (B) 12 h, (C) 15 h, and (D) 24 hours; (b) FT-IR spectrum of the fabricated MIL-53(Fe).

53(Fe) electrodes were performed in $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (0.005 M) and 0.1 M KCl solution. CVs were recorded at different scan rates of 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, and 75 mV s^{-1} . EIS spectra were measured with frequency range: 100 kHz to 100 mHz, $E_{\text{AC}} = 5 \text{ mV}$, $E_{\text{DC}} = 180 \text{ mV}$. Cadmium ions in aqueous solutions were detected using the MOF-based electrochemical sensors with DPV measurements. The electrolyte solutions contained cadmium ions (in ABS) with the concentrations of 150, 200, 250, 300, 350, 400, and 450 nM. A deposition potential of -1.2 V was applied for 120 s under stirring. After preconcentration, DPV measurements were recorded from -1.1 to -0.3 V with a pulse amplitude of 50 mV and width of 50 ms. Before the next detection, the desorption process was performed under the potential of 0.4 V for 100 s to remove the residual metal ions.

3. Results and Discussion

3.1. Characterizations of MIL-53(Fe). The XRD patterns of as-prepared MIL-53(Fe) samples with various hydrothermal times including 8, 12, 15, and 24 hours are presented in Figure 1(a). It can be seen that the samples prepared with the hydrothermal time of 8 hours (Figure 1(a), curve A) and 24 hours (Figure 1(a), curve D) have specific peaks of the MIL-53(Fe); however, there are several peaks belonging to other crystals [31, 34]. Meanwhile, the XRD patterns of samples prepared with the hydrothermal time of 12 or 15 hours (Figure 1(a), curves B and C, respectively) show only characteristic peaks of MIL-53(Fe) at 9.5, 12.5, and 18.2 degrees of 2-theta [31, 34]. These peaks shift slightly compared to the previous reports due to the different reaction conditions [35, 36]. Comparing XRD patterns of sample B and sample C (samples were synthesized with the hydrothermal time of 12 and 15 hours, respectively), the hydrothermal time for the formation of MIL-53(Fe) was finally chosen to be 12 hours because of the sharper and higher characteristic peaks, which implied that the crystals were formed completely. The FT-IR spectrum of the MIL-53(Fe) (Figure 1(b)) exhibits the typical vibrational bands of the car-

boxylic acid function in the region of $1400\text{--}1700 \text{ cm}^{-1}$. The adsorption band of the carboxyl group of the ligand coordinated to the Fe(III) ion is visible at 1585 cm^{-1} . The peak at 749 cm^{-1} corresponds to the C-H bonding vibration of the benzene rings [37, 38]. Moreover, the presence of the Fe-O vibration at 545 cm^{-1} indicates the formation of a metal-oxo bond between the carboxylic group of terephthalic acid and the Fe(III) [39].

The surface morphology of the MIL-53(Fe) was investigated by using SEM that is shown in Figure 2(a), which can be observed that the MIL-53(Fe)'s particle size is quite small and homogeneous with the distribution of the particle size around $0.8 \mu\text{m}$ (Figure 2(b)). The TEM images (Figures 2(c) and 2(d)) indicate that there are small pseudospherical particles in the range of 5–8 nm which were attached to the surface of the MIL-53(Fe) crystals [26]. The small particle size and the homogeneous particle size distribution of the obtained MIL-53(Fe) have an important role in improving the repeatability and reproducibility of electrochemical sensors.

3.2. Electrochemical Characterizations of MIL-53(Fe). Figure 3 shows the CV (Figure 3(a)) and EIS spectra (Figure 3(b)) of the GCE/bare (curve A) and GCE/MIL-53(Fe) (curve B) electrodes performed in $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (0.005 M) and 0.1 M KCl solution. It can be seen that there are two peaks on the two CV curves corresponding to the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ and the reduction of $\text{Fe}(\text{CN})_6^{3-}$ (Figure 3(a)). In the case of the GCE/MIL-53(Fe) electrode (curve B), the peak current is higher than that of the bare GCE electrode (curve A). This result can be attributed to the increase in the electroactive area when the MIL-53(Fe) was loaded on the GCE, leading to the accumulation of the electroactive species on the electrode surface and the increase in the current density. The EIS spectra (Figure 3(b)) of the two different electrodes consist of two parts: a semicircle which characterizes the charge transfer process and a linear region which characterizes the diffusion process. These EIS spectra can be simulated by an equivalent circuit based on the Randles model (Figure 3(b), inset). This equivalent circuit

FIGURE 2: (a) SEM image; (b) particle diameter distribution; (c, d) TEM images of the synthesized MIL-53(Fe).

FIGURE 3: (a) Cyclic voltammograms of (A) GCE/bare and (B) GCE/MIL-53(Fe) electrodes; (b) EIS spectra (Nyquist plots) of (A) GCE/bare and (B) GCE/MIL-53(Fe) electrodes (inset: Randles equivalent circuit). Experimental conditions: $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (0.005 M) and 0.1 M KCl solution. CVs were recorded at a scan rate of 30 mV s^{-1} . EIS spectra were measured with frequency range 100 kHz to 100 mHz, $E_{AC} = 5 \text{ mV}$, $E_{DC} = 180 \text{ mV}$.

consists of a solution resistance (R_s), a charge transfer resistance (R_{ct}), a constant phase element (Q_{CPE}), and a Warburg diffusion coefficient (W). Fitted R_{ct} results of the GCE/MIL-53(Fe) and bare GCE were 425Ω and 828Ω , respectively, which implied that the MIL-53(Fe) layer-modified GCE with the small particle size, the homogeneous particle size distribution,

and the high electrochemically effective surface area was able to significantly enhance the electrochemical response of the working electrode. These EIS results are suitable for the CV results obtained in Figure 3(a).

CVs of the GCE/MIL-53(Fe) electrode in 0.1 M KCl solution containing $5 \text{ mM Fe}(\text{CN})_6^{3-/4-}$ at different scan rates

FIGURE 4: (a) Cyclic voltammograms of the GCE/MIL-53(Fe) electrode in 0.1 M KCl solution containing 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at different scan rates of 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, and 75 mV s^{-1} ; (b) the relationships between the currents of anodic and cathodic peaks and the square root of the scan rate ($v^{1/2}$) and their corresponding linear fit lines: I_{pa} , the red line with the triangle symbols, and I_{pc} , the blue line with the circle symbols; (c) the relationships between the potentials of anodic and cathodic peaks and $\ln v$ and their corresponding linear fit lines: E_{pa} , the green line with the square symbols, and E_{pc} , the orange line with the star symbols.

from 25 to 75 mV s^{-1} are shown in Figure 4(a). From these obtained data, the relationships between the currents of anodic and cathodic peaks and the square root of the potential scan rate are plotted in Figure 4(b), i.e., with the relationship between I_{pa} vs. $v^{1/2}$ (marked by the red line with the triangle symbols)

$$y = 0.0014 \times v^{1/2} - 1.2563 \times 10^{-4} \quad (R^2 = 0.9857) \quad (1)$$

and I_{pc} vs. $v^{1/2}$ (the blue line with the circle symbols)

$$y = -0.0014 \times v^{1/2} + 1.0267 \times 10^{-4} \quad (R^2 = 0.9903). \quad (2)$$

In the cases of both anodic and cathodic peaks, the peak currents expressed linear dependence on the square root of the potential scan rate, indicating that the electrochemical

processes occurred in a diffusion-controlled regime on the MIL-53(Fe)-modified GCE electrode [40]. Besides, the relationships between the potentials of anodic and cathodic peaks and $\ln v$ were investigated, and their corresponding linear fit lines for each set of experimental data have been shown in Figure 4(c), i.e., E_{pa} vs. $\ln v$ (the green line with the square symbols)

$$y = 0.0178 \times \ln v + 0.3099 \quad (R^2 = 0.9940) \quad (3)$$

and E_{pc} vs. $\ln v$ (the orange line with the star symbols)

$$y = -0.0292 \times \ln v + 0.0294 \quad (R^2 = 0.9969). \quad (4)$$

The gradually increasing trend of the potential peak difference ($\Delta E = E_{pa} - E_{pc}$) with the potential scan rate v

FIGURE 5: DPV results of (a) GCE/bare and (b) GCE/MIL-53(Fe) electrodes measured in 20 μM Cd(II) and 0.1 M ABS (pH = 5.0) solution.

demonstrates that the electrochemical processes which happened on the GCE/MIL-53(Fe) electrode surface are quasireversible [41]. Moreover, as can be seen in Figure 4(c), both the potentials of anodic and cathodic peaks depend linearly on the natural logarithm of the scan rate, and these relationships can be expressed by the following equations [41, 42]:

$$E_{\text{pa}} = E^0 + m \left[0.78 + \ln \left(\frac{D^{1/2}}{k^0} \right) - 0.5 \ln m \right] + 0.5m \ln \nu, \quad (5)$$

$$m = \frac{RT}{(1 - \alpha)nF}, \quad (6)$$

$$E_{\text{pc}} = E^0 - m' \left[0.78 + \ln \left(\frac{D^{1/2}}{k^0} \right) - 0.5 \ln m' \right] - 0.5m' \ln \nu, \quad (7)$$

$$m' = \frac{RT}{\alpha nF}, \quad (8)$$

where ν (V s^{-1}) is the scan rate, E^0 (V) is the formal standard potential, α is the charge transfer coefficient, n is the number of transported electrons, k^0 (cm s^{-1}) is the electron transfer rate constant, D ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient, R is gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is working temperature ($T = 298 \text{ K}$), and F is Faraday's constant ($F = 96480 \text{ C mol}^{-1}$). The values of α and n can be calculated from the slopes of E_{pa} vs. $\ln \nu$ and E_{pc} vs. $\ln \nu$, and the results are that the value of α is 0.379 and the value of n is 1.161. The value of n verified that the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ and the reduction of $\text{Fe}(\text{CN})_6^{3-}$ which occurred on the GCE/MIL-53(Fe) electrode surface are through monoelectronic steps. The diffusion coefficients (D_{O} and D_{R}) of ferri- and ferrocyanide ions in 0.1 M KCl medium at 25°C are $7.20 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ and $6.66 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$, respectively [43]. From the intercepts of E_{pa} vs. $\ln \nu$ and E_{pc} vs. $\ln \nu$ and using $E^0 = (E_{\text{pa}} + E_{\text{pc}})/2 = 0.19 \text{ V}$ [41], the values of k^0 were calculated as

$1.069 \times 10^{-3} \text{ cm s}^{-1}$ and $1.489 \times 10^{-3} \text{ cm s}^{-1}$ for the anodic and the cathodic branches, respectively, and the average value was $1.279 \times 10^{-3} \text{ cm s}^{-1}$. These results further confirmed that, in the considered scan rate range, the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ and the reduction of $\text{Fe}(\text{CN})_6^{3-}$ which occurred on the GCE/MIL-53(Fe) electrode surface are quasireversible.

The electrochemically effective surface area (A) of modified electrodes is an important factor increasing electrochemical active sites, enhancing electrochemical response, and improving sensitivity of electrochemical sensors [44]. In this work, the electrochemically effective surface area of the GCE/MIL-53(Fe) electrode was determined by CV data analysis by using the Randles-Sevcik equation for quasireversible reactions as follows [45]:

$$I_p = 3.01 \times 10^5 \alpha^{1/2} n^{3/2} A C_0 D^{1/2} \nu^{1/2}, \quad (9)$$

where ν (V s^{-1}), α , n , and D ($\text{cm}^2 \text{s}^{-1}$) were mentioned in Equations (5)–(8). A (cm^2) is the electrochemically effective surface area of the electrode, C_0 (mol cm^{-3}) is the concentration of redox species, and I_p (A) is the redox peak current. From Equation (9) and using the slope of the linear dependence of the anodic peak current on the square root of the potential scan rate (Figure 4(b)), the value of A of the GCE/MIL-53(Fe) electrode was calculated to be 0.453 cm^2 . Thus, the electrochemically effective surface area of the modified GCE electrodes using the synthesized MIL-53(Fe) is significantly larger than that of the GCE electrodes ($A_{\text{GCE}} = 0.071 \text{ cm}^2$). The above EIS and CV results verified that the synthesized MIL-53(Fe) material was successfully immobilized on the GCE electrode surface, the electrochemical activity of the GCE/MIL-53(Fe) electrode was stable, and the MIL-53(Fe) with a high electrochemically effective surface area was able to significantly enhance the electrochemical response of the WE. These data also further confirmed that in this study, the drop-casting method used to immobilize the MIL-53(Fe) on the WE surface was simple, convenient, and effective.

3.3. Detection of Cd(II) Ions Using MIL-53(Fe)-Based Electrochemical Sensors. To assess the ability of GCE/MIL-53(Fe) as an electrochemical sensor for detection of cadmium (Cd(II)) ions in aqueous solutions, the DPV of the GCE/bare and GCE/MIL-53(Fe) electrodes were recorded in 0.1 M ABS (pH = 5.0) solution containing 20 μM Cd(II) (Figure 5). As can be observed in Figure 5 (curve a), with GCE, no obvious response was observed when the accumulation process was carried out for 120 s at -1.2 V in the solution containing 20 μM Cd^{2+} and 0.1 M ABS buffer (pH = 5.0). This result implies that with the bare GCE, the ability to be used as an electrochemical sensor for detection of cadmium ions in aqueous solutions was almost negligible.

In contrast, the DPV result of GCE/MIL-53(Fe) (Figure 5, curve b) showed a strong response peak at -0.75 V with the peak current $I_{\text{peak}} = 37.29 \mu\text{A}$, which characterizes the presence of Cd(II) ions in the aqueous solution, although the concentration of cadmium ions is relatively low

FIGURE 6: (a) DPV results of GCE/MIL-53(Fe) electrodes in Cd(II) solutions (with 0.1 M ABS (pH = 5.0)). Cd(II) concentrations (from A to G): 150, 200, 250, 300, 350, 400, and 450 nM; (b) response of the electrochemical sensors to different concentrations of Cd(II) ions.

TABLE 1: Comparison of the electrochemical sensor with someone else's in the previous literature.

Surface modification	Linear range (M)	Detection limit (M)	Reference
GCE/chitosan-carbon nanotubes	$1.334 \times 10^{-5} - 3.950 \times 10^{-5}$	7.1×10^{-6}	[47]
GCE/LAL* -AuNPs	$3.0 \times 10^{-7} - 1.4 \times 10^{-6}$	3.0×10^{-7}	[48]
GCE/MIL-100(Cr)	$0 - 1.0 \times 10^{-5}$	4.4×10^{-8}	[49]
GCE/porous carbon-PdNPs	$5.0 \times 10^{-7} - 5.5 \times 10^{-6}$	4.1×10^{-8}	[50]
GCE/MIL-53(Fe)	$1.5 \times 10^{-7} - 4.5 \times 10^{-7}$	1.6×10^{-8}	This work

*LAL: laser ablation in liquid.

(20 μ M). This result implies that the electrochemical sensor based on the MIL-53(Fe)-modified GCE can be used for determination of Cd(II) ions in aqueous solutions.

These obtained results can be attributed to the MIL-53(Fe) material with abundant adsorption sites and a large surface area, which can adsorb Cd(II) ions from the aqueous solution, leading the Cd(II) ion enrichment process onto the GCE/MIL-53(Fe) surface. Therefore, the electrochemical measurements were performed to detect the presence of Cd(II) ions on the electrode surface at low concentration. In addition, the enhanced current at the GCE/MIL-53(Fe) electrode compared to the bare GCE also indicates that the obtained MIL-53(Fe) with the high electrochemically effective surface area exhibits electrocatalytic activity to the reduction of the target. These above results suggest that using MIL-53(Fe) material in development of the electrochemical sensor for detection of Cd(II) ions is totally suitable.

Figure 6(a) shows the DPV response results of the GCE/MIL-53(Fe) with different Cd(II) concentrations. As can be seen, the increase in the concentration of Cd(II) target caused an increase in the peak current (I_{peak}) of the responses. The change in the electrochemical signal was obtained even at low concentration of Cd(II) ions (150 nM). And this phenomenon becomes more obvious when the target concentra-

tion continues to rise (up to 450 nM). The above results are explained that when Cd(II) ions in the aqueous solutions increase, the amount of Cd(II) ions accumulated on the surface of the MIL-53(Fe) layer increases, which leads to increasing in response current of the DPV results. The sensitivity of the electrochemical sensors was investigated by plotting I_{peak} versus different Cd^{2+} concentrations (Figure 6(b)). It shows that a linear relationship between I_{peak} vs. $[\text{Cd}^{2+}]$ in the range from 150 nM to 450 nM is $I_{\text{peak}} (\mu\text{A}) = 0.2946 + 0.0017 \times [\text{Cd}^{2+}] (\text{nM})$ with a correlation coefficient of $R^2 = 0.9809$. Based on a signal-to-noise ratio characteristic of 3 (S/N = 3) [32, 46], the detection limit of Cd^{2+} ions on GCE/MIL-53(Fe) was estimated to be 16 nM. The fabricated electrochemical sensor was compared to someone else's which has been reported in the previous studies (Table 1). Results in Table 1 indicate that the GCE/MIL-53(Fe) in this work has a great applied potential for Cd^{2+} determination on the terms including simple fabrication, direct detection, rapid analysis time, and high sensitivity.

4. Conclusion

We have synthesized the metal-organic framework MIL-53(Fe) using the effective hydrothermal method with

optimized synthesis conditions. The synthesized MIL-53(Fe) was characterized by XRD, SEM/TEM, and FT-IR measurements, and the obtained results indicated that the formed MIL-53(Fe) was a single phase with narrow size distribution and the mean size was around 800 nm. A layer of MIL-53(Fe)-modified glassy carbon electrode (GCE/MIL-53(Fe)) was fabricated via the simple drop-casting technique. The CV and EIS measurements of the GCE/MIL-53(Fe) electrode indicated that the MIL-53(Fe) layer with the small particle size and the high electrochemically effective surface area was able to increase the electrochemical response and improve the sensitivity of the electrochemical sensor. The novel electrochemical sensor based on the MIL-53(Fe) was designed and developed to detect Cd(II) ions in aqueous solutions, and the detection limit of the sensor was 16 nM. The evaluated results demonstrated that the metal-organic framework MIL-53(Fe)-modified glassy carbon electrode (GCE/MIL-53(Fe)) has great promising for Cd²⁺ ion sensing in water samples with expressed advantages such as high sensitivity, direct detection, and rapid analysis time.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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