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Electrochimica Acta



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Doping ZIF-67 with transition metals results in bimetallic centers for electrochemical detection of Hg(II)



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ARTICLE INFO

Article history: Received 12 December 2020 Revised 9 April 2021 Accepted 1 May 2021 Available online 6 May 2021

Keywords: Electrochemical detection Mercury Metal-organic framework SWASV Transition metal

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Development of robust methods for rapid detection of heavy metal ions and associated chemical species in water is challenging. Different mercury species are ubiquitous in the environment; they bio-amplify and undergo methylation into organo-Hg species. We developed a new electrochemical method for rapid screening of free Hg^{2+} in water by square wave anodic stripping voltammetry (SWASV) on a metalorganic framework (MOF) platform using ZIF-67 as starting substrate. Bimetallic MOF structures were fabricated by doping iron, manganese or nickel ions into ZIF-67 using a facile NaOH treatment. The GCE was modified with Ni, Mn, or Fe doped ZIF-67 nanocomposites to enhance performance for Hg²⁺ detection. When compared to pure ZIF-67/GCE, the Hg²⁺ detection sensitivity by the metal ions-doped ZIF-67/GCE was increased by 260%. The detection limit was improved by 60%. The Fe doping on ZIF- $67 (Fe_x Co_y)$ significantly improves electroanalytical performance due to the formation of iron oxide on ZIF-67. The GCE modified with Fe₁Co₁ nanocomposite showed the best performance for electrochemical detection of Hg²⁺. Besides, the cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) data also confirmed that Fe doping of the ZIF-67 enhanced the electron transfer rate at the solid-liquid interface. Hg^{2+} detection and quantification at this new chemically modified sensing electrode were not interfered by Cd^{2+} , Pb^{2+} , and Cu^{2+} . The Fe_1Co_1 modified GCE is stable when used repeatedly for ten cycles. The spike recovery of 0.3 to 1.00 μ M Hg²⁺ with Fe₁Co₁ modified GCE was always above 99.0%. The chemically modified sensor with Fe_1Co_1 holds a promise in monitoring Hg^{2+} at trace concentrations.

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1. Introduction

Heavy metals are ubiquitous on the earth's crust; however, the pollution results from their uses in anthropogenic activities such as mining, industrial, domestic and technological applications [1]. Heavy metal-induced toxicity and carcinogenicity involve many mechanistic aspects, some of which are not well understood. Each

metal has unique physic-chemical properties that confer to its specific toxicological mechanisms of action. Most heavy metals (and metalloids) are systemic toxicants that depend mainly on their particular chemical species [2]. For example, mercury occurs primarily in three states, Hg⁰, Hg²⁺ and methylated Hg, that exert contrasting toxicity. Therefore, the development of rapid detection methods of metal ions and chemical species is a timely need in rapid screening of environmental pollution.

Many spectroscopic techniques are available for metal/ metalloids detection which include atomic absorption spectroscopy (AAS) [3], inductively coupled plasma mass spectrometry (ICPS) [4], cold vapour atomic fluorescence spectrometry (CVAFS) [5], atomic emission spectroscopy (AES) [6]. These methods have the advantage of high accuracy and low detection limit. Usually, they require complicated, pretreatment procedures, and cost-intensive, equipment and trained operators, which limit their in-situ and

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real-time applications. On the contrary, electrochemical methods provide with an attractive alternative solution for metal ions detection due to their high resolution, fast response, simple operation, portability and low cost [7,8]. Further, these methods can be extended to identify chemical species of metal ions. Square wave anodic stripping voltammetry (SWASV) is an emerging electrochemical analysis technology, which is widely used in heavy metal ions detection. Compared with other electrochemical methods, SWASV is particularly suitable for metal ions detection due to high selectivity & sensitivity, low detection limit, broad detection range and fast analysis speed [9]. The mechanism of detection can be described simply by an adsorption-desorption model. First, the heavy metal ions(M²⁺) are adsorbed to the active layer and then diffused into the electrode surface under the concentration gradient. When a deposition potential is applied to the electrode, the heavy metal ions are reduced to a metallic form (M). Then a scanning potential is applied to the electrode to observe the stripping current [10].

The basis of the electrochemical analysis is the redox reaction of the target analyte that occurs on the modified electrode material, therefore, selecting the appropriate electrode and the interface rationally are the key to achieve outstanding electrical analysis performance [11]. Compared with conventional glassy carbon electrode, chemically modified electrode can improve the accumulation effect of the target analyte and accelerate the electron transfer rate, thus enhancing the sensitivity of electrical analysis and significantly broadening the application scenario of electrochemical detection.

Metal-organic frameworks (MOFs) are organic-inorganic hybrid materials with porous properties, which have received extensive attention in different fields over the past 20 years [12-14]. Zeolitic imidazolate frameworks (ZIFs) that topologically isomorphic with zeolites is a type of important MOFs. Up to now, hundreds of ZIFs structures have been discovered, most of which exhibit excellent thermal and chemical stability due to their microporous structure, large specific surface area and adjustable pore size [15]. They have shown wide application potential in the fields of energy storage [16,17], adsorption [18,19], catalysis [20,21], gas separation [22,23], etc. Nevertheless, the research on the electrochemical analysis of ZIFs materials is rarely reported; it is significant to explore the application in HMIs detection. Besides, element doping, as a method of adjusting the physical and chemical properties of nanomaterials, can often play an unexpected positive role. Hui Yang et al. [24] successfully applied the doping strategy to the regulation of gas adsorption and photo-catalytic performance, and produced a high-performance photo drive catalyst microporous Cu@ZIF-67, with strong gas adsorption capacity and high efficiency in visible-light-driven photo-catalytic degradation methyl orange. Wei Hong et al. [25] introduced Fe elements into ZIF-67 by simple sodium hydroxide-mediated approach to preparing a Fe-Co bimetallic MOF. Electrochemical measurements verify that incorporation of Fe during the MOF preparation can reduce the R_{ct} significantly, which finally enhances the OER activity. Inspired by this view, the electronic structure of ZIFs can be adjusted by introducing foreign elements into the lattices, which may facilitate the realization of specific electrochemical analytical properties.

In this work, transition metal elements doped ZIF-67 were synthesized by an improved sodium hydroxide-mediated method [24], and manganese, ferric, and nickel ions were individually doped into the substrate. A series of metal ions doped ZIF-67 composites were used to construct the electrochemical sensing interface and detect Hg²⁺ by square wave anodic stripping voltammetry. The surface morphology and structure of ZIF-67 nanocomposites were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The electrochemical analytical performance of different ZIF-67 nanocomposites modified electrode for the determination of Hg²⁺ was investigated. To further investigate the mechanism by which metal ions doping contributes to the electrochemical analysis, the electrochemical properties of the material itself were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The repeatability, stability and anti-interfering ability of ZIF67 nanocomposites in the detection of Hg²⁺ were then investigated. Finally, the newly developed electrochemical sensor was used to detect Hg²⁺ concentration in natural water bodies.

2. Experimental

2.1. Reagents and materials

Analytical grade 2-methylimidazole $(C_4H_6N_2)$, sodium hydroxide (NaOH), iron chloride hexahydrate (FeCl₃•6H₂O), manganese chloride tetrahydrate (MnCl₂•4H₂O), nickel chloride hexahydrate (NiCl₂•6H₂O) were purchased from Sinopharm Chemicals (China). Cobalt nitrate hexahydrate (Co(NO₃)₂•6H₂O), mercuric chloride (HgCl₂) were obtained by Aladdin Chemistry Co. Ltd. (Shanghai, China). All the chemicals were used as received for the experiments. NaAc-HAc buffer solutions with different pH values were prepared by adjusting the volume ratio of 0.1M acetic acid (HAc) solution and 0.1M sodium acetate (NaAc) solution. The ultra-pure water (electric conductivity 18.25 MΩ•cm) was used throughout the experimental process (NANO pure® DiamondTM UV water system).

2.2. Instruments

All electrochemical measurements were carried out with a high-precision potentiostat (CHI 660D ChenHua Instr., Shanghai, China) in three-electrode configurations: 3 mm diameter glassy carbon electrode (CHI 104 ChenHua Instr., China), or modified GCE working electrode, Ag/AgCl reference electrode (The internal solution is a saturated KCl solution) and Pt counter electrode. To determine crystalline phases of synthesized ZIF-67 materials, the X-ray diffraction analysis (XRD) was carried out with Cu K α radiation. (PANalytical X-Pert PRO MPD, Holland). The surface morphology of the solid materials was characterized by a field emission scanning electron microscope (FESEM, Quanta 200 FEI, USA) and highresolution transmission electron microscopy (HRTEM, JEM-2100F, Japan). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Esca lab 250Xi (Thermo Fisher Scientific, Waltham, MA, USA) system using a monochromatic Al K α source (1320eV, 140W). Fourier transform infrared spectrometer (FTIR) analyses of the samples were conducted on a Nicolet 67, Thermo Nicolet Co., USA.

2.3. Synthesis of pure and transition-metal doped ZIF-67

ZIF-67 was prepared according to a modified sodium hydroxidemediated method [25]. In brief, 5 mmol NaOH was dissolved in 5 mL of water and then mixed with 5 mL of a solution containing 16.8 mmol (1.38 g) 2-methylimidazole under stirring (solution A); 0.8 mmol Co(NO)₃•6H₂O (0.23 g) was added into 6 mL of water (solution B). After that, solution B was slowly added into solution A with a pipette and the resultant solution was allowed to react at ambient conditions under stirring for three h (stirring rate 300 rpm). The solid was separated by centrifugation, and washed three times with methanol, and dried overnight at 60°C (sample named as ZIF-67). We used a similar process to fabricate Fe doped ZIF-67 with following minor modifications. First, a given proportion of cobalt and iron or nickel dopants were added into solution B (Fe³⁺:



Fig. 1. transmission electron microscopy (TEM) images of (a) pure ZIF-67; (b)Mn₁Co₁; (c) Fe₁Co₁ and (d)Ni₁Co₁.

 Co^{2+} = 1:2, 1:1 or 2:1). The samples thus prepared were designated as Fe₁Co₂, Fe₁Co₁, Fe₂Co₁ and Mn_xCo_y and Ni_xCo_y.

2.4. Fabrication of modified electrodes

Before modification, the GCE surface was polished with 1.0, 0.3, and 0.05 μ m alumina slurries followed by sequential sonication in 1:1 HNO₃, ethanol, and deionized water for 3 min to obtain a clean surface. Then 3 mg ZIF-67 was mixed with 3 mL water and homogenized by sonication for 30 min. Afterwards, 5 μ L suspension was pipetted onto the cleaned GCE surface and dried at the room temperature. The same procedure was repeated to prepare modified GCE electrodes using differently doped ZIF nanocomposites.

2.5. Electrochemical measurements

The electrochemical performance of the chemically modified GCE-solution interface was carried out by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The Hg²⁺ detection method was developed using square wave anodic stripping voltammetry (SWASV) mode. For the previous experiments, the required metal ion solutions (e.g. Hg²⁺, Cd²⁺, Cu²⁺ and Pb²⁺) were prepared by diluting respective metal ion stock solutions as received from the manufacturer. The EIS experiments were carried out under following experimental conditions: AC amplitude: 5 mV; frequency range: 10^{-1} ~ 10^{6} Hz, dc potential, 180 mV. In SWASV experiments following experimental conditions were used: The initial and final potential in SWV are -0.2 V and 0.8 V, respectively. step potential 4 mV, amplitude 25 mV, frequency 15 Hz and 1.2 V desorption potential (200 s). All experiments were triplicated, and average values are shown in the manuscript.

3. Results and discussion

3.1. Material characterization

The surface morphology of ZIF-67 and Fe-doped ZIF-67 was examined observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1 shows transmission electron microscopy (TEM) images of the bare ZIF-67 and Fe, Mn or Ni doped ZIF-67. As shown in Fig. 1(a), The crystallinity of ZIF-67 is a rhombic dodecahedron with a size around 1µm. In agreement with published data [26,27] the bright edges and dark centers in TEM images confirm well-crystallized solid [26,27]. When the ZIF-67 is doped with Mn, Fe or Ni, the outer boundaries of the composites are blurred, however, the rhombic dodecahedron skeletal structure is well preserved. Distortion of the surface coating is marked in Metal doped ZIF-67. The differently doped ZIF-67 images show a marked effect on exterior coating with specific elements doping. With the introduction of the iron component, the edges of ZIF-67 blurred with a dimension reduction. When nickel was doped into ZIF, lamellar structures seem stacking. The surface morphology of Fe-doped ZIF-67 was characterized by SEM, and the results were shown in Fig. S1. With the increase of the Fe doping concentration, the edges of ZIF-67 became blurred, and the size reduced. And a few lamellar structures were formed on the surface when the molar ratio of Fe and Co ions reaches 2:1; the generated nanosheets started to stack. Some researchers suggest that The formation of two-dimensional nanosheets is due to coordination interactions of 2-methylimidazole in methanol matrix which, results in the transformation of the structure from rhombic dodecahedron to a two-dimensional nanosheet shell structure [28].

Fig. 2(a) shows XRD patterns of pure ZIF-67 and Fe doped ZIF-67. The diffraction pattern of ZIF-67 is consistent with that reported elsewhere [29,30], which shows successfully synthesized ZIF-67. The pattern for Fe_xCo_y has several peaks that can be wellindexed to Fe_2O_3 and FeO [31,32]. However, weak characteristic diffraction peaks of iron oxides are observed because of its low loadings and weak crystallization, and it also implies good dispersion of small Fe_2O_3 and FeO clusters on the ZIF-67 surface. The sharp diffraction peak of 18.04° of Fe_1Co_1 suggested that the nanostructures are well crystallized. The XRD spectra of Mnand Ni-doped ZIF-67 are displayed in Fig. S2, and corresponding diffraction peaks of metal oxides were found.

FT-IR measurements were used to identify surface functional group species and consider the molecular structure in Fe_xCo_y nanostructures. As shown in Fig. 2(b), each absorption peak in the spectrum is matched with the corresponding vibration, two peaks at 1055 and 1390 cm⁻¹ correspond to the presence of the



Fig. 2. a) X-ray diffraction (XRD) patterns of pure ZIF-67, Fe₁Co₂, Fe₁Co₁ and Fe₂Co₁; (b) Fourier transform infrared spectroscopy (FT-IR) of pure ZIF-67, Fe₁Co₂, Fe₁Co₁ and Fe₂Co₁.



Fig. 3. Optimization of experimental conditions for Hg(II) determination: (a) supporting electrolytes, (b) deposition potential, (c) deposition time and (d) pH values on Square wave anodic stripping voltammetry (SWASV) responses of the Fe₁Co₁ modified glass carbon electrode (GCE) in 0.1 M NaAc-HAc containing 0.5 μM Hg(II).

benzene ring groups [33]. The characteristic peaks at 2922 and 3133 cm⁻¹ are attributed to the C-H bonds in aliphatic and aromatic groups, respectively; the distinct peaks at 1598 cm⁻¹ correspond to the C=N stretching vibration in 2-methylimidazole [34]. The bands at 1350-1500 cm⁻¹ are ascribed to the stretching vibration of imidazole ring; the bands observed in the region of 900-1350 cm⁻¹ could be attributed to the plane vibration of the imidazole ring. The bands at 500-800 cm⁻¹ are attributed to the out of plane vibration of imidazole ring [35]. Besides, it is noteworthy that the characteristic peak at 1384 cm⁻¹ gradually intensifies with the increase of iron content, which may be due to the excessive substitution reaction between Fe ions and Co ions.

3.2. Experimental parameters optimization

To optimize SWASV electrochemical detection of Hg(II) by Fe_1Co_1 modified GCE, the following parameters were considered:

supporting electrolyte, solution pH, deposition potential and time. Fig. 3(a) shows the voltammetric response to 0.5 μ M Hg(II) using three supporting electrolytes (0.1 M, pH 5.0): PBS, NaAc-HAc, and NH₄Cl-HCl. The deposition potential and deposition time were set to -1.1 V and 160 s, respectively. No significant current signal was observed in the NH₄Cl-HCl solution. A broad stripping peak appeared in PBS solution, and its stripping peak position has deviated from the standard stripping potential of Hg(II). Optimum sensitivity for Hg²⁺ detection is observed in NaAc-HAc solution, a well-defined and sharp current peak was observed. The huge difference obtained in different background electrolytes may be due to the formation of complexes between metal ions and the supporting electrolyte. Therefore 0.1 M NaAc-HAc electrolyte was selected in further experiments. Considering that pH values of the accumulation solution exhibit a significant and predictable effect on preconcentration, we prepared a series of HAc-NaAC buffer solutions with pH ranging from 3.0 to 6.0. Similarly, the deposition



Fig. 4. SWASV responses of (a) pure ZIF-67, (b) Fe₁Co₂, (c) Fe₁Co₁ and (d) Fe₁Co₂ modified electrodes toward Hg(II) at different concentrations in 0.1 M NaAc-HAc solution (pH 5.0). The insets show the corresponding calibration plots.

potential and time of this experiment were set to -1.1 V and 160 s respectively. As shown in Fig. 3(b), the stripping current showed a trend of first increased and then reach a peak at 5.0. When pH < 5.0, the competition between H⁺ and Hg(II) towards the sensor is observed; When pH > 5.0, Hg(II) tends to hydrolyze in an alkaline environment. The stripping current is optimal around pH 5.0 for Hg²⁺ detection with modified GCE sensor. Hence, the pH was set around 5.0 for subsequent experiments in the development of Hg²⁺ detection method.

The effect of deposition potential on stripping signal was examined using 0.5 µM Hg(II) at pH 5.0 in 0.1 M NaAc-HAc. In our experiments, keeping the other conditions constant, we varied the deposition potential: -0.7, -0.8, -0.9, -1.0, -1.1, -1.2 V. And the deposition time was 160 s. The results show in Fig. 3(c), the current intensity increased with the potential, when the potential reached -1.0 V, the maximum current appeared; when the voltage exceeded -1.0 V, the current signal decreased significantly. The above phenomena can be attributed to the increase in the amount of Hg(II) adsorption, and when the specific current intensity value is reached, a large number of H⁺ in the buffer solution were reduced to H₂, which covers the surface of Fe₁Co₁/GCE and hinders the adsorption of Hg(II) [36]. Finally, Fig. 3(d) depicts the effect of deposition time (60, 90, 120, 150, 180, and 210 s) on the stripping signal toward Hg(II). As expected, the peak current signal maintained an increasing trend as the deposition time increases. When the time exceeded 150 s, the growth of the current slowed down, which can be attributed to the saturation of the modified material surface, which could not provide additional sites for Hg(II) reduction [37]. Therefore, to achieve a balance between experimental time and stripping efficiency, 150 s was chosen as the deposition time.

3.3. Comparison of electroanalytical performance of transition-metal doped ZIF-67

Under the optimized experimental conditions, the analytical performance of the ZIF-67 modified GCE, and Fe_xCo_v /ZIF-67 modified GCE for Hg²⁺ detection was examined. Fig. 4 shows the SWASV responses of the chemically modified GCE electrode with the variation of Hg²⁺ concentration. A well-defined and sharp peak increased gradually with the Hg(II) concentration, showing that the ZIF-67 nanocomposite is applicable for trace detection of Hg(II). The resultant calibration curve plotted with current (µA) vs Hg(II) concentration (µM) shows a high correlation coefficient, further demonstrates the accuracy and validity of linearity analysis. Meanwhile, it indicated that the desorption treatment at the potential of 1.2 V for 200 s can effectively refresh electrode surface. The chemical modifications on GCE exhibit higher sensitivity than bare GCE (Fig. S3) which show that the ZIF-67 nanomaterials enhance the electroanalytical performance to Hg(II) detection. The results of the Mn-doped and Ni-doped ZIF-67 samples are shown in Fig. 5.

For comparison, the sensitivity and limits of detection (LOD, 3δ method) of pure ZIF-67 materials and transition-metal doped ZIF-67 are determined. The limit of detection (LOD) were calculated by following equations [38]:

$$LOD = \frac{3\sigma}{S}$$

σ is the signal-to-noise ratio, *S* is the slope of the calibration equation. The small variations of the error bars prove the high stability of the experimental results in Hg²⁺ detection. Fig. 6(a) shows the order of sensitivity of the modified electrode toward Hg(II): Fe doped ZIF-67 > Ni-doped ZIF-67 > Mn-doped ZIF-67 >



Fig. 5. SWASV responses of (a) Mn_1Co_2 , (b) Mn_1Co_1 , (c) Mn_1Co_2 , (d) Ni_1Co_2 , (e) Ni_1Co_1 , (f) Ni_2Co_1 modified electrodes toward Hg(II) at different concentrations in 0.1 M NaAc-HAc solution (pH 5.0). The insets show the corresponding calibration plots.



Fig. 6. Comparison of (a) sensitivity and (b) limit of detection (LOD) for SWASV determination of Hg(II) by pure ZIF-67, Mn_xCo_y, Fe_xCo_y, Ni_xCo_y modified GCEs, respectively.



Fig. 7. (a) Survey XPS spectrum of Fe_1Co_1 nanocomposites; High-resolution XPS spectra of (b) Fe 2p, (c) Co 2p, (d) O 1s, (e) N 1s and (f) C 1s regions for the Fe_1Co_1 nanocomposites.

pure ZIF-67. Compared with pure ZIF-67, the sensitivity of Hg²⁺ detection after metal ions doping can be increased up to 22.1% in some cases and can reach almost 260%. The LOD values obtained for GCEs modified with different ZIF-67 composites are shown in Fig. 6(b). The observed detection limit and the sensitivity values confirm that our method can meet the requirements recommended by the WHO for Hg(II) detection in drinking water [39]. In this respect, Fe doping is also relatively advantageous, with LOD only 40% of that of pure ZIF-67. The linear range, sensitivity and detection limit of this work, including the data of the sensing platform in other works, are summarized in Table 1. In summary, Fe doping can significantly improve the performance of the sensitivity and LOD, and the mechanism involved would be further discussed later.

3.4. Study on the mechanism for Improved electroanalytical performance of Fe-Doped ZIF-67

3.4.1. Investigation of the surface chemical state of Fe_1Co_1 nanocomposite

The overall XPS survey scan of Fe_1Co_1 (Fig. 7a) shows the presence of C 1s (282.6 eV), N 1s (397.6 eV), O 1s (529.1 eV), Co 2p, and

Table. 1

Comparison of electroanalysis performance with previously reported values of different electrodes for electrochemical detection of Hg(II)

Modified Electrode	Linear range (µM)	Sensitivity (µA/µM)	LOD (nM)	Ref
Graphene-MnO ₂ N-doped G/GCE [Ru(bpy)3] ²⁺ /GO/ Au NH ₂ -CMS/GCE Fe ₃ O ₄ -chitosan/GCE Fe ₁ Co ₁ /GCE	12–210 0.07–9 0.1–1.2 1–1.9 0.4–1.1 0.1–1.1	0.106 15.734 3.71 29.086 9.65 41.5	2000 10 350.20 370 95.7 7.82	[40] [41] [42] [43] [44] This work

Fe peaks [45]. The Fe 2p peak and the Co LM2 Auger peak overlap to a certain extent. Our data show that Fe 2p has a doublet, and Co LM2 has a singlet. The Fe has a distinct oxidation state; Fe 2p3 peak corresponds to 711.2 eV, which is consistent with the reported values for Fe₃O₄ [33]. Two prominent peaks with binding energies of 781.2 eV and 797.5 eV can be observed in the XPS peak for Co 2p (Fig. 7b), corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$, and the difference in binding energy between the two peaks is 16.3 eV, which agrees well with the standard Co²⁺ spectrum. There are also



Fig. 8. The CV (a) and EIS (b) measured with bare, pure ZIF-67, Fe₁Co₂, Fe₁Co₁, and Fe₂Co₁ modified GCE in the solution of 5 mM Fe(CN₆)^{3-/4-} containing 0.1 M KCl. The inset in Fig. 8(b) is the equivalent circuit.

two shakeup satellite peaks at 786.5 eV and 802.8 eV, which can be attributed to the binding energies of Co $2p_{3/2}$ and Co $2p_{1/2}$ [46]. In high-resolution N 1s spectra (Fig .7e), N 1s resolved into two peaks centered at 398.79 and 399.53 eV correspond to pyridinic-N, and pyrrolic-N, respectively [47]. In the high-resolution spectra of O 1s, in addition to the corresponding C=O and C-O peaks, there are also peaks of metal oxides located at 529.8 eV, thus consistent with the previous characterization results, confirming the presence of Fe₃O₄.

3.4.2. Electrochemical characterization of Fe₁Co₁ nanocomposite

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods are used to characterize the electrochemical performance of the sensing interface, which can reveal that information about the kinetics of electron transfer during redox reactions. All electrodes characterization was performed in 5 mM $Fe(CN_6)^{3-/4-}$ and 0.1 M KCl solutions.

Fig. 8(a) shows the cyclic voltammograms measured with bare ZIF-67, Fe1Co2, Fe1Co1 and Fe2Co1 modified working GCEs. All electrodes are cycled more than three times in CV mode, and the last measurement was taken for the comparison. Compared with the bare GCE, the redox peak interval of all modified GCE electrodes tended to increase, and this shows successful loading of the material onto the GCE surface. Among the materials used for electrode modification, Fe1Co1 exhibited the largest peak current, which conforms that Fe doping at this ratio enhances the redox process. Electrochemical impedance spectroscopy (EIS) is widely applied to analyze the electron transfer resistance of target materials. Fig. 8(b) shows a typical Nyquist diagram, the semicircle diameter at high frequencies corresponds to the electron transfer resistance(Ret), and the linear portion at low frequencies corresponds to the diffusion-limited processes [48]. The inset simulates the equivalent circuit, where R_s, CPE, W_o and R_{et}, represent the solution resistance, constant phase element, Warburg impedance and electro transfer resistance, respectively. The parameters of each component after fitting to the equivalent circuit are shown in Table S1. The R_{et} of bare GCE is smallest (R_{et} ~114 $\Omega)\!,$ and after modifying it with ZIF-67, the Ret value reaches the maximum(Ret ~1263 Ω). According to previous data [49], ZIF-67 is weakly conductive, which is responsible for the increase in electron transfer impedance. Among all modified electrodes, the Ret value of Fe₁Co₁/GCE was at the minimum (R_{et} ~198 Ω), indicating that the doping of Fe element effectively accelerate the electron transfer rate at the electrode-solution interface and enhance the electronic conductivity of the ZIF-67 material.

3.5. Interference measurements

The electrochemical detection of Hg^{2+} is always interfered by the presence of Pb^{2+} , Cd^{2+} and Cu^{2+} in Hg^{2+} in the matrix. There-

fore, we evaluated the interfering effect of Cd^{2+} , Pb^{2+} and Cu^{2+} on Hg²⁺ detection by Fe₁Co₁ modified GCE. The interference experiments were divided into two modes as single-element and multielement interference, and the concentration of the added interfering ions was set as 0.7 μ M. Fig. 9(a, b, c) show the single-element interference patterns; the presence of Cd^{2+} and Pb^{2+} in the matrix solution had no significant effect on the signal of Hg²⁺, while the presence of Cu^{2+} reduced the current response of Hg^{2+} . This is ascribed to the amalgamation of electrochemically reduced Cu⁰ and Hg^0 . The current response of Hg^{2+} decreases slightly when several interfering ions coexist; it is partly due to amalgamation and the competition of remaining ions to a limited number of sites on the electrode surface. Conversely, there was a varying degree of improvement of the Cd^{2+} , Pb^{2+} and Cu^{2+} stripping signal with increasing of Hg^{2+} concentration in solution, which was the result of the mercury film first formed on the electrode to enhance the enrichment process. The linear fitting data for Hg^{2+} in single-element interference and multi-element interference mode are shown in Fig. S4. the Hg²⁺ peak shape and selectivity remain excellent. As the Hg²⁺ concentration increased, the height of the peak maintained a good linear growth trend. Above experiments prove that Fe₁Co₁ modified glassy carbon electrode has a strong anti-interference ability when detecting Hg²⁺, and with potential to be used in simultaneous detection of multiple heavy metal ions.

3.6. Stability and reproducibility

The stability of the Fe_1Co_1 modified GCE in repeated use was examined by measuring the stripping currents of 0.7 µM Hg²⁺ in twelve cycles with the same electrode for two weeks. As shown in Fig. 10(a), the variation of the stripping current kept within a reasonable range, and the calculated relative standard deviation (RSD) is 1.93%. The results confirm the high stability of Fe_1Co_1 GCE, which can be reused generally for at least two weeks. Besides, reproducibility of the data was examined using six Fe_1Co_1 GCE (marked as E1, E2, E3, E4, E5, E6) under the same optimized experimental conditions. In Fig. 10(b), the RSD value obtained from the measurements of Hg²⁺ using six electrodes is 2.11%, indicating the robustness of the electrode fabrication. In short, the stability and reproducibility of Fe_1Co_1 GCE make it promising for applications in Hg²⁺ in environmental samples.

3.7. Real sample analysis

To further evaluate the performance of the modified electrode in practical applications, the SWASV method was used to analyze the Hg^{2+} in real-world water samples collected from Nanfei River (Sample 1) and Hubing Lake (Sample 2) in Hefei, China. The filtered water samples (by 0.22 µm membranes) were diluted ten



Fig. 9. SWASV responses of the Fe₁Co₁/GCE towards Hg(II) when adding (a) 0.7 µM Cd²⁺, (b) 0.5 µM Pb²⁺, (c) 0.5 µM Cu²⁺, and (d) 0.7 µM Cd²⁺, Pb²⁺, Cu²⁺, simultaneously.



Fig. 10. Stability and reproducibility toward Hg(II) by Fe₁Co₁/GCE (a) SWASV responses toward 0.7µM Hg(II) during twelve cycles. (b) SWASV responses to 0.7µM Hg(II) measured with six Fe₁Co₁/GCE.

Table. 2Determination of spiked Hg^{2+} in real samples.(n=3)

Samples	Hg^{2+} added (μM)	Hg^{2+} found (μM)	Recovery (%)	RSD
	0.3	0.294	98	2.7
Sample I	0.6	0.607	101.2	2.1
	1.0	0.978	97.8	1.8
	0.3	0.310	103.3	1.1
Sample II	0.6	0.589	98.2	2.3
	1.0	1.021	102.1	1.4

times using 0.1 M, pH 5.0 HAc-NaAc buffer solution. Both samples do not contain Hg^{2+} in water. A spike recovery test was carried out using 0.3, 0.6 and 1.0 μ M spike solutions. Prior to the addition of Hg^{2+} , no obvious current signal was observed using Fe₁Co₁/GCE by SWASV method, indicating that the real water sample did not contain Hg^{2+} . A recovery test was performed by adding Hg^{2+} at concentrations of 0.3, 0.6 and 1.0 μ M to diluted water samples. The

spike recoveries at each level were determined, and the data are given in Table 2. Always the spiked recoveries are between 97.8-103.3 %. The RSD values range between 1.1 % and 2.7 %. The results show that the Hg²⁺ detection by Fe₁Co₁/GCE by SWASV method is not influenced by the matrix of the real-world water samples, and the Fe₁Co₁/GCE sensor has potential in Hg²⁺ detection of environmental samples.

4. Conclusions

We synthesized Mn, Fe, or Ni-doped ZIF-67 nanocomposites in large quantities by a facile sodium hydroxide mediation approach. When compared to bare ZIF-67, when ZIF-67 is doped with metal ions, the electrochemical signal of Hg²⁺ detection has enhanced. Our data showed that Fe₁Co₁ modified GCE offers excellent performance for trace detection of Hg²⁺ with a sensitivity (41.5 μ A/ μ M) and a limit of detection (7.82 nM), which exceeds the requirements of analytical methodology specified by the WHO for Hg²⁺ detection in drinking water. The Fe₁Co₁ modified GCE showed excel-

lent stability and reproducibility for Hg^{2+} detection. The Fe_1Co_1 modified GCE sensor shows 1.1%-2.7% spiked recoveries for Hg^{2+} in the real-water matrix. Transition metal ions doping provide a new strategy for the application of metal-organic frameworks in electrochemical sensor developments with a promising prospect.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit authorship contribution statement

Xing Chen: Conceptualization, Supervision, Writing - review & editing, Funding acquisition. **Ji-Xing Zhao:** Methodology, Formal analysis, Investigation, Writing - original draft. **Jia-Wei Wang:** Formal analysis, Investigation. **Yao Liu:** Methodology, Investigation, Formal analysis. **Lian-Chao Wang:** Formal analysis, Writing - review & editing. **Rohan Weerasooriya:** Writing - review & editing. **Yu-Cheng Wu:** Investigation, Writing - review & editing.

Acknowledgement

The authors acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 21777164), National Key R&D Program of China (Grant No. 2019YFC0408500), Fundamental Research Funds for the Central Universities (Grant No. PA2019GDQT0019). R. W. acknowledges the Program of Distinguished Professor in B&R Countries (Grant No. G20200012010).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2021.138539.

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