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Integrating catalytic role of gold nanoparticles with *in-situ* confinement effect of zirconium-based metal-organic frameworks for electrochemical determination of methylmercury

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ABSTRACT

Catalytic redox reactions and size matching effect between the target molecule and sensing material are reliable methods for highly efficient determination of heavy metal ions. In this work, the electrochemical determination of methylmercury (CH_3Hg^+) was carried out gold nanoparticles (AuNPs) incorporated into four zirconium-based metal organic frameworks (MOF) with different pore diameters, namely MOF-801, (University of Oslo) UiO-66, UiO-67, UiO-68. The work relates the role of dicarboxylic ligands of different lengths to the AuNPs load capacity and the adsorption and reduction of CH_3Hg^+ . The voltammetric properties of CH_3Hg^+ at different modified electrodes were studied by differential pulse anodic stripping voltammetry (DPASV). It was found that the CH_3Hg^+ electrochemical behavior was greatly influenced by the pore confinement effect of MOFs. Under the optimal conditions, the pore sizes of Au/UiO-67 are matched to CH_3Hg^+ molecule and they showed the highest response current. The possible reduction process of CH_3Hg^+ at the sensitive interface was explored by X-ray photoelectron spectroscopy (XPS) and chronoamperometry (CA). These four Au/MOFs modified GCE can also be used in detection of CH_3Hg^+ spiked in river water, confirming their potential application in the rapid detection of methylmercury in environmental samples.

1. Introduction

Mercury is a toxic heavy metal element that can accumulate in living organisms [1,2]. Methylated mercury is particularly hazardous due to its stronger toxicity than inorganic mercury [3]. Indeed, the search for a highly sensitive determination method of CH_3Hg^+ has been a long-standing challenge that has triggered tremendous studies. Recently, electrochemical methods have achieved a series of significant results in the characterization and quantification of toxic micropollutants with the advantages of strong response signal, high stability, simple operation and inexpensive instrumentation [4,5]. In spite of this, direct electrochemical determinations for organomercury compounds such as CH_3Hg^+ have rarely been reported due to their high stability and toxicity. Besides, electrochemical methods for methylmercury determination are mainly performed using noble metal electrodes or noble metal nanoparticle modified electrodes in a strong acid electrolyte.

Under these conditions, the high catalytic performance of noble metal (e.g., gold, silver, and platinum) is the key to electrochemical signal amplification [6–8]. When the size of noble metal nanoparticles goes down to a few nanometers, the high surface energy makes them to aggregate and form larger particles [9–11]. Therefore, more electrocatalytic sites and uniform dispersion of catalysts on the modified electrodes are required.

Metal organic frameworks (MOFs) are considered to be a promising nanostructure for sensing applications due to their large active surface area, abundant metal sites, ordered structure, easy functionalization, etc. [12–14]. In particular, nanometres-sized cages in MOFs can effectively adsorb and captures the target analytes and diffuse them across the sensing surface through the nanoscale inner and outer walls [15]. MOFs obtained by the reaction of high-valent metal ions (e.g. Fe³⁺, Cr³⁺, Al³⁺, Zr⁴⁺) with carboxylate ligands, such as the MIL and UiO series MOFs, possess strong coordination bonds sufficient to prevent the

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destructive effects of water molecules [16-18]. There has been a growing interest in UiO-based MOFs due to their remarkable hydrothermal stability in electrochemical determination [19,20]. Kemmegne-Mbouguen et al. [21] synthesized graphene foam/Zr-MOF nanocomposites (GF/UiO-66) modified glassy carbon electrode for simultaneous detection of acetaminophen (AC) and tryptophan (TRYP). The LOD of AC and TRYP were obtained as 7×10^{-8} M and 6×10^{-8} M, respectively. For enhancing the electrical conductivity of UiO-66-NH₂, Ru et al. [22] anchored gallium oxide hydroxide (GaOOH) on its surface. The prepared UiO-66-NH₂/GaOOH nanocomposites were used to determine four HMI (Cd^{2+} , Cu^{2+} , Hg^{2+} and Pb^{2+}) in real sample. Zhang et al. [23] reported the preparation of UiO-67/carbon paste electrode (CPE) for the electrochemical sensing of hydroquinone with a LOD of 3.6×10^{-9} M Interestingly, the importance of the functionalization and pore size of MOFs has been highlighted in the relevant reports. Cai et al. [24] prepared three ferrocene-doped MOF (Fc-MOF) films with different pore sizes (15 \sim 47 Å) and the effects of different MOF pore sizes on diffusion process between electrons and ions were clarified. Deng et al. [25] encapsulated platinum nanoparticles into UiO-66, UiO-67 and UiO-68, respectively, and investigated the effect of carrier structure on the electro-oxidation properties for N_2H_4 . Xia et al. [26] investigated the difference in the adsorption performance of UiO-66, NU-1000 and MOF-525 on tetracycline (TC). The results showed that the MOFs with a pore size slightly larger than the target molecule had the highest adsorption performance. However, there are few works reporting the electrochemical determination of CH₃Hg⁺ form within MOFs materials based on size matching effect.

In previous works we have developed a procedure for the determination of CH_3Hg^+ using AuNPs/ZIF67 nanoparticles modified GCE [27]. The MOFs were chosen as the substrate for loading AuNPs permitted to greatly improve the sensitivity of the determination. Indeed, the focal point of our work is to explore the effect of pore characteristics of MOFs for CH_3Hg^+ determination. The pore size of MOFs can be regulated by varying the size of the ligand. Here, four Zr-MOFs (MOF-801, UiO-66, UiO-67, UiO-68) were used as carriers loaded with AuNPs to construct electrochemical interfaces for determination of CH_3Hg^+ by DPASV. The significant differences in the AuNPs load capacity of four Zr-MOFs and the electrochemical performance of different Au/MOFs were observed. The possible preconcentration mechanism of CH_3Hg^+ at Au/MOFs/GCE was investigated and the effects of common interfering ion signals were analysed. Ultimately, CH_3Hg^+ in natural water samples were determined using the optimized procedure.

2. Experimental and methods

2.1. Reagents and apparatus

Zirconium(IV) chloride (ZrCl₄), N, N'-dimethylformamide (DMF), methanol, acetone, tetra chloroauric acid tetrahydrate (HAuCl₄·4H₂O), sodium acetate anhydrous (NaAc), ethanoic acid (HAc), and diethylene triamine pentaacetic acid (DTPA) were received from Shanghai Chemical Reagent Co. Ltd. Fumaric acid (FC), benzene-1,4-dicarboxylate acid (BDC), biphenyl-4,4'-dicarboxylate acid (BPDC), p-terphenyl-4,4'dicarboxylate acid (TPDC) were obtained from Shanghai Macklin Biochemical Co., Ltd. All solvents and reagents were of analytical grade and were used without further purification.

The morphology of Au/MOFs was investigated by field emission scanning electron microscopy (FESEM, Quanta 200 FEG, FEI, USA) at 10 kV accelerating voltage and high-resolution transmission electron microscopic (HRTEM, JEM-2100F, JEOL, Japan) at 200 kV accelerating voltage. X-ray powder diffraction (XRD) of the Au/MOFs nanocomposite was examined using X-ray diffraction (X'Pert PRO MPD) by Cu K α irradiation ($\lambda = 0.15,406$ nm) from 5° to 80° (2 θ). X-ray photoelectron spectroscopic (XPS) analysis was performed on PHI 5000 Versa Probe, USA. Fourier transform infrared spectra (FT-IR) were collected from a Nicolet 67 (Thermo Nicolet Co., USA) with the scanning range of 4000 to

 500 cm^{-1} . The pore size and specific surface area of the prepared materials were obtained by the Brunauer-Emmett-Teller (BET) method using Autosorb-IQ3 (Quantachrome, USA) at 77 K.

2.2. Fabrication of Au/MOFs nanoparticles

MOF-801 and UiO-66, 67, 68 were synthesized according to previous method reported [28]. In short, 0.233 g ZrCl₄ (1 mmol) and 1 mmol of the corresponding ligand were dissolved in 80 mL DMF and 2 mL HAc. After ultrasonic stirring to mix thoroughly, the mixture solutions were then placed into a Teflon-lined stainless-steel autoclave heated to 120 °C for 24 h The reaction products obtained were centrifuged and washed three times with DMF, methanol and acetone, respectively. The corresponding ligands used were as follows: MOF-801-FC, UiO-66-BDC, UiO-67-BPDC, UiO-68-TPDC.

Au/MOFs nanoparticles were prepared via the following procedure. The 20 mg MOFs were dispersed in 100 mL ultrapure water and sonicated. Then, 3 mL HAuCl₄·4H₂O (10 mg/mL) were added and the above system was stirred for 6 h Afterwards, the supernatant was removed by centrifugation, and 5 mL NaBH₄ (0.05 mol/L) solution were added to continue stirring for 30 min. The product was washed by with ultrapure water for three times and dried at 60 °C. The prepared materials are named as: Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68.

2.3. Preparation of modified electrodes

Prior to modification, the glassy carbon electrode was polished with alumina powder slurries. Then, sequentially ally cleaned with nitric acid solution, ethanol solution and ultrapure water. 2 mg nanocomposites prepared were dispersed into 1.0 mL of ultrapure water and sonicated for 10 min to obtain 2 mg/mL suspension of Au/MOFs. Then, 5.0 μ L of Au/MOFs suspension were deposited onto the GCE surface and dried in a nitrogen atmosphere. The obtained modified electrodes were marked as Au/MOF GCE, Au/UiO-66 GCE, Au/UiO-67 GCE, and Au/UiO-68 GCE.

2.4. Electrochemical measurements

An electrochemical system with three electrodes was used for all measurements with a 10 mL electrolytic cell and an electrochemical workstation using CHI 760e computer-controlled potentiate (ChenHua Instruments, Shanghai, China). The working electrode, counter electrode and reference electrode were bare or modified GCE (3 mm in diameter), platinum wire and Ag/AgCl electrode containing 3.3 mol/L KCl, respectively. The cyclic voltammetry (CV) parameters were used as follows: scanning potential range, -0.2 V to 0.6 V; scan rate, 0.1 V/s; sample interval, 0.001 V. For the measurements of electrochemical impedance spectroscopy (EIS), the frequency range was tested from 1000,000 to 1 Hz along with an amplitude of 0.005 V. The electrochemical behavior of the modified electrodes for CH₃Hg⁺ determination was performed by DPASV. All Au/MOFs modified electrodes were measured in 0.1 M NaAc-HAc (pH:5.0) at -0.8 V for 900 s. The parameters of DPASV were as follows: Increase E, 5 mV; Amplitude, 50 mV; pulse width, 50 ms; sample width, 40 ms; pulse period, 0.1 s; Unless otherwise stated, these parameters were will always be used in subsequent experiments. Chronoamperometry of Au/MOFs modified GCE was performed in 0.1 M PBS (pH 7.0) upon adding increasing amounts (from 0 to 40 μ g/L) of CH₃Hg⁺ at the applied potential of -1.0 V (vs. Ag/ AgCl).

3. Results and discussion

3.1. The morphology and structure of au/mofs

The SEM images of MOF-801, UiO-66, UiO-67, and UiO-68 are illustrated in Fig. S1. The morphology of the MOF-801, UiO-66 and UiO-67 shows typical regular octahedral shapes with the particle size of

approximately 500 nm, 150 nm, and 3 µm, respectively (Fig. S1a-c). UiO-68 mainly presents irregular spherical particles with rough surface (Figure S1d). The excessively functional ligand length makes strong instability during synthesis, which in turn causes the collapse of the octahedral structure. Fig. 1(a~d) shows a typical SEM image of Au/ MOF. It can be observed that almost all gold nanoparticles were deposited on the MOFs, even after thorough washing. It can be noted from the micrographs that AuNPs were uniformly dispersed on Zr/ MOFs. Meanwhile, histograms shows that the particle size of these NPs is about 15-25 nm (Fig. 1). Fig. 1(a. c) shows the octahedral shapes of MOF-801 and UiO-67 was perfectly maintained after loading of AuNPs. And the octahedral angles of UiO-66 become rounded and smooth, showing a spherical structure. TEM images of Au/MOFs further revealed that the MOFs immobilized Au nanoparticles were highly dispersed with average size of 15–25 nm (Fig. 1e–h). In addition, the overall structural integrity of the MOFs was preserved but there are some local defects or minor deformations in the framework, which are mainly caused by the particle sizes of the AuNPs larger than the cavitary size of MOFs. In the upper right inset of the TEM image, the gold nanoparticles exhibited highly faceted and twinned features. The lattice fringes spacing was around 0.22 nm in Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68, which corresponds to the (111) planes of the face-centered cubic (fcc) Au [29] . The lattice stripe spacing in Au/UiO-67 was 0.204 nm, which corresponded to the (200) crystal plane of Au nanoparticles [30]. Present results depicted the successful synthesis of AuNPs in crystalline form. In contrast, AuNPs are very uniformly distributed on the UiO-67 carrier, which can generate more active sites, leading to higher catalytic activity.

Fig. 2 shows the XRD patterns of the simulated MOFs and MOFs with Au/MOFs. The as-prepared MOF-801, UiO-66, UiO-67, and UiO-68 (red curve) matches well with the simulated signals (black curve), confirming the successful fabrication of MOFs nanoparticles. The characteristic peak corresponding to (111), (200), (220), and (311) planes of Au was observed for Au/MOFs at $2\theta = 38.23^{\circ}$, 44.45°, 64.59°, and 77.62°, respectively (blue curve) [31]. There is hardly any difference between the primary XRD peak of the Au/MOFs and the corresponding MOFs after loading with Au NPs, except for Au/UiO-68. It is demonstrated that the incorporation of Au NPs does not change the structural integrity of MOF-801, UiO-66, and UiO-67 (Fig. 2a–c). However, a significant loss of crystallinity can be observed in Fig. 2(d), indicating that the doping of Au NPs does disrupts the crystal structure of UiO-68. Fig. S2 illustrates the FTIR spectrum of the synthesized Au/MOFs. The large broad band around $3000-3700 \text{ cm}^{-1}$ is attributed to the O—H stretching band of

surface adsorbed water molecules [31]. In the MOF organic functional ligands, the stretched bands corresponding to the different carboxylate groups vibrations in the benzene rings appear in the spectral region 1800–1300 cm⁻¹ [32]. The peaks at 875, 763 and 700 cm⁻¹ correspond to the C—H vibration, O—H bend and OCO bend in carboxylic acid ligands, respectively. Peak at 657 cm⁻¹ is attributed to the μ 3-O stretch. The peaks at 667 cm⁻¹ belong to the Zr-(OC) bond [33,34].

The chemical composition and elemental distribution of Au/MOFs were further analysed by XPS (Fig. S3). The results of XPS survey spectrum shows that Au/MOFs are composed of C, Zr, O and Au (Fig. S3 a). In Fig. S3 (b), the peaks at binding energies of 182.7 and 185.2 eV correspond to Zr 3d3/2 and Zr 3d5/2, implying that Zr-O linkage existed in the skeleton of Au/MOFs [35]. In Fig. S3 (c), the O1s spectrum shows three peaks at 530.7 eV, 531.8 eV and 532.9 eV which were attributed to Zr-O, surface adsorbed oxygen and hydroxyl groups, respectively [36]. In addition, the peak area ratios of -OH in Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 were 0.09%, 0.08%, 0.21%, and 0.20%, respectively. It was shown that more -OH functional groups were exposed in Au/UiO-67, which could improve the interaction between target ion and potential adsorption sites [37]. In Fig.Fig. S3 (d), the peaks of Au 4f were divided into Au $4f^{5/2}$ (87.8 eV) and Au $4f^{7/2}$ (84.1 eV), proving the presence of Au [38]. It is noteworthy that the AuNPs load capacity varied among the four nanocomposites prepared. According to the XPS survey, the Au content in Au/MOF-801, Au/UiO-66, Au/UiO-67 and Au/UiO-68 was 0.91%, 1.16%, 1.84%, and 0.93%, respectively. The results show with UiO-67 as a carrier, the suitable pore confinement and larger specific surface area are more favourable to the load of gold nanoparticles. Overall, Zr 3d, and Au 4f show the same positive shift pattern in binding energy with increasing functional ligand chain length. In general, the binding energy shift is related to the electron effect, and its increase implies a decrease in the electron density.

3.2. Electrochemical characterization of the modified electrode

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of Au/MOFs GCE was studied in 5 mM Fe(CN₆)^{3-/4-} containing 0.1 M KCl. When the modified GCE were scanned in the voltage range of $-0.2 \sim 0.6$ V, a well-defined pair of redox peaks was observed (Fig. 3a). Among them, the Au/MOF-801 GCE has a low peak current. However, the enhanced redox currents at the Au/UiO-66, 67, 68 modified electrode surfaces can be explained by the increased pore size of the MOFs favouring the electron transfer of the redox probes. Fig. 3(b) shows the Nyquist diagrams of Au/MOF-801, Au/UiO-66, Au/UiO-67,



Fig. 1. SEM images of Au/MOF-801(a), Au/UiO-66(b), Au/UiO-67(c), and Au/UiO-68(d). TEM of and HRTEM (in the inset) images of Au/MOF-801(e), Au/UiO-66 (f), Au/UiO-66(h).



Fig. 2. XRD patterns of simulated MOFs, MOFs and Au/MOFs; MOF-801(a), UiO-66(b), UiO-67(c), and UiO-68(d).



Fig.Fig.3. The CV curves (a), Nyquist plots of EIS (b) and the equivalent circuit diagram (inset of Fig. 3(b)) of Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 in 5 mM Fe(CN₆)^{3-/4-} containing 0.1 M KCl.

and Au/UiO-68. The semicircle of the high-frequency part corresponds to the electron transfer resistance of the electrode interface, which is further analyzed using an equivalent circuit model [39]. The Ret values of the different electrodes obtained by equivalent circuit fitting are listed in Table S1(Supporting Information). The Ret values of Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 modified electrodes were 382.5 Ω , 323.4 Ω , 229.1 Ω , and 275.4 Ω , respectively. Among them, the Au/UiO-67 has the lowest electron transfer resistance and the excellent electron transfer ability result from the better for loading Au NPs.

According to the voltammetric behavior of the methylmercury

reduction in aqueous media in acidic solutions, the mechanism of the electrochemical reduction on Au^0 or Hg^0 electrodes is as follows [40, 41]:

 $CH_3Hg^+ + e^- \rightleftharpoons CH_3Hg^-$ (1)

$$2CH_3Hg' \rightarrow (CH_3Hg)_2$$
 (2a)

 $(CH_3Hg)_2 \rightarrow (CH_3)_2 Hg + Hg^0$ (2b)

$$CH_{3}Hg' + H^{+} + e^{-} \rightarrow CH_{4} + Hg^{0}$$
(3)

Reaction 1 is a reversible electron transfer process that produced methyl mercury radical (CH₃Hg⁻). Reaction 2 consists of two reactions, CH₃Hg in a fast dimerization reaction to form dimethylmercury ((CH₃Hg)₂), followed by a relatively slow reaction to form dimethylmercury ((CH_3)₂ Hg) and Hg⁰ [41]. In addition to the dimerization, CH₃Hg⁻ may also react with the solvent and be directly reduced to Hg⁰ (Reaction 3) [42]. The voltammetric behavior of CH_3Hg^+ at Au/MOFs modified electrodes was studied by DPASV. Comparison of the CH₃Hg⁺ adsorption amount on Au/UiO-67 modified GCE surface with and without voltage during pre-enrichment process are shown inFig. S4. Fig. S4 (a) shows the EDS mapping data of Au, Zr and Hg on Au/UiO-67 in 0.1 M HAc-NaAc containing 50 μ g/L CH₃Hg⁺, deposited at -0.8 V for 900 s. The results shows that the wt% of Hg element range around 0.2%, which is much higher than in the absence of voltage (Fig. S4 b). This proves that the stripping process on the modified electrode occurs only when metallic mercury is pre-formed on the electrode surface [41].

3.3. Optimization of experimental parameters

The influence of solution pH, deposition potential and time on the stripping signals of 10 μ g/L CH₃Hg⁺ was explored in 0.1 M NaAc-HAc solution. It can be observed that the response current values of CH₃Hg⁺ shows the same trend on Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 GCE. The effect of solution pH on the electro-catalytic oxidation of 10 μ g/L CH₃Hg⁺ at the Au/MOFs/GCE was evaluated in the pH range from 3.0 to 7.0. The highest response peak current was recorded at the pH value of 5.0 (Fig. S5.a), which was chosen as the optimal pH value. As shown at Fig. S5.b. the peak current of CH₃Hg⁺ increased gradually when the deposition potential negatively shifted, and the maximum current was achieved at -0.8 V. With further

decreasing deposition potential, the current conversely decreased, which may be due to H_2 evolution in the vicinity of the electrode hindering CH_3Hg^+ accumulation [43]. Therefore, -0.8 V was selected for the subsequent experiments. Accumulation can improve the loading amount of target on the working electrode, and then may amplify the electrochemical signals. As shown in Fig. S5. (c), the intensity of the response current increased with increasing accumulation time, after which an accumulation time of 900 s was chosen for the next DPV experiments.

3.4. Voltammetric determination of CH_3Hg^+ with au/mofs gce

To investigate the analytical applicability of Au/MOFs/GCE, DPASV were recorded in 0.1 M HAc-NaAc (pH 5.0) containing concentration of CH_3Hg^+ changed between 1 and 25 µg/L shown as Fig. 4. The peak current of CH₃Hg⁺ linearly increases with its concentrations at Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 GCE. The linear regression equations for CH_3Hg^+ were y = 0.074x - 0.136 ($R^2 = 0.981$) at Au/MOF-801 GCE, y = 0.216x - 0.475 (R² = 0.986) at Au/UiO-66 GCE, y =0.363x - 0.045 GCE (R² = 0.997) at Au/UiO-67, and y = 0.221x + 0.108 $(R^2 = 0.996)$ for at Au/UiO-68 GCE (x is the concentration (µg/L) and y is the peak current (µA)). The LODs based on a signal-to-noise ratio of 3 (S/N = 3) at each Au/MOFs/GCE were found to be 0.786 µg/L, 0.374 μ g/L, 0.159 μ g/L, and 0.398 μ g/L for CH₃Hg⁺. Overall, the experimental sensitivities of the Au/MOFs modified electrode followed the order: Au/ MOF-801 < Au/UiO-66 < Au/UiO-68 < Au/UiO-67. Compared to four Zr-MOFs with different pore diameters, the results showed Au/UiO-67 has higher sensitivity and a lower LOD, which may be attributed to the cages diameter in UiO-67 matching well with $\rm CH_3Hg^+$ molecule, that enhances the interaction effect between Au/UiO-67 and CH₃Hg⁺. In



Fig.4. DPASV at GCEs loaded with Au/MOF-801(a), Au/UiO-66(b), Au/UiO-67(c), and Au/UiO-68(d) in 0.1 M HAc-NaAc (pH 5.0) containing CH_3Hg^+ at different concentrations. Inset is the calibration plot of the peak currents versus the concentration of CH_3Hg^+ ranging from 1 to 25 μ g/L.

addition, Au/UiO-68 has poor electronic conductivity due to structural collapse, which is unfavorable for electrochemical determination of CH_3Hg^+ [25]. In addition, the comparisons of electrochemical performance of the Au/MOFs with other previously reported for electrochemical determination of CH_3Hg^+ is listed in Table S2.

3.5. Possible electrochemical determination mechanism

3.5.1. Effect of pore characteristics

The framework structures of MOF-801, UiO-66, UiO-67, and UiO-68 were created based on crystallographic information files (Fig. 5). The metal center of all four MOFs is connected to 12 linkers to form the fcu network structure with octahedral cage and tetrahedral cages [44]. The octahedron cavity of MOF-801, UiO-66, Au/UiO-67, and UiO-68 vary with increasing diameter size, \sim 7 Å, \sim 12 Å, \sim 16 Å, and \sim 20 Å respectively [45]. The nitrogen adsorption-desorption isotherms and pore size distribution curves of Au/MOFs are shown in Fig. S6. Au/MOF-801, Au/UiO-66 Au/UiO-67, and Au/UiO-68 shows the type I isotherm, which refers to the microporous material. The average pore diameter was 4.5 Å, 9.6 Å, 13.08 Å and 17.34 Å, respectively, for Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68. Since the size of CH_3Hg^+ is about 4.5 \times 4.5 \times 5.2 Å, the pore size of Au/MOF-801 is too small to accommodate CH₃Hg⁺. However, the pore size of Au/UiO-66 Au/UiO-67, and Au/UiO-68 are large enough to accommodate CH₃Hg⁺. On one hand, as the MOF pore size increases it will promote the effective movement of ions through the pores. On the other hand, increasing the MOF pore size leads to a larger distance between the active sites. Therefore, the rate of redox electron transfer is suppressed [24]. The sensitivity of CH_3Hg^+ determination by Au/UiO-67 modified GCE was the highest among these Au/MOFs. This may be due to the fact that Au/UiO-67 has a pore size matching well with the CH₃Hg⁺, which facilitates the balance between the electron transfer rate of redox and the diffusion of CH₃Hg⁺.

3.5.2. Electrochemical kinetic studies

In order to explore the electrocatalytic ability of four sensing interfaces toward CH₃Hg⁺, the electrocatalytic parameters were evaluated by chronoamperometry (CA). Fig. 6 shows the time-current relationship at various concentrations of CH₃Hg⁺ on Au/MOF-801, Au/UiO-66, Au/ UiO-67, and Au/UiO-68 modified GCE. Among them, the electrolyte solution of the CA reaction system was 0.1 M HAc-NaAc and the added concentration of CH₃Hg⁺ was 0, 10, 20, 40 µg/L. It can be observed that the response current changes with the addition of CH₃Hg⁺, which indicates the electrocatalytic effect of the modified electrochemical sensitive interface toward CH₃Hg⁺. In addition, The I_L/I_{cat} linearly increases with the square root of time at Au/MOF-801, Au/UiO-66, Au/ UiO-67, and Au/UiO-68 GCE (in the inset of a~d). Therefore, the catalytic rate constant (K_{cat}) at the reaction interface is estimated from the Cottrell equation [46]:

$$\frac{I_{cat}}{I_t} = \left(\pi K_{cat} C_0 t\right)^{1/2}$$

I_{cat}: the respond currents of working electrodes with CH₃Hg⁺; I_L: the respond currents of working electrodes without CH₃Hg⁺. The calculated electrocatalytic rate constants for Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 GCE were 15.074 s^{-1} /gL⁻¹, 33.290 s^{-1} /gL⁻¹, 55.032 s^{-1} /gL⁻¹, and 26.539 s^{-1} /gL⁻¹, respectively.

In addition, the number of electrons transferred at different modified electrodes surface toward CH_3Hg^+ were estimated by CV in 0.1 M NaAc-HAc (pH 5.0) containing 200 µg/L CH_3Hg^+ at various scan rates in the range of $0.05 \sim 0.4 \text{ Vs}^{-1}$. From the results shown in Fig. S7, the oxidation peak currents linearly increase with the square roots of scan rate, indicating that it is a typical diffusion-controlled electrochemical process [25]. Besides, the oxidation peak potentials (E_p) shifted with the increase of scan rate. There was a close fit to linearity between E_p and ln (v). as shown in the illustration in Fig. S7. According to the Laviron's equation as following [47]:

$$E_p = \frac{RT}{\alpha nF} ln \frac{k^0 RT}{\alpha nF} - \frac{RT}{\alpha nF} lnv$$

Where R is the gas constant, T is the temperature, α is the transfer coefficient, k^0 is the standard rate constant, n is the electron transfer number, F is the Faraday constant. For Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 modified electrodes, the electrons transferred number were calculated to be 3.13, 4.65, 6.43 and 3.16, respectively. It was found that the electrocatalysis of Au/MOFs modified GCE toward CH₃Hg⁺ was greatly influenced by the pore confinement effect of MOFs. MOFs are used as carriers, the electrocatalytic properties of composites increase with the increase of ligand length except that the structure collapses.

3.5.3. XPS

The surface interactions between CH_3Hg^+ and MOFs were analyzed by XPS (Fig. 7). From the XPS survey spectrum of Au/MOFs after adsorption of CH_3Hg^+ in Fig. 7(a), the peaks observed are Zr 3d, C 1 s, O 1 s centered at about 183.0, 284.2 and 531.1 eV, respectively. Furthermore, the binding energy at 101.3 eV are assigned to Hg 4f peak, which indicated that Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/ UiO-68 have a certain adsorption capacity for CH_3Hg^+ . The high resolution XPS spectrum of Hg 4f is illustrated in Fig. 7(b), the two peaks centered at about 101.5 and 105.6 eV are attributed to Hg 4 f_{7/2} and Hg 4f_{5/2}. However, the adsorbed Hg contents in four materials make some difference. The atomic percentages of Hg in the four materials followed



Fig.5. Framework structures of CH₃Hg⁺ molecule, Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 (Atom colours: zirconium-sky blue; carbon-dark gray; oxygen-red. Hydrogen atoms are omitted.).



Fig. 6. The current response and the plots of I_{cat}/I_L vs. $t^{1/2}$ (in the inset) of Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 modified GCE by chronomperometry at different concentrations of CH_3Hg^+ (0 $\mu g/L \sim 40 \ \mu g/L$) at the applied potential of $-1.0 \ V$ (vs. Ag/AgCl).

the order: Au/MOF-801(0.09%) < Au/UiO-66(0.11%) < Au/UiO-68 (0.13%) < Au/UiO-67(0.16%). The result displays that the Au/UiO-67 as an electrode modification material is more favorable for CH₃Hg⁺ adsorption among these four materials. Fig. 7(c) shows the spectrum of Au 4f of Au/MOFs before and after adsorption of CH₃Hg⁺ with peaks of Au 4f_{7/2} at 84.7 ~ 85.3 eV and Au 4f_{5/2} at 88.2 ~ 89.1 eV It can be observed that the Au peak in all four materials is slightly shifted after the adsorption of CH₃Hg⁺. The shift of the Au peak of Au/UiO-67 (0.28 eV) is obviously higher than that of Au/MOF-801 (0.02 eV), Au/UiO-66 (0.06 eV) and Au/UiO-68 (0.19 eV). The advantages of Au/UiO-67 may be attributed to the stronger interaction between Au and CH₃Hg⁺, which improve the electrochemical determination performance of CH₃Hg⁺.

3.6. Assessment of chemical interference

Anti-interference is an important parameter for electrode modification materials. The interfering effect on CH_3Hg^+ determination by Au/ MOFs modified GCE were performed in 0.1 M HAc-NaAc (pH 5.0) containing common interferents (Fig. 8). According to the electrochemical reduction mechanism, inorganic Hg^{2+} has a great influence on the determination of CH_3Hg^+ because their stripping current peaks have the same reduction potential [8,48]. 10-fold excess of Hg^{2+} exhibited approximately 75% interference rate at Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 modified GCE. The interference rate was reduced to less than 10% after the addition of DTPA, indicating that DTPA can eliminate the chemical interference of Hg^{2+} in the determination of CH_3Hg^+ . The principle is that DTPA can complex Hg^{2+} and shift the reduction potential in the negative direction [47]. The stable response for CH_3Hg^+ were observed after the addition of common heavy metal ions such as Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Fe^{2+} , and As^{3+} . 10-fold excess of these metal ions exhibited less than 10% of interference (Fig. 8). Besides, the effects of anions such as NO_3^- , NO_2^- , and Cl^- on the electrochemical signal of methylmercury detection were also investigated. The results show that the addition of anions does not change the peak currents of CH_3Hg^+ more than 5%.

3.7. Method reproducibility and stability

As shown in Fig. 9, the repeatability of the Au/MOFs/GCE was evaluated by determining the relative standard deviation (RSD) of the peak current for 10 μ g/L CH₃Hg⁺. After seven consecutive days of measurements, the calculated RSD values for Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 modified GCE were 6.7%, 9.9%, 4.6% and 15.0%, respectively (Fig. 9a). As shown in Fig. 9(b), the stripping peak currents of the CH₃Hg⁺ on the Au/MOFs/GCE were reproducible, with RSD of Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 modified GCE for CH₃Hg⁺ detection were 9.8%, 5.9%, 4.5%, and 5.5%, respectively. The RSD for CH₃Hg⁺ on Au/UiO-67 GCE was lower than 5%, which indicates superb repeatability and reproducibility.

3.8. Analysis of natural water samples

To evaluate the applicability of Au/MOFs, the recovery experiment for CH_3Hg^+ determination was also executed. The actual water samples were taken from Hubingtang Lake, Hefei University of Technology, China. Prior to measurement, impurities in the water were filtered out using a 0.45 µm filter membrane. And then samples were mixed in 0.1 M



Fig. 7. XPS spectra of Au/MOFs after adsorption of CH₃Hg⁺. (a) full view; (b) Hg 4f; (c) Au 4f of Au/MOFs before and after adsorption of CH₃Hg⁺.



Fig. 8. The effect of common ions on the peak current of $10 \ \mu g/L \ CH_3Hg^+$ at Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 modified GCE in 0.1 M HAc-NaAc (pH 5.0). The deposition potential: -0.8 V, the deposition time:900 s.

HAc-NaAc buffer (pH=5.0) at a ratio of 1:9. Four different modified electrodes were used to detect of the mixed solution, no obvious CH_3Hg^+ response signals founded. Besides, the real water samples were analyzed by ICP-MS and ion chromatography. The relevant data were shown in Table S3 and no detectable mercury species were found. The reliability of the constructed sensing interface for CH_3Hg^+ detection in real samples was demonstrated. These results obtained from the Au/MOFs modified GCE are listed in Table S3 for comparison. The standard recovery rate of CH_3Hg^+ on Au/MOF-801, Au/UiO-66, Au/UiO-67, and

Au/UiO-68 modified GCE exceed 90% and the RSD is lower than 5.0%. This indicates that electrochemical sensors based on Au/MOFs GCE have great potential for the detection of CH_3Hg^+ in real samples.

4. Conclusions

In summary, the electrochemical behavior of CH₃Hg⁺ on Au/MOF-801, Au/UiO-66, Au/UiO-67, and Au/UiO-68 was studied and the pore confinement effect of MOFs were considered. It is shown that the pore characteristics of MOFs may have a great influence on the electrochemical detection of CH₃Hg⁺. Among them, Au/UiO-67 modified GCE showed a higher sensitivity (0.363 μ A/ μ gL⁻¹) and a lower limit of detection (0.159 μ g/L) for CH₃Hg⁺. The superior catalytic activity of Au/UiO-67 for the reduction of CH_3Hg^+ probably owing to the synergistic effects of pore confinement and gold catalysis. MOFs are used as carriers, the molecular accessibility and the electrocatalytic properties improve with the increase of ligand length, but excessive length can make the structure collapse. Further insight into the structureconductivity-catalytic mechanism relationship was obtained and the anti-interference performance and stability of Au/MOFs-modified GCE were evaluated. Our strategy exploits the adjustable pore size for MOFs, and it provides guidance for improving the performance of electrochemical sensor devices.

CRediT authorship contribution statement

Yao Liu: Methodology, Investigation, Formal analysis, Writing – original draft. Zhang-Jun Ding: Methodology, Investigation, Writing – original draft. Zhao-Gang Ding: Investigation, Supervision. Rohan Weerasooriya: Writing – review & editing. Xing Chen: Conceptualization, Supervision, Writing – review & editing, Funding acquisition.



Fig. 9. (a) The DPASV peak currents of Au/MOFs modified GCE toward 10 μ g/L CH₃Hg⁺ in the seven consecutive days. (b) The DPASV peak currents of five Au/MOFs modified GCE toward 10 μ g/L CH₃Hg⁺ (N: electrodes number).

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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2023.143374.

References

- C.A. Eagles-Smith, E.K. Silbergeld, N. Basu, P. Bustamante, F. Diaz-Barriga, W. A. Hopkins, K.A. Kidd, J.F. Nyland, Modulators of mercury risk to wildlife and humans in the context of rapid global change, Ambio 47 (2018) 170–197.
- [2] F. Beckers, J. Rinklebe, Cycling of mercury in the environment: sources, fate, and human health implications: a review, Crit. Rev. Environ. Sci. Technol. 47 (2017) 693–794.
- [3] A.G. Bravo, S. Bouchet, J. Tolu, E. Björn, A. Mateos-Rivera, S. Bertilsson, Molecular composition of organic matter controls methylmercury formation in boreal lakes, Nat. Commun. 8 (2017) 14255.
- [4] X.Y. Lang, H.Y. Fu, C. Hou, G.F. Han, P. Yang, Y.B. Liu, Q. Jiang, Nanoporous gold supported cobalt oxide microelectrodes as high-performance electrochemical biosensors, Nat. Commun. 4 (2013) 2169.
- [5] R.Y. Ding, Y.H. Cheong, A. Ahamed, G. Lisak, Heavy metals detection with paperbased electrochemical sensors, Anal. Chem. 93 (2021) 1880–1888.
- [6] M. Korolczuk, A. Stepniowska, Stripping voltammetric determination of methylmercury in the presence of inorganic mercury, Electroanalysis 22 (2010) 2087–2091.
- [7] Rebecca Lai, Eva L. Huang, Feimeng Zhou, D.O. Wipf, Selective determination of methylmercury by flow-injection fast-scan voltammetry, Electroanalysis 10 (1998) 926.
- [8] M. Korolczuk, I. Rutyna, New methodology for anodic stripping voltammetric determination of methylmercury, Electrochem. Commun. 10 (2008) 1024–1026.

- [9] G. Malta, A. Kondrat Simon, J. Freakley Simon, J. Davies Catherine, L. Lu, S. Dawson, A. Thetford, K. Gibson Emma, J. Morgan David, W. Jones, P. Wells Peter, P. Johnston, C.R.A. Catlow, J. Kiely Christopher, J. Hutchings Graham, Identification of single-site gold catalysis in acetylene hydrochlorination, Science 355 (2017) 1399–1403.
- [10] X. Chen, X.X. Ke, Y. Liu, R. Weerasooriya, H. Li, Y.C. Wu, Photocatalytically induced Au/mpg-C₃N₄ nanocomposites for robust electrochemical detection of Cr (VI) in tannery wastewater, J. Environ. Chem. Eng. 9 (2021) 9.
- [11] J.Y. Liu, H.J. Yu, L. Wang, Effective reduction of 4-nitrophenol with Au NPs loaded ultrathin two dimensional metal-organic framework nanosheets, Appl. Catal. A Gen. 599 (2020), 117605.
- [12] F.M. Zhang, L.Z. Dong, J.S. Qin, W. Guan, J. Liu, S.L. Li, M. Lu, Y.Q. Lan, Z.M. Su, H.C. Zhou, Effect of imidazole arrangements on proton-conductivity in metal-organic frameworks, J. Am. Chem. Soc. 139 (2017) 6183–6189.
- [13] L.Y. Wang, H. Xu, J.K. Gao, J.M. Yao, Q.C. Zhang, Recent progress in metal-organic frameworks-based hydrogels and aerogels and their applications, Coord. Chem. Rev. 398 (2019), 213016.
- [14] A.E. Thorarinsdottir, T.D. Harris, Metal-organic framework magnets, Chem. Rev. 120 (2020) 8716–8789.
- [15] S. Kempahanumakkagari, K. Vellingiri, A. Deep, E.E. Kwon, N. Bolan, K.H. Kim, Metal–organic framework composites as electrocatalysts for electrochemical sensing applications, Coord. Chem. Rev. 357 (2018) 105–129.
- [16] Y. Bai, Y.B. Dou, L.H. Xie, W. Rutledge, J.R. Li, H.C. Zhou, Zr-based metal-organic frameworks: design, synthesis, structure, and applications, Chem. Soc. Rev. 45 (2016) 2327–2367.
- [17] C. Wang, X. Liu, N.K. Demir, J.P. Chen, K. Li, Applications of water stable metalorganic frameworks, Chem. Soc. Rev. 45 (2016) 5107–5134.
- [18] H.M. He, Q. Sun, W.Y. Gao, J.A. Perman, F.X. Sun, G.S. Zhu, B. Aguila, K. Forrest, B. Space, S.S. Ma, A stable metal-organic framework featuring a local buffer environment for carbon dioxide fixation, Angew. Chem. Int. Ed. 57 (2018) 4657–4662.
- [19] J.F. Chang, X. Wang, J. Wang, H.Y. Li, F. Li, Nucleic acid-functionalized metalorganic framework-based homogeneous electrochemical biosensor for simultaneous detection of multiple tumor biomarkers, Anal. Chem. 91 (2019) 3604–3610.
- [20] H.W. Zhang, Q.Q. Zhu, R.R. Yuan, H.M. He, Crystal engineering of MOF@COF core-shell composites for ultra-sensitively electrochemical detection, Sens. Actuators B Chem. 329 (2021), 129144.
- [21] J.C. Kemmegne-Mbouguen, F.P. Tchoumi, E. Mouafo-Tchinda, H.W. Langmi, S. E. Bambalaza, N.M. Musyoka, C. Kowenje, R. Mokaya, Simultaneous quantification of acetaminophen and tryptophan using a composite graphene foam/Zr-MOF film modified electrode, New J. Chem. 44 (2020) 13108–13117.
- [22] J. Ru, X.M. Wang, X.L. Cui, F.B. Wang, H. Ji, X.Z. Du, X.Q. Lu, GaOOH-modified metal-organic frameworks UiO-66-NH₂: selective and sensitive sensing four heavymetal ions in real wastewater by electrochemical method, Talanta 234 (2021), 122679.
- [23] T. Zhang, J.Z. Wei, X.J. Sun, X.J. Zhao, H.I. Tang, H. Yan, F.M. Zhang, Continuous and rapid synthesis of UiO-67 by electrochemical methods for the electrochemical detection of hydroquinone, Inorg. Chem. 59 (2020) 8827–8835.
- [24] M. Cai, Q. Loague, A.J. Morris, Design rules for efficient charge transfer in metalorganic framework films: the pore size effect, J. Phys. Chem. Lett. 11 (2020) 702–709.
- [25] M. Deng, X.J. Bo, L.P. Guo, Encapsulation of platinum nanoparticles into a series of zirconium-based metal-organic frameworks: effect of the carrier structures on electrocatalytic performances of composites, J. Electroanal. Chem. 815 (2018) 198–209.
- [26] J. Xia, Y.X. Gao, G. Yu, Tetracycline removal from aqueous solution using zirconium-based metal-organic frameworks (Zr-MOFs) with different pore size and

Y. Liu et al.

topology: adsorption isotherm, kinetic and mechanism studies, J. Colloid Interface Sci. 590 (2021) 495–505.

- [27] Y. Liu, R. Weerasooriya, X. Chen, The metal-organic framework supported gold nanoparticles as a highly sensitive platform for electrochemical detection of methyl mercury species in the aqueous environment, J. Hazard. Mater. 431 (2022), 128608.
- [28] M.J. Katz, Z.J. Brown, Y.J. Colon, P.W. Siu, K.A. Scheidt, R.Q. Snurr, J.T. Hupp, O. K. Farha, A facile synthesis of UiO-66, UiO-67 and their derivatives, ChemComm 49 (2013) 9449–9451.
- [29] Z. Haibao, L. Guang, Z. Xian, X.Y. Tian, Preparation and optical properties of Au nanoparticle "Sandwich" structure (AuNPs/ZNNs/AuNPs) substrate based on ZnO nanosheets template, Mater. Chem. Phys. 268 (2021), 124715.
- [30] G.J. Guan, M. Low, S.H. Liu, Y.Q. Cai, S.Y. Zhang, D.S. Geng, C. Liu, Z.P. Zhang, Y. Cheng, M.S. Bharathi, Y.W. Zhang, M.Y. Han, Destabilization of thiolated gold clusters for the growth of single-crystalline gold nanoparticles and their selfassembly for SERS detection, Part Part Syst. Charact. 32 (2015) 588–595.
- [31] M.M.G. Fouda, J.S. Ajarem, S.N. Maodaa, A.A. Allam, M.M. Taher, M.K. Ahmed, Carboxymethyl cellulose supported green synthetic features of gold nanoparticles: antioxidant, cell viability, and antibacterial effectiveness, Synth. Met. 269 (2020), 116553.
- [32] S.N. Tambat, P.K. Sane, S. Suresh, N.O. Varadan, A.B. Pandit, S.M. Sontakke, Hydrothermal synthesis of NH₂-UiO-66 and its application for adsorptive removal of dye, Adv. Powder Technol. 29 (2018) 2626–2632.
- [33] X.Y. Shi, X.D. Zhang, F.K. Bi, Z.H. Zheng, L.J. Sheng, J.C. Xu, Z. Wang, Y.Q. Yang, Effective toluene adsorption over defective UiO-66-NH₂: an experimental and computational exploration, J. Mol. Liq. 316 (2020), 113812.
- [34] Z.L. Jin, Y.K. Zhang, Q.X. Ma, Orthorhombic WP co-catalyst coupled with electron transfer bridge UiO-66 for efficient visible-light-driven H-2 evolution, J. Colloid Interface Sci. 556 (2019) 689–703.
- [35] P. Hu, X.P. Liang, M. Yaseen, X.D. Sun, Z.F. Tong, Z.X. Zhao, Z.X. Zhao, Preparation of highly-hydrophobic novel N-coordinated UiO-66(Zr) with dopamine via fast mechano-chemical method for (CHO-/Cl-)-VOCs competitive adsorption in humid environment, Chem. Eng, J. 332 (2018) 608–618.
- [36] Z.Q. Yang, X.W. Tong, J.N. Feng, S. He, M.L. Fu, X.J. Niu, T.P. Zhang, H. Liang, A. Ding, X.C. Feng, Flower-like BiOBr/UiO-66-NH₂ nanosphere with improved photocatalytic property for norfloxacin removal, Chemosphere 220 (2019) 98–106.
- [37] Z.S. Li, Q. Li, R. Jiang, Y. Qin, Y. Luo, J.S. Li, W. Kong, Z.G. Yang, C. Huang, X. Qu, T. Wang, L. Cui, G. Wang, S.C. Yang, Z.Y. Liu, X.H. Guo, An electrochemical sensor

based on a MOF/ZnO composite for the highly sensitive detection of Cu(ii) in river water samples, RSC Adv. 12 (2022) 5062–5071.

- [38] G. Kumar, L. Tibbitts, J. Newell, B. Panthi, A. Mukhopadhyay, R.M. Rioux, C. J. Pursell, M. Janik, B.D. Chandler, Evaluating differences in the active-site electronics of supported Au nanoparticle catalysts using Hammett and DFT studies, Nat. Chem. 10 (2018) 268–274.
- [39] R.X. Xu, X.Y. Yu, C. Gao, Y.J. Jiang, D.D. Han, J.H. Liu, X.J. Huang, Nonconductive nanomaterial enhanced electrochemical response in stripping voltammetry: the use of nanostructured magnesium silicate hollow spheres for heavy metal ions detection, Anal. Chim. Acta 790 (2013) 31–38.
- [40] R.C. Heaton, H.A. Laitinen, Electroanalytical studies of methylmercury in aqueous solution, Anal.Chem. 46 (1974) 547–553.
- [41] A. Królicka, A. Bobrowski, A. Kowal, Effects of electroplating variables on the voltammetric properties of bismuth deposits plated potentiostatically, Electroanalysis 18 (2006) 1649–1657.
- [42] V.A. Kurmaz, V.P. Gul'tyai, Electrode reactions and electroanalysis of organomercury compounds, Russ. Chem. Rev. 79 (2010) 307–350.
- [43] C.C. Bi, X.X. Ke, X. Chen, R. Weerasooriya, Z.Y. Hong, L.C. Wang, Y.C. Wu, Assembling reduced graphene oxide with sulfur/nitrogen- "hooks" for electrochemical determination of Hg(II), Anal. Chim. Acta 1100 (2020) 31–39.
- [44] Q.Y. Yang, V. Guillerm, F. Ragon, A.D. Wiersum, P.L. Llewellyn, C. Zhong, T. Devic, C. Serre, G. Maurin, CH₄ storage and CO₂ capture in highly porous zirconium oxide based metal-organic frameworks, ChemComm 48 (2012) 9831–9833.
- [45] J.M. Mayers, R.W. Larsen, The effect of cavity size on ruthenium (II) tris-(2,2bipyridine) photophysics encapsulated within zirconium based metal organic frameworks, Inorganica Chim. Acta 526 (2021).
- [46] Y.Z. Yang, Q.X. Wang, W.W. Qiu, H.X. Guo, F. Gao, Covalent immobilization of Cu-3(btc)(2) at chitosan-electroreduced graphene oxide hybrid film and its application for simultaneous detection of dihydroxybenzene isomers, J. Phys. Chem. C 120 (2016) 9794–9803.
- [47] X. Chen, X.T. Sun, M.S. Cui, Y. Liu, K.P. Cui, R. Weerasooriya, Electrochemical determination of methylmercury via modulating bandgap of sulfur doped graphitic carbon nitride, J. Environ. Chem. Eng. 9 (2021), 105510.
- [48] O. Abollino, A. Giacomino, M. Malandrino, S. Marro, E. Mentasti, Voltammetric determination of methylmercury and inorganic mercury with an home made gold nanoparticle electrode, J. Appl. Electrochem. 39 (2009) 2209–2216.