

Polyoxometalate-incorporated metal–organic frameworks as electrochemical sensors for ascorbic acid, dopamine and uric acid

Shuang Liu¹, Li-Ping Wang¹, Jia-Jia Li¹, Xiang-Jie Bo¹, Dong-Ying Du¹ , and Zhong-Min Su²

¹ National & Local United Engineering Laboratory for Power Battery, Department of Chemistry, Northeast Normal University, Changchun 130024, China

² State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun 130021, China

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 Address correspondence to dudy540@nenu.edu.cn



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ABSTRACT: Real-time analysis of small-molecule metabolites such as ascorbic acid (AA), dopamine (DA), and uric acid (UA) is valuable for investigating biological systems and supporting disease diagnosis. As a representative metal-organic framework (MOF), MIL-101(Cr) combines strong chemical stability with a large specific surface area, demonstrating considerable potential in numerous fields. Herein, we demonstrated a series of polyoxometalate (POM)-incorporated bimetallic MOF composites, MIL-101(Cr₂Fe)-POM-T (POM = SiW₁₂ or PW₁₂, T = 180 or 220), which were evaluated as electrochemical sensors for measuring AA, DA, and UA. Among them, MIL-101(Cr₂Fe)-PW₁₂-220 delivered the strongest electrochemical sensing response in 0.1 M PBS (pH = 7.0). After optimization, MIL-101(Cr₂Fe)-PW₁₂-220 demonstrated a broad linear detection range (412–6550, 1–160, and 2–160 μM) and low limits of detection (51.1, 0.385, and 0.644 μM, S/N = 3) when AA, DA, and UA were measured individually. In addition, MIL-101(Cr₂Fe)-PW₁₂-220 also enabled AA, DA, and UA analysis in human serum samples, supported by its broad linear range, low detection limits, selectivity, and stability.

KEYWORDS: metal-organic frameworks; polyoxometalates; electrochemical sensors; ascorbic acid; dopamine; uric acid

1 Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), typically composed of metal ions (or clusters) and organic linkers, represent an emerging class of highly ordered porous materials [1–5]. Owing to their tunable structures and outstanding physicochemical properties, MOFs have found extensive applications in various fields such as gas adsorption and separation [6–9], catalysis [10–12], sensing [13–15], and drug delivery [16]. Since the Yaghi group reported the significant breakthrough in multivariate MOFs [17], multi-component MOFs exhibiting complementary or conflicting properties have emerged as a research hotspot within the scientific community [18–20]. Polyoxometalates (POMs) represent a well-defined library of inorganic clusters with Lewis and Bronsted acidities that can be used as efficient solid-acid catalysts for a range of organic reactions [21]. Diversified material-design strategies including heteroatom doping, bimetallic regulation and heterostructure construction have been proven to be effective pathways to boost the electrocatalytic performance of electrode materials [22–25]. However, their practical applications were often restricted by

high water-solubility and low conductivity. Furthermore, incorporating POMs into porous MOFs endows the composites with outstanding redox and proton conductivity, significantly improving their catalytic activities [26–27], which is an efficient strategy to address these limitations [28–32]. Therefore, recent studies have increasingly focused on preparing POM-containing MOFs and exploring their applications.

Three critical endogenous small compounds, namely ascorbic acid (AA), dopamine (DA), and uric acid (UA), play indispensable roles in diverse biological metabolic processes. AA (vitamin C) plays a crucial role in numerous bodily processes, including collagen synthesis and iron absorption. Deficiency in AA increases susceptibility to pneumonia and heart disease [33–34]. DA is an important monoamine neurotransmitter in human metabolism, the central nervous system, cardiovascular function, renal function, endocrine function, and hormonal systems [35–36]. As the final product of purine metabolism, UA holds significant physiological and pathological importance for the human body. Elevated concentrations of UA in bodily fluids may lead to conditions such as gout, kidney stones, and hypertension. Low uric acid levels have been associated with multiple sclerosis and certain

genetic disorders [37]. Rapid and reliable quantitative assays for three key biomolecules (AA, DA, and UA) delivers important research merits covering biomedical, neurochemistry, clinical diagnosis, and pathological mechanism. Various methods have been explored for the detection of AA, DA, and UA, such as high-performance liquid chromatography [38], chemiluminescence [39], capillary electrophoresis [40], and ultraviolet-visible spectroscopy [41]. However, the electrochemical method has garnered increasing attention due to its rapid response, high sensitivity, excellent stability, and outstanding selectivity [42-44].

Taking these points into account, a stable porous MOF, MIL-101(Cr), was selected as the parent MOF to construct POM-incorporated MOF composites, (i) MIL-101(Cr) showed good resistance to air, water and common solvents, and has two kinds of mesoporous cages with sizes of ~ 3.4 and ~ 2.9 nm (Fig. S1) [45]; (ii) the sizes of Keggin-type POM units matched with the zeotype quasispherical cages in MIL-101(Cr) [46], and POMs possess unique redox and electrochemical properties [47]; and (iii) the application of transition-metal clusters in catalysis makes heterometallic clusters increasingly attractive owing to the synergistic effects between different metal species [48-49]. Fortunately, a series of POM-incorporated bimetallic MOF materials, MIL-101(Cr₂Fe)-POM-T (POM = SiW₁₂ or PW₁₂, T = 180 or 220), were synthesized at different temperatures. Furthermore, MIL-101(Cr₂Fe)-POM-T-modified electrodes were fabricated and assessed for electrochemical sensing of three physiological small molecules. Under the optimization condition (0.1 M PBS, pH = 7.0), MIL-101(Cr₂Fe)-PW₁₂-220 stood out with the maximum electrochemical signal responses among all tested candidates. Because of its broad linear range, low detection limits, selectivity, and stability, MIL-101(Cr₂Fe)-PW₁₂-220 was further applied to the practical analysis of AA, DA, and UA in human serum samples.

2 Experimental

2.1. Synthesis of MIL-101(Cr)

MIL-101(Cr) was prepared according to the reported method [35]. Cr(NO₃)₃·9H₂O (400.0 mg, 1.00 mmol) and H₂BDC (164.0 mg, 1.00 mmol) were placed in a 15 mL stainless steel autoclave lined with Teflon. Then, distilled water (5.0 mL) and concentrated nitric acid (0.1 mL) were introduced before heating at 220 °C for 8 h. After the vessel cooled naturally to room temperature, the solid was isolated by centrifugation at 8000 rpm. The product was washed three times with distilled water and then dried at 60 °C for 12 h.

2.2. Synthesis of MIL-101(Cr₂Fe)

A mixture of Cr(NO₃)₃·9H₂O (266.7 mg, 0.67 mmol), Fe(NO₃)₃·9H₂O (134.7 mg, 0.33 mmol), and H₂BDC (164.0 mg, 1.00 mmol) was placed in a 15 mL Teflon-lined stainless steel autoclave. Next, distilled water (5.0 mL) and concentrated nitric acid (0.1 mL) were introduced before the mixture was heated at 220 °C for 8 h. After natural cooling to room temperature, the precipitate was collected by centrifugation at 8000 rpm. The product was washed three times with distilled water and dried at 60 °C for 12 h.

2.3. Syntheses of MIL-101(Cr₂Fe)-SiW₁₂-T (T = 180 or 220)

A mixture of Cr(NO₃)₃·9H₂O (88.9 mg, 0.22 mmol), Fe(NO₃)₃·9H₂O (44.9 mg, 0.11 mmol), H₄SiW₁₂O₄₀ (8.3 mg, 0.0028 mmol), and H₂BDC (54.7 mg, 0.33 mmol) was placed in a 15 mL Teflon-lined stainless steel autoclave. Distilled water (5.0 mL) was introduced before hydrothermal treatment at either 180 °C or 220 °C for 20 h. After natural cooling to room temperature, the precipitated solids were isolated by centrifugation at 8000 rpm. The products were washed three times with distilled water and dried at 60 °C for 12 h.

2.4. Syntheses of MIL-101(Cr₂Fe)-PW₁₂-T (T = 180 or 220)

A mixture of Cr(NO₃)₃·9H₂O (266.7 mg, 0.67 mmol), Fe(NO₃)₃·9H₂O (134.7 mg, 0.33 mmol), H₃PW₁₂O₄₀ (288.0 mg, 0.10 mmol) and H₂BDC (164.0 mg, 1.00 mmol) was placed in a 15 mL Teflon-lined stainless steel autoclave. Distilled water (5.0 mL) was then introduced, and the mixture was heated at either 180 °C or 220 °C for 12 h. After natural cooling to room temperature, the crude solids were recovered by centrifugation at 8000 rpm. The products were washed three times with distilled water and dried at 60 °C for 12 h.

3 Results and discussion

3.1. Design and preparation

Because of its high surface area and large pore volume, MIL-101(Cr) is desirable for incorporating small guest fragments. In addition, the introduction of iron(III) not only enhanced materials' chemical stability but also improved their catalytic activities [50]. Moreover, the introduction of POM fragments into MOF materials combines the advantages of POMs and MOFs, featuring specific structures and abundant redox sites [51]. In this sense, MIL-101(Cr) was chosen as the host MOF. The bimetallic MIL-101(Cr₂Fe) was synthesized by introducing transition metal iron(III) ions via solvothermal synthesis. Furthermore, Keggin-type POM units were incorporated into MIL-101(Cr₂Fe) at different temperatures through a one-pot method, yielding the POM-incorporated MOF composites (Fig. S2), MIL-101(Cr₂Fe)-POM-T (POM = SiW₁₂ or PW₁₂, T = 180 or 220).

As demonstrated by the powder X-ray diffraction (PXRD) patterns, the peak positions of the as-prepared MIL-101(Cr) agreed with those of the simulated one (Fig. 1(a)) [52], confirming the successful synthesis of the MOF framework. In addition, MIL-101(Cr₂Fe) and the MIL-101(Cr₂Fe)-POM-T series showed PXRD patterns closely matching those of the prepared MIL-101(Cr). These observations indicated that adding iron centers and POM units preserved the parent MOF framework.

Furthermore, the Fourier-transform infrared (FT-IR) spectra of these samples were performed (Fig. S3). These spectra not only contain typical infrared bands belonging to MIL-101(Cr), but also contain typical bands belonging to Keggin-type POM structures. After the introduction of Fe(III) centers, a peak was observed at 575 cm⁻¹ for MIL-101(Cr₂Fe) and MIL-101(Cr₂Fe)-

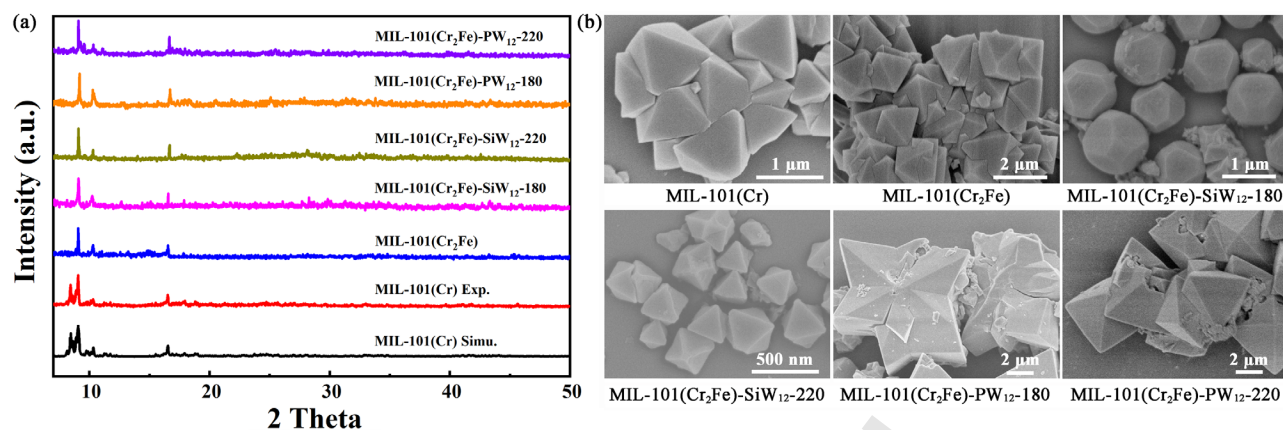


Figure 1 (a) PXRD patterns and (b) SEM images of MIL-101(Cr), MIL-101(Cr₂Fe) and MIL-101(Cr₂Fe)-POM-T series.

POM-T series, which can be attributed to the Fe–O stretching vibration [53]. These results confirmed the successful introduction of Fe(III) sites into parent MIL-101(Cr). After immobilization of POM species, MIL-101(Cr₂Fe)-POM-T samples exhibited additional characteristic peaks at 974, 881, and 808 cm⁻¹, which can be attributed to the stretching vibrations of W=O_d, W–O_b–W, and W–O_c–W bonds (O_d = terminal oxygen atoms, O_b = bridging oxygen atoms connecting pairs of metal atoms not sharing a central atom, and O_c = bridging oxygen atoms connecting pairs of metal atoms sharing a central atom) [54], respectively. In addition, the characteristic peaks at 926 and 1080 cm⁻¹ can be assigned to the stretching vibrations of Si–O_a and P–O_a bonds of MIL-101(Cr₂Fe)-SiW₁₂-T and MIL-101(Cr₂Fe)-PW₁₂-T (O_a = central oxygen atoms), respectively. These characteristic peaks confirmed that the POM species remain intact after immobilization. The small magnitude of peak shifts suggested that MIL-101(Cr₂Fe)-POM-T composites were obtained by the combination of POM and MOF components rather than a simple physical mixture.

The XPS analysis of MIL-101(Cr₂Fe)-PW₁₂-220 and MIL-101(Cr₂Fe) was used to determine the oxidation states of the metal centers. As shown in Fig. S4(a), the binding energies were observed at 577.52 and 587.15 eV for Cr 2p_{3/2} and Cr 2p_{1/2}, supporting the presence of Cr³⁺ species [55]. The peaks at 712.02 and 725.81 eV corresponded to Fe 2p_{3/2} and Fe 2p_{1/2} (Fig. S4(b)), suggesting the presence of the Fe³⁺ sites in MIL-101(Cr₂Fe) and MIL-101(Cr₂Fe)-PW₁₂-220 [56]. Furthermore, the peaks occurred at 34.96 and 37.21 eV corresponding to W 4f_{7/2} and W 4f_{5/2} (Fig. S5), indicating the peak position of the W⁶⁺ centers in MIL-101(Cr₂Fe)-PW₁₂-220 [57].

In addition, inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to quantify the metal contents in MIL-101(Cr₂Fe), MIL-101(Cr₂Fe)-PW₁₂-220, and MIL-101(Cr₂Fe)-SiW₁₂-220. The ratios of the chromium to iron were close to 2:1, which agreed with the feed ratios for their syntheses (Table S1). Based on the W/Cr ratios of 0.72 and 0.81, the POM contents were calculated to be 25.18 wt% and 20.63 wt% in MIL-101(Cr₂Fe)-PW₁₂-220 and MIL-101(Cr₂Fe)-SiW₁₂-220 (Table S2). Correspondingly, their corresponding formula were presented in Table S3.

The morphology of the MIL-101(Cr₂Fe)-POM-T series was

examined by scanning electron microscopy (SEM). The as-synthesized MIL-101(Cr) and MIL-101(Cr₂Fe) particles exhibited a regular and smooth octahedral morphology (Fig. 1(b)). In addition, MIL-101(Cr₂Fe)-POM-220 retained the octahedral shape as synthesized at 220 °C. However, MIL-101(Cr₂Fe)-PW₁₂-180 displayed octahedral agglomeration, and MIL-101(Cr₂Fe)-SiW₁₂-180 was truncated octahedron in shape. These results suggested that reaction systems were more likely to yield octahedral samples when reacting at 220 °C than at 180 °C. Relatively speaking, there were significant differences in the particle sizes of these samples (Fig. S6), yet no specific pattern of variation is evident. Additional energy-dispersive X-ray (EDX) analysis was performed on all obtained materials, aiming to fully characterize their inherent elemental makeup. Cr, Fe, and W were detected in the EDS spectra of the MIL-101(Cr₂Fe)-POM-T series (Fig. S7). Moreover, elemental mapping analysis was further carried out (Figs. S8 – S11). As described in Figs. S10 – S11, chromium, iron, and tungsten were homogeneously distributed throughout the entire structure of MIL-101(Cr₂Fe)-POM-220. Compared with MIL-101(Cr) and MIL-101(Cr₂Fe) (Figs. S8 and S9), the results suggested that POM species were successfully incorporated into the parent MOF.

N₂ adsorption-desorption analysis was used to examine the porous structures of the MIL-101(Cr₂Fe)-POM-T series. As shown in Fig. S12, MIL-101(Cr₂Fe)-POM-T exhibited typical type-I behaviors of microporous materials [45]. The measured nitrogen uptakes of MIL-101(Cr), MIL-101(Cr₂Fe) and MIL-101(Cr₂Fe)-POM-T were 1076.40, 714.76, 622.31, 592.50, 531.50, and 501.73 cm³·g⁻¹, with corresponding Brunauer–Emmett–Teller (BET) surface areas of 2723.43, 721.10, 1821.44, 1521.56, 1320.48, and 1312.07 m²·g⁻¹ (Table S4). The nitrogen uptake and BET areas of the MIL-101(Cr₂Fe)-POM-T series decreased after the introduction of POM units. This is because part of the cages was occupied by POM units, further confirming that POM units were successfully incorporated into MIL-101(Cr₂Fe)-POM-T [58]. In addition, nitrogen uptake and BET areas of the MIL-101(Cr₂Fe)-POM-T series were close to those documented in the literature [56, 59]. After

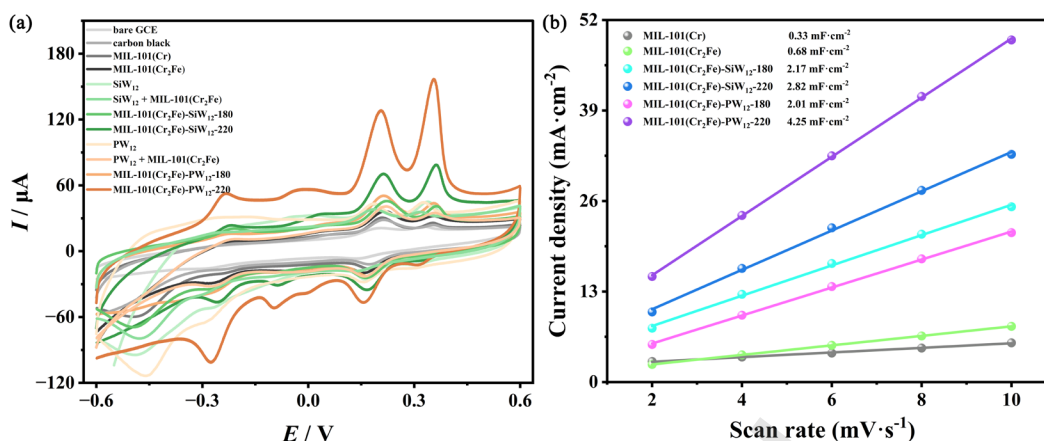


Figure 2 (a) CV curves and (b) double-layer capacitive of MIL-101(Cr), MIL-101(Cr₂Fe), and MIL-101(Cr₂Fe)-POM-T series.

comprehensive analysis of the nitrogen adsorption and BET data, it was clearly observed that lower N₂ uptake and BET areas were recorded for the composites synthesized at 220 °C compared with those prepared at 180 °C. This phenomenon perhaps resulted from the more efficient introduction and homogeneous distribution of POM species in the MOF cages, which were promoted at higher temperatures.

In addition, UV-Vis spectra were collected for the MIL-101(Cr₂Fe)-POM-T series (Fig. S13), as well as MIL-101(Cr₂Fe) and MIL-101(Cr) were also examined for comparison. For MIL-101(Cr), a distinct absorption peak appeared at 250 nm, along with two weaker bands at approximately 430 and 580 nm. These features can be assigned to $\pi \rightarrow \pi^*$ transitions and spin-allowed d-d transitions of the Cr³⁺ centers, which was consistent with previous reports [60]. The absorption peaks of MIL-101(Cr₂Fe) closely resembled that of MIL-101(Cr). In contrast, MIL-101(Cr₂Fe)-POM-T exhibited a broader peak covering the range of 250–300 nm, following the incorporation of POM units. This result can be attributed to the characteristic absorption of Keggin-type POMs around 260 nm, originating from O $\rightarrow$ W charge transfer [61]. Moreover, the absorption intensities were enhanced at 430 and 580 nm after POM introduction [51].

3.2. Electrochemical characterization

To validate the electrochemical performance of different materials, electrochemical measurements were performed in 0.1 M KCl solution containing 5.0 mM [Fe(CN)₆]^{3-/4-} (1:1) using cyclic voltammetry (CV). As shown in Fig. S14, the peak-current signals of POM-incorporated MOF composites were markedly stronger than those of MIL-101(Cr) and MIL-101(Cr₂Fe). Among them, MIL-101(Cr₂Fe)-PW₁₂-220 demonstrated the strongest electrochemical response. Additionally, CV curves were obtained for MIL-101(Cr₂Fe)-PW₁₂-220 at different scan rates (Fig. S15(a)). Further analysis revealed a linear dependence between peak currents and the square roots of scan rates (Fig. S15(b)), indicating that the electrochemical reaction was a diffusion-controlled process.

In addition, the electrochemical impedance spectroscopy (EIS) measurements were performed to study the impedance

change, and the corresponding Nyquist plots were described in Fig. S16. To understand the interface behavior more intuitively, the Randles equivalent circuit was presented after fitting the impedance data by Z-view software (inset of Fig. S16) [62]. In general, the charge-transfer resistance (R_{ct}) at the surface can be assessed from the diameter of a semicircle at high frequencies. And, the R_{ct} value varies inversely with the electrochemical activity. Compared with the bare glassy carbon electrode (GCE) and carbon black-modified electrode, MOF-modified electrodes show markedly reduced R_{ct} values (Table S5). Relatively, the semicircle diameters of MIL-101(Cr₂Fe)-POM-T series were smaller than those of MIL-101(Cr) and MIL-101(Cr₂Fe), and the corresponding R_{ct} values were reduced. These results suggested that the introduction of Fe(III) centers and POM species accelerates the electron transfer on the electrode surface. Among them, MIL-101(Cr₂Fe)-PW₁₂-220 possesses the smallest R_{ct} value, suggesting that the incorporation of PW₁₂ species at 220 °C is more effective at modulating the pore microenvironment—and consequently influencing interfacial charge transfer—than introducing SiW₁₂ species or synthesizing at 180 °C.

3.3. Electrochemical detection

As essential biomolecules existing in bodily fluids, fast and accurate measurement of AA, DA, and UA is valuable in biomedical, neurochemical, diagnostic, and pathological research. The porous POM-incorporating MIL-101(Cr₂Fe)-POM-T series offers a useful basis for designing and optimizing electrochemical sensors.

The current responses of different electrodes were investigated for AA, DA, and UA detection (Fig. 2(a)). Compared with the bare GCE and carbon black, MIL-101(Cr) and MIL-101(Cr₂Fe) exhibited certain electrochemical responses. As expected, the MIL-101(Cr₂Fe)-POM-T series exhibited markedly higher peak current responses than MIL-101(Cr) and MIL-101(Cr₂Fe) (Figs. S17 and S18). Meanwhile, the electrochemical sensing performance of pure POM materials and physical mixtures of POM and MIL-101(Cr₂Fe) was far from those of the MIL-101(Cr₂Fe)-POM-T composites. These results suggested that chemical composites exhibited

superior electrochemical detection performance, compared with simple physical mixtures. MIL-101(Cr₂Fe)-POM-220 exhibited higher peak currents than those of MIL-101(Cr₂Fe)-POM-180 (Fig. S19), suggesting that higher temperature facilitates the synthesis of POM-incorporated MOF composites with superior electron transfer properties. These results were consistent with EIS measurements (Fig. S16). Among them, MIL-101(Cr₂Fe)-PW₁₂-220 exhibited the strongest electrochemical response, far exceeding that of MIL-101(Cr₂Fe)-SiW₁₂-220. In previous molecular orbital studies, the LUMO energy of PW₁₂O₄₀³⁻ lies slightly lower than that of SiW₁₂O₄₀⁴⁻ under similar conditions [63-64]. In this sense, PW₁₂O₄₀³⁻ more readily accepts electrons from the analyte molecules than that of SiW₁₂O₄₀⁴⁻. Therefore, the electrochemical redox reactions were promoted on the MIL-101(Cr₂Fe)-PW₁₂-220-modified electrode compared to MIL-101(Cr₂Fe)-SiW₁₂-220. Relatively, the particle size and morphology have a negligible effect on the electrochemical detection behavior of these materials, primarily because their dimensions are in the micrometer range. We believe that the more significant impact stems from the synergistic effect between POM species and parent MOF frameworks after introducing iron(III) centers and POM units. The anodic peaks of MIL-101(Cr₂Fe)-PW₁₂-220 were found at potentials of approximately -0.027, 0.203, and 0.335 V for AA, DA, and UA detection (Fig. 2(a)) [50, 65], respectively, displaying three well-separated oxidation peaks. MIL-101(Cr₂Fe)-PW₁₂-220 exhibited a well-distinguish activity for the three analytes, thereby enabling the three analytes to be distinguished electrochemically.

To investigate the intrinsic catalytic activity in depth, electrochemical surface area (ECSA) measurements were performed under a series of gradient scan rates [66-67]. The ECSA values of MIL-101(Cr₂Fe)-POM-T series were assessed via the double-layer capacitance (C_{dl}) obtained from the CV curves (Fig. S20). As shown in Fig. 2(b), the C_{dl} increased markedly after POM incorporation relative to MIL-101(Cr) and MIL-101(Cr₂Fe). Among them, MIL-101(Cr₂Fe)-PW₁₂-220 exhibited the maximum C_{dl} value (4.25 mF·cm⁻²), suggesting that MIL-101(Cr₂Fe)-PW₁₂-220 possessed a corresponding maximum ECSA value. These results indicated that MIL-101(Cr₂Fe)-PW₁₂-220 had the largest population of accessible active sites.

To further evaluate the electrochemical behavior of MIL-101(Cr₂Fe)-PW₁₂-220, scan-rate effects on peak currents were examined in 0.1 M PBS solution at pH = 7.0 within the scan rate range of 25 to 300 mV·s⁻¹ (Fig. S21(a)). Furthermore, peak current varied linearly with the square root of scan rate (Fig. S21(b) and Table S6), indicating that the oxidation reactions of AA, DA, and UA on MIL-101(Cr₂Fe)-PW₁₂-220 electrode surface were governed by diffusion [68].

3.3.1. Optimization

To investigate the impact of operating conditions on detection efficiency, relevant parameters were optimized systematically. Two key factors were focused on: (i) the mass ratio of POM-based MOF composite to carbon material and (ii) the pH values of buffer solution. Under conditions where all three analytes were simultaneously present, MIL-101(Cr₂Fe)-PW₁₂-220 exhibited optimal current response when the mass ratio was 1:2

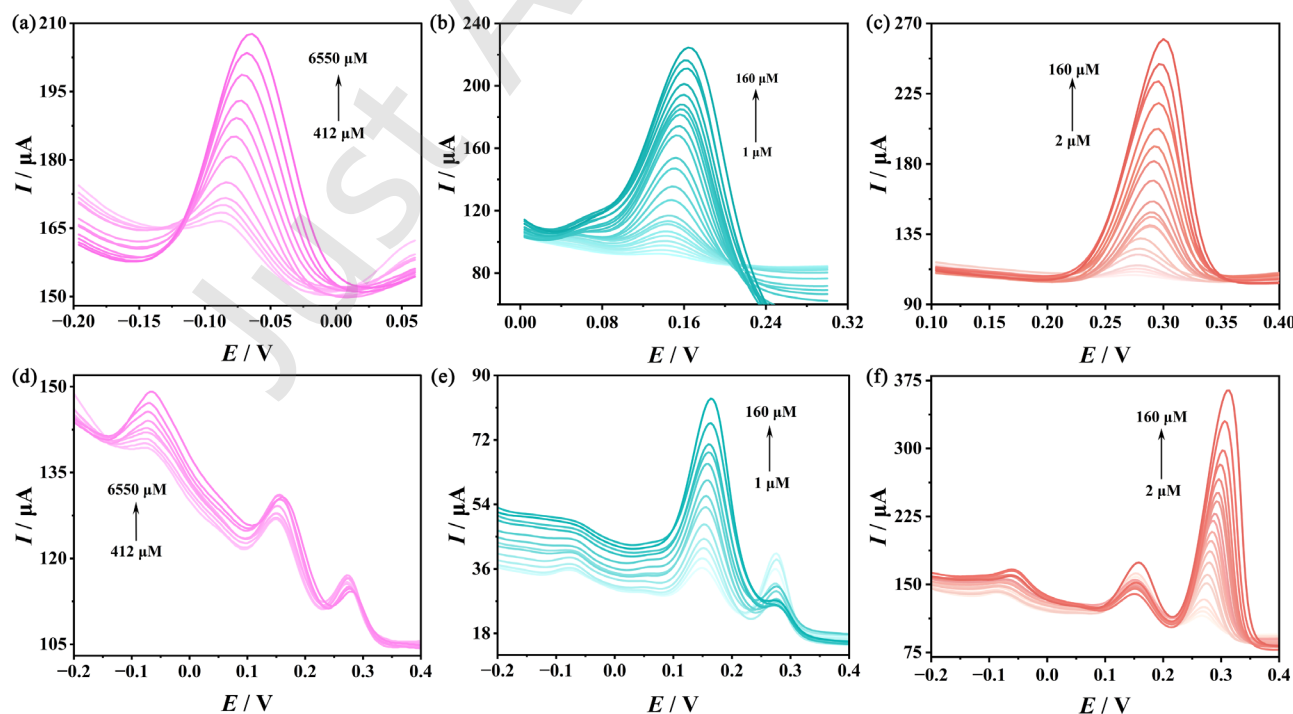


Figure 3 DPV curves of MIL-101(Cr₂Fe)-PW₁₂-220 for the individual detection of (a) AA, (b) DA, and (c) UA with varying concentrations in 0.1 M PBS solution (pH = 7.0); DPV curves of MIL-101(Cr₂Fe)-PW₁₂-220 for the detection of (d) AA ([DA]: 5 μM and [UA]: 5 μM), (e) DA ([AA]: 400 μM and [UA]: 5 μM), and (f) UA ([AA]: 400 μM and [DA]: 5 μM) with different concentrations in 0.1 M PBS solution (pH = 7.0).

(Fig. S22).

As shown in Fig. S23(a), the oxidation peak potential progressively shifted to more negative direction with pH value increasing from 5.0 to 9.0, indicating proton participation occurred in the reaction [69]. The oxidation peak potentials exhibited a good linear relationship with pH values (Fig. S23(b)). The slopes were respective 55.1, 53.6, and 57.1 mV/pH for AA, DA, and UA detection (Table S7), approaching the theoretical value of 59.2 mV/pH. This result suggested that the number of protons and electrons was equal participating in the electrochemical oxidation reaction of AA, DA, and UA (Fig. S24) [70]. The oxidation peak currents increased from 5.0 to 7.0 and then decreased, with the maximum occurring at pH = 7.0 (Fig. S23(c)). The pH of the buffer solution influenced the electrochemical behaviors, which is consistent with proton participation in the electrode reaction [71]. Therefore, subsequent experiments were conducted at a pH value of 7.0.

3.3.2. Individual and simultaneous determination

To evaluate the individual sensing performance of MIL-101(Cr₂Fe)-PW₁₂-220, electrocatalytic oxidation of AA, DA, and UA was examined by varying their concentrations in PBS (pH = 7.0). The linear concentration ranges were evaluated via differential pulse voltammetry (DPV) (Fig. 3(a)-(c)). Peak currents rose as the concentrations of AA, DA, and UA increased. Within the concentration ranges of 412–6550, 1–160, and 2–160 μ M, the peak currents varied linearly with concentration of AA, DA, and UA (Fig. S25). Therefore, the following relationships were obtained: as for AA, I_{pa} (μ A) = 0.016 [AA] – 0.715 ($R^2 = 0.9949$, 412–1000 μ M) and I_{pa} (μ A) = 0.008 [AA] + 10.377 ($R^2 = 0.9942$, 1000–6550 μ M); as for DA, I_{pa} (μ A) = 2.630 [DA] – 0.314 ($R^2 = 0.9940$, 1–10 μ M) and I_{pa} (μ A) = 0.928 [DA] + 19.694 ($R^2 = 0.9949$, 10–160 μ M); as for UA, I_{pa} (μ A) = 1.084 [UA] + 0.420 ($R^2 = 0.9991$, 2–10 μ M) and I_{pa} (μ A) = 0.974 [UA] + 6.231 ($R^2 = 0.9943$, 10–160 μ M). The calculated limits of detection (LODs) were 51.1, 0.385, and 0.644 μ M for the individual detection of AA, DA, and UA ($S/N = 3$), respectively.

To achieve high selectivity, sensitivity, and discrimination performance, DPV curves were conducted to test the variation trends corresponding to one analyte against its concentrations in the presence of another two analytes. As shown in Fig. 3(d), only the oxidation peak response of AA increased with rising AA concentrations while keeping the concentrations of DA and UA constant. DA and UA produced no measurable interference in AA detection, with their oxidation peaks remaining virtually unchanged. Similarly, the presence of another two analytes did not cause interference when the concentrations of DA and UA were increased (Fig. 3(e) and (f)). The oxidation peaks of the three analytes exhibited linear relationships with their concentrations in the range of 412–6550 ([DA]: 5 μ M and [UA]: 5 μ M), 1–160 ([AA]: 400 μ M and [UA]: 5 μ M), and 2–160 μ M ([AA]: 400 μ M and [DA]: 5 μ M) (Fig. S26). The LODs were 67.2, 0.429, and 0.708 μ M for AA, DA, and UA ($S/N = 3$), respectively. Taken together, these experiments showed that, MIL-101(Cr₂Fe)-PW₁₂-220 demonstrated the ability to selectively

detect the three biomolecules in solutions without interference from another two species.

Additionally, the electrochemical sensing performance of MIL-101(Cr₂Fe)-PW₁₂-220 was investigated with varying concentrations of AA, DA, and UA when they coexisted in a system. As described in Fig. 4(a), three resolved oxidation peaks were observed at –0.061, 0.168, and 0.313 V, respectively, corresponding to the oxidation of AA, DA, and UA. The potential differences (ΔE) between adjacent oxidation peaks were 0.229, 0.374, and 0.145 V, respectively. The AA, DA, and UA oxidation peaks did not overlap, indicating that MIL-101(Cr₂Fe)-PW₁₂-220 exhibited excellent discrimination during the simultaneous detection of these three biomolecules. Furthermore, when the concentrations of AA, DA, and UA varied concurrently in a coexisting state, the intensities of their corresponding oxidation peak also changed (Fig. 4(a)). The linear regression equations were obtained relating the oxidation peak responses of AA, DA, and UA to their concentrations (Fig. S27), with linear ranges of 508–4650, 1–100, and 2–100 μ M, respectively. The resulting LODs were 75.7, 0.143, and 0.497 μ M for AA, DA, and UA ($S/N = 3$), respectively.

Compared with other MOF or POM-based materials in the documented literature (Tables S8 and S9), MIL-101(Cr₂Fe)-PW₁₂-220 exhibited comparable detection activity [72–73]. The linear ranges for AA and DA detection were broader than most classical MOFs and POM-based materials like HKUST-1 [74], MOF-235 [75], MIL-125(Ti-Al)-75%NH₂ [76], PVIM-Co₂POM/NCNT [77], and CuBTC@CrMo₆ [78], while it was narrower than GO-ZIF-67 for UA detection [79]. The microenvironments of the MIL-101(Cr₂Fe)-POM-T series were tuned by the introduction of Fe(III) sites and POM species, thus arising synergistic effect between POM species and parent MOF frameworks and improving the electrochemical activities toward the detection of AA, DA, and UA. This adjustment establishes MIL-101(Cr₂Fe)-PW₁₂-220 as a potentially practical analytical platform featuring a broader linear range and a lower LOD.

3.4. Selectivity, reproducibility and stability

To further investigate the interference capability, MIL-101(Cr₂Fe)-PW₁₂-220 was used to measure AA, DA, and UA simultaneously in 0.1 mol·L^{–1} PBS (pH = 7.0) while containing 100-fold concentrations of inorganic salts (including sodium chloride, magnesium sulphate, potassium chloride, calcium chloride, sodium carbonate, disodium hydrogen phosphate, and sodium bicarbonate) or 50-fold concentrations of organic molecules (including urea, glucose (Glu), sucrose (Suc), fructose (Fru), citric acid (CA), glycine (Gly), L-cysteine (L-Cys)). It can be clearly seen that the interference substances produced negligible changes in the simultaneous signals of AA, DA, and UA (Fig. 4(b)). These results suggested that MIL-101(Cr₂Fe)-PW₁₂-220 showed satisfactory selectivity for simultaneous measurement of AA, DA, and UA.

Additionally, the reproducibility was tested using five newly prepared MIL-101(Cr₂Fe)-PW₁₂-220/GCE electrodes was

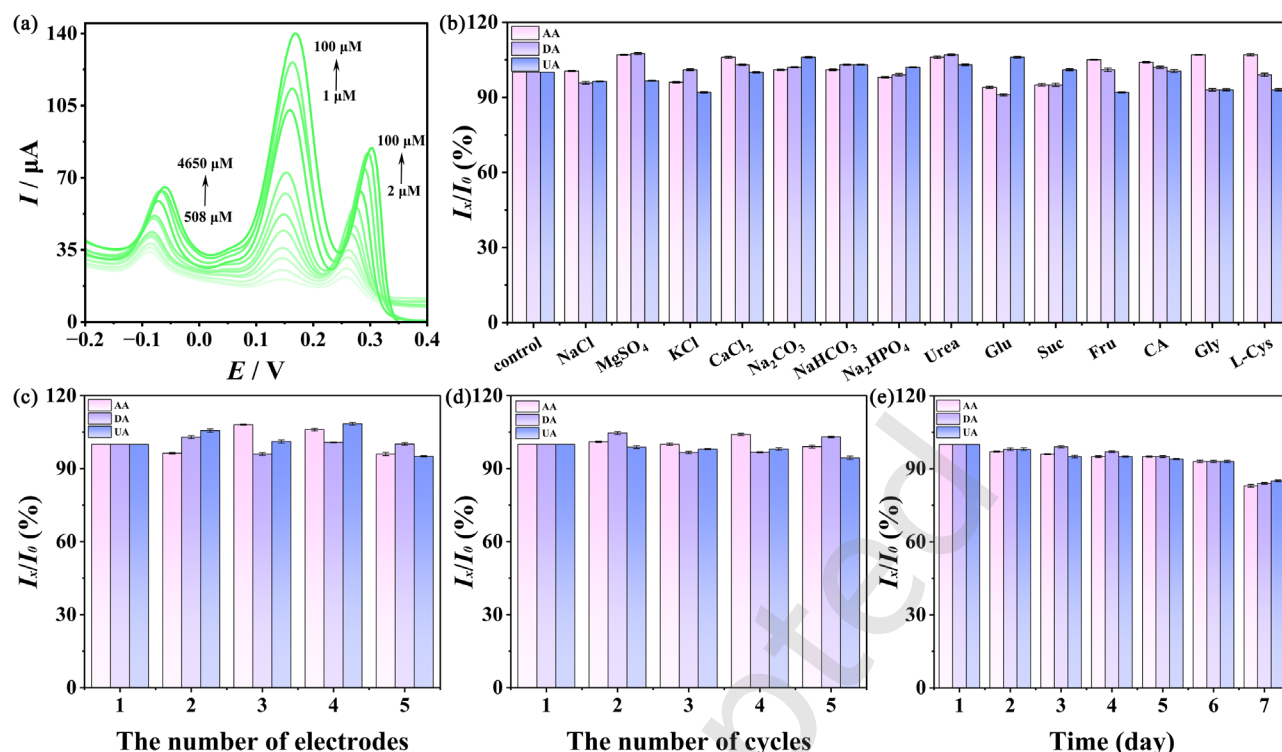


Figure 4 (a) DPV curves of MIL-101(Cr₂Fe)-PW₁₂-220 for the simultaneous determination of AA, DA, and UA with varying concentrations in 0.1 M PBS (pH = 7.0). (b) Selectivity, (c) reproducibility, (d) stability, and (e) long-term stability of MIL-101(Cr₂Fe)-PW₁₂-220 for the simultaneous detection of AA, DA, and UA.

examined under identical conditions (Fig. 4(c)). The relative standard deviation (RSD) values were 5.64%, 2.52%, and 5.07% for AA (500 μ M), DA (100 μ M), and UA (100 μ M) ($n = 5$), respectively, indicating that MIL-101(Cr₂Fe)-PW₁₂-220 exhibited excellent reproducibility. Furthermore, the stability of MIL-101(Cr₂Fe)-PW₁₂-220 was explored by means of two methods. Firstly, the performance of a freshly-prepared MIL-101(Cr₂Fe)-PW₁₂-220/GCE electrode was evaluated through a series of repeated measurements in a mixed solution of AA (500 μ M), DA (100 μ M), and UA (100 μ M). The RSD values were 1.83%, 3.80% and 2.16% for AA, DA, and UA (Fig. 4(d)), respectively. Secondly, the long-term stability of MIL-101(Cr₂Fe)-PW₁₂-220 was investigated towards AA, DA, and UA detection by storing the MIL-101(Cr₂Fe)-PW₁₂-220/GCE electrode at room temperature for 7 days (Figs. S28 and 4(e)). Therefore, MIL-101(Cr₂Fe)-PW₁₂-220 showed good stability over the storage period.

Furthermore, the FT-IR spectrum of MIL-101(Cr₂Fe)-PW₁₂-220 was recorded after 7-day durability test. Compared with the as-synthesized MIL-101(Cr₂Fe)-PW₁₂-220, the characteristic peaks assigned to the parent framework and the Keggin fragment were well retained (Fig. S29), without obvious variations in peak shape or position. This result suggested that the structure of MIL-101(Cr₂Fe)-PW₁₂-220 remains intact after electrochemical detection. In addition, the UV-Vis spectrum and EDS analysis of the electrolyte were further monitored after 7-day storage. No characteristic absorption peaks of PW₁₂ units were observed (Fig. S30). Meanwhile, no W element was detected (Fig. S31). These results further confirmed that the

encapsulated PW₁₂ units did not leach from the composite. These results indicated that MIL-101(Cr₂Fe)-PW₁₂-220 showed good durability over the electrochemical sensing process.

3.5. Real samples analysis

The excellent selectivity, reproducibility, and stability endows MIL-101(Cr₂Fe)-PW₁₂-220 with great potential for detecting AA, DA, and UA in real samples. To evaluate analytical reliability, MIL-101(Cr₂Fe)-PW₁₂-220-modified electrode was used to determine AA, DA, and UA individually in real samples *via* the standard addition method. Herein, human serum samples were diluted tenfold with 0.1 M PBS (pH = 7.0) prior to analysis. The results were presented in Table S10. Based on the results, the calculated recovery rates were ranged from 98.0% to 102.0%, suggesting that MIL-101(Cr₂Fe)-PW₁₂-220 provided satisfactory accuracy for measuring of AA, DA, and UA in human serum samples.

4 Conclusions

In summary, we successfully prepared a series of POM-modified bimetallic MOF composites, MIL-101(Cr₂Fe)-POM-T series (POM = SiW₁₂ or PW₁₂, T = 180 or 220), which served as electrochemical sensors for detecting AA, DA, and UA individually and simultaneously. Among them, MIL-101(Cr₂Fe)-PW₁₂-220 gave the strongest electrochemical responses in 0.1 M PBS (pH = 7.0) with wide linear ranges and low LODs. More importantly, MIL-101(Cr₂Fe)-PW₁₂-220 exhibited satisfactory reliability when measuring AA, DA, and UA in human serum samples owing to its excellent selectivity,

reproducibility, and stability. The current work not only enriches the multivariate POM-modified MOF family, but also offers a useful platform for electrochemical analysis of small biomolecules. Further studies of the design of POM-based MOF sensors for the electrochemical detection of biomolecules is currently being conducted in our lab.

Electronic Supplementary Material: Supplementary material (XPS, EDX, UV-Vis, CV data) is available in the online version of this article at <https://doi.org/10.26599/POM.2026.9140168>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

S. L.: Data collection, formal analysis, data curation, and writing – original draft. L.-P. W.: Data curation, and formal analysis. J.-J. L.: Formal analysis. X.-J. B.: Methodology, and resources. D.-Y. D.: Data curation, funding acquisition, project administration, and writing – review & editing. Z.-M. S.: project administration. All the authors have approved the final manuscript.

Ethics statement

Human serum samples were collected from healthy subject in compliance with all the ethical guidelines under a protocol (ID 202602032) that was approved by Northeast Normal University. Subject gave written informed consent before participation in the study.

Use of AI statement

None.

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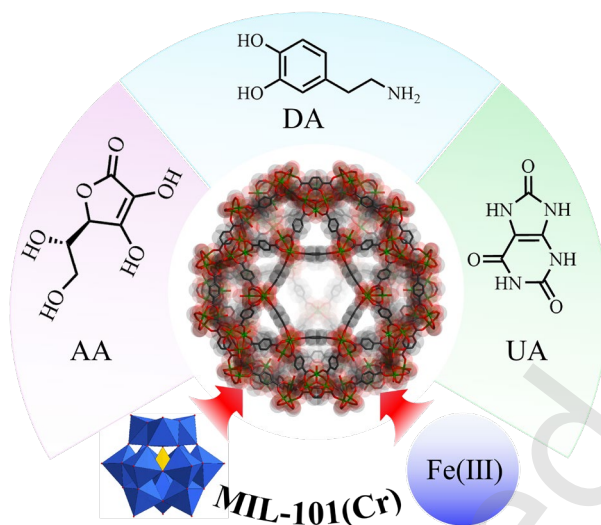
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A family of polyoxometalate (POM)-incorporated bimetallic MOF composites, MIL-101(Cr₂Fe)-POM-T series, was obtained by incorporating POM units and Fe(III) centers, which was subsequently used for electrochemical sensing of small biomolecules.