Electrochemical Sensor for the Detection of 1-Hydroxypyrene Based on Composites of PAMAM-Regulated Chromium-Centered Metal–Organic Framework Nanoparticles and Graphene Oxide

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ABSTRACT: A nanocomposite was formed by combining graphene oxide (GO) with chromium-centered metal–organic framework (Cr-MOF) nanoparticles regulated by the dendrimer polyamidoamine (PAMAM). PAMAM can successfully regulate the synthesis of Cr-MOF; in doing so, the size of Cr-MOF is reduced, its original morphology is maintained, and it has good crystallinity. A simple ultrasonication method was used to make the Cr-MOF/GO hybrid nanocomposite. Various characterization methods confirmed the successful synthesis of PAMAM/Cr-MOF/GO nanocomposites. The PAMAM/Cr-MOF/ERGO modified electrode could be used with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) to study the electrochemical behaviors of 1-hydroxypyrene (1-OHPyr). The results indicated that the constructed PAMAM/Cr-MOF/ERGO electrochemical sensor had a significantly enhanced electrocatalytic effect on the electrochemical reduction of 1-OHPyr compared with the sensors with no PAMAM and the ERGO sensor, which could be ascribed to the synergetic effect from the high porosity of Cr-MOF and the high conductivity of ERGO, as well as the further electron transport action of the nanocomposite. Under the optimal conditions, the reduction peak current and concentration of 1-OHPyr showed a good linear relationship in the range of 0.1–1.0 and 1.0–6.0 μM, and the detection limit of 1-OHPyr was calculated to be 0.075 μM. Moreover, the PAMAM/Cr-MOF/ERGO electrochemical sensor constructed in this paper can be expected to provide some instructions for the construction of electrochemical sensing platforms and wider potential applications.

INTRODUCTION

As one of the representatives of persistent organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are widely found in the atmosphere, water, soil, food, and so forth.1−4 PAHs can enter the human body through various exposure pathways, such as respiration, diet, and contact; quite a few PAHs are known to be carcinogenic and mutagenic, such as benzo[a]-pyrene, so human exposure to PAHs is an important factor to reveal their toxicity and carcinogenic risk.5,6 Therefore, increasing attention has been given to the prediction of the internal exposure level of PAHs. After entering the body, some PAHs are metabolized into hydroxyl PAHs (OH-PAHs), which are excreted with urine and mostly exist in a combined state with glucuronic acid. The OH-PAHs in urine can effectively reflect the recent exposure to PAHs, and the samples are easy to collect. Therefore, OH-PAHs in urine have been widely used as biomarkers to evaluate PAH exposure levels in the human body.7,8 Among them, 1-hydroxypyrene (1-OHPyr) can more accurately indicate the total internal exposure level of PAHs. The PAH exposure levels and the amount of 1-OHPyr in urinary issue have also been demonstrated to be correlated in some occupational settings.9−11 Many methods for 1-OHPyr analysis have been developed such as HPLC−MS, GC−MS, and LC−MS/MS, but most of the equipment used is large, expensive, and difficult to operate, laborious sample pretreatment and toxic reagents are used, and the pretreatment processes are time-consuming.12−14 Therefore, a novel, simple, effective, fast, and low-cost approach for the determination of urinary 1-OHPyr is urgently needed. Studies on electrochemical sensors in 1-OHPyr analysis are beginning to be reported.7,8,15−17 The OH-PAH structure contains electrochemically active hydroxyl groups, so they can be used for electrochemical detection. In the electrochemical analysis of trace substances in a complex...
matrix, the key to realizing simple, fast, selective, and sensitive detection lies in the selection of electrode-modified coatings.

Metal–organic frameworks (MOFs), formed by the self-assembly of metal ions connected with organic ligands, have gained widespread attention in the field of synthesis and applications over the past few decades owing to their intriguing properties, including large surface areas, high porosity, adjustable pore sizes, available functionality, and ordered crystal structures. The large surface area of MOFs enables them to increase the loading capacity of the target, which provides innate sensitivity for electrochemical detection. The high porosity of the MOFs allows guest molecules to selectively diffuse into the pores depending on the shape and size. Another contribution to selectivity comes from weak interactions between the MOFs and guest molecules, such as hydrogen bonds, π–π interactions, open metal sites, and van der Waals forces. However, the instability of MOFs in water limits their use in electrochemical analysis because most electrochemical reactions occur in the aqueous phase. A chromium-based MOF (Cr-MOF), which is constructed from chromium ions and terephthalate ligands, shows excellent chemical and hydrothermal stability, a large surface area, large pore windows, and numerous unsaturated chromium sites, making it favorable for electrochemical sensors. In addition, the Cr-MOF has been reported to be an attractive solid-phase extraction sorbent for OH-PAHs in urine samples of coke-oven workers based on the solid-phase extraction sorbent for OH-PAHs in urine samples.23−25

Figure 1. TEM images of Cr-MOF (A), PAMAM/Co-MOF (B), and PAMAM/Cr-MOF/GO (C). SEM images of Cr-MOF (D), PAMAM/Co-MOF (E), and PAMAM/Cr-MOF/GO (F).

metal nanoparticles, conducting polymers, and so forth, which gives them both the advantages of MOFs and good electrical conductivity; additionally, the synergistic effects of MOF composites would further broaden the application in the field of electrochemical sensors. As a representative material of carbon nanomaterials, graphene oxide (GO) has been widely used in the synthesis of MOF nanocomposites due to its abundant oxygen-containing functional groups, large specific surface area, good electrical conductivity, robust mechanical properties, and other inherent advantageous properties. The introduction of GO can not only enhance the adsorption capacity of the target by π–π stacking, hydrogen bonding, and other forces but also effectively improve the conductivity of MOF nanocomposites, which could result in a synergistic effect to improve the electrochemical active area and sensitivity of the electrochemical sensing. In addition, the addition of GO possessing excellent stability in aqueous solutions could greatly improve the poor stability of MOF nanocomposites and dispersion degree in water so as to significantly enhance electrochemical and electrocatalytic performances. Because graphene’s rapid electron transport occurs on the surface of edge plane and defects, GO has been reduced to defective reduced GO (RGO) by various methods to improve the electrocatalytic properties of graphene-MOF composites, such as chemically reduced, electrochemically reduced, and so on. Additionally, the morphology and pore size of the nanocomposite were improved by introducing polymer surfactants or chemical modification and hybridization of the MOF in an in situ assembly. The result is that the electrochemical performance of MOF-based composite materials is enhanced more than that of single-component MOFs due to the combination of the merits of both MOFs and other materials.

In this work, the dendritic macromolecule PAMAM was first introduced to regulate the synthesis of Cr-MOF nanoparticles to further increase the specific surface area, optimize the pore structure, reduce the size, and improve the performance. Then, a highly dispersible, stable, and electrocatalytic nanocomposite material of PAMAM/Cr-MOF/GO was synthesized by employing a simple ultrasound technique, which was based on the addition and synergy of hydrogen bonding, π–π stacking, and metal coordination. The morphology, structure, and some characteristics of PAMAM/Cr-MOF nanoparticles and the obtained nanocomposite were characterized by transmission electron microscopy (TEM), energy-dispersive spectrometry, scanning electron microscopy (SEM), UV–vis spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction...
(XRD), nitrogen adsorption–desorption isotherms, and thermogravimetric analysis (TGA). A certain amount of PAMAM reduced the size of Cr-MOF nanoparticles and improved the dispersibility of the nanocomposites, and a high

Figure 2. TEM elemental mapping images (A–E) and EDX spectra (F) of PAMAM/Cr-MOF.

Figure 3. (A) UV–vis absorption spectra and the photographs (inset) of GO (a), PAMAM/Cr-MOF (b), and PAMAM/Cr-MOF/GO (c). (B) FT-IR spectra of GO (a), PAMAM/Cr-MOF (b), and PAMAM/Cr-MOF/GO (c). (C) XPS profile of PAMAM/Cr-MOF. (D) XRD patterns of Cr-MOF (a), PAMAM/Cr-MOF (b), and PAMAM/Cr-MOF/GO (c).
specific surface area was obtained while maintaining the morphology of the Cr-MOF nanoparticles. Electrochemical reduction technology was used to convert the GO components in PAMAM/Cr-MOF/GO to their reduced state (ERGO). Compared to chemically reduced GO, electrochemical reduction technology leaves out toxic reducing agents; thus, it is simpler, faster, and more environmentally friendly. Herein, for the first time, an electrochemical sensor based on a PAMAM/Cr-MOF/ERGO nanocomposite was fabricated for the qualitative and quantitative analysis of urinary 1-OHPyr. The results showed that enhanced electrical signals on the nanocomposite-modified electrode were obtained compared with the individual material; thus, a new path has emerged to adjust the synthesis and broaden the potential application capabilities of MOFs in the field of electrochemical analysis.

## RESULTS AND DISCUSSION

Characterization of Materials. The texture of Cr-MOF, PAMAM/Cr-MOF, and PAMAM/Cr-MOF/GO nanocomposites can be observed in the TEM and SEM images presented in Figure 1. A large number of regular octahedrons with perfect crystallinity are observed in the graph of the PAMAM/Cr-MOF (Figure 1B,E). Moreover, the size of PAMAM/Cr-MOF was reduced from 1 μm to approximately 200 nm after PAMAM was added, which is expected to increase the specific surface area and favor the formation of nanocomposites. In addition, the effects of PAMAM on the morphology and size of PAMAM/Cr-MOF were investigated; the SEM images are presented in Figure S1. As shown in Figure S1, as the PAMAM volume increased from 25 to 75 μL, the size of PAMAM/Cr-MOF decreased gradually and the octahedrons disappeared when the volume reached 75 μL, which confirmed that PAMAM regulated the synthesis of Cr-MOF. The mechanism can be explained by the fact that when PAMAM is added to the synthesis process of Cr-MOF, it will adhere to the Cr-MOF surface as a surfactant and will act as a capping agent to slow down the relative growth rate of some crystal faces with Cr-MOF, thus controlling the morphology and size of the Cr-MOF. In this experiment, the size of the Cr-MOF decreased when the amount of PAMAM increased, which might be because PAMAM slowed the growth rate of all crystal faces of Cr-MOF at the same rate. High-resolution TEM elemental mapping images of the PAMAM/Cr-MOF confirm the chemical distribution of C, O, N, and Cr, indicating that PAMAM binds to Cr-MOF and regulates its synthesis (Figure 2). The images of the PAMAM/Cr-MOF/GO composites (Figure 1C,F) showed that the morphology of the PAMAM/Cr-MOF was maintained well, and some obvious wrinkles in accordance with the characteristics of GO were well-coated across the surface of the octahedrons, resulting in some three-dimensional hole structures.

The inset of Figure 3A shows photographs of the GO (photograph a), PAMAM/Cr-MOF (photograph b), and PAMAM/Cr-MOF/GO (photograph c) aqueous solutions. The photographs show that the aqueous solution of GO is a uniform yellowish-brown color, indicating that the synthesized GO has good dispersion in water. However, the PAMAM/Cr-MOF aqueous solution was stable for several minutes after being dissolved by ultrasound and then the PAMAM/Cr-MOF slowly accumulated at the bottom of the tube, which suggested that the synthesized PAMAM/Cr-MOF had poor dispersion in water. Interestingly, when GO was sonically mixed with PAMAM/Cr-MOF, a slightly darker dispersion solution with no precipitation for least 1 week was obtained, indicating that GO could effectively endue the composite with good solubility and dispersibility in water. The binding mechanism of PAMAM/Cr-MOF and GO was explored by UV–vis absorption spectroscopy and is shown in Figure 3A. A typical UV–vis spectrum with a strong broad absorption peak at 228 nm and a weak shoulder peak at 300 nm was observed due to the existence of GO, which corresponded to \( \pi \rightarrow \pi^* \) transitions of oxidized domains and \( n \rightarrow \pi^* \) transitions within the C()==O bonds, respectively (curve a).

In the PAMAM/Cr-MOF/GO solution, a red shift from 228 to 247 nm was found (curve c), which indicated that the degree of electron conjugation within the GO layer had been restored after the decoration of PAMAM/Cr-MOF. This may be because \( \pi \) electron coupling between the PTA in the PAMAM/Cr-MOF and the unoxidized domain of GO layers was easily accomplished. In addition, the absorption peak at 300 nm almost disappeared, suggesting that GO may also interact with PAMAM/Cr-MOF through hydrogen bonds or Cr–O coordination bonds. Wang et al. studied GO and Cu-MOF composites and also confirmed this mechanism.

The interaction between GO and PAMAM/Cr-MOF was further confirmed by FT-IR, and the corresponding spectra are displayed in Figure 3B. GO showed bands at 3301 and 1726 cm\(^{-1}\), arising from the \(-OH\) stretch and C==O stretch, respectively. The peaks at 1402, 1218, and 1042 cm\(^{-1}\) can be attributed to the C–OH bending vibrations and stretching vibrations of C–O in alkoxy C–O and C–O–C, respectively, while the peak at 1619 cm\(^{-1}\) arises from the skeleton vibration of the unoxidized graphite layer. For PAMAM/Cr-MOF, peaks appeared in the region of 1800–1300 cm\(^{-1}\), which were in accordance with previous reports in the literature, and were related to the asymmetric and symmetric stretching vibration peaks of –COO and C–C vibrations. The bands at 1550 and 1402 cm\(^{-1}\) were assigned to the asymmetric and symmetric stretching of –COO in BDC with a separation of 147 cm\(^{-1}\), which indicated that the coordination mode of the carboxylate binding with Cr\(^{3+}\) was bridging. The peak at 1256 cm\(^{-1}\) could be ascribed to C–N bonds. The stretching vibrations of primary and tertiary amines appeared at 1161 and 1116 cm\(^{-1}\), which were broadened in the nanocomposite indicating the formation of hydrogen bonds. The peak position of PAMAM/Cr-MOF/GO (curve c) was analogous to that of PAMAM/Cr-MOF, and only the C==O peak of GO shifted to 1700 cm\(^{-1}\), which confirmed the existence of \( \pi \rightarrow \pi \) packing. In addition, the band at 1550 cm\(^{-1}\) shifted to 1543 cm\(^{-1}\), and the peak at 1619 cm\(^{-1}\) broadened compared to PAMAM/Cr-MOF. All of the abovementioned results confirmed that PAMAM/Cr-MOF successfully became an integral component with the GO domain, which could favor efficient charge transfer within the composite.

To detect the elemental composition and content of the material surface and provide electronic structure information, XPS analysis was performed, and the results are presented in Figure 3C and Table 1. C 1s, O 1s, N 1s, and Cr 2p are displayed in the full survey. The Cr 2p spectra of Cr-MOF and the composite exhibit the binding energy peaks of Cr 2p\(_{3/2}\) and Cr 2p\(_{1/2}\) at 587.07 and 577.39 eV, respectively, corresponding to Cr\(^{3+}\). The C 1s spectra of PAMAM/Cr-MOF (Figure S2A) present three bands at 284.77, 286.15, and 288.64 eV, which correspond to C==C, C–N, and C==O bonds, respectively. However, the binding energy of C–N shifts to 287.02 eV (Figure S2C) due to the low electron density, which
Cr-MOF was not disrupted during ultrasonic preparation. The intensity was slightly reduced, indicating that the structure of the material was preserved. The BET surface area, pore size, and pore volume of Cr-MOF and PAMAM/Cr-MOF were 954.9941 m² g⁻¹, 1.678013 cm² g⁻¹, and 2.0 nm, respectively. The peak at 400.96 eV in the N 1s spectra may be attributed to NH₃, the terminal group of PAMAM not involved in the reaction; however, no N was detected in the spectra of PAMAM/Cr-MOF/GO which may be because XPS measures elements within 10 nm of the surface, whereas N is encapsulated within the composite material. The contents of C in the nanocomposite increased while the Cr content and O content decreased (Table 1), indicating that GO was successfully incorporated into the PAMAM/Cr-MOF structure.

The XRD patterns of Cr-MOF, PAMAM/Cr-MOF, and PAMAM/Cr-MOF/GO are depicted in Figure 3D. Good crystallinity was reflected in both Cr-MOF and PAMAM/Cr-MOF, and the main characteristics of the diffraction peaks were at 3.32, 5.19, 5.91, 8.46, 9.07, 10.35, and 16.5° which are in accordance with the literature. This phenomenon effectively demonstrated that PAMAM did not affect the formation of the structure of Cr-MOF when regulating its synthesis. The well-defined Cr-MOF structure was preserved in the diffraction pattern of PAMAM/Cr-MOF/GO, but the intensity was slightly reduced, indicating that the structure of Cr-MOF was not disrupted during ultrasonic preparation.

Nitrogen adsorption–desorption measurements of PAMAM/Cr-MOF were performed. As shown in Figure S3A, the Cr-MOF and PAMAM/Cr-MOF present type-I adsorption–desorption isotherms, which are characteristic of microporous nanostructures. In addition, the Brunauer–Emmett–Teller (BET) surface area, pore size, and pore volume of Cr-MOF and PAMAM/Cr-MOF were 954.9941 m² g⁻¹, 2.0 nm, and 1.221768 cm³ g⁻¹ and 3282.5937 m² g⁻¹, 2.0 nm, 1.678013 cm³ g⁻¹ 2.0 nm, respectively. The BET surface area of PAMAM/Cr-MOF was larger than that of the Cr-MOF. Such superior characteristics of PAMAM/Cr-MOF provide favorable conditions for the adsorption of 1-OHPyr, which is consistent with the fact that MIL-101 (Fe) has been reported to be used for the determination of PAHs in water. The strong adsorption capacity of PAHs is inseparable from the large specific surface area and pore size of the MOF.

To sufficiently determine the content of the signal component in the hybrids and the thermal stabilities, TGA for the GO (curve a), PAMAM/Cr-MOF (curve b), and PAMAM/Cr-MOF/GO composites (curve c) was performed under a N₂ atmosphere. From Figure S3B, all of the substances started to lose weight below 100 °C, which is caused by the thermal desorption of water molecules physically adsorbed on the surface. Then, for GO, apparent weight loss occurred at approximately 200 °C, which may be attributed to the loss of oxygen-containing groups of GO. The TGA curve of Cr-MOF showed that decomposition started at 200 °C, and the slower weight loss occurred until 500 °C, indicating that the structure of PAMAM/Cr-MOF collapsed due to the removal of PTA from the framework. The TGA curve (c) of the PAMAM/Cr-MOF/GO composite showed the expected thermal properties which are in complete agreement with the combined thermal decomposition behavior of GO and PAMAM/Cr-MOF.

Electrochemical Behavior of 1-OHPyr on PAMAM/Cr-MOF/ERGO/GCE. To explore the properties of PAMAM/Cr-MOF/GO composites, the electrochemical behavior of 1-OHPyr was studied on several modified electrodes, including bare GCE, ERGO/GCE, PAMAM/Cr-MOF/GCE, and PAMAM/Cr-MOF/ERGO/GCE. Figure 4 shows the cyclic voltammetry (CV) curves of the GCE (curve a), PAMAM/Cr-MOF/GCE (b), ERGO/GCE (c), Cr-MOF/ERGO/GCE (e), and PAMAM/Cr-MOF/ERGO/GCE (e) in 0.05 M PBS (pH 2.0) containing 0.2 M NaCl. Curve f is the CV curve of PAMAM/Cr-MOF/ERGO/GCE in 0.05 M PBS (pH 2.0) containing 0.2 M NaCl without 1-OHPyr.

![Image](https://doi.org/10.1021/acsomega.1c04765)

**Figure 4.** CV curves of 5 μM 1-OHPyr at GCE (a), PAMAM/Cr-MOF/GCE (b), ERGO/GCE (c), Cr-MOF/ERGO/GCE (e), and PAMAM/Cr-MOF/ERGO/GCE (e) in 0.05 M PBS (pH 2.0) containing 0.2 M NaCl. Curve f is the CV curve of PAMAM/Cr-MOF/ERGO/GCE in 0.05 M PBS (pH 2.0) containing 0.2 M NaCl without 1-OHPyr.

| Table 1. XPS Elemental Composition of PAMAM/Cr-MOF and PAMAM/Cr-MOF/GO |
|-------------------------|-------|-------|-------|-------|
| material                | C     | O     | N     | Cr    |
| PAMAM/Cr-MOF            | 56.71 | 31.6  | 4.56  | 4.21  |
| PAMAM/Cr-MOF/GO         | 66.71 | 31.6  | 4.56  | 4.21  |

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To determine how the scan rates affect the peak current responses to better explain the electrochemical reaction mechanism, this factor was discussed on a scale of 10−200 mV s⁻¹. Figure 6A,B shows that the peak currents of 1-OHPyr increased with the scan rate (v) and presented good linear correlations according to the following equations:

$$I_{pc} (\mu A) = 1.062 + 431.7v (V \cdot s^{-1}) (r = 0.993)$$

$$I_{pa} (\mu A) = -0.8144 - 333.7v (V \cdot s^{-1}) (r = 0.993)$$

indicating that the reaction of 1-OHPyr on the PAMAM/Cr-MOF/ERGO/GCE surface took place in the adsorption-controlled process.

**Effect of pH.** In electrochemical analysis, the supporting electrolyte has a corresponding influence on the electrochemical properties of the electrode and the target response. As Figure 7A shows, we investigated the effect of different pH values of the supporting electrolyte on the electrocatalytic performance via CV. The oxidation peak and reduction peak currents of 1-OHPyr gradually decreased as the pH value increased, and the peak potentials gradually shifted to the negative peak direction, indicating that protons participated in the electrode reaction. When the pH was 2.0, the peak current of the 1-OHPyr redox was the largest, so a PBS solution with a pH of 2.0 was adopted as the best supporting electrolyte. The relationship between the peak currents and pH values of the supporting electrolyte is depicted in Figure S4. Moreover, a good linear relationship is found between the formal potential ($E'^{0}$) and pH, and the linear equation is

$$E'^{0} (V) = 0.291 - 0.068 \cdot \text{pH} (r = 0.98)$$

The slope of -68 mV pH⁻¹ was close to the theoretical value of -59 mV pH⁻¹, indicating that the same number of electrons was involved in charge transfer and proton transfer, which is consistent with the findings reported in the literature. Moreover, the electrical signals of 1-OHPyr are the largest at pH 2.0. Hence, the PBS solution with a pH of 2.0 was adopted as the best supporting electrolyte.
Effects of Deposition Potential and Deposition Time. The surface of the electrode will have some new functions after modification, which will be beneficial in improving the sensitivity, selectivity, stability, and reproducibility of detection. The enrichment efficiency depends largely on the electrode modification material. ERGO and the organic ligand of PAMAM/Cr-MOF could offer a π-π stacking system to adsorb 1-OHPyr via π−π stacking interactions. Meanwhile, because of the abundant pores and large specific surface area of PAMAM/Cr-MOF, it plays a great role in the enrichment. To improve the sensitivity of the detection of 1-OHPyr, the reduction peak current of 1-OHPyr was monitored after it was preliminarily oxidized on the electrode surface, and the deposition potential and deposition time are important conditions in the preoxidation process. As an anion, it is more reasonable to choose a positive deposition potential for 1-OHPyr. Therefore, the deposition potential and deposition time effects were studied. As depicted in Figure S5A, the reduction peak current of 1-OHPyr first increased and then decreased with a positive shift of the deposition potential within the range of 0.5−1.0 V. The reduction peak current reached the maximum value when the deposition potential was 0.7 V, so 0.7 V was taken as the best deposition potential. The deposition time was actually a synergistic accumulation comprising both the time the target was enriched onto the materials on the electrode surface and the time needed for the electro-oxidation process. The effect of deposition time was researched under a controlled deposition potential (Figure S5B). As observed from the variation tendency, the peak current of 1-OHPyr increased with the extension of the deposition time within the range of 10−60 min, and the growth rate seemed to decrease from 40 min. Considering the analysis speed, 40 min was adopted as the optimal deposition time.

Quantitative Detection of 1-OHPyr. Differential pulse voltammetry (DPV) was used to evaluate the analytical performance of the PAMAM/Cr-MOFs/GO-based biosensor toward the detection of 1-OHPyr under the optimal conditions selected above. Figure 8 shows the typical DPV voltammograms for the different 1-OHPyr concentrations, and we find that the reduction current response increases with increasing concentration. It can also be observed that the peak currents were linearly proportional to the values of concentrations within two concentration ranges, such as 0.1−1.0 and 1.0−6.0 μM, with a detection limit of 0.075 μM calculated based on LOD = KSb/S (Sb is the standard deviation of blank parallel determinations of 11 determinations and S is the slope of the calibration curve of results), and the linear regression equations were Ipc (μA) = 21.62 + 93.74c (μM) when the r was 0.998 and Ipc (μA) = 73.14 + 40.39c (μM) when the r was 0.997. The different linear relationships are related to the different adsorption behaviors on the surface of the material electrode at different concentrations. The lower the concentration of the target substance adsorbed on the electrode surface, the easier it can be converted into products, leading to high sensitivity. However, at higher levels, the probability of fouling on the electrode surface is due to the increase in reaction products, especially for porous MOFs, and the diffusion of reaction products is relatively slow, resulting in a relatively low slope. In addition, the sensitivity of the sensor could be calculated by S/A as 1309.76 μA μM−1 cm−2, where S and A are the slope of the calibration curve and the electrochemically active surface area of the modified electrode, respectively. The performances of the constructed sensor were compared with those of the existing electrochemical methods for the detection of 1-OHPyr, and the information in terms of electrode materials, linear range, and LOD is listed in Table 2.

Stability, Reproducibility, and Selectivity. Stability and reproducibility are important performance indicators of electrochemical sensors. The constructed PAMAM/Cr-MOF/ERGO/GCEs were placed at 4 °C for 7 days and 14 days and then measured and the responses retained 92.5 and 81.1% of the initial responses, respectively. Reproducibility refers to the consistency of the results of multiple measurements under different electrode modifications. Five PAMAM/Cr-MOF/ERGO/GCEs were prepared for a series of measurements to study the reproducibility of the sensor, and the results showed a relative standard deviation (RSD) of 7.56%. These results revealed that the electrochemical sensor has good stability and reproducibility. Repeatability refers to the consistency of the results obtained from successive measurements under one electrode modification. Due to the properties of 1-OHPyr and the interaction between the nanomaterial and 1-OHPyr, enrichment should be carried out before measurements are taken to increase the detection sensitivity of 1-OHPyr. The modified electrode that had been used cannot be used for repeated measurements because of the high concentration of 1-OHPyr remaining on the electrode surface, which would affect the subsequent measurements.

Furthermore, prior to the detection of real samples, the anti-interference ability of the material also needs to be discussed because the actual sample not only has 1-OHPyr but also has many other complex physiological interferences. The 100-fold concentrations of K+, Ca2+, Mg2+, Cl−, CO32−, and SO42− had no interference on the peak current of 1-OHPyr. In addition, there is a large amount of uric acid (UA) in human urine, which is the main final metabolite of purine and is electroactive; therefore, it is necessary to investigate whether UA interferes with 1-OHPyr detection. As shown in Figure S6, the oxidation potential of UA (0.594 V) was well-separated from 1-OHPyr (0.182 V), and the influence on the current response of 1-OHPyr can be ignored after the addition of UA at a concentration of 100 times. All these results suggested that PAMAM/Cr-MOF/ERGO/GCE has a good anti-interference ability for the determination of 1-OHPyr.

Urine Sample Analysis. The fabricated electrochemical sensor was utilized to analyze human urine samples. Since I-
OHPyr in human urine is mostly in the form bound with glucuronic acid and the form has no electrochemical activity, the enzyme hydrolysis method was adopted to treat the actual urine samples. In total, three levels of standard solution were added to the urines for six parallel tests and then the recovery was calculated to verify the feasibility of the method. The analysis results are presented in Table 3. The recoveries for the spiked 1-OHPyr were in the range of 91.8 and 108%, indicating that the electrochemical sensor constructed in this experiment is feasible for use in the analysis of 1-OHPyr in actual samples.

### MATERIALS AND METHODS

**Chemicals.** 325 mesh high-purity flake graphite (purity ≥99.6 wt %) was obtained from Nanjing XFNANO Materials Tech Co., Ltd. (P. R. China). Sodium nitrate was obtained from Tianjin Kaitong Chemical Reagent Co., Ltd. (P. R. China). Potassium permanganate and hydrogen peroxide were purchased from Tianjin Kaitong Chemical Reagent Co., Ltd. (P. R. China). All the other chemicals were analytical reagents and used directly without further purification.

**Apparatus.** Field emission SEM (FESEM) was performed on a Hitachi model SU8020 microscope (Japan). TEM was performed on a JEM-2100 electron microscope (JEOL, Japan). FT–IR spectra were obtained on a Thermo Nicolet iS50 FT–IR spectrometer (Thermo Scientific, P. R. China). XPS was conducted on a Thermo Fisher ESCALAB 250Xi XPS spectrometer with a monochromatic X-ray source (Thermo Scientific, P. R. China). XRD was performed on a Bruker D8-ADVANCE X-ray diffractometer (Germany). TGA was conducted on a NETZSCH STA449 F3 thermal gravimetric analyzer (Germany). N2 adsorption–desorption measurements were performed on a Micromeritics ASAP 2460 at 77 K (USA). Electrochemical measurements were performed on a CHI 660E electrochemical workstation (P. R. China). A conventional three-electrode system was used, including a modified GCE as the working electrode, a saturated calomel electrode as the reference electrode, and a platinum wire as the auxiliary electrode. The pH values were measured with a Sartorius PB-10 pH meter (Germany).

**Preparation of the PAMAM/Cr-MOF/GO Nanocomposite.** GO was synthesized from high-purity flake graphite using a modified Hummers’ method.58 PAMAM/Cr-MOF was synthesized by modifying a hydrothermal method reported in the literature.39 First, Cr(NO3)3·9H2O (8.00 mg) and a certain amount of PAMAM were mixed with 9.5 mL of ultrapure water, followed by transfer to a Teflon-lined stainless-steel reactor containing 332.0 mg of PTA; the solution was stirred for 40 min. Then, 100 μL of HF was added and stirred evenly. Finally, the sealed reactor was placed in an oven and programmed temperature control was used as follows: the temperature was increased to 220 °C for 30 min and the reactor was held at that temperature for 8 h; then, the temperature was decreased to 30 °C at a rate of 5 °C/h and maintained at that temperature for 36 h; and then, the reactor was gradually cooled to room temperature. A uniform green solution was obtained, and unreacted TPA crystals were also found. To remove the excess TPA and other molecules, the as-synthesized PAMAM/Cr-MOF was further purified by washing with hot DMF and ethanol at 60 °C three times. The purified product was centrifuged at 15 000 rpm for 10 min and dried overnight in a vacuum at 150 °C. Meanwhile, a conventional Cr-MOF was also synthesized. The PAMAM/Cr-MOF composite was obtained by adding 1.0 mg of Cr-MOF into 1.0 mL of 0.5 mg mL−1 GO solution, followed by sonication for 2 h in an ice bath to obtain a uniform dispersion, which was performed at low temperature, shaken well every 10 min, and finally stored at 4 °C for use.

**Construction of the PAMAM/Cr-MOF/GO/GCE.** Prior to modification, the GCE was polished with a 0.05 μm Al2O3 suspension and then sequentially sonicated in ethanol and ultrapure water to obtain a mirror-like electrode surface. After cleaning, the electrode was dried by a stream of N2. PAMAM/Cr-MOF/GO suspensions (8.0 μL) were drop-coated on the surface of the well-polished GCE and then dried. A 4.0 μL 0.5% Nafion solution was applied to enhance stability
and it was dried again. As a control, PAMAM/Cr-MOF/GCE and GO/GCE were fabricated using a similar procedure. The electrochemical reduction of GO was implemented following previous reports.60 Briefly, the modified GCE was immersed in predeoxygenated 0.1 M PBS (pH 7.0) and CV scanning was performed in the range of −1.5−0.6 V for at least 10 cycles at a scan rate of 50 mV s\(^{-1}\) until the curves stabilized, illustrating that GO was sufficiently restored. The modified electrode was expressed as PAMAM/Cr-MOF/ERGO/GCE. ERGO/GCE was also prepared following the same procedure.

**Electrochemical Measurements.** Electrochemical measurements of 1-OHPyr by CV and DPV were performed in 0.05 M PBS (pH 2.0) containing 0.2 M NaCl. CVs were carried out in the range of 0.7 to −0.5 V at a scanning speed of 0.1 V s\(^{-1}\). When DPV was applied for determination, a deposition potential of 0.7 V was performed for 40 min to form diquinonepyrene through the electroattraction accumulation and electro-oxidation, and DPV voltammograms were recorded from 0.7 to −0.5 V with the following parameters: increment potential, 0.004 V; pulse amplitude, 0.05 V; pulse width, 0.05 s; sample width, 0.0167 s; pulse period, 0.5 s; and quiet time, 2 s. The reduction peak obtained is used as an analytical signal for 1-OHPyr. All test solutions weredeoxygenated prior to use with high-purity nitrogen. The preparation of PAMAM/Cr-MOF/ERGO/GCE and determination of 1-OHPyr are shown in Scheme 1.

**Pretreatment of Urine Samples.** Urine samples were pretreated according to the following procedure.7 Briefly, 10.0 mL of urine was thawed at room temperature, thoroughly mixed, and then transferred to a 50 mL conical flask. For enzymatic hydrolysis, after mixing with 5.0 mL of HAc-NaAc buffer solution (0.5 M, pH = 5.0) and adjusting with 0.2 M HCl, 20.0 μL of β-glucuronidase was then added to the abovementioned solution. The mixture was put in a water bath at 37 °C for 2 h and then centrifuged for 10 min at 2500 rpm. After that, 5 mL of hexyl hydride was added to the supernatant to extract the enzymolysis products; this step was repeated twice. Finally, the hexyl hydride was dried with a flow of N\(_2\), and the residue was redissolved in 10 mL of PBS (0.05 M, pH = 2.0). The abovementioned process was performed under dark conditions if possible.

**CONCLUSIONS**

In summary, we introduced the dendrimer PAMAM to regulate the preparation of Cr-MOF nanoparticles, which exhibit perfect crystallinity, reduced size, and high specific surface areas. Moreover, a facile method based on ultrasonication was applied to the preparation of the PAMAM/Cr-MOF/GO nanocomposite, showing excellent dispersibility in water. An electrochemical sensor was constructed by modifying the nanocomposite on a GCE, and the GO in the material was then converted to an excellent electrically conductive reduction form (ERGO) by a simple and effective electroreduction method. The proposed sensor showed an increasing current response compared with the ERGO-based sensor, which was ascribed to the synergistic effect between the high conductivity of ERGO and the high porosity of PAMAM/Cr-MOF, which brought the nanocomposite-accelerated electron transfer and increased the effective specific surface area. Under optimal experimental conditions, this method has been successfully used for the detection of 1-OHPyr in human urine with satisfying reproducibility and excellent anti-interference ability. Therefore, the results show that the synthesis method of PAMAM/Cr-MOF/ERGO opens up new possibilities and approaches for the synthesis and construction of other highly sensitive electrochemical sensing materials in the future.
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Notes
The authors declare no competing financial interest.

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