Supporting information

Two-dimensional conductive phthalocyanine-based metal-organic frameworks for electrochemical nitrite sensing

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Table S1 Comparisons of analytical performance of nitrite on the modified electrodes (from 2018-2020)

Table S2 Determination of nitrite in 0.1 M PBS on the NiPc-MOF electrode (under optimized conditions, n = 3)

References
S.1 Synthesis of NiPc-MOF nanosheets
In a typical synthesis, NiPc-NH$_2$ (60 mg) and NiCl$_2$ 6H$_2$O (42 mg) were both dissolved in DMSO (80 mL). Then, the mixed solution was heated to 70 °C, followed by the continuous addition of 1.0 mL aqueous ammonia (NH$_3$ H$_2$O). After that, the final dark red mixture was softly stirred for 12 h under air at 70 °C. After cooling to room temperature, the resulting black powder was collected by filtration and the solid product was washed thoroughly with hot DMSO (20 mL * 3), deionized water (20 mL * 3) MeOH (20 mL * 3), and acetone (20 mL * 3) serially. The product as a pure black powder (~65 mg, yield 93.2%) was collected and stored in refrigerator. All raw materials were purchased from chemical reagent company in the USA (Fisher and Sigma-Aldrich) without further purification.

S.2 Fabrication of the NiPc-MOF electrode
To prepare the 2D NiPc-MOF nanosheets modified electrode, a bare GCE (ø = 4 mm) was polished with alumina slurry (different particle sizes ranging from 50 μm to 10 μm) and then in turn ultrasonically washed in distilled-water and ethanol for 5 min, respectively. 1 mg of 2D NiPc-MOF nanosheets was dispersed into 1 mL ethanol for ultrasonication lasting for 30 min. Then, the prepared suspension was mixed with 5.0 % nafion until a well-dispersed solution was achieved. After that, 10 μL of the uniform mixture solution was cast on the polished GCE and then dried naturally, through which the modified electrode (NiPc-MOF@GCE) was obtained. Also, the NiPc@GCE was fabricated via the same way.

S.3 Physical characterizations
Morphological structure was observed employing a transmission electron microscope (TEM, JEM-2100, JEOL) equipped with scanning transmission electron microscope energy-dispersive X-ray spectroscopy (STEM-EDX, Gatan Inc.). The transmission spectrum was recorded by Fourier transform infrared (FTIR) spectrometer ( Nicolet 380, Thermo Fisher, USA) in a range from 400 cm$^{-1}$ to 4000 cm$^{-1}$. Atomic force microscopy (AFM, FEI SIRION200) was used to study the morphology of the as-prepared sample. In addition, X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, Thermo Fisher, USA), and powder X-ray diffraction spectra (PXRD; BL14B station, Shanghai) were recorded to investigate the internal structure of 2D NiPc-MOF nanosheets. All the electrochemical tests were performed on an electrochemical workstation (CHI 760E, CH instruments, Inc., USA).

S.4 Electrochemical measurements
All electrochemical measurements were carried out using an electrochemical workstation (CHI 760E, CH instruments, Inc., USA) with a typical three-electrode system consisting of the working electrode (WE), counter electrode (CE) and reference electrode (RE). Herein, the glassy carbon electrode (GCE, ø = 4 mm) coated with the as-prepared catalyst loading was used as the WE, the Pt wire and the saturated Ag/AgCl electrode as the CE and RE, respectively. The mass loading of 2D NiPc-MOF nanosheets was about 0.03 mg cm$^{-2}$. The electrocatalytic performance of 2D NiPc-MOF electrode was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 0.1 M buffer solution. The electrochemical impedance (EIS) measurements were performed inside the three-electrode electrochemical cell. EIS study was performed within frequency range of 100 kHz to 0.1 Hz with an AC amplitude of 10 mV. An equivalent Randles circuit model was used to fit the data to calculate the charge transfer resistance $R_{ct}$ for each catalyst system. All potentials were referenced to the Ag/AgCl electrode if no specified. All the tests were carried out at room temperature (~25 °C).
Figure S1. Different views of the theoretical structure of 2D NiPc-MOF nanosheets.

Figure S2. XPS spectrum of Ni 2p.
**Figure S3.** EDX spectrum of NiPc-MOF nanosheet corresponding to Fig. 1c.

**Figure S4.** AFM image and height profile (inset) along the marked white line of the as-prepared sample.
Figure S5. FT-IR spectrum of NiPc-MOF nanosheets.

Figure S6. BET characterization of NiPc-MOF nanosheets.
Figure S7. (a) Cyclic voltammograms of 1.0 M nitrite in 0.1 M PBS (pH 7.0) on the NiPc-MOF electrode, at different scan rates from 20 to 120 mV s\(^{-1}\). (b) Linear variation of oxidation peak current (\(I_{pa}\)) versus the square of scan rates related to the nitrite oxidation. (c) Linear variation of peak currents versus scan rates related to the nitrite oxidation. (d) Linear variation of \(E_{pa}\) and log\(v\).

Figure S8. (a) Histograms of oxidation peak current (\(I_{pa}\)) of NiPc-MOF electrode for nitrite oxidation in the electrolyte of acetic acid, NaAc-HAc buffer, PBS and NaOH. (b) Histograms of oxidation peak current (\(I_{pa}\)) of NiPc-MOF electrode for nitrite versus pH values of 0.1 M PBS.
**Figure S9.** (a) EIS simulation patterns of NiPc electrode and NiPc-MOF electrode with details (b).

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>R1/Ω</th>
<th>R2/Ω</th>
<th>CPE1-T</th>
<th>CPE1-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPc</td>
<td>0.11476</td>
<td>1680</td>
<td>3.8*10^{-5}</td>
<td>0.70571</td>
</tr>
<tr>
<td>NiPc-MOF</td>
<td>-18.05</td>
<td>803.8</td>
<td>4.8*10^{-4}</td>
<td>0.37364</td>
</tr>
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</table>

**Figure S10.** CV measurements of (a) NiPc electrode and (b) NiPc-MOF electrode in 5.0 mM [Fe(CN)₆]³⁻/⁴⁻ containing 0.1 M KCl between 0.1 V and 0.6 V at a scan rate of 50 mV s⁻¹.
S.5 The effect of scan rates on electrochemical reaction kinetics

To evaluate kinetic characteristic for the nitrite oxidation at NiPc-MOF electrode, CV measurements were recorded in 0.1 M PBS with 0.1 M nitrite at different scan rates (Fig. S7a). As shown, the current responses of redox peak increased with increasing scan rate from 20 mV s\(^{-1}\) to 120 mV s\(^{-1}\). Furthermore, the oxidation peak currents were linear with the square root of scan rates, the relevant regression equation is given as follows: \(I/\mu A = 1.58\sqrt{\text{scan rate}} + 25.51\), \(R^2 = 0.9997\) (Fig. S7b), rather than \(I/\mu A = 0.101 \times \text{scan rate} + 31.24\), \(R^2 = 0.98\) (Fig. S7c), indicating that the redox of nitrite at the NiPc-MOF electrode is the diffusion-controlled mechanism, not the surface-controlled process. Additionally, it can be seen in Fig. S7d that the anodic peak potential \((E_{pa})\) was linearly proportional to the logarithm of scan rate \((\log v)\) from the same range (20-120 mV s\(^{-1}\)). The corresponding equation of linear regression can be expressed as \(E_{pa} = 0.05\log v + 1.04\) with the correlation coefficient \((R^2)\) of 0.9998. For an irreversible process, \(E_{pa}\) could be described by the following Eq. (1)\(^2\):

\[
E_{pa} = K + \frac{2.3RT}{2(1-a)nF}\log v
\]

Where, \(K\) is a constant, \(n\) is the number of involved electrons in the rate-determining step, \(R\), \(T\) and \(F\) are gas constant (8.3145 J K\(^{-1}\) mol\(^{-1}\)), room temperature (298.15 K) and Faraday constant (96,485.33 A mol\(^{-1}\)), \(a\) is the transfer coefficient, respectively. Among the above parameters, the value of \(a\) can reflect the reaction mechanism during nitrite oxidation\(^3\). By assuming one electron \((n = 1)\) in rate-determining step\(^4\), the value of \(a\) will be calculated as 0.53 \((a > 0.5)\). It means the reaction favors product formation rather than reactants\(^3\), which may explain why the nitrite oxidation possesses a better electrocatalytic mechanism on the NiPc-MOF electrode.

S.6 Optimization of experimental conditions
To build a better sensing environment, the species of electrolyte and its pH are non-negligible factors for nitrite oxidation. So, phosphate buffer solution (PBS), NaAc-HAc buffer, NaOH and acetic acid are primarily selected for further study in the following experiments. Fig. S8a displays the histograms of the oxidation peak currents ($I_p$) of NiPc-MOF electrode with the above supporting electrolytes during nitrite oxidation. Among them, 0.1 M PBS is preferred to use for nitrite oxidation due to it shows the largest $I_p$. Then, to evaluate the impact of the pH, the pH values of 0.1 M PBS buffer ranging from 5.5 to 8.0 was chosen, and the consequent oxidation peak currents are plotted as a function of pH in Fig. S8b. It is observed that the current response of nitrite increases as pH value increases from 5.5 to 7.5 and then decreases at 8.0. The result of the low current response at low pH value may be due to the production of N$_2$O which results in the decrease of the peak current in a strongly acidic environment. However, nitrite oxidation becomes more difficult as pH values arrives 8.0 due to the lack of enough protons. Accordingly, the optimum applied pH 7.5 for nitrite sensing was determined for the subsequent analytical experiments.
**Table S1** Comparisons of analytical performance of nitrite on the modified electrodes (from 2018-2020 year)

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrode</th>
<th>Technique</th>
<th>Linear range</th>
<th>LOD</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$O$_4$-rGO/CNTsa</td>
<td>GCE</td>
<td>Amperometric i-t</td>
<td>0.1 μM-8 mM</td>
<td>1 μM</td>
<td>6</td>
</tr>
<tr>
<td>CoTL-MethPc/MWCNTsb</td>
<td>GCE</td>
<td>DPVc</td>
<td>50-1050 nM</td>
<td>35 nM</td>
<td>7</td>
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<tr>
<td>CoPc/MWCNTc</td>
<td>GCE</td>
<td>DPV</td>
<td>0.01-1050 mM</td>
<td>2.11 μM</td>
<td>8</td>
</tr>
<tr>
<td>a-Fe$_2$O$_3$/CNTs hybrids</td>
<td>GCE</td>
<td>Amperometric i-t</td>
<td>0.5-4000 μM</td>
<td>0.15 μM</td>
<td>9</td>
</tr>
<tr>
<td>TiO$_2$-Ti$_3$C$_2$TX/CTAB/CS</td>
<td>GCE</td>
<td>DPV</td>
<td>0-1.25 mM</td>
<td>0.85 μM</td>
<td>10</td>
</tr>
<tr>
<td>Au/CNHNf</td>
<td>GCE</td>
<td>Chronoamperometry</td>
<td>0.05–1150 μM</td>
<td>0.017 μM</td>
<td>11</td>
</tr>
<tr>
<td>GO-Ag</td>
<td>GCE</td>
<td>LSVg</td>
<td>1.0-1000 μM</td>
<td>0.24 μM</td>
<td>12</td>
</tr>
<tr>
<td>SFh</td>
<td>GCE</td>
<td>Amperometric i-t</td>
<td>0.02–3600 μM</td>
<td>6.3 μM</td>
<td>13</td>
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<td>CaFe$_2$O$_4$</td>
<td>SPEi</td>
<td>Amperometric i-t</td>
<td>0.016–1921 μM</td>
<td>6.6 μM</td>
<td>14</td>
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<tr>
<td>Poly(TazoCoPc)/CNPi</td>
<td>GCE</td>
<td>Amperometric i-t</td>
<td>0.02–1 μM</td>
<td>0.006 μM</td>
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<tr>
<td>CoTM-QOPc/CNPk</td>
<td>GCE</td>
<td>Chronoamperometry</td>
<td>0.1–350 μM</td>
<td>0.033 μM</td>
<td>16</td>
</tr>
<tr>
<td>2D NiPc-MOF</td>
<td>GCE</td>
<td>DPV</td>
<td>0.01-1150 mM</td>
<td>2.3 μM</td>
<td>This work</td>
</tr>
</tbody>
</table>

a rGO/CNTs, reduced graphene oxide and carbon nanotubes.
b CoTL-MethPc/MWCNTs, tetra L-Methionine cobalt (II) phthalocyanine/Multi-wall carbon nanotubes.
c DPV, Differential pulse voltammogram.
d CoPc, Cobalt phthalocyanine.
e TiO$_2$-Ti$_3$C$_2$TX nanohybrid, hexadecyl trimethyl ammonium bromide (CTAB) and chitosan (CS)
f CNHN, CuNi-based hollow nanoarchitecture
g LSV, linear sweep voltammogram.
h SF, Strontium ferrite
i SPE, screen-print electrode
j Poly(TazoCoPc)/CNP, tetraazo-bridged cobalt phthalocyanine polymer
k CoTM-QOPc/CNP, Cobalt (II) tetra methyl-quinoline oxy bridged phthalocyanine
l GCE, glassy carbon electrode
Table S2 Determination of nitrite in 0.1 M PBS on the NiPc-MOF electrode (under optimized conditions, n = 3)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added/mM</th>
<th>Found/mM</th>
<th>Recovery/%</th>
<th>RSD/% (n = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M PBS</td>
<td>#1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>100</td>
<td>101.7</td>
<td>101.7</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>500</td>
<td>498.4</td>
<td>99.6</td>
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<tr>
<td></td>
<td>#4</td>
<td>1000</td>
<td>989.3</td>
<td>98.9</td>
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<tr>
<td>Tap water</td>
<td>#1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>100</td>
<td>93.6</td>
<td>93.6</td>
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<td></td>
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<td>508.2</td>
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<tr>
<td></td>
<td>#4</td>
<td>1000</td>
<td>976.4</td>
<td>97.6</td>
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References