Supporting Information

Nickel porphyrin-based covalent organic frameworks modified electrode for the electrochemical detection of acetaminophen

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Reagents and apparatus

All solvents and reagents obtained from commercial sources were used without further purification. 2,3,6,7-tetra (4-formylphenyl) tetrathiafulvalene (TTF-4CHO), and 5,10,15,20-tetrakis (para-aminophenyl)-21H, 23H-porphyrin (TAPP-2H) was purchased from J&K China Chemical Ltd. (Shanghai, China). $Ni(OAc)_2 \cdot 4H_2O$, 1, 4-Dioxane (≥ 99.7%), dicalcium phosphate (KCl), sodium phosphate dibasic (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), potassiumhexacyanoferrate (II) ($K_4[Fe(CN)_6$), potassium hexacyanoferrate (III) ($K_3[Fe(CN)_6]$), and 1,3,5-trimethylbenzene was purchased from Aliddin Reagent (Shanghai, China). tetrahydrofuran (THF), acetone, phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), and acetaminophen (ACOP) from Macklin Reagent (Shanghai, China). All aqueous solutions are prepared using ultrapure water (Milli-Q, Millipoll) with resistance values > 18.2 MΩ.cm.

Scanning electron microscopy (SEM) images were recorded using a Nova Nano SEM 450 scanning electron microscope from Hitachi Co., Japan. Transmission electron microscopy (TEM) images were taken on a JEM-2100 transmission electron microscope from JEOL Ltd., Japan. X-ray diffractometer (XRD) was recorded using an X'Pert3Powder from PANalytical, Netherlands. The X-ray photoelectron spectrum (XPS) was recorded on an ESCALAB 250X spectrometer from Thermo-VG Scientific Co., USA, equipped with an ultra-high vacuum generator. The current responses were recorded using a CHI 660E electrochemical workstation (Shanghai Chenhua Instruments Co., China). All electrochemical measurements at room temperature were conducted using a three-electrode system consisting of a modified glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. A 0.1 M phosphate buffered (PB) (pH = 3.0) solution was used as the electrolyte throughout the experiment.

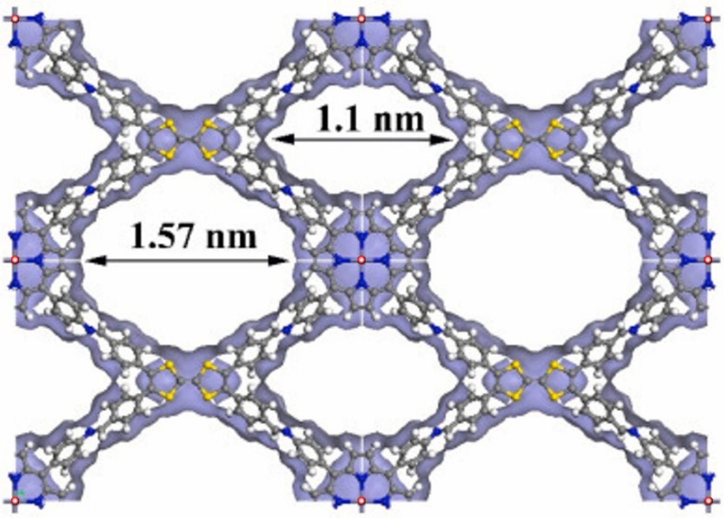
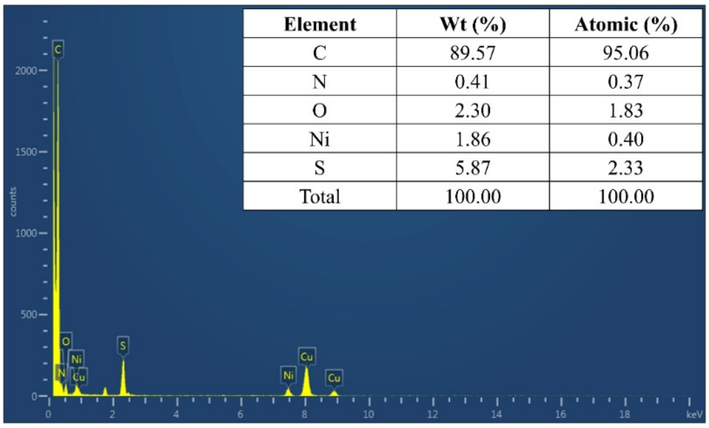


Fig. S1. The porous structure of COF-Ni material.

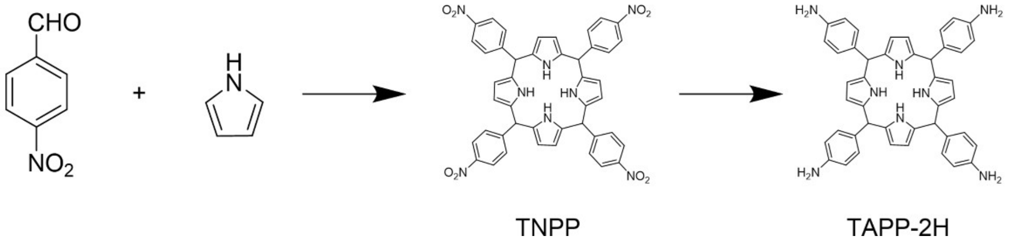


Element	Wt (%)	Atomic (%)
C	89.57	95.06
N	0.41	0.37
O	2.30	1.83
Ni	1.86	0.40
S	5.87	2.33
Total	100.00	100.00

Fig. S2. The element content in COF-Ni material

Synthesis of 5,10,15,20-tetrakis (4-aminophenyl) porphyrin (COF-H)

In a 200 ml flask, p-nitrobenzaldehyde (3.7 g, 20.44 mmol), acetic anhydride (4 mL, 42.33 mmol) and propionic acid (100 mL) was added and heat to 150°C to reflux with stirring. Then 3.3 mL of propionic acid mixed with 1.66 mL (20.44 mmol) of pyrrole was added and continue refluxing under stirring for 30 min. After that cooled to room temperature and stand undisturbed for 24 h. Then the crude product was affording through vacuum filtered as black solid, then washed with 100 mL water for 6 times. Put the crude product in a 100 °C vacuum oven for 24 h to drying to obtain purple-black solid. After that, the solid was mixed with 80 mL of pyridine and refluxed for 1 h, then cooled to room temperature and stored at -4°C overnight to get black precipitate. Then the solvent was removed through vacuum filtered and washed the filter cake with acetone for several times until the filtrate become colorless. The second step is the reduction of nitro to amino groups. 2.0 g (2.5 mmol) of TNPP was dissolved in 100 mL of concentrated hydrochloric acid. 40 mL of concentrated hydrochloric acid solution containing 9.0 g (40 mmol) of $SnCl_2 \cdot 2H_2O$ was added dropwise to the porphyrin solution within 20 min at room temperature under stirring, and then the temperature was raised to 80 °C for 30 min. The dark green TAPP-2H hydrochloride solid was separated by ice bath cooling, the hydrochloride was dispersed in 200 ml of deionized water, neutralized with concentrated ammonia to pH = 9, and the solid was collected by centrifugation and dried under vacuum at 60 °C. The product was extracted with chloroform by using a Soxhlet extractor, and solvent was removed by rotary evaporation to give a bright purple TAPP-2H crystal. The synthesis of COF-H was carried out following the same protocol as for COF-Ni, by replacing the TAPP-Ni with TAPP-2H (13.5 mg, 0.02 mmol).



Scheme S1. Synthesis of TAPP-2H

Optimization of amount of COF-Ni material on GCE

The amount of the modified material has an important effect on the performance of the electrochemical sensor. If the amount of modification material is too little, the conductive carbon plane cannot be paved so that the material is unevenly distributed on the GCE surface and the catalytic performance is poor. If the amount of modification material is too much, the material film formed on the GCE surface will be too thick, which will affect the overall conductivity of the electrode. Therefore, the oxidation peak current of ACOP increases first and then decreases with the concentration (Figure S3a, b) and volume (Figure S3c, d) of the COF-Ni dispersion. Based on this result, the dispersion concentration of 2 mg mL^{-1} and the modification volume of 7 μL were finally determined.

Optimization of pH

The pH value of the buffer has an effect on the oxidation peak current of ACOP on COF-Ni/GCE, and this change was evaluated by setting the pH gradient from 2.0 to 6.0, increasing one unit each time. As shown in Figure S3e, f, the oxidation peak current of ACOP increases with the increase of pH and reaches the maximum at pH = 3.0. At the same time, it can be observed that with the increase of pH, the oxidation peak potential of ACOP moves to the negative half axis, which indicates that hydrogen ions are involved in the whole redox reaction process. The pink line in Figure S3f shows the linear relationship between different pH values and the oxidation peak current of ACOP. The corresponding linear equation is $E_p = -0.0415\ \mathrm{pH} + 0.763$ ($R^2 = 0.992$). The slope is − 41.5 mV pH^{-1}, which is close to the Nernst value of − 59 mV pH^{-1} at 25 °C. According to the Nernst equation [1], the number of electrons and protons transferred is equal. Figure S3g shows the linear relationship between E_p and ln v. The equation was $E_p\ (V) = 0.0111 \ln v + 0.377$ ($R^2 = 0.992$). According to the Laviron equation:

$$Ep = E^{\theta} + \frac{RT}{\alpha nF} ln \frac{RTK_s}{\alpha nF} - \frac{RT}{\alpha nF} lnv$$

where E^{θ} represents the formal redox potential, R is molar gas constant (8.314 J K^{-1} mol^{-1}), T is temperature (298 K), Ks is the standard rate constant of the reaction, α is the transfer coefficient (which can be assumed to be 0.5 for an irreversible process) and *F* is Faraday's constant (96480 C mol^{-1}), The number of electrons transferred (*n*) in the process can be calculated to be 2.05 for ACOP. Therefore, the possible oxidation pathways of ACOP can be inferred as shown in Figure S4.

The effect of scan rate

In order to explore the kinetics of electrode reaction, the relationship between the scan rates and the oxidation peak current of ACOP is studied by using CVs. As shown in Figure S3h and i, the oxidation peak current of ACOP increases with the increase of the scan rate. A linear relationship is obtained between the scan rate and oxidation peak current of ACOP. The linear regression equation is I (μA) = 0.707 $v^{1/2}$ + 1.51 (R^2 = 0.995). Such results show that the reaction process of ACOP on the COF-Ni/GCE is a classical diffusion-controlled process [2].

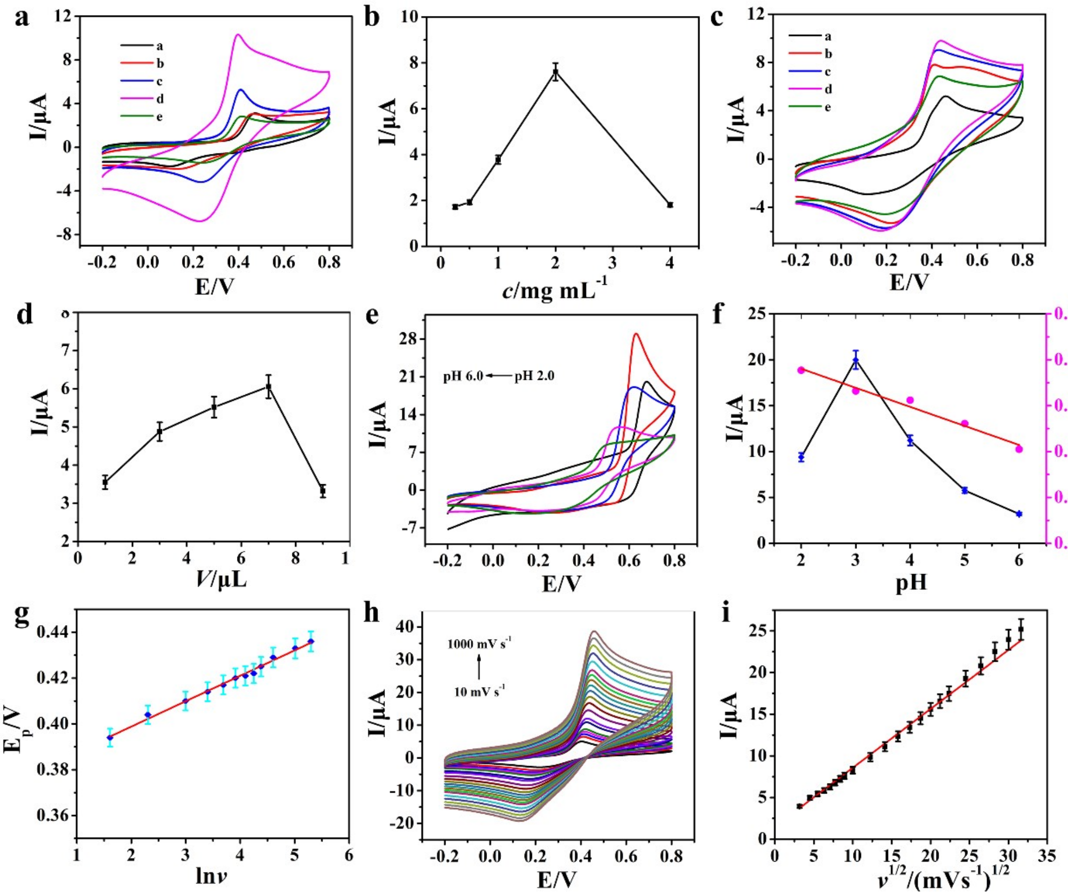


Figure S3. CVs curves of COF-Ni dispersion with (a) different concentration (a: 0.25 mg mL^{-1}, b:

0.5 mg mL^{-1}, c: 1 mg mL^{-1}, d: 2 mg mL^{-1}, e: 4 mg mL^{-1},) and (c) different volume (a: 1 μL, b: 3 μL, c: 5 μL, d: 7 μL, e: 9 μL) modified GCE in 0.1 M PB solution; The relationship between the oxidation peak current of ACOP and the (b) concentration and (d) volume of COF-Ni dispersion; (e) CV curves of COF-Ni/GCE in different pH (2.0, 3.0, 4.0, 5.0, 6.0) of 0.1 M PB solution; (f) The oxidation peak currents and peak potentials of ACOP *vs* different pH; (g) The relationship between E_p of ACOP and ln v; (h) CV curves of COF-Ni/GCE in 0.1 M PB (pH 3.0) solution with different scan rates ranging from 10 to 1000 mV s^{-1}; (i) The relationship between the oxidation peak currents of ACOP and $v^{1/2}$.

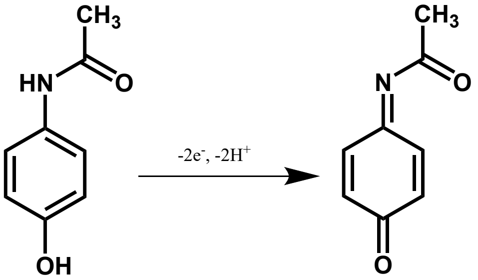


Figure S4. Oxidation pathway of ACOP.

Reference

1. R. Li, L. Yao, Z. Wang, W. Lv, W. Wang, F. Kong and W. Wang, *J. Electrochem. Soc*. 2019, **166**, B212.
2. Y. Zhang and X. Bai, *J. Electrochem. Soc*. 2020, **167**, 027541.