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Covalent Organic Frameworks-TpPa-1 as an Emerging Platform for Electrochemical Sensing

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Abstract: Covalent organic frameworks (COFs) are a new type of metal-free porous architecture with a well-designed pore structure and high stability. Here an efficient electrochemical sensing platform was demonstrated based on COFs TpPa-1 constructed by 1,3,5-triformylphloroglucinol (Tp) with p-phenylenediamine (Pa-1), which possesses abundant nitrogen and oxo-functionalities. COFs TpPa-1 exhibited good water dispersibility and strong adsorption affinities for Pd^{2+} and thus was used as loading support to modify Pd^{2+} . The Pd^{2+} -modified COFs TpPa-1 electrode (Pd^{2+} /COFs) showed high electrocatalytic activity for both hydrazine oxidation reaction and nitrophenol reduction reaction. In addition, TpPa-1-derived nitrogen-doped carbon presented high activity for the electro-oxidation of reduced glutathione (GSH), and sensitive electrochemical detection of GSH was achieved. The presented COFs TpPa-1 can be utilized as a precursor as well as support for anchoring electro-active molecules and nanoparticles, which will be useful for electrochemical sensing and electrocatalysis.

Keywords: covalent organic frameworks; electrochemical sensor; hydrazine; nitrophenol; nitrogen doped carbon; reduced glutathione



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1. Introduction

The synthesis and construction of efficient electrode materials to gain high sensitivity and selectivity is crucial for electroanalysis. The successful development of nonenzymatic electrochemical sensors depends critically on electrode materials with excellent electrocatalytic properties because many analytes are electrochemically inactive when using traditional electrodes. Up to now, different categories of materials, including noble metals, metal oxides, and carbons (such as CNT and graphene), have been applied in electrochemical sensing [1]. Recently, porous materials have demonstrated advantages in constructing electrochemical sensors due to their high specific surface areas and powerful adsorption and loading capability [2].

Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), as two emerging families of crystalline porous materials, have been explored in electroanalysis and electrocatalysis [3,4]. Compared to conventional porous materials such as zeolites, porous oxides, and carbons, MOFs and COFs show some intriguing features for electrochemical applications, including inter-connected porosity, tunable intra-framework chemical functionality, and high surface area [5]. Wang et al. synthesized graphene aerogel (GA) and metal-organic framework (MOF) composites via the in situ growth of the MOF UiO-66-NH₂ crystal on the GA matrix. The interface showed high sensitivity and selectivity for the electrochemical sensing of multiple heavy-metal ions. GA was employed as the backbone for UiO-66-NH₂, which also improved the electrical conductivity of the composites by accelerating the electron transfer in the matrix. UiO-66-NH₂ provided a binding site for heavy-metal ions due to the interaction between hydrophilic species and metal cations [6]. Xu et al. developed a facile furazolidone sensor based on COFs [7]. In this work, 1,3,5-tris-(4-amino-phenyl) benzene (TAPB) and terephthalaldehyde (TPA) were used as monomers to synthesize the COF, which was then self-assembled on the

surface of the NH_2 -CNTs via a simple and rapid one-pot strategy at room temperature. The prepared COF@ NH_2 -CNT composites exhibited a high surface area and excellent conductivity, thus achieving high sensitive detection of furazolidone. However, most MOFs are not chemically stable in water. If the MOF is unstable in the aqueous buffer used for electroanalysis, the MOF coating modified on the electrode surface may suffer from dissolving or converting into MOF-derived metal hydroxides or oxides [8]. Unlike MOFs, COFs are regularly integrated into metal-free crystalline organic structures through strong covalent bonds between the organic building blocks, leading to more robust frameworks and relatively lower densities. Many COFs possess the sp^2 carbon networks with a high degree of p-conjugation and thus lead to at least a modest electronic conductivity, which facilitates the electron transfer rate. Furthermore, the presence of electronegative atoms (N and O) and π bonds within COFs can allow more specific target analyte recognition through the formation of hydrogen bonds or π - π bonds, thus improving the sensitivity and selectivity of COF-based electrochemical sensors [7]. These unique characteristics of COFs make them promising materials for electrochemical sensing.

COFs-derived porous carbons are also considered ideal platforms for electrochemical sensing due to their high conductivity, porosity, chemical and thermal stability, high electrocatalytic activity, and powerful supporting performances for anchoring molecules and nanomaterials. Most intrinsic electrocatalytic activities are contributed to the oxo-functionalities and edge-plane-like sites (defects) present on the surface of carbon materials [9]. COFs are often rich with nonmetal elements such as N, B, S, and P, which can induce heteroatom doping into derived carbons. Heteroatom doping forms charge delocalization and changes in the electronic structure due to the difference in atomic size, bond length, and coordination between the carbon atoms and dopants, leading to abundant defect sites [10]. N-doping can increase the surface polarity and wettability of the electrodes and also improve the electrocatalytic activity and adsorption [11,12]. Here COFs TpPa-1 constructed by 1,3,5-triformylphloroglucinol (Tp) with p-phenylenediamine (Pa-1) possess abundant nitrogen and oxo-functionalities, which was demonstrated for Pd^{2+} immobilization and fabricating nitrogen-doped porous carbon. The presented electrocatalysts showed high responses for hydrazine oxidation, nitrophenol reduction, and glutathione (GSH) oxidation.

2. Experimental

2.1. Chemicals and Solutions

GSH, palladium chloride (PdCl_2), hydrazine (wt. 80%), graphite powder, liquid paraffin, p-nitrophenol (PNP), and o-nitrophenol (ONP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). COFs-TpPa-1 was purchased from Nanjing XFNano Materials Tech Co., Ltd. (Nanjing, China) The pore size of COFs-TpPa-1 is in the range of 1.5–1.8 nm with a BET specific surface area of $\sim 1360 \text{ m}^2/\text{g}$. All of the other chemicals were of analytical reagent grade and used without further purification.

2.2. Apparatus

The morphologies were characterized by scanning electron microscopy (SEM) (Hitachi SU8010, Tokyo, Japan) and transmission electron microscopy (TEM) (JEM-2100, JEOL, Tokyo, Japan). The X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo ESCALAB 250 Xi spectrometer (Waltham, MA, USA) fitted with a monochromatic Al K α X-ray source. X-ray diffraction patterns were collected by a Bruker D8 (Billerica, MA, USA) advance powder X-ray Cu K α radiation diffractometer. All of the electrochemical experiments were conducted on a CHI 750E electrochemical workstation with a conventional three-electrode system consisting of a modified working electrode, platinum coil auxiliary electrode, and Ag/AgCl (saturated KCl) reference electrode. Electrochemical impedance spectra (EIS) were carried out in 0.1 M KCl containing 5.0 mM $\text{Fe}(\text{CN})_6^{3-}/4-$ in the frequency range of 1 MHz to 0.1 Hz at 0.25 V.

2.3. Electrode Preparation and Modification

2.3.1. Preparation of Pd²⁺/COFs/GCE

Prior to modification, the glassy carbon electrode (GCE) (3 mm diameter, 0.07 cm²) was successively polished with 1, 0.3, and 0.05 µm alumina paste to a mirror finish and then rinsed with deionized water followed by ultrasonic treatment in water and ethanol, respectively. The COFs-modified GCE (COFs/GCE) was prepared by dropping 10.0 µL COFs aqueous suspension (2.0 mg/mL) on a cleaned GCE and dried at room temperature. In order to anchor Pd²⁺, the prepared COFs/GCE was dipped in 10 mM PdCl₂ solution for 30 min, which was then washed with water and left to dry at room temperature (Pd²⁺/COFs/GCE). Pd²⁺/GCE was prepared by soaking the GCE in Pd²⁺ solution by electroless deposition. The electroactive surface areas of the different electrodes could be calculated by the Randles–Sevcik equation using the CV responses of the corresponding electrodes in 0.1 M KCl solution in the presence of 5.0 mM K₃Fe (CN)₆ at different scan rates at 298 K (Figures S1–S3).

2.3.2. Preparation of PCs/CPE

The nitrogen-doped porous carbon materials (PCs) were prepared by calcination. A number of COFs were calcined at 800 °C (heating rate of 10 °C min^{−1}) for 80 min under nitrogen flow in the tubular furnace, and black carbonized materials were obtained after cooling to room temperature naturally. To prepare the PCs modified electrode, 3.0 mg PCs were ultrasonically dispersed in 1.0 mL water for 1 h. The carbon paste electrode (CPE) was prepared by thoroughly mixing 1 mg of the graphite powder and 300 µL of liquid paraffin using an agate mortar and pestle for 40 min. Then, a suitable amount of the above mixture was filled firmly into one glass tube. The electrical contact was made by inserting a copper wire into the paste in the inner hole of the tube. Finally, 5.0 µL of 3.0 mg/mL PC suspension was dropped onto the freshly prepared CPE surface and dried at room temperature (PCs/CPE).

3. Results and Discussion

3.1. Electrochemical Sensing of Hydrazine

3.1.1. Characterization of Pd²⁺/COFs/GCE

The surface morphology and elemental composition of Pd²⁺/COFs/GCE were investigated by SEM and XPS. As shown in Figure 1, the SEM image of Pd²⁺/COFs/GCE shows the rough and inter-connected porous surface. The morphology is mainly composed of complicated long strips, indicating that COFs were modified on the GCE surface. XPS was also carried out to explore the surface composition and chemical states (Figure 2). The characteristic peaks of C, N, O, and Pd elements are found in the XPS survey spectrum (Figure S4). The O1s XPS spectrum exhibits four peaks centered at 530.79, 531.96, 533.18, and 535.29 eV (Figure 2a), which can be attributed to C–OH, C=O, C–O, or H–O, and chemisorbed oxygen in carboxylic groups or water (H–O–H), respectively [13]. The abundant oxo functionalities present on COFs can improve their dispersion in water, which is beneficial for the modification of COFs on the electrode surface. The N1s XPS spectra show two characteristic peaks at 400.06 and 403.53 eV (Figure 2c), which are assigned to the C=N and C–N groups, respectively [14]. Figure 2b displays the XPS Pd3d spectra of Pd²⁺/COFs, including two peaks at 338.10 and 343.40 eV, corresponding to the peak of the low energy band (Pd3d 3/2) and high energy band (Pd3d 5/2), respectively. The Pd²⁺ species might be attached to COFs via N coordination [15]. The results confirm the existence of Pd on the composite surface, and the Pd²⁺ is successfully loaded on the COFs. The XPS data showed that the atomic amount of Pd is 0.16%. In order to investigate the stability of COFs, the XRD patterns of COFs, Pd²⁺/COFs, and Pd²⁺/COFs soaked in 0.1 M NaOH were performed (Figure 3). The characteristic peaks of these samples observed in XRD patterns were in accord with the reported literature [15,16] and remained unchanged, indicating that Pd²⁺ modification and NaOH solution soaking did not change the crystalline structure. The

results showed that COF-TpPa-1 possessed good chemical stability. It was also found that COF-TpPa-1 was still stable even though soaked in 1.0 mol/L HNO_3 , 6.0 mol/L NaOH , and HCl for three days [16].

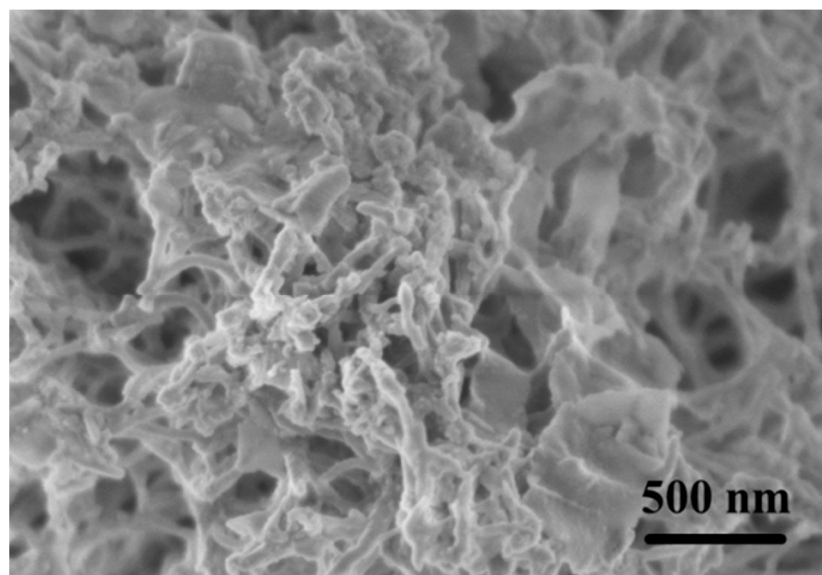


Figure 1. SEM image of $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$.

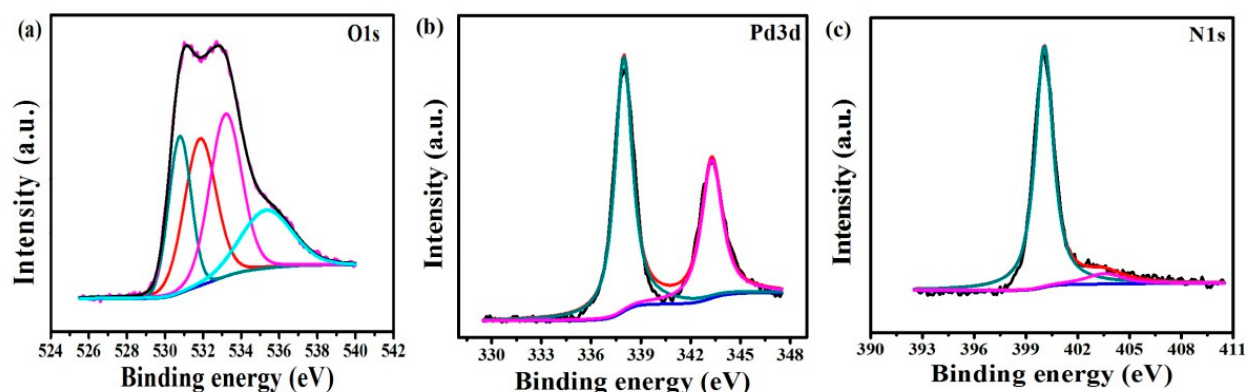


Figure 2. XPS (a) O1s, (b) Pd3d and (c) N1s spectra of $\text{Pd}^{2+}/\text{COFs}$.

3.1.2. Electrochemical Oxidation of Hydrazine

Figure 4 shows the CVs of COFs/GCE , $\text{Pd}^{2+}/\text{GCE}$, and $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ in 0.1 M NaOH in the absence and presence of 5.0 mM hydrazine at a scan rate of 100 mV s^{-1} . At COFs/GCE , the hydrazine oxidation began at the potential of 0.25 V (Figure 4a) and reached the oxidation peak at about 0.75 V. However, for $\text{Pd}^{2+}/\text{GCE}$, two oxidation peaks were observed at -0.25 and 0.75 V, respectively (Figure 4b). Pd^{2+} was reduced to Pd metal by electroless deposition when GCE was immersed in a Pd^{2+} solution [17]. The first oxidation wave was ascribed to the electrocatalytic activity of Pd, while the second one originated from the bare GCE. $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ showed three oxidation peaks at -0.50 , -0.33 , and 0 V (Figure 4c), and no oxidation peak was found at about 0.75 V. This indicates that $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ demonstrated the lowest oxidation over-potential among these modified electrodes, suggesting that the combination of Pd^{2+} and COFs formed new catalytic sites and thus enhanced the oxidation of hydrazine. The different electrodes were also investigated by EIS (Figure S5). The electron transfer rate of different electrodes follows the order: Bare GCE > $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ > COFs/GCE . The higher charge transfer resistance of COFs/GCE is attributed to the lower electrical conductivity.

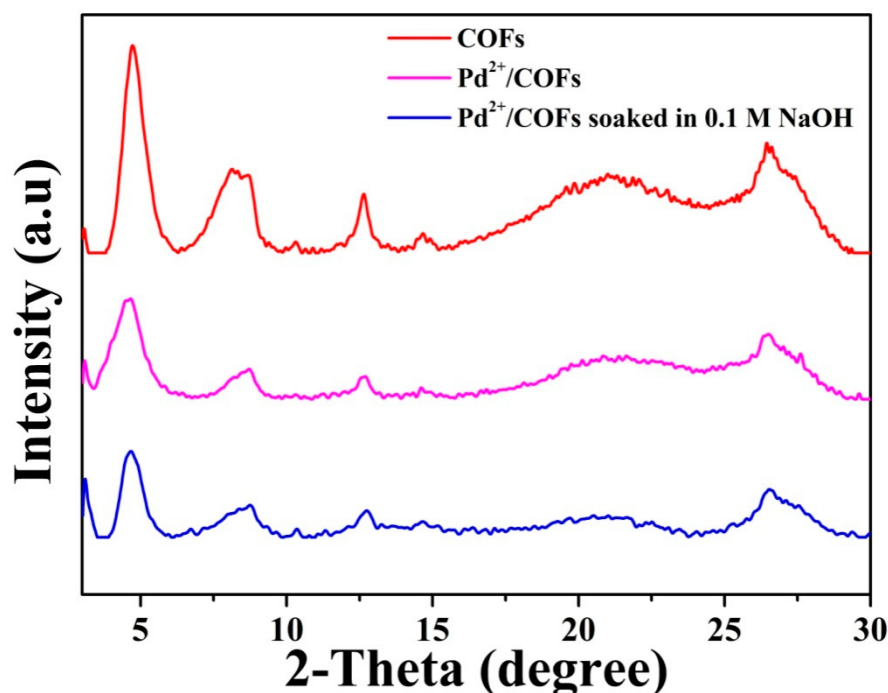


Figure 3. XRD patterns of COFs, Pd²⁺/COFs and Pd²⁺/COFs soaked in 0.1 M NaOH for 24 h.

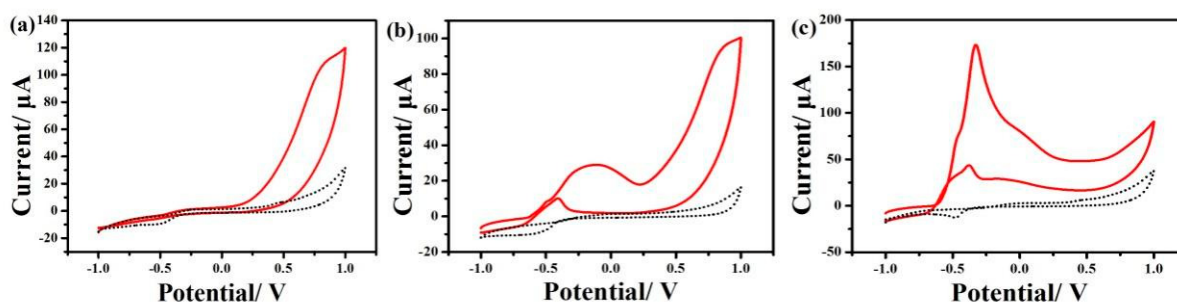


Figure 4. CVs of COFs/GCE (a), Pd²⁺/GCE (b), Pd²⁺/COFs/GCE (c) in the absence (dotted line) and presence (solid line) of 5 mM hydrazine at a scan rate of 100 mV s^{−1}, respectively. (Electrolyte: 0.1 M NaOH).

3.1.3. Analytical Performances for Hydrazine

Figure 5 shows the amperometric current–time response of Pd²⁺/COFs/GCE to the successive additions of hydrazine in 0.1 M NaOH. Upon each successive addition of different concentrations of hydrazine, a stair-shaped plot was raised rapidly and then reached a steady-state oxidation current within 2 s. The inset (a) of Figure 5 shows a linear response over a concentration range from 0.5 μM to 1.6 mM with a sensitivity of 10 μA μM^{−1} cm^{−2} and a detection limit of 0.2 μM (S/N = 3). Table S1 summarizes the sensing performances of hydrazine with Pd²⁺/COFs/GCE and other modified electrodes presented in the literature. The results show that Pd²⁺/COFs/GCE demonstrated an excellent analytical performance for hydrazine, owing to the high electrocatalytic activity.

In order to explore the selectivity of Pd²⁺/COFs/GCE, the interference test was also examined at Pd²⁺/COFs/GCE with 50.0 μM hydrazine in 0.1 M NaOH containing 0.5 mM of the possible interference substances such as KCl, NaCl, Na₂SO₄, NaBr, CaCl₂, NaAc, glucose, (NH₄)₂SO₄, NaNO₃, and NaNO₂ (Figure S6). It was found that 100-fold interferents almost did not interfere with the determination of hydrazine. Moreover, a remarkable current response with the addition of hydrazine was observed again after adding the mentioned interference species. The results indicate that our proposed Pd²⁺/COFs/GCE sensor displays excellent selectivity towards the electrochemical oxidation of hydrazine.

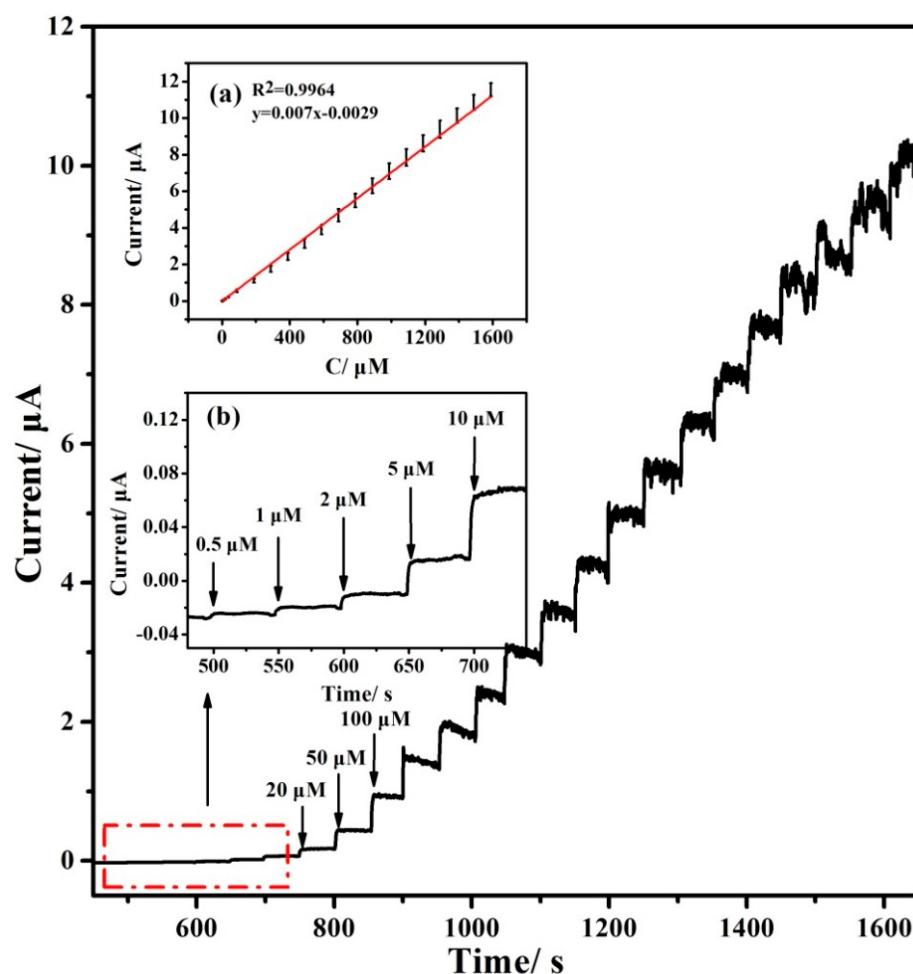


Figure 5. Amperometric responses of the $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ to successive additions of various concentrations of hydrazine in 0.1 M NaOH at -0.1 V. (Inset: (a) the corresponding calibration plot, (b) the amplified response curve.).

The long-term stability of the sensor was further tested by a continuous operation. After 1000s of continuous i-t running for $10.0 \mu\text{M}$ hydrazine, the electrode still retained 89% of its initial value. In addition, ten successive analyses of $10.0 \mu\text{M}$ hydrazine using the same electrode showed a relative standard deviation (RSD) value of 4.5%. A reproducible experiment was also evaluated by using five parallel electrodes for the same solution, and the RSD of the current response was found to be 6.4%, suggesting an acceptable reproducibility.

3.1.4. Sample Analysis of Hydrazine

To confirm the practical applicability of the proposed sensor, the validity of $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ for the determination of hydrazine spiked in real samples was tested by a standard addition method (Figure S7). The prepared sensor presented acceptable recoveries of hydrazine in lake water samples (Table S2).

3.2. Electrochemical Sensing of ONP and PNP

3.2.1. Electrochemical Behaviors of ONP and PNP

The electrochemical behaviors of ONP and PNP were investigated at bare GCE (a), COFs/GCE (b), and $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ (c) by CV at a scan rate of 50 mV s^{-1} in 0.1 M PBS (pH = 7.0) (Figure 6). The CVs of these electrodes in 0.1 M PBS are shown in Figure S8. For PNP, three redox peaks were observed, with one main irreversible cathodic peak located at -0.79 V (R_1) and a pair of reversible redox peaks centered at about 0.08 V (R_2) and 0.14 V (O_1) at bare GCE and COFs/GCE. $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ also exhibited the same redox peaks,

but the peak of R_1 shifted to -0.56 V. However, at bare GCE and COFs/GCE, upon the addition of ONP, four redox peaks, including the three peaks and an additional oxidation peak (O_2) appeared at -0.68 (R_1), -0.30 (R_2), -0.25 (O_1), and -0.23 V (O_2), respectively. Pd^{2+} /COFs/GCE demonstrated the same redox peaks but a much lower R_1 peak (-0.54 V). This indicated that Pd^{2+} /COFs/GCE presented superior electrocatalytic activity towards the R_1 reduction process of ONP and PNP, which was ascribed to the combination of the high catalytic performance of Pd^{2+} and efficient supporting effect of COFs.

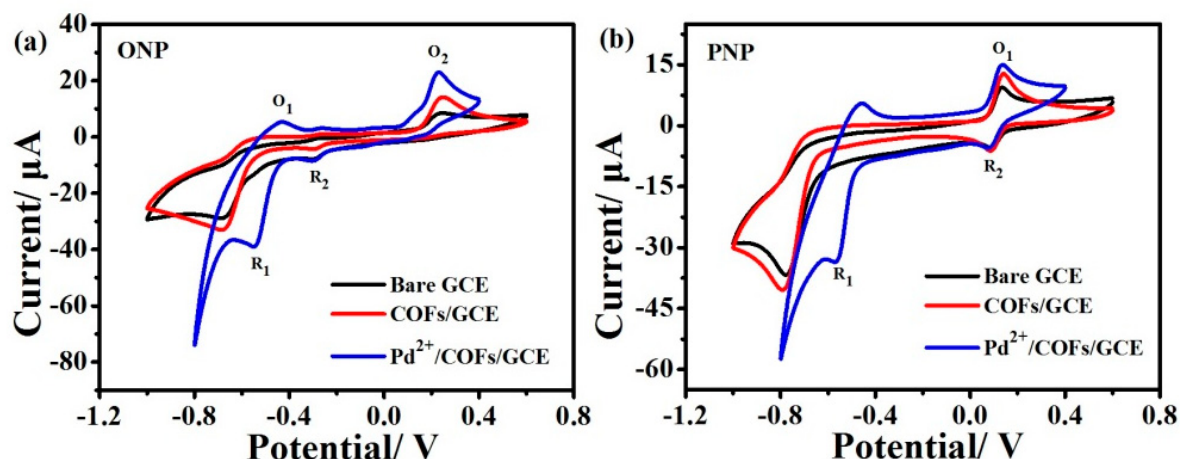
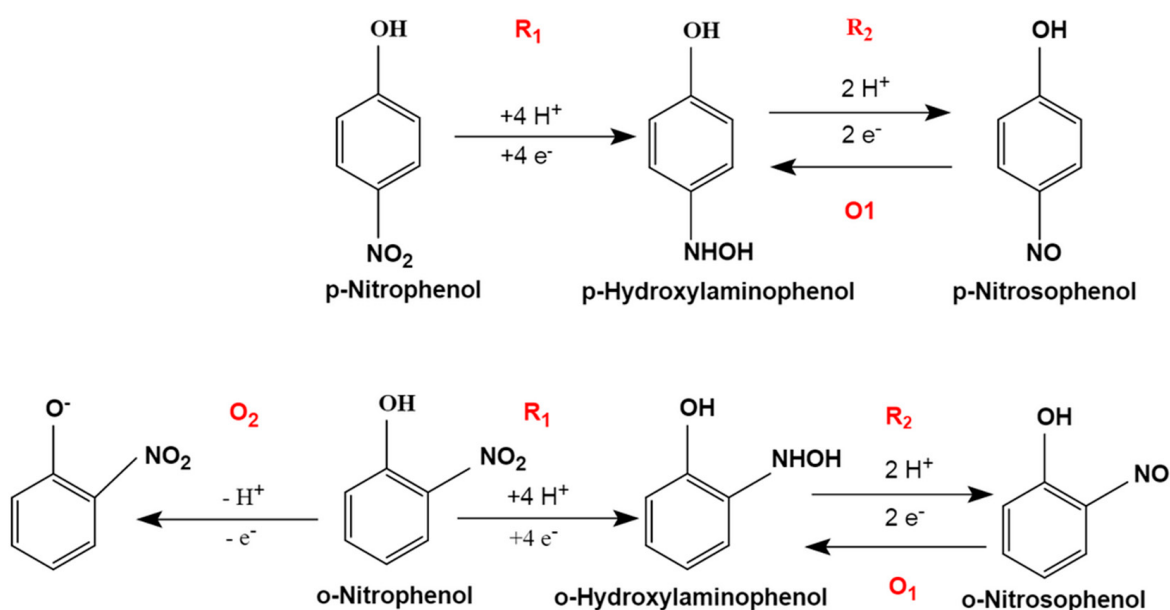


Figure 6. CVs of bare GCE, COFs/GCE, Pd^{2+} /COFs/GCE in the presence of $500 \mu\text{M}$ nitrophenol ((a): ONP, (b): PNP) at a scan rate of 50 mV s^{-1} in 0.1 M PBS ($\text{pH} = 7.0$).

When the potential was scanned negatively, both ONP and PNP could be reduced to hydroxylaminophenol through a four-electron and four-proton transfer process (R_1). Reversible transformation (O_1/R_2) between hydroxylaminophenol and nitrosophenol then occurred with the potential scanning back. In addition, the phenolic group of ONP gave further oxidation through a proton and an electron transfer process (O_2). The detailed reaction mechanism was proposed as Scheme 1 [18]:



Scheme 1. Electrochemical reaction mechanism of PNP and ONP at the Pd^{2+} /COFs/GCE.

To further investigate the electrochemical performance of Pd^{2+} /COFs/GCE, the effect of the scan rate on the redox peak current (I_{pc}) was studied (Figure S9). The results showed

that the peak currents of ONP and PNP were quadratic functions of the square root of the scan rate ($v^{1/2}$), which suggested that the reactions of ONP and PNP on the surface of $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ were mixed controlled processes (surface-controlled at lower scan rates but diffusion-controlled at higher scan rates).

Next, the effect of the pH on the cathodic peak current and potential (R_1) of ONP and PNP (500 μM) was studied by DPV on the $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ in 0.1 M PBS (Figure S10). The reduction peak current of both ONP and PNP increased firstly and then decreased and reached the maximum at pH = 7.0. In the basic solution, the protonation of PNP and ONP decreases, and the electron density of the nitro group increases due to the decrease in proton concentration, thus hampering the electrochemical reduction of PNP and ONP [19]. Therefore, pH 7.0 was selected for further electrochemical experiments.

3.2.2. Analytical Performances for ONP and PNP

Under optimal conditions, the DPV response of $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ for different concentrations of ONP and PNP in 0.1 M PBS (pH = 7.0) was investigated, respectively (Figure 7a,b). The reduction peak current increased gradually with the concentration of ONP and PNP and exhibited a log–log linear relationship in the range of 5.0 μM –2.0 mM. The detection limit of ONP and PNP was estimated to be 1.6 and 1.3 μM ($S/N = 3$), respectively. $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ was also applied for the simultaneous detection of ONP and PNP. Figure 7c clearly shows the well-separated reduction peak for ONP and PNP. The calibration curves reveal the favorable linear relationships between the logarithm of peak current and the logarithm of concentrations (5.0 μM –2.0 mM), with 1.8 and 0.9 μM for ONP and PNP, respectively. The electrochemical sensing performances based on $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ and other reported sensors are summarized in Table S3. The results show that the $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ sensor exhibits comparable performances with the reported methods for the detection of ONP and PNP.

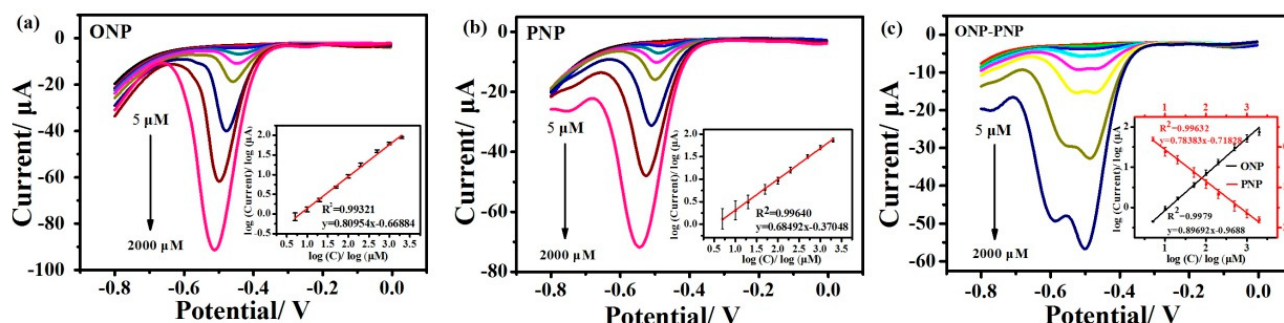


Figure 7. DPV of $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ with individual addition of (a) ONP and (b) PNP (5, 10, 20, 50, 100, 200, 500, 1000, and 2000 μM) into 0.1 M PBS (pH = 7.0), respectively. Inset: Linear relationship between logarithm of peak current and logarithm of concentrations of (a) ONP and (b) PNP. DPV of $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ with simultaneous addition of the same concentration of (c) ONP and PNP (5–2000 μM) into 0.1 M PBS (pH = 7.0). Inset: Linear relationship between logarithm of peak current and logarithm of concentrations of (c) ONP and PNP.

The antifouling property of different electrodes was investigated by successive CVs in the ONP and PNP solution, respectively (Figures S11–S13). The results showed that COFs/GCE exhibited the best antifouling property because of the hydrophilicity of COFs. For ONP, $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ showed improved antifouling properties than GCE in the first six cycles. However, for PNP, both $\text{Pd}^{2+}/\text{COFs}/\text{GCE}$ and bare GCE exhibited lower antifouling properties.

3.3. Electrochemical Sensing of GSH

3.3.1. Characterization of PC

The morphology of the PCs was characterized by SEM and TEM images. The SEM image of PCs shows the overlapping structure of stratified lamellae (Figure S14a). As

shown in Figure S14b, the flake morphology can be observed in the TEM image of PCs. Furthermore, XPS characterization was employed to investigate the elemental compositions and chemical states of PCs. Figure 8 shows the XPS spectra of PCs containing C, N, and O elements. The C 1s spectra suggest the coexistence of C-C (283.60 eV), C=C (284.50 eV), C=O (287.70 eV), and π - π (292.30 eV) in PCs (Figure 8a) [20]. The N1s XPS spectra show two characteristic peaks at 397.10 and 400.00 eV (Figure 8b), which are attributed to the C=N and C-N groups, respectively [10]. Figure 8c displays the O 1s XPS spectrum of PCs, including two peaks at 531.30 and 532.20 eV, representing the C=O and C-O bonds, respectively [21]. The XPS spectra suggest that a large number of functional groups are present on the surface of the PCs.

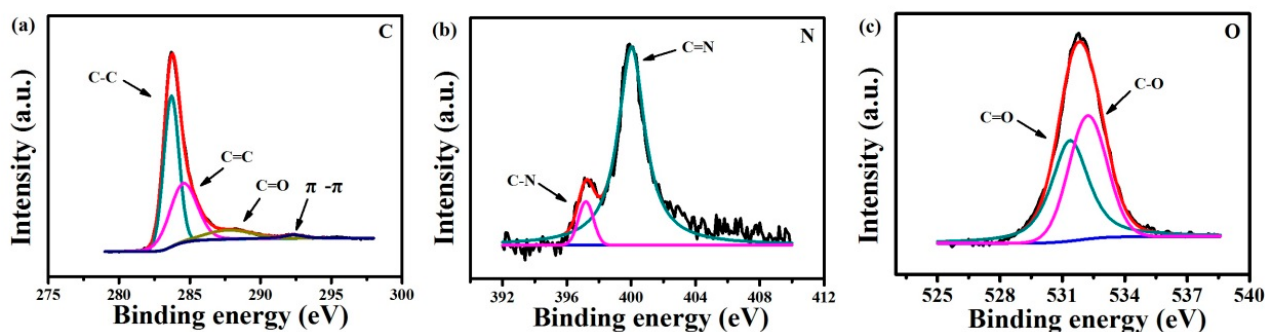


Figure 8. XPS (a) C, (b) N and (c) O spectra of PCs.

3.3.2. Electrochemical Oxidation of GSH

GSH is an important antioxidant in protecting cells from oxidative damage by oxidizing to form glutathione disulfide (GSSG), and the balance of GSH and GSSG acts as an indicator of many human illnesses such as several cancers, Parkinson's disease, Alzheimer's, and HIV [22]. Metal and non-metal electrocatalysts have been explored for the non-enzymatic detection of biological thiols [23–25]. Non-metal electrocatalysts consist of redox-active organic molecules [23,26] and carbon materials, including carbon nanotube [27], ordered mesoporous carbon [28], graphene oxide [29], graphene oxide nanoribbons [30], and derived carbon [31]. In fact, the oxo-functionalities present on these carbons contribute to the electrocatalytic activity towards thiols. Recently, nitrogen-doped carbon has proven effective in not only improving the electrical conductivity but also promoting defect sites in the carbon network for better catalytic activity towards GSH [32]. Here, the N-doped PCs with abundant oxo-functionalities were explored for the electro-oxidation of GSH. Figure 9 shows the CV response for the electrochemical oxidation of GSH at PCs/CPE in 0.1 M PBS (pH 7.0) at a scan rate of 50 mV s^{−1}. As can be seen, in the absence of GSH, no anodic peak was observed on the PCs/CPE. However, in the presence of GSH, it could be noticed that a remarkable anodic current emerged at about 0.10 V, and the anodic peak was observed at 0.25 V, which could be ascribed to some oxygen-containing functional groups on PCs promoting the oxidation of GSH [26]. Furthermore, there was a very small anodic peak at 0.28 V, and this could be attributed to the edge plane-defective sites on PCs [33]. Furthermore, no cathodic current peak appeared in the CV curves, confirming that the GSH oxidation was a fully irreversible process. The results suggest that the N-doping and the oxo-functionalities present on PCs enhance the rate of electron transfer and exhibit efficient electrocatalytic activity for the oxidation of GSH.

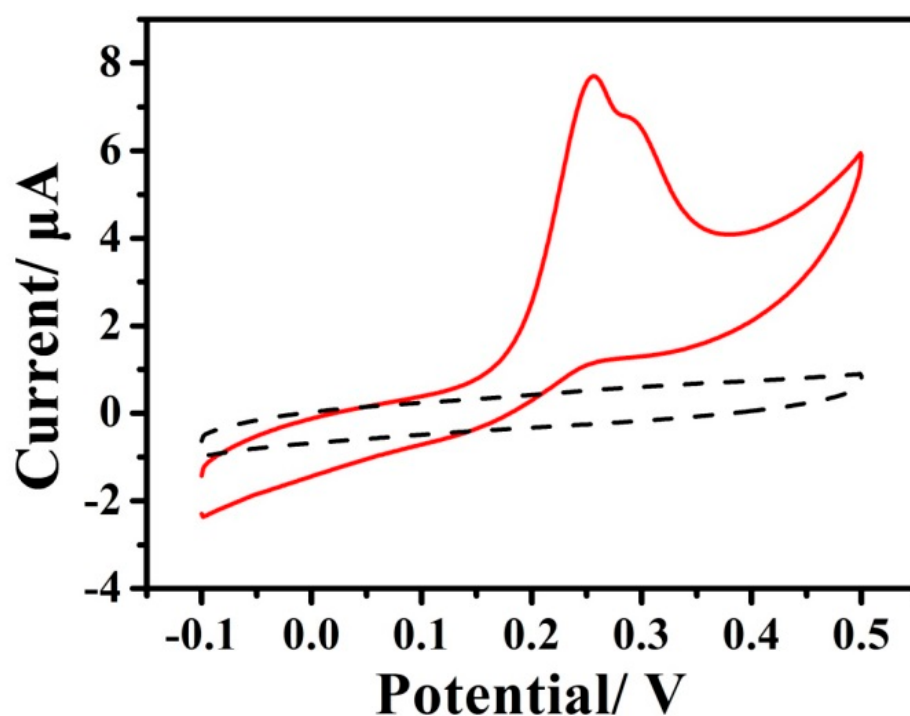


Figure 9. CV of PCs/CPE in the absence (dotted line) and presence (solid line) of 5 mM GSH in 0.1 M PBS (pH = 7.0). Scan rate: 50 mV s^{-1} .

The pH value is a crucial factor for the electrochemical oxidation of GSH, which was examined in 0.1 M PBS with various pH values containing 5.0 mM GSH on the PCs/CPE (Figure S15). The anodic peak current of GSH increased firstly and then decreased as the solution pH value increased from 3.0 to 5.0 and reached a maximum at pH = 4.0. Accordingly, pH = 4.0 is selected as the optimal condition for further detection. GSH is an important tripeptide consisting of L-cysteine, L-glutamine, and glycine with $\text{pK}_{\text{a}1} = 2.12$ (carboxylic acid of glutaminic acid), $\text{pK}_{\text{a}2} = 3.59$ (carboxylic acid of glycine), $\text{pK}_{\text{a}3} = 8.75$ (thiol of cysteine), and $\text{pK}_{\text{a}4} = 9.65$ (ammonium of glutaminic acid) [34]. Gilbertson et al. investigated the interaction and catalytic oxidation mechanisms between GO and GSH. It was found that the synergism between the adjacent epoxide and hydroxyl groups on the GO surface contributed to the catalytic oxidation of GSH [35]. It was speculated that the pH value of the solution is related to both the activity of oxo-functionalities and the ionization of GSH.

3.3.3. Analytical Performances for GSH

Under the optimal conditions, the amperometric responses of the PCs/CPE were conducted by successive injections of various concentrations of GSH into the stirred 0.1 M PBS (pH = 4.0) solution (Figure 10). Upon each addition of 200 μM GSH, a well stair-shaped amperometric response was raised quickly and reached a steady-state oxidation current within 5 s. The inset (a) of Figure 10 shows the response current of the PCs/CPE to various concentrations of GSH, and it is clear that the current increased rapidly with the addition of GSH. The enhancement of response current is ascribed to the excellent electrocatalytic property of the PCs/CPE. Figure 10b displays the linear correlation between the GSH oxidation current and concentration ranging from 5.0 μM to 1.2 mM and 1.2 to 6.4 mM, respectively. The limit of detection was calculated to be 2 μM ($\text{S/N} = 3$). Nevertheless, as the GSH concentration increased gradually, the sensitivity of the prepared sensor slightly decreased owing to the binding of the sulfur moiety to the electrode surface caused by the oxidation of GSH [26].

metric curve of Pd²⁺/COFs/GCE with 50 µM hydrazine and 500 µM of interferences such as KCl, NaCl, Na₂SO₄, NaBr, CaCl₂, NaAc, glucose, (NH₄)₂SO₄, NaNO₃, and NaNO₂. (Electrolyte: 0.1 M NaOH); Figure S7: Amperometric curve of Pd²⁺/COFs/GCE for the detection of hydrazine spiked in water samples at −0.1 V. (Electrolyte: 0.1 M NaOH); Figure S8: CVs of Bare GCE, COFs/GCE, and Pd²⁺/COFs/GCE in 0.1 M PBS at a scan rate of 50 mV s^{−1} (pH = 7.0); Figure S9: CVs of 500 µM of (a) ONP and (b) PNP on Pd²⁺/COFs/GCE with different scan rates (20–200 mV s^{−1}) in 0.1 M PBS (pH = 7.0). (Inset: the corresponding calibration plot.); Figure S10: DPV curves of 500 µM of (a) ONP and (b) PNP on Pd²⁺/COFs/GCE in 0.1 M PBS (pH = 7.0) with different pH values (1–5: 6.5, 7.0, 7.5, 8.0, and 8.5). Plots of I_{pc} vs. pH for (c) ONP and (d) PNP; Figure S11: Successive CVs of Bare GCE (a), COFs/GCE (b), and Pd²⁺/COFs/GCE (c) in the presence of 500 µM nitrophenol ONP at a scan rate of 50 mV s^{−1} in 0.1 M PBS (pH = 7); Figure S12: Successive CVs of Bare GCE (a), COFs/GCE (b), and Pd²⁺/COFs/GCE (c) in the presence of 500 µM nitrophenol PNP at a scan rate of 50 mV s^{−1} in 0.1 M PBS (pH = 7.0); Figure S13: Normalized peak current of bare GCE, COFs/GCE, and Pd²⁺/COFs/GCE in the presence of 500 µM nitrophenol (a: ONP, b: PNP) at a scan rate of 50 mV s^{−1} in 0.1 M PBS (pH = 7.0) for ten cycles; Figure S14: SEM (a) and TEM (b) images of PCs; Figure S15: CVs of 5 mM of GSH on (a) PCs/CPE in 0.1 M PBS with different pH values (1–5: 3.0, 3.5, 4.0, 4.5 and 5.0). Plots of I_{pc} vs. pH for (b) GSH; Figure S16: Amperometric responses of PCs/CPE to additions of various concentrations of GSH in 0.1 M PBS (pH = 4.0) at 0.25 V. (Inset: the corresponding calibration plot.); Figure S17: Amperometric responses of PCs/CPE to successive additions of various concentrations of GSH spiked in serum in 0.1 M PBS (pH = 4.0) at 0.25 V; Figure S18: Amperometric responses of PCs/CPE for the detection of GSH spiked in human serum in 0.1 M PBS (pH = 4.0) at 0.25 V; Table S1: Comparison of the Pd²⁺/COFs/GCE for different parameters with previously reported hydrazine electrodes; Table S2: Determination of hydrazine spiked in water samples; Table S3: Comparison of different modified GCE for detection of ONP and PNP; Table S4: Comparison of different modified electrodes for electrochemical sensing of GSH; Table S5: Determination of GSH spiked in human serum by successive additions; Table S6: Determination of GSH spiked in human serum by a non-successive addition method. References [36–68] were cited in the Supplementary Materials.

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References

1. Liu, H.Y.; Weng, L.Y.; Yang, C. A review on nanomaterial-based electrochemical sensors for H₂O₂, H₂S and NO inside cells or released by cells. *Microchim. Acta* **2017**, *184*, 1267–1283. [CrossRef]
2. Liu, C.S.; Li, J.J.; Pang, H. Metal-organic framework-based materials as an emerging platform for advanced electrochemical sensing. *Coord. Chem. Rev.* **2020**, *410*, 213222. [CrossRef]
3. Yan, Y.; He, T.; Zhao, B.; Qi, K.; Liu, H.F.; Xia, B.Y. Metal/covalent-organic frameworks-based electrocatalysts for water splitting. *J. Mater. Chem. A* **2018**, *6*, 15905–15926. [CrossRef]
4. Yuan, B.Q.; Liu, D.; Yin, H.J.; Zhang, D.J. Materials for Electroanalysis Based on Advanced Frameworks. *Front. Chem.* **2021**, *3*, 638338. [CrossRef]
5. Chuang, C.H.; Kung, C.W. Metal-organic frameworks toward electrochemical sensors: Challenges and opportunities. *Electroanalysis* **2020**, *32*, 1885–1895. [CrossRef]
6. Lu, M.X.; Deng, Y.J.; Luo, Y.; Lv, J.P.; Li, T.B.; Xu, J.; Chen, S.W.; Wang, J.Y. Graphene aerogel–metal–organic framework-based electrochemical method for simultaneous detection of multiple heavy-metal ions. *Anal. Chem.* **2019**, *91*, 888–895. [CrossRef] [PubMed]

7. Sun, Y.F.; Waterhouse, G.I.; Xu, L.H.; Qiao, X.G.; Xu, Z.X. Three-dimensional electrochemical sensor with covalent organic framework decorated carbon nanotubes signal amplification for the detection of furazolidone. *Sens. Actuators B Chem.* **2020**, *321*, 128501. [\[CrossRef\]](#)
8. He, W.H.; Ifraemov, R.; Raslin, A.; Hod, I. Room-Temperature Electrochemical Conversion of Metal-Organic Frameworks into Porous Amorphous Metal Sulfides with Tailored Composition and Hydrogen Evolution Activity. *Adv. Funct. Mater.* **2018**, *28*, 1707244. [\[CrossRef\]](#)
9. Beitollahi, H.; Movahedifar, F.; Tajik, S.; Jahani, S. A review on the effects of introducing CNTs in the modification process of electrochemical sensors. *Electroanalysis* **2019**, *31*, 1195–1203. [\[CrossRef\]](#)
10. Hu, X.W.; Long, Y.; Fan, M.Y.; Yuan, M.; Zhao, H.; Ma, J.T.; Dong, Z.P. Two-dimensional covalent organic frameworks as self-template derived nitrogen-doped carbon nanosheets for eco-friendly metal-free catalysis. *Appl. Catal. B Environ.* **2019**, *244*, 25–35. [\[CrossRef\]](#)
11. Yang, L.; Cai, Z.; Hao, L.; Ran, L.L.; Xu, X.; Dai, Y.; Pan, S.Y.; Jing, B.J.; Zhou, J.L. Increase of structural defects by N doping in MoS₂ cross-linked with N-doped CNTs/carbon for enhancing charge transfer in oxygen reduction. *Electrochim. Acta* **2018**, *283*, 448–458. [\[CrossRef\]](#)
12. Sun, F.; Liu, X.Y.; Wu, H.B.; Wang, L.J.; Gao, J.H.; Li, H.X.; Lu, Y.F. In situ high-level nitrogen doping into carbon nanospheres and boosting of capacitive charge storage in both anode and cathode for a high-energy 4.5 V full-carbon lithium-ion capacitor. *Nano Lett.* **2018**, *18*, 3368–3376. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Wang, J.; Yin, D.G.; Guo, X.D.; Luo, Z.Y.; Tao, L.Y.; Ren, J.J.; Zhang, Y. Fabrication of a Covalent Organic Framework-Based Heterojunction via Coupling with ZnAgInS Nanosphere with High Photocatalytic Activity. *Langmuir* **2022**, *38*, 4680–4691. [\[CrossRef\]](#)
14. Zhong, X.; Lu, Z.P.; Liang, W.; Hu, B.W. The magnetic covalent organic framework as a platform for high-performance extraction of Cr (VI) and bisphenol a from aqueous solution. *J. Hazard. Mater.* **2020**, *393*, 122353. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Wang, F.N.; Zhang, J.X.; Shao, Y.H.; Jiang, H.; Liu, Y.F.; Chen, R.Z. Pd nanoparticles loaded on two-dimensional covalent organic frameworks with enhanced catalytic performance for phenol hydrogenation. *Ind. Eng. Chem. Res.* **2020**, *59*, 18489–18499. [\[CrossRef\]](#)
16. Li, Z.D.; Zhang, H.Q.; Xiong, X.H.; Luo, F. U (VI) adsorption onto covalent organic frameworks-TpPa-1. *J. Solid State Chem.* **2019**, *277*, 484–492. [\[CrossRef\]](#)
17. Choi, H.C.; Shim, M.; Bangsaruntip, S. Spontaneous reduction of metal ions on the sidewalls of carbon nanotubes. *J. Am. Chem. Soc.* **2002**, *124*, 9058–9059. [\[CrossRef\]](#)
18. Wang, Q.Z.; Li, R.; Zhao, Y.J.; Zhe, T.T.; Bu, T.; Liu, Y.N.; Sun, X.Y.; Hu, H.F.; Zhang, M.; Zheng, X.H. Surface morphology-controllable magnetic covalent organic frameworks: A novel electrocatalyst for simultaneously high-performance detection of p-nitrophenol and o-nitrophenol. *Talanta* **2020**, *219*, 121255. [\[CrossRef\]](#)
19. Afzali, F.; Zavar, M.H.A.; Rounaghi, G.; Ashraf, N.J.E.A. Gold digital versatile disc platform modified with nano-porous mercury/gold amalgam as a solid-state disposable electrochemical sensor for detection of para-nitrophenol. *Electrochim. Acta* **2016**, *209*, 654–660. [\[CrossRef\]](#)
20. Chen, X.; Wang, X.; Fang, D. A review on C1s XPS-spectra for some kinds of carbon materials. *Fuller. Nanotub. Carbon Nanostruct.* **2020**, *28*, 1048–1058. [\[CrossRef\]](#)
21. Cao, S.; Yang, J.X.; Li, J.; Shi, K.; Li, X.K. Preparation of oxygen-rich hierarchical porous carbon for supercapacitors through the co-carbonization of pitch and biomass. *Diamond Relat. Mater.* **2019**, *96*, 118–125. [\[CrossRef\]](#)
22. Townsend, D.M.; Tew, K.D.; Tapiero, H.J.B. The importance of glutathione in human disease. *Biomed. Pharmacother.* **2003**, *57*, 145–155. [\[CrossRef\]](#)
23. Harfield, J.C.; Batchelor-McAuley, C.; Compton, R.G. Electrochemical determination of glutathione: A review. *Analyst* **2012**, *137*, 2285–2296. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Hanko, M.; Švorc, L.; Planková, A.; Mikuš, P. Overview and recent advances in electrochemical sensing of glutathione—A review. *Anal. Chim. Acta* **2019**, *1062*, 1–27. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Nesakumar, N.; Berchmans, S.; Alwarappan, S. Chemically modified carbon based electrodes for the detection of reduced glutathione. *Sens. Actuators B Chem.* **2018**, *264*, 448–466. [\[CrossRef\]](#)
26. Yuan, B.Q.; Xu, C.Y.; Zhang, R.C.; Lv, D.H.; Li, S.J.; Zhang, D.J.; Liu, L.; Fernandez, C. Bioelectronics, Glassy carbon electrode modified with 7, 7, 8, 8-tetracyanoquinodimethane and graphene oxide triggered a synergistic effect: Low-potential amperometric detection of reduced glutathione. *Biosens. Bioelectron.* **2017**, *96*, 1–7. [\[CrossRef\]](#)
27. Lee, P.; Compton, R.G. Selective electrochemical detection of thiol biomarkers in saliva using multiwalled carbon nanotube screen-printed electrodes. *Sens. Actuators B Chem.* **2015**, *209*, 983–988. [\[CrossRef\]](#)
28. Zhou, M.; Ding, J.; Guo, L.P.; Shang, Q.K. Electrochemical behavior of L-cysteine and its detection at ordered mesoporous carbon-modified glassy carbon electrode. *Anal. Chem.* **2007**, *79*, 5328–5335. [\[CrossRef\]](#)
29. Yuan, B.Q.; Zeng, X.Y.; Xu, C.Y.; Liu, L.; Ma, Y.H.; Zhang, D.J.; Fan, Y. Electrochemical modification of graphene oxide bearing different types of oxygen functional species for the electro-catalytic oxidation of reduced glutathione. *Sens. Actuators B Chem.* **2013**, *184*, 15–20. [\[CrossRef\]](#)
30. Wu, S.; Lan, X.Q.; Huang, F.F.; Luo, Z.Z.; Ju, H.X.; Meng, C.G.; Duan, C.Y. Selective electrochemical detection of cysteine in complex serum by graphene nanoribbon. *Biosens. Bioelectron.* **2012**, *32*, 293–296. [\[CrossRef\]](#)

31. Zhang, T.; Li, H.D.; Liu, M.X.; Zhou, H.; Zhang, Z.C.; Yu, C.; Wang, C.Y.; Wang, G.X. Improved the specificity of peroxidase-like carbonized polydopamine nanotubes with high nitrogen doping for glutathione detection. *Sens. Actuators B Chem.* **2021**, *341*, 129987. [\[CrossRef\]](#)
32. Wang, Y.; de Carvalho, N.A.; Tan, S.S.; Gilbertson, L.M. Leveraging electrochemistry to uncover the role of nitrogen in the biological reactivity of nitrogen-doped graphene. *Environ. Sci. Nano* **2019**, *6*, 3525–3538. [\[CrossRef\]](#)
33. Ndamani, J.C.; Bai, J.; Qi, B.; Guo, L.P. Application of electrochemical properties of ordered mesoporous carbon to the determination of glutathione and cysteine. *Anal. Biochem.* **2009**, *386*, 79–84. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Gotoh, T.; Iguchi, H.; Kikuchi, K.I. Separation of glutathione and its related amino acids by nanofiltration. *Biochem. Eng. J.* **2004**, *19*, 165–170. [\[CrossRef\]](#)
35. Wang, Y.; Basdogan, Y.; Zhang, T.Y.; Lankone, R.S.; Wallace, A.N.; Fairbrother, D.H.; Keith, J.A.; Gilbertson, L.M. Interfaces, Unveiling the synergistic role of oxygen functional groups in the graphene-mediated oxidation of glutathione. *ACS Appl. Mater. Interfaces* **2020**, *12*, 45753–45762. [\[CrossRef\]](#)
36. Wang, L.; Teng, Q.Q.; Sun, X.T.; Chen, Y.T.; Wang, Y.M.; Wang, H.; Zhang, Y.F. Facile synthesis of metal-organic frameworks/ordered mesoporous carbon composites with enhanced electrocatalytic ability for hydrazine. *J. Colloid Interface Sci.* **2018**, *512*, 127–133. [\[CrossRef\]](#)
37. Wang, L.; Meng, T.J.; Jia, H.X.; Feng, Y.; Gong, T.; Wang, H.; Zhang, Y.F. Electrochemical study of hydrazine oxidation by leaf-shaped copper oxide loaded on highly ordered mesoporous carbon composite. *J. Colloid Interface Sci.* **2019**, *549*, 98–104. [\[CrossRef\]](#)
38. Gharani, M.; Bahari, A.; Ghasemi, S. Preparation of MoS₂-reduced graphene oxide/Au nanohybrid for electrochemical sensing of hydrazine. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 7765–7777. [\[CrossRef\]](#)
39. Yao, Y.Q.; Han, X.H.; Yang, X.H.; Zhao, J.; Chai, C.P. Detection of Hydrazine at MXene/ZIF-8 Nanocomposite Modified Electrode. *Chin. J. Chem.* **2021**, *39*, 330–336. [\[CrossRef\]](#)
40. Zhang, X.J.; Zheng, J.B. Amperometric hydrazine sensor based on the use of a gold nanoparticle-modified nanocomposite consisting of porous polydopamine, multiwalled carbon nanotubes and reduced graphene oxide. *Mikrochim. Acta.* **2020**, *187*, 89. [\[CrossRef\]](#)
41. Vishnu, N.; Kumar, A.S.; Badhulika, S. Selective in-situ derivatization of intrinsic nickel to nickel hexacyanoferrate on carbon nanotube and its application for electrochemical sensing of hydrazine. *J. Electroanal. Chem.* **2019**, *837*, 60–66. [\[CrossRef\]](#)
42. Li, S.; Feng, W.S.; Gao, X.H.; Guo, A.M.; Li, H.J. Copper-based materials derived from metal-organic frameworks for electrochemical sensing of hydrazine. *Micro Nano Lett.* **2021**, *16*, 478–483. [\[CrossRef\]](#)
43. Asadi, F.; Azizi, S.N.; Ghasemi, S. Preparation of Ag nanoparticles on nano cobalt-based metal organic framework (ZIF-67) as catalyst support for electrochemical determination of hydrazine. *J. Mater. Sci. Mater. Electron.* **2019**, *30*, 5410–5420. [\[CrossRef\]](#)
44. Avanes, A.; Hasanazadeh-Karamjavan, M.; Shokri-Jarcheloo, G. Electrocatalytic oxidation and amperometric determination of hydrazine using a carbon paste electrode modified with beta-nickel hydroxide nanoplatelets. *Mikrochim. Acta* **2019**, *186*, 441. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Duan, C.Q.; Dong, Y.H.; Sheng, Q.L.; Zheng, J.B. A high-performance non-enzymatic electrochemical hydrazine sensor based on NiCo₂S₄ porous sphere. *Talanta* **2019**, *198*, 23–29. [\[CrossRef\]](#)
46. Ghasemi, S.; Hosseini, S.R.; Hasanpoor, F.; Nabipour, S. Amperometric hydrazine sensor based on the use of Pt-Pd nanoparticles placed on reduced graphene oxide nanosheets. *Mikrochim. Acta* **2019**, *186*, 601. [\[CrossRef\]](#)
47. Maleki, A.; Rezaee, R.; Daraei, H.; Shahmoradi, B.; Amini, N. Fabrication of a sensitive electrochemical sensor to environmental pollutant of hydrazine in real water samples based on synergistic catalysis of Ag@C core-shell and polyalizarin yellow R. *J. Alloys Compd.* **2018**, *763*, 997–1004. [\[CrossRef\]](#)
48. Shahid, M.M.; Rameshkumar, P.; Basirunc, W.J.; Wijayantha, U.; Chiu, W.S.; Khiew, P.S.; Huang, N.M. An electrochemical sensing platform of cobalt oxide@gold nanocubes interleaved reduced graphene oxide for the selective determination of hydrazine. *Electrochim. Acta* **2018**, *259*, 606–616. [\[CrossRef\]](#)
49. Mousavi-Majd, A.; Ghasemi, S.; Hosseini, S.R. Zeolitic imidazolate framework derived porous ZnO/Co₃O₄ incorporated with gold nanoparticles as ternary nanohybrid for determination of hydrazine. *J. Alloys Compd.* **2022**, *896*, 162922. [\[CrossRef\]](#)
50. Vinoth, S.; Sampathkumar, P.; Giribabu, K.; Pandikumar, A. Ultrasonically assisted synthesis of barium stannate incorporated graphitic carbon nitride nanocomposite and its analytical performance in electrochemical sensing of 4-nitrophenol, Ultrasonics Sonochemistry. *Ultrason. Sonochem.* **2020**, *62*, 104855. [\[CrossRef\]](#)
51. Zhou, Y.Y.; Zhao, J.; Li, S.H.; Guo, M.J.; Fan, Z. An electrochemical sensor for the detection of p-nitrophenol based on a cyclodextrin-decorated gold nanoparticle-mesoporous carbon hybrid. *Analyst* **2019**, *144*, 4400–4406. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Ansari, A.A.; Alam, M.; Ali, M.A. Nanostructured CeO₂: Ag platform for electrochemically sensitive detection of nitrophenol. *Colloids Surf. A.* **2021**, *613*, 126116. [\[CrossRef\]](#)
53. Suresh, R.; Giribabu, K.; Manigandan, R.; Kumar, S.P.; Munusamy, S.; Muthamizh, S.; Narayanan, V. Polyaniline Nanorods: Synthesis, Characterization, and Application for the Determination of para-Nitrophenol. *Anal. Lett.* **2015**, *49*, 269–281. [\[CrossRef\]](#)
54. Alam, M.M.; Asiri, A.M.; Rahman, M.M. Electrochemical detection of 2-Nitrophenol using a glassy carbon electrode modified with BaO Nanorods. *Chem. Asian J.* **2021**, *16*, 1475–1485. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Nejati, K.; Asadpour-Zeynali, K.; Rezvani, Z.; Peyghami, R. Determination of 2-nitrophenol by electrochemical synthesized Mg/Fe layered double hydroxide sensor. *Int. J. Electrochem. Sci.* **2014**, *9*, 5222–5234.

56. Yin, H.S.; Zhou, Y.L.; Ai, S.Y.; Cui, L.; Zhu, L.S. Electrochemical determination of 2-Nitrophenol in Water Samples using Mg-Al-SDS Hydrotalcite-Like Clay modified glassy carbon electrode. *Electroanalysis* **2010**, *22*, 1136–1142. [[CrossRef](#)]
57. Li, J.H.; He, L.Z.; Jiang, J.B.; Xu, Z.F.; Liu, M.Q.; Liu, X.; Tong, H.X.; Liu, Z.; Qian, D. Facile syntheses of bimetallic Prussian blue analogues ($K_xM[Fe(CN)_6] \cdot nH_2O$, $M = Ni, Co$, and Mn) for electrochemical determination of toxic 2-nitrophenol. *Electrochim. Acta* **2020**, *353*, 136579. [[CrossRef](#)]
58. Chu, L.; Han, L.; Zhang, X.L. Electrochemical simultaneous determination of nitrophenol isomers at nano-gold modified glassy carbon electrode. *J. Appl. Electrochem.* **2011**, *41*, 687–694. [[CrossRef](#)]
59. Zhang, J.J.; Cui, S.Q.; Ding, Y.P.; Yang, X.X.; Guo, K.; Zhao, J.T. Bioelectronics, Two-dimensional mesoporous $ZnCo_2O_4$ nanosheets as a novel electrocatalyst for detection of o-nitrophenol and p-nitrophenol. *Biosens. Bioelectron.* **2018**, *112*, 177–185. [[CrossRef](#)]
60. Hryniewicz, B.M.; Orth, E.S.; Vidotti, M. Enzymeless PEDOT-based electrochemical sensor for the detection of nitrophenols and organophosphates. *Sens. Actuators B Chem.* **2018**, *257*, 570–578. [[CrossRef](#)]
61. Wu, W.T.; Chen, X.; Jiao, Y.T.; Fan, W.T.; Liu, Y.L.; Huang, W.H. Versatile Construction of Biomimetic Nanosensors for Electrochemical Monitoring of Intracellular Glutathione. *Electroanal. Chem.* **2022**, *134*, e202115820.
62. Zhao, L.Z.; Zhao, L.; Miao, Y.; Zhang, C.X. Selective electrochemical determination of glutathione from the leakage of intracellular GSH contents in HeLa cells following doxorubicin-induced cell apoptosis. *Electrochim. Acta* **2016**, *206*, 86–98. [[CrossRef](#)]
63. Lee, P.T.; Goncalves, L.M.; Compton, R.G. Electrochemical determination of free and total glutathione in human saliva samples. *Sens. Actuators B Chem.* **2015**, *221*, 962–968. [[CrossRef](#)]
64. Yuan, B.Q.; Zhang, R.C.; Jiao, X.X.; Li, J.; Shi, H.Z.; Zhang, D.J. Amperometric determination of reduced glutathione with a new Co-based metal-organic coordination polymer modified electrode. *Electrochem. Commun.* **2014**, *40*, 92–95. [[CrossRef](#)]
65. Kannappan, S.; Bhat, L.R.; Nesakumar, N.; Babu, K.J.; Kulandaisamy, A.J.; Rayappan, J.B.B. Design and development of a non-enzymatic electrochemical biosensor for the detection of Glutathione. *Electroanalysis* **2022**, *34*, 1–12. [[CrossRef](#)]
66. Abbas, M.N.; Saeed, A.A.; Ali, M.B.; Errachid, A.; Zine, N.; Baraket, A.; Singh, B. Biosensor for the oxidative stress biomarker glutathione based on SAM of cobalt phthalocyanine on a thioctic acid modified gold electrode. *J. Solid State Electrochem.* **2019**, *23*, 1129–1144. [[CrossRef](#)]
67. Xu, H.Y.; Xiao, J.J.; Liu, B.; Griveau, S.; Bedioui, F. Enhanced electrochemical sensing of thiols based on cobalt phthalocyanine immobilized on nitrogen-doped graphene. *Biosens. Bioelectron.* **2015**, *66*, 438–444. [[CrossRef](#)]
68. Saranya, S.; Geetha, B.; Deepa, P.N. Simultaneous detection of glutathione, threonine, and glycine at electrodeposited RuHCF/rGO-modified electrode. *Ionics* **2019**, *25*, 5537–5550. [[CrossRef](#)]