We report on the design of a bio-inspired composite as a noble-metal-free electrocatalyst for the oxygen reduction reaction (ORR). The composite is made from the assembly of pyridine-functionalized graphene (G-py) and a 3D metal–organic framework (MOF) deposited onto a glassy carbon electrode (GCE). The 3D heme-like MOF was synthesized from tetrakis(4-carboxyphenyl)porphyrin iron(III) chloride and Zn₆ clusters for the assembly of the stable porous coordination network. G-py, which possesses an axial ligand to anchor to the centers of porphyrin in the MOF, results in a significant change in the electronic and geometric structure of centers, which enhances the rate of ORR and durability during cycling in acidic media. The occurrence potential of the ORR by the composite is shifted to the positive potential near 100 mV. Our results introduce a new strategy for the rational design of inexpensive and highly stable oxygen reduction electrocatalysts for fuel cells without the requirement of pyrolysis.

Introduction

The reduction of oxygen is not only a significant reaction in biological systems, but it is also a challenging part of fuel cells and metal air batteries. Undoubtedly, fuel cells are one of the most important alternatives to fossil fuels if we consider the astonishing increase in the consumption of energy. Such electrochemical energy conversion systems have become attractive because of their cleanliness and high efficiency. However, the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode remains the bottleneck for the use of fuel cells. Pt and its alloys of various sizes and shapes have been used extensively as cathode catalysts, but their widespread use has been severely limited by their high cost, scarcity, and low stability, especially in acidic media. Therefore, a tremendous motivation has been created for the synthesis of cheap, high-performance, and accessible electrocatalysts to replace Pt. Cheaper noble metals, metal oxides, metal chalcogenides, metal macrocycle (M-N-C) catalysts, and carbon-based materials have attracted great attention as alternatives. Since Jasinski reported the electroactivity of cobalt phthalocyanine for the ORR, this group of metal macrocycles (Fe, Co) has been placed at the center of numerous investigations. To overcome the degradation of metal macrocycles, metal porphyrins or phthalocyanines accompanied by carbon supports involve high-temperature pyrolysis, which results in metal nitrogen carbon hybrids with enhanced stability and activity. In some cases, pyrolysis was not achieved, and metal macrocycles were connected to the carbon support through covalent bonding or π–π interactions. For example, You et al. synthesized a material in which cobalt [5,15-(p-aminophenyl)-10,20-(pentafluorophenyl) porphyrin] was attached covalently to graphene oxide. However, most of the investigations on synthetic M-N-C catalysts focused on four-coordinate systems (M-NₓC) and few attempts have been made to alter the coordination environment of the metal center. With inspiration from cytochrome c oxidase, Cao and co-workers designed a new ORR electrocatalyst that uses pyridine-functionalized carbon nanotubes (CNTs) to anchor iron phthalocyanine molecules and provide the axial ligand as the fifth ligand for the Fe center.

Recently, a new approach to develop high-performance electrocatalysts using the template-free pyrolysis of metal-porphyrin-based conjugated mesoporous polymer frameworks has been proposed. Accordingly, Wu et al. prepared a self-supported ORR electrocatalyst from the pyrolysis of cobalt-porphyrin-based conjugated mesoporous polymer (CoP-CMP) frameworks. The resulting materials showed catalytic activity and stability in both alkaline and acidic media.

Metal–organic frameworks (MOFs), which consist of metal ions or clusters connected by organic linkers, constitute one of the most substantial progresses in the field of nanoporous materials and have many practical applications, such as gas...
storage, gas separation, catalytic activity, drug delivery, and sensors. As MOFs possess a high density of metal ion sites and a high surface area, these porous frameworks are interesting as sacrificial materials to be pyrolyzed in the synthesis of nonprecious metal catalysts. Although some MOFs have been used as a sacrificial precursor to prepare ORR catalysts, only a few examples of preserved MOF structures (no pyrolysis step) have been reported. For the first time, in 2012 Jahan et al. reported on a composite graphene/2D Fe porphyrin MOF structure (G-dye-FeP) with enhanced electrocatalytic activity towards the ORR in an alkaline medium. In addition, Mao et al. demonstrated that Cu-btc (btc = 1,3,5-benzetricarboxylic acid) MOF modified with bipyridine as an auxiliary ligand exhibited a stable electrocatalytic activity towards the ORR. Another example is a porous MOF that contains Cu centers and fully activated nanocages as a noble-metal-free electrocatalyst for the ORR.

Hence, with a rational choice of building blocks, porous materials with delicate functions that provide many appropriate interactions for catalytic purposes can be constructed. To the best of our knowledge, some MOFs are made up of porphyrins as building blocks, but only a few porphyrin-based MOFs exist with Fe and Co centers. Feng and co-workers employed tetrakis(4-carboxyphenyl)porphyrin-FeIII Cl (FeTCPPCl) as a heme-like ligand and highly stable Zr6 clusters as nodes for the synthesis of a 3D Zr-MOF with superb features such as ultra high stability, accessible mesoporous channels for substrate molecules, and a high surface area. Given the successful role of PCN-222 (porous coordination network) in peroxidase mimic applications and stability in acidic media, we concluded that this MOF was one of the best candidates for our goal. For postsynthetic modification, stability improvement, and to mimic cytochrome c oxidase, we have designed a new composite of PCN-222 with pyridine-functionalized graphene (G-py), which exhibits a highly efficient catalytic performance for the ORR and stability in acidic media. G-py possesses an axial ligand to anchor to the Fe centers of porphyrin building blocks in PCN-222, which changes the coordination environment of the metal centers. Moreover, graphene nanosheets provide an easy way for fast electron transfer to the active sites through the axial ligands. In other words, pyridine functions as a connector to pass the charge to the Fe center and increases the electrocatalytic activity of PCN-222 to facilitate the ORR.

**Results and Discussion**

**Synthesis and description of catalysts**

Graphene nanosheets were decorated with the pyridinium moiety through a diazonium reaction (Scheme 1). The presence of pyridine on the graphene nanosheets was proved by using CHN analysis and FTIR spectroscopy. The structure, stability, and morphology of G-py were investigated by using UV/Vis spectroscopy, SEM, XRD, and thermogravimetric analysis (TGA). FeTCPPCl and ZrCl4 were employed for the solvothermal synthesis of PCN-222, which has hexagonal mesostructures.

Scheme 1. Preparation of G-py.

Scheme 2. Synthesis of PCN-222.

Scheme 3. Preparation of PCN-222-G-py.

The CHN elemental analysis of G-py indicates the presence of 6.47 wt% of nitrogen, which is evident from the connection of pyridine ligand to the graphene sheets. The UV/Vis spectrum of graphene oxide shows λmax = 228 nm, which corresponds to π–π* transitions of aromatic C=C bonds, and a shoulder peak at λ ≈ 308 nm caused by n–π*

**Characterization of G-py**

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The presence of pyridine on the r-GO sheets can be observed by peaks at \( \tilde{v} = 802, 1515-1652, \) and 1339 cm\(^{-1}\), which correspond to C–H pyridine (out-of-plane bending), C=C stretching, and C=N pyridine stretching, respectively. Moreover, the C=O vibration of COOH appears at \( \tilde{v} = 1741 \) cm\(^{-1}\) in G-py.[44, 46] The spectrum of PCN-222 shows two peaks at \( \tilde{v} = 1691 \) and 1417 cm\(^{-1}\) assigned to the COO (asymmetric) and COO (symmetric) stretching vibrations, respectively. The peaks at \( \tilde{v} = 2920-3090, 1557-1603, \) and 1326 cm\(^{-1}\) are attributed to the C=H bond of the benzene and pyrrole ring, C=C (phenyl and pyrrole) stretching functional groups, and pyrrole deformation, respectively. C–H (out-of-plane bending of the phenyl rings) is observed at \( \tilde{v} = 712 \) and 804 cm\(^{-1}\).[50] For the composites, because of the anchoring of the pyridine function to the Fe center, the intensity of the Fe–N peak located at \( \tilde{v} = 1000 \) cm\(^{-1}\) increases. Some of the peaks of PCN-222 appear in the spectra of the composites. Furthermore, the C=C stretching vibration mode covers the \( \tilde{v} \approx 1600 \) cm\(^{-1}\) zone.

The thermal stability of PCN-222 (activated) and the composites (10, 25, and 50 wt %) were investigated by using TGA. In the PCN-222 sample, weight is lost gradually at \( \approx 350-800 \) °C, and no weight loss occurs up to 350 °C (Figure S4).[43] For composites, the amount of remnant liberated after thermal pyrolysis diminishes with the increasing content of G-py in the composite from 10 to 50 wt % (Figure 3). The proportion of residue for the composites (10, 25, and 50 wt %) are 32.69, 19.37, and 6.8%, respectively.[36]

To determine the morphology of the samples, SEM images were recorded (Figure 4). The SEM images of the functionalized graphene nanosheets were investigated by using TGA (Supporting Information).

Characterization of PCN-222 and PCN-222-G-py

It is necessary to know which changes in the MOF structure and its properties are created by the presence of graphene. Therefore, optical properties, vibrational bands, and the structure of the MOF and its composites were studied.

The absorption spectra of TPPCOOMe, [TPP-COOMe]Fe\(^{0}\)Cl, PCN-222, and PCN-222-G-py (25 wt %) are shown in Figure 1b. For TPPCOOMe, the Soret band (transition from \( \pi \) to LUMO) at \( \lambda = 419 \) nm and Q bands (HOMO→LUMO) at \( \lambda = 514, 549, 589, \) and 646 nm can be observed. If Fe is inserted into the porphyrin to form [TPP-COOMe]Fe\(^{0}\)Cl, the number of Q bands is reduced from four to two at \( \lambda = 570 \) and 609 nm and a Soret band appears with a blueshift at \( \lambda = 414 \) nm.[40] The UV/Vis spectrum of PCN-222 shows part of the Soret band along with broadening. In the spectrum of PCN-222-G-py, the Soret band appears with a blueshift compared to that of PCN-222. No clear shift can be monitored for a physical mixture of PCN-222 and G-py (Figure S2). This shows that PCN-222-G-py possesses a different electronic structure to PCN-222.[23, 36] Furthermore, the presence of r-GO in PCN-222-G-py creates a new band at \( \lambda = 244 \) nm, which corresponds to G-py.

FTIR spectra of GO, G-py, PCN-222, and PCN-222-G-py (25 wt %) are shown in Figure 2. In GO, the C=O stretching vibrations of carboxyl and carbonyl groups are observed at \( \tilde{v} = 1727 \) cm\(^{-1}\). The O–H stretching vibration at \( \tilde{v} = 3412 \) cm\(^{-1}\) and the C–O stretching vibration at \( \tilde{v} = 1058 \) cm\(^{-1}\) can be observed. The peaks at \( \tilde{v} = 1622, 1382, \) and 1235 cm\(^{-1}\) are assigned to C–C from the unoxidized sp\(^{2}\) C–C bond, the stretching vibration of C=O of carboxylic acid, and C–OH stretching, respectively.[23, 45, 47] In the spectrum of G-py, the intensities of the peaks associated with the oxygen groups decrease dramatically and some of them vanish.[43] The presence of pyridine on the r-GO sheets can be observed by peaks at \( \tilde{v} = 1515–1652, \) and 1339 cm\(^{-1}\), which correspond to C–H pyridine (out-of-plane bending), C=C stretching, and C=N pyridine stretching, respectively. Moreover, the C=O vibration of COOH appears at \( \tilde{v} = 1741 \) cm\(^{-1}\) in G-py.[44, 46] The spectrum of PCN-222 shows two peaks at \( \tilde{v} = 1691 \) and 1417 cm\(^{-1}\) assigned to the COO (asymmetric) and COO (symmetric) stretching vibrations, respectively. The peaks at \( \tilde{v} = 2920–3090, 1557–1603, \) and 1326 cm\(^{-1}\) are attributed to the C=H bond of the benzene and pyrrole ring, C=C (phenyl and pyrrole) stretching functional groups, and pyrrole deformation, respectively. C–H (out-of-plane bending of the phenyl rings) is observed at \( \tilde{v} = 712 \) and 804 cm\(^{-1}\).[50] For the composites, because of the anchoring of the pyridine function to the Fe center, the intensity of the Fe–N peak located at \( \tilde{v} = 1000 \) cm\(^{-1}\) increases. Some of the peaks of PCN-222 appear in the spectra of the composites. Furthermore, the C=C stretching vibration mode covers the \( \tilde{v} \approx 1600 \) cm\(^{-1}\) zone.

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peak at a binding energy (BE) of 711.5 eV for PCN-222, which demonstrates the presence of Fe$^{3+}$ inside the porphyrin core, whereas the binding energy of the Fe 2p$_{3/2}$ in the spectrum of PCN-222-G-py (25 wt%) increases to 712.29 eV because of the anchoring of the pyridine function to the Fe center (Figure 5a). The coordination of pyridine as an axial ligand to the Fe center decreases the electron density from the core because pyridine is a π-acceptor ligand according to the Mössbauer spectra reported previously, which is in good agreement with our results. Therefore, the Fe centers in PCN-222-G-py (25 wt%) have more positive charge than those in PCN-222. The presence of the more positive centers in PCN-222-G-py (25 wt%) is desirable for the adsorption of O$_2$ molecules in the first step of the ORR.

In the N 1s region, a single peak at BE = 398.9 eV related to the Fe–N bond in the porphyrin core of PCN-222 accompanied with a satellite can be observed (Figure 5b). In PCN-222-G-py (25 wt%), the N 1s peak splits into two bands located at BE = 398.9 and 400.7 eV, which correspond to the pyridinic N of G-py and the “pyrrole-type” N of the porphyrin core, respectively.

XRD patterns of PCN-222 and the composites are presented in Figure 6. For the MOF, most peaks are located in the small-angle region because of the mesoporous nature of PCN-222. This is in agreement with that reported previously for PCN-222. In the composites (10 and 25 wt%), the main diffraction pattern of PCN-222 is preserved and the increase of the amounts of G-py, as an impurity, reduces the clarity of the peaks related to PCN-222, which suggests that the MOF structure is mainly retained and the graphene layers induce a slight distortion. PCN-222-G-py (50 wt%) has a completely amorphous phase because of the high amount of G-py in the material.

**Investigation of the presence of graphene nanosheets inside the framework**

PCN-222-G-py (25 wt%) was dissolved in 2 M NaOH solution and washed with water and ethanol to remove impurities from Figure 2. FTIR spectra of i) GO, ii) G-py, iii) PCN-222, and iv) PCN-222-G-py (25 wt%).

Figure 3. TGA plots of freshly synthesized PCN-222-G-py (10, 25, and 50 wt%).
The precipitate was dried and then dispersed in DMF with sonication for 30 min. The presence of r-GO sheets was revealed by using SEM (Figure 7a) and Raman spectroscopy. The Raman spectrum presented in Figure 7b shows the D band ($\tilde{v} = 1320 \text{ cm}^{-1}$) and G band ($\tilde{v} = 1590 \text{ cm}^{-1}$) of the graphene sheet.\(^{[56]}\)

Electrochemical characterization of the modified electrode

The electroactivity of the constructed modified electrodes was evaluated by studying the redox reactions of Fe(CN)$_6^{3-/4-}$ (Figure 8a) by using cyclic voltammetry (CV). As observed, the peak currents increased after the introduction of modifiers on the electrode surface compared to those obtained on the bare glassy carbon electrode (GCE). Moreover, a decrease of the peak potential difference ($\Delta E_p = E_{p,a} - E_{p,c}$) of the ferricyanide redox reaction on the surface of the modified electrodes led to the enhancement of the charge transfer kinetics. These results confirm the significant improvement of the electrochemical activity of GCE as a consequence of the electrode surface modification and, therefore, the effectiveness of the synthesized modifiers.

As confirmed previously, the presence of PCN-222 and G-py (as PCN-222-G-py (25 wt%)) on the surface of the electrode increases its effective surface area. To evaluate the effective surface area of the various modified electrodes, the CVs of 0.1 M KCl solution that contained 1 mM K$_3$Fe(CN)$_6$ as a redox probe were recorded at different scan rates. The electroactive surface area was estimated according to the Randles–Sevcik equation [Eq. (1)].\(^{[57]}\)

$$i_{p,c} = 2.69 \times 10^5 n^{1.5} A C_D^{0.5} v^{0.5}$$  \(1\)
Electrocatalytic behavior of optimized PCN-222-G-py towards the ORR

The electrochemical reduction of oxygen was investigated on the modified and bare GCE surfaces to clarify the differences between their electrocatalytic activities. The CVs recorded in 0.5 M H₂SO₄ solution saturated with O₂ at GCE, PCN-222-GCE, PCN-222-G-py (10 wt %)-GCE, PCN-222-G-py (25 wt %)-GCE, and PCN-222-G-py (50 wt %)-GCE are given in Figure 8b. In N₂-saturated solution, no clear cathodic peak appeared within the potential range of +0.5 to −0.5 V. However, in the O₂-saturated solution, a reduction peak was observed, which reveals the occurrence of the ORR process. Oxygen shows a broad and weak reduction peak, with a peak current of approximately −1.45 mA at −0.395 V on the bare GCE (curve a), whereas for PCN-222-GCE, PCN-222-G-py (10 wt %)-GCE, PCN-222-G-py (25 wt %)-GCE, and PCN-222-G-py (50 wt %)-GCE the cathodic peak currents of the ORR are enhanced significantly, and well-defined irreversible reduction peaks appear at E_{pa} = −0.031, 0.018, 0.082, and 0.080, respectively. The thin layer of PCN-222, PCN-222-G-py (10 wt %), PCN-222-G-py (25 wt %), or PCN-222-G-py (50 wt %) coated on the GCE surface increased the peak current of oxygen reduction by 15.1, 16.2, 43.1, and 61.6 times, respectively, compared to bare GCE (curves b–e). As shown, the reduction peak current of oxygen was further enhanced by increasing the amount of G-py in the PCN-222-G-py composite, which reveals the effectiveness of the prepared composites. These results confirm the high electrocatalytic activities of the employed modifiers, which lead to the significant enhancement of the ORR kinetics.

CVs of GO-GCE, G-py-GCE, and PCN-222-G-py (25 wt %)-GCE recorded in 0.5 M H₂SO₄ solution saturated with O₂ with a potential sweep rate of 50 mV s⁻¹ are shown in Figure 9a. At GO-GCE, a very small peak with a high overvoltage was observed at −0.4 V. The deposition of r-GO directly on the GCE (G-py-GCE) results in the appearance of a broad peak with a high background current for the ORR at −0.165 V. Interestingly, the observation of a well-shaped reduction peak with a higher peak current at more positive potentials on the surface of PCN-222-G-py (25 wt %)-GCE reveals the enhanced electron transfer kinetics of the related process. Notably, the background current of the bare electrode increased significantly after its surface modification by G-py. In contrast, the use of GO or PCN-222-G-py as a modifier leads to a lower increase in the background current, which is more reliable for quantification purposes as the Faraday current can be detected sensitively. The observed improvement in the electrocatalytic activity may be caused by the synergistic effects of framework porosity and the electrocatalytic activity of PCN-222 as well as the high surface area and good electrical conductivity of r-GO in the structure of the PCN-222-G-py composite.

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A linear relationship between the peak potential $E_{p,c}$ and the logarithm of scan rate (Figure 9c) can be expressed by Equation (2):

$$E_{p,c} = -99.54 \log \nu + 270.63$$

in which $R^2 = 0.994$, $E_{p,c}$ is in mV and $\nu$ is in mVs$^{-1}$. According to the Laviron equation [Eq. (3)] for an adsorption-controlled irreversible process$^{[58]}$, a value of 0.59 was obtained for the term $an$.

$$E_p = E^o + (2.303RT/anF) \log (RTk^o/anF) - (2.303 RT/anF) \log \nu$$

Here, $E^o$, $\alpha$, $n$, and $k^o$ are the formal potential, transfer coefficient, number of electrons involved in the rate-determining step of the electrode process, and the electrochemical rate constant, respectively, and the other symbols have their usual meanings. If we consider that $\alpha = 0.5$, the value of $n$ was calculated to be 1, which reveals the involvement of one electron in the rate-determining step of the electroreduction of $O_2$.

The durability of PCN-222-G-py (25 wt %) as an ORR catalyst for the cathode was evaluated. The test was performed by recording successive CVs in 0.5 M $H_2SO_4$ saturated with $O_2$ at a sweep rate of 50 mV S$^{-1}$. The results exhibited a very slow current attenuation over 100 scans, which suggests the good stability and acceptable performance of the modified electrode.

**Role of the pyridine connection**

To explore the key role of the pyridine connection to the Fe centers, we examined another sample for the ORR in which the nanosheets of r-GO are not functionalized with pyridine. This sample (PCN-222/r-GO (25 wt %)) was prepared according to the following procedure.

First, PCN-222(Fe) (1.5 mg) and r-GO (0.5 mg; 25 wt %, based on the mass of PCN-222) were dispersed in 2 mL of water by sonication for 30 min. The prepared PCN-222/r-GO suspension (4 mL) was drop-casted onto the GCE surface. The electrode was allowed to dry at room temperature for 30 min. Again, the PCN-222/r-GO suspension (4 mL) was loaded onto the GCE and allowed to dry for 30 min.

The CV recorded in 0.5 M $H_2SO_4$ solution saturated with $O_2$ at PCN-222/r-GO (25 wt %)-GCE is shown in Figure S6. A comparison between the results of PCN-222, PCN-222/r-GO (25 wt %), and PCN-222-G-py (25 wt %) revealed that GCE modification using the PCN-222/r-GO (25 wt %) suspension increased the peak current of the ORR by 1.1 times compared to that of PCN-222-GCE. Moreover, PCN-222-G-py (25 wt %)-GCE increased the peak current of the ORR by 2.8 times compared to that of PCN-222-GCE. Furthermore, the cathodic peak potentials of the ORR at PCN-222/r-GO (25 wt %)-GCE and PCN-222-G-py (25 wt %)-GCE appeared at $E_{p,c} = 0.012$ and 0.082 V, respectively. These results indicate that the use of a mixture of PCN-222 and r-GO nanosheets without the pyridine connection as a modifier can enhance the ORR peak current at more posi-
tive potentials than that of PCN-222 because of the good electrical conductivity of r-GO. However, if pyridine ligands were connected to the iron porphyrins and a path for electron transfer was constructed in the composite (PCN-222-G-py), the peak current increased significantly and was located at a more positive potential. Generally, the creation of a chemical pathway to pass the electrons is the main reason to use pyridine, which leads to the significant amplification of the electrochemical oxygen reduction kinetics.

Stability and repeated use of PCN-222-G-py (25 wt%)

As some proton exchange membrane (PEM) fuel cells use acidic media, the stability of the electrocatalyst in an acidic medium is necessary. The stability of the GCE modified by the prepared composite was evaluated by recording 100 successive CVs in 0.5 M H$_2$SO$_4$ solution saturated with O$_2$ at a scan rate of 50 mV s$^{-1}$ (Figure S7a). Small changes in the peak potential (5 mV after 100 cycles) and a decrease of the peak current with the increasing number of CV cycles were observed because of the decline of O$_2$ concentration. In the next step, O$_2$ was purged into the acidic solution and another 100 successive CVs were recorded. Notably, the same results were obtained in both steps, which reveal the good stability of the prepared modified electrode. Similar results were obtained for PCN-222 (Figure S7b).

The repeatability of PCN-222-G-py-GCE and PCN-222-GCE was investigated by immersing PCN-222-G-py-GCE and PCN-222-GCE in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution and recording CV, and the electrodes were left in solution for 24 h. Then, CVs were recorded in the same O$_2$-saturated solution. Similar results were obtained, which reveals the good repeatability of the prepared modified electrodes (the peak potential change was less than 10 mV). These results are in good agreement with that reported previously for the stability of PCN-222 in acidic media by using XRD.$^{[43]}$

Methanol tolerance test

One of the disadvantages of direct methanol fuel cells is that the Pt/C commercial catalyst is prone to methanol poisoning. As a good electrocatalyst is inert to methanol oxidation, we have investigated the methanol crossover effect for PCN-222-G-Py. No clear response for PCN-222-G-Py-GCE is detected in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution with 3 M methanol (Figure S8). Thus the composite has a selectivity for the ORR accompanied by a tolerance of methanol crossover effects. According to the previous report of Jahan et al., the Pt/C catalyst shows a distinct oxidation peak caused by the methanol oxidation reaction.$^{[59]}$

Advantages of the 3D structure of the designed electrocatalyst

To explore the advantages of the 3D structure of the electrocatalyst, other samples such as Fe-TCPP/r-GO (1.5 mg Fe-TCPP and 0.5 mg r-GO in 2 mL water) were examined (Supporting Information). The results indicate the necessity to use a 3D structure such as a MOF for the preparation of the electrocatalyst. If the iron porphyrins that are responsible for the ORR are located in a 3D structure, they have better operation because of the specific properties of MOFs such as good stability under harsh conditions and an appropriate dispersion in solvent. Furthermore, the 3D structure of the MOF prevents the aggregation of iron porphyrins. Therefore, the access of O$_2$ to the active center of the electrocatalyst is easier.

The demetalation of porphyrins during the ORR is an unavoidable process.$^{[24]}$ Notably, the Fe centers in PCN-222-G-py (25 wt%) have an axial ligand. Probably, the demetalation of porphyrins in the building blocks of PCN-222 takes place slowly because of the extra coordination bond.

Comparison between the activity and stability of PCN-222-G-py (25 wt%) and Pt/C electrodes

According to a report published previously,$^{[59]}$ the cathodic peak for the ORR at a GCE loaded with Pt (20 wt%)/C is at $-0.2$ V with a current density of $\approx 2$ mA cm$^{-2}$ in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution. Our PCN-222-G-py (25 wt%)-GCE shows the potential peak at 0.082 V with a current density of 3.55 mA cm$^{-2}$ under the same conditions (Figure S10a). These results demonstrate that the use of PCN-222-G-py (25 wt%) as a GCE modifier leads to the occurrence of the ORR at a more positive potential with a current density of approximately 1.8 times of that of Pt/C.

To compare the stability of PCN-222-G-py (25 wt%) and commercial Pt (20 wt%)/C, the chronoamperometry of PCN-222-G-py (25 wt%)-GCE was measured at a constant voltage of $-0.2$ V in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution. The composite was cycled continuously for 1000 s. After a 47.5% loss in the initial current density, a very slow attenuation can be observed in Figure S11a. In comparison, Pt (20 wt%)/C shows a current loss of 58%.$^{[59]}$ This result suggests the good durability of the PCN-222-G-py (25 wt%) catalyst.

Conclusions

We have designed a new composite from a 3D porphyrin-based metal–organic framework (MOF) and graphene nanosheets that has a highly stability and good performance as an electrocatalyst for the oxygen reduction reaction in acidic media. Our results revealed that the presence of graphene and the MOF enhance the electrocatalytic activity of the final composite synergistically because of the pyridine functional groups that connect the graphene sheets and the MOF to provide an easy transfer of electrons, which facilitates oxygen reduction. The use of a glassy carbon electrode (GCE) modified with the prepared PCN-222-G-py composite shifted the oxygen reduction reaction onset potential positively (477 mV) compared to a bare GCE and with an increased peak current that is 43.1 times higher than that of the bare GCE.
Experimental Section

Materials
Methyl 4-formylbenzoate, pyrrole, propionic acid, 4-aminopyridine, N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), acetone, FeCl₃·4H₂O, ZrCl₄, H₂SO₄, HCl, and H₂O₂ were purchased from Merck Chemical Co. (Darmstadt, Germany, www.merck.de). Graphite powder, Na₂CO₃, NaBH₄, KMnO₄, NaNO₃, and NaNO₂ were obtained from Sigma Aldrich Chemical Co. Sodium dodecylbenzenesulfonate (SDBS) and benzoic acid were obtained from Acros Organics and LobaChemie, respectively.

Apparatus
SEM images were recorded by using a LEO 1455VP operated at an acceleration voltage of 10 kV. FTIR spectra were recorded at RT by using a Bruker (Tensor 27) spectrometer. The samples were ground with KBr and pressed into disks. UV/Vis spectra were recorded by using a UV/Vis PerkinElmer Lambda 35 spectrophotometer. Powder XRD was performed by using a Phillips PW 1800 X-ray diffractometer with a CuKα line (1 = 1.54060 Å) as the incident beam. TGA was performed by using a Mettler Toledo TGA/SDTA 851 instrument under N₂ at a heating rate of 10 °C·min⁻¹. XPS was performed by using a Gamma data-scienta ESCA200 hemispherical analyzer equipped with an AlKα X-ray source (1486.6 eV) with a monochromator. The binding energies were calibrated relative to the C1s peak at 285 eV. Voltammetric experiments were performed by using an Autolab PGSTAT30 digital potentiostat/galvanostat. All the measurements were recorded at RT by using a three-electrode system with a GCE as the working electrode, Pt wire as the counter electrode, and Ag/AgCl (1 mM KCl) as the reference electrode. Typically, CVs were performed at a scan rate of 50 mV·s⁻¹. All potentials were measured and reported using a Ag/AgCl reference electrode. The CV experiments were conducted in N₂ and O₂-saturated 0.5 M H₂SO₄ for the ORR.

Synthesis of graphene oxide (GO)
GO was prepared using a modified Hummers and Offeman’s method. Typically, graphite (500 mg), NaNO₃ (5.9 mmol, 500 mg), and concentrated H₂SO₄ (23 mL) were stirred in an ice bath for 15 min. Next, KMnO₄ (25.3 mmol, 4000 mg) was added slowly. After the addition of KMnO₄, the reaction was continued at 35 °C for 2 h under stirring to form a thick green paste. Excess water (50 mL) was added very slowly followed by stirring for 1 h, and the temperature was increased to (90 ± 5) °C. Finally, water (100 mL) was added, followed by the slow addition of H₂O₂ (30%, 3 mL). The color of the mixture changed to yellow brown during the dropwise addition of H₂O₂. The product was collected by filtration and washed with HCl solution (5%) and then repeatedly washed with water. The final product was dried under reduced pressure. by outgassing. The resulting r-GO was collected by filtration and washed with plenty of water.

Synthesis of pyridine-functionalized graphene (G-py)
The functionalization of graphene was achieved with pyridine groups using the diazonium reaction. Briefly, NaN₂O₃ (70 mmol, 4900 mg) was dissolved in H₂O (7 mL) and then cooled on an ice bath. Further, 4-aminopyridine (4·AP; 70 mmol, 6580 mg) was dissolved in 4 M HCl (5 mL) and then cooled in an ice bath. The solution of NaN₂O₃ was added dropwise to the 4·AP solution. The resulting yellow solution was kept at 0 °C in an ice bath under stirring for 30 min. At the same time, r-GO (150 mg) was dispersed in 1 wt% aqueous SDBS surfactant in water (150 mL) by using a bath sonicator for 1 h. The r-GO solution was cooled to 0 °C in an ice bath, and the yellow solution of NaN₂O₃ and 4·AP was added dropwise, and the temperature was maintained at 0 °C to prevent the decomposition of diazonium salts. The mixture was maintained in an ice bath at 0 °C for around 4 h. Next, the reaction mixture was stirred at RT for another 4 h. Finally, the solution was filtered and washed several times with water, ethanol, DMF, and acetone.

Synthesis of FeTCPPCl
FeTCPPCl was prepared according to a procedure described previously in three steps as follows:

1) 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin (TPPCOMe)
In a 500 mL three-necked flask, methyl p-formylbenzoate (42 mmol, 6900 mg) was dissolved in propionic acid (100 mL). Then, pyrrole (43 mmol, 3.0 mL) was added dropwise, and the solution was heated to reflux for 12 h. After the reaction mixture was cooled to RT, the precipitates were collected by suction filtration and washed with methanol, ethyl acetate, and THF. After drying in an oven, a purple solid was obtained as the pure product (1.9 g, 2.24 mmol, 21% yield).

2) 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)-porphyrinatoiron(III) chloride (TPPCOMe·FeCl₃)
TPPCOMe·FeCl₃ (1 mmol, 854 mg) and FeCl₃·4H₂O (12.8 mmol, 2500 mg) were added to DMF (100 mL), and the mixture was heated to reflux for 6 h. After cooling to RT, H₂O (150 mL) was introduced. The resulting precipitate was collected by filtration and washed with H₂O (50 mL) twice. The obtained solid was dissolved in CHCl₃ and washed three times with 1 M HCl and twice with water. The organic layer was then dried over anhydrous magnesium sulfate and evaporated to give a quantitative yield of dark brown crystals.

3) 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinatoiron(III) chloride (FeTCPPCl)
The obtained ester (750 mg) was stirred in THF (25 mL) and MeOH (25 mL), and a solution of KOH (46 mmol, 2630 mg) in H₂O (25 mL) was added. The mixture was heated to reflux for 12 h. After cooling to RT, THF and MeOH were evaporated. Water was then added to the resulting water phase, and the mixture was heated until the solid was dissolved fully. Afterwards, the homogeneous solution...
was acidified with 1 M HCl until no further precipitate was detected. The brown solid was collected by filtration, washed with water, and dried in vacuum. FTIR (KBr): υ = 3447 (m), 3050 (w), 2650 (w), 1694 (s), 1604 (s), 1560 (m), 1402 (s), 1300 (m), 1268 (s), 1201 (m), 1174 (m), 1102 (m), 999 (s), 866 (m), 796 (s), 765 (s), 717 cm⁻¹ (m).

Synthesis of PCN-222(Fe)

PCN-222 was prepared according to a method reported previously by Feng. \[\text{ZnCl}_2 \] (0.32 mmol, 75 mg), FeTCPPCl (0.056 mmol, 50 mg), and benzoic acid (220 mmol, 2700 mg) in DEF (8 mL) were dissolved ultrasonically in a 20 mL Pyrex vial. The vial was heated in an oil bath at 120 °C under stirring with a stir bar for 24 h. After cooling to RT, a dark brown powder was obtained by centrifugation. FTIR (KBr): υ = 3444 (m), 2980 (w), 1691 (w), 1603 (s), 1557 (s), 1417 (vs), 1326 (s), 1178 (m), 1000 (s), 871 (w), 804 (m), 770 (m), 712 cm⁻¹ (s).

Activation of the PCN-222 sample

To remove the unreacted starting materials and trapped benzoic acid, as-synthesized PCN-222 (~100 mg) was immersed in DMF (40 mL) at 120 °C for 12 h. Afterwards, the sample was centrifuged and washed with DMF and acetone. Fresh acetone was added, and the sample was maintained for 24 h. Finally, the extract was deca
tered carefully and dried under vacuum for 6 h.

Preparation of composite (PCN-222-G-py)

PCN-222(Fe) (10 mg) was dispersed in a mixture of DMF (5 mL) and ethanol (3 mL). Various amounts of G-py (10, 25, and 50 wt %, based on the mass of PCN-222) were added to the mixture. The final mixture was sealed in a small capped vial and sonicated for 30 min. Again, asuspension of sample (4 mL) was loaded onto the GCE surface. The electrode was allowed to dry at RT for 30 min. Again, a suspension of sample (4 mL) was dropped onto the GCE and allowed to dry for 30 min.

Acknowledgements

Financial support by the Alzahra University is gratefully acknowl
dged.

Keywords: electrochemistry · fuel cells · graphene · metal-
organic frameworks · reduction

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Catalytic properties of PCN-222

Before use, a GCE was polished mechanically with alumina slurry and washed with DMF and acetone. Fresh acetone was added, and the sample was maintained for 24 h. Finally, the extract was deca
tered carefully and dried under vacuum for 6 h.
