Fabrication of a polyoxotungstate/metal–organic framework/phosphorus-doped reduced graphene oxide nanohybrid modified glassy carbon electrode by electrochemical reduction and its electrochemical properties

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Hybrid nanocomposites based on polyoxometalates (POMs), metal–organic frameworks (MOFs), and graphene oxide (GO) have a unique set of properties. They have specific properties such as high acidity, oxygen-rich surface, and good redox capability from POMs. In contrast, they do not have weaknesses of POMs such as a low surface area, and high solubility in aqueous media. Herein, a novel organic–inorganic nanohybrid compound based on H$_2$PW$_{12}$O$_{40}$ (PW$_{12}$), a Co-based MOF, and GO was prepared. The prepared hybrid nanocomposite (PW$_{12}$/MOF/GO) was characterized using different techniques. Then, a PW$_{12}$/MOF/GO nanocomposite modified glassy carbon electrode (GCE) was fabricated by the drop-casting method and next was dried at room temperature. Then, the PW$_{12}$/MOF/GO/GCE was subjected to electrochemical reduction at a constant potential of −1.5 V, in 0.1 M H$_3$PO$_4$ solution containing 0.10% w/v PW$_{12}$/MOF/GO additive. The morphology, electrochemical activity, and stability of the modified electrode (PW$_{12}$/MOF/PgERGO/GCE) were studied with FE-SEM coupled with EDS, CV, and amperometry. The obtained results confirmed that the PW$_{12}$/MOF/PgERGO/GCE could be effective in hydrogen evolution reaction (HER). The electrochemical activity of the PW$_{12}$/MOF/PgERGO/GCE due to the desirable microstructure of the electrocatalyst (e.g. high active surface area and homogeneous distribution of the PW$_{12}$/MOF/PgERGO), and also the synergistic effect of the blocks, is more than those of PW$_{12}$/GCE, MOF/GCE, PW$_{12}$/MOF/GCE, and PgERGO/GCE. Moreover, the PW$_{12}$/MOF/PgERGO/GCE showed an excellent long-term stability under the air atmosphere.

1. Introduction

Polyoxometalates (POMs) are a large class of metal oxide clusters, consisting of early transition metal oxoanions with shared oxygen atoms exhibiting well-defined connectivity. POMs, especially Keggin-type POMs, have wide applications in various fields such as catalysis, optics, magnetism, medicine, environmental science, and electrochemistry, due to their exclusive molecular structure, electronic features, and excellent redox properties. One of the attractive properties of POMs is that the anionic cluster can undergo a fast, stepwise, reversible, and multi-electron transfer reaction while keeping the structural integrity. These numerous redox properties make them potential candidates for surface modification, and electrocatalytic studies. However, their use as catalysts is one of the interesting fields for researchers, because of their high acidity, oxygen-rich surface, and redox capability. Despite these special characteristics, POMs still show some weaknesses for their use as a catalyst. First, POMs have a low specific surface area (<10 m$^2$ g$^{-1}$), which consequently reduces the availability of reactants, and secondly, their high solubility in aqueous solutions results in low recyclability.

To overcome these challenges and improve electrochemical properties and electrocatalytic performances, immobilization or dispersion of POMs onto porous materials has been proposed.

In the last few decades, many porous solids have been investigated as immobilizers for POMs, like silica, conducting polymers, ion-exchange resin, and carbon materials. Since discovering metal–organic frameworks (MOFs), these porous materials have been widely used as potential supports for POMs. MOFs are inorganic–organic hybrid crystalline materials are fabricated from metal-containing nodes and organic linkers through coordination bonds. These materials have attracted considerable attention in recent years due to their large surface areas, adjustable pore size, and designable functionalities. MOFs have shown great potential in gas storage and separation, catalysis, sensing, drug delivery, proton...
conduction,

27,28 solar cells,

29,30 supercapacitors31,32 and

biomedicine.15,16 In addition, MOFs are as a suitable platform

for the introduction of guest molecules due to the high acces-

sibility of their internal surface area and regular long-range

channels. To date, several active sites have been successfully

embedded in the cages of MOFs, such as noble metals,33 metal

oxides,34,35 enzymes,36,37 and POMs.40,41

The first report of a POM/MOF hybrid was presented in 2005

by Ferey et al.41 In this study, K2PW12O40·nH2O successfully was

incorporated into big cages of the highly stable Cr-based MOF,

MIL-101, using the impregnation method.

Up to now, several other thermal and stable chemical MOFs

such as Materials of Institute Lavoisier Framework Series (MIL

Series),38,39 Zeolite Imidazole Framework Series (ZIF Series),40

and Cu-BTC41,42 frameworks applied as supports for POMs

hosting for using in catalysis.

The most examined POMs that have been incorporated into

MOFs are the well-known Keggin [XM12O40] 3− and Wells–Daw-

son [X2M18O62] 3− (X = Si, P, etc.; M = Mo, W, V, etc.) POMs and

their derivatives.43,44

There are many benefits to using MOFs as a host matrix to

capsule POMs. First, their extremely high surface areas and

confined cages/channels allow the homogeneous distribution of

POM in the MOF host to be ensured. This phenomenon prevents

the aggregation of POMs, and improves their stability and

recyclability. Secondly, the very regular cages and channels of

MOFs provide a high substrate selectivity, or, in other words, only

specific substrates/products can access the active POM sites.

Thirdly, due to the excellent interaction and electron transfer

between the MOF and the POM, an enhanced synergistic catalytic

effect is typically observed. Finally, the POM@MOF hybrids not

only combine the exciting properties of POM and MOF, but also

allow the weaknesses as mentioned above of POMs to be

resolved, and the catalytic performance significantly increased.2

On the other hand, immobilization or entrapment of POMs

on various supporting carbon materials has concerned signifi-

cant attention. Among the carbon materials, graphene exten-

sively studied in nanotechnology fields due to its excellent

chemical stability, high surface area, extraordinary conduc-

tivity, and good mechanical properties.10,12

Graphene was discovered at Manchester University by Andre

Geim and Kostya Novoselov in 2004.52 It is an allotrope of

carbon-containing a single layer of atoms arranged in a two-

dimensional (2D) hexagonal lattice nanostructure.53

It is the thinnest and most robust known material in the

universe.54 Graphene is a good choice for POMs support mate-

rials to overcome the limitations of POMs such as high solu-

bility in polar solvents and low specific surface area (SSA).55 In

addition, the unique features of POMs, especially in catalysis,56

electrocatalysis,57 and capacitance,58 enhance because of the

large SSA and excellent electrical conductivity of graphene.

Recently, numerous reports have submitted on the nano-

composites of reduced graphene oxide (RGO) and poly-

oxometalates (POMs).59–61 However, the RGO is processed from

GO through UV-phoretoreduction,62,63 and chemical reduction

with hazardous materials.64 However, using these approaches,

POM/RGO composites are obtained in powder form, which

must be deposited on the surface of electrode by the drop-

casting technique. The drop-casting technique has inherent

defects like lack of control over the film thickness and low

stability.65 The self-assembly method is the best way to create

stable and uniform modified surfaces. Recently, the preparation

of RGO from GO by the electrochemical reduction method has

attracted a lot of attention due to its easy and green preparation

method.65–68 Chen et al. directly deposited RGO onto a glassy

carbon electrode (GCE) through cyclic voltammetric (CV)

reduction of a GO colloidal solution. The graphene-modified

electrode was applied to simultaneously determine of hydro-

quinone and catechol.66 Guo et al. investigated the preparation

Scheme 1  Schematic diagram of stepwise electrode modification processes.
method and electrocatalytic property of H₄SiMo₁₂O₄₀ and chitosan/ERGO multilayer composite films on indium tin oxide (ITO) electrode by electrochemical growth method. Tao Wei et al. firstly synthesized H₅PMo₁₀V₂O₄₀/BTC/RGO nano-composites for lithium-ion batteries (LIBs) by a facile one-pot method. Wen Zhang and co-workers prepared a POM/MOF/RGO hybrid material via a facile hydrothermal process. The prepared hybrid material is used to detect dopamine (DA). The POM/MOF/RGO/GCE presented an excellent catalytic activity toward oxidation of DA owing to matching functionality and structure between the POM, MOF, and RGO.

Recently, many reports have verified that heteroatom doping into graphene (e.g., B, N, P, and S) can increase the electrical conductivity and electrocatalytic activity of RGO in supercapacitor electrodes, lithium-ion batteries, fuel cells, and dye-sensitized solar cells. The preparation of the P-doped graphene monolayer film modified electrode by the electrochemical reduction approach has many benefits. But, few studies have reported concerning the POM/P@ERGO modified electrode and its derivatives. Therefore fabrication of these modified electrodes still have challenges.

In this work, a new PW₁₂O₄₀ₙH₂O/[Co(TPA)(bimb)(H₂O)₂]ₙ/GO nanocomposite has been dropped onto the GCE using drop-casting method followed by an electrochemical reduction process (PW₁₂/MOF/P@ERGO). For this purpose, PW₁₂/MOF/GO nanocomposite was dropped onto the GCE. Then the modification procedure completed through the electrochemical reduction of GO to RGO at a constant potential of −1.5 V, for 60 s in a H₃PO₄ aqueous solution (0.1 M) containing PW₁₂/MOF/GO (0.10% w/v) as an additive. The PW₁₂/MOF nanocomposite can interact with P@ERGO via P⁺ and π-electrons of MOF without any impact on the electronic structure of PW₁₂ Keggin type. The synergistic effects of these four-blocks, and specific microstructure of PW₁₂/MOF/P@ERGO nanocomposite provide enhanced electrochemical activity of the modified electrode. Then, electrochemical behavior, stability, repeatability, reproducibility of the modified electrode were investigated, comprehensively.

### 2. Experimental section

#### 2.1. Materials

The [Co(TPA)(bimb)(H₂O)₂]ₙ as a Co-based MOF was synthesized according to the previous literature. The 1,4-bis(imidazole)butane (abbreviated as bimb) was prepared according to the previous literature. Tungstophosphoric acid (H₃PW₁₂O₄₀n abbreviated as PW₁₂), cobalt(n) nitrate hexahydrate (Co(NO₃)₂·6H₂O), terephthalic acid (abbreviated as TPA), dimethylformamide (abbreviated as DMF), graphite powder (<20 μm), and other chemicals were of analytical grade and

| Compound   | \(\tilde{v}(\text{C=O})\) | \(\tilde{v}(\text{COO}^-)\) | \(\tilde{v}(\text{C-O})\) | \(\tilde{v}(\text{P-O}_a)\) | \(\tilde{v}(\text{W-O}_b)\) | \(\tilde{v}(\text{W-O}_c)\) |
|------------|----------------|----------------|----------------|-----------------|----------------|----------------|
| PW₁₂       | —              | —              | —              | 1074            | 968            | 887            |
| PW₁₂/MOF   | 1627, 1485     | 1585           | —              | 1056            | 953            | 886            |
| MOF        | 1585, 1360     | —              | —              | —               | —              | —              |
| GO         | 1627, 1402     | 1574           | 1137           | —               | —              | —              |
| PW₁₂/MOF/GO| 1625, 1445     | 1164           | 1060           | 952             | 882            | 819            |

\(O_a\) central oxygen. \(O_b\), \(O_c\) bridging oxygen. \(O_d\) terminal oxygen.
purchased from commercial sources (Merck or Sigma) and used without further purification. Phosphate buffer saline solutions (PBS, 0.11 M) were prepared by mixing the stock solutions of 0.10 M KCl and 0.01 M H₃PO₄ and then adjusting the pH with 0.5 M NaOH aqueous solution.

2.2. Physical methods

The percent of immobilized PW₁₂ on the GO was determined from inductively coupled plasma-optical emission spectrometry (Optima 7300 V ICP-OES spectrometer Brochure-PerkinElmer) by measuring of tungsten contents in the PW₁₂/MOF/GO. FTIR spectra in ATR mode were recorded using a Spectrum Two FT-IR spectrometer (PerkinElmer) in the 4000–600 cm⁻¹ range. The crystalline structure of the PW₁₂, [Co(TPA)(bimb)(H₂O)₂]ₙ, PW₁₂/MOF, GO, and PW₁₂/MOF/GO was confirmed using an X-ray diffraction (XRD, PANalytical XPERT-PRO X-ray diffractometer equipped with Cu Kα radiation, λ = 0.1541 nm). The morphologies of the PW₁₂/MOF/GO, and GO were studied by transmission electron microscope (TEM, EM10C-100 kV series, Zeiss Co., Germany). The surface morphology and elemental analysis of the bare GCE, P@ERGO/GCE, and PW₁₂/MOF/P@RGO/GCE were determined using

Fig. 3 TEM images of (A) GO (a, b) and (B) PW₁₂/MOF/GO (a–d) at different magnifications.
2.4. Synthesis of PW12/MOF

A mixture of bimb (0.095 g, 0.5 mmol), Co(NO3)2·6H2O (0.320 g, 1.0 mmol), TPA (0.085 g, 0.5 mmol), and PW12 (0.288 g, 1.0 mmol) was dissolved in 25.0 mL DMF and 25.0 mL distilled water. After stirring for 30 minute at room temperature, the reaction suspension was transferred to the Teflon-lined stainless-steel autoclave (100 mL), kept at 160 °C under autogenous pressure for 72 h. Then the autoclave was cooled to room temperature with rate of 5 °C h⁻¹. Reddish-pink crystals were collected by filtration. Then obtained crystals washed with distilled water, and dried in the open air (about 45% yield based on cobalt).

2.5. Synthesis of PW12/MOF/GO

GO was prepared by oxidizing graphite flakes via modified Hummers’ method. As-prepared GO (0.100 g) in distilled water (10 mL) was exposed to sonication for 30 minute to achieve a homogeneous suspension. Then 1.000 g of PW12/MOF was added. After the sonication for 20 minute, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated in an oven at 180 °C for 24 h. The black precipitates were filtered, washed with distilled water, and dried at 60 °C for 12 h to obtain PW12/MOF/GO.

2.6. Fabrication of PW12/MOF/P@ERGO/GCE

The surface of the GCE was polished with α-alumina slurries (α-Al2O3, the particle size of 0.30, 0.10, and 0.05 μm) to remove the contaminants. Then it was electrochemically cleaned in 0.5 M H2SO4 solution by repetitive cycling in the potential range from −1.0 to 1.0 V (vs. Ag/AgCl) until a stable CV scan is achieved. After rinsing with deionized water, and drying at room temperature, 5.0 μL of the PW12/MOF/GO suspension (0.010 g in 2.0 mL ethanol) was drop-cast onto the bare GCE. Finally, the electrode surface was dried under room temperature overnight at air atmosphere, and washed with deionized water. Then, electrochemical reduction of GO to RGO was performed in 0.01 M H3PO4 containing different concentrations of PW12/MOF/GO as additive (0.0, 0.01, 0.05, 0.10, 0.15, and 0.20% w/v) using chronoamperometry in the potential of −1.5 V at various times (30, 45, 60, and 120 s). A better analytical signal was found in the presence of 0.10% w/v PW12/MOF/GO and at time 60 s. Therefore, 0.10% w/v additive and time 60 s were selected as optimum conditions in the fabrication of the modified GCE. PW12/GCE, MOF/GCE, PW12/MOF/GCE, and P@ERGO/GCE, as the control electrodes were constructed by a similar technique in 0.01 M H3PO4 in the absence of the additive. The schematic design of the preparation procedure of the modified GCE is displayed in Scheme 1.

2.7. Electrochemical experiment

The electrochemical experiments were done in an electrochemical cell with a volume of 90 mL, containing 5 mL of H2SO4 (0.5 M, pH 0.5) solution. The CV, and amperometry methods were used to investigate of electrochemical behavior, effective...
electroactive surface area, and stability of the modified electrode.

3. Results and discussion

3.1. Characterization

The loading percentage of PW$_{12}$ on GO was estimated 0.83% by ICP spectroscopy. ATR-FTIR spectrum of PW$_{12}$/MOF/GO is shown in Fig. 1. To prove of structure, ATR-FTIR measurements of PW$_{12}$, PW$_{12}$/MOF, MOF, and GO were also recorded as shown in Fig. 1, curves a, b, c, and d, respectively. The information is summarized in Table 1.

The ATR-FTIR spectra of PW$_{12}$, PW$_{12}$/MOF, and PW$_{12}$/MOF/GO show four characteristic peaks, that are related to the stretching vibration of P–O$_a$, W–O$_b$, O$_c$–W, and W–O$_d$. The presence of these asymmetric stretching vibration peaks in PW$_{12}$/MOF, and PW$_{12}$/MOF/GO propose that the POM moiety of the hybrid compounds has maintained its Keggin structure. Moreover, the peaks around 1625, 1445, 1574, and 1164 cm$^{-1}$ in PW$_{12}$/MOF/GO that is assigned to the stretching vibrations of C=C aromatic, COO$, and C–O confirm the existence of MOF, and GO (compare curve e with c, and d).

The XRD patterns of PW$_{12}$, PW$_{12}$/MOF, MOF, GO, and PW$_{12}$/MOF/GO are presented in Fig. 2. As displayed in Fig. 2b, PW$_{12}$/MOF shows peaks about 8.2°, 19.1°, 30.8°, 35.4°, 40.4°, and 53.2°, respectively of the PW$_{12}$ (Fig. 2a). However, a sharp peak about at 8.2°, and a broad peak at 30.8°, which are overlapped with the peaks of PW$_{12}$, can be credited to the Co-based MOF (Fig. 2c). Fig. 2d shows a broad diffraction peak 26.4°, which is correspond to the (002) plane of GO nanosheets.$^{41,42}$ In Fig. 2e, the characteristic XRD peaks of PW$_{12}$/MOF/GO appeared at nearly similar locations without a significant shift in its peaks position compared to those of PW$_{12}$, and MOF. However, the peak (002) of GO was not appeared because of peak overlap with the peak of PW$_{12}$, and MOF which has a higher crystallinity.

The specific surface areas and pore size distributions of the MOF, and PW$_{12}$/MOF were measured by N$_2$ adsorption-desorption isotherms. As shown in Fig. 4A and B, both samples exhibited a type-IV isotherm curve with an H4 hysteresis loop, often associated with narrow slit-like pores. The BET surface areas, total pore volumes, and mean pore diameters for MOF, and PW$_{12}$/MOF are 277 m$^2$ g$^{-1}$, and 697 m$^2$ g$^{-1}$, 0.22 cm$^3$ g$^{-1}$, 0.47 cm$^3$ g$^{-1}$, 32 nm, and 27 nm, respectively. The pore size distributions were calculated from the adsorption isotherms using the BJH model as shown in the inset of Fig. 4A and B. These confirm that the MOF, and PW$_{12}$/MOF mainly contain micropores (1.6 nm), and mesopores (10.6 nm), respectively.

Fig. 5 (A) FE-SEM images (a, b), EDS pattern (c) and EDS element mapping (d, e) of the bare GCE, (B) FE-SEM images (a, b), EDS pattern (c) and EDS element mapping (d–f) of P@ERGO/GCE, and (C) FE-SEM images (a, b), EDS pattern (c) and EDS element mapping (d–i) of PW$_{12}$/MOF/P@ERGO/GCE.

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The morphology of the PW₃₂/MOF/P@ERGO/GCE was characterized using FE-SEM, and compared with bare GCE, and P@ERGO/GCE. The FE-SEM images confirmed that the bare GCE (Fig. 5A, images a, b) have a mirror-like surface, which was changed to roughly and heterogeneously surface after the modification by P@ERGO, and PW₃₂/MOF/P@ERGO (Fig. 5B and C, images a, b). Additionally, the EDS patterns of the bare and modified GCEs are presented in Fig. 5A–C image c. The EDS spectra and elemental mappings approve the presence of C, and O in the bare GCE (Fig. 5A, images c–e), C, O, and P in the P@ERGO/GCE (Fig. 5B, images c–f) and C, W, O, N, Co, and P elements on the PW₃₂/MOF/P@ERGO/GCE (Fig. 5C, images c–i).

3.2. Electrochemical activity of PW₃₂/MOF/P@ERGO/GCE

The electrochemical behaviors of the bare GCE, MOF/GCE, PW₃₂/GCE, PW₃₂/MOF/GCE, P@ERGO/GCE, and PW₃₂/MOF/P@ERGO/GCE were investigated using the CV method in 0.5 M H₂SO₄ (Fig. 6). As shown in curve a, the bare GCE did not show any significant peak. In contrast, MOF/GCE, PW₃₂/GCE, PW₃₂/MOF/GCE, P@ERGO/GCE, and PW₃₂/MOF/P@ERGO/GCE displayed a cathodic peak (peak I) about at −0.2 V (vs. Ag/AgCl), that can correspond to hydrogen evolution reaction (HER). However, the peak I current in PW₃₂/MOF/P@ERGO/GCE (curve f) is more significant than MOF/GCE (curve b), PW₃₂/GCE (curve c), PW₃₂/MOF/GCE (curve d), and P@ERGO/GCE (curve e). This result confirms a synergistic effect of four blocks that can promote the electron transfer more effectively.

3.2.1. Effect of scan rate. The CVs of the PW₃₂/MOF/P@ERGO/GCE in H₂SO₄ (0.5 M) at different scan rates were presented in Fig. 6B. As shown in the inset of Fig. 6B, the peak I current depends linearly on the square root of scan rate from 10 to 400 mV s⁻¹. The results show that the HER at the modified electrode undergoes a diffusion-controlled process.

3.2.2. Effect of pH. In Fig. 6C, the impact of buffer pH on the electrochemical activity of the PW₃₂/MOF/P@ERGO/GCE was examined at different pH values (pH 0.5–8.0), using the CV method. As shown in Fig. 6C, peak I, which corresponds to HER, is only seen at pH 0.5 (curve a). This phenomenon can be due to the stability of POMs-based modified electrodes⁹,¹⁰ and also the performance of HER at acidic pH.⁸³,⁸⁴ Therefore, pH 0.5 was considered the optimal pH, and further studies were performed at this pH.

3.3. Optimization of coating parameters

Optimizing of coating parameters is essential to achieve a modified electrode with enhanced electrochemical behavior. Some important parameters, including type, and concentration of electrolyte additive, and deposition time, were investigated. These parameters can affect the electrochemical property of the
modified electrode. The following experiments were performed using CV in H₃PO₄ (0.01 M) at the constant potential of −1.5 V, as shown in Fig. 7. The prepared modified electrode was signified as PW₁₂/MOF/P@ERGO/GCE through the text.

3.3.1. Effect of the electrolyte additive type. Fig. 7A, presents the effect of type of electrolyte additive (without additive, MOF, PW₁₂/MOF, GO, and PW₁₂/MOF/GO additive), on the electrochemical activity of the modified surface. The modified GCE, which is prepared in the presence of PW₁₂/MOF/GO additive (curve e), shows a more faradaic peak current (iₚ, peak I) to other cases (curves a, b, c, and d). This phenomenon proves that PW₁₂/MOF/GO additive, due to the synergistic effects of these blocks, and its microstructure can improve the electrochemical activity of PW₁₂/MOF/P@ERGO/GCE.

3.3.2. Effect of electrolyte additive concentration. An optimum concentration of PW₁₂/MOF/GO additive was determined by electrochemical measurements in a wide range of additive concentrations (between 0.01 and 0.20% w/v) in 0.01 M H₃PO₄ aqueous solution. As displayed in Fig. 7B, the maximum peak I current of the modified electrode appeared in the presence of 0.10% w/v PW₁₂/MOF/GO additive (curve e), which has the highest current to other cases (curves a, b, c, and d). This phenomenon proves that PW₁₂/MOF/GO additive, due to the synergistic effects of these blocks, and its microstructure can improve the electrochemical activity of PW₁₂/MOF/P@ERGO/GCE.

3.3.3. Effect of the electrodeposition time. The electrodeposition time is a crucial variable to be worth discussing. The effect electrodeposition time of 0.10% w/v PW₁₂/MOF/GO additive on the peak I current of PW₁₂/MOF/GO/GCE was performed from 30 s to 120 s at −1.5 V (vs. Ag/AgCl). To determine the optimum electrodeposition time, the CV curves of PW₁₂/MOF/P@ERGO in the presence of PW₁₂/MOF/GO additive (0.10% w/v) at different times were recorded. As shown in Fig. 7C, the modified GCE at 60 s have the most prominent peak I current than 30 s, 45 s, and 120 s, illustrating that it has a more electrochemical active area. Therefore, prepared PW₁₂/MOF/GO/GCE in the presence of 0.10% w/v PW₁₂/MOF/GO additive at 60 s was set as modified GCE, and it chosen to continue the subsequent electrochemical tests. Such excellent performance of the modified GCE at 60 s can be for the following reason. With increasing deposition time up to 60 s, the thickness of the P@ERGO structure is raising, which leads to better electrochemical performance. However, a longer electrodeposition time of 120 s gave a PW₁₂/MOF/P@ERGO/GCE film with a thicker layer, which serves as a barrier layer and imparts resistance to the electron transfer.

3.4. Electrochemical studies of [Fe(CN)₆]³⁻/⁴⁻ on the PW₁₂/MOF/P@ERGO/GCE

The electron transfer characteristics of the bare and the modified GCEs were appraised using voltammetric responses of the [Fe(CN)₆]³⁻/⁴⁻ redox couple on the PW₁₂/MOF/P@ERGO/GCE.
P@ERGO/GCE also shows a significative decrease in peak currents when compared to bare GCE (c), PW12/MOF/GCE (d), P@ERGO/GCE (e), and PW12/MOF/P@ERGO/GCE in PBS solution (10.0 mM) at different pHs; scan rate: 50 mV s⁻¹.

The bare GCE displays a redox couple separated by 92.9 mV with currents (Fig. 8A, curve a). The immobilization of MOF, PW12, and P@ERGO on the GCE leads to decrease in faradaic peak currents (Fig. 8A, curve b, c, and e). These modifiers serve as a kinetic barrier to charge transfer between [Fe(CN)₆]³⁻/⁴⁻ and GCE surface, and decrease iₚ. Moreover, PW12/GCE, and P@ERGO/GCE also shows a significant increase in ∆Eₚ (Fig. 8A, curve c, e). The PW12, and P@ERGO modifiers with negatively charges due to electrostatic repulsion with [Fe(CN)₆]³⁻/⁴⁻ increase the ∆Eₚ. However, a lesser ∆Eₚ accompanied by an increasing of iₚ was established for the PW12/MOF/GCE, and PW12/MOF/P@ERGO/GCE (Fig. 8A, curves d, f). It confirms that the synergistic effect of blocks can enhance the electron transfer kinetic at the GCE surface. The obtained quantitative information is given in Table 2.

Electrochemical studies showed that variation of the electrolyte pH effects on the electrochemical properties of PW12/MOF/P@ERGO/GCE. Fig. 8B presents CVs of this modified electrode in [Fe(CN)₆]³⁻/⁴⁻ (0.5 mM) at various pHs (pH 3 to pH 9). As shown, the ∆Eₚ increases and the iₚ decreases by increasing pH. However, almost no peak could be observed at pHs higher than 6. Indeed, with increasing pH, the concentration of OH⁻ increases. Therefore, the positively charged surface of the modified electrode is gradually neutralized. Thus, the electrostatic attraction between the surface of PW12/MOF/P@ERGO/GCE and redox probe decreases and eventually disappears.

The electroactive surface area of the bare GCE, and PW12/MOF/P@ERGO/GCE was estimated by CV measurements in [Fe(CN)₆]³⁻/⁴⁻ (0.5 mM) containing KCl (0.1 M) at different scan rates (Fig. 9A and C, respectively). The electroactive surface area was calculated by using following Randles Sevck equation (eqn (1)).

\[ i_p = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} v^{1/2} C_p \]  

where \( i_p \) represents the anodic or cathodic peak current, \( n \) is the number of electrons transferred, \( A \) stands for the area of the electroactive surface (cm²), \( D_0 \) denotes the diffusion co-efficient of [Fe(CN)₆]³⁻/⁴⁻ (7.6 × 10⁻⁹ cm² s⁻¹), \( v \) symbolize the scan rate (V s⁻¹), and \( C_p \) represents the concentration of the probe solution (M). The electroactive surface area of PW12/MOF/P@ERGO/GCE is calculated to be 6.032 cm², according to the calibration equation of \( i_p = 2.239 v^{1/2} - 11.695 \) \((R^2 = 0.974)\) presented in Fig. 9D which is about 8.5 times larger than the bare electrode electroactive surface area (0.704 cm²) with calibration equation of \( i_p = 0.2615 v^{1/2} + 0.218 \) \((R^2 = 0.9974)\) (Fig. 9B). Indeed, the high electroactive surface area of the PW12/MOF/P@ERGO/GCE enhanced its electrochemical activity, which was shown in the previous parts.

### Table 2. Electrochemical parameters extracted from CVs on the bare and modified GCEs in the presence of [Fe(CN)₆]³⁻/⁴⁻ (0.5 mM) in PBS (10.0 mM, pH 3) containing KCI (0.1 M) as supporting electrolyte (Fig. 8A)

| Electrode                  | ∆Eₚ/mV ± SD⁺ | ip[mA] ± SD⁻ | iₚ[mA] ± SD⁻ |
|----------------------------|--------------|---------------|---------------|
| Bare GCE                  | 92.9 ± 1.2   | 1.68 ± 0.18   | 1.52 ± 0.13   |
| MOF/GCE                   | 80.0 ± 1.1   | 0.98 ± 0.06   | 0.99 ± 0.08   |
| PW12/GCE                  | 107.0 ± 2.1  | 1.43 ± 0.17   | 1.73 ± 0.14   |
| PW12/MOF/GCE              | 80.0 ± 0.9   | 2.12 ± 0.15   | 2.47 ± 0.12   |
| P@ERGO/GCE                | 115.8 ± 1.1  | 1.53 ± 0.19   | 1.55 ± 0.17   |
| PW12/MOF/P@ERGO/GCE       | 79.0 ± 1.2   | 2.12 ± 0.11   | 2.27 ± 0.12   |

⁺ SD: standard deviation (from 3 data point).

3.5. Stability, repeatability, and reproducibility

Attaining a highly stable sensor is one of the main aims of analytical electrochemistry. The POM-based modified electrodes are usually stable in acidic aqueous solutions. The stability of the PW12/MOF/P@ERGO/GCE was estimated by chronoamperometry (I-t) measurement at the fixed potential of...
**Fig. 9** CVs obtained in the presence of $\text{[Fe(CN)}_6\text{]}^{3-/-4-}$ (0.5 mM) redox probe, in PBS solution (10.0 mM, pH 3) containing KCl (0.1 M) as supporting electrolyte, (A) on the bare GCE at different scan rates from 10 to 300 mV s$^{-1}$, (B) variations of the absolute value of cathodic peak currents on the bare GCE with square root of scan rates, (C) on the PW$_{12}$/MOF/P@ERGO/GCE at different scan rates from 40 to 150 mV s$^{-1}$, and (D) variations of the absolute value of cathodic peak currents on the PW$_{12}$/MOF/P@ERGO/GCE with square root of scan rates.

**Fig. 10** (A) Stability investigation of PW$_{12}$/MOF/P@ERGO/GCE by chronoamperometry ($I$–$t$) measurement at the fixed potential of $-0.175$ V in 0.5 M H$_2$SO$_4$, (B) long-term stability of PW$_{12}$/MOF/P@ERGO/GCE in 0.5 M H$_2$SO$_4$ during a period of 30 days, (C) repeatability test of PW$_{12}$/MOF/P@ERGO/GCE in 0.5 M H$_2$SO$_4$, scan rate 50 mV s$^{-1}$, inset shows histogram of the peak I current of each measurement, and (D) reproducibility test of PW$_{12}$/MOF/P@ERGO/GCE in 0.5 M H$_2$SO$_4$, scan rate 50 mV s$^{-1}$, inset shows histogram of the peak I current of each modified GCE.
–0.175 V in 0.5 M H2SO4 solution. As seen in Fig. 10A, the performance of PW12/MOF/P@ERGO/GCE is very stable up to 4 hours of measurement.

The long-term stability of the modified electrode was also investigated. For this purpose, peak I current of the PW12/MOF/P@ERGO/GCE stored at ambient conditions over a month was recorded (Fig. 10B).

The results displayed that peak I current of the modified electrode remained at 99.97% of its primary current after 7 days, 99.92% after 14 days, 99.79% after 21 days, and 99.72% after a month.

The repeatability and reproducibility were also confirmed by repeatedly test. To certify the repeatability of PW12/MOF/P@ERGO/GCE, four different CV tests were repeated with one modified GCE surface (Fig. 10C). The reproducibility was estimated using four same modified electrodes by CV (Fig. 10D). The results confirmed that the modified electrode has excellent repeatability and reproducibility with relative standard deviation (RSD) of 2.61% and 4.80%, respectively.

4. Conclusions

In summary, the preparation method of a novel modified GCE based on POM, MOF, and RGO hybrid nanocomposite (PW12/MOF/P@ERGO/GCE) under the optimum conditions and its electrochemical properties has been investigated, comprehensively. The simplicity of preparation, high stability, good repeatability, and reproducibility are the features of the modified electrode. The modified GCE revealed a specific reduction peak that could be attributed to the HER processes. The PW12/MOF/P@ERGO/GCE show a high electroactive surface area of 6.032 cm2 resulting from the synergistic effect of PW12, MOF, and P@ERGO, and the porous structure of the hybrid modifier. Furthermore, electrochemical measurements proved that different factors such as type and concentration of the electrolyte additive, and electrodeposition time affect the electrochemical activity of the modified GCE.

Conflicts of interest

There are no conflicts to declare.

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