Nanostructure polyoxometalates containing Co, Ni, and Cu as powerful and stable catalysts for hydrogen evolution reaction in acidic and alkaline solutions

Ali A. Ensafi*, E. Heydari-Soureshjani, B. Rezaei

Department of Chemistry, Isfahan University of Technology, Isfahan 84156–83111, Iran

Abstract

A new form of $[PW_{11}MO_{39}]^{5-}@Ru$ -reduced graphene oxide (rGO) (M: Co, Ni, and Cu) was prepared by depositing $[PW_{11}MO_{39}]^{5-}$ on the surface of Ru-rGO. The behaviour of the polyoxometalates (POMs) toward hydrogen evolution reaction (HER) was studied in acidic and alkaline media. Different techniques were used for the characterization of the nanocomposites. These included voltammetry and electrochemical impedance spectroscopy to determine the electrocatalytic properties of the nanocomposites toward HER, and Tafel plots to calculate the kinetic parameters and to identify the possible mechanisms involved in the HER process. Results showed that HER on $[PW_{11}MO_{39}]^{5-}@Ru$ -rGO electrodes obeyed the Volmer-Heyrovsky mechanism. The enhanced HER rates on the modified electrodes were attributed not only to the presence of POM nanoparticles on the electrode surface but also to the resulting enhanced surface areas. These results demonstrate the effective performance of the nanocomposites used as HER catalysts in acidic and alkaline media in conformance with green chemistry objectives. The catalysts are especially advantageous for their desirable capacity, durability, favorable kinetics, and low price.

* Corresponding author. Tel.: +98 31 33912351; Fax: +98 31 33912350; E-mail: Ensafi@cc.iut.ac.ir, aaensafi@gmail.com, ensafi@yahoo.com.

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Introduction

Hydrogen (H_2) has been identified as one of the most important and a potential source of energy not only because of its pollution-free and zero-carbon emission properties but also for its higher energy performance and easy storage [1,2]. The production of inexpensive hydrogen is a key factor in exploiting this abundant source of energy and in commercializing the Hydrogen Evolution Reaction (HER) as a new technology [5–7] which has attracted a lot of attention because of its importance for energy harvesting and green chemistry [3,4]. The synthesis of proper catalysts for HER forms the cornerstone in the development of hydrogen economy [8–10]. For this purpose, a variety of metals and alloys have been experimentally tested as electrocatalyst materials for use in HER. Among these, the Keggin-type polyoxometalates (POMs) have found wide applications in both chemistry and electrochemistry [11].

POMs are fascinating transition-metal oxide nanoclusters with a considerable structural diversity that have potential applications in catalysis, photochemistry, and materials science [12]. One advantage of POMs is that they lend themselves to modifications in composition and properties in response to reaction requirements. In addition, they are non-explosive, non-volatile, and easy to handle [11]. POMs exhibit the same properties as metal oxide semiconductors in that they are constructed by the d^0 electronic structure of transition metal oxygen anion clusters, which makes them the most promising class of hydrogen evolution catalysts [13]. They also offer such properties as super-acidity and good proton conductivity; hence, they adsorb more H^+ and affect the electrocatalytic reaction to improve ultimately upon the kinetics of hydrogen evolution reaction. In addition, coupling of Co, Ni, and Cu as

post-transition metals with W or Mo in the structure of POMs is of great interest as this can change the electronic state and give rise to enhanced active sites and conductivity [14].

Graphene was discovered in 2004 and soon attracted a lot of attention as a two-dimensional carbon material because of its large surface area, high electrical conductivity, great electrocatalytic activity, and low-cost production [15,16]. It is a good choice for the deposition of nanoparticles and acceleration of electrochemical kinetics during electrocatalytic reactions. In the construction of nanohybrid materials, POMs are good candidates as nano-building blocks due to their multiple charge transfer reactions and individual electronic and optical properties [17].

In this study, three POM compounds are initially synthesized with different earth-abundant transition metals. In a second stage of the study, $[\text{PW}_{11}\text{MO}_{39}]^{5-}$ (M: Co, Ni, and Cu) are decorated on Ru-reduced graphene oxide (Ru-rGO) as efficient electrocatalysts for HER. This will be followed by investigating the effects of POMs as catalysts for the hydrogen evolution reaction in both alkaline and acidic solutions and comparisons will be made among the synthesized POMs in terms of their behaviour under different operating conditions and in different applications. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction pattern (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX) are used for the structural characterization of the electrocatalysts. Finally, electrochemical studies are used to explore the capabilities of these catalysts for HER. Results show that the synthesized electrocatalysts enjoy a high efficiency and long-term stability exhibiting different behaviours in the HER process in alkaline and acidic solutions.

Synthesis of exfoliated graphene oxide

Graphite oxide was produced by chemical oxidation of natural pure graphite powder (99.999%). The modified Staudenmaier method was used for preparing graphene oxide (GO) [18]. For this purpose, 10.0 g potassium chloride, 10 mL HNO_3 (63% w/w), and 20 mL H_2SO_4 (98% w/w) were mixed with 1.00 g of graphite. The mixture was continuously stirred for approximately 100 h before a 5.0 wt% HCl aqueous solution was used to rinse the resulting GO. The product was then repeatedly washed with distilled water until the pH of the outflow reached 7.0 when the final product was dried at room temperature. Finally, the resulting GO was dispersed in water (0.5 mg mL^{-1}) and placed in an ultrasonic bath for two h to obtain the desired exfoliated graphene oxide (EGO) [18].

Preparation of Ru-rGO

In a conical flask, 1000 mg of the GO obtained in the previous stage was added to 500 mL of water and the mixture was ultrasonicated at room temperature for 240 min (8 min on and 4 min off) until a homogeneous dark suspension was produced, indicating the perfect dispersion of GO. Then, 107 mg of Triton X-100 and 250 mg of Ru were added to the spinning suspension and refluxed for 12 h at 100°C . The final product was collected by filtration and dried at room temperature. Then, 5.0 g NaBH_4 , as a reducing agent, was used to improve the reduction of GO to rGO [19].

Synthesis of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\text{PW}_{11}\text{MO}_{39}]$ (where M is: Co, Ni and Cu)

To a solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (1.54 mol L^{-1}) was added 0.266 g of Na_2HPO_4 plus $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and/or $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, and/or $\text{Cu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$. While the solution was being stirred, nitric acid (1.0 mol L^{-1}) was added until pH reached about 4.8. The mixture was then heated up to $80\text{--}85^\circ\text{C}$ to which was added drop-wise a solution of 9.0 mmol (2.90 g) tetra n-butyl ammonium chloride monohydrate in 10 mL of water. The final product was

filtered using water followed by ethanol and finally with ether [19]. The product was then dried overnight at room temperature. Subsequently, the product was purified using 50 mL of acetonitrile and the filtering mixture was washed two times with distilled water. In the process of adding acetonitrile, a small amount of nitric acid was added whenever the colour of the mixture turned green until the colour changed back from green to yellow [19]. The final product was then dried in an oven at 90 °C.

Preparation of $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (where M is: Co, Ni, and Cu)

POM was synthesized as described in the previous section. A suspension of Ru-rGO was prepared by dispersing 90 mg of Ru-rGO into 300 mL of water. The suspension was added to the POM reaction mixture slowly and the mixture was then refluxed for 12 h at 100 °C. The selected ratio for the synthesis POM on the surface of Ru-rGO were 2.08: 25.39: 1.00: 2.68 g for Ru-rGO, Na_2WO_4 , Na_2HPO_4 and the transition metals salt, respectively. The final product was collected by filtration, dried in a vacuum oven, and named $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (where M is: Co, Ni, and Cu) [19].

Preparation of the modified electrodes

The glassy carbon electrode (GCE) was polished with emery paper followed by alumina (0.05 μm) for 3 min, sonicated in ethanol plus water (50:50), washed with water, and finally dried. The catalyst ink was prepared as follows: under ultrasonication, 2.50 mg of $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (where M is: Co, Ni, and Cu) was dispersed in 1.0 mL H_2O . Subsequently, 10 μL of the ink was deposited onto a GCE. After the solvent (water) had evaporated, 10 μL of Nafion solution (2.0%) was dropped onto the surface of the modified-GCE and dried at room temperature. The resulting agglomerate was used as a working electrode.

Results and discussion

Structural characterization of $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (M: Co, Ni, and/or Cu)

FT-IR, XRD, TEM, FE-SEM, and EDX were used for the structural characterization of $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (M: Co, Ni, and/or Cu). The FT-IR spectra of $[PW_{11}NiO_{39}]^{5-}$ are shown in Fig. 1A (a). The FT-IR spectra of $[PW_{11}MO_{39}]^{5-}$ (where M is Co and Cu) were the same as those of $[PW_{11}NiO_{39}]^{5-}$ with special bands for POM, which can be ascribed to the terminal W-O_t (stretching modes: 964 cm⁻¹), edge-sharing W-O_b-W (896 cm⁻¹), and corner sharing W-O_c-W (804 cm⁻¹). The asymmetric vibrations of P-O of the tetrahedral PO₄ were found at 1078 and 1043 cm⁻¹, which display characteristic vibration patterns of the POMs in the 700–1100 cm⁻¹ region and are present in the FT-IR spectrum of $[PW_{11}MO_{39}]^{5-}$ (where M is Co, Ni, and/or Cu). The C-H scissoring vibrations of CH₃-N⁺ moiety appeared at 1467 cm⁻¹, while the peaks at 2852 and 2925 cm⁻¹ belong to the symmetric and asymmetric stretching vibrations of -CH₂ group of [(n-C₄H₉)₄N]. [19] Also, the FT-IR spectra of: b) Ru-rGO and $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (where M is Co (c), Ni (d), and Cu (e)) presented all the characteristic peaks corresponding to $[PW_{11}MO_{39}]^{5-}$ and Ru-rGO. The broad peak centred at about 3469 cm⁻¹ is attributed to the O-H stretching vibration of rGO (Fig. 1A). Also, the absorption bands under 700 cm⁻¹ are imputed to the characteristic peak of M-O (where M is: Co, Ni or Cu) and W-O vibrations in the lattice of POM.

The XRD patterns of: a) Ru-rGO, b): $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (where M is: Ni, c) Cu, and d) Co are shown in Fig. 1B. The XRD patterns indicate the presence of Co, Ni, and Cu as well as the formation of POMs on the surface of Ru-rGO [20].

Fig. 2 shows the FE-SEM images of A): Ru-rGO and B): $[PW_{11}CoO_{39}]^{5-}@Ru-rGO$ at different magnitudes. The morphology of the surface was evaluated using these images. Increasing the POM to rGO ratio also increased both the nanoparticle aggregates and their

size so that POM structure became visible on the substrate while the active sites of POMs and the surface area of the electrocatalyst reduced, ultimately reducing the current density of HER.

Figs. 3 (a, b, c, and d) show the TEM images of Ru-rGO, $[\text{PW}_{11}\text{MO}_{39}]^{5-}$ (where M is: Co, Ni, and Cu). These images reveal the typically small nanoparticles of $[\text{PW}_{11}\text{MO}_{39}]^{5-}$ (where M is: Co, Ni, and Cu) attached onto the surface of Ru-rGO. The images confirm the identical size of the nanoparticles of $[\text{PW}_{11}\text{MO}_{39}]^{5-}$ with a mean diameter of $15(\pm 2.0)$ nm.

EDX analysis of the $[\text{PW}_{11}\text{MO}_{39}]^{5-}@\text{Ru-rGO}$ confirmed the formation of nanocomposites. Tungsten (W), M (where M is: Co, Ni, and Cu), O, P and Ru peaks are clearly observed in the EDX spectra (Results reported in Table 1). Electrostatic interaction might have caused the formation of POM@Ru-rGO via the strong adsorption between POM and Ru-rGO [19,20].

Investigation of HER ability in alkaline and acidic media

Figs. 4 (A and B) present the LSV curves of $[\text{PW}_{11}\text{MO}_{39}]^{5-}@\text{Ru-rGO}$ (where M is: Co, Ni, and Cu) in 2.0 mol L^{-1} KOH and in 0.5 mol L^{-1} H_2SO_4 solution. The cathodic current density shows the hydrogen evolution rate. Judging from the results obtained, the electrocatalyst behaved differently in the two situations. In an acidic solution, POM had the opportunity to exploit its properties to play the main catalytic role while the transition metals played the critical role in the alkaline solution.

The properties of d-orbital and the catalytic activities of such transition metals as Ni, Co, and W are compatible with each other in HER. According to the theory of electron bond, unpaired d-orbital acts as a hole to create an adsorption bond with the electrons of s or p-orbitals of the adsorbents. Addition of an empty d-orbital improves the reception of the electron pair of the hydrogen [21,22]. Also, the presence of tungsten (W) in the POM creates a high ionic radius, a desirable charge, and an access to the empty orbital for the formation of

π -bond of the metal-oxygen to improve upon the hydrogen evolution activity. According to Fig. 4A, the catalytic activity of $[\text{PW}_{11}\text{MO}_{39}]^{5-}@\text{Ru-rGO}$ in an alkaline solution increased in the order M: $\text{Cu}<\text{Ni}<\text{Co}$. This is due to the presence of more unpaired orbitals of Co than in the other electrocatalysts in which the POM does not exhibit any catalytic behavior in the alkaline solution. Fig. 4B shows the hydrogen evolution in the H_2SO_4 solution. Clearly, the current densities of the nanohybrids increased in the order M: $\text{Co}<\text{Ni}<\text{Cu}$. Comparison of the ionic radius of tungsten with those of Co, Ni, and Cu reveals that a cavity was created after the tungsten atom was replaced with either of Co, Ni, or Cu. The hole size increased with increasing ionic radius as a result of replacing $\text{Co}<\text{Ni}<\text{Cu}$ so that the protons were able to penetrate into the POM structure more easily.

POM in acidic solutions acts as a catalyst and the three types of the electrocatalysts synthesized in this study demonstrated this catalytic behavior (Fig. 5). Heterogeneous catalysis is the surface-type catalysis (Mode a, Fig. 5) that takes place on a solid surface. The modes b and c in Fig. 5 illustrate the bulk type catalysis whose reactions are 3D as opposed to mode a [23,24]. When the diffusion of the reactant molecules in the lattice, rather than in the pores, are faster than the reaction rate, a pseudo-liquid phase is created on which the catalytic reaction can perform (Fig. 5b) and the products are liberated in the gas or liquid phase on the surface [23,24].

The acidic protons in POM come in the three types of: a) H^+ , b) H_3O^+ , and c) H_5O_2^+ attached to the polyanions. The polyanions can interact weakly with H_3O^+ and H_5O_2^+ via hydrogen bonding, as shown in Fig. 6 [23,24].

Table 2 shows the comparison between the efficiency of recently reported electrocatalysts for HER. According to this table the electrocatalyst activity of POMs didn't investigate in the alkaline solution. This electrocatalyst has an acceptable response in $2.0 \text{ mol L}^{-1} \text{ KOH}$

solution. The Tafel slop and potential at the $J = -10 \text{ mA cm}^{-2}$ are better or approximately equal or better than the other catalysts.

Linear polarization

Tafel analysis was conducted to determine the electrode kinetics. The cathode exchange current densities, i_0 (A), were calculated using the Tafel plots and reported in Table 1. The generation of hydrogen gas on the surface of the electrodes is a multi-step electrochemical process ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). The reaction mechanisms of HER in acid and alkaline solutions may be explained as follows [25]:

1. Electrochemical hydrogen adsorption (Volmer Reaction; Eqs. 1 and 2):

2. Electrochemical desorption (Heyrovsky Reaction; Eqs. 3 and 4):

3. Chemical desorption (Tafel Reaction; Eq. 5):

HER starts with the Volmer Reaction that is an electrochemical adsorption of H^+ . This is followed in the second step by the Tafel Reaction in which two adsorbed H atoms are combined with each other or with a solvated proton (the Heyrovsky Reaction), resulting in the generation of gaseous hydrogen [25,26]. Eqs. (1) to (4) prove the competition between chemical adsorption and desorption for hydrogen atoms on the electrocatalyst surface. The

Sabatier principle shows that, to generate the gaseous hydrogen, a good HER catalyst should form an adequately strong bond with the adsorbed H_{ads} to facilitate the proton electron-transfer process and a weak one to allow for the facile bond breaking. The difficulty associated with the direct measurement of the surface-intermediate bonding energy makes it hard to establish a quantitative relationship between the rates of electrochemical HER reaction and the energetics of the H_{ads} intermediates. The linear part of the Tafel curve indicates that the Volmer Heyrovsky was the major mechanism involved in the electrocatalysis.

Long-term stability

The stability of a catalyst is critical for its activity. To test the stability of the $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (M: Co, Ni, and Cu), 1000 cycles of the HER process were consecutively performed in 2.0 mol L^{-1} KOH and in 0.5 mol L^{-1} H_2SO_4 . Fig. 7 (A and B, $[PW_{11}MO_{39}]^{5-}@Ru-rGO$ (where M is: a): Co, b): Ni and c): Cu) presents the LSV curves on the 1st and 1000th CV cycles (ranging from 0.20 to -1.00 V in 0.5 mol L^{-1} H_2SO_4 and from -0.70 to -1.70 V in 2.0 mol L^{-1} KOH at a scan rate of 25 mV s^{-1}). The two almost overlapping curves indicate that $[PW_{11}CoO_{39}]^{5-}@Ru-rGO$ in 0.5 mol L^{-1} H_2SO_4 exhibited an excellent long-term electrochemical stability. According to Fig. 7A, the electrocatalysts exhibited an excellent stability in a long-term electrochemical process in the alkaline media due to the slight loss in the cathodic current density. Based on the results in Fig. 7B, it was concluded that the current density of the HER increased after 1000 scans. This was probably the result of increasing surface porosity from the 1st to the 1000th scan. Transition metals are unstable in acidic solutions, which gives rise to their gradual leak to enhance the active porosity on the electrode surface. To verify this, AFM images of $[PW_{11}CoO_{39}]^{5-}@Ru-rGO$ before and after 1000 scans were prepared (not shown here) to find that porosity was

enhanced after 1,000 scans. Furthermore, cyclic voltammetry was used to measure the active surface areas of $[\text{PW}_{11}\text{MO}_{39}]^{5-}@\text{Ru-rGO}$ (where M is: Co, Ni, and Cu), on the 1st and the 1000th scans, in 5.0 mmol L⁻¹ $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 mol L⁻¹ KNO_3 . Fig. 8A shows the voltammograms of $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$ in 5.0 mmol L⁻¹ $\text{Fe}(\text{CN})_6^{3-/4-}$ before and after the 1000 scan in 0.5 mol L⁻¹ H_2SO_4 . Clearly, electrode porosity increased after 1000 scans. The surface areas of the electrodes on the 1st and the 1000th scans were measured using the Randles-Sevcik equation, $i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C$, in which, n: the number of electrons, A: the surface area of the working electrode, i_p : peak current, D: diffusion coefficients for ferrocene and ferricenium ions, v: the scan rate, and C: the bulk concentration of the electroactive species of the voltammograms. The surface areas of the electrode were measured to be 5.73 and 25.23 (cm²) before and after the 1000th scan, respectively. The chronoamperometry technique was used to confirm the results obtained on the catalyst stability. Figs. 8 (B and C) show the (i-t) curves of $[\text{PW}_{11}\text{MO}_{39}]^{5-}@\text{Ru-rGO}$ (where M is: Co, Ni, and Cu) in acidic and alkaline media, respectively. The applied potential in the H_2SO_4 0.5 mol L⁻¹ solution and that in the KOH 2.0 mol L⁻¹ one were -0.45 V and -1.45 V for 14400 s, respectively, indicating that the electrocatalysts were highly durable in both acidic and alkaline solutions.

Electrochemical impedance spectroscopy examination

Efficient electron transfer and hydrogen evolution rates are the two important indicators of an excellent HER electrocatalyst. In the Nyquist plots of the electrodes, semicircles as shown in Fig. 9, were observed at higher overpotentials ($\eta > 500$ mV at the 1st and $\eta > 400$ after the 1000th scan in an acidic solution, and $\eta > 1.35$ V at the 1st and 1000th scans in an alkaline solution). Fig. 9A shows the Nyquist plots of $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$ in H_2SO_4 solution: a) at the 1st scan, and b): after the 1000th scan. Fig. 9B shows the Nyquist plots of

[PW₁₁CoO₃₉]⁵⁻@Ru-rGO in the KOH solution: a) at the 1st scan, and b): after the 1000th scan. The Nyquist plots from the EIS responses for [PW₁₁MO₃₉]⁵⁻@Ru-rGOs (where M is: Co and Ni) in H₂SO₄ and [PW₁₁MO₃₉]⁵⁻@Ru-rGOs (where M is: Ni and Cu) in the KOH solution were the same as those for [PW₁₁CuO₃₉]⁵⁻@Ru-rGO.

It is seen that the Nyquist plots look like semicircles with decreasing diameters as the overpotential values increase; this demonstrates that the mechanism of the reaction is controlled by charge transfer. The semicircles are, therefore, related to the electrode kinetics [26]. The decrease in the semicircles of the Nyquist plots indicates that the current density, i.e. the rate of hydrogen evolution, is incremented although the Nyquist plots were drawn after 1000 scans. According to these plots, the charge transfers and kinetics of the electrocatalysts improved after 1000 scans. Overall, it may be claimed that the reaction is kinetically controlled because of the quick mass transport rate. HER activities are improved with increasing surface roughness and intrinsic activity. It was postulated that the Randles Equation without a diffusion equivalent circuit could be used as a model for the modified electrode-electrolyte interface [27], as shown in Fig. 9. The EIS and the cathodic polarization results are in reasonable agreement.

Conclusion

Of utmost importance to HER efficiency is the selection of catalyst materials. Hence, studies have been devoted to the investigation of many metals, alloys, and composites to determine their effects on improved HER capability. A number of active materials have been developed and applied for industrial hydrogen generation. It has been found that noble metals, unfortunately, lose their activity and viability with time while they are also costly and easily poisoned. Keggin-type structures are the most widely investigated as catalysts because of their stability and ease of synthesis. It was, therefore, the objective of this study to develop

a new technique for developing inexpensive and efficient HER catalysts which can be easily prepared. For this purpose, $[\text{PW}_{11}\text{MO}_{39}]^{5-}@\text{Ru-rGO}$ (where M is: Co, Ni, and Cu) nanocomposites which exhibit a porous morphology, excellent activity, and low overpotentials were synthesized. The POMs' ability toward HER revealed differences in their behavior, as catalysts, in acidic and alkaline solutions. It was found that while the catalytic behavior of POM was dominant in an acidic solution, it was the catalytic behavior of the transition metal that dominated in an alkaline solution.

Acknowledgements

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Table 1. EDS information of the electrocatalysts.

A): $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$.

Element	Line	Intensity (c s^{-1})	Atomic (%)	Conc. (Wt.%)
O	K _a	9.97	30.11	4.89
P	K _a	7.76	4.09	1.29
Co	K _a	34.78	18.06	10.80
Ru	L _a	14.27	7.18	7.36
W	L _a	34.99	40.57	75.67
Total			100.00	100.00

B): $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$.

Element	Line	Intensity (c s^{-1})	Atomic (%)	Conc. (Wt.%)
O	K _a	0.65	13.61	1.81
P	K _a	2.12	7.51	1.93
Ni	K _a	3.95	15.28	7.43
Ru	L _a	3.45	11.76	9.85
W	L _a	6.78	51.84	78.98
Total			100.00	100.00

C): $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$.

Element	Line	Intensity (c s^{-1})	Atomic (%)	Conc. (Wt.%)
O	K _a	66.91	38.58	7.60
P	K _a	66.66	7.39	2.83
Cu	K _a	88.73	12.34	9.53
Ru	K _a	91.87	9.48	10.41
W	L _a	146.00	32.21	69.64
Total			100.00	100.00

Table 2. Comparison between the efficiency of reported electrocatalyst in the HER.

Electrocatalyst	Electrolyte		Potential (vs. Ag/AgCl) at $J=10\text{mA}/\text{cm}^2$		Tafel slop (mV/dec)		Ref.
	H ₂ SO ₄	KOH	H ₂ SO ₄	KOH	H ₂ SO ₄	KOH	
Pd ⁰ @Polyoxometalate	0.5 M	not applicable	-0.25 V	-	52 to 83	-	[28]
Pt(1mM)@Polyoxometalates	0.5 M	not applicable	-0.50V	-	32	-	[29]
SiW ₁₂ /CoTMPyP	0.1 M	not applicable	-0.50 V	-	53	-	[30]
[PW ₁₁ Pt-NiO ₃₉] ⁻ @PDDA-CNT	0.5 M	not applicable	-0.25 V	-	60	-	[19]
[PW ₁₁ Pt-NiO ₃₉] ⁻ @PDDA-rGO	0.5 M	not applicable	-0.27 V	-	65	-	[19]
[PW ₁₁ CoO ₃₉] ⁵⁻ @Ru-rGO	0.5 M	2.0 M	-0.32	-1.55	42.60	59.76	Present study
[PW ₁₁ NiO ₃₉] ⁵⁻ @Ru-rGO	0.5 M	2.0 M	-0.30	-1.58	40.42	68.96	Present study
[PW ₁₁ CuO ₃₉] ⁵⁻ @Ru-rGO	0.5 M	2.0 M	-0.41	-1.65	36.56	107.95	Present study

Table 3. Information obtained from the Tafel curves for the HER in 2.0 mol L⁻¹ KOH and 0.5 mol L⁻¹ H₂SO₄ solution.

Electrocatalyst	Tafel slope (V dec ⁻¹)		α		i_0 (A)	
	H ₂ SO ₄	KOH	H ₂ SO ₄	KOH	H ₂ SO ₄	KOH
1	42.60	59.76	1.39	0.99	2.53 (e-18)	2.12 (e-26)
2	40.42	68.96	1.46	0.86	1.48 (e-13)	1.08 (e-25)
3	36.56	107.95	1.62	0.55	2.67 (e-17)	1.01 (e-18)

1: [PW₁₁CoO₃₉]⁵⁻@Ru-rGO; 2: [PW₁₁NiO₃₉]⁵⁻@Ru-rGO; and 3: [PW₁₁CuO₃₉]⁵⁻@Ru-rGO.

Legends for the figures

Fig. 1. **A):** FT-IR spectra of **(a):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}$; **(b):** $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$, **(c):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$ and **(d):** $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$ and **B):** XRD pattern for **(a):** $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$, **(b):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$ and **(c):** $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$.

Fig. 2. SEM image of **(A):** Ru-rGO, and **(B):** $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$ in different magnitude.

Fig. 3. TEM images of **(a):** Ru-rGO, **(b):** $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$, **(c):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$ and **(d):** $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$.

Fig. 4. Polarization curve of **(a):** $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$; **(b):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$ and **(c):** $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$ in **A):** alkaline and **B):** acidic solution. (Conditions: 2.0 mol L^{-1} KOH and 0.5 mol L^{-1} H_2SO_4 with a scan rate of 25 mV s^{-1}).

Fig. 5. Three kinds of catalysis for POMs: **(a):** surface type; **(b):** pseudo liquid: bulk type (I), **(c):** bulk type (II).

Fig. 6. Models offered for the situation of H^+ .

Fig. 7. Linear polarization curve before and after 1000 cycles for **(a):** $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$, **(b):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$, and **(c):** $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$ in **A):** alkaline and **B):** acidic solution. (Conditions: 2.0 mol L^{-1} KOH and 0.5 mol L^{-1} H_2SO_4 with a scan rate of 25 mV s^{-1}).

Fig. 8. **A):** Cyclic voltammograms of $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$ in 5.0 mmol L^{-1} $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 mol L^{-1} KNO_3 **(a):** before, and **(b):** after 1000 scan; (i-t) curves for **(a):** $[\text{PW}_{11}\text{CoO}_{39}]^{5-}@\text{Ru-rGO}$, **(b):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$, and **(c):** $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$ in **(A):** 0.5 mol L^{-1} H_2SO_4 and **(B):** 2.0 mol L^{-1} KOH.

475 **Fig. 9.** Nyquist plots from EIS responses of, **A):** $[\text{PW}_{11}\text{CuO}_{39}]^{5-}@\text{Ru-rGO}$ in 0.5 mol L^{-1}
 476 H_2SO_4 , **(a):** 1st scan at various HER overpotentials in order of -200, -400, -600, -800 mV and
 477 **(b):** after 1000st scan at various HER overpotentials in order of -400, -425, -450, -475, -500,
 478 -525, -550, -575, -600, -625 and -650 mV; and **B):** $[\text{PW}_{11}\text{NiO}_{39}]^{5-}@\text{Ru-rGO}$ in $\text{KOH } 2.0 \text{ mol}$
 479 L^{-1} , **(a):** 1st scan at various HER overpotentials in order of -1.40, -1.60 and -1.80 V and after
 480 1000st scan at various HER overpotentials in order of -1.40, -1.45, -1.50, -1.55, 1.60, 1.65,
 481 1.70, 1.75 and 1.80 V (from up to down).
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