

Supporting Information

Designing a hybrid nanomaterial based on Cr-containing polyoxometalate and graphene oxide as an electrocatalyst for the hydrogen evolution reaction

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Materials

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Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), disodium hydrogen phosphate (Na_2HPO_4), nitric acid (HNO_3), 3-aminopropyltrimethoxysilane (APTS), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{Cr}(\text{acac})_3$ complex, toluene, and methanol were purchased from Merck. The graphite powder was purchased from Sinchem Company. Nafion solution (5 wt%) was purchased from electrochemiabaspar-Iran.

Equipment

Chemical analyses of samples were carried out with VARIAN VISTA-MPX ICP-OES spectrometer. CHN analysis was conducted with using Thermo Finnigan (Flash 1112 series EA) CHN analyzer. X-ray diffraction (XRD) patterns were collected using a X'Pert Pro instrument with $\text{Cu K}\alpha$ radiation. Field emission Scanning Electron Microscope (FE-SEM) imaging and energy dispersive X-ray (EDX) spectroscopy were carried out on a TESCAN MIRA III instrument for micro-elemental analysis and mapping. Fourier transform infrared spectroscopy (FT-IR) spectra were measured through a Perkin-Elmer Spectrum RXI spectrometer using the standard KBr pellet method. Transmission electron microscopy (TEM) images were taken on a Zeiss-EM10C instrument with an accelerating voltage of 100 kV. Samples were prepared for TEM analysis by placing a few droplets of a suspension of the specimen in ethanol on a polymer microgrid supported on a Cu grid. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS Ultra HSA spectrometer equipped with a monochromatized $\text{Al K}\alpha$ X-ray source (1468.71 eV). Specific surface area of each sample was analyzed with Brunauer-Emmett-Teller (BET) N_2 method using a surface area analyzer (BEISORP Mini/Microtrac BEL Corp, Japan). ^{31}P NMR spectra of the products were recorded on Bruker Avance 300.

Preparation of $\text{PMo}_{11}\text{-Cr-GO}$

A solution of $\text{PMo}_{11}\text{-Cr}$ (200 mg) in deionized water (10 mL) was added to a mixture of GO (500 mg) in deionized water (10 mL). After stirring for 3 h, the solid was collected via centrifugation, rinsed with cold water, and dried to obtain $\text{PMo}_{11}\text{-Cr-GO}$.

Preparation of $\text{PMo}_{12}\text{-mGO}$, $\text{PMo}_{11}\text{-mGO}$, and Cr-mGO

First, 200 mg of mGO was dispersed in deionized water (10 mL). Next, a mixture of 200 mg of precursor (PMo_{12} , PMo_{11} , or $\text{Cr}(\text{acac})_3$) in 10 mL of deionized water was added to the mixture. After stirring for 3 h, the solid was collected via centrifugation, rinsed with cold water, and dried to obtain $\text{PMo}_{12}\text{-mGO}$, $\text{PMo}_{11}\text{-mGO}$, and Cr-mGO , respectively.

Testing conditions for electrochemical analysis

Electrochemistry measurements of the samples were carried out on a PalmSens electrochemical workstation with a three-electrode setup: Ag/AgCl as the reference electrode, glassy carbon electrode as the working electrode, and graphite rod as the counter electrode. HER polarization curves were collected at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ via LSV in H_2SO_4 0.5 M. The working electrodes were scanned for several times until the signals were stabilized and then the data for polarization curves were collected.

^{31}P NMR spectra

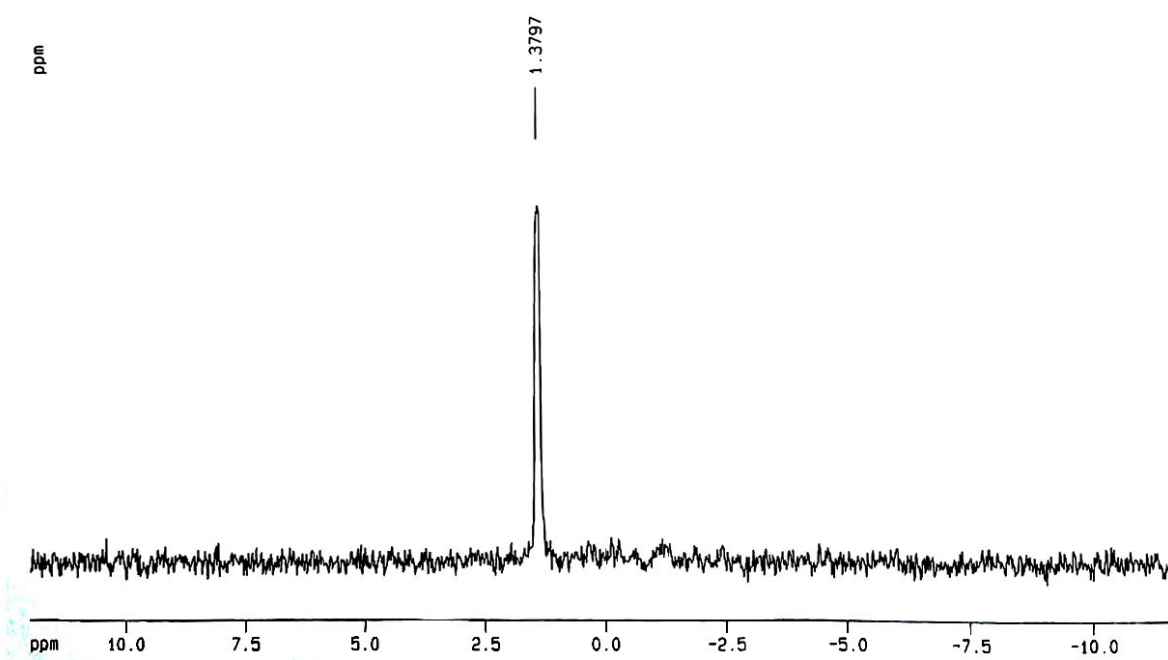
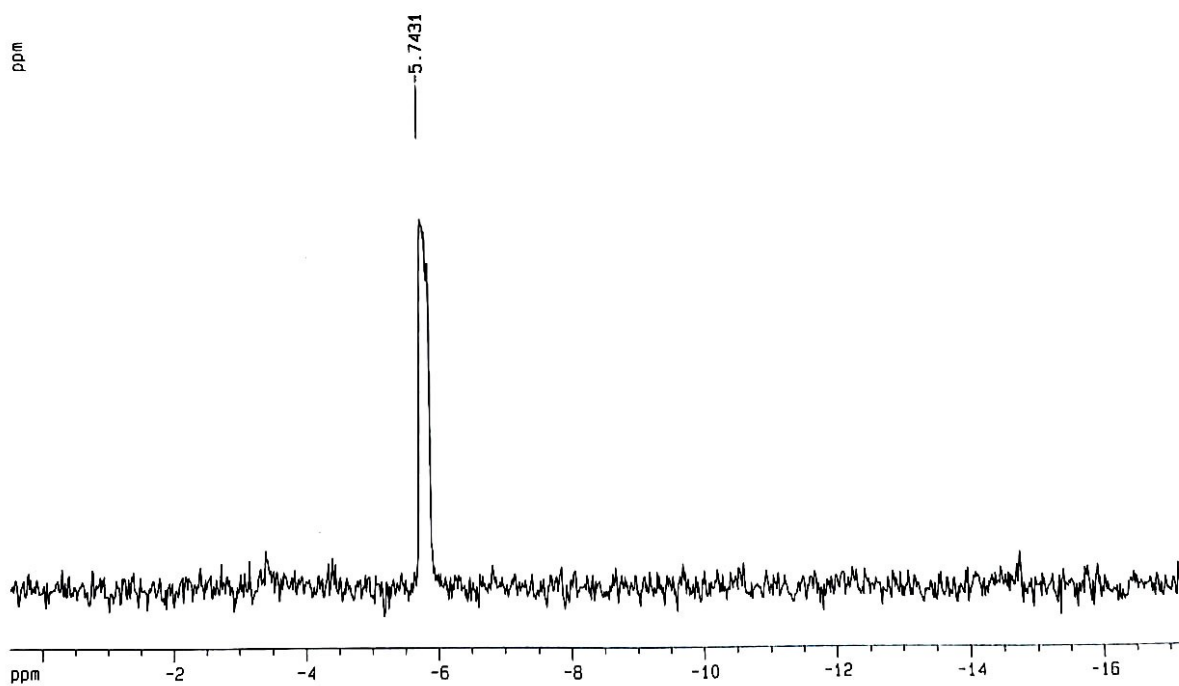


Fig. S1. ^{31}P NMR spectra of PMo_{12} (top) and PMo_{11} (bottom).

Elemental analysis

Table S1. The results of elemental analysis of P₂Mo₁₁-Cr.

No.	Element	Percent (Calculated)	Mole (%)
1	C	5.35 (5.31)	0.445
2	P	1.27 (1.37)	0.041
3	Mo	45.01 (46.71)	0.469
4	Cr	2.39 (2.30)	0.046
5	Na	5.76 (6.10)	0.250

Thermogravimetric analysis

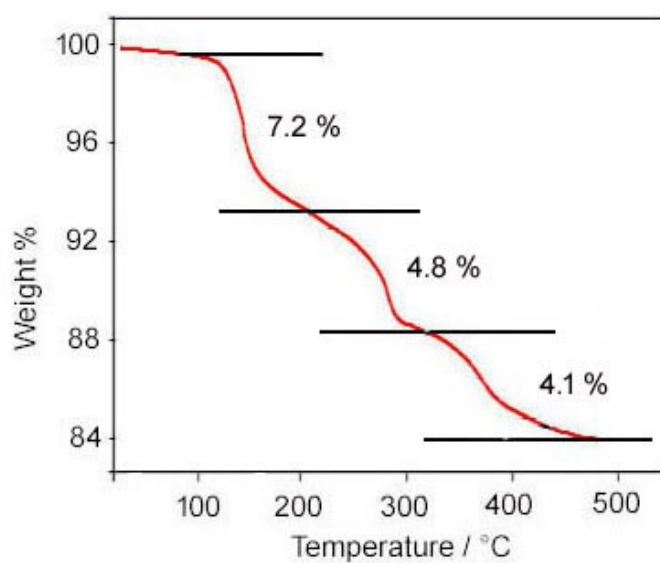


Fig. S2. TGA curve of P₂Mo₁₁-Cr.

Cyclic voltammetry and electrochemical analyses

The cyclic voltammetry (CV) analyses of $\text{PMo}_{11}\text{-Cr-mGO}$, $\text{PMo}_{11}\text{-Cr}$, PMo_{11} , $\text{Cr}(\text{acac})_3$, and GO modified GCE conducted in the 0.5 M H_2SO_4 solution indicate the electrocatalytic HER activity of $\text{PMo}_{11}\text{-Cr-mGO}$ as a heterogeneous catalyst (Fig. S3). In fact, there is no any peak in the CV curves of PMo_{11} , $\text{Cr}(\text{acac})_3$, and GO in the range of 0.1-0.45 V. However, in the CV curve of $\text{PMo}_{11}\text{-Cr}$, a hump can be observed at around +0.36 V vs RHE assigned to the oxidation of Cr^{III} . The oxidation process of Cr^{III} is irreversible, with its corresponding reduction wave appearing at 0.19 V vs RHE.¹ Furthermore, the CV analysis of $\text{PMo}_{11}\text{-Cr-mGO}$ indicates an irreversible cycle too. The observed shift could be attributed to strong interaction of PMo_{11} species with $\text{Cr}(\text{acac})_2$ species which results in decreasing the electron density on the PMo_{11} and the stabilization of its energy levels.^{2,3} Therefore, $\text{PMo}_{11}\text{-Cr}$ immobilized on mGO represents enhanced catalytic properties in the HER process.

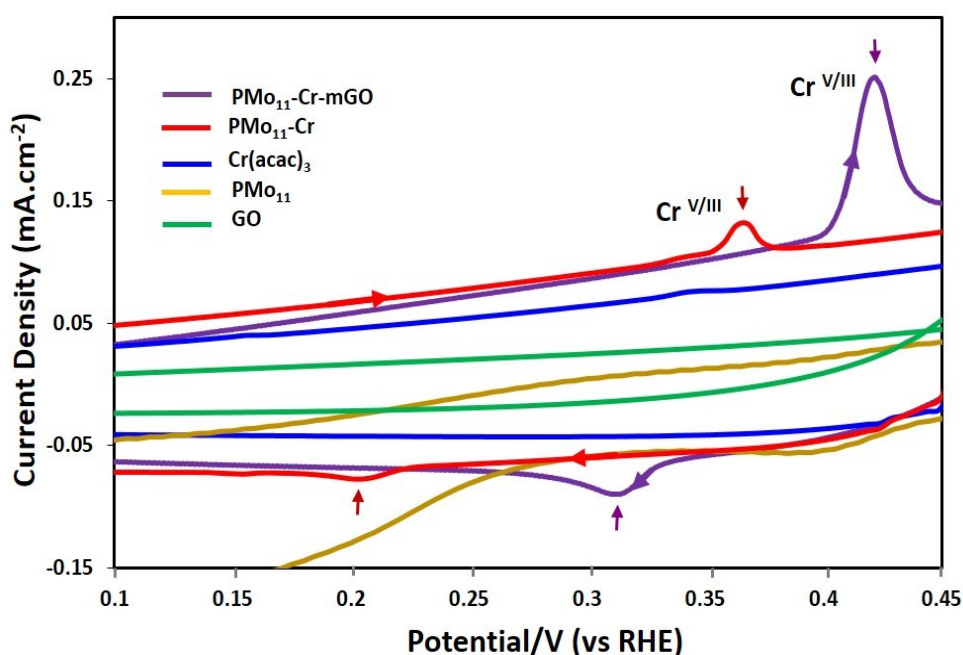


Fig. S3. CV curves of $\text{PMo}_{11}\text{-Cr-mGO}$, $\text{PMo}_{11}\text{-Cr}$, PMo_{11} , $\text{Cr}(\text{acac})_3$, and GO in 0.5M H_2SO_4 . Scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$.

References

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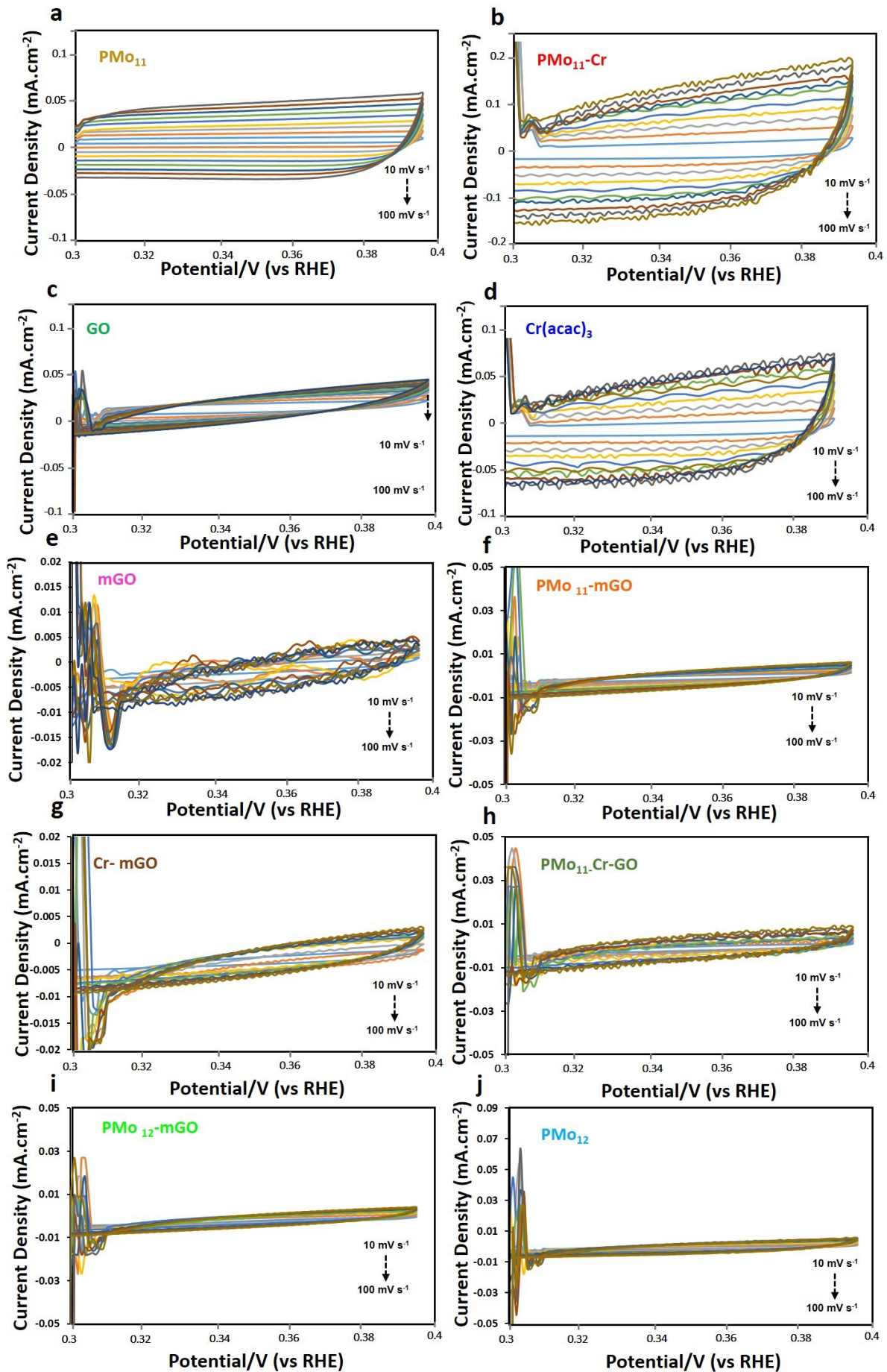


Fig. S4. CV curves in the region of 0.3~0.4 V vs. RHE for the (a) P_{Mo}₁₁, (b) P_{Mo}₁₁-Cr, (c) GO, (d) Cr(acac)₃, (e) mGO, (f) P_{Mo}₁₁-mGO, (g) Cr-mGO, (h) P_{Mo}₁₁-Cr-GO, (i) P_{Mo}₁₂-mGO, and (j) P_{Mo}₁₂.

Table S2. The double layer capacitance and ECSA of P_{Mo}₁₁-Cr-mGO, P_{Mo}₁₁-Cr, P_{Mo}₁₁, Cr(acac)₃, mGO, P_{Mo}₁₁-mGO,

No.	Sample	C _{dl} (mF.cm ⁻²)	ECSA (m ² .g ⁻¹)
1	P _{Mo} ₁₁ -Cr-mGO	32	46.7
2	P _{Mo} ₁₁ -Cr	7	10.23
3	Cr(acac) ₃	4	5.85
4	P _{Mo} ₁₁	2	~3
5	GO	0.5	~1
6	mGO	-	-
7	P _{Mo} ₁₁ -mGO	0.3	~0.5
8	P _{Mo} ₁₂ -mGO	-	-
9	P _{Mo} ₁₁ -Cr-GO	-	-
10	P _{Mo} ₁₂	-	-
11	Cr-mGO	-	-

P_{Mo}₁₂-mGO, P_{Mo}₁₁-Cr-GO, P_{Mo}₁₂, Cr-mGO, and GO.

