**INTRODUCTION**

Electrochemical hydrogen evolution reaction (HER) provides a cost-efficient and sustainable method to generate $H_2$ effectively, which is an important component of developing green energy technologies (1). To date, Pt-based nanomaterials are widely considered as the state-of-the-art electrocatalysts for HER. However, the high cost and natural scarcity severely hamper their large-scale applications. Therefore, substantial efforts have been devoted to exploring cheap, efficient, and durable alternatives of Pt for hydrogen production. Recently, nonprecious metal-based catalysts have been studied extensively for HER such as carbides (2), nitrides (3), dichalcogenides (4), phosphides (5), and oxides (6); yet still, their HER activities and stabilities are far from satisfactory. In addition, to meet different applications, catalysts that function well over a wide pH range are highly regarded. For instance, water electrolyzers based on proton exchange membrane technology require catalysts operation in acidic solution; microbial electrolysis cells need catalysts that function well under neutral condition, and alkaline water electrolysis demands catalysts that operate in strongly basic media (7). Hence, designing and developing efficient, durable, and scalable HER catalysts working well in a pH-universal electrolysis system become important yet challenging.

The single-atom catalysts (SACs) maximize the efficiency of metal atoms utilization, enabling reasonable use of metal resources and achieving atomic economy, which is highly desirable for electrocatalysis (8). Unfortunately, the increased surface free energy renders SACs with only one kind of single metal site that tend to agglomerate, leading to a significant decline in performance. Compared to the single-atom components, the multiatom catalysts with tunable electronic environments could further improve the intrinsic activity and stability. In multiatom catalytic system, the metal cluster centers will offer a range of unique and often unexpected catalytic properties (9); the strong chemical interactions between neighboring atom-atom can efficiently stabilize the individual species and prevent agglomeration, thereby creating highly stable active sites. Within this context, dispersing metal atoms on support into a minimal cluster or dinuclear category could modulate the electronic structure by adjusting the ligand atom (10), coordination number (CN) (11), and structural distortion (12). In particular, the heteronuclear metal atom catalysis would optimize activity, stability, and selectivity through tuning metal active centers, which are not observable in their individual monometallic systems (13). Thus, it is very reasonable to expect that the dual-atom catalysts (DACs) with interacted biatomic metal cores could maximize the atom utilization and greatly improve the catalytic activity. However, synthesis and characterization of binuclear metal clusters remain a huge challenge, owing to the lack of atomic-scale control techniques under the harsh synthesis condition and the difficulty in identifying the exact non-crystallographic structures and active sites. Therefore, it is urgent and challenging to controllably synthesize DACs, as well as provide in-depth insight into the synthetic mechanism of heteronuclear species and the local environment associated with catalytic performance.

Polyoxometalates (POMs), a special class of metal oxide anion nanoclusters, feature stability, solubility, compatibility with nearly all other materials (i.e., supports, additives, and solvents), and diverse structural topologies, ensuring them attractive in broad fields of...
science. Moreover, the variable CN and geometry of POMs with separated units can inhibit agglomeration of metal atoms during the pyrolysis process. While MoO₄ clusters derived from POMs have been reported (14), they have not yet been explored to construct heteronuclear diatomic catalysts. Here, we report bimetallic DAC consisting of O-coordinated W-Mo heterodimer anchored in N-doped graphene (W₁Mo₁-NG); the W—O—Mo—O—C configuration of which is distinct from the reported dual-metal sites using traditional methods. The W- and Mo-based POMs are used as precursors for producing W-Mo DAC, which is prepared through a hydrothermal reaction followed by chemical vapor deposition (CVD) process. In W₁Mo₁-NG, heteronuclear W-Mo dual atoms are immobilized in the NG vacancies and stabilized through W—O and Mo—O bonds. The W and Mo atoms are respectively located in oxygen-bridged [WO₄] tetrahedron and distorted [MoO₆] octahedron units; W atom is bridged with Mo atom via O atom, functioning as a bimetallic dimer system. The distinctive W—O—Mo—O—C configuration with strong covalent interactions works as stable and excellent catalyst toward HER in pH-universal electrolysis. The electron delocalization of O-coordinated W-Mo heterodimer results in a favorable adsorption behavior of H and improved HER kinetics, ultimately enhancing the intrinsic activity.

RESULTS

W₁Mo₁-NG DAC

W₁Mo₁-NG electrocatalyst was synthesized through a three-step procedure, as schematically illustrated in Fig. 1A. A precursor solution was first prepared by sonicating tungstic acid, molybdate, and graphene oxide (GO) in water. The Na₂WO₄·2H₂O and (NH₄)₆Mo₇O₂₄·4H₂O were selected as W and Mo sources, respectively. The well-mixed precursor solution was then subjected to a hydrothermal reaction, in which paired W-Mo species were formed and anchored into partially reduced GO (p-RGO). Subsequently, the homogeneous mixture was freeze-dried to minimize restacking of p-RGO sheets. Last, the W₁Mo₁-NG DAC was obtained with CVD treatment in the NH₃/Ar gas at 800°C. For comparison, a series of DACs with various CVD times and molar ratios of W/ Mo (table S1), together with homonuclear diatomic Mo and W supported on NG (denoted as Mo₂-NG and W₂-NG, respectively), were also synthesized. Further details of the experiments were provided in Materials and Methods.

The formation mechanism of W₁Mo₁-NG DAC was based on POMs self-assembly chemistry. Specifically, Na₂WO₄·2H₂O and (NH₄)₆Mo₇O₂₄·4H₂O were added to GO suspension (Fig. 1B, 1) in an ultrasonic bath (pH 6.1 to pH 6.3). Afterward, in the hydrothermal process, protonation of carboxyl anion occurred (Fig. 1B, 2), followed by the removal of protonated carbonyl and epoxy on GO (Fig. 1B, 3); the delocalized π-electron system and H⁺ underwent protonation to obtain positively charged p-RGO (Fig. 1B, 4) (15). In a mild acidic solution, protonation promoted Mo(VI) oxo in MoO₄²⁻ fragment transformed to Mo hydroxido and lastly to Mo aquo ligands ([MoO₄(H₂O)₂]²⁻) (16), while the hydrogenentustate anion ([WO₃(OH)]⁻) from WO₃²⁻ fragment retained the tetrahedral coordination (17). Hence, heteronuclear W-Mo species could be obtained through self-assembly of [WO₃(OH)]⁻ and [MoO₄(H₂O)₂]²⁻ with dehydration condensation reaction; before aggregation and rearrangement, the heteronuclear W-Mo species could be captured and stabilized with protonated p-RGO sheets as counterion (Fig. 1B, 5) (18). Because of the intensive coupling of negatively charged W-Mo dimer anions and positively charged protonated p-RGO sheets, the O-coordinated W-Mo heterodimers could be electrostatically attracted onto the p-RGO sheets without any additives. As a result, the hydrothermal self-assembly process created a tremendous opportunity for heteronuclear W-Mo dual atoms to anchor in p-RGO through strong covalent interactions. Where small amount of low-nuclear MM’Oₓ, MMOVₓ, and M’M’Oₓ (M, M’ = Mo, W) clusters could also formed. Last, uniform W₁Mo₁-NG DAC (Fig. 1B, 6) was prepared by ammonia annealing. During CVD process, further reduction of p-RGO and N doping occurred simultaneously. The successful synthesis of W₁Mo₁-NG DAC is contributed to the structural asymmetry between the protonated p-RGO sheets and metal precursors in mild acidic solution, in which protonated p-RGO sheets working as counterion inhibit WO₄²⁻ and MoO₄²⁻ fragments aggregating into block materials (19). The general synthetic strategy of heteronuclear DAC can also be extended to other POM systems, such as vanadium, niobium, and tantalum, which provides an alternative way to develop atomically dispersed catalysts with higher complexity.

Structural characterization of W₁Mo₁-NG DAC

The morphology and structure of W₁Mo₁-NG were initially investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and aberration-corrected high-angle annular dark-field scanning TEM (AC HAADF-STEM). As revealed in Fig. 2A and fig. S1, W₁Mo₁-NG and RGO have similar morphological features. As a result, the W₁Mo₁-NG DAC is contributed to the structural asymmetry between the protonated p-RGO sheets and metal precursors in mild acidic solution, in which protonated p-RGO sheets working as counterion inhibit WO₄²⁻ and MoO₄²⁻ fragments aggregating into block materials (19). The general synthetic strategy of heteronuclear DAC can also be extended to other POM systems, such as vanadium, niobium, and tantalum, which provides an alternative way to develop atomically dispersed catalysts with higher complexity.

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ratio of D band to G band ($I_D/I_G$) for $W_1Mo_1$-NG (1.16) is higher than that of NG (1.05), which indicates that structural defects are introduced into $W_1Mo_1$-NG. Furthermore, the Brunauer-Emmett-Teller surface areas of $W_1Mo_1$-NG and NG are 566 and 268 m$^2$ g$^{-1}$, respectively (Fig. 3B), and the main pore size is centered at 3.5 nm (Fig. 3B, inset). These results suggest that the interacted W and Mo atoms can effectively inhibit the agglomeration of NG sheets and generate a considerable amount of voids (fig. S6), which provides nucleation sites for W-Mo heterodimers. The defective $W_1Mo_1$-NG with porous structure and large surface area can effectively promote the electrolyte permeation and charge transfer. In XRD patterns, no diffraction peaks of metal-based crystalline phases in DACs, such as...
Unary W- or Mo-based carbides/nitrides/oxides, are detected (Fig. 3C). However, XPS survey spectrum confirms that W\textsubscript{1}Mo\textsubscript{1}-NG consists of W, Mo, N, O, and C elements (Fig. 3D), consistent with the EDS elemental mapping (Fig. 2G). The atomic concentrations of W and Mo in W\textsubscript{1}Mo\textsubscript{1}-NG determined by XPS are 0.38 and 0.36 atomic %, respectively, which are close to the inductively coupled plasma mass spectrometry (ICP-MS) results [5.01 and 2.55 weight % (wt %), respectively] (table S2). Notably, all these DACs have relatively high metal loading of 7.5 wt %, which could not be achieved with conventional deposition-reduction method (13). The Mo 3d XPS of W\textsubscript{1}Mo\textsubscript{1}-NG shows two peaks at 235.6 and 232.4 eV (Fig. 3E), corresponding to Mo 3d\textsubscript{3/2} and Mo 3d\textsubscript{5/2} core energy levels, respectively, validating the presence of Mo(VI) (20). For W 4f XPS (Fig. 3F), W ions have two well-defined peaks at 37.5 and 35.3 eV in W\textsubscript{1}Mo\textsubscript{1}-NG.
ascribed to the W 4f_{5/2} and W 4f_{7/2}, respectively, being consistent with high oxidation state of W(VI) (21). The Mo 3d in W_{1}Mo_{1}-NG has some shift toward low binding energy compared to Mo_{2}-NG, whereas the W 4f in W_{1}Mo_{1}-NG shifts positively relative to W_{2}-NG. These microdisplacements indicate the altering of local electronic structure for heteronuclear W_{1}Mo_{1}-NG system, which could be ascribed to the W-Mo heterodimers. Moreover, the control samples with various ratios of W/Mo and CVD times were also subjected to XPS measurements. For Mo 3d and W 4f spectra, the varying metal ratio triggers an electron transfer at a certain CVD time (fig. S7), while adjusting the CVD time with a fixed metal ratio does not introduce any changes (fig. S8). As a result, the local electronic structure of W-Mo heterodimers can be effectively modulated via adjusting the ratio of W/Mo. As revealed in Fig. 3G, the deconvoluted peaks around 530.2 and 530.8 eV are attributed to the structural perturbation of W-Mo heterodimers. The fitted peak at 533.2 eV can be assigned to C-O bond. (H) High-resolution N 1s spectra of W/Mo_{1}-NG, Mo_{2}-NG, and W_{2}-NG. The fitted peak at 399.2 eV, 401.4 eV, and 402.3 eV respectively, can be assigned to pyridinic-N (398.0 eV), pyrrolic-N (399.2 eV), and graphitic-N (401.4 eV) species (Fig. 3H), demonstrating the presence of oxygen-containing functional groups and a short-range order in stacked graphene layers. The Mo 3d in W_{1}Mo_{1}-NG confirms that W-Mo heterodimers are O-coordinated within W_{1}Mo_{1}-NG; the peak around 532.0 eV derives from oxygen vacancy (O_v) (24). Notably, peak areas of O_v are different; W_{1}Mo_{1}-NG has higher O_v concentration than single metal–doped Mo_{2}-NG and W_{2}-NG, in accordance with the electron paramagnetic resonance spectra (fig. S9). Because the oxygen-containing functional groups are easily detached from fluffy NG during CVD process, the concentration of O_v may be positively correlated with the specific surface area. Meanwhile, the N 1s spectra are deconvoluted into three characteristic peaks of pyridinic-N (398.0 eV), pyrrolic-N (399.2 eV), and graphitic-N (401.4 eV) species (Fig. 3H), demonstrating the NG, while W–N bond only appears in W_{2}-NG, suggesting W atoms coordinating with N atoms. Metal carbides are absent in the C 1s spectra of DACs (fig. S10). Distinctly, the metal centers in
$W_1Mo_1$-NG and $Mo_2$-NG are O-coordinated, while the W(VI) in $W_2$-NG are co-coordinated with O and N atoms.

To probe the local coordination chemistry of DACs, we conducted x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). In the Mo K-edge XANES (Fig. 4A), $W_1Mo_1$-NG and $Mo_2$-NG exhibit a shoulder peak (♦) in the pre-edge region, suggesting the formation of distorted [MoO$_x$] octahedron with Mo=O bond (25). Moreover, according to the linear relationship between the Mo oxidation state and the energy position (♦) (26), the average oxidation state of Mo ions in $W_1Mo_1$-NG and $Mo_2$-NG is close to 6, which matches well with the XPS results (Fig. 3E). Figure 4B shows the $k^2$-weighted Fourier transform (FT)-EXAFS spectra at Mo K-edge. As expected, $W_1Mo_1$-NG and $Mo_2$-NG have two strong peaks at 1.25 and 1.88 Å, which could be attributed to Mo=O and Mo=O bonds, respectively. Comparing with Mo foil, no apparent peaks (2.43 and 2.96 Å) for Mo=O bonds are detected in both $W_1Mo_1$-NG and $Mo_2$-NG, confirming the absence of Mo nanoparticles, in line with the STEM observation. For the W L$_3$-edge XANES spectra, the oxidation state of W ions in $W_1Mo_1$-NG and $W_2$-NG is higher than W powder but lower than WO$_3$ (Fig. 4C). The primary peak around 10,210 eV is attributed to the electronic transition from 2$p_3/2$ to unoccupied 5d orbital (27). In comparison with W$_2$-NG, $W_1Mo_1$-NG exhibits higher intensity of white line, which demonstrates the electron deficiency at W atoms by introducing Mo atoms, suggesting strong interactions between heteronuclear W-Mo atoms and NG support. Furthermore, the main peak of $W_1Mo_1$-NG (10,210.12 eV) moves toward low energy compared to $W_2$-NG (10,210.71 eV) and WO$_3$ (10,210.74 eV), revealing the low CN environment of W atoms in $W_1Mo_1$-NG (28). As displayed in the FT-EXAFS spectra at W L$_3$-edge (Fig. 4D), $W_1Mo_1$-NG and $W_2$-NG have only one prominent peak located at 1.36 Å assigned to the W-O coordination. The weak peaks at 2.86 and 3.20 Å correspond to the W-Mo and W-W contributions for $W_1Mo_1$-NG and $W_2$-NG, respectively, indicating that W atoms within $W_1Mo_1$-NG and $W_2$-NG are atomically distributed. To confirm the adjacent properties of the metal atoms, we conducted wavelet transform (WT)-EXAFS. As shown in Fig. 4E, the WT signal related to Mo=O bond in Mo foil is not detected in both $W_1Mo_1$-NG and $Mo_2$-NG, further confirming the absence of Mo-containing nanoparticles. Compared to MoO$_3$, $W_1Mo_1$-NG and $Mo_2$-NG show two intensity maxima at 3.9 and 9.3 Å$^{-1}$, which are respectively associated with the Mo=O and Mo=O/W/Mo paths, consistent with the Mo K-edge FT-EXAFS results. For WT-EXAFS at W L$_3$-edge (Fig. 4F), $W_1Mo_1$-NG and NG show the intensity maxima at 4.1 and 3.9 Å$^{-1}$ for W=O and W=O/N paths, respectively, which are close to the W-O bond (4.2 Å$^{-1}$) in WO$_3$ reference, but distinct from the W-O bond (7.3 Å$^{-1}$) of W powder. Moreover, WT signal at 9.2 Å$^{-1}$ of $W_1Mo_1$-NG and $W_2$-NG should be derived from the W=O-Mo and W=O/N=O-W contributions, respectively. Unambiguously, by combining the WT results at Mo K-edge and W L$_3$-edge, the metal atoms are confirmed to be bridged via extra O or N atoms in the $W_1Mo_1$-NG, $Mo_2$-NG, and $W_2$-NG. To determine the configuration of these DACs, we used density functional theory (DFT) calculations to deduce the bimetal models based on the FT-EXAFS experimental spectra and fitted curves. The EXAFS fitting results exhibit that the Mo atom has four coordinating interactions of Mo=O (1.79 Å), Mo=O (1.99 Å), Mo=O=C/N (2.66 Å), and Mo=W (3.29 Å) and the corresponding CN values are 1.9, 2.2, 1.1, and 0.9, respectively (table S3). Meanwhile, the four coordination paths of W atom at 1.83, 2.01, 2.67, and 3.29 Å are respectively assigned to W=O, W=O=O/C=O, and W=Mo with corresponding CN of 2.1, 1.7, 1.2, and 1.1 (table S4). The EXAFS fitting curves at $R$-space and $k$-space are consistent well with experiment spectra of $W_1Mo_1$-NG (Fig. 4, G and H). Then, possible W-Mo heterodimer models were constructed and optimized with DFT calculations based on the coordination environment (fig. S11). For the O-coordinated $W_1Mo_1$-NG model (Fig. 4G, inset), the W=O, Mo=O, and O-bridged W=Mo paths length are 1.75, 1.71, and 3.54 Å (fig. S12), respectively, in good agreement with EXAFS fitting data (1.79, 1.79, and 3.29 Å, respectively). As a result, the geometry of heteronuclear W-Mo atoms anchored in NG vacancy by four O atoms and two C atoms is the most possible actual configuration. Wherein one W atom binding with O atom to form W-O motif, which further binds with a neighboring Mo atom to form a W-O-Mo-O–C configuration, while the W and Mo atoms respectively exist in the [WO$_4$] tetrahedron and distorted [MoO$_6$] octahedron units. Quantitative EXAFS fitting results for homonuclear systems are also summarized in Fig. 4, I and J and fig. S13. Note that the local coordination of Mo atom in $Mo_2$-NG resembles that of $W_1Mo_1$-NG, suggesting similar local environment around the Mo center, while for $W_2$-NG, the CN of the W=O/N path (second shell) is 2.3, which is higher than that of $W_1Mo_1$-NG (1.7). According to the EXAFS fitting and DFT calculation results, the homonuclear Mo$_2$ and W$_2$ dual atoms are determined to be inlaid in NG with seven O and N atoms, respectively (fig. S14). Other coordination configurations are excluded by comparing the EXAFS fitting and XPS results (fig. S15). Compared to homonuclear Mo$_2$-NG and W$_2$-NG, the coaxial line of W-Mo atoms is not parallel to the NG plane, which gives rise to structural deformation. The structural perturbation of W-Mo heterodimers can effectively modulate the electronic structure of the W, Mo, and O atoms in the defective NG, ensuring high intrinsic activity. Obviously, the paired metal atoms in $W_1Mo_1$-NG ($W=O=Mo=O=C$) and $Mo_2$-NG ($Mo=O=Mo=O=C$) are anchored in NG by O atoms, while paired W atoms in W$_2$-NG ($W=N=W=W=C$) are anchored in NG by N atoms. Usually, the metal atoms are dispersed on N-doped carbon support in SACs with form of M–N–C (M refers to transition metals). Unambiguously, the bulk oxides of W and Mo can be converted to the corresponding nitriles in an NH$_3$ atmosphere at high temperature (29). In this work, the energy provided during the CVD process probably fails to reach the dissociation energy of M=O bonds (M = W, Mo) in W-Mo and Mo$_2$ dimers obtained via hydrothermal process, thus keeping M=O coordination. For the tungstate system, the structural stability of isolated dinuclear tungsten oxide is extremely poor (30), so that the weaker W=O bond cannot survive in the high temperature CVD process compared to W=N bond. Consequently, we have prepared DAC with W=O–Mo=O–C configuration through facile self-assembly of W- and Mo-based POMs, followed by CVD procedure. In $W_1Mo_1$-NG, the O-coordinated W-Mo heterodimer with distorted structure provides the possibility to modulate the electronic structure around the W, Mo, and O atoms, thereby improving the electrocatalytic activity.

**Electrocatalytic HER performance**

The HER performance of DACs was investigated in 0.5 M H$_2$SO$_4$ and 1.0 M KOH solutions using a standard three-electrode setup. All potentials were referenced to a reversible hydrogen electrode (RHE) and without iR compensation. The commercial Pt/C and raw NG were tested for comparison. As illustrated in Fig. 5A, $W_1Mo_1$-NG...
exhibits excellent catalytic activity toward HER, giving a near-zero onset potential ($U_{\text{onset}}$) in acidic electrolyte. As a consequence of polarization, W$_{1}$Mo$_{1}$-NG produces cathodic geometric current density ($j$) of 10 mA cm$^{-2}$ at an overpotential of 24 mV ($\eta_{10} = 24$ mV), which is much lower than those of Mo$_{2}$-NG (145 mV), W$_{2}$-NG (156 mV), raw NG (200 mV), and other counterparts (fig. S16). Impressively, W$_{1}$Mo$_{1}$-NG delivers a high cathode current density at overpotential ($\eta$) above 50 mV, which is even superior to that of commercial Pt/C.
catalyst. Distinctly, this overpotential ($\eta_{10} = 24$ mV) is the lowest among the reported earth-abundant HER catalysts, such as CoP/NiCoP nanotadpoles (125 mV) (31), Ni$_2$P/Ni@C (149 mV) (32), and Fe$_3$Co/NC (298 mV) (2), as well as other catalysts (table S5). Specifically, W$_1$Mo$_1$-NG affords a small Tafel slope of 30 mV dec$^{-1}$, which is much lower than those of Mo$_2$-NG (175 mV dec$^{-1}$), W$_2$-NG (107 mV dec$^{-1}$), and NG (173 mV dec$^{-1}$) (Fig. 5B), reflecting that W$_1$Mo$_1$-NG has highest HER kinetic process through the Volmer-Tafel mechanism and the surface recombination step is the rate-limiting step (33). The exchange current density ($j_0$) of W$_1$Mo$_1$-NG is calculated...
to be 1.78 mA cm$^{-2}$, which is much higher than those of Mo$_2$-NG (1.50 mA cm$^{-2}$), W$_2$-NG (0.33 mA cm$^{-2}$), and NG (0.67 mA cm$^{-2}$) (fig. S17). Distinctly, W$_1$Mo$_1$-NG has such a lower Tafel slope and larger $j_0$ value than those of Mo$_2$-NG, W$_2$-NG, and raw NG, suggesting the superior HER kinetics and enhancing the intrinsic activity of W$_1$Mo$_1$-NG. In addition, in alkaline electrolyte (Fig. 5, C and D), W$_1$Mo$_1$-NG exhibits a small $U_{\text{onset}}$ of $\pm 26$ mV, upon which the cathodic current density elevates substantially at more negative potentials; W$_1$Mo$_1$-NG delivers $\eta_{00}$ of 67 mV, which is much lower than those of Mo$_2$-NG (247 mV), W$_2$-NG (223 mV), NG (281 mV), other counterparts, and reported transition metal–based HER catalysts (fig. S18 and table S6). The Tafel slope of W$_1$Mo$_1$-NG is 45 mV dec$^{-1}$, which is lower than those of Mo$_2$-NG (124 mV dec$^{-1}$), W$_2$-NG (94 mV dec$^{-1}$), and NG (128 mV dec$^{-1}$). Similarly, the $j_0$ of W$_1$Mo$_1$-NG is calculated to be 0.26 mA cm$^{-2}$, which is much higher than those of Mo$_2$-NG (0.19 mA cm$^{-2}$), W$_2$-NG (0.04 mA cm$^{-2}$), and NG (0.08 mA cm$^{-2}$) (fig. S19). The results reveal that W$_1$Mo$_1$-NG has more favorable HER kinetics than Mo$_2$-NG, W$_2$-NG, and NG under both acidic and alkaline media. We further compared the HER activity with recently reported tungsten and molybdenum electrocatalysts (Fig. 5E). It is evident that W$_1$Mo$_1$-NG DAC requires the lowest $\eta_{00}$ (24 and 67 mV, respectively) in 0.5 M H$_2$SO$_4$ and 1.0 M KOH, outperforming almost all W- and Mo-based HER catalysts. In addition, the electrochemical double-layer capacitance ($C_{\text{dl}}$) was measured by performing cyclic voltammetry (CV) at various scan rates (Fig. 5F). W$_1$Mo$_1$-NG has the $C_{\text{dl}}$ values of 7.20 and 6.18 mF cm$^{-2}$, which are better than those of Mo$_2$-NG (5.26 and 4.15 mF cm$^{-2}$), W$_2$-NG (6.01 and 4.72 mF cm$^{-2}$), and NG (2.06 and 1.80 mF cm$^{-2}$) in 0.5 M H$_2$SO$_4$ and 1.0 M KOH solutions, respectively (figs. S20 and S21), suggesting that the heteronuclear W$_1$Mo$_1$-NG system can subjoin active surface area (22). Furthermore, geometric current density has been widely used to evaluate the activity of electrocatalysts. However, there is considerable dispute on its effectiveness especially in the case of highly porous electrocatalysts (5). To exclude the effect of surface area and compare the intrinsic HER activity, geometric current density was normalized by electrochemical active surface area (ECSA; $j_{\text{ECSA}}$) and to further identify the catalysts’ intrinsic activity. As shown in fig. S22, W$_1$Mo$_1$-NG delivers the $j_{\text{ECSA}}$ values of 1100.49 and 165.00 mA cm$^{-2}$ at $n = 100$ mA, which are markedly higher than those of Mo$_2$-NG (32.28 and 11.50 mA cm$^{-2}$), W$_2$-NG (34.40 and 3.63 mA cm$^{-2}$), NG (46.60 and 11.83 mA cm$^{-2}$), and Pt/C (262.82 and 69.64 mA cm$^{-2}$) in 0.5 M H$_2$SO$_4$ and 1.0 M KOH solutions, respectively. These reveal that W$_1$Mo$_1$-NG has better intrinsic activity than Mo$_2$-NG, W$_2$-NG, and NG, even outperforming benchmark Pt/C in pH-universal electrolyte (8).

In addition, to gain further insight into the intrinsic catalytic activity, we measured the turnover frequency (TOF) per active site. Thus, the number of active sites was titrated from integrated charge of anodic CV cycles at phosphate buffer solution (pH 7) (fig. S23) (34). Evidently, W$_1$Mo$_1$-NG affords the highest TOF values of 2.36 and 0.42 H$_2$ s$^{-1}$ at $n = 100$ mA, which are about 59, 42, and 26, 21 times higher than those of Mo$_2$-NG (0.04 and 0.01 H$_2$ s$^{-1}$) and W$_2$-NG (0.09 and 0.02 H$_2$ s$^{-1}$) in 0.5 M H$_2$SO$_4$ and 1.0 M KOH, respectively (Fig. 5G). The results indicate that heteronuclear W$_1$Mo$_1$-NG system delivers prominent catalytic hydrogen production capacity compared to homonuclear Mo$_2$-NG and W$_2$-NG. This superior catalytic performance is related to the distinctive W–O–Mo–O–C configuration, which provides a unique electronic structure and improves electrical conductivity, notably affecting on the electron transfer from the catalyst surface to adsorbed species (35). Besides, electrochemical impedance spectroscopy (EIS) technique was also performed. Among them, W$_1$Mo$_1$-NG DAC yields small charge-transfer resistance ($R_{\text{ct}}$) (1 and 2 ohms) in 0.5 M H$_2$SO$_4$ and 1.0 M KOH, which are much lower than those of Mo$_2$-NG (5 and 10 ohms), W$_2$-NG (4 and 10 ohms), and NG (40 and 20 ohms), respectively (fig. S24). The Mo$_2$-NG and W$_2$-NG both exhibit lower $R_{\text{ct}}$, than that of raw NG, indicating that the foreign metal atoms doping facilitate electron transport at the electrode/electrolyte interface. Notably, the HER performance of W$_1$Mo$_1$-NG catalyst is extremely superior to Mo$_2$-NG and W$_2$-NG, which can be attributed to the atomic W–O–Mo–O–C moity having favorable local electronic structure. Here, the highest performance of W$_1$Mo$_1$-NG is achieved with feed molar ratio for W/Mo of 7:13 at CVD processing time of 3 hours, indicating that the synergy of W and Mo species decreases the reaction kinetic barrier for HER. Since the self-assembly of POMs strongly depended on the pH and the concentration of metal precursors, W$_1$Mo$_1$-NG heterocatalysts with W/Mo molar ratio of 1:1 are successfully synthesized with feed molar ratio for W/Mo of 7:13, based on XPS, ICP-MS, x-ray absorption, and DFT results. When the feed molar ratio of W/Mo precursors is 1:1, the loadings of W and Mo atoms in the catalyst is 6.82 and 1.02 wt %, respectively (table S2). Under this condition, the paired W-Mo atoms are not dominant amount, which weakens the synergetic effect of W and Mo atoms and reduces HER activity. As a result, the optimal performance in HER is achieved on W$_1$Mo$_1$-NG with electron delocalization of paired W-Mo atoms. The stability and durability of W$_1$Mo$_1$-NG were further analyzed. As illustrated in Fig. 5H, the polarization curve of W$_1$Mo$_1$-NG exhibits negligible differences compared with the initial curve after 10,000 even 50,000 CV cycles in 0.5 M H$_2$SO$_4$. Meanwhile, the polarization curves before and after 50,000 HER cycles in 1.0 M KOH also remain virtually unchanged (fig. S25). Furthermore, we performed aggressive long-term stability test on W$_1$Mo$_1$-NG by galvanostatic measurement at a current density of $\pm 10$ mA cm$^{-2}$ at room temperature (25°C) (Fig. 5I). After 100,000 s, W$_1$Mo$_1$-NG DAC still retains 98% of the initial overpotential in 0.5 M H$_2$SO$_4$ and 95% in 1.0 M KOH solutions, respectively, higher than those of Pt/C with 93 and 82%. Again, to further study the effect of temperature on stability, W$_1$Mo$_1$-NG electrocatalyst was also verified by chronopotentiometric curves in 0.5 M H$_2$SO$_4$ and 1.0 M KOH solutions below (5°, 10°, 15°, and 20°C) and above (40°, 60°, 80°, and 90°C) room temperature. As exhibited in fig. S26, W$_1$Mo$_1$-NG exhibits substantially constant overpotentials over the temperature range 5° to 90°C for 100,000 s, highlighting the excellent stability over a wide temperature range. Besides, the XRD characterization reveals no evidence phase transition for W$_1$Mo$_1$-NG after cycling test (fig. S27). The chemical valence states of W and Mo ions remain almost unchanged, further signifying the robustness of the heteronuclear W$_1$Mo$_1$-NG catalyst (fig. S28). In particular, the HER activity of W$_1$Mo$_1$-NG DAC remains undegraded even storing for more than 2 years, confirming the remarkable chemical stability (fig. S29). The excellent physicochemical stability can be attributed to the robust W–O–Mo–O–C configuration with strong W–O and Mo–O bonds inherited from the W- and Mo-based POMs, respectively.

### DFT calculation

To understand that the O-coordinated W$_1$Mo$_1$-NG system promotes the catalytic reaction over wide range of pH 0 to pH 14, we performed the correlative theoretical calculations based on DFT studies. In
W-Mo atoms are anchored in NG vacancies through oxygen atoms. Results, the DFT geometry optimization indicates that the O-bridged structure is constructed by switching their coordinated O and N atoms while maintaining the metal centers unchanged. On the basis of EXAFS fitting results, the DFT geometry optimization indicates that the O-bridged structure is constructed by switching their coordinated O and N atoms while maintaining the metal centers unchanged. While, for the homonuclear Mo2-NG and W2-NG models, atomic H adsorbs on terminal O atoms linked with metal centers (Fig. 6, B and C). We calculated $\Delta G_{\text{H}}$ on the abovementioned sites for DACs, and the results are summarized in Fig. 6D and fig. S30. For heteronuclear W1Mo1-NG system, according to the Sabatier principle, we focused on six nonequivalent active sites: Mo-coordinated terminal O, O1; W-coordinated terminal O, O2; bridging oxygen in Mo–O–C motif, O4 and O5; bridging oxygen in Mo–O–W motif, O6; Mo-coordinated C, C3. Specifically, the bridged oxy POMs is preferred for proton adsorption; thus, bridging oxygen in W–O–Mo–O–C configuration inherited from POMs shows optimal $\Delta G_{\text{H}}$ in electrocatalytic HER. The $\Delta G_{\text{H}}$ of these six nonmetal sites locates far optimal value than those of homonuclear Mo2-NG and W2-NG, implying that the heteronuclear W1Mo1-NG with diverse binding sites is more active than the homonuclear catalysts. Obviously, W1Mo1-NG system with six nonmetal sites guarantees optimal $\Delta G_{\text{H}}$ throughout the entire pH range, indicating that W–O–Mo–O–C configuration can redistribute the electronic structure, which affords an improved electron environment for HER. In particular, the O1 site provides a low $\Delta G_{\text{H}}$ of $-0.065 \text{ eV}$, which is close to the optimal condition and even lower than that of commercial Pt catalyst ($-0.10 \text{ eV}$). For O-coordinated W1Mo1-NG DAC, $\Delta G_{\text{H}}$ can reach the optimal value (marked with dash line) at any pH, which is consistent with the electrochemical test results, suggesting that the unique O-coordinated W-Mo heterodimer is the active ingredient for HER under given pH condition. Moreover, when W-Mo heterodimers are coordinated with N atoms and tuned O/N atoms, the coordination environment of metal atoms is inconsistent with the EXAFS fitting and XPS results, and the corresponding W–O–Mo–O–C, W–N–Mo–N–C and W–O–Mo–(N, O)–C models show positive $\Delta G_{\text{H}}$ from 1.760 to 2.347 eV with no H adsorption (fig. S31), further demonstrating the validity of the W–O–Mo–O–C model. In contrast, the experimentally determined O-coordinated Mo2-NG and N-coordinated W2-NG systems exhibit the $\Delta G_{\text{H}}$ of $-3.172 \text{ eV}$ and $-1.250 \text{ eV}$, respectively, indicating overbonding of H, thereby leading to the sites blocking. Furthermore, the other N/O-coordinated Mo2 and W2 homodimer configurations display $\Delta G_{\text{H}}$ ranging from 1.09 to 2.278 eV (figs. S32 and S33), where the coordination of Mo and W atoms actually contradicts with the EXAFS fitting and XPS results, confirming the structural rationality of O-coordinated Mo2-NG and N-coordinated W2-NG models. Thus, according to the DFT calculation results, the O-coordinated W1Mo1-NG system has a near–optimum synergistic effect and gives more favorable $\Delta G_{\text{H}}$ for HER than O-coordinated Mo2-NG and N-coordinated W2-NG systems as well as other Mo–O and W atom–nucleated structures.

To investigate the electronic structure of W1Mo1-NG DAC with improved HER activity, we perform the Bader charge analysis to quantitatively chemical analyze the differences among the DACs (see Materials and Methods). The W1Mo1-NG, Mo2-NG and W2-NG systems give almost identical Bader charge value for O atom with 6.83 e. However, the O-coordinated W1Mo1-NG delivers a Bader volume of 291 pm³, which is much larger than those of Mo2-NG (206.6 pm³) and W2-NG (149.8 pm³). In addition, as shown in Fig. 6, E and F, electrons are delocalized in W1Mo1-NG system, well corresponding to the much larger Bader volume, indicating that the O-coordinated W-Mo heterodimer has strong covalent character with weak ionic property. Compared to heteronuclear W1Mo1-NG, the homonuclear Mo2-NG and W2-NG exhibit growing ionic nature because the electrons are strongly localized around coordination atoms (Fig. 6, G and H), via which the electrons from the metal centers are partially depleted to the coordinated O sites, leading to strong overbinding of H. Besides, the projected density of states (PDOS) on Mo, W, and O atoms was further performed to detect the electronic band structure of W1Mo1-NG. As illustrated in Fig. 6l, for three DAC systems, the Mo, W, and O atoms exhibit unoccupied states, deriving from the covalent bonding between metal ions and O atoms; the density of states (DOS) around the Fermi level ($E_F$) is dominated by O 2p orbital. Notably, heteronuclear W1Mo1-NG exhibits an increased DOS for the occupied states from 0.30 eV to the $E_F$ (the shadowed part in Fig. 6l) due to the delocalized electrons (37), corresponding to the favorable adsorption behavior of H. Meanwhile, the delocalized electrons for W1Mo1-NG system can reduce the adsorption energy between the active sites and water in alkaline solution (37), which could lower the energetic barrier for the reorganization of the interfacial water network, thereby enhancing the hydrogen evolution rate (38). Besides, the results also suggest that W1Mo1-NG with delocalized electrons offers enhanced electrical conductivity compared to Mo2-NG and W2-NG, in accordance with EIS results (fig. S24). As a result, the distinctive W–O–Mo–O–C configuration with delocalized electrons ensures the optimal $\Delta G_{\text{H}}$ and enhances reaction kinetics, thereby improving the HER activity in pH-universal electrolyte. In W1Mo1-NG system, the overlap of the electron clouds between W site and O site deforms the electron cloud of Mo site, and vice versa, which could cause distortion of the structure and electron redistribution, resulting in the electron delocalization of the W–O–Mo–O–C configuration (39). In addition, since the terminal O atom is the most promising active site, we extracted the bonding and antibonding states of H adsorbed on terminal O atom by projected crystal orbital Hamilton population (pCOHP) analysis. Fig. 6g displays the –pCOHP curves of the H–O coupling in the adsorption configurations. In O-coordinated W1Mo1-NG and Mo2-NG systems, O 2s and O 2p valence orbitals are actively participating in the hybridization with H. The antibonding states of Mo2-NG system (1.67 eV) move to higher energy level compared to W1Mo1-NG system (0.50 eV), indicating strong interaction with hydrogen (40), which corresponds to the excessive adsorption strength of Mo2-NG ($\Delta G_{\text{H}} = -3.172 \text{ eV}$). Whereas, in N-coordinated W2-NG system, the O 2p and O 2p valence orbitals are participating in the hybridization with H, which causes an antibonding state (0.40 eV) above the $E_F$, ensuring strong interaction with hydrogen ($\Delta G_{\text{H}} = -1.25 \text{ eV}$).

**DISCUSSION**

In summary, we have developed a facile two-step method to prepare the W1Mo1-NG DAC via a hydrothermal self-assembly of pH-dependent POMs and GO, followed by CVD process. In W1Mo1-NG, O-coordinated W-Mo heterodimers are anchored in NG; W and Mo
atoms are respectively located in oxygen-bridged [WO₄] tetrahedron and distorted [MoO₆] octahedron. The distinctive W─O─Mo─O─C configuration is the active site for HER, which guarantees excellent catalytic activity and high stability. DFT results reveal that electron delocalization of W₁Mo₁-NG system affords the desirable ΔGₜ and good HER kinetics, thereby promoting HER activity. These results suggest that the self-assembly of POMs can be a versatile method for preparing atomic-scale catalysts with uniform distributed active ingredients.

**MATERIALS AND METHODS**

**Materials synthesis**

Na₂WO₄·2H₂O and (NH₄)₆Mo₇O₂₄·4H₂O precursors were added to aqueous suspension of GO to form a homogeneous solution. Subsequently, the resulting mixture was transferred to a Teflon-lined autoclave and heated at 190°C for 12 hours. The as-prepared product was freeze-dried to produce a spongy column. Sponge column of p-RGO with O-coordinated W-Mo heterodimers was obtained by...
freeze drying of the product after hydrothermal synthesis. Last, the nanocomposite was reacted with NH3/Ar at 800°C in a CVD apparatus to obtain Mo2-NG, W1Mo1-NG, W2-NG, and NG catalysts. The details are shown in the Supplementary Materials.

Materials characterization
A JEOL JSM-7001F SEM and JEOL 2100 field emission gun TEM were used to examine the morphology. AC HAADF-STEM images and EDS elemental mappings were carried out by a Cs-corrected FEI Titan G2 60-300 equipped with a Super-X EDS detector and operated at 300 kV. Chemical compositions and elemental oxidation states were checked by XPS spectra (PHI-5702). X-ray absorption spectra (XANES and EXAFS) of W L3- and Mo K-edges were measured on VESPERs beamline at the Canadian Light Source, by scanning a double-crystal Si(111) monochromator and collecting emitted x-ray fluorescence.

Computational details
The first-principles calculations based on the DFT were performed within spin-polarized generalized gradient approximation. Core electron states were represented by the projector augmented-wave method (41) as implemented in the Vienna ab initio simulation package (42). The Perdew-Burke-Enzerhof (43) exchange correlation functional and a plane wave representation for the wave function with a cutoff energy of 450 eV were used. Lattice parameters and geometry of crystal were fully optimized on the basis of the criteria of a maximum atomic force of 0.01 eV Å−1 and energy convergence with a cutoff energy of 450 eV were used. Lattice parameters and energy convergence with a cutoff energy of 450 eV were used. Lattice parameters and energy convergence with a cutoff energy of 450 eV were used.

where asterisk means adsorption on the graphene substrate. The COHP analyses were performed by LOBSTER program (@Maintz16CCC37) (45).

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/23/eaba5868/DC1

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