Grain boundary controlling is an effective approach for manipulating the electronic structure of electrocatalysts to improve their hydrogen evolution reaction performance. However, probing the direct effect of grain boundaries as highly active catalytic hot spots is very challenging. Herein, we demonstrate a general water-assisted carbothermal reaction strategy for the construction of ultrathin Mo$_2$C nanosheets with high-density grain boundaries supported on N-doped graphene. The polycrystalline Mo$_2$C nanosheets are connected with N-doped graphene through Mo–C bonds, which affords an ultra-high density of active sites, giving excellent hydrogen evolution activity and superior electrocatalytic stability. Theoretical calculations reveal that the $d_{z^2}$ orbital energy level of Mo atoms is controlled by the MoC$_3$ pyramid configuration, which plays a vital role in governing the hydrogen evolution activity. The $d_{z^2}$ orbital energy level of metal atoms exhibits an intrinsic relationship with the catalyst activity and is regarded as a descriptor for predicting the hydrogen evolution activity.

Owing to the high gravimetric specific energy density and environmentally friendly characteristics, hydrogen energy has emerged as one of the most promising alternatives to fossil fuels [1]. Electrochemical hydrogen evolution reaction (HER) provides an attractive way for efficient H$_2$ production from water electrolysis, in which catalysts are critical for developing renewable energy conversion technologies [1]. To date, platinum (Pt)-based materials are considered to be the most active HER catalysts, but the scarcity and high cost of Pt rigorously hamper their widespread applications [1]. Therefore, developing earth-abundant alternatives to Pt-based catalysts for achieving efficient H$_2$ generation is highly desirable. Molybdenum carbide (Mo$_2$C), an excellent early transition-metal carbide, has intensely...
awakened ever-growing interest as a promising HER electrocatalyst because its electronic structure is virtually analogous to that of Pt metal\textsuperscript{15}. Nevertheless, Mo\textsubscript{2}C surface shows excessively strong Mo–H binding energy, which hinders the desorption of adsorbed H to generate H\textsubscript{2}, severely deteriorating the electrochemical HER activity\textsuperscript{21,22}.

Grain boundaries (GBs), as a type of planar defect, are effective to directly tune the surface atomic and electronic structure, significantly altering the intrinsic reactivity of nanocrystalline materials\textsuperscript{23,24}. Specifically, GBs create lattice distortion regions in Mo\textsubscript{2}C polycrystals by stabilizing dislocations, which could provide an optimized electronic structure for tailoring the binding energy of Mo–H, consequently accelerating the H\textsubscript{2} production. However, conventional bulk materials are typically limited to the surface GB density, which is not available for practical catalytic reactions due to the relatively low accessibility of active sites. Compared with bulk counterparts, ultrathin two-dimensional (2D) nanostructures possess sufficient interplanar active sites and shorter reactant/product diffusion length, and have been intensively reported as promising candidates for HER\textsuperscript{10}. Currently, most of the Mo\textsubscript{2}C nanostructures are synthesized from either high-temperature carburization of costly/toxic molybdenum precursors (e.g., Mo foil, MoO\textsubscript{2}, and Mo\textsubscript{2}CO\textsubscript{3}) with carbonaceous gases (e.g., CH\textsubscript{4}, C\textsubscript{6}H\textsubscript{6}, and CO\textsubscript{2})\textsuperscript{25} or the selectively etching layered ternary Mo-containing phases\textsuperscript{26}. Nevertheless, in the former method, the resultant carbide surface generally suffers from severe car contamination from the pyrolysis of carbonaceous gases, inhibiting the exposure of active sites; in the latter, the delamination yield and defect controllability of Mo\textsubscript{2}C sheets derived in aqueous fluoride-containing acidic solutions are not satisfactory. In this context, nearly all the above-mentioned methods can only introduce small changes in the structural and chemical configuration of Mo\textsubscript{2}C catalysts, resulting in poor tunability for altering the catalytic performance. Therefore, a facile approach for developing high-density and fully exposed GBs on ultrathin 2D Mo\textsubscript{2}C nanostructure is highly desired.

Herein, we propose an effective strategy to achieve ultrathin Mo\textsubscript{2}C nanosheets (NSs) with rich GBs supported on N-doped graphene (H-Mo\textsubscript{2}C/NG) via hydrothermal and water-assisted carbothermal reactions. During the carbonization process, water induces the structural evolution of Mo\textsubscript{2}C nanocrystals from nanoparticles (NPs) to NSs and controls the GB density of Mo\textsubscript{2}C NSs as well. The high-density GBs in Mo\textsubscript{2}C NSs provide an ultra-high fraction of active sites, significantly improving the inherent HER activity of H-Mo\textsubscript{2}C/NG. Theoretical calculations show that the GBs in Mo\textsubscript{2}C NSs modulate the configuration of Mo\textsubscript{3} pyramids, which thereby regulates the Mo d\textsubscript{3z\textsuperscript{2}} orbital energy level, manipulating the Mo–H bond strength of H-Mo\textsubscript{2}C/NG catalyst and influencing the HER activity. This work opens up an avenue for the development of high-efficiency catalysts through GB engineering.

Results
Controllable construction of ultrathin Mo\textsubscript{2}C NSs with high-density GBs
Mo\textsubscript{2}C NSs supported on N-doped graphene (NG) were constructed in situ by facile hydrothermal and water-assisted carbothermal reactions (Fig. 1a). Typically, graphene oxide (GO) and (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}·4H\textsubscript{2}O were dissolved into deionized water and then the homogeneous solution was subjected to a hydrothermal reaction to obtain a homogeneous mixture composed of amorphous MoO\textsubscript{3} supported on reduced GO sheets (MoO\textsubscript{3}/RGO) (Supplementary Fig. 1). Next, the mixture was freeze-dried and then treated at 800 °C under NH\textsubscript{3}/Ar gas. Finally, only Mo\textsubscript{2}C NPs decorated on NG were obtained when the MoO\textsubscript{3}/RGO intermediate was water-free. However, when MoO\textsubscript{3}/RGO intermediate contained sufficient water concentration (18.56 wt%), Mo\textsubscript{2}C NSs with high-density GBs were constructed in situ and anchored on NG. Further details of the experiments were provided in Methods.

To illustrate the growth behavior of Mo\textsubscript{2}C nanocrystals with the assistance of water, density functional theory (DFT) calculations were performed. As shown in Fig. 1b, two theoretical model systems consisting of initial MoO\textsubscript{3} without H\textsubscript{2}O (I\textsubscript{SNP}) and with H\textsubscript{2}O (I\textsubscript{SNS}) are constructed, and the structural evolution mechanisms of Mo\textsubscript{2}C products are discussed from a reaction enthalpy (\Delta H) viewpoint. During the carbonization process, I\textsubscript{SNP} and I\textsubscript{SNS} first absorb heat and dissociate into transition states of T\textsubscript{SNP} and T\textsubscript{SNS}, respectively, and they then react with C atoms in RGO to form Mo\textsubscript{2}C. Generally, RGO has different types of C atoms, namely, the highly reactive carbon at the edge and the relatively inertness carbon of the six-membered C-ring far away from the edge\textsuperscript{41}. Because H-bonded graphene has a structure analogous to benzene (Ph), the chemical properties of the compounds can be thought to be similar\textsuperscript{42}. For simplicity, the C atoms extracted from the edge of the graphene lattice, as well as the free Ph radicals, react with T\textsubscript{SNP} and T\textsubscript{SNS} to produce T\textsubscript{SNP}-C, T\textsubscript{SNP}-Ph, T\textsubscript{SNS}-C, and T\textsubscript{SNS}-Ph, respectively. Of course, these model structures are much simpler than those in the actual experiment, yet, they are sufficient to study the interaction between two substances. Theoretical calculations show that \Delta H values for T\textsubscript{SNP} and T\textsubscript{SNS} reacting with C atoms are both negative, which indicates that the C atoms from RGO can carbonize MoO\textsubscript{3} to form Mo\textsubscript{2}C. In anhydrous atmosphere, C atoms are chemically intercalated into common MoO\textsubscript{3} motifs, reducing MoO\textsubscript{3} into Mo\textsubscript{2}C NPs decorated on defective NG. In addition, the reaction \Delta H\textsubscript{TS} for T\textsubscript{SNP} to produce T\textsubscript{SNP}-Ph is 2.45 eV, suggesting that T\textsubscript{SNP} fails chemically bind with the six-membered C-ring. But the reaction \Delta H\textsubscript{TS} for T\textsubscript{SNS} to produce T\textsubscript{SNS}-Ph is -1.45 eV, which indicates that T\textsubscript{SNS} tends to combine with six-membered C-ring on RGO basal plane, thus inducing the lateral arrangement of Mo\textsubscript{2}C lattice along 2D direction\textsuperscript{43}. In general, common MoO\textsubscript{3} without H\textsubscript{2}O can only react with carbon on RGO edge, producing Mo\textsubscript{2}C NPs. While MoO\textsubscript{3} with H\textsubscript{2}O not only reacts with the edge C atoms but also readily combines with six-membered C-ring along the RGO basal plane: in this situation, epitaxial growth is carried out to enlarge the Mo\textsubscript{2}C domain, achieving a coalesced NSs with several micrometers in lateral size. Especially, in the presence of H\textsubscript{2}O, due to the guest–host interaction between H\textsubscript{2}O and MoO\textsubscript{3},\textsuperscript{44} a unique Mo–O configuration is obtained and anchored on RGO, which serves as the nucleation site for Mo\textsubscript{2}C growth. As the activated carbon species encounter the Mo–O configuration, the dense seeds begin to individually nucleate at multiple regions. Consequently, these simultaneously grown nanocrystals merge together seamlessly and eventually form multi-faceted Mo\textsubscript{2}C NSs, which thereby hinders the growth of Mo\textsubscript{2}C grains in the radial orientation, leaving behind numerous GBs. In this situation, the RGO intermediate not only provides C source for Mo\textsubscript{2}C growth, but also acts as a robust support for Mo\textsubscript{2}C nanodomains to nucleate and finally splice into NSs; in turn, the formed Mo\textsubscript{2}C NSs are covalently connected with underneath NG sheets through Mo–C bonds, which ensures the high inherent stability of Mo\textsubscript{2}C hybrids.

Morphologies and structures of the Mo\textsubscript{2}C hybrids were characterized with atomic force microscopy (AFM), transmission electron microscopy (TEM), and high-angle annular dark-field scanning TEM (HAADF-STEM) measurements. For Mo\textsubscript{2}C/NG, Fig. 2a, b and Supplementary Fig. 2 show that high-density and discrete Mo\textsubscript{2}C NPs (diameter <5 nm) are uniformly loaded on NG layers. In contrast, in H-Mo\textsubscript{2}C/NG, GB-rich Mo\textsubscript{2}C NSs with a uniform thickness of ~1.0 nm, corresponding to 2–3 layers of unit cells, are well-distributed on NG (Fig. 2c, d and Supplementary Figs. 3, 4), affording a very high proportion of exposed active sites. Procession electron diffraction (PED) measurements under TEM were employed to collect orientation maps and extract GB density. As shown in Fig. 2e and Supplementary Fig. 5, the crystallographic orientations of each grain in the polycrystalline microstructure are random, and especially abundant intersections between domain walls can be observed. The GB density of Mo\textsubscript{2}C NSs in Mo\textsubscript{2}C hybrids is summarized in Supplementary Fig. 6, where the statistical region of each sample is ~20,000 nm\textsuperscript{2}. Obviously, H-Mo\textsubscript{2}C/NG possesses the highest GB density of 138 ± 3 μm\textsuperscript{-1}, clearly demonstrating that the water content in MoO\textsubscript{3}/RGO effectively manipulates the GB

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density of Mo$_2$C NSs, consistent with TEM results (Supplementary Figs. 7–9 and Supplementary Note 1). It is worth mentioning that the supply of NH$_3$ (Supplementary Fig. 10 and Supplementary Note 2) and the sufficient oxygen-containing functional groups on GO surface (Supplementary Figs. 11–14 and Supplementary Note 3) are necessary for the formation of GB-rich Mo$_2$CN Ss. Furthermore, tens of HAADF-STEM images clearly reveal that Mo$_2$C NSs composed of individual grains with nanometer size (Fig. 2f and Supplementary Fig. 15), which forms chemically connected interfaces with numerous GBs and triple junctions, indicating full exposure of high-density active sites in electrocatalysis.

**Atomic structure of GBs on Mo$_2$C NSs in H-Mo$_2$C/NG**

We employed HAADF-STEM characterization to examine the atomic structure of GBs. The inspection of dozens of boundary locations systematically found that the nanocrystalline grains in Mo$_2$C NSs are seamlessly stitched with irregular GBs (Fig. 3 and Supplementary Fig. 16). Figures 3a, a1–a3 obviously display that two Mo$_2$C nanograins form a corrugated GB with an angle of 15°, as well as stacking faults (SFs) and off-centered Mo columns. Furthermore, a conspicuous strain concentration is discovered in the vicinity of the GB (Fig. 3b). Compressive strain ($-0.136 \pm 0.036$) and tensile strain ($0.801 \pm 0.484$ and $0.107 \pm 0.086$) coexist (Supplementary Fig. 17), ensuring that the...
The lattice, which modifies fcc/hcp heterophase GBs regulate the atomic arrangement of Mo2C. Hcp phases of Mo2C nanocrystals are strongly controlled by carbon sources. Figures 3c1, c2 show representative HAADF-STEM images of fcc/hcp GB superstructures. Along the fcc/hcp heterophase edges, both hcp phase with “ABAB” stacking and fcc phase with “ABCABC” stacking, with the coexistence of twin boundaries (TBS) and SFs are observed along the close-packed [110] and [1120] directions. This fcc/hcp heterophase GBs regulate the atomic arrangement of Mo2C lattice, which modifies the electronic structure of Mo2C hybrid, thus enhancing the efficiency of hydrogen production. In fact, the fcc and hcp phases of Mo2C nanocrystals are strongly controlled by carbon activity. Meanwhile, the reaction ΔH calculation clearly reveal that in anhydrous system, only the C atoms from graphene edges participate the formation of hcp Mo2C, while in aqueous system, carbon sources from edge and basal plane of the graphene lattice are both active and readily react with the unique Mo–O configuration to produce Mo2C NSs with a mixed fcc and hcp phases (Fig. 1b). On the basis of the aforementioned characterizations, the crystalline structure of Mo2C NSs can be schematically illustrated in Fig. 3f, where the hcp/hcp and fcc/hcp GBs appear alternately. As a result, atomic structure analyzes clarify the atomic configuration at GBs in Mo2C NSs and reveal the obvious lattice distortion, accompanied by abundant atomic step edges, dislocations, TBS, and SFs, which can effectively alter the surface electronic structure.

Crystal and surface electronic structure of Mo2C hybrids were investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. The diffraction patterns of H-Mo2C/NG and Mo2C/NG in Fig. 4a match with the hcp Mo2C (PDF#35-0787), which confirms the identity of Mo2C. Compared to Mo2C/NG, the diffraction peak intensity of H-Mo2C/NG is significantly enhanced with a narrower full width at half maxima, indicating that the introduction of water enables the epitaxial growth of Mo2C grains to harvest large-sized NSs. No diffraction peaks of fcc Mo2C are detected in Mo2C hybrids (Supplementary Fig. 20), which could be attributed to the strong destruction of the periodic structure for the fcc lattice because of the alternating arrangement of fcc and hcp Mo2C lattices. Moreover, the Mo 3d spectra of H-Mo2C/NG and Mo2C/NG are deconvoluted into four pairs of peaks (Fig. 4b), indicating that four oxidation states for molybdenum species (+2, +3, +4, and +6) exist in Mo2C hybrids. Compared to Mo2C/NG, a negative shift of 0.17 eV is observed on Mo2+ in H-Mo2C/NG, indicating the electron accumulation of Mo atoms near GBs in Mo2C NSs, which is beneficial to weaken the binding strength of Mo–H and thus enhance the HER activity. Meanwhile, the Mo–C resonance in C K-edge X-ray absorption near-edge structure (XANES) spectra for H-Mo2C/NG shifts to a higher photon energy zone compared to that of Mo2C/NG (Fig. 4c), which could be attributed to the enhanced orbital hybridization between the C and Mo elements, that caused by lattice distortion near GBs, facilitating...
electron transfer. In addition, to further understand the role of water during carbonization process, a series of Mo$_2$C hybrids synthesized with various water contents were also subjected to XPS measurement. As water content increases, the peak intensity of Mo–C (Supplementary Fig. 21) and Mo–N (Supplementary Fig. 22) species increases slightly, indicating that water promotes the formation of nitrogen-doped Mo$_2$C. As revealed by the theoretical calculation that the reaction ΔH of TS$_{NS}$ to produce TS$_{NS}$-N (−1.05 eV) is lower than that...
of TS$_{\text{Ne}}$ to produce TS$_{\text{Ne}}$N ($\sim$0.31 eV) (Supplementary Fig. 23), indicating that unique Mo–O configuration induced by water prefers to bind with N atoms forming Mo–N species.

To precisely probe the local coordination structure of GBs in Mo$_2$C nanosheets, XANES and extended X-ray absorption fine structure (EXAFS) at Mo K-edge were conducted. Compared to H-Mo$_2$C/NG-7.14 and Mo$_2$C/NG, the pre-edge of H-Mo$_2$C/NG obviously shifts to lower energy (Fig. 4d), indicating the increased average electron density around Mo atoms, consistent with XPS results. The details of Mo local environment can be described through the Fourier-transformed EXAFS (FT-EXAFS) in $k$-space. Mo$_2$C hybrids exhibit relatively weak Mo–Mo paths in H-Mo$_2$C/NG (2.38 and 2.95 Å) compared to H-Mo$_2$C/NG-7.14 (2.29 and 2.87 Å); these Mo paths can be attributed to Mo$_2$O$_2$ and Mo$_2$O$_3$ caused by the oxidation of molybdenum species in ambient atmosphere, respectively. The Mo$_2$+ and Mo$_3$+ are assigned to carbides and nitrides, respectively, which are known to serve as active sites for HER. c K-edge XANES spectra of H-Mo$_2$C/NG and Mo$_2$C/NG. The characteristic resonances of C = C π* and C–C σ* originating from NG support. d Mo K-edge XANES spectra of H-Mo$_2$C/NG, H-Mo$_2$C/NG-7.14, Mo$_2$C/NG, and the reference samples. H-Mo$_2$C/NG-7.14 and Mo$_2$C/NG have a higher half-edge energy than that of bulk Mo$_2$C reference, which arises from the charge-transfer from Mo to C atoms on the NG-supported Mo$_2$C. e Mo K-edge Fourier transform EXAFS spectra of H-Mo$_2$C/NG, H-Mo$_2$C/NG-7.14, Mo$_2$C/NG, and the reference samples. f EPR spectra of H-Mo$_2$C/NG and Mo$_2$C/NG. H-Mo$_2$C/NG shows the EPR signals at $g_1 = 1.930$ (Mo–N species$^3$), $g_2 = 1.870$ and $g_3 = 2.056$ (Mo$^4+$ species$^3$), followed by $g_4 = 2.111$ and $g_5 = 2.156$ (the resonance on conduction electrons$^3$).

**Electrocatalytic HER performance**

The catalytic performance of Mo$_2$C hybrids was investigated by a three-electrode system in 0.5 M H$_2$SO$_4$ and 1.0 M KOH solutions (see more details in Methods). As revealed in Fig. 5a, H-Mo$_2$C/NG shows the highest HER performance among all catalysts in acidic media, and only requires an overpotential of 10 mV to achieve the geometric current density of −10 mA cm$^{-2}$ ($\eta_{10}$), significantly superior to the Mo$_2$C/NG ($\eta_{10} = 138$ mV) and even Pt/C catalyst ($\eta_{10} = 19$ mV). Furthermore, the Tafel slope of H-Mo$_2$C/NG is 38 mV dec$^{-1}$ (Fig. 5b), which far surpasses that of Mo$_2$C/NG (137 mV dec$^{-1}$) and is even comparable to that of state-of-the-art Pt/C catalyst (34 mV dec$^{-1}$), suggesting that H-Mo$_2$C/NG possesses more fast kinetics with the Heyrovsky reaction as the rate-determining step$^1$. The exchange current density ($j_0$) of H-Mo$_2$C/NG is...
ENG (0.80 mA cm\(^{-2}\)) with the highest GB density achieves the best HER performance in alkaline media. H-Mo2C/NG merely requires 57 mV and respectively, which are comparable to commercial Pt/C catalyst. H-Mo2C/NG also affords a lower Tafel slope of 48 mV dec\(^{-1}\), significantly better than those of Mo2C/NG (3.70 and 6.23 µA cm\(^{-2}\)) and Pt/C (80.16 and 9.86 µA cm\(^{-2}\)), respectively, revealing better intrinsic HER activity of Mo2C/NG with Mo2C/NG in 1.0 M KOH. Inset is cyclic voltammetry (CV) cycles of H-Mo2C/NG. galvanostatic measurement of H-Mo2C/NG. galvanostatic measurement of H-Mo2C/NG in 1.0 M KOH at \(\eta = -100\), -200, and -300 mA cm\(^{-2}\), respectively. additionally, to gain insight into the superior catalytic activity of H-Mo2C/NG, the turnover frequency (TOF) was calculated (supplementary Fig. 29 and supplementary note 4). As displayed in Fig. 5e, H-Mo2C/NG affords the TOF values of 21.33 and 3.81 H\(_2\) s\(^{-1}\) at \(\eta = 110\) mV in acidic and alkaline electrolytes, respectively, which are quite larger than those of Mo2C/NG (0.57 and 1.08 H\(_2\) s\(^{-1}\)), as well as other control samples (Supplementary Fig. 30), confirming the high HER activity of H-Mo2C/NG. to further identify the intrinsic activity of H-Mo2C/NG, geometric current density (\(j\)) was normalized by electrochemical active surface area (ECSA, \(j_{\text{ECSA}}\)). which was determined by deriving the electrochemical double-layer capacitance (\(C_{\text{dl}}\)). The \(C_{\text{dl}}\) of H-Mo2C/NG (23.8 mF cm\(^{-2}\)) is slightly higher than that of Mo2C/NG (19.7 mF cm\(^{-2}\)) by 10.57 mF cm\(^{-2}\) at \(\eta = 50\) mV in 0.5 M H\(_2\)SO\(_4\) and 1.0 M KOH (supplementary Figs. 31, 32), which are evidently higher than those of Mo2C/NG (3.70 and 6.23 µA cm\(^{-2}\)) and Pt/C (80.16 and 9.86 µA cm\(^{-2}\)), respectively, revealing better intrinsic HER activity of H-Mo2C/NG with calculated to be 5.47 mA cm\(^{-2}\), which is much higher than that of Mo2C/NG (0.80 mA cm\(^{-2}\)) (supplementary table 2), further underscoring favorable HER kinetics. Meanwhile, H-Mo2C/NG also demonstrates promising HER activity in alkaline media. H-Mo2C/NG merely requires overpotentials of 63 and 163 mV to reach -10 and -100 mA cm\(^{-2}\), respectively, which are comparable to commercial Pt/C catalyst (\(\eta_{\text{0.05}} = 57\) mV and \(\eta_{100} = 173\) mV) and significantly better than those of Mo2C/NG (\(\eta_{\text{0.05}} = 107\) mV and \(\eta_{100} = 388\) mV) (Fig. 5c). Compared to Mo2C/NG catalyst, H-Mo2C/NG also affords a lower Tafel slope of 48 mV dec\(^{-1}\) (Fig. 5d) and higher \(j_{0}\) value (0.75 mA cm\(^{-2}\)), which reveals the same favorable HER kinetics as in acidic media for H-Mo2C/NG. To further study the effect of GBs on HER activity, we performed electrocatalytic hydrogen evolution tests on a series of Mo2C hybrids. Obviously, as the water content increases, the \(\eta_{\text{0.05}}\) and Tafel slopes on Mo2C hybrids firstly decrease and then increase (supplementary Figs. 25-28), where H-Mo2C/NG with the highest GB density achieves the best HER performance. These results suggest that the GBs in Mo2C NSs can effectively enhance the intrinsic HER activity of the Mo2C hybrids.
noted that most synthesized 2D Mo2C catalysts cannot withstand a electrocatalytic HER process (Supplementary Fig. 37). It should be indicated that H-Mo2C/NG possesses much fast electron transfer resistance ($R_\text{ct}$) (2.5 and 2.1 $\Omega$) in 0.5 M H2SO4 and 1.0 M KOH, respectively, which is much lower than those of Mo2C/NG (5.5 and 12.5 $\Omega$) and other control samples (Supplementary Fig. 33). This result indicates that H-Mo2C/NG possesses much fast electron transfer kinetics during HER process, which is attributed to the unique structure of Mo2C NSs with chemically connected GBs, shortening the electron transfer pathway between active sites.

For real applications, the stability and durability of H-Mo2C/NG were further analyzed. As illustrated in Supplementary Fig. 34, after 10,000 or even 50,000 cycles in 0.5 M H2SO4 and 1.0 M KOH, the shifts of polarization curves for H-Mo2C/NG are negligible compared with the initial curves. Meanwhile, we performed aggressive long-term stability examine on H-Mo2C/NG by continuous galvanostatic measurement (Fig. 5g). After 100,000 s of operation at $j = -200$, and $-300$ mA cm$^{-2}$, the potentials of H-Mo2C/NG only increase by 8, 14, and 38 mV in 0.5 M H2SO4, and 11, 13, and 36 mV in 1.0 M KOH, respectively. In contrast, the potentials of Pt/C catalyst at $j = -200$ mA cm$^{-2}$ increase by 136 and 110 mV in 0.5 M H2SO4 and 1.0 M KOH, respectively. TEM characterization shows that Mo2C nanocrystals in H-Mo2C/NG still maintain an ultrathin nanosheet structure with highly exposed high-density GBs after electrochemical cycling (Supplementary Fig. 33). The chemical valence state of Mo species remains almost unchanged, further indicating the robustness of H-Mo2C/NG in the electrocatalytic HER process (Supplementary Fig. 37). It should be noted that most synthesized 2D Mo2C catalysts cannot withstand a high current density and operate for a long-lasting lifetime in a wide pH range because of the weak interfacial adhesion with adjacent nanocrystals or substrates. In this work, the excellent physicochemical stability of H-Mo2C/NG can be attributed to the chemical connection of Mo2C GBs and strong interaction of Mo2C NSs with NG sheets through Mo−C bonds. Moreover, the general synthetic strategy of GB-rich NSs can also be extended to other transition metal carbide systems (Supplementary Fig. 38), such as vanadium (Supplementary Fig. 39), niobium (Supplementary Fig. 40), tantalum (Supplementary Fig. 41), and tungsten (Supplementary Fig. 42), and yield excellent HER performances in pH-universal electrolyte (Supplementary Fig. 43), demonstrating the generality of this method, which provides an alternative way to develop high-efficiency catalysts through GB engineering.

**DFT calculations**

To understand the correlation between the electronic structure and catalytic performance in GB-rich Mo2C plane, DFT calculations were conducted. According to the HAADF-STEM images of Mo2C NSs (Fig. 3 and Supplementary Figs. 16, 19), the computational models of fcc/hcp, fcc/fcc, and hcp/hcp GBs were constructed, respectively. The DFT calculation shows that the fcc/hcp Mo2C slab surface exhibits various kinds of trigonal pyramid-like structures (Supplementary Fig. 44), in which Mo atom locates at top and pyramidally coordinates with three C atoms at bottom, forming a typical trigonal pyramid (MoC3) configuration (Fig. 6a). Depending on the height of the pyramid-shaped MoC3 skeleton on the fcc/hcp Mo2C superlattice surface, the corresponding configuration of MoC3 can be schematically classified into three types: (i) approximative triangular plane (S1), (ii) intermediate height (S2), and (iii) high height (S3). The hcp Mo2C surface consists of S1 and S3 structures, in which the S3 structure typically represents common bulk Mo2C configuration and is predominant; on the fcc Mo2C surface, MoC3 pyramids only present S3 structure. Notably, the
The dense polycrystalline Mo$_2$C NSs with massive irregular GBs are near the fcc/fcc and hcp/hcp homophase Mo$_2$C GBs also display close-tinct energy levels (Fig. 6a). In the electrocatalytic HER process, the dependence on the Mo energy level. As a result, the intrinsic HER activity exhibits a strong are s u l t, t h e D F Tr e s u l t sc o n level is more relevant to the active site of the catalysts. Therefore, the optimized adsorption free energy and fast HER kinetics can be achieved by manipulating the bond strength between the H 1 s orbital and Mo d$_{xz}$ orbital.

The bond strength is defined as:

$$E = \frac{\int (S \cdot F_{d_{xz}})}{E_s - E_{d_{xz}}}$$

(1)

Where $E_s$ and $F_{d_{xz}}$ are the energy levels of H 1 s orbital and Mo d$_{xz}$ orbital, respectively. S is orbit overlap population of H 1 s orbital and Mo d$_{xz}$ orbital. Within these contexts, we calculated the H adsorption free energy ($H_{ads}$) of surface Mo atoms on the model of fcc/hcp GB, and studied its relationship with the Mo d$_{xz}$ orbital energy level (Fig. 6c). Where the numerical fitting over the calculated $H_{ads}$ and the Mo d$_{xz}$ orbital energy level follows the similar function as the Eq. (1) of bond strength, that is, the adsorption energy varies with the Mo d$_{xz}$ orbital energy level. As a result, the intrinsic HER activity exhibits a strong dependence on the Mo d$_{xz}$ orbital energy level, which rationalizes the role of d$_{xz}$ orbital energy level as one of the most important activity descriptors for HER in Mo$_2$C systems. Compared with the state-of-the-art descriptors such as band-energy theory and work function that describe the properties of the whole surface, the d$_{xz}$ orbital energy level is more relevant to the active site of the catalysts. Therefore, the descriptor d$_{xz}$ orbital energy level could be used as a figure of merit for designing transition metal catalyst with well-defined active sites for electrocatalytic HER reaction. Additionally, the $H_{ads}$ on the Mo atoms near the fcc/fcc and hcp/hcp homophase Mo$_2$C GBs also display close-to-zero values, such as -0.044, 0.035, and 0.038 eV (Supplementary Figs. 45 and 46), which also contribute to the excellent HER activity. As a result, the DFT results confirm that GBs in ultrathin Mo$_2$C NSs can significantly alter the electronic structures of H-Mo$_2$C/NG electrocatalyst, and the intrinsic HER activity strongly depends on the Mo d$_{xz}$ orbital energy level controlled by the MoC$_3$ pyramid configuration.

### Discussion

In summary, ultrathin Mo$_2$C NSs with rich GBs supported on NG have been developed by facile hydrothermal and water-assisted carbothermal reactions with GO as carbon source. During carbonization process, water induces structural evolution of Mo$_2$C nanocrystals from NPs to NSs and controls the GB density of Mo$_2$C NSs as well. In H-Mo$_2$C/NG, the dense polycrystalline Mo$_2$C NSs with massive irregular GBs are chemically connected to NG through Mo−C bonds, which afford ultra-high fraction of active sites for electrolysis, exhibiting high reproducibility in terms of structure and performance. The inherent HER activity of H-Mo$_2$C/NG electrocatalyst strongly depends on the d$_{xz}$ orbital energy level of Mo atoms, which is controlled by the MoC$_3$ pyramid configuration. This work provides a horizon for rationally designing GB interfaces of transition metal electrocatalysts to achieve excellent HER activities, and establishes a descriptor of the d$_{xz}$ orbital energy level for the design of high-performance catalysts.

### Methods

#### Chemicals

All chemicals were purchased from commercial sources (Sigma Aldrich, Energy Chemical) without further purification. GO was synthesized from graphite flakes by the improved Hummers method.

#### Synthesis of H-Mo$_2$C/NG

First, the GO suspension was prepared by adding 0.16 g GO into 80 mL deionized water and sonicating for 10 h. Typically, 0.4470 g (NH$_4$)$_2$Mo$_3$O$_9$·4H$_2$O were added into the GO suspension and sonicated for another 4 h. Subsequently, above mixture was transferred to a Teflon-lined autoclave and heated at 190 °C for 12 h to harvest MoO$_3$/RGO intermediate. Next, the MoO$_3$/RGO intermediate was freeze-dried to obtain sponge columns with various water contents, including 0, 0.41, 7.14, 13.52, 18.56, 30.98, and 43.28 wt%. The MoO$_3$/RGO with various water contents were put into a tubular quartz furnace for heat treatment. After pumping and purging the system with Ar for 30 min, the temperature was ramped at 10 °C min$^{-1}$ up to 800 °C with the feeding of Ar (150 scm) and NH$_3$ (100 scm). The reaction was allowed to proceed for 3 h and the final product was fast cooled to room temperature by quickly removing the sample from the hot zone of the furnace under the protection of flowing Ar. The final catalysts were named H-Mo$_2$C/NG-X, where X was the water content retained in MoO$_3$/RGO intermediate, for example, H-Mo$_2$C/NG-7.14 (the water content was 7.14 wt%). In our report, H-Mo$_2$C/NG-0 and H-Mo$_2$C/NG-18.56 were denoted as H-Mo$_2$C/NG and Mo$_2$C/NG unless otherwise specified, respectively.

#### Material characterization

Morphological structure characterizations of Mo$_2$C hybrids were performed on SEM (JEOL-JSM-7001F) and TEM (FEI Titan ChemisSTEM, FEI Talos F200X, FEI Titan Themis). HAADF-STEM images were carried out by a Cs-corrected FEI Titan G2 60-300 equipped with a Super-X ED detector. The LADIA package was used to analysis the strain states of Mo$_2$C nanocrystals during the loading and unloading of tensile stress. The surface electronic structure was checked by XPS spectra (XPS, PHI-7002). The C and N K-edge XANES spectra were measured at the photoemission end-station at beamline BL10B in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. X-ray absorption spectra (XANES and EXAFS) of Mo K-edge were measured on VESERS beamline at the Canadian Light Source, by scanning a double crystal Si (111) monochromator and collecting emitted X-ray fluorescence.

#### Electrochemical measurements

Electrochemical measurements were conducted on a typical three-electrode system (CH Instruments 760E). All potentials were referenced to a reversible hydrogen electrode (RHE) and without IR compensation. The binder solution was prepared by mixing of 5 wt% Nafion solution (40 μl) with 1 mL of 4:1 v/v deionized water/ethanol. The catalyst ink was then prepared by dispersion of 2 mg Mo$_2$C hybrids (H-Mo$_2$C/NG, Mo$_2$C/NG, and control samples) into binder solution followed by ultrasonication for 2 h. In Mo$_2$C hybrids, molybdenum atoms are the active species, and molybdenum loading (~ 8 wt%, Supplementary Table 5) is basically the same. To maintain the same metal load, 5 mg Pt/C catalyst (20 wt% Pt on graphitized carbon, Johnson Matthey) ink was prepared in the same way. The ink (10 μL) was then dripped onto a carbon fiber paper (CPF, 5 mm × 5 mm) as the working electrode. The electrode was allowed to dry at room temperature for at least 24 h before measurement. After drying, a catalyst (Mo$_2$C hybrids and Pt/C) mass loading of 0.038 mg cm$^{-2}$ was obtained. A graphite rod
as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. All potentials were referenced to RHE: \( E_{\text{RHE}} = E_{\text{SCE}} + (0.242 + 0.059 \times \text{pH}) \text{V} \). In 0.5 M H\(_2\)SO\(_4\) and 1.0 M KOH solutions, the polarization curves were obtained at the electrode potential of 0 to 0.45 V using a scan rate of 50 mV s\(^{-1}\). The electrochemical EIS was performed from 10\(^{-2}\) to 10\(^{5}\) \text{Hz} with an AC voltage of -5 mV. Galvanostatic charge discharge curves of H-Mo\(_2\)C/NG were recorded at \( j = -100, -200, \) and -300 mA cm\(^{-2}\). Prior to all measurements, the electrochemical system was purged with H\(_2\) bubbles for 30 min, and then conducted all electrochemical measurements at room temperature (25 \text{C}) under ambient atmosphere.

DFT calculations
The first-principles calculations based on the DFT were performed within generalized gradient approximation (GGA). Core electron states were represented by the projector augmented-wave method as implemented in the Vienna ab initio simulation package (VASP)\(^{13,14}\). The Perdew-Burke-Ernzerhof exchange-correlation functional and a plane wave representation for the wave function with a cut-off energy of 450 eV were used\(^3\), more details can be found in Supporting Information (Supplementary Note 6). The atomic coordinates of the H adsorption on the fcc/hcp GB model to generate Fig. 6e are listed in VASP CONTCAR format (Supplementary Data 1).

Data availability
The data supporting the findings of this study are available within the article and its Supplementary Information. Additional data are available from the corresponding authors on reasonable request. Source data are provided with this paper.

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Author contributions
Y.Y., Y.Q., Z.L., and X.F. conceived the experiment and scientific discussions. Y.Y. carried out the syntheses and electrocatalysis measurements. H.L., L.C., X.C., S.W., B.Z., Z.Z., S.C., W.Y., J.D., L.S., W.Z., R.F., J.Z., K.D., and X.-M.Z. carried out the characterizations. Z.L. and X.L. performed the atomic resolution microscopy and PED. Y.Q. carried out the computational investigation and provided the theoretical analysis. Y.Y. and X.F. wrote the paper. All the authors discussed the results and revised the paper.

Competing interests
The authors declare no competing interests.

Additional information

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