Hydrogen production from water splitting is one of the most promising approaches to achieve carbon neutrality when high-performance electrocatalysts are ready for the sluggish hydrogen evolution reaction (HER). Although earth-rich and cheap transition metal carbides (TMCs) are potential HER electrocatalysts, their platinum-like electronic structures are severely hampered by their strong binding with hydrogen intermediates (H\textsuperscript{2+}). Here, a universal “balance effect” strategy is proposed, where nitrogen-doped graphene (NG) is introduced to weaken the interactions of TMCs (M = Mo, W, Ti, and V) with H\textsuperscript{2+}. Hydrogen binding energies calculated by the density functional theory show that the TMCs coupled with NG appear to be thermo-neutral. Stemming from different work functions of TMCs and NG, partial electrons transfer from TMC to the NG surface, resulting in optimized electronic structures of these electrocatalysts. These optimized electronic structures balance hydrogen adsorption and desorption, leading to synergistically-enhanced HER kinetics. The overpotentials and Tafel slopes of the HER on these TMC@NG electrocatalysts are thus pronouncedly reduced in both acidic and alkaline solutions. This universal strategy provides a novel approach to design effective and stable TMCs as superior HER electrocatalysts. It can be expanded to other electrocatalysts for sustainable hydrogen production in different media.

1. Introduction

Global energy crisis and serious environmental pollution have severely urged our society to explore green and sustainable energy sources as the substitutes to replace conventional fossil fuels. As one of the most promising green energy, hydrogen has been paid much attention in past years, due to its zero CO\textsubscript{2}-emission and its high energy density\textsuperscript{[1–4]}. To efficiently produce hydrogen and at an industrial scale, electrochemical water splitting (H\textsubscript{2}O $\rightarrow$ H\textsubscript{2} + 1/2 O\textsubscript{2}) has been proposed as an effective method\textsuperscript{[5]}. On the other hand, hydrogen evolution reaction (HER) features sluggish kinetics. In these regards, various electrocatalysts have been designed and synthesized to accelerate this reaction\textsuperscript{[6]}. Up to date, most of remarkable HER electrocatalysts are still based on the Pt metal. Originating from a high price and the scarcity of the Pt metal, these Pt-based HER electrocatalysts are unfortunately not possible for industrial applications\textsuperscript{[7–10]}. Development of earth-abundant or cost-effective electrocatalysts with excellent HER performance (e.g., high efficiency and long-term stability) is thus still highly demanded for hydrogen production\textsuperscript{[10]}. Among various alternatives to the Pt-based electrocatalysts, transition metal carbide (TMC) has been deemed to be one of the most promising candidates to replace the Pt-based electrocatalysts, thanks to its unique “Pt-like behavior”\textsuperscript{[11–13]}. Inside a TMC, the d-band of a transition metal (TM) is significantly broadened, stemming from the hybridization between the d-orbitals of a TM and the s-/p-orbitals of a carbon atom in the...
related carbide. The resultant d-band state of a TMC is actually quite similar to the Pt metal.[14,15] TMCs also exhibit superior electrical conductivities and broader pH applicability when compared with TM oxides/sulfides/phosphides/nitrides.[16,17] In these regards, the kinetics of HER on the TMCs has been much boosted or the HER performance on the TMCs is outstanding (e.g., high catalytic activity and long-term stability). Unfortunately, the density of empty d-bands in most TMCs is high, results in the strong binding of a TMC electrocatalyst with hydrogen intermediate (H*)[18] In other words, the Heyrovsky or a Tafel step during the HER is severely inhibited on a TMC electrocatalyst, again resulting in the sluggish HER kinetics.[14,19] Although tremendous efforts have been devoted to weakening these binding interactions via intrinsically regulation of electronic structures of TMCs (e.g., heteroatom doping, heterointerface construction),[12,15] a universal route to optimize the d-band structure of TMCs is still missing in literature up to date.

To solve such a challenge, we propose a universal strategy, so-named “balance effect” to promote the HER activity of a TMC, where a second phase is introduced into a TMC to weaken its binding with H*. The second phase that was selected in this study is the nitrogen-doped graphene (NG) weaken its binding with H*. The second phase that was selected in this study is the nitrogen-doped graphene (NG) in that NG possesses a distinctly positive hydrogen-binding energy (ΔG1/2). A balanced electronic structure of on an NG-integrated TMC (TMC@NG) electrocatalyst is thus expected between a TMC electrocatalyst that features strong binding ability toward H* and a NG electrocatalyst that owns a distinctly positive ΔG1/2. Namely, hydrogen adsorption and generation can be tailored on the TMC@NG electrocatalyst. In this contribution, we report about theoretical verification of such a concept by means of density functional theory (DFT) calculations, followed by the details on the synthesis, characterization of several ultrafine NG-encapsulated TMC nanoparticles that are templated on carbon nanotubes (TMC@NG/CNTs). The HER performance of these TMC@NG/CNT electrocatalysts is highlighted with respect to their overpotentials and Tafel slopes in both the acidic and alkaline media. It is believed that this universal route is valid to other electrocatalysts that feature strong binding interactions with hydrogen and thus creates possibilities to design low-cost and long-term stable HER electrocatalysts for efficient hydrogen production, even at an industrial scale.

2. Results and Discussion

As a proof-of-concept, the DFT calculations were first performed to estimate the binding energies between H* and TMC@NG, TMC or NG by use of the Mo2C@NG, WC@NG, TiC@NG, and VC@NG model electrocatalysts (Figure S1, Supporting Information). The ΔG1/2 values on them are −0.744, −0.398, −0.709, and −0.487 eV, respectively. They values are much smaller when compared to the ΔG1/2 value of NG (0.532 eV), indicating the strong binding interaction between H* and different TMCs. In other words, both H* desorption and H2 production processes are much impeded on the TMCs (Figure 1a). The incorporation of TMCs with NG makes the ΔG1/2 values of the TMCs modulate to be thermo-neutral, which are 0.012, −0.083, 0.478, and 0.120 eV for the Mo2C@NG, WC@NG, TiC@NG, and VC@NG model electrocatalysts, respectively. Based on these ΔG1/2 values, a volcano curve of these model electrocatalysts was drawn (Figure 1b). Clearly, the TMC@NG electrocatalysts efficiently compromise the reaction barriers of H* adsorption and desorption steps.[23] Among these model TMC electrocatalysts, this balance effect on an Mo2C@NG model electrocatalyst is particularly pronounced.

To further confirm this proposed balance effect inside the TMC@NG electrocatalysts, a series of TMC@NG electrocatalysts were synthesized by means of a solvothermal method (Figure 1c). In the first step, polyaniline (PANI)-encapsulated TM oxide (TMO@PANI) precursors are obtained using an aniline polymerization process. The confinement of PANI is beneficial to avoid the aggregation of TMCs nanoparticles at high temperatures during the following reaction steps. Subsequently, the TMO@PANI precursors are transformed to TMC@NG/CNT during a facile magnesium thermal reaction process, where CNTs are used as both carbon source and the template.[24–26] During the course of this process, the PANI is carbonized to NG, which is further anchored to the TMCs, leading to the generation of the TMC@NG/CNT electrocatalysts. It is expected that an NG layer prevents the damage of the TMCs or the TMC@NG/CNT electrocatalysts are expected to feature high stability.

Clearly, these electrocatalysts feature different ability or efficiencies toward hydrogen adsorption and desorption (Figure 1d). An NG electrocatalyst is good at hydrogen desorption but poor at hydrogen adsorption in that an NG electrocatalyst possesses a distinctly positive ΔG1/2.[20–22] In contrast, on a TMC electrocatalyst, hydrogen adsorption is more pronounced or efficient than hydrogen desorption since the empty d-bands in most TMCs can bind strongly with H*.[18] After the introduction of an NG phase into a TMC, a balanced electronic structure of a TMC@NG is thus expected between a TMC and an NG. In this context, hydrogen adsorption and generation can be tailored on a TMC@NG electrocatalyst. The regulation of electronic structures of these TMC@NG electrocatalysts is named as a universal “balance effect” throughout this paper.

Since the proposed balance effect on an Mo2C@NG model electrocatalyst is particularly pronounced among these model electrocatalysts, the detailed characterization of an Mo2C@NG electrocatalyst is shown as a case study in the following section. First, the crystal structures of the Mo2C@NG/CNT and Mo2C/CNT electrocatalysts together with an MoO2@PANI precursor were examined by means of X-ray diffraction (XRD). In terms of XRD patterns of an MoO2@PANI precursor (Figure S2a, Supporting Information), the characteristic peaks appeared at 26.0°, 37.0°, and 53.5° are assigned to the (111), (211), and (312) planes of an MoO2 phase (PDF#65-1273), respectively. With respect to the Mo2C@NG/CNT and Mo2C/CNT electrocatalysts, their typical XRD peaks are located at 34.3°, 38.0°, 39.4°, and 52.1° (Figure 2a). These peaks correspond to the (100), (002), (101), and (102) facets of an Mo2C phase (PDF#65-8766) respectively. These results indicate successful synthesis of a hexagonal Mo2C phase in both electrocatalysts. The peak shown at about 26.2° is ascribed to the (002) plane of a graphite phase, originating from the NG/CNT component (Figure S2b, Supporting Information). The mass ratio of Mo in the Mo2C@NG/CNT electrocatalyst was then probed by means of inductively
coupled plasma optical emission spectrometer. It is 40.93 wt%, corresponding to an Mo2C mass loading of 43.49 wt% in the Mo2C@NG/CNT catalyst. To measure surface areas of both Mo2C@NG/CNT and Mo2C/CNT electrocatalysts, their N2 adsorption/desorption tests (Figure S3, Supporting Information) were conducted. The estimated surface area of the Mo2C@NG/CNT electrocatalyst is larger than that of the Mo2C/CNT electrocatalyst, confirming more active sites on the Mo2C@NG/CNT electrocatalyst or its potential as a more efficient HER electrocatalyst. In addition, the Raman spectra of the Mo2C@NG/CNT and Mo2C/CNT electrocatalysts were recorded (Figure 2b). The Raman peaks located at around 814 and 989 cm\(^{-1}\) for both electrocatalysts again confirm the formation of an Mo2C phase.\[27,28\] Other two distinct peaks appeared at about 1347 and 1584 cm\(^{-1}\) stem from the D-band and G-band of a carbon-based substrate, respectively.\[29,30\]

To elucidate the surface states of the Mo2C@CNT and Mo2C@NG/CNT electrocatalysts, X-ray photoelectron spectroscopy (XPS) was employed. The recorded XPS spectra were calibrated using C 1s (284.6 eV). In their XPS survey spectra (Figure S4, Supporting Information), the existence of the Mo, C, N, and O elements is clearly observed. In the high-resolution C 1s XPS spectrum of the Mo2C@NG/CNT electrocatalyst (Figure S5a, Supporting Information), the peaks at 284.0, 284.6, 285.5, 286.1, and 288.7 eV are attributed to the C−Mo, C−C, C=C, C−N, and O−C=O bonds, respectively.\[31,32\]

In the high-resolution N 1s XPS spectra of the Mo2C@NG/CNT and NG/CNT electrocatalysts (Figure S5b, Supporting Information), four types of N species are found: namely pyridinic N at 397.5 eV, pyrrolic N at 398.7 eV, graphitic N at 399.9 eV, and oxidized N at 401.3 eV.\[33\] The binding energies of these N species in the Mo2C@NG/CNT electrocatalyst are obviously more negative when compared with those of the NG/CNT electrocatalyst. Therefore, a part of electrons transfer from Mo sites to NG in the Mo2C@NG/CNT electrocatalyst. In addition, the density of Mo2C nanoparticles is also found to affect the amounts of these N species. In the Mo 3d XPS spectra of the Mo2C@NG/CNT (Figure 2c) and the Mo2C/CNT (Figure S6, Supporting Information) electrocatalysts, six peaks are deconvoluted into Mo\(^{2+}\), Mo\(^{4+}\), and Mo\(^{6+}\) species (Table S1, Supporting Information).\[34,35\] The Mo\(^{2+}\) species is from the Mo2C component, while the Mo\(^{4+}\) and Mo\(^{6+}\) species are supposed to lead to increased stability and catalytic activity.
result from the Mo\textsubscript{2}C oxidation when exposed to air, namely the MoO\textsubscript{2} and MoO\textsubscript{3} components, respectively.\[^{36}\] The binding energy of the Mo\textsubscript{2}C\textsuperscript{+} species in the Mo\textsubscript{2}C@NG/CNT electrocatalyst is more positive when compared with that in the Mo\textsubscript{2}C/CNT electrocatalyst. This result confirms again a part of electrons transfers from Mo sites to NG in the Mo\textsubscript{2}C@NG/CNT electrocatalyst.

The local coordination environment and electronic states of the Mo\textsubscript{2}C@NG/CNT electrocatalyst were further checked using the X-ray absorption fine structure spectroscopy. In addition to the Mo K-edge X-ray absorption near-edge structure (XANES) spectra of the Mo\textsubscript{2}C@NG/CNT electrocatalyst, the XANES spectra of the Mo\textsubscript{2}C/CNT electrocatalyst, an Mo foil, and an MoO\textsubscript{3} film were also recorded as the references (Figure 2d). The Mo\textsubscript{2}C@NG/CNT electrocatalyst exhibits different atomic configurations, suggesting its unique coordination environment around Mo atoms. This statement is also verified by the corresponding k space oscillation (Figure S7, Supporting Information).\[^{37}\] The Mo K-edge XANES spectra of the Mo\textsubscript{2}C@NG/CNT and Mo\textsubscript{2}C/CNT electrocatalysts indicate their similar valence states because the absorption energy of the Mo\textsubscript{2}C@NG/CNT electrocatalyst is close to that of the Mo\textsubscript{2}C/CNT electrocatalyst. The white line in the Mo K-edge derives from the electrons transited from the 2p-optial to a vacant 3d-optial. The peak intensity of the white line in the Mo\textsubscript{2}C@NG/CNT electrocatalyst is lower than that of the Mo\textsubscript{2}C/CNT electrocatalyst. This results from partial electron transfer from Mo atoms to NG, consistent with the result obtained from their XPS spectra.

Furthermore, the Fourier transform (FT) of the Mo extended XAFS (EXAFS) of the Mo\textsubscript{2}C@NG/CNT electrocatalyst, the Mo\textsubscript{2}C/CNT electrocatalyst, an Mo foil, and an MoO\textsubscript{3} film

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**Figure 2.** Characterization: a) XRD patterns and b) Raman spectra of the Mo\textsubscript{2}C/CNT and Mo\textsubscript{2}C@NG/CNT electrocatalysts. c) High-resolution XPS spectra of Mo 3d in the Mo\textsubscript{2}C@NG/CNT electrocatalyst. d) The normalized XANES spectra and e) FT-EXAFS curves at the Mo K-edge of the Mo\textsubscript{2}C@NG/CNT and Mo\textsubscript{2}C/CNT electrocatalysts as well as an Mo foil and an MoO\textsubscript{3} film. f) Wavelet transforms for the k\textsuperscript{2}-weighted Mo K-edge EXAFS of the Mo\textsubscript{2}C@NG/CNT and Mo\textsubscript{2}C/CNT electrocatalysts. g) TEM and h) HRTEM images of the Mo\textsubscript{2}C@NG/CNT electrocatalyst. i) The size distribution of Mo\textsubscript{2}C nanoparticles in the Mo\textsubscript{2}C@NG/CNT electrocatalyst.
were studied (Figure 2e). The peak in the EXAFS curve of the Mo@NG/CNT electrocatalyst is attributed to a Mo–C bond with a length of about 1.3 Å, which is shorter than that in the Mo/CNT electrocatalyst. This result re-confirms that the electrons are transferred from the Mo sites to NG. Other peaks in the EXAFS curve of the Mo@NG/CNT electrocatalyst can be assigned to the Mo–O and Mo–Mo bonds, respectively. Their bond lengths are about 1.6 and 2.6 Å, respectively. In comparison to those of the Mo/CNT electrocatalyst, an Mo foil, and an MoO3 film,

Among the wavelet transforms for the k2-weighted Mo K-edge EXAFS curve of the Mo@NG/CNT and the Mo/CNT electrocatalysts (Figure 2f) as well as an Mo foil and an MoO3 film (Figure S8, Supporting Information), the Mo@NG/CNT electrocatalyst exhibits the highest peak intensity, which corresponds to an Mo–Mo bond with a length of about 8.6 Å in the Mo@NG/CNT electrocatalyst. The length of this Mo–Mo bond is similar to that (8.5 Å) in the Mo/CNT electrocatalyst, but different from that in either an Mo foil (8.2 Å) or an MoO3 film (9.8 Å). The peak intensity of the Mo–C bond in the Mo@NG/CNT electrocatalyst is lower than that of the Mo/CNT electrocatalyst, revealing an apparent, local, and unsaturated coordination of the Mo@NG/CNT electrocatalyst. Consequently, partial electrons are transferred from Mo sites to NG, leading to the formation of an electron-rich NG layer.

The morphology of the Mo@NG/CNT electrocatalyst, especially the location and distribution of active Mo sites were investigated by means of transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Ultrafine Mo nanoparticles (yellow arrows) are clearly seen on the surface of CNTs (Figure 2g). The lattice of these anchored Mo nanoparticles features a d-spacing of 0.22 nm, which obviously belongs to the (101) plane of an MoC phase. The estimated thickness of an NG layer is about 0.36 nm (Figure 2h), evidencing its monolayer structure. The average size of the Mo@NG nanoparticles synthesized on the CNTs is about 1.3 nm (Figure 2i), ensuring an increased specific surface area of the Mo@NG nanoparticles and further their optimized HER activity. As control experiments, the morphology of the TMC@N-doped CNT electrocatalyst was also investigated by means of TEM and HRTEM (Figure S9, Supporting Information), where the anchored Mo nanoparticles are obviously agglomerated and overgrown on the surface of the CNTs. Such a uniform structure is not conducive to expose more active sites and expected to feature sluggish electrode kinetics. This phenomenon provides the evidence that the existence of NG significantly prevents the agglomeration and overgrowth of Mo nanoparticles during the magnesium thermal reaction. Further characterization of these Mo nanoparticles was carried out by means of high-resolution scanning TEM that was operated under a high-angle annular dark-field mode as well as corresponding energy-dispersive X-ray spectrometer elemental mapping (Figure S10, Supporting Information), where the uniform distribution of Mo, C, and N elements is confirmed in the Mo@NG/CNT electrocatalyst.

The HER performance of the Pt/C, Mo@NG/CNT, Mo2C/CNT, and NG/CNT electrocatalysts were assessed by recording their linear sweep voltammograms (LSVs) in both acidic and alkaline media. When a current density of −10 mA cm−2 is harvested on the Mo@NG/CNT electrocatalyst, the overpotentials of 160 and 135 mV are achieved in 0.5 M H2SO4 (Figure 3a) and 1 M KOH (Figure 3b), respectively. These overpotentials are much lower than those of the Mo2C/CNT and NG/CNT electrocatalysts under identical conditions.

To explore the effect of Mo2C loading on the HER performance of the Mo@NG/CNT electrocatalyst, the loading amount of Mo2C in such an electrocatalyst was varied during its synthesis process. The LSVs of the Mo@NG/CNT-1, Mo@NG/CNT-3, Mo@NG/CNT-7, and Mo@NG/CNT-9 electrocatalysts were then tested in both 0.5 M H2SO4 and 1 M KOH. As-obtained overpotential decreases with an increase of the loading amount of Mo2C in the Mo@NG/CNT electrocatalyst (Figure S11, Supporting Information). The minimum overpotential for the HER is noticed on the Mo@NG/CNT-7 electrocatalyst.
The corresponding Tafel slope of the Mo2C@NG/CNT electrocatalyst is 65 mV dec−1 in 0.5 M H2SO4 (Figure 3c), much smaller than that of the Mo2C/CNT electrocatalyst (106 mV dec−1) and that (196 mV dec−1) of the NG electrocatalyst. In 1 M KOH, the Tafel slope of the Mo2C@NG/CNT electrocatalyst is 41 mV dec−1 (Figure 3d), which is superior to that of the Mo2C/CNT electrocatalyst (78 mV dec−1) and the NG electrocatalyst (124 mV dec−1). These Tafel slopes imply that the HER mechanism on the Mo2C@NG/CNT electrocatalyst follows a Volmer–Heyrovsky route in both alkaline and acid media. Beyond these experiments, the HER performance of the Mo2C@N-doped CNT electrocatalyst was evaluated and further compared with that of the Mo2C@NG/CNT electrocatalyst. The overpotential and Tafel slope of the Mo2C@N-doped CNT electrocatalyst are larger than those of the Mo2C@NG/CNT electrocatalyst in both 0.5 M H2SO4 (Figure S13a,b, Supporting Information) and 1 M KOH (Figure S13c,d, Supporting Information). These results demonstrate the excellent structure of the Mo2C@NG/CNT electrocatalyst guarantees its superior HER performance in both acidic and alkaline media.

As an important indicator of an HER electrocatalyst for practical applications, the stability of the Mo2C@NG/CNT electrocatalyst during the long-term HER was investigated in both acidic and alkaline solutions. After running the HER for 20 h at a potential of either −160 mV (vs RHE) in 0.5 M H2SO4 (Figure 3e) or −135 mV (vs RHE) in 1 M KOH (Figure 3f), the monitored current densities in both cases remain stable during the whole process, indicating high stability of the Mo2C@NG/CNT electrocatalyst toward the HER. To further confirm the durability of the Mo2C@NG/CNT electrocatalyst, its characterization after such stability tests was conducted by means of TEM, XRD, and XPS. The XRD patterns of the Mo2C@NG/CNT electrocatalyst remain unchanged after these stability tests (Figure S14, Supporting Information). In the recorded XPS spectra (Figure S15, Supporting Information), no obvious changes of C 1s, N 1s, and Mo 3d features of the Mo2C@NG/CNT electrocatalyst are observed even after running the HER for over 20 h. As confirmed from the TEM and HRTEM images of the Mo2C@NG/CNT electrocatalyst after these stability tests (Figure S16, Supporting Information), its morphology and crystal structure remain similar with those of the fresh one. To further support this conclusion, the cyclic voltammetric measurements of the Mo2C@NG/CNT electrocatalyst were also conducted within a potential window of 0 to −0.16 (vs RHE) in 0.5 M H2SO4 and within a potential window of 0 to −0.14 (vs RHE) in 1 M KOH for 1000 cycles. The 1000th LSV recorded in the acidic (the inset of Figure 3e) and alkaline (the inset of Figure 3f) media feature similar shapes with their 1st LSV, respectively. The variation of the current densities in the LSVs before and after 1000 cycles of cyclic voltammetric measurements is negligible in both 1 M KOH and 0.5 M H2SO4. Therefore, the Mo2C@NG/CNT electrocatalyst exhibits excellent chemical and structural stability during the long-term HER test in both the 0.5 M H2SO4 and 1 M KOH. The merit of long-term HER stability of the Mo2C@NG/CNT electrocatalyst toward the HER is assumed to result from the unique configuration of NG and Mo2C since NG can completely prevent the dissolution of Mo2C nanoparticles from the electrocatalyst surface in the electrolytes.

To assess outstanding HER activity of this Mo2C@NG/CNT electrocatalyst, another crucial parameter of an electrocatalyst—electrochemically active surface area (ECSA) of the Mo2C@NG/CNT electrocatalyst was calculated. It is known that the ECSA value of an electrocatalyst is linearly dependent on its double-layer capacitance (Cdl).[18] For comparison, the cyclic voltammograms of several electrocatalysts studied in this work were recorded at different scan rates (Figure S17, Supporting Information). In 0.5 M H2SO4 the calculated Cdl values of the Mo2C@NG/CNT, Mo2C/CNT, and NG/CNT electrocatalysts are 8.1, 6.8, and 3.9 mF cm−2, respectively (Figure S18a, Supporting Information). In 1 M KOH they are 14.2, 8.0, and 3.6 mF cm−2, respectively (Figure S18b, Supporting Information). Clearly, the Mo2C@NG/CNT electrocatalyst possesses the largest ECSA and the highest roughness factor in both acidic and alkaline media (Table S2, Supporting Information). Compared with those of the Mo2C/CNT and NG/CNT electrocatalysts, the ECSA-normalized LSVs of the Mo2C@NG/CNT electrocatalyst exhibit the lowest overpotentials at the same current density in both acidic (Figure S18c, Supporting Information) and alkaline solutions (Figure S18d, Supporting Information). It has to point out that the Mo2C@NG/CNT electrocatalyst owns incomparable intrinsic catalytic activity and a high ECSA.[19] To further explore this statement, Nyquist plots of these electrocatalysts were also recorded, where the Mo2C@NG/CNT electrocatalyst shows lower charge-transfer resistances than the Mo2C/CNT electrocatalyst in both acidic (Figure S19a, Supporting Information) and alkaline solutions (Figure S19b, Supporting Information) media. Again, the favorable charge transfer on the Mo2C@NG/CNT electrocatalyst during the HER process is proved.[40,41] The superior HER activity of the Mo2C@NG/CNT electrocatalyst is assumed to be originated from the introduction of NG, enhanced intrinsic activity of an Mo2C electrocatalyst, and the weakened ΔG_H*. In other words, the balance effect existed in this electrocatalyst results in significantly improved HER performance. Note that in the Mo2C@NG/CNT electrocatalyst, the CNTs act as only the substrate and do not feature catalytic ability toward the HER. The DFT calculations were then conducted only using the Mo2C@NG model electrocatalyst to unveil as-mentioned optimization mechanism. The difference of the charge density of the Mo2C@NG electrocatalyst (Figure 4a; Figure S20, Supporting Information) reveals that the electrons transfer from Mo atoms to N atoms via a route of Mo→C→N. The C atoms in NG play the dual roles: as both electron acceptors and electron donors. The electron transfer effectively activates C atoms in NG, endowing excellent HER activity of this electrocatalyst. Moreover, the ΔAG_H* values of C1, C2, C3, N, Mo, and C3 sites were investigated to disclose the actual active centers of the Mo2C@NG electrocatalyst. The calculated ΔAG_H* value of the C3 site is only 0.012 eV (Figure 4b), much lower than the ΔAG_H* values of other sites (Table S3, Supporting Information). The C3 site is thus the active center in the Mo2C@NG electrocatalyst. Compared with the Mo2C electrocatalyst, the simulated density of state (DOS) of the Mo2C@NG electrocatalyst exhibits more occupations at the Fermi level (Figure 4c).
These results confirm that the incorporation of Mo₂C with NG simultaneously optimizes both the conductivity of Mo₂C as well as the adsorption strength of hydrogen and its radicals, ultimately leading to the improved HER catalytic activity.[42]

As for the HER activity of TM-based electrocatalysts, the d-band center ($\varepsilon_d$) is known as an effective descriptor.[43,44] In this regard, the $\varepsilon_d$ of the Mo₂C@NG electrocatalyst was calculated using a similar approach (Figure 4d). It is $-1.05$ eV, much smaller than that ($-0.76$ eV) of the Mo₂C electrocatalyst. Therefore, the Mo₂C@NG electrocatalyst exhibits a weakened hydrogen adsorption energy than the Mo₂C electrocatalyst.[45] The overlap of H 1s-orbital with C 2p-orbitals below the Fermi level in the Mo₂C@NG electrocatalyst is larger than that in the NG electrocatalyst (Figure S21, Supporting Information), illustrating that the bond strength between C and H atoms in the Mo₂C@NG electrocatalyst is stronger than that in the NG electrocatalyst.

To analyze the bond strength of the C—H bond in more detail as well as to obtain the antibonding/bonding states between C and H atoms, a crystal orbital Hamilton population (COHP) bonding analysis was performed on the Mo₂C@NG and NG electrocatalysts (Figure 4e). The bond strength between C and H atoms was quantitatively determined by taking the integral of $\triangle \text{ICOHP}$ up to the Fermi level. The calculated $\triangle \text{ICOHP}$ value for the Mo₂C@NG electrocatalyst is 4.66, larger than that (4.07) of the NG electrocatalyst. This larger $\triangle \text{ICOHP}$ is thus associated with a stronger bonding interaction between C and H* on the Mo₂C@NG electrocatalyst than on the NG electrocatalyst. Namely the C site in the Mo₂C@NG electrocatalyst has a more robust H* binding than that in the NG electrocatalyst. [46,47] These results confirm the validity of as-proposed “balance effect.” In short, hydrogen adsorption and desorption are balanced by optimizing the electronic structure of the Mo₂C@NG electrocatalyst.

To explore the activation mechanisms of the Mo₂C@NG electrocatalyst toward the HER, the kinetic energy barriers of both a Volmer step and a Heyrovsky step were calculated for the
Mo$_2$C@NG, Mo$_2$C, and NG electrocatalysts. In an acidic solution (Figure 4f), an H$^+$ ion is first adsorbed at the C$_1$ site to form an H$^*$ radical (namely following a Volmer step). This radical is then combined with an electron and an H$^+$ ion, leading to the generation of H$_2$ (namely following a Heyrovsky step). The ΔG$_{\text{H*}}$ value of a Volmer step on the Mo$_2$C@NG electrocatalyst is 0.012 eV (Figure 4g), much smaller than that on the Mo$_2$C (-0.744 eV) and NG (0.532 eV) electrocatalysts. Moreover, the energy barrier of a Heyrovsky step on the Mo$_2$C@NG electrocatalyst is 0.434 eV, lower than that on the NG (-0.441 eV) and Mo$_2$C (0.459 eV) electrocatalysts. In alkaline media (Figure 4h), two main stages are considered, including water dissociation to form an adsorbed H$^*$ radical (followed by a Volmer step) and hydrogen generation (followed by a Heyrovsky step). [48] The electron-rich N site in the Mo$_2$C@NG electrocatalyst significantly reduces the energy barrier of water dissociation to 0.411 eV (Figure 4i). Whereafter, the C$_1$ sites serve as the active sites for the Heyrovsky step. The energy barrier of this step on the Mo$_2$C@NG electrocatalyst is 0.012 eV. These theoretical calculation results indicate that the “balance effect” by coupling Mo$_2$C with NG efficiently optimizes the electronic structure of the Mo$_2$C@NG electrocatalyst, decreases the energy barrier of both Volmer and Heyrovsky steps, and eventually improves the HER performance of the Mo$_2$C@NG electrocatalyst in both acidic and alkaline media.

To further confirm the universality of the proposed “balance effect” (namely by introducing NG into TMCs), a series of similar TMC@NG/CNT (M = W, Ti, and V) electrocatalysts were synthesized. Their XRD results of these TMC@NG/CNT electrocatalysts (Figure 5a) prove their successful synthesis.

![Figure 5](image-url)

**Figure 5.** Universal TMC@NG/CNT electrocatalysts toward the HER: a) XRD patterns of three TMC@NG/CNT electrocatalysts. b) The iR-corrected LSVs and c) Tafel slopes of three TMC@NG/CNT and three TMC/CNT electrocatalysts in 0.5 M H$_2$SO$_4$. d) The iR-corrected LSVs and e) Tafel slopes of three TMC@NG/CNT and three TMC/CNT electrocatalysts in 1 M KOH. f) Overpotential comparison of three TMC@NG/CNT electrocatalysts with three TMC/CNT electrocatalysts at a current density of 10 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$ and 1 M KOH. The scan rate in (b,d) is 5 mV s$^{-1}$.

For example, the characteristic peak located at ~26° is associated with the (002) facets of the NG/CNT component. The HER performance of the TMC@NG/CNT and TMC/CNT electrocatalysts were then examined in both acidic and alkaline media. When a current density of 10 mA cm$^{-2}$ is reached in 0.5 M H$_2$SO$_4$, the overpotentials of the WC@NG/CNT, TiC@NG/CNT, and VC@NG/CNT electrocatalysts during the HER are 253, 268, and 428 mV, respectively (Figure 5b). These values are much lower than their pristine TMC/CNT electrocatalysts. Their Tafel slopes of these TMC@NG/CNT electrocatalysts also exhibit obvious drops in an acidic solution (Figure 5c). The Tafel slope of the TiC@NG/CNT electrocatalyst decreases over 71% in comparison to the Ti/CNT electrocatalyst. The WC@NG/CNT electrocatalyst has the lowest Tafel slope (60 mV dec$^{-1}$). Likewise, in 1 M KOH, the overpotentials (Figure 5d) and Tafel slopes (Figure 5e) of these TMC@NG/CNT electrocatalysts are lower than those of the corresponding TMC/CNT electrocatalysts. The WC@NG/CNT electrocatalyst features again the best HER activity (e.g., the lowest overpotentials of 304 mV at a current density of 10 mA cm$^{-2}$ and a Tafel slope of 76 mV dec$^{-1}$). The Tafel slopes of the TiC@NG/CNT and VC@NG/CNT electrocatalysts are reduced from 118 and 112 mV dec$^{-1}$ in acidic media to 80 and 82 mV dec$^{-1}$ in alkaline media, respectively. From the overpotential comparison of these TMC@NG/CNT and TMC/CNT (M = Mo, W, Ti, and V) electrocatalysts at a current density of 10 mA cm$^{-2}$ (Figure 5f), one can conclude that the introduction of NG into these TMCs enhances the HER performance of dec$^{-1}$ in alkaline media, respectively. From the overpotential comparison of these electrocatalysts in both
acidic and alkaline media, this “balance effect” is thus a universal strategy to effectively regulate hydrogen adsorption and desorption on the resultant electrocatalysts, leading to the production of high-performance electrocatalysts for efficient or promoted hydrogen generation.

3. Conclusion

A universal strategy—“balance effect” by the incorporation of the TMCs with NG, is proposed to achieve synergistically-enhanced HER kinetics. The DFT calculations confirm that the hydrogen adsorption energy on the TMC@NG electrocatalysts is thermoneutral. Both the overpotentials and Tafel slopes of the TMC@NG/CNT electrocatalysts for the HER are pronouncedly reduced in both acidic and alkaline solutions. These superefficient HER electrocatalysts profit from the optimization of their electronic structures and unique structural configurations. The electrons are proved to transfer from TMC to NG, bringing in balanced hydrogen adsorption and desorption and eventually promoted hydrogen generation. Meanwhile, the specific surface areas of hydrogen adsorption and desorption on the resultant electrocatalysts, leading to the production of high-performance electrocatalysts for efficient or promoted hydrogen generation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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