Tuning orbital orientation endows molybdenum disulfide with exceptional alkaline hydrogen evolution capability

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Molybdenum disulfide is naturally inert for alkaline hydrogen evolution catalysis, due to its unfavorable water adsorption and dissociation feature originated from the unsuitable orbital orientation. Herein, we successfully endow molybdenum disulfide with exceptional alkaline hydrogen evolution capability by carbon-induced orbital modulation. The prepared carbon doped molybdenum disulfide displays an unprecedented overpotential of 45 mV at 10 mA cm\(^{-2}\), which is substantially lower than 228 mV of the molybdenum disulfide and also represents the best alkaline hydrogen evolution catalytic activity among the ever-reported molybdenum disulfide catalysts. Fine structural analysis indicates the electronic and coordination structures of molybdenum disulfide have been significantly changed with carbon incorporation. Moreover, theoretical calculation further reveals carbon doping could create empty 2p orbitals perpendicular to the basal plane, enabling energetically favorable water adsorption and dissociation. The concept of orbital modulation could offer a unique approach for the rational design of hydrogen evolution catalysts and beyond.

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Sustainable hydrogen production in an economical way is the key to building new hydrogen-based energy systems. Water electrolysis driven by renewable energy sources such as solar, wind, or geothermal energy has been regarded as the most promising way for sustainable hydrogen production⁶–⁹. Despite the fact that water electrolysis is first discovered in an acidic condition, alkaline electrolysis is more preferred in industrial plants, due to the robustness of electrode materials, long lifetime, and cheap electrolyzer construction¹. Electrocatalysts, as the heart of the electrolysers, significantly affect the cell efficiency⁵. Unfortunately, precious platinum-based materials till now are still the state-of-the-art hydrogen evolution reaction (HER) catalysts in both acidic and alkaline conditions⁶,⁷. In this regard, developing non-noble metal-based HER catalysts to replace Pt has been one of the focal points over the past decades⁸–¹⁴.

Molybdenum disulfide (MoS₂), a typical cost-effective layered transition metal dichalcogenide¹³–¹⁸, has been proved both theoretically and experimentally to be highly active for HER catalysis in acidic condition¹⁶–²⁶. The edge Mo and S atoms with a free energy of H adsorption close to zero are commonly believed to be the catalytic sites¹⁹,²⁷–³⁰. Unfortunately, MoS₂ is found to be inactive in alkaline condition²⁷,³¹,³², while the alkaline catalysis is more practically viable. The inert alkaline electrolysis is mainly attributed to the sluggish water adsorption and dissociation dynamics, which is, in essence, determined by the intrinsic structural feature of MoS₂¹⁹,³³–³⁵. As the dominated orbital compositions of the conduction band in MoS₂, both the Mo 4d⁰ orbital in the central sublayer and the S 3pₓᵧ orbitals in the outermost sublayers possess unfavorable charge interaction with water molecule due to the steric effect (dₓ²) and unsuitable orbital orientation (3pₓᵧ) in the basal plane, which essentially hinder the water adsorption and dissociation on MoS₂ (Fig. 1). Although improving the conductivity of MoS₂³¹,³⁶,³⁷ or surface modification with water adsorption components¹⁹,³³,³⁴ has shown enhanced alkaline electrolysis, the overall performance of MoS₂ is still far from being satisfactory for practical alkaline electrolysis and studies on this issue are also very limited. Moreover, the understanding of the alkaline catalytic essences especially at atomic levels is also absent. Therefore, rationally tailoring the catalytic sites to endow MoS₂ with efficient alkaline HER catalytic activity is highly desirable but extremely challenging as well.

To essentially manipulate the intrinsic properties of MoS₂ for alkaline HER catalysis, tuning the orbital orientation of the MoS₂ layer to promote water adsorption and dissociation dynamics is the key. Considering carbon with smaller atomic radius and less electrons owns more empty and lower-energy 2p valence orbitals than sulfur, partially substituting S with carbon in MoS₂ could generate sp² hybrid sites in the outermost sublayers of MoS₂, which consequently vacate one p orbital perpendicular to the basal plane for water adsorption and activation. Herein, we successfully endow MoS₂ nanosheets with exceptional alkaline HER activities by carbon-induced surface orbital orientation modulation. Carbon is in-situ incorporated into MoS₂ through a unique incomplete sulfurization of Mo₂C. The prepared carbon doped MoS₂ (C–MoS₂) nanosheets display an unprecedented overpotential of 45 mV at 10 mA cm⁻² in alkaline condition, which represents the best alkaline HER activity among the ever-reported MoS₂-based catalysts. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) systematically reveal the structural and electronic evolution of MoS₂ after carbon doping. Moreover, density functional theory (DFT) analysis indicates carbon doping can generate empty p orbitals perpendicular to the basal plane of MoS₂ for water adsorption and dissociation, which is essential for the alkaline HER catalysis. More importantly, the capability to endow materials with the properties which are not readily available in nature by rational orbital modulation offers a new vision for the design of HER catalysts and beyond.

**Results**

**Synthesis and structural characterization of C–MoS₂.** C–MoS₂ and MoS₂ were synthesized via a controlled sulfurization of Mo₂C, which is illustrated in Fig. 2a. Mo₂C as the precursor was obtained by a previously developed method (details, see Methods)³⁸. Then, the as-synthesized Mo₂C was controllably sulfurized to C–MoS₂ and MoS₂ in a home-built tube furnace with sulfur powder as the sulfur source and argon as the carrier gas (details, see Methods). The synthesized Mo₂C, C–MoS₂, and MoS₂ were further characterized by field-emission scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectrum, and transmission electron microscopy (TEM), respectively. SEM images in Supplementary Fig. 1 indicate the carbon fibers of the carbon cloth (CC) substrate are uniformly coated with porous Mo₂C thin film, which becomes rougher after sulfurization treatment. XRD patterns (Fig. 2b) clearly reveal the Mo₂C (JCPDS No. 00-035-0787) can be well converted to hexagonal MoS₂ (JCPDS No. 01-073-1508) after controlled sulfurization treatment. The sharp diffraction feature of MoS₂ with deep sulfurization suggests improved crystallinity. In addition, the sulfurization process can also be revealed by Raman spectroscopy (Supplementary Fig. 2). The fingerprint bands of Mo₂C located at 662.5, 816.4, and 991.8 cm⁻¹ disappear after sulfurization treatment⁴⁰; meanwhile, new bands centered at around 376 and 402 cm⁻¹ emerge, which can be assigned to the in-plane (E₂g) and out-plane (A₁g) Mo–S phonon mode vibration of MoS₂, respectively⁴⁰. Moreover, the wavenumbers of E₂g and A₁g of C–MoS₂ display a positive shift relative to the MoS₂, probably due to the susceptibility of electron–phonon coupling induced by carbon doping¹¹,⁴². Taken together, all these results illustrate sulfurization treatment can well control the conversion from Mo₂C to MoS₂.

Furthermore, TEM was employed to acquire the microstructural features of Mo₂C, C–MoS₂, and MoS₂, as shown in Supplementary Fig. 3 and Fig. 2c. The high-resolution TEM (HRTEM) images exhibit well-resolved lattice fringes, where the interplanar spacing of 0.23 nm is assigned to the (101) plane of Mo₂C and 0.62 nm is assigned to the (002) plane of MoS₂, respectively. Interestingly, both C–MoS₂ and MoS₂ prepared by sulfurization treatment are composed of ultrathin layered MoS₂ nanosheets. It is also worth mentioning that no obvious carbon coating is observed on the surfaces of Mo₂C, C–MoS₂, and

![Fig. 1 The orbital analysis of the MoS₂. The top-view (upper) and side-view (lower) orbital compositions of the conduction band in MoS₂](image-url)
Mo$_2$C, C

at 231.1 and 228.0 eV in Mo$_2$C, while a pair of new peaks located C, Mo, and S elements in C

suggesting possible carbon doping in the MoS$_2$. Obviously, the typical characteristics of Mo

distribution of C, Mo, and S elements in C

be assigned to the Mo 3d$^{3/2}$ and Mo 3d$^{5/2}$ of Mo

respectively. Strikingly, the Mo 3d pre

edge regions are further assigned. The whole spectral intensity at 231.1 and 228.0 eV in Mo$_2$C, while a pair of new peaks located at 232.6 and 229.5 eV after deep sulfurization, which can be assigned to the Mo 3d$^{3/2}$ and Mo 3d$^{5/2}$ of Mo–S bond in MoS$_2$, respectively. Strikingly, the Mo 3d profiles in C–MoS$_2$ exhibit obvious shoulders at the lower binding energy region, suggesting the existence of multiple chemical states of Mo. The Mo 3d spectrum of C–MoS$_2$ can be further deconvoluted into two pairs of peaks corresponding to the chemical states of S–Mo–S and S–Mo–C, which indicates carbon has been substitutionally doped into the MoS$_2$ lattices (The fitting parameters are summarized in Supplementary Table 1). Meanwhile, the C 1s spectra of C–MoS$_2$ and Mo$_2$C (Supplementary Fig. 4, the fitting parameters in Supplementary Table 2) also support the existence of Mo–C bonds in C–MoS$_2$. In addition, the slight shift of S 2s position suggests the chemical environments around S atoms also slightly changes after carbon doping, which could be originated from the electronegativity difference between C and S.

To probe the evolution of localized coordination environment in MoS$_2$ induced by carbon doping, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) are performed. Figure 3b shows the Mo K-edge XANES spectra of Mo$_2$C, C–MoS$_2$, Mo$_2$C, and Mo foil, in which Mo foil is used as the reference. Apparently, the Mo foil possesses the smallest energy of absorption edge. Moreover, the enlarged Mo K-edge XANES curves (inset, Fig. 3b) reveal that the near-edge absorption energy of C–MoS$_2$ located between Mo$_2$C and Mo$_2$C indicates the average electron density around Mo in C–MoS$_2$ is higher than Mo$_2$C but lower than Mo$_2$C, which is consistent to the XPS Mo 3d spectra and also suggests the existence of Mo–C bonds in C–MoS$_2$. In addition, Mo K-edge extended EXAFS oscillation functions $k^2\chi(k)$ of Mo$_2$C, C–MoS$_2$, Mo$_2$C, and MoS$_2$ mixed with small amounts of Mo$_2$C (denoted as Mo$_2$C + MoS$_2$) are presented in Supplementary Fig. 5a, respectively. Clearly, the oscillation of C–MoS$_2$ is very similar to MoS$_2$, but quite different from Mo$_2$C and Mo$_2$C + MoS$_2$, convincingly indicating the C–MoS$_2$ possesses similar structure to MoS$_2$ and there is no obvious Mo$_2$C remaining in C–MoS$_2$. Moreover, the XPS depth profiling analysis also does not show obvious existence of Mo$_2$C (Supplementary Fig. 5b). Figure 3c displays the corresponding R-space curves of Mo after $k^2\chi(k)$ weighted Fourier transform. The shoulder peaks at around 1.9 and 2.9 Å in MoS$_2$ are originated from the Mo–S and Mo–Mo vectors, respectively. Considering the positions of Mo–C and Mo–O are very close and no obvious Mo–O states are observed in the XPS Mo 3d spectra, we reasonably believe the peak at 1.3 Å in C–MoS$_2$ could be assigned to the Mo–C bond. To more clearly reveal the coordination structures in C–MoS$_2$, wavelet transform (WT) with high resolution in both k and R spaces of Mo K-edge EXAFS oscillation are further performed. The whole WT contour spectra are shown in the Fig. 3d (the upper). The intensity maxima at $R = 1.9$ and 2.9 Å are attributed to the Mo–S and Mo–Mo bonds, respectively. Owing to the small bond length difference between Mo–C and Mo–S, more-refined first shell analysis of MoS$_2$ and C–MoS$_2$ is further carried out (Fig. 3d, the lower). Apparently, MoS$_2$ possesses only one contour centered at about $k = 5.4$ Å$^{-1}$, originated from the Mo–S bond, while C–MoS$_2$ presents one more maximum intensity at $k = 4.6$ Å$^{-1}$, which is very close to the Mo–C in Mo$_2$C centered at about $k = 4.5$ Å$^{-1}$ (Supplementary Fig. 6a) and far from the Mo–O in MoO$_2$ with the maximum intensity at $k = 6.0$ Å$^{-1}$ (Supplementary Fig. 6b), and thus can be well assigned to the Mo–C. Meanwhile, we also conduct the EXAFS fitting in the range of 1.1 to 2.3 Å by using the Mo–O and Mo–C path at 1.3 Å, respectively (Supplementary Fig. 6c,d). Based on the fitting parameters presented in the Supplementary Table 3, the R$_f$ value for the Mo–O model (2.9%) is much larger than that of the Mo–C path (1.1%), further suggesting the Mo–C path is more likely than the Mo–O path in the C–MoS$_2$. In light of the formation of Mo–C in C–MoS$_2$, the coordination environment of MoS$_2$ may also alter with carbon doping. Furthermore, the EXAFS
and Mo foil. 

Normalized Mo K-edge XANES spectra. Inset: the enlarged Mo K-edge XANES spectra.

Distribution of Fourier-transformed EXAFS signal of C

Faradaic efficiency of the catalytic performance toward HER.

C-MoS2 delivers higher current density and lower current onset potential dependent HER activities of C–MoS2.

Alkaline hydrogen evolution catalysis of C–MoS2. The alkaline HER catalysis is evaluated in 1.0 M KOH solution using a typical three-electrode system with the studied materials as the working electrodes, Hg/HgO as the reference electrode and graphite rod as the counter electrode. Figure 4a shows the linear sweep voltammetry (LSV) curves of CC, Mo2C, C–MoS2, MoS2, and Pt/C with a scan rate of 5 mV s–1, in which the blank CC and benchmark Pt/C are used as control samples. Impressively, C–MoS2 delivers higher current density and lower current onset potential than CC, MoS2, and Mo2C, indicating carbon doping can substantially improve the catalytic activity toward HER in alkaline condition. Carbon doping enables the overpotential of C–MoS2 at 10 mA cm–2 to be as low as 45 mV, which is much better than the 200 mV of Mo2C and 228 mV of MoS2 and even close to the catalytic activity of Pt/C (30 mV). Although the performance of C–MoS2 is not the best among all kinds of the HER catalysts including non-precious and precious catalysts, C–MoS2 represents the best alkaline HER activity among the ever-reported MoS2 (Fig. 4b and Supplementary Table 5 and 6) [19,32–34,36,37,46–48], which could provide valuable insights for the active site engineering. The faradaic efficiency of the C–MoS2 for HER catalysis is estimated to be around 97%. Given that temperature can well control the sulfurization degrees, we also study the sulfurization degree-dependent HER activities (Supplementary Fig. 8). With the increase of the sulfurization temperatures, the HER overpotentials display an inverse volcano-shaped feature. At the temperature below 500 °C, Mo2C cannot be completely converted to MoS2 and the corresponding catalytic activity is far less than that of the C–MoS2, further revealing C doping probably plays vital role in the HER catalysis. To probe the effects of carbon contents, we further study the carbon content dependent HER activities of C–MoS2 (Supplementary Fig. 9). Obviously, with the increase of carbon concentration, the catalytic activity of C–MoS2 increases and reaches a maximum value. However, further increasing the C ratio will result in performance decay probably due to too much destroy of the layered structures of MoS2, suggesting moderate carbon doping in MoS2 is essential for the HER catalysis. Additionally, Tafel slope can be used to probe the effects of carbon dopants on the rate-determining steps during HER process. Figure 4c displays the corresponding Tafel curves. The derived Tafel slope of MoS2 is around 129 mV dec–1, suggesting the alkaline HER catalysis on MoS2 undergoes Volmer mechanism and water dissociation is the rate-determining step. Importantly, C–MoS2 exhibits a substantially decreased Tafel slope of 46 mV dec–1, clearly revealing the sluggish water dissociation behavior has been significantly improved after carbon doping. Meanwhile, the exchange current densities for Mo2C, MoS2, C–MoS2, and Pt/C derived by Tafel extrapolation are 0.12, 0.25, 0.87, and 1.28 mA cm–2, respectively. Clearly, although the exchange current density of C–MoS2 is a little smaller than that of Pt, it is still substantially larger than that of MoS2, also suggesting carbon doping can change the intrinsic catalytic activities of MoS2 for alkaline HER catalysis.

Considering surface area may also affect the HER catalytic performance, we further estimate the electrochemical surface area of MoS2 and C–MoS2 are fitted through the Artemis to get detailed structural parameters (Supplementary Fig. 7 and Fig. 3e). The coordination number of Mo–S is fitted to be around 6 for the MoS2, while the coordination number of Mo–S is deceased to 4.8 and the coordination number of Mo–C is 1.1 in the C–MoS2. The detailed fitting parameters are summarized in Supplementary Table 4. Although we cannot exclude the existence of Mo2C clusters in C–MoS2 that is beyond the detection limits of the currently used characterization techniques, our experimental results clearly reveal that carbon is most probably doped into the lattices of MoS2 in the form of Mo–C bond.

Fig. 3 Chemical states and coordination structures of C–MoS2. a XPS core-level Mo 3d spectra of Mo2C, MoS2, and C–MoS2, respectively. b The normalized Mo K-edge XANES spectra. Inset: the enlarged Mo K-edge XANES spectra. c Fourier transform (FT) of Mo K-edge of Mo2C, C–MoS2, MoS2, and Mo foil. d The whole contour plots of wavelet transform (WT) of MoS2 and C–MoS2 (upper) and the more-refined first shell analysis (lower). e Radial distribution of Fourier-transformed EXAFS signal of C–MoS2.
areas of the studied materials by deriving the electrochemical double layer capacitance \( (C_{dl}) \) from the cyclic voltammetry studies (Supplementary Fig. 10). The C-MoS\textsubscript{2} is found to have a larger \( C_{dl} \) of 54 mF cm\(^{-2} \) than MoS\textsubscript{2} (19 mF cm\(^{-2} \)) and Mo\textsubscript{2}C (27 mF cm\(^{-2} \)), indicating carbon doping treatment can also increase the surface area of C-MoS\textsubscript{2}. To eliminate the influence of surface area and reveal the intrinsic catalytic behavior, turnover frequency (TOF), a surface area independent figure of merit, is calculated to gain the intrinsic per-site activity, as shown in Fig. 4d. Impressively, the TOF values of C-MoS\textsubscript{2} are significantly larger than those of MoS\textsubscript{2} and Mo\textsubscript{2}C, clearly revealing carbon doping can essentially promote the per-site activity for HER catalysis. Additionally, electrochemical impedance spectroscopy (EIS) in Fig. 4e presents that C-MoS\textsubscript{2} possesses a smaller charge transfer resistance \( (R_{ct}) \) of 32.1 \( \Omega \) than MoS\textsubscript{2} (83.7 \( \Omega \)) and Mo\textsubscript{2}C (59.7 \( \Omega \)), further suggesting carbon doping in MoS\textsubscript{2} can also substantially boost the interfacial electron-transfer kinetics. Besides carbon doping, the superior electrochemical behavior of C-MoS\textsubscript{2} is also attributed to the unique carbon doping strategy without involving carbon deposition on the catalyst surface. We also use a conventional post-doping method to introduce carbon and study their electrochemical performance, shown in Supplementary Fig. 11. TEM image clearly illustrates obvious carbon shell deposited on the surface of MoS\textsubscript{2}, which results in decreased catalytic performance probably due to the blocked active sites for catalysis (Supplementary Fig. 12). Given that the MoS\textsubscript{2} is derived from Mo\textsubscript{2}C which may have tiny amounts of carbon remaining, MoS\textsubscript{2} with minimum carbon interference is also prepared by thermal sulfurization of ammonium molybdate (Supplementary Fig. 13). Electrochemical studies reveal that the HER performance of the newly prepared MoS\textsubscript{2} is far less than that of C-MoS\textsubscript{2}, also suggesting carbon dopants play vital roles in the HER catalysis of C-MoS\textsubscript{2}. Finally, the stability of C-MoS\textsubscript{2} is evaluated by polarization cycling and chronoamperometric test, both of which display superior catalytic stability for alkaline electrolysis (Fig. 4f).

XPS and XAFS are further employed to evaluate the C-MoS\textsubscript{2} after the stability test (Supplementary Fig. 14). Impressively, there is no big difference in chemical and bonding states in C-MoS\textsubscript{2} before and after the durability test, suggesting the robustness of the C-MoS\textsubscript{2} for HER catalysis.

**Discussion**

To decipher the modulation essence of the carbon dopants in C-MoS\textsubscript{2} for alkaline HER catalysis at the atomic level, DFT calculations are further carried out. The C content used in the C-MoS\textsubscript{2} model is based on the area ratio of Mo–C and Mo–S states in the XPS Mo 3d of C-MoS\textsubscript{2}. In light of the charge balance after carbon doping, we also introduce sulfur vacancies (Vs) in the structural models. To equally distribute the positions of the C dopants and S vacancies, we considered seven different configurations, as shown in Supplementary Fig. 15. Supplementary Fig. 16 shows one of the typical structures of C-MoS\textsubscript{2}, where the C dopants are pulled into the sublayer of MoS\textsubscript{2} due to the formed stronger Mo–C bond with shorter bond length than the original Mo–S bond. Detailed bond length information is provided in Supplementary Fig. 17. The electron density difference images in Supplementary Figs 18 and 19 clearly reveal that the introduction of carbon can significantly break the unified surface electron distribution of MoS\textsubscript{2}. More importantly, the orbital analysis in Fig. 5a and b indicates the carbon dopants prefer to form the sp\(^2\) hybrid orbitals (highlighted by red dash circle in Fig. 5a), which thus vacates an unhybridized 2p\(_x\) orbital perpendicular to the basal plane (highlighted by red dash circle in Fig. 5b). This 2p\(_x\) orbital orientation can maximize the head-on orbital overlapping to form sigma bonds, which can potentially offer active sites for water adsorption and activation. This orbital orientation is also consistently observed on the other structural configurations of C-MoS\textsubscript{2}, as shown in Supplementary Fig. 15. Additionally, the detailed partial density of states (PDOS) analysis
(Supplementary Fig. 20) indicates that carbon doping can well increase the electrical conductivity of the MoS2 and thus could benefit the electron transportation and enhance the catalytic activity. Although conductivity is important for electrocatalysis, we reasonably believe the exceptional alkaline HER activity of C–MoS2 is mainly stemmed from the C-induced orbital tuning for water adsorption and dissociation, considering 1-T MoS2 with better conductivity does not exhibit such exceptional activity.46 Moreover, the electrostatic potential mapping images (Fig. 5c and Supplementary Fig. 21) and the electron density difference slices (Supplementary Fig. 22) further reveal superior water adsorption on the basal plane of C–MoS2, which is confirmed by the apparent charge transfer and the formation of remarkable chemical bonding orbital between water and C–MoS2 (Fig. 5c), while no apparent orbital bonding or charge interaction occurs on MoS2 (Fig. 5d). We also consider the MoS2 model with only sulfur vacancies. Structural analysis indicates sulfur vacancies indeed do not have obvious effects on the orbital orientation tuning (Supplementary Fig. 23a). The corresponding water adsorption energy on the defected MoS2 (MoS2-Vs) is around −0.23 eV, which is only slightly higher than that on the MoS2. Meanwhile, we also experimentally prepare MoS2 with sulfur vacancies via a typical hydrogen treatment and study their electrochemical properties. The overall performance of the hydrogen treated MoS2 is still far less than that of C–MoS2 (Supplementary Fig. 23b), suggesting the sulfur vacancy may not be the main factor for the exceptional alkaline HER activity of the C–MoS2. Taken together, all the structural information consistently suggest that carbon doping can effectively manipulate the orbital orientation and create more active sites on the basal plane of MoS2 for water adsorption and activation.

Besides structural information, alkaline HER catalytic pathways on the basal plane of MoS2 and C–MoS2 are further studied. Figure 5e shows the relative energy profiles of water adsorption and dissociation on MoS2 and C–MoS2, respectively. As expected, the basal plane of MoS2 is almost inert for alkaline HER catalysis, with poor water adsorption and giant water dissociation energy barrier. Impressively, carbon doping enables the HER catalysis to proceed on a much lower potential energy surface. Specifically, C–MoS2 owns more favorable adsorption energies (−0.53 eV for RC1 & −0.25 eV for RC2) and much lower transition state energy barrier (0.70 eV for TS1 & 1.15 eV for TS2). From the water adsorption/dissociation configurations on C–MoS2 (Fig. 5e), H2O is adsorbed on the C site, while the nearby S sites assist water dissociation by attracting the H in water molecule. In addition, we also performed the catalytic pathway of Mo2C (001) (Supplementary Fig. 24). Obviously, the reaction on the Mo2C proceeds on a potential energy surface with much higher energy barrier than that on C–MoS2. Moreover, the generated hydrogen adsorbed intermediate (Sur-H) is so stable that the adsorbed hydrogen needs overcome 1.37 eV for H desorption from the carbon site of the surface, which could potentially impede the HER catalysis. The studies on the catalytic pathways clearly reveal carbon doping could intrinsically boost the water adsorption and dissociation kinetics and thus endow MoS2 with exceptional alkaline catalysis by tuning the orbital orientations on the basal plane.

In summary, we have demonstrated carbon doping can intrinsically endow MoS2 with exceptional alkaline HER catalytic capability by tuning the orbital orientation. In comparison with the inert alkaline HER activity of MoS2, the prepared C–MoS2 achieves an overpotential of 45 mV at 10 mA cm−2, which is very close to the commercial Pt/C and also represents the best catalytic activity among the ever-reported MoS2 for alkaline HER catalysis. XPS and XAS analysis reveal that the electronic and coordination structures of MoS2 have been significantly altered after carbon doping. DFT studies further indicate that carbon-induced empty 2p orbitals perpendicular to the basal plane of MoS2 enable energetically favorable water adsorption and dissociation, and thus promote the alkaline HER catalytic kinetics. The capability to intrinsically manipulate the catalytic activities by orbital modulation could offer a powerful platform to rationally design HER catalysts and beyond.
Methods

Reagents and chemicals. Ammonium molybdate (NH4)6Mo7O24·4H2O. Potassium hydroxide, Cetyltrimethyl ammonium bromide (CTAB), Thiourea and Sublimed sulfur were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. CC was purchased from Shanghai Hesien Electric Co., Ltd.

Synthesis of MoC. Typically, 3.708 g ammonium molybdate and 1.638 g CTAB were dissolved in 30 mL and 180 mL deionized water with ultrasonic assistance, respectively. Then, the two solutions were mixed homogeneously by magnetically stirring for 30 min, and further aged for another 24 h to obtain a uniform emulsion. A volume of 15 mL of the as-prepared emulsion was transferred into a 20 mL Teflon-lined stainless steel autoclave with the pretreated CC (CC, 2.53 cm2, pretreated with nitric acid and deionized water, respectively) as the growth substrate. After keeping the autoclave at 200 °C for 20 h, the CC was taken out, cleaned by deionized water and dried at vacuum oven at 60 °C overnight. Finally, MoC was obtained by annealing the prepared samples at 900 °C for 6 h in a home-built tube furnace system under argon atmosphere.

Synthesis of C-MoS2 and MoS2. C-MoS2 and MoS2 were prepared by a temperature-controlled sulfurization process. The as-prepared MoC was sulfurized in a tube furnace system for 2 h with powdered sulfur as the sulfur source and argon as the carrier gas (flowing rate at 20 scm). The sulfurization temperatures can be tuned from 500 to 900 °C. The optimized C-MoS2 was achieved at 600 °C with a partial sulfurization, while MoS2 was fabricated at 900 °C with a deep sulfurization. As comparison, a post-doping strategy was employed to dope carbon electrodes, respectively. All the measurements were conducted in 1.0 M KOH HgO electrode and graphite rod were employed as the reference and counter electrodes, respectively. 

Mott-Schottky measurements were carried out using the CASTEP program in Material Studio package of Accelrys Inc51. The exchange-correlation functional was employed by the Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (LDA) with the ultrasoft pseudopotentials (USP). The van der Walls interactions was considered by the DFT dispersion correction (DFT-D). The number of plane wave was determined by an energy cutoff of 450 eV. The Brillouin zone was sampled by a 2 × 2 × 1 k-points grid for the structure optimizations and double k-points meshes were employed for the density of states (DOS) calculations, respectively. A complete linear synchronous transitions (LST) and quadratic synchronous transitions (QST) approach was used for the transition state searching. The convergence tolerances were set to 2.0 × 10⁻⁸ eV per atom for energy, 0.002 Å for maximum displacement, and 0.05 eV Å⁻¹ for maximum force. The models were formed by a periodic slab repeated in 6 × 2 × 1 direction.

Fourier transform k-space range of 3.1 Å⁻¹ was set to the best-fit value of 0.85 determined from fitting the data of MoS2. In order to fit the curves in the R-range of 1.1–3.4 Å, we considered Mo=C, Mo–Mo and Mo=S paths as the central-peripheral. For each path, the structural parameters, like coordination number (N), interatomic distance (R), and edge-energy shift (ΔE0) were fitted and used for the refining parameters, like coordination number (N), interatomic distance (R), and edge-energy shift (ΔE0) were fitted and used for the refining.

Density functional theory calculation. All the DFT calculations were carried out using the CASTEP program in Material Studio package of Accelrys Inc51. The exchange-correlation functional was employed by the Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (LDA) with the ultrasoft pseudopotentials (USP). The van der Walls interactions was considered by the DFT dispersion correction (DFT-D). The number of plane wave was determined by an energy cutoff of 450 eV. The Brillouin zone was sampled by a 2 × 2 × 1 k-points grid for the structure optimizations and double k-points meshes were employed for the density of states (DOS) calculations, respectively. A complete linear synchronous transitions (LST) and quadratic synchronous transitions (QST) approach was used for the transition state searching. The convergence tolerances were set to 2.0 × 10⁻⁸ eV per atom for energy, 0.002 Å for maximum displacement, and 0.05 eV Å⁻¹ for maximum force. The models were formed by a periodic slab repeated in 6 × 2 × 1 direction.

Data availability

The authors declare that the main data to support the findings of this study are available within the article and its Supplementary Information. Extra data are available from the corresponding author upon request.

Received: 17 August 2018 Accepted: 28 February 2019 Published online: 14 March 2019

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Acknowledgements
We thank the financial support of the National Key Research and Development Program of China (2017YFA0206703), National Science Fund of China (No. 21771169, 11225243, 11505187), the Fundamental Research Funds for the Central Universities (WK2060190074, WK2060190081, and WK2310000066), USTC start-up funding, and Recruitment Program of Global Expert. We also acknowledge the beamline BL10B at National Synchrotron Radiation Laboratory, and the Beamline BL14W1 at Shanghai Synchrotron Radiation Facility for XPS and XAFS characterizations. The numerical calculations in this paper have been done on the supercomputing system in the Supercomputing Center of University of Science and Technology of China.

Author contributions
G.W. and Y.Q. designed and supervised the project. Y.Z. and S.N. conducted the project and contributed equally to this work. J.Y., Y.W., and J.Z. conducted XPS and XAS measurements. J.C., Y.X., and J.Z. performed SEM and TEM characterization. X.L. and S.N. provided the DFT calculation. G.W., Y.Z., and X.L. wrote and revised the manuscript, and all the authors discussed the results and commented on the manuscript.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-019-09210-0.

Competing interests: the authors declare no competing interests.

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Journal peer review information: Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

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