Hydrogen production by water electrolysis is a centralized energy technology for indirect conversion and storage of sustainable but intermittent energy sources, such as solar energy, wind energy, and tide energy.[1,2] Due to high intrinsic catalytic activity, excellent chemical stability, and earth abundance, 2D layered transition metal dichalcogenides (e.g., MoS$_2$ and WS$_2$) have been regarded as the most promising candidates in substituting noble-metal platinum for catalyzing the cathodic hydrogen evolution reaction (HER) in water splitting.[3–5] Recently, theoretical and experimental studies have demonstrated that only the coordinatively unsaturated sulfur (S) and molybdenum (Mo) atoms along the edges of S-Mo-S molecular layers in semiconducting 2H-MoS$_2$ are the catalytically active sites, while a significant proportion of S atoms in 1T-MoS$_2$ basal planes are inert.[6,7] Although extensive efforts have been paid to maximally expose the active edge sites of 2H-MoS$_2$ for promoting the HER catalytic activities of MoS$_2$-based catalysts,[8–10] it is still a daunting challenge to realize extremely high density of active sites in 2H-MoS$_2$ due to inherently high surface energy of the edges and instabilities of the coordinatively unsaturated edge atoms.[9,11] Metallic IT-MoS$_2$ has recently been proposed to display excellent HER activity due to its superior HER energetics on the basal plane.[11–14] Nevertheless, the metastable nature of IT-MoS$_2$ poses a vital concern for long-term operational stability in practical applications.[15,16] Therefore, it holds great significance to develop effective strategies for triggering the catalytic ability of inert 2H-MoS$_2$ basal planes.

Heteroatom doping has been identified to be a promising route in enhancing the intrinsic activities of pristine active sites and/or triggering new active centers in MoS$_2$-based HER catalysts.[17–20] It has been predicted that doping transition metal atoms (Fe, Co, Ni, and Cu) into 2H-MoS$_2$ edges can enhance HER catalytic activity of S-edge sites. Unfortunately, the experimental results have demonstrated that the edge doping has very weak influences on the apparent HER activities of doped and edge-terminated MoS$_2$ catalysts, which is possibly attributed to the decrement of intrinsic activities of Mo-edge sites.[21] Some recent reports have theoretically demonstrated that the incorporation of dopant atoms (e.g., Pt, Pd, Co, and Ni) can trigger HER catalytic activity in the inert 2H-MoS$_2$ basal planes, while the effects of the doping atoms in the edges and basal planes on HER activity of free MoS$_2$ nanosheets are hardly distinguished experimentally.[21–20] Besides, poor conductivity and restacking of MoS$_2$ nanosheets are two important factors, which depress HER catalytic activity in reported MoS$_2$-based electrocatalysts.[27–30] Taken together, multiscale electronic and
structural engineering would be more effective to upgrade apparent HER activities of MoS₂-based catalysts by synergistically enhancing the intrinsic activity of each active site and raising the density of electrochemically accessible active sites.

In this work, we systematically investigated the effects of ruthenium (Ru) doping into the basal plane of 2H-MoS₂ on its HER activity. Experimentally, we prepared composition-tunable Ru-doped MoS₂ nanosheets, which epitaxially sheath around multiwalled carbon nanotube (CNT). This unique core/shell structure of Ru-MoS₂/CNT can ensure fast charge transfer, efficient mass transport, and exclusive exposure of the basal plane atoms of Ru-MoS₂. Electrochemical characterizations indicate that Ru-doping significantly promotes HER catalytic activities of Ru-MoS₂/CNT in terms of exchange current density, onset potential, and Tafel slope. Theoretically, density functional theory (DFT) calculations reveal that Ru-doping in MoS₂ effectively modulates the electronic properties of the adjacent in-plane S atoms, which displays optimum hydrogen binding energy and significantly reduced energy barriers for water adsorption and dissociation.

Ru-MoS₂/CNT was prepared according to our previously reported method for the synthesis of MoS₂/CNT with the introduction of RuCl₃ as the dopant source (see experimental details in the Supporting Information). The detailed structural features of representative Ru-MoS₂/CNT with Ru doping amount of 5 at% were first investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Except for a weak diffraction signal around 26.2° from CNT, other diffraction peaks in the XRD pattern of 5%Ru-MoS₂/CNT are indexed to hexagonal 2H-MoS₂ (Figure S1, Supporting Information). Z-contrast scanning TEM (STEM) and bright-field TEM images indicate that the microstructural units of 5%Ru-MoS₂/CNT feature hollow tubular structure with smooth surface (Figure 1a,b). High-resolution TEM images show that few-layered MoS₂ nanosheets epitaxially sheath around the CNT core (Figure 1c and Figure S2, Supporting Information). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping results confirm highly uniform distribution of Mo, S, and Ru elements in the Ru-MoS₂ shell around CNT (Figure 1d). It is noted that cubic phase RuS₂ nanocrystals (~3–8 nm in size) were intimately grown on CNT when MoCl₅ was completely replaced by RuCl₃ in the synthesis of Ru-MoS₂/CNT (Figure S3, Supporting Information). However, there are no diffraction peaks assignable to RuS₂ in the XRD pattern of Ru-MoS₂/CNT with Ru doping amount up to 10 at% (Figure S4 and Table S1, Supporting Information). Because the atomic number of Ru is very close to that of Mo and the Ru-doping amount is relatively low, no obvious peak shifts are observed in the XRD patterns of Ru-MoS₂/CNT. TEM characterizations further confirm the absence of observable crystalline RuS₂ species in 10%Ru-MoS₂/CNT (Figure S5, Supporting Information). Furthermore, our theoretical calculation results have demonstrated that Ru atoms could be stably doped into 2H-MoS₂ by substituting Mo atoms and coordinating to six S atoms (Figure S6, Supporting Information). In light of above results, it could be firmly validated that Ru atoms are uniformly doped into the MoS₂ shell of Ru-MoS₂/CNT (Figure 1e).

Multiple spectroscopic characterizations were performed to investigate the structural and electronic properties of Ru-MoS₂/CNT. Raman spectra of CNT, MoS₂/CNT, and 5%Ru-MoS₂/CNT were acquired to probe the effects of Ru-doping on the crystalline structure of MoS₂ and the interactions between the CNT core and Ru-MoS₂ shell (Figure 2a). Both MoS₂/CNT and 5%Ru-MoS₂/CNT exhibit two characteristic in-plane (E₁₂₉) and out-of-plane (A₁₅) vibration peaks of 2H-MoS₂. The inappreciable shift and broadening of E₁₂₉ and A₁₅ peaks as well as
similar intensity ratio of E\textsubscript{2g}/A\textsubscript{1g} indicate that Ru-doping does not introduce substantial structural defects or lattice strain in MoS\textsubscript{2}.\textsuperscript{32} In the high-frequency region, the Raman spectra of these three samples exhibit two distinct peaks centered at 1348 and 1590 cm\textsuperscript{-1}, which are associated with the D and G vibration modes of graphitic structure, respectively.\textsuperscript{33} Notably, the intensity ratios of D/G in Raman spectra of MoS\textsubscript{2}/CNT and 5%Ru-MoS\textsubscript{2}/CNT are reduced to 0.76 and 0.73, respectively, significantly smaller than that of CNT (1.07), suggesting partial removal of oxygen-containing defects on CNT (Figure S7, Supporting Information). The decrease of defects on CNT is due to the removal of oxygen-containing groups and reordering of graphitic basal planes during thermal sulfidation in the preparation of Ru-MoS\textsubscript{2}/CNT.\textsuperscript{34} The less defective CNT core could endow higher charge mobility in Ru-MoS\textsubscript{2}/CNT. Additionally, the disappearance of 2D vibration peaks in the Raman spectra of MoS\textsubscript{2}/CNT and 5%Ru-MoS\textsubscript{2}/CNT is probably caused by the strains at the interfaces between CNT core and MoS\textsubscript{2} or Ru-MoS\textsubscript{2} shells, indicating a strong interface interaction that is favorable to the charge transfer.\textsuperscript{34–36}

X-ray photoelectron spectroscopy (XPS) analyses were further performed to study the electronic effects on Ru-MoS\textsubscript{2}/CNT induced by Ru-doping. All the adventitious carbon peaks in XPS spectra of the surveyed samples were first calibrated to 284.5 eV (Figure 2b). Compared to those of MoS\textsubscript{2}/CNT, both Mo 3d and S 2p XPS spectra of 5%Ru-MoS\textsubscript{2}/CNT show a shift of 0.25 (±0.02) eV toward low binding energy, which is probably attributed to the combined effect of the work function change and altered electronic structures of Mo and S in Ru-MoS\textsubscript{2}/CNT and RuS\textsubscript{2}/CNT with different Ru-doping amount (Figure 2c,d).\textsuperscript{37,38} The negative shifts of Mo 3d and S 2p spectra are consistently observed in Ru-MoS\textsubscript{2}/CNT with different Ru-doping amount (Figure S8, Supporting Information). Notably, the bonding energy peaks of S 2p and Ru 3p core levels in RuS\textsubscript{2}/CNT are significantly different from those in Ru-MoS\textsubscript{2}/CNT, displaying a positive shift of 0.65 eV and a negative shift of 0.78 eV, respectively (Figure 2d,e). The energy shift is also observed in the Ru 3d XPS spectra (Figure 2b). These results not only indicate that the chemical states of Ru atoms in Ru-MoS\textsubscript{2}/CNT are significantly different from those in RuS\textsubscript{2}/CNT but also provide a powerful evidence that Ru atoms are stably doped into MoS\textsubscript{2} lattice.

Alkaline HER is more competitive to be enrolled in large-scale hydrogen production in viewing that very few low-cost electrocatalysts possess satisfactory activities and stabilities for anodic oxygen evolution reaction in acidic or neutral media.\textsuperscript{39–53} Herein, the electrocatalytic HER performance of Ru-MoS\textsubscript{2}/CNT hybrids was evaluated in alkaline 1 m KOH electrolyte. The polarization curves in Figure 3a show that the HER activities of Ru-MoS\textsubscript{2}/CNT are significantly higher than that of MoS\textsubscript{2}/CNT and sensitive to Ru doping amount. 5%Ru-MoS\textsubscript{2}/CNT exhibits the highest electrocatalytic activity among these Ru-MoS\textsubscript{2}/CNT hybrids and is even better than RuS\textsubscript{2}/CNT (Figure S9, Supporting Information). Specifically, for achieving \( j = -10 \) mA cm\textsuperscript{-2}, 5%Ru-MoS\textsubscript{2}/CNT requires an
overpotential of 50 mV, which is about 141 and 36 mV smaller than that of MoS$_2$/CNT and 2%Ru-MoS$_2$/CNT, respectively (Table S2, Supporting Information). The Tafel slopes of both MoS$_2$/CNT and Ru-MoS$_2$/CNT are in the range from 40 to 120 mV dec$^{-1}$ (Figure 3b and Figure S10, Supporting Information), suggesting the Volmer–Heyrovsky HER mechanism.[29] The remarkably small Tafel slope of 5%Ru-MoS$_2$/CNT over that of MoS$_2$/CNT suggests superior HER kinetics in 5%Ru-MoS$_2$/CNT.[54,55] Better HER activity of 5%Ru-MoS$_2$/CNT than MoS$_2$/CNT is also reflected by its faster electrode kinetics in view of its smaller charge transfer resistance derived from the electrochemical impedance spectrum (EIS) (Figure 3c). The difference of electrochemically accessible surface area (ECSA) of MoS$_2$/CNT, 2%Ru-MoS$_2$/CNT, and 5%Ru-MoS$_2$/CNT electrodes was estimated by determining their double-layer capacitance ($C_{dl}$) by a reported cyclic voltammetry method (Figure S11, Supporting Information).[40] It can be found that the $C_{dl}$ increases as the rise of Ru-doping amount in Ru-MoS$_2$/CNT (Figure 3d).

Considering their structural similarities, the correlation of $C_{dl}$ and Ru content in Ru-MoS$_2$/CNT indicates more active sites are generated by Ru-doping in Ru-MoS$_2$/CNT. However, the slight increase of ECSA of Ru-MoS$_2$/CNT over MoS$_2$/CNT cannot fully account for their significantly enhanced HER activities.

The catalytic durability of 5%Ru-MoS$_2$/CNT was assessed by accelerated degradation test (ADT) and chronopotentiometry. A negligible negative shift of the polarization curve is observed after 5000 continuous cyclic voltammetry sweeps in the potential window between −0.15 and 0.05 V at a scan rate of 100 mV s$^{-1}$ (Figure 3e). Additionally, only a slightly increased overpotential of 23 mV is required to achieve a current density of $-10$ mA cm$^{-2}$ after continuous operation over 36 h (Figure 3f). The periodically recorded H$_2$ Faradaic efficiencies during the chronopotentiometry test are determined to be nearly 100% by online gas chromatograph (Figure 3f). Post-HER characterizations including TEM, EDS, Raman, and XPS analyses show that the compositions, morphology, and structure of 5%Ru-MoS$_2$/CNT...
have no observable changes after the chronopotentiometry test (Figures S12 and S13, Supporting Information). These results are indicative of excellent durability of 5%Ru-MoS2/CNT for alkaline HER. Thus, the outstanding electrocatalytic activity and durability enable 5%Ru-MoS2/CNT to be a promising candidate to compete with other HER catalysts for being used in water electrolysis (Table S3, Supporting Information).

Density functional theory (DFT) calculations were performed to deeply understand the roles of Ru-doping in improving HER activity of Ru-MoS2/CNT. In our theoretical model, a 4 × 4 unit cell of MoS2 with Ru-doping density θ = 1/16 adopts a representative basal plane configuration with isolated Ru doping atom. The calculated total density of states (DOS) of MoS2 reveal a bandgap of 1.21 eV, which is consistent with previously reported theoretical and experimental results (Figure 4a).[22,56] The Fermi level of Ru-MoS2 moves closer to the conduction band, indicative of a n-type Ru doping. Additionally, some new gap states appear around the Fermi level in Ru-MoS2. These hybridized electronic states have been revealed to be responsible for enhanced hydrogen binding at the in-plane S sites.[18,22] For alkaline HER, it has been reported that the energy barriers for water adsorption and dissociation as well as hydrogen binding energy all strongly correlate with HER activity on catalyst surface.[57–59] As shown in Figure 4b, Ru-MoS2 shows much smaller water adsorption energy change than that of pristine MoS2, indicating that water molecules are more easily adsorbed on Ru-MoS2 surface to afford the proton source for HER.[59] After the theoretical identification that in-plane S sites are the active centers, our calculation results show that water dissociation energy barrier is remarkably lowered at the in-plane S sites neighboring to the doped Ru atoms in Ru-MoS2 (Figure S14, Supporting Information). Moreover, the hydrogen adsorption free energy (ΔG_H) on the Ru-bonded in-plane S sites is strikingly reduced to about 0.19 eV, which is very close to thermoneutral value of ΔG_H (Figure 4c,d). According to Sabatier principle, a moderate ΔG_H is conducive to the balance of hydrogen adsorption and desorption, and thus improving HER thermodynamics and kinetics.[6] The superiority of the improved ΔG_H on Ru-MoS2 has also been demonstrated by significantly enhanced acidic HER activity of Ru-MoS2/CNT (Figure S15, Supporting Information). Thus, the theoretical results reveal that Ru-doping can efficiently activate the inert basal plane S sites in MoS2 for HER by synergistically improving the water adsorption, dissociation, and hydrogen adsorption/desorption.

In summary, we have designed and synthesized a novel core/shell structured Ru-MoS2/CNT catalyst and demonstrated its superior catalytic performance toward HER. In combination with theory and experiment, we proved that Ru-doping into basal planes of MoS2 is feasible and is an effective methodology for activating the S atoms of inert 2H-MoS2 basal planes for HER. The multiscale electronic and structural engineering strategy developed in this work will open up many new opportunities in exploring cost-effective electrocatalysts based on transition metal dichalcogenides for practical applications.

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.

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