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# Interfacial modulation of Ru catalysts by B, N co-doped porous carbon-confined MoC quantum dots for enhanced hydrogen evolution reaction performance<sup>†</sup>

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The development of high-performance electrocatalysts that rival Pt catalysts is crucial for efficiently driving hydrogen evolution reaction (HER) to produce H<sub>2</sub>. Herein, we engineer a sophisticated interfacial modulation of the Ru catalyst by constructing B, N co-doped porous carbon confined ultra-small MoC quantum dots (MoC@BNC) as an advanced catalyst carrier and stimulator. Combined experimental and theoretical calculations prove enhanced electron interaction between the Ru catalysts and the MoC quantum dots. Additionally, the B, N co-doped carbon substrate further refines the electronic structure of MoC, reinforcing the modulation of Ru catalysts. The Ru/MoC@BNC catalyst embodies a boosted H<sub>2</sub>O dissociation ability with a lowered H bonding strength, which promises an outstanding HER performance with an overpotential of 14 mV at 10 mA/cm<sup>2</sup> in an alkaline solvent. Furthermore, robust catalytic stability is achieved with almost zero deterioration after the cycling test. This result exemplifies the importance of interfacial manipulation of the Ru catalyst to promote HER catalytic performance.

# 1. Introduction

Hydrogen  $(H_2)$ , as a green and efficient carbon-free energy source, has demonstrated great potential to address the energy crisis and climate change.1-3 To embrace the H2-fueled society in the future, reliable H<sub>2</sub> production technology is the crucial premise. At present, electrochemical water splitting (with electricity derived from renewable energy) has been demonstrated to be a decent approach to producing H2.4-6 Efficient catalyst exploitation is pivotal to accelerate the hydrogen evolution reaction (HER) for large-scale H<sub>2</sub> production.<sup>7,8</sup> Platinum (Pt)-based catalysts are regarded as the state-of-the-art catalyst for HER in an acid solvent, which guarantees almost a zero overpotential.9 However, two or three times activity attenuation is encountered for Pt catalyst when working in an alkaline environment, due to the involvement of more sluggish HO-H splitting procedures.<sup>10</sup> Meanwhile, the superiority of Pt catalyst is largely discounted considering its expensive price and scarcity, which necessitates the exploration of high-performance non-Pt catalysts for HER in an alkaline environment to promote the practical application.<sup>11</sup>

Benefitting from the attractive price (at least 1/3 of Pt) and remarkable H bonding ability, Ruthenium (Ru) based catalysts have stood out to be a competitive non-Pt candidate.12-14 However, the catalytic performance of the Ru catalyst still should be boosted due to the over-strong Ru-H bond, which leads to a kinetically slow Tafel pathway.<sup>15</sup> Meanwhile, Ru with high cohesive energy tends to aggregate in the electrolyte, leading to stability deterioration during the HER process.<sup>16</sup> To address the above demerits, engineering a suitable carbon substrate, which owns superiority of high specific surface area, remarkable electron conductivity, outstanding chemical stability, etc., to confine Ru catalyst both geometrically and electrically has been proven to be a valid strategy. The abundant anchoring sites on the surface of carbon could tether the small Ru nanoparticles to facilitate active site exposure.<sup>17,18</sup> Moreover, the interfacial electronic interaction may manipulate the electronic structure of the Ru catalyst to optimize H adsorption, thereby increasing the intrinsic activity.<sup>19,20</sup> Zhang et al. utilized carbon dots to coordinate with Ru clusters, which demonstrated an enlarged active surface and promoted electron conductivity, leading to an excellent HER performance.<sup>21</sup> Li et al. successfully developed C<sub>60</sub> molecules tethered Ru catalyst, which induced electrons flowing from Ru to C<sub>60</sub> through the Ru-O-C<sub>60</sub> interface. The electronic metal-support interaction optimized the H adsorption and promoted H<sub>2</sub> productivity.<sup>22</sup> To better realize the efficacy of the carbon support, surface functionalization or heteroatom doping are the most common tactics. Baek et al. applied -COOH functionalized carbon nanotubes to support ultra-fine Ru catalysts.<sup>23</sup> The Ru-C sites possessing a proper H binding strength were verified to be the plausible root for enhancing HER activity. Zhou et al. constructed a Mott-Schottky hybrid by loading Ru clusters on the N-doped carbon nanofiber.24 A builtin electric field was created in the interface to steer the electron transfer from Ru to the N-doped carbon surface, which prompted a fast charge delivery and a lowered intermediate adsorption, leading to an excellent HER performance. Zhang et al. built Ru-

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S bonds by loading Ru on N, S co-doped hollow carbon sphere to tune the electronic and coordination environment of the Ru catalyst, which resulted in the optimizing of \*H adsorption energy.<sup>25</sup> Wang et al. reported the function of N, P co-doped carbon to electronically modulate and confine Ru catalyst to guarantee a stable HER performance.<sup>26</sup> We recently engineered a B, N co-doped polar carbon surface to establish an electron communication with the Ru catalyst, which exerted a moderate electronic modulation of the Ru catalyst to stimulate the H<sub>2</sub>O activation capability.<sup>9</sup>

Transition metal carbide (TMC), exemplified by molybdenum carbide (MoC), shares a noble-metal analogical electronic structure.<sup>27-29</sup> Despite the pessimistic activity when using sole MoC directly as the HER catalyst, an optimistic chance holds in applying MoC as a promising catalyst support to better disperse and engender a strong metal and support interaction (SMSI) with the supported catalyst.28,30 Tremendous progress has been achieved for the MoC-supported catalyst to stimulate the catalytic performance, wherein the interfacial electronic modulation was affirmed to be supremely pivotal.<sup>31</sup> However, MoC is traditionally synthesized by high-temperature calcination, which inevitably causes particle agglomeration and specific surface area reduction, leading to limited surface exposure. Considering the advantageous features of highly porous carbon material for HER, it will be intriguing to build advanced catalyst support by binding highly dispersed MoC nanoparticles.32,33 The MoC quantum dots with enlarged accessible surfaces could guarantee maximized interfaces with the catalyst to enhance the interfacial modulation effect. Taking a further step, by surface modification of the carbon substrate by heteroatom doping, the electronic structure of MoC could be further tailored, which will cause electronic feedback to the loaded catalyst to tune the interfacial interaction.<sup>34,35</sup>

In this work, ultra-dispersed MoC quantum dots (with a mean size of about 1.8 nm) are successfully implanted on the surface of B, N co-doped porous carbon material, which is further applied to confine Ru clusters. The relationship between catalyst structure and HER performance is profoundly investigated. This work will offer meaningful guidance for the further development of Ru-based catalyst for HER.

# 2. Experimental

# 2.1 Materials

Melamine was purchased from Sinopharm Chemical Reagent Co., Ltd. glucose, ammonium heptamolybdate tetrahydrate  $((NH_4)_6Mo_7O_{24}\cdot 4H_2O)$ , ethanol anhydrous, Commercial 20% Pt/C, were purchased from Macklin. H<sub>3</sub>BO<sub>3</sub> was purchased from Aladdin Industrial Co., Ltd. Ruthenium chloride trihydrate (RuCl<sub>3</sub>·xH<sub>2</sub>O), and Nafion solution (5 *wt.*%) were purchased from Sigma-Aldrich. All solvents and chemicals were used as bought without further purification.

# 2.2 Material synthesis

**2.2.1 Synthesis of MoC@BNC.** 3.03 g of melamine, 0.20 g of glucose, 0.014 g of  $H_3BO_3$ , 0.07 g of  $(NH_4)_6Mo_7O_{24}$ · $4H_2O$  were dissolved in 40 mL of deionized (DI) water under stirring, which was heated to 80 °C for about 5 h, until the solvent was completely evaporated. Then, the collected white solids were dried in an oven at

60 °C overnight and calcined under Ar atmosphere at 800 °C for 2 h to produce MoC@BNC.

**2.2.2** Synthesis of MoC@NC, BNC, NC. Synthesis procedure of MoC@NC was similar to that of MoC@BNC except that  $H_3BO_3$  was not added. BNC was synthesized by avoiding adding of  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ . NC was produced without the presence of  $H_3BO_3$  and  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ .

**2.2.3** Synthesis of Ru/MoC@BNC, Ru/MoC@NC, Ru/NC catalyst. Ru catalyst was loaded on the support by an incipient impregnation method. After vacuum drying at 60 °C for 12 h, the sample was reduced at 500 °C for 2 h in a 10 *vol.*% H<sub>2</sub> (Ar balanced) atmosphere. The product was named as Ru/MoC@BNC, Ru/MoC@NC, and Ru/NC, respectively.

# 2.3 Structure characterizations

Emission scanning electron microscope (SEM) and energy dispersion spectrum (EDS) were characterized by a Nippon Electron JSM-7800F. Transmission electron microscopy (TEM) was collected by a JEOL JEM-2100. The power X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Ultima IV with Cu-Ka radiation. X-ray photoelectron spectroscopy (XPS) was performed on PHI 5000 Versa Probe III using an Al Kα radiation source (1486.6 eV). Inductive Coupled Plasma Emission Spectrometer (ICP) was carried out using Agilent ICP-OES/730. N<sub>2</sub> adsorption-desorption was measured by a Quantachrome, Autosorb-IQ3. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the pore size distribution was obtained with the Non-Barrett-Joyner-Halenda (BJH) method. Raman spectra was investigated on a Raman spectrometer (Renishaw inVia) with a laser wavelength ( $\lambda$ ) of 532 nm.

## 2.4 Density functional theory (DFT) calculation method

The details of density functional theory (DFT) calculation methods are provided in **Supplementary Information**.

# 2.5 Electrochemical measurements

All tests were conducted on an auto lab workstation, using 1.0 M KOH as the electrolyte and a three-electrode configuration. Clean platinum plate and mercury Mercury (II) oxide electrode were used as the counter electrode and reference electrode, respectively. To prepare the working electrode, 3 mg of catalyst, 200 µL of DI water, and 600 µL of ethanol were mixed evenly, and 20 µL of Nafion solution was added, which was ultrasound treated for 20 minutes. Then, 20 µL of the above solution was drop-added on the surface of the rotating platinum carbon electrode with an area of 0.19 cm<sup>2</sup> and was dried naturally. Linear sweep voltammetry (LSV) was obtained at a scanning rate of 10 mV s<sup>-1</sup> in alkaline electrolyte. All polarization curves were adjusted to 95% iR correction. Stability was assessed by chronoamperometric and cyclic voltammetry (CV) tests. Electrochemical impedance spectroscopy (EIS) measurements were performed at 0.95 V (vs. RHE). CV test within the scanning speed range of 20-120 mV s<sup>-1</sup> was performed to calculate the electrochemical double-layer capacitances (C<sub>dl</sub>). The electrochemical active surface area (ECSA) was estimated by the following equation: ECSA= $C_{dl}/C_s$ ,  $C_s$ =40  $\mu$ F cm<sup>-2.12</sup> The potential data of the Hg/HgO electrode (E (vs. Hg/HgO)) was transformed into potential vs. reversible hydrogen electrode (RHE) according to the following equation.9

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# E (vs. RHE) = E (vs. Hg/HgO) + Eq Hg/HgO + 0.059 × pH 3. Results and discussions

As schematically depicted in Fig. 1, MoC@BNC was prepared by a simple one-pot solvothermal method, which involved the spontaneous assembly of melamine, glucose, and H<sub>3</sub>BO<sub>3</sub> as well as the *in-situ* chelating of the Mo ions. After calcination at 800 °C, B, N co-doped porous carbon confined ultra-small MoC quantum dots (MoC@BNC) was obtained. XRD pattern of the synthesized sample in Fig. 2a shows typical peaks at 36.41°, 42.30°, 61.36°, and 73.50°, attributed to  $\alpha$ -MoC (JCPSD Card No.89-2868).<sup>36</sup> On the other hand, the peak at 26.3° is assigned to graphitic carbon.37 MoC@BNC was further washed with methanol to completely remove the possible formation of  $B_2O_3$ . It can be seen from the XRD characterization in Fig. S1<sup>†</sup> that both the washed sample and the un-washed sample show similar XRD patterns. This may indicate that B is incorporated in the substrate rather than present in the form of boron oxide. The SEM image in Fig. 2b shows a flack morphology. The corresponding EDS elemental mapping analysis demonstrates the uniform distribution of Mo, C, B, and N atoms (Fig. 2c). This suggests that B and N atoms have been successfully doped in the carbon matrix and MoC nanoparticles are uniformly dispersed on the surface of BNC substrate. The TEM image (Fig. 2d) proves the presence of MoC quantum dots with a mean particle size of about 1.8 nm as suggested by the particle size distribution in Fig. 2e. The lattice spacing in the inset of the enlarged TEM is calculated to be 0.25 nm, which is consistent with the (111) crystal plane of  $\alpha$ -MoC.<sup>36</sup> This further indicates that MoC quantum dots anchored on BNC substrate are successfully prepared. As a comparison, MoC@NC was also prepared, which demonstrated a flake-like morphology and small MoC quantum dots (Fig. S2<sup>†</sup>), similar to that of MoC@BNC. To elucidate the electro-modulation effect of the doped carbon substrate on the loaded MoC, XPS was carried out. From Fig. 2f, the Mo 3d XPS spectra can be deconvoluted into Mo2+ at 228.8/232.0 eV (Mo  $3d_{5/2}/3d_{3/2}$ ) corresponding to  $\alpha$ -MoC, the Mo<sup>4+</sup>/Mo<sup>6+</sup> peaks at 229.4/232.8 eV (Mo  $2d_{5/2}$ ) and 233.8/235.9 eV (Mo  $3d_{2/3}$ ) corresponding to MoO<sub>2</sub>/MoO<sub>3</sub> due to the unavoidable oxidation of  $\alpha$ -MoC when exposed to air.<sup>36</sup> It can be observed that the Mo 3d XPS peak of the MoC@BNC has a positive shift of 0.43 eV compared to that of MoC@NC, indicating the enhanced electron delocalization of the MoC after B introduction, inducing electron transfer from MoC to the BNC substrate. The B 1s XPS spectrum for MoC@BNC shows a negative shift compared with BNC (Fig.  $S3^{\dagger}$ ), which is consistent with the result of the Mo 3*d* XPS peak. This consolidates the strong electronic interaction between the



Fig. 1 Schematic illustration for preparing Ru/MoC@BNC catalysts.

**Fig. 2** (a) XRD, (b) SEM image, (c) EDS elemental mapping of Mo, C, B, and N, (d) TEM image and (e) MoC particle size distribution of MoC@BNC. (f) Mo 3*d* XPS spectra of MoC@BNC and MoC@NC.

B, N co-doped carbon substrate leading to electron-deficient MoC quantum dots.

Ru catalyst was subsequently loaded on the surface of MoC@BNC using a post-impregnation method (as schematically depicted in Fig. 1). The Ru and Mo content is determined to be 4.0 wt.% and 17.0 wt.%, respectively by the ICP-OES analysis (Table S1<sup>†</sup>). As shown in Figs. 3a-b, Ru/MoC@BNC inherits the morphology of MoC@BNC. Ru catalysts with a particle size of about 1.8 nm are evenly dispersed on the surface, following a similar distribution to the Mo element. HR-TEM in Fig. 3c explicitly demonstrates the hetero-junction structures of Ru intertwined by MoC quantum dots. This suggests that the presence of small MoC quantum dots helps tethering Ru catalysts due to the strong interaction, which establishes a maximized MoC-Ru interface and an enhanced interfacial electronic modulation of Ru catalysts. To further identify the presence structures of Ru for Ru/MoC@BNC, we calculated the formation energy  $(E_f)$  for different catalysts, wherein Ru exists beside MoC, Ru is positioned on top of MoC, while Ru is located on BNC without contact with MoC. As the models and the  $E_{\rm f}$  value shown in Fig. S4<sup>+</sup>, it is found that Ru prefers to position beside MoC to form Ru-MoC hetero-junctions.

As a comparison, Ru/MoC@NC catalyst was prepared, which possessed a close hetero-structure to Ru/MoC@BNC (Fig. S5<sup>†</sup>). Meanwhile, the reference catalyst of Ru/NC shows larger Ru nanoparticles (~2.7 nm) compared with that of Ru/MoC@NC Ru/MoC@BNC (Fig. S6<sup>†</sup>). XRD patterns for and Ru/MoC@BNC and Ru/MoC@NC (Fig. 3d) show the absence of Ru, which may be due to the ultra-small size of the Ru particles. On the other hand, the XRD peaks at 38.37°, 42.10°, 43.73°, 58.18°, 69.41°, and 78.38° in line with the Ru (100), (002), (101), (102), (110), and (103) are observed for Ru/NC (Fig. 3d).<sup>38</sup> This could be due to the larger particles of Ru on the NC support without MoC quantum dots, which sufficiently validates the important role of MoC quantum dots in facilitating the dispersion of Ru nanoparticles due to the strong interaction between MoC quantum dots and Ru. By the analysis of XPS spectra in Fig. 3e, it could be found that Ru 3p XPS peak of Ru/MoC@NC has a positive shift of about 1.0 eV compared with Ru/NC catalyst, indicating a strong electron transfer between Ru nanoparticles and MoC@NC. Moreover, upon careful comparison, it is found that the Ru 3p XPS peak of Ru/MoC@BNC exhibits a slight negative shift compared to

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80

10 µn

0.9



#### Journal Name (a) c)(d) ▼Ru ◆MoC Ru/MoC@BNC Intensity (a.u. Ru/MoC@NC Ru/NC 10 um 20 40 60 2 Theta $(\theta)$ (b) Ru Mo C В N 10 µm 10 µm 10 µm 10 µm 10 µm (e) Ru 3p (f) (g) 462.5 eV d(V)/d(r) cc/g/nm G:1593 cm Ru/MoC@BNC D<mark>:1350 cm</mark>-1 ı/MoC@BN Ru/MoC@BNC Intensity (a.u.) Intensity (a.u.) I<sub>D</sub>:I<sub>C</sub>=0.88 Ru/MoC Volume (cc/g) Ru/NC 462.9 eV Ru/MoC@NC I<sub>D</sub>:I<sub>G</sub>=0.85 6 Pore size (nm) Ru/NC 461.9 eV I<sub>D</sub>:I<sub>G</sub>=0.52 Ru/NC 0.3 900 1200 1500 1800 0.0 0.6 460 470 480 490 Binding Energy (eV) Raman Shift (cm-1) $P/P_0$

Fig. 3 (a) SEM image, (b) Ru, Mo, C, B, N, and O EDS elemental mapping and (c) TEM image of Ru/MoC@BNC. (d) XRD patterns, (e) Ru 3p XPS spectra, (f) Raman spectra, and (g) N<sub>2</sub> adsorption-desorption isotherms (the inset is the BJH pore size distribution) of Ru/MoC@BNC, Ru/MoC@NC, and Ru/NC.

Ru/MoC@NC. To explain this phenomenon, a Bader charge analysis of the Ru catalyst was carried out. It is found that the average charge of Ru in Ru/MoC@BNC is 7.639 e, which is higher than 7.628 e for Ru/MoC@NC. This indicates a slightly higher electron density of Ru in Ru/MoC@BNC than Ru/MoC@NC. Considering that electrons are transferred from MoC to BNC in MoC@BNC, therefore the BNC substrate is electron-enriched. By subsequently loading Ru at the interface of MoC and BNC (as the structure model shown in Fig. S4<sup>†</sup>), the contact of Ru with the electron-rich BNC can help maintain Ru with a higher electron density, which can explain the XPS result.

Fig. 3f displays the Raman spectra of the catalyst, which shows two wide peaks at 1350 cm<sup>-1</sup> (D band) and 1593 cm<sup>-1</sup> (G band). The higher  $I_D/I_G$  value in Ru/MoC@BNC (0.88) and Ru/MoC@NC (0.85) compared to that of Ru/NC (0.52) suggests a higher structural defects degree in the carbon matrix, which may benefit the electron transfer during the water-splitting process.39 The N2 adsorption-desorption isotherms and pore size distribution curves are shown in Fig. 3g and Table S2<sup>†</sup>. It can be seen that the isotherms for all the catalysts exhibit the presence of slight hysteresis loops. A gradual uptake of nitrogen gas indicates the mesoporous structure of the catalysts.<sup>40-42</sup> The BET-specific surface area is calculated to be 227.0 m<sup>2</sup> g<sup>-1</sup> for Ru/MoC@BNC, 218.3 m<sup>2</sup> g<sup>-1</sup> for Ru/MoC@NC and 250.0 m<sup>2</sup> g<sup>-1</sup> <sup>1</sup> for Ru/NC. In addition, the pore size distribution curve shows that the catalyst contains a mean pore size of about 3.5 nm. Such highly porous structure may be due to the release of abundant

gas from the decomposition of the carbon precursor (melamine and glucose).43-46

The HER performance was evaluated in a KOH aqueous solution (1.0 M) at a scanning rate of 5 mV s<sup>-1</sup> at ambient temperature and pressure. As the linear sweep voltammetry (LSV) curve shown in Figs. 4a-b, Ru/MoC@NC demonstrates an impressive overpotential ( $\eta$ ) of 18 mV and 98 mV to achieve the current density of 10 mA cm<sup>-2</sup> and 100 mA cm<sup>-2</sup>, which is remarkably lower than that of Ru/NC (33 mV and 163 mV) and even outperforming the benchmark Pt/C catalyst (27 mV and 147 mV). This prominently highlights the significance of the interfacial electronic modulation of Ru by MoC quantum dots for the intrinsic HER catalytic activity improvement. More interestingly, Ru/MoC@BNC exhibits a continuously improved activity with a further lowered overpotential of 14 mV and 80 mV to reach a current density of 10 mA cm<sup>-2</sup> and 100 mA cm<sup>-2</sup>. This signifies the important function of the B, N doping for the electronic tuning of the Ru-MoC system. The HER performance of MoC@BNC and MoC@NC was first evaluated, which demonstrate overpotentials of 304 mV and 316 mV, respectively at a current density of 10 mA cm<sup>-2</sup> (Fig. S7<sup>†</sup>), far inferior to that of Ru/MoC@BNC. The poor catalytic performance of the MoCbased catalyst may be attributed to the low hydrogen adsorptionfree energy.47 Besides, three samples of Ru/MoC@B1NC, Ru/MoC@B2NC (corresponding to Ru/MoC@BNC), and Ru/MoC@B<sub>3</sub>NC was constructed by adjusting the adding amount of boron precursors during the preparation. From the



**Fig. 4** (a) Polarization curve of Ru/MoC@BNC in 1.0 M KOH electrolyte at 5 mV s<sup>-1</sup>, along with those of Ru/MoC@NC, Ru/NC, and Pt/C for comparison. (b) The overpotential at 10, 50 and 100 mA cm<sup>-2</sup>. (c) Tafel plots of Ru-based catalysts and commercial Pt/C. (d) Comparison of  $\eta_{10}$  of Ru/MoC@BNC with representatively reported HER electrocatalysts. (e) Nyquist plots of Ru-based catalysts. (f) The capacitive current at 0.1 V as a function of scan rate for Ru/MoC@BNC, inset: cyclic voltammograms of Ru/MoC@BNC with different rates from 20 to 120 mV s<sup>-1</sup>. (g) Polarization curves of Ru/MoC@BNC, inset: i–t curve of Ru/MoC@BNC at a constant overpotential of 20 mV for 45 h.

HER performance in **Fig. S8** $\dagger$ , it could be seen that Ru/MoC@B<sub>2</sub>NC (Ru/MoC@BNC) has the highest activity. Therefore, B precursor was fixed at the optimal amount for the following catalyst design and application.

The Tafel polarization curve is used to investigate the kinetics as displayed in **Fig. 4c**. Ru/MoC@BNC shows the smallest Tafel slope of 25.5 mV dec<sup>-1</sup>, which is even lower than the Pt/C catalyst (33.2 mV dec<sup>-1</sup>). This is consistent with the LSV results, validating again the superior catalytic activity of Ru/MoC@BNC for HER. By comparing the reported Ru-based HER catalysts, Ru/MoC@BNC stands out to be one of the most active catalysts, which is even better than some reported Pt-based catalysts (**Fig. 4d** and **Table S3**†).

By comparing the electrochemical impedance spectra (EIS) (Fig. 4e), Ru/MoC@BNC exhibits the smallest diameter, indicating the lower internal electron transfer resistance.<sup>6,48</sup> Therefore, Ru/MoC@BNC has the fastest electron mobility, which may be attributed to the facilitated electron interaction between Ru and the substrate. The double-layer capacitance value (C<sub>dl</sub>) is calculated by the respective cyclic voltammetry (CV) curve (Figs. 4f, S9a-b<sup>†</sup>, S10<sup>†</sup>), which is proportional to the electrochemical active surface area (ECSA). Ru/MoC@BNC shows the highest C<sub>dl</sub> value (28.8 mF cm<sup>-2</sup>) compared with other catalysts, validating the augmentation of the accessible active sites. The catalytic current density was further normalized based

on the ECSA and the mass of Ru, as shown in the Figs. S11<sup>+</sup>, S12<sup>†</sup>. The results show that the HER activity of the Ru/MoC@BNC catalyst is indeed better than Ru/MoC@NC, and Ru/NC, confirming its higher intrinsic activity. In addition to the catalytic activity, durability is another important indicator for evaluating the catalytic performance.49,50 From the cycling stability test in Fig. 4g, it can be seen that Ru/MoC@BNC exhibit a robust electrocatalytic performance with negligible deactivation after 2000 cycles. The excellent stability of Ru/MoC@BNC catalyst could be further evidenced by the durable electric operation at  $\eta$ =20 mV within 45 h (inset in Fig. 4g). The samples after stability testing were collected and characterized. From the SEM and EDS elemental mapping analysis in Figs. S13a-b<sup>†</sup>, it could be seen the catalyst maintains its original lamellar morphology and Ru are still well dispersed. TEM characterization in Fig. S13c<sup>+</sup> indicates that Ru has a small particle size of about 1.8 nm without aggregation in the reacted catalyst. These results may confirm the robust stability of the Ru/MoC@BNC catalyst.

The density functional theory (DFT) calculations were performed to elucidate the electronic structure and HER mechanism of the catalysts. The optimized structures and corresponding H adsorption geometries of the catalyst are summarized in **Figs. 5a-f**. The corresponding Gibbs free energies of H adsorption ( $\Delta G_H$ ) over different catalysts are elaborately

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**Fig. 5** (a-c) The optimized structures and (d-f) the corresponding H adsorption structures. (g) The Gibbs free energies of H adsorption. (h) Calculated free energies of the alkaline HER process for Ru/MoC@BNC, Ru/MoC@NC, and Ru/NC. (i-j) The 3d charge density differences of Ru/MoC@NC and Ru/MoC@BNC composite. The yellow and cyan color represent the accumulation and loss of charges, respectively.

depicted (**Fig. 5g**). It can be seen that the addition of MoC in the catalyst system could significantly reduce the  $\Delta G_H$  from -0.807 eV (Ru/NC) to -0.359 eV (Ru/MoC@NC). This prominently underlines the promoting effect of the MoC quantum dots for the tuning of Ru catalyst to optimize the H adsorption strength. While, for Ru/MoC@BNC,  $\Delta G_H$  is further decreased to be - 0.332 eV. Therefore, B doping in the carbon substrate could further improve the HER performance by providing a more ideal  $\Delta G_H$ .

Moreover, the free energies of the alkaline HER process were also calculated. The optimized adsorption structures of \*OH+\*H are displayed in **Fig. S14**<sup>†</sup>. From **Fig. 5h**, it can be seen that the HER activity is mainly restricted by the process of \*OH and \*H evolution. The Ru/MoC@BNC has the most ideal free energies of the alkaline HER process, with moderate endothermic energy for \*OH transformation to OH<sup>-</sup> and the lowest endothermic energy of \*H evolution.

To explore the root reason for HER improvement, the charge density difference and Bader charge of the Ru/MoC@NC composite was calculated. As displayed in Fig. 5i, the yellow area is near the MoC, the blue area is around Ru. Thus, there is a charge transfer from Ru to MoC quantum dots at the interface of Ru/MoC@NC composite. Consequently, the introduction of MoC in Ru/MoC@NC composite weakens the  $\Delta G_H$  of Ru active site (H adsorption sites). For Ru/MoC@BNC composite, the charge density differences indicate that the blue area is mainly around MoC and BNC substrate (Fig. 5j). Therefore, B doping could lead to the charge loss of MoC and BNC substrate. The Bader charge analysis indicates that the charge difference between two bridge Ru atoms (active sites) in Ru/MoC@BNC and Ru/MoC@NC are 0.011 e and 0.103 e, respectively. The small charge difference of Ru active sites could weaken the H binding strength and lead to slight structural deformation.<sup>9</sup> As a result, B incorporation in Ru/MoC@BNC could further weaken the  $\Delta G_{\rm H}$  and improve the HER performance.

# 4. Conclusion

In summary, a judicious interfacial modulation has been successfully implemented to boost the HER performance of Ru

catalysts. The B, N co-doped carbon substrate can induce charge redistribution of MoC quantum dots, which further profoundly enhances the electronic interaction with Ru catalyst. The corresponding Ru/MoC@BNC exhibits high catalytic activity in 1.0 M KOH with a low overpotential of 14 mV at 10 mA cm<sup>-2</sup>, and excellent structural stability and durability. Theoretical calculations indicate that the high HER activity of Ru/MoC@BNC is attributed to the charge regulation of Ru-MoC with BNC, leading to optimization of the \*OH and \*H evolution-free energies. This study could offer meaningful guidance for the further development of Ru-based catalysts for HER with precise tailoring of the electronic structure.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Data availability

The data supporting this article have been included as part of the Supplementary Information.

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# **Data Availability Statement**

The data supporting this article have been included as part of the Supplementary Information.