ORIGINAL ARTICLE

Mo₂C nanoparticles embedded within bacterial cellulose-derived 3D N-doped carbon nanofiber networks for efficient hydrogen evolution

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Molybdenum carbide (Mo₂C) has been considered as a promising non-noble-metal hydrogen evolution reaction (HER) electrocatalyst for future clean energy devices. In this work, we report a facile, green, low-cost and scalable method for the synthesis of a Mo₂C-based HER electrocatalyst consisting of ultrafine Mo₂C nanoparticles embedded within bacterial cellulose-derived 3D N-doped carbon nanofiber networks (Mo₂C@N-CNFs) using 3D nanostructured biomass as a precursor. The electrocatalyst exhibits remarkable HER activity (an overpotential of 167 mV achieves 10 mA cm⁻² and a high exchange current density of 4.73×10^{-2} mA cm⁻²) and excellent stability in acidic media as well as high HER activity in neutral and basic media. Further theoretical calculations indicate a strong synergistic effect between Mo₂C nanoparticles and N-CNFs in the Mo₂C@N-CNF catalyst, which leads to an impressive HER performance.

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INTRODUCTION

As a clean and sustainable energy source, hydrogen has been considered the most promising alternative to traditional fossil fuels for future energy systems.^{1,2} An attractive and effective method for producing hydrogen is electrochemical water splitting in an electrolyzer using a sustainable electricity source.^{1,3} Currently, although the most efficient electrocatalysts for hydrogen evolution reaction (HER) are platinum-based catalysts, their high cost and scarcity limit large-scale commercial application.^{4,5} Therefore, substantial efforts have been dedicated to the search for robust non-noble-metal HER catalysts.¹ Remarkable advances have been made recently regarding the use of transition metal dichalcogenides, phosphides, carbides, nitrides and borides as promising non-noble-metal catalysts for HER.^{1,2,4–7}

Among these non-noble-metal HER catalysts, molybdenum carbide (Mo₂C), which features a d-band electronic structure and catalytic properties similar to those of platinum, has been demonstrated as an active and stable HER catalyst, even in the form of bulky particles.^{8–13} Previous research has revealed that the coupling of Mo₂C particles with nanocarbons is an excellent strategy for improving the HER

activity,^{8,9,14–16} because of the following reasons: (1) carbon supports create a resistanceless path for rapid electron transfer and also effectively inhibit Mo₂C nanoparticle aggregation; (2) coupling conjugation can downshift the d-band center of molybdenum by inducing a charge transfer from molybdenum to carbon, thus achieving a relatively moderate Mo-H bond strength for enhanced H desorption.^{8,15} In particular, if the carbon supports are electrochemically active N-doped nanocarbons, their synergistic effects become more significant.^{17–19} However, most of the methods reported for preparing Mo₂C/nanocarbon electrocatalysts inevitably involve complex or dangerous synthetic procedures and expensive precursors, therefore hampering their practical applications.^{8,9,16–19}

Bacterial cellulose (BC), a low-cost and environmentally friendly biomass, can be produced on an industrial scale via the microbial fermentation process.²⁰ Our recent studies demonstrated that BC was an excellent precursor for producing heteroatom-doped carbon nanofiber (CNF) aerogels for energy storage and conversion.^{21–23} In this work, using BC as 3D nanostructured carbon source, we report a facile method for synthesizing a non-noble-metal HER electrocatalyst consisting of ultrafine Mo₂C nanoparticles embedded within 3D

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N-doped carbon nanofiber networks (Mo₂C@N-CNFs) via a solid-state reaction between (NH₄)₆Mo₇O₂₄ and BC. Owing to the low-cost biomass precursor and simple preparation process, our developed method is environmentally friendly, inexpensive and easy to scale up. The prepared Mo₂C@N-CNF catalyst possesses relatively high specific surface area and porosity, 3D electrochemically active N-doped carbon fibrous networks and ultrafine Mo₂C nanoparticles. When used as electrocatalysts for HER, the BC-derived Mo₂C@N-CNFs exhibit remarkable activity in a wide range of pH values (pH 0–14). Furthermore, theoretical calculations reveal that the high HER activity results from a strong synergistic effect between the Mo₂C nanoparticles and N-CNFs.

MATERIALS AND METHODS

Materials

Raw materials of purified BC pellicles with fiber content of ~1% (vol/vol) were provided by Ms C. Y. Zhong (Hainan Yeguo Foods Co., Ltd, Hainan, China). All chemicals were of analytical grade, commercially available from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and used as received without further purification.

Preparation of Mo₂C@N-CNF aerogels

The as-received gel-like white purified BC pellicles were rinsed several times with deionized water and cut into rectangular slices (5.0 × 2.0 cm²) with a sharp blade. Five BC slices were immersed in 500 ml ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) aqueous solution with various concentrations (0.5, 1.5, 2.5, 5.0, 7.5 mM) under vigorous magnetic stirring for 3 days at room temperature to obtain BC/(NH₄)₆Mo₇O₂₄ hybrid hydrogels. The as-obtained hydrogel slices were frozen in liquid nitrogen (−196 °C) and freeze-dried in a bulk tray dryer at a sublimation temperature of −50 °C and a pressure of 0.04 mbar to evaporate the water. Finally, the dried BC/(NH₄)₆Mo₇O₂₄ hybrid aerogels were pyrolyzed under flowing N₂ at 800 °C for 2 h to generate black Mo₂C@N-CNF aerogels.

Preparation of reference samples (that is, N-CNF and CNF aerogels)

The preparation processes for N-CNF aerogels are similar to those of Mo₂C@N-CNF aerogels. The only difference is that the solution chosen for immersion of BC slices was 15 mM NH₄Cl aqueous solution. For the preparation of pure CNF aerogels, no immersion solution was required, and the other preparation processes were the same as those for the Mo₂C@N-CNF aerogels.

Characterization

Scanning electron microscopy was performed on a Zeiss Supra 40 scanning electron microscope (Oberkochen, Germany) at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained using a Hitachi H7650 transmission electron microscope (Hitachi, Tokyo, Japan), equipped with a CCD imaging system, at an acceleration voltage of 120 kV. X-ray diffraction was performed using a Philips X'Pert PRO SUPER X-ray diffractometer (Philips, Almelo, Netherlands) equipped with graphite monochromatic Cu K α radiation (λ = 1.54056 Å). X-ray photoelectron spectra (XPS) were recorded on an X-ray photoelectron spectrometer (ESCALab MKII, Thermo Scientific, Waltham, MA, USA) with Mg K α radiation (1253.6 eV) as an excitation source. Thermogravimetric analysis (TGA) was performed using a TGA Q5000IR analyzer under air flow with a temperature ramp of 10 °C min^{−1}. Raman scattering spectra were recorded with a Renishaw System 2000 spectrometer (Renishaw plc, Hoffman Estates, IL, USA) using the 514.5-nm line of Ar⁺ for excitation. N₂ sorption analysis was conducted using an ASAP 2020 accelerated surface area and a porosimetry instrument (Micromeritics, Norcross, GA, USA), equipped with an automated surface area, at 77 K using Barrett–Emmett–Teller (BET) calculations for the surface area. The pore size distribution plot was based on the original density functional theory model. High-resolution TEM (HRTEM), selected area electron diffraction, scanning transmission electron microscopy and element mappings were

performed using a JEM-ARM 200F atomic resolution analytical microscope (JEOL, Tokyo, Japan) operating at an acceleration voltage of 200 kV. Elemental mappings were collected using a Gatan GIF Quantum 965 instrument (Gatan Inc., Pleasanton, CA, USA).

Electrocatalytic HER measurements

The electrochemical measurements were performed in a conventional three-electrode cell using an IM6e electrochemical workstation (Zahner-Elektrok, Germany) controlled at room temperature. A 5.0-mm-diameter glassy carbon disk (disk geometric area of 0.196 cm²) served as the substrate for the working electrode. The glassy carbon electrode was polished to a mirror finish and thoroughly cleaned before use. A saturated calomel electrode (SCE) and platinum foil were used as the reference and counter electrodes, respectively. For the stability study, a graphite rod was used as the counter electrode to avoid the possible contribution of dissolved Pt species to the HER.

The catalyst ink was prepared by blending 5 mg of each catalyst with 50 μ l Nafion solution (5 wt%) and 950 μ l ethanol via sonication. An amount of 10 μ l of the dispersion was transferred onto the glassy carbon disk, producing a catalyst loading of 0.255 mg cm^{−2}. Finally, the as-prepared catalyst film was dried at room temperature. Using this electrode as the working electrode, electrochemical measurements were measured in 0.5 M H₂SO₄, 0.1 M phosphate buffer saline (PBS) and 1 M KOH, which were prepared using deionized water. Linear sweep voltammetry was measured at 1600 r.p.m. (to remove the *in situ*-formed H₂ bubbles on the rotating disk electrode) with a sweep rate of 2 mV s^{−1} to obtain the polarization curves. Long-term stability tests were performed by continuous linear sweep voltammetry scans from −0.4 to +0.1 V (vs reversible hydrogen electrode (RHE)) at a sweep rate of 100 mV s^{−1}. Electrochemical impedance spectroscopy (EIS) was conducted at various overpotentials with a 10 mV AC potential from 100 000 to 0.01 Hz. For the hydrogen bubbling experiment on carbon fiber paper, the electrode was prepared by loading 1 mg cm^{−2} of catalyst on carbon fiber paper (Toray, Tokyo, Japan). The obtained carbon fiber sheet was dried under vacuum and used as the working electrode. The applied potential was −0.7 V vs SCE (Supplementary Movie S1). In all measurements, SCE was used as the reference and was calibrated with respect to RHE. In 0.5 M H₂SO₄, E (RHE) = E (SCE) + 0.269 V; in 0.1 M PBS, E (RHE) = E (SCE) + 0.664 V; and in 1 M KOH, E (RHE) = E (SCE) + 1.050 V. All potentials reported in our manuscript are given against RHE.

Computational details

Density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package^{24,25} and the Perdew–Burke–Ernzerhof exchange–correlation functional correction.²⁶ To describe the van der Waals interaction, the DFT–D₂ method of Grimme was adopted.²⁷ A 400-eV kinetic energy cutoff was chosen for plane-wave basis set, and Monkhorst–Pack k-point sampling was used.²⁸ Residual forces were within 0.02 eV/Å for geometry optimizations.

The Gibbs free energy (ΔG_{H^+}) is expressed as follows:

$$\Delta G_{H^+} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S,$$

where ΔE_{H^*} , ΔE_{ZPE} and ΔS are the adsorption energy of atomic hydrogen on the given surface, zero point energy correction and entropy change of H⁺ adsorption, respectively. The zero point energy correction can be estimated by the equation $\Delta E_{ZPE} = E_{ZPE}(H^*) - 1/2E_{ZPE}(H_2)$, where $E_{ZPE}(H_2)$ is calculated as 0.284 eV, in good agreement with previous reports.^{19,29} The value of ΔS can be calculated using the equation $\Delta S = S(H^*) - 1/2S(H_2) \approx -1/2S(H_2)$ owing to the negligible entropy of hydrogen in the adsorbed state. At 1 bar and 300 K, $T\Delta S$ is approximately −0.205 eV.^{19,30} The value of ΔE_{H^*} is calculated as $\Delta E_{H^*} = E_{tot} - E_{sub} - 1/2E_{H_2}$, where E_{tot} and E_{sub} are the energies of H absorbed systems and the clean given surface, respectively, and E_{H_2} is the energy of molecular H₂ in the gas phase.

Theoretical models

The correlative theoretical models, as shown in Supplementary Figure S1, were constructed to simulate the Mo₂C@N-CNF materials and the reference materials, including CNFs, N-CNFs, Mo₂C and Mo₂C@CNFs. In our models, graphene and N-doped graphene were used to simulate CNFs and N-CNFs

(Supplementary Figure S1a and b). The hexagonal Mo₂C was adopted, and the calculated lattice parameters were $a = b = 6.08 \text{ \AA}$, $c = 4.72 \text{ \AA}$, in accordance with previous experimental and theoretical studies.^{31,32} Four layers of Mo-C atoms with Mo-termination were used to describe the Mo₂C (001) surface in which the bottom layer was fixed (Supplementary Figure S1c). The models constructed by covering the 5×5 supercell of graphene and N-doped graphene on a 2×2 supercell of the Mo₂C (001) surface were adopted to simulate Mo₂C@CNFs and Mo₂C@N-CNFs (Supplementary Figure S1d and e). Owing to the mismatch (approximately 1.2%) between graphene or N-doped graphene and Mo₂C (100), the lattice parameter of Mo₂C was slightly adjusted to match that of the graphene or N-doped graphene surface. The corresponding lattice parameters of all models are presented in Supplementary Table S1. Based on the DFT calculation results, the Gibbs free energy (ΔG_{H^+}) can be obtained to evaluate the HER activity of the CNFs, N-CNFs, Mo₂C, Mo₂C@CNFs and Mo₂C@N-CNFs. Supplementary Table S2 reports the $\Delta E(H^*)$, $E_{ZPE}(H^*)$, ΔE_{ZPE} and $\Delta G(H^*)$ values of the H⁺ adsorbed on the surface of different models.

RESULTS AND DISCUSSION

Figure 1 shows the procedures for preparing Mo₂C@N-CNF aerogels. Small BC hydrogels were first immersed in (NH₄)₆Mo₇O₂₄ solutions for 3 days and were then freeze-dried to obtain BC/(NH₄)₆Mo₇O₂₄ hybrid aerogels. Subsequently, the hybrid aerogels were pyrolyzed under a N₂ atmosphere to generate black Mo₂C@N-CNF aerogels. Owing to the simple processes and low-cost precursors, our developed method is easy to scale up. It should be noted that the N-dopants in CNFs originated from NH₄⁺ of (NH₄)₆Mo₇O₂₄ during the pyrolysis process, which is similar to other BC-derived N-doped CNFs prepared by annealing BC with ammonium salt.²¹ The crystalline phase compositions of the products obtained at different concentrations of (NH₄)₆Mo₇O₂₄ solution were first examined by X-ray diffraction (Supplementary Figure S2). A broad peak near 22° can be attributed to the (002) planes of graphitic carbon. The other X-ray diffraction peaks at 34.4, 37.9, 39.6, 61.6 and 74.6° are attributed to the diffractions of the (100), (002), (101), (110) and (112) faces, respectively, of hexagonal Mo₂C (JCPDS 35-0708) (Supplementary Figure S3). It is found that the carbon peak is substantially reduced when the concentrations of (NH₄)₆Mo₇O₂₄ solution are increased from 0.5 to 7.5 mM and the signals of Mo₂C in Mo₂C@N-CNFs are enhanced. Interestingly, with an excess of (NH₄)₆Mo₇O₂₄ (7.5 mM), a weak peak

of MoO₂ appears. These results provide strong evidence of a solid-state reaction between (NH₄)₆Mo₇O₂₄ and BC.^{8,14} Electrochemical measurements show that the samples prepared in 2.5 mM (NH₄)₆Mo₇O₂₄ solution possess the highest HER activities (Supplementary Figure S4a), probably because optimization of the chemical compositions and microstructure could be realized at this concentration.^{18,19} Furthermore, the variation tendency of the R_{ct} determined from the semicircle registered at low frequencies (high Z') was highly consistent with the polarization curves (Supplementary Figure S4b), indicating that the samples prepared in 2.5 mM (NH₄)₆Mo₇O₂₄ solution create the fastest electrode kinetics. Therefore, the Mo₂C@N-CNF catalysts discussed below were prepared at this concentration unless otherwise specified. For comparison, CNF aerogels and N-doped CNF (N-CNF) aerogels were also prepared.

Detailed Mo₂C@N-CNF composition information was further investigated using Raman and TGA. Two significant peaks are observed in the Raman spectrum at 1347 and 1593 cm⁻¹, which correspond to the D and G bands of carbon, respectively (Supplementary Figure S5a).^{15,16} Based on the TGA results, the N-CNF and Mo₂C contents in Mo₂C@N-CNFs are estimated as ca. 49.4 wt.% and ca. 50.6 wt.%, respectively (Supplementary Figure S5b). The presence of massive carbon materials in Mo₂C@N-CNFs has an important role in prohibiting the growth of Mo₂C nanocrystallites and stabilizing the ultrafine particles.¹¹ XPS analysis was conducted to elucidate the chemical composition and element bonding configurations in Mo₂C@N-CNFs (Supplementary Figure S6). As expected, the XPS survey spectrum confirms the presence of C, Mo, N and O in Mo₂C@N-CNFs. The N 1s XPS spectrum shows that two types of nitrogen species exist, that is, pyridinic and graphitic nitrogen atoms in the hybrid,^{19,22} and the surface N content is ca. 2.4 at.%. Additionally, the Mo 3d can be deconvoluted into six peaks assignable to Mo²⁺ (228.9, 232.6 eV), Mo⁴⁺ (230.0, 233.1 eV) and Mo⁶⁺ (233.5, 236.1 eV) species.^{17,33} Mo²⁺ is assigned to Mo₂C, and Mo⁴⁺ (MoO₂) and Mo⁶⁺ (MoO₃) originate from superficial oxidation of Mo₂C owing to air contact, which is consistent with previous reports.^{15,34}

The microstructure of Mo₂C@N-CNFs was characterized by scanning electron microscopy and TEM (Figures 2a and b). The as-prepared Mo₂C@N-CNF aerogel displays a 3D network microstructure with 10–20 nm nanofibers, which originated from the intrinsic

Figure 1 The synthesis procedure of Mo₂C@N-CNF electrocatalysts from BC.

Figure 2 Characterization of Mo₂C@N-CNFs electrocatalysts. (a) SEM, (b–d) TEM images, (e) magnified TEM image, (f) HRTEM image, (g) SAED pattern, (h) STEM and (i) corresponding element mappings of Mo₂C@N-CNFs.

structure of BC. Remarkably, the nanofibers interconnect with each other by many junctions, resulting in abundant interconnected macropores and excellent conductive properties. As far as we know, this is the first report of a Mo₂C-based HER electrocatalyst with a 3D nanostructure. A closer TEM examination of the nanofiber network clearly reveals that many ultrafine Mo₂C nanoparticles are embedded within the N-CNF matrix (Figures 2c and d). Judging from the magnified TEM image in Figure 2e, the size of the Mo₂C nanoparticles (darker area indicated by green circles) is ultrasmall and typically <5 nm, although some nanoparticles seem to aggregate and appear as large clusters. The HRTEM image clearly shows a set of lattice fringes with an interplanar distance of 0.229 nm (Figure 2f), which corresponds to the (101) planes of hexagonal Mo₂C, further confirming that the phase composition of these nanoparticles is Mo₂C. Additionally, typical nanostructured carbons are also found around Mo₂C, clearly indicating that the Mo₂C nanoparticles are embedded within N-CNFs. The selected area electron diffraction pattern shows the polycrystalline nature of Mo₂C@N-CNFs (Figure 2g), and all polycrystalline rings match well with carbon and Mo₂C (Supplementary Figure S7). Furthermore, scanning transmission electron microscopy

and corresponding element mappings (Figures 2h and i) show that the C, Mo, N and O atoms are homogeneously distributed within the hybrids, providing further evidence that the Mo₂C nanocrystals are uniformly distributed within the N-CNF matrices. In addition, the nitrogen adsorption/desorption measurement for the Mo₂C@N-CNF aerogel gives a relatively high specific BET surface area of 81.98 m² g^{−1} (Supplementary Figure S8a). The pore size distribution curve shows that the Mo₂C@N-CNF aerogel possesses a hierarchically porous structure containing many micropores centered at 1.5 nm and mesopores centered between 7.5 and 30 nm (Supplementary Figure S8b). The high specific BET surface area and hierarchically porous structure creates a high electrode/electrolyte contact area, thus facilitating the high HER electrochemical performance of the Mo₂C@N-CNF catalyst.^{9,11}

The electrocatalytic HER activity of the Mo₂C@N-CNF aerogel was first evaluated using a standard three-electrode electrochemical configuration with a catalyst loading of 0.255 mg cm^{−2} in 0.5 M H₂SO₄. For comparison, the original CNF aerogel, N-CNF aerogel, commercially available Mo₂C (com-Mo₂C) and 20 wt.% Pt/C (Johnson Matthey) were also tested using the same loading amount. Figure 3a

Figure 3 Electrocatalytic HER performance of Mo₂C@N-CNFs and reference samples. (a) Polarization curves and (b) Tafel curves of Mo₂C@N-CNFs, CNF aerogel, N-CNF aerogel, commercial available Mo₂C and 20 wt% Pt/C catalysts. (c) Nyquist plots of Mo₂C@N-CNFs collected at different overpotentials. (d) Stability test for Mo₂C@N-CNFs by CV scanning for 2000 cycles in 0.5 M H₂SO₄ solution.

shows the corresponding polarization curves. As expected, the Pt/C catalyst exhibits the best HER activity with a near-zero overpotential. Although the CNF aerogel displays poor performance, the N-CNF aerogel shows improved activity with an onset overpotential (the potential at which the cathodic current density is 1 mA cm⁻²) of 302 mV, supporting the positive role of N-doping for HER activity. It is found that com-Mo₂C has low HER activity, with an onset overpotential of 313 mV, whereas the Mo₂C@N-CNF catalyst produces the same current density at a much lower overpotential of 105 mV, indicating the positive effect of the ultrasmall size of the Mo₂C nanoparticles as well as the coupling effect between Mo₂C and N-CNFs in the Mo₂C@N-CNF catalyst. In addition, to produce a current density of 10 mA cm⁻², Mo₂C@N-CNFs require an overpotential of only 192 mV. Remarkably, when the loading of the Mo₂C@N-CNF catalyst is increased from 0.255 to 1.020 mg cm⁻², the HER performance is dramatically enhanced, and an overpotential of only 167 mV is needed to achieve 10 mA cm⁻² (Supplementary Figure S9), which favorably compares with those of many previously reported non-precious HER catalysts measured in an acidic medium (Supplementary Table S3). The turnover frequency of the Mo₂C@N-CNF catalyst was estimated via previously reported methods.³⁵ Mo₂C@N-CNFs achieve turnover frequencies of 1.03 and 3.79 s⁻¹ at overpotentials of 200 and 300 mV at pH 0, respectively. These values compare favorably with those of other reported non-precious HER catalysts.³⁶ Furthermore, a video recording of the Mo₂C@N-CNF-modified carbon fiber paper electrode showed vigorous

H₂ effervescence at an overpotential of 431 mV, indicating the remarkable HER performance of Mo₂C@N-CNF electrocatalysts (Supplementary Movie S1). Using the cyclic voltammetric method, we investigated the double layer capacitance (*C_{dl}*) at the solid-liquid interface (Supplementary Figure S10), which is proportional to the effective electrochemical surface area.^{37,38} The Mo₂C@N-CNFs exhibit a high *C_{dl}* of 11.34 mF cm⁻² at 0.22 V, which is slightly less than that of the high specific surface area Vulcan XC-72R carbon black-supported Pt catalyst (12.58 mF cm⁻²) and comparable to those of many reported excellent non-precious HER catalysts, such as edge-terminated MoS₂,³⁷ g-C₃N₄ nanoribbon-graphene³⁹ and 3D CoSe₂/carbon fiber felt.³⁸ Thus the high HER activity of Mo₂C@N-CNFs can be associated with its relatively high BET-specific surface.

To probe the HER kinetics of the catalysts, Tafel plots were fitted to the Tafel equation ($\eta = a + b \log(j)$), where *b* is the Tafel slope. As shown in Figure 3b, the Pt/C catalyst exhibits a Tafel slope of 30.8 mV dec⁻¹, consistent with the reported values.^{30,37,40} The Tafel slope of Mo₂C@N-CNFs is 70.0 mV dec⁻¹, which is much lower than that of reference catalysts such as CNFs (214.5 mV dec⁻¹), N-CNFs (195.4 mV dec⁻¹) and com-Mo₂C (114.5 mV dec⁻¹), indicating a higher HER rate and favorable kinetics for Mo₂C@N-CNFs. The Tafel slope value of Mo₂C@N-CNFs falls within the range of 40–120 mV dec⁻¹, suggesting that the HER taking place on the Mo₂C@N-CNF surface follows a Volmer–Heyrovsky mechanism, and the rate of the discharge step is consistent with that of the desorption step.⁴⁰ Next the exchange current density (*j₀*) was

calculated by extrapolating the Tafel plot to an overpotential of 0 V, which might profoundly reflect the intrinsic electrochemical reaction rate. As expected, the Mo₂C@N-CNFs exhibits a j_0 of $4.73 \times 10^{-2} \text{ mA cm}^{-2}$, which is much higher than those of CNFs ($2.74 \times 10^{-2} \text{ mA cm}^{-2}$), N-CNFs ($3.36 \times 10^{-2} \text{ mA cm}^{-2}$) and com-Mo₂C ($7.38 \times 10^{-4} \text{ mA cm}^{-2}$) (Supplementary Figure S11). The j_0 of Mo₂C@N-CNFs also outperforms many non-precious HER electrocatalysts reported in the literature (Supplementary Table S3).

Because the Tafel plots derived from polarization curves are always affected by factors such as different choices of overpotential regions and different methods of IR compensation,¹⁷ we further performed EIS investigations on Mo₂C@N-CNFs to explore the HER kinetics. Figure 3c displays the Nyquist plots at applied overpotentials from 100 to 200 mV, showing the classical two time-constant behavior at all applied overpotentials.^{8,14} Thus experimental data were fitted using an equivalent circuit consisting of a series resistance R_s (the ohmic resistance) in series with two parallel branches: one reflecting the charge-transfer process ($C_{dl} - R_{ct}$) and the other related to the surface porosity ($C_{d2} - R_p$) (Supplementary Figure S12a).^{8,14} Supplementary Figure S12b shows the R_{ct} determined from the semicircle registered at low frequencies (high Z'), which is found to be overpotential dependent. The R_{ct} sharply drops from 631.0 to 16.0 Ω when the overpotential increases from 100 to 200 mV. Because the small R_{ct} means rapid charge transfer kinetics, the above results clearly indicate that the charge transfer kinetics are dramatically accelerated upon increase of the overpotential. The plot of overpotential vs $\log R_{ct}^{-1}$ shows that the Tafel slope is 60.8 mV dec⁻¹ (Supplementary Figure S12c), which is slightly less than that derived from the polarization curve (70.0 mV dec⁻¹). These results can be explained by the fact that the Tafel slope obtained from the EIS tests only relates to charge-transfer kinetics and does not include contributions from the catalyst resistance, which are different from those extracted from the polarization curves. In addition, the Tafel slope of 60.8 mV dec⁻¹ further indicates that the Mo₂C@N-CNFs might follow a Volmer–Heyrovsky mechanism during the HER process and that the electrochemical desorption step is rate limiting.

Catalytic stability is another important criterion for a good HER electrocatalyst. We performed an accelerated degradation test (ADT) of the Mo₂C@N-CNF catalyst to evaluate its stability by cyclic voltammetric sweeping between -0.4 to 0.1 V in 0.5 M H₂SO₄ at a scan rate of 100 mV s⁻¹. Figure 3d shows the HER polarization curves for the Mo₂C@N-CNFs before and after 2000 cycles. The observation of negligible current change strongly indicates that Mo₂C@N-CNFs

exhibit excellent HER electrocatalytic stability in 0.5 M H₂SO₄. To uncover the superior HER stability, we also examined the Mo₂C@N-CNFs after ADT by TEM, HRTEM and element mappings (Supplementary Figure S13 and S14). TEM and HRTEM observations indicate that the nanofibrous network morphology and the nanoparticles embedded in N-CNF structure are well retained after ADT (Supplementary Figure S13). In addition, element mappings also show that the C, Mo, N and O elements are still uniformly distributed over the nanofibers (Supplementary Figure S14), consistent with those of the Mo₂C@N-CNF catalyst before ADT. The above results demonstrate that the microstructure and composition of Mo₂C@N-CNFs are highly stable during ADT, which results in its excellent stability.

Currently, most of developed non-precious HER electrocatalysts work well only in acidic media, whereas almost all of the best non-noble oxygen evolution reaction electrocatalysts function well only in basic or neutral media.⁴¹ Non-precious HER catalysts that work well in basic or neutral media are highly desirable to realize overall electrochemical water splitting by inexpensive electrocatalysts. Therefore, the HER activity of Mo₂C@N-CNFs was also investigated in 1 M KOH (pH 14) and 0.1 M PBS (pH 7) solutions (Supplementary Figure S15). The polarization curve of Mo₂C@N-CNFs in 1 M KOH shows a small overpotential of 168 mV, achieving a significant hydrogen evolution with a current density of 10 mA cm⁻² (Supplementary Figure S15a). Impressively, an overpotential of only 261 mV can produce a notably high current density of 50 mA cm⁻². This HER activity in basic media is among the best reported activities of various types of non-precious electrocatalysts (Supplementary Table S4). Additionally, the Mo₂C@N-CNFs exhibits a notably small Tafel slope of 47.1 mV dec⁻¹ at an overpotential range from 100 mV to 150 mV, comparable to that of Pt/C (39.9 mV dec⁻¹) (Supplementary Figure S15b). In neutral media, the electrocatalytic activity of Mo₂C@N-CNFs is relatively lower than those at pH 0 and pH 14. For instance, Mo₂C@N-CNFs require an overpotential of 437 mV to produce a current density of 10 mA cm⁻² at pH 7 (Supplementary Figure S15c). Nevertheless, the HER activity in neutral media is better than that of Mo₂C embedded N-doped carbon nanotubes,¹⁷ cobalt-embedded nitrogen-rich carbon nanotubes⁴¹ and metallic cobalt@cobalt-oxo/hydroxo phosphate,⁴² among others. The Tafel slope at pH 7 is 76.7 mV dec⁻¹, which is similar to that of high-quality Pt/C catalyst (58.1 mV dec⁻¹) (Supplementary Figure S15d). These results clearly indicate that Mo₂C@N-CNFs is a highly active electrocatalyst over a wide pH range (pH 0–14). Significantly, the Mo₂C@N-CNF electrocatalyst also exhibits good stability under both pH 7 and 14 (Supplementary Figure S16). Few previously reported non-noble-metal HER catalysts exhibit high HER performance over the pH range of 0–14.^{11,17,41}

Finally, we performed DFT calculations to understand the remarkable HER performance of Mo₂C@N-CNFs (Supplementary Figure S1, Figure 4). For most electrocatalysts, the entire HER pathway ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) can be described by a three-state diagram consisting of (1) an initial state $\text{H}^+ + \text{e}^-$, (2) an intermediate adsorbed H^* and (3) the final product $1/2 \text{H}_2$ (Figure 4).^{30,43} The Gibbs free energy of the intermediate state $|\Delta G_{\text{H}^*}|$ can serve as a good measure for the HER activity of various catalysts (the smaller $|\Delta G_{\text{H}^*}|$, the better the activity toward HER). The optimal value of $|\Delta G_{\text{H}^*}|$ is zero. For example, the $|\Delta G_{\text{H}^*}|$ value of the most efficient catalyst Pt is ca. 0.09 eV.³⁰ Among the five catalysts (Figure 4), CNFs shows the most highly positive ΔG_{H^*} value, suggesting negligible HER activity. After N-doping, the ΔG_{H^*} value of the N-CNFs is dramatically reduced, showing an enhanced initial H^* adsorption and thus improved HER activity. However, the ΔG_{H^*} of N-CNFs is still a largely positive value

Figure 4 HER free energy diagram calculated at the equilibrium potential for Mo₂C@N-CNFs and other reference electrocatalysts.

(0.897 eV), indicating weak H⁺ adsorption and easy product desorption. By contrast, Mo₂C exhibits a largely negative ΔG_{H^+} value of -0.834 eV, indicating that chemical adsorption of H⁺ on its surface is too strong. Impressively, coupling of Mo₂C with N-CNFs into a hybrid results in the smallest $|\Delta G_{H^+}|$ value for Mo₂C@N-CNFs, which indicates mediated adsorption-desorption behavior. From the viewpoint of thermodynamics, Mo₂C@N-CNFs is the most HER electrocatalytically active among these catalysts.⁴³ Indeed, the DFT calculations match well with the above experimental results. Additionally, comparison of the $|\Delta G_{H^+}|$ values of Mo₂C@N-CNFs and Mo₂C@CNFs clearly proves that the N dopants in CNFs can effectively improve the HER performance of Mo₂C@N-CNF catalysts. Therefore, the strong synergistic effect between Mo₂C nanoparticles and N-CNFs has a critical role in the high HER activity of our developed Mo₂C@N-CNF catalyst.

CONCLUSIONS

In summary, ultrafine Mo₂C nanoparticles embedded within BC-derived 3D N-doped carbon nanofiber networks have been successfully synthesized by a simple, green, low-cost and scalable method using 3D nanostructured biomass (that is, BC) as a precursor. The hybrid catalysts exhibit remarkable HER electrocatalytic activity over a wide pH range of 0–14. Both the experimental results and theoretical calculations indicate that a strongly synergistic effect exists between the ultrafine Mo₂C nanocrystalline material and N-CNFs in Mo₂C@N-CNFs, which results in its superior HER activity. We believe that this work encourages further research on the development of more facile and low-cost strategies for synthesis of novel nanostructured materials for a wide variety of energy applications, including HER, oxygen evolution reaction and lithium ion batteries.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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