Heterointerface engineering in bimetal alloy/metal carbide for superior hydrogen evolution reaction

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Abstract

Developing noble-metal-free electrocatalysts for hydrogen evolution reaction (HER) is highly desirable to realize the hydrogen energy economy. Nanostructures and carbon-based hybrids are introduced to increase active-site abundance and to promote mass transportation. Herein, we reported a facile strategy for the in situ synthesis of bimetallic alloy-metal carbide heterostructures on ultra-fine chitin derived N-doped carbon nanofibers (NCNFs). The chitin nanofibers have abundant functional groups including hydroxyl (−OH) and amino (−NH2), which can strongly catch the metal ions. After the carbonization process, the Mo0.84Ni0.16-Mo2C nanoparticles were in situ formed throughout the whole NCNFs. Owing to the unique 3D nanofibers network structure, large specific surface area and synergistic effects between the Mo0.84Ni0.16 alloy and Mo2C, the Mo0.84Ni0.16-Mo2C/NCNFs electrocatalysts exhibit excellent HER activity with low overpotentials of 183 mV (10 mA cm−2) and Tafel slope of 71 mV dec−1 in alkaline solution. Heterointerface engineering can optimize the chemical configurations of active sites toward intrinsically boosted HER kinetics. The Mo0.84Ni0.16-Mo2C/NCNFs display temperature-dependent HER activity and the 750°C is the best carbonization temperature. In addition, the electrocatalysts exhibit outstanding stability during continuous HER electrolysis. This work provides a simple strategy to fabricate bimetal alloy metal carbide heterostructures.

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1. Introduction

Due to the severe global energy crisis and environmental pollution, clean and sustainable energy sources and carriers have drawn considerable attention. Hydrogen is thought to be an ideal candidate by virtue of its high mass energy density and renewability. Efficient electrocatalytic water splitting is regarded as an attractive method for large-scale hydrogen production [1,2]. Platinum (Pt) group metals are established as the effective hydrogen evolution reaction (HER) electrocatalyst. However, the high cost and low abundance in earth limit their widespread application [1,3]. Therefore, it is necessary to develop alternative noble-metal free electrocatalysts for HER.

In the recent years, most efforts have been made in developing non-noble-based catalysts, such as Fe, Ni and Co. Their metal alloys, chalcogenides, carbides and phosphides have been considered as promising alternatives to the Pt-based catalyst [4–8]. Recently, bimetallic alloys have showed great HER activity in alkaline solution benefiting from the synergistic effect between adjacent atoms [9–12]. Meanwhile, it is indispensable to choose highly conductive matrix with high specific surface area (such as carbon nanotubes, graphene, and carbon nanofiber) [13–16]. Compared with other carbon materials, biomass-derived carbon has attracted growing concern due to its abundant resource, low cost and environmental friendliness [16–19]. Chitin nanofibers have been extracted from crab and shrimp waste by a series of hydrolysis treatment and...
ultrasonic exfoliation. They have abundant hydroxyl and amino groups, which are the excellent substrates for the anchoring of metal nanoparticles due to their strong electrostatic attraction, coordination, and chelation with metal ions [20]. In addition, the three-dimensional (3D) nanofibers networks constructed by superfine chitin nanofibers (10 nm in diameter) can dramatically enhance the specific surface area and be beneficial to excellent electrolyte wettability and fast ion penetration [16].

In this work, we have proposed a facile approach for the in situ synthesis of Mo0.84Ni0.16-Mo2C heterostructures on chitin aerogel derived N doped ultra-thin carbon nanofibers (NCNFs). The chitin nanofibers have abundant functional groups including hydroxyl (–OH) and amino (–NH2), which can strongly catch the metal ions [21]. After the carbonization process, the Mo0.84Ni0.16-Mo2C nanoparticles were in situ formed throughout the whole NCNFs. Owing to the unique 3D nanofibers network structure, large specific surface area and synergistic effects between the Mo0.84Ni0.16 alloy and Mo2C, the Mo0.84Ni0.16-Mo2C/NCNFs electrocatalysts exhibit excellent HER activity with low overpotentials of 183 mV (10 mA cm−2) and Tafel slope of 71 mV dec−1 in alkaline solution. Heterointerface engineering can optimize the chemical configurations of active sites toward intrinsically boosted HER kinetics. The Mo0.84Ni0.16-Mo2C/NCNFs display temperature-dependent HER activity and the 750 °C is the best carbonization temperature. In addition, the electrocatalysts exhibit outstanding stability during continuous HER electrolysis for 10 h. This work provides a simple strategy to fabricate bimetal alloy metal carbide heterostructures, opening a new avenue to take advantage of earth-abundant biomass in energy conversion application.

2. Experimental details

2.1. Materials

The raw chitin powder was purchased from Golden-Shell Pharmaceutical Co. Ltd. (Zhejiang, China). Ammonium molybdate tetrahydrate ((NH4)6Mo7O24·4H2O, AR), nickel chloride hexahydrate (NiCl2·6H2O, AR), sodium hydroxide (NaOH), acetic acid (CH3COOH) and tertiary butyl alcohol (t-BuOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. All the reagents were used as received.

2.2. Preparation of the chitin nanofibers hydrogels

The general synthesis procedure of the chitin nanofibers hydrogels were reported in previous papers [21,22]. In short, chitin nanofibers hydrogels were prepared as follows: partially deacetylated chitin (DE-Chitin) was obtained in NaOH solution (33 wt%) at 90 °C for 2 h. The partially deacetylated chitin was washed with deionized water and then was dispersed in CH3COOH solution with the pH adjusted to 3 under constant stirring. The chitin nanofibers were prepared by ultrasonic exfoliation in an ice bath for 30 min. After removing the insoluble substance, the chitin nanofibers suspension was concentrated to about 1 wt% by rotary evaporation. At last, the as-prepared chitin nanofiber dispersion (10 g, solid content is 100 mg) was put in an ammonia atmosphere to obtain chitin nanofibers hydrogels.

2.3. Preparation of the Mo0.84Ni0.16-Mo2C/NCNFs hybrid nanofibers

To obtain the Mo0.84Ni0.16-Mo2C/NCNFs hybrid nanofibers, 200 mg (NH4)6Mo7O24·4H2O and 100 mg NiCl2·6H2O were dissolved in 20 mL deionized water. The as-prepared chitin nanofibers hydrogels (solid content is 100 mg) were cut into little pieces and were mixed in solution with continuous oscillation for 12 h. The obtained mixture was dissolved in t-BuOH solution for 24 h and then they were frozen and vacuum-dried in a freezer dryer to gain aerogels. At last, the as-prepared materials were heated from 30 to 300 °C and maintained for 1 h. Then, the samples were pyrolyzed at 750 °C for 2 h in a tube furnace under Ar atmosphere to obtain the Mo0.84Ni0.16-Mo2C/NCNFs (heating rate is 3 °C min−1). The sum of the (NH4)6Mo7O24·4H2O and NiCl2·6H2O is 300 mg in mixed solution. The Mo–Ni heterostructures synthesized with mass ratio of Mo and Ni precursor of 1:2, 1:1 and 2:1 are denoted as Mo–Ni–1-1/2-1 NCNFs, Mo–Ni–1-1/NCNFs and Mo–Ni–2-1/NCNFs, respectively. Further, in order to investigate the temperature effects on the HER activity of Mo0.84Ni0.16-Mo2C/NCNFs, we synthesized the Mo0.84Ni0.16-Mo2C/NCNFs prepared at different temperatures of 650, 750, 850 and 950 °C, respectively.

2.4. Materials characterization

The structures of the as-prepared nanomaterials were characterized by transmission electron microscopy (TEM, JEM, Japan, JEM-2100 plus) and scanning electron microscopy (SEM, Hitachi, Japan, S-4800). The elemental mappings were performed on a scanning transmission electron microscope (STEM, Philips, Tecnai G2 F30 STEMWIN) operating at 200 kV. The physical surface area and pore size distributions were determined through N2 adsorption and desorption measurements, which were calculated by using Brunauer-Emmett-Teller (BET) method by N2 adsorption at 77 K (ASAP2020 Micromeritics, Instrument Corp.). The compositions of the as-prepared materials were investigated by X-ray diffraction with Cu Kα radiation (λ = 0.1542 nm) (XRD, Bruker D8 Adv, D2 PHASER). The surface elementals composition and chemical state were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos, Axis supra). Raman spectrum was obtained on a Raman spectrometer (Renishaw 1000 NR) with 582 nm excitation line.

2.5. Electrochemical measurement

Electrochemical measurements were performed in a conventional three-electrode cell with a potentiostat (CHI 660E). Typically, 3 mg of sample and 25 μL Naion solution (5 wt%) were dispersed in 1 mL water-isopropanol solution with volume ratio of 1:1 by sonication for 1 h to form a homogeneous ink. Then 5 μL of the dispersion was loaded onto a glassy carbon electrode (GCE, 3 mm in diameter). The as-prepared electrode, the graphite rod and the saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively.

Electrochemical measurements were measured in 1 M KOH and 0.5 M H2SO4 solution. Linear sweep voltammetry was measured with a sweep rate of 2 mV s−1 to obtain the polarization curves, E (RHE) = E (SCE) + 0.244 + 0.059 pH V. Electrochemical impedance spectroscopy (EIS) measurements were carried out from 100 Hz to 0.1 Hz with amplitude of 10 mV at a potential of 240 mV. To estimate the electrochemically active surface area (ECSA), the electrocatalysts were cycled in the potential region from 0.17 to 0.47 V vs RHE under various scan rates from 20 to 120 mV s−1. According to the linear relationship between the capacitive currents and the scan rate, the slope k of the fitting line can be obtained. The value of capacitance of the double layer (Cdl) was equal to k/2 (0.3 V vs RHE), which is linearly proportional to the electrochemically active surface area of the electrode. Further, the specific capacitance C can be calculated by C = Cdl/m, where m is the area loading amount of the catalyst. In addition, the ECSA can be calculated by assuming a standard value of 40 μF/cm2: ECSA = C/40 μF/cm2 [23]. The long-term stability tests were conducted by continuous cycle voltammetry sweep from 0.17 to 0.47 V vs RHE at a scan rate of 100 mV s−1.
The chronoamperometry test was performed at current density of 50 mA cm⁻² for 10 h.

3. Results and discussion

The synthetic procedure of the Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs is illustrated in Fig. 1. Chitin nanofibers (ChNFs) dispersion was cross-linked in closed container of ammonium hydroxide to fabricate the chitin nanofibers hydrogel. Afterwards, the ChNF hydrogels were immersed in the precursor solution containing (NH₄)₆MoO₄·4H₂O and NiCl₂·6H₂O. The ChNFs have abundant functional groups including hydroxyl (–OH) and amino (–NH₂), which can strongly catch the metal ions, forming the MoO₄²⁻/Ni²⁺/ChNF hybrid precursor. The as-prepared MoO₄²⁻/Ni²⁺/ChNF hydrogels were freeze-dried after solvent exchanging to obtain MoO₄²⁻/Ni²⁺/ChNF aerogels. Through the carbonization process, the Mo₀.₈₄Ni₀.₁₆-Mo₂C heterostructure nanoparitcles were in situ formed throughout the whole NCNFs, leading to the formation of the Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs hybrid materials.

As shown in Fig. 2a-c, the as-prepared Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs aerogels exhibit distinct nanofiber-based 3D structures, and the superfine NCNFs exhibit average diameter of about 5–10 nm. There are larger amounts of Mo₀.₈₄Ni₀.₁₆-Mo₂C nanoparticles (NPs) anchored throughout the whole NCNFs. In addition, the Mo₀.₈₄Ni₀.₁₆-Mo₂C NPs are surrounded by carbon shells, which can strongly protect the NPs from aggregation during the carbonization process. The high-resolution transmission electron microscope (HRTEM) images indicate the formation of Mo₀.₈₄Ni₀.₁₆-Mo₂C heterostructures, as shown in Fig. 2d–f. The clearly visible interplanar distances with lattice fringe spacings of 0.212 nm correspond to the (200) planes of Mo₀.₈₄ phases. The lattice fringe spacings of 0.244 and 0.228 nm are attributed to (111) and (101) planes of Mo₀.₈₄Ni₀.₁₆ alloy phase. The HRTEM results confirm that the Mo₀.₈₄Ni₀.₁₆ alloy and Mo₂C phase both formed on the NCNFs, forming the heterostructures. The corresponding high angle annular dark field scanning TEM (HAADF-STEM) and STEM energy dispersive spectra (STEM-EDS) element mapping images are shown in Fig. 2g and h. Fig. 2h displays the uniform elemental distribution of C and N, suggesting the N-doped carbon of NCNFs. The elements distribution of Mo and Ni are according with the NP morphology, demonstrating the successful synthesis of Mo₀.₈₄Ni₀.₁₆-Mo₂C heterostructures on the surface of NCNFs. The formation of Mo₀.₈₄Ni₀.₁₆-Mo₂C heterostructure would effectively facilitate the electronic interaction and promote electron transfer in the electrocatalytic reaction [24,25]. The Mo–Ni heterostructures synthesized with mass ratio of Mo and Ni precursors of 1:2, 1:1 and 2:1 were denoted as Mo–Ni-1-2/NCNFs, Mo–Ni-1-1/NCNFs and Mo–Ni-2-1/NCNFs, respectively. Fig. S1 shows the pure NCNFs and Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs (Mo–Ni-2-1/NCNFs) prepared at different temperatures ranged from 650 to 950 °C. With the increased temperatures, the NCNFs become to fuse with each other and the 3D networks begin to collapse. In addition, as shown in Fig. S2 and S3, the higher temperatures lead to the formation of the larger sized Mo₀.₈₄Ni₀.₁₆-Mo₂C NPs due to the Oswald ripens. The collapse of the NCNFs also make the NPs easily collided with each other and coalesce into larger sizes.

Structural features of the as-prepared samples were revealed by X-Ray diffraction (XRD). Fig. 3a shows the XRD patterns of samples with mass ratio of Mo and Ni precursor of 1:2, 1:1 and 2:1. All the samples exhibit a broad band at 2θ = 21.5°, corresponding to the amorphous carbon. The peaks at 2θ = 36.8° and 42.6° are assigned to (111) and (200) planes of Mo₀.₈₄Ni₀.₁₆ alloy phase (JCPDS No.50-1270), suggesting the formation of Mo₀.₈₄Ni₀.₁₆ alloy. The peak at 2θ = 39.4° can be attributed to (101) planes of Mo₂C phase (JCPDS No.35-0787). The Mo₀.₈₄Ni₀.₁₆ alloy phases and Mo₂C phases all formed at different mass ratio of Mo and Ni, demonstrating that the Mo₀.₈₄Ni₀.₁₆-Mo₂C heterostructures are in situ synthesized on the NCNFs. Fig. S4 displays the Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs prepared at different temperatures. Higher temperatures exhibit the sharp diffraction peaks for Mo₀.₈₄Ni₀.₁₆ and Mo₂C phases, confirming the larger sizes of the Mo₀.₈₄Ni₀.₁₆-Mo₂C NPs due to the Oswald ripens. Fig. 3a shows that the Mo₀.₈₄Ni₀.₁₆-Mo₂C only consists of Mo₀.₈₄Ni₀.₁₆ and Mo₂C with the Mo–Ni ratio of 2:1. Although Mo₀.₈₄Ni₀.₁₆ alloy and Mo₂C are both generated when Mo–Ni ratio is 1:1 and 1:2, and in addition, there were NiC₃ phase generated at the Mo–Ni ratios of 1:1 and 1:2. As shown in Fig. S4, with the increased reaction temperature, the peak intensity for Mo₂C phases become stronger. Therefore, higher temperatures would lead to the formation of Mo₂C phases. The Mo₀.₈₄Ni₀.₁₆-Mo₂C heterostructures are accurate synthesized at Mo–Ni ratio of 2:1 and the best temperature of 750 °C.

In addition, we also synthesized the Ni/NCNFs (without (NH₄)₆MoO₄·4H₂O) and Mo₂C/NCNFs (without NiCl₂·6H₂O) hybrid as control at the same condition (Fig. S5). The Ni/NCNFs exhibits the characteristic peaks of metal Ni phases (JCPDS No.04-1270), indicating that there are only metallic Ni formed on NCNFs. For the Mo₂C/NCNFs, the XRD pattern only displays the characteristic peaks of the Mo₂C phase (JCPDS No.35-0787), indicating that there are only Mo₂C phase formed without any metallic Mo phases.

The Raman spectra of Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs are shown in Fig. 3b and Fig. S6. The D and G bands located at 1320 and 1595 cm⁻¹ are ascribed to carbon atoms in disordered graphitic form and E₂g vibration of carbon atoms in sp² form, respectively. The surface/edge defect of the material was evaluated by the relative intensity of D to G peak (ID/IG). The ID/IG of Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs >1, suggesting that the Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs possess large amounts of defects, which may pose positive effects on the electrocatalytic activity. The remaining peaks at 819 and 993 cm⁻¹ correspond to stretching vibration of Mo–C–Mo and Mo–C bonds [26], proving the formation of Mo₂C. The bands at 660, 706, 902, 954 cm⁻¹ correspond to Mo=O and Mo=O [27], this is due to oxidation, induced by high laser power and increased scan rate at ambient conditions [28].

The specific surface area and the porous 3D networks of Mo–Ni–2-1/NCNFs prepared at different temperature were determined by Brunauer-Emmett-Teller (BET) method. As shown in Fig. 4, the carbonation temperatures at 650, 750, 850, 950 °C correspond to specific surface area of 27.8, 158, 119.3, 16 m² g⁻¹. BET results reveal that the Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs prepared at 750 °C obtain the highest specific surface area of 158 m² g⁻¹, according to the N₂ adsorption-desorption isotherms (Fig. 4b) at high relative pressure (P/P₀ = 0.3). The average pore size of as-prepared Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs hybrid 3D networks is about 61 nm (Fig. 5b), indicating that there are sufficient mesopores (2–50 nm) and macropores (>50 nm) for effective electrochemical activation of Mo₀.₈₄Ni₀.₁₆ alloy and Mo₂C [29].

The surface chemical compositions and chemical states of Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs were further investigated by X-ray
photoelectron spectroscopy (XPS). For Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs, the wide-scan XPS spectrum exhibits the signals of Mo 3d, Ni 2p, C 1s, N 1s and O 1s (Fig. S8). The C 1s spectrum (Fig. 5a) can be deconvoluted into four different peaks located at 288.7, 286.1, 284.7, and 283.3 eV, corresponding to the C–O, C–N, C–C and C–Mo bonds, respectively [30–32]. The N 1s spectrum (Fig. 5b) exhibits characteristic peaks centered at 394.6, 398.1 and 400.8 eV, corresponding to the pyridinic-N, pyrrolic-N and graphitic-N, respectively. The Mo 3d XPS spectra (Fig. 5c) display four distinct doublets. The peaks with binding energies (BEs) at 233.1 and 235.4 eV can be ascribed to the Mo$^{6+}$ ions. The peaks at 233.7 and 231.3 eV are attributed to Mo$^{4+}$ ions [33]. The peaks with BEs at 228.6 and 232.1 eV correspond to Mo$^{2+}$ ions, which are ascribed to the Mo$_2$C phases. The peaks with BEs at 231.3 and 228.1 eV are correspond to Mo$^{0}$, which are ascribed to the Mo–Ni alloy phases [34]. The observed Mo$^{4+}$ and Mo$^{6+}$ ions are ascribed to the partial oxidation of Mo$_2$C in air. The high-resolution Ni 2p XPS spectra can be deconvoluted into two doublets (Fig. 5d). The characteristic peaks of Ni 2p located at 852.8 and 870.0 eV correspond to the metallic Ni. The peaks with BEs at 855.8 and 873.6 eV belong to the Ni$^{2+}$ ions caused by the surface oxidation [12,24]. The XPS results indicate the existence of metallic Ni and Mo and Mo$_2$C phases, confirming the formation of Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C heterostructures on NCNFs.

The electrocatalytic HER performance of the as-prepared catalysts was investigated by using a three-electrode setup system in
1 M KOH. The commercial Pt/C (20 wt%) was used as control. Linear sweep voltammetry (LSV) was used to investigate the HER activity of NCNFs, Mo2C/NCNFs, Mo–Ni–1-2/NCNFs, Mo–Ni–1-1/NCNFs and commercial Pt/C (20 wt%), respectively. All polarization curves were collected without iR correction. As shown in Fig. 6a, obviously, the pure NCNFs aerogels show poor HER activity. The Mo2C/NCNFs, Ni/NCNFs, the Mo–Ni–1-2/NCNFs and Mo–Ni–1-1/NCNFs require 218, 330, 220 and 220 mV versus RHE to obtain 10 mA cm−2, respectively, which were larger than that of the Mo–Ni–2-1/NCNFs. Tafel slopes were applied to study the kinetics of HER process. The commercial Pt/C electrocatalyst shows higher Tafel slope of about 127 mV dec−1 in 1 M KOH. The Tafel slope of Mo–Ni–2-1/NCNFs is 71 mV dec−1, which is lower than that of Mo–Ni–1-2/NCNFs (77 mV dec−1) and Mo–Ni–1-1/NCNFs (86 mV dec−1). The Mo–Ni–2-1/NCNFs shows the lower Tafel slope of 71 mV dec−1, when compared with the Pt/C electrocatalyst.

To explore the resource of its advantage in HER over the other three electrocatalysts, electrochemical impedance spectroscopy (EIS) is an effective method. Here, the EIS of these electrocatalysts were measured in the range of 105 Hz to 10−2 Hz. The obtained Nyquist plots are shown in Fig. 6c. It is obvious that only one semicircle can be observed for three samples. Apparently, the Mo–Ni–2-1/NCNFs electrocatalyst shows the smallest diameter of the semicircle, indicating the lowest charge transfer resistance, which can be calculated as 30 Ω. The charge transfer resistance of Mo–Ni–2-1/NCNFs and Mo–Ni–1-2/NCNFs are 99 and 60.4 Ω. The small resistance in Mo0.84Ni0.16-Mo2C/NCNFs suggests that the electrons can move quickly on its surface, which is benefit for the improvement of HER activity.

Electrochemical active surface area (ECSA) was estimated by double-layer capacitances (Cdl, Fig. 6d) calculated from the CV curves (Fig. S9) at a series of different sweep rates (20–120 mV s−1). The Cdl values of Mo–Ni–2-1/NCNFs, Mo–Ni–1-1/NCNFs and Mo–Ni–2-1/NCNFs are 9.14, 9.28 and 18.7 mF cm−2 at 0.4 V vs RHE.
respectively. Afterwards, the values of ECSA can be calculated to be 228.5, 232 and 467.5 cm² by assuming a moderate value of 40 μF/cm². Mostly, the largest ECSA imply that the Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs could provide more active sites.

Fig. 5. High-resolution (a) C 1s, (b) N 1s, (c) Mo 3d and (d) Ni 2p XPS spectra of Mo₀.₈₄Ni₀.₁₆-Mo₂C/NCNFs.

Fig. 6. (a) Polarization curves of the NCNFs, Mo₂C/NCNFs, Ni/NCNFs, Mo–Ni–1-2/NCNFs, Mo–Ni–1-1/NCNFs and Mo–Ni–2-1/NCNFs and commercial Pt/C (20 wt%) electrocatalysts in 1 M KOH. (b) The corresponding Tafel plots of the various electrocatalysts. (c) Nyquist plots performed at overpotential of 240 mV for Mo–Ni–1-2/NCNFs, Mo–Ni–1-1/NCNFs and Mo–Ni–2-1/NCNFs. (d) Linear fitting for the capacitive currents of the catalyst vs various scan rates of Mo–Ni–1-2/NCNFs, Mo–Ni–1-1/NCNFs and Mo–Ni–2-1/NCNFs.
The HER performance of samples in acid solutions is shown in Fig. 7. As shown in the Fig. 7, the overpotential required to drive the cathodic current densities of 10 mA cm$^{-2}$ is 229 mV for Mo–Ni–2–1/NCNFs, which is smaller than that of Mo$_2$C/NCNFs (274 mV), Ni/NCNFs (545 mV), Mo–Ni–1–2/NCNFs (246 mV) and Mo–Ni–1–1/NCNFs (240 mV), respectively. Obviously, the Mo–Ni–2–1/NCNFs shows the best HER performance. The Tafel slope of Mo–Ni–2–1/NCNFs, which is smaller than that of Mo$_2$C/NCNFs (274 mV), Ni/NCNFs (545 mV), Mo–Ni–1–2/NCNFs (246 mV) and Mo–Ni–1–1/NCNFs (240 mV), respectively. In the Mo–Ni–1–2/NCNFs, Mo–Ni–1–1/NCNFs and Mo–Ni–2–1/NCNFs were calculated to be 77 mV dec$^{-1}$, 79 mV dec$^{-1}$ and 76 mV dec$^{-1}$, respectively. In addition, the charge-transfer resistance value of Mo–Ni–2–1/NCNFs (31 Ω) is much lower than Mo–Ni–1–2/NCNFs (60 Ω) and Mo–Ni–1–1/NCNFs (99 Ω), implying Mo–Ni–2–1/NCNFs has good electron transfer ability. In acid solution, the C$_{dl}$ values of Mo–Ni–1–2/NCNFs, Mo–Ni–1–1/NCNFs and Mo–Ni–2–1/NCNFs are 2.83, 5.65 and 7.32 mF cm$^{-2}$. Therefore, the Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs show good HER performance in both alkaline and acid solution. The Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs exhibits the highest HER activity when compared with the Ni/NCNFs and Mo$_2$C/NCNFs, suggesting the synergistic effects between the Mo$_{0.84}$Ni$_{0.16}$ alloy and Mo$_2$C. The Mo–Ni alloy provides two types of active sites that facilitate the HER process in alkaline solutions [12]. At the same time, due to more efficient charge transfer kinetics, heterostructures have been demonstrated to be effective in reducing the HER overpotential [25,35]. In the Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs electrocatalysts, the Mo$_{0.84}$Ni$_{0.16}$ alloy can improve the intrinsic activity and conductivity of Mo$_2$C [24]. Generally, the reaction kinetics of HER is limited by the lack of protons under alkaline conditions. Therefore, an additional water-dissociation step is required to provide protons for the subsequent reactions. The Ni atoms in the MoNi alloy are revealed to be favorable sites for water dissociation, whereas the Mo atoms possess almost ideal free energy for hydrogen absorption/desorption [24]. The synergistic effect between the two metals thus leads to a high intrinsic activity for alkaline HER.

Further, we investigated the temperature effects on the HER activity of Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs. Fig. 8a shows the LSV curves of the Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs prepared at different temperatures of 650, 750, 850 and 950 °C, respectively. As shown in Fig. 8a, the overpotentials (10 mA cm$^{-2}$) of Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs prepared at 650, 750, 850 and 950 °C are 197, 183, 212 and 234 mV, respectively. The corresponding Tafel slopes of the samples are 78, 71, 79, 78 mV dec$^{-1}$, respectively (Fig. 8b). The electrochemical results demonstrated that Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs prepared at 750 °C exhibit the best HER performance. In addition, compared with other reported MoNi-based electrocatalysts, the Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs also shows a good HER activity (Table S1). From Fig. 8c, it is shown that the Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs prepared at 750 °C also obtain the lowest charge transfer resistance of 30 Ω than the Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs (650 °C) (40 Ω), Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs (850 °C) (43 Ω) and Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs (950 °C) (56.4 Ω). ECSA was also calculated from the CV curves (Fig. S10) at a series of different sweep rates (20–120 mV s$^{-1}$). Fig. 8d displayed the C$_{dl}$ of Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs prepared at 650–950 °C Table 1 summarizes the HER performance over the as-prepared samples. The Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs prepared at 750 °C acquire the highest ECSA values of 18.7 mF cm$^{-2}$, suggesting the larger amounts of active sites for HER.

The results indicate that increased carbonized temperatures from 650 to 950 °C will not lead to the continuous increased HER activity. The excessive temperature would result in the larger sizes of NPs and the collapse of the 3D networks. The catalyst Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs (750 °C) show best HER activity in alkaline solution. In addition, the Mo$_{0.84}$Ni$_{0.16}$-Mo$_2$C/NCNFs (750 °C) shows the largest specific surface area (158 m$^2$ g$^{-1}$), which could provide more active sites and improve its HER performance.
factors together lead to the best HER performance at carbonation temperature of 750 °C.

Chitin is a kind of natural polymer containing nitrogen, and the chitin nanofibers can be converted into N-doped carbon nanofibers after carbonization process. According to some relevant paper, N-doped carbon nanofibers matrix may pose positive effects on the electrocatalytic activity. We used carbon black (CB) and carbon nanotube (CNT) without nitrogen doping as the substrate to investigate the effects of N-doped carbon on the electrocatalytic HER. The electrocatalytic HER performance of the as-prepared

Table 1
Summary of HER performances over the as-prepared samples.

<table>
<thead>
<tr>
<th>samples</th>
<th>$r_{10}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_{dl}$ (mF cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo–Ni–1–2/NCNFs</td>
<td>220</td>
<td>77</td>
<td>99</td>
<td>9.14</td>
</tr>
<tr>
<td>Mo–Ni–1–1/NCNFs</td>
<td>220</td>
<td>86</td>
<td>60.4</td>
<td>9.28</td>
</tr>
<tr>
<td>Mo–Ni–2–1/NCNFs (650 °C)</td>
<td>197</td>
<td>78</td>
<td>40</td>
<td>9.24</td>
</tr>
<tr>
<td>Mo–Ni–2–1/NCNFs (750 °C)</td>
<td>183</td>
<td>71</td>
<td>30</td>
<td>18.7</td>
</tr>
<tr>
<td>Mo–Ni–2–1/NCNFs (850 °C)</td>
<td>212</td>
<td>79</td>
<td>43</td>
<td>5.5</td>
</tr>
<tr>
<td>Mo–Ni–2–1/NCNFs (950 °C)</td>
<td>234</td>
<td>78</td>
<td>56.4</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Chitin is a kind of natural polymer containing nitrogen, and the chitin nanofibers can be converted into N-doped carbon nanofibers after carbonization process. According to some relevant paper, N-doped carbon nanofibers matrix may pose positive effects on the electrocatalytic activity. We used carbon black (CB) and carbon nanotube (CNT) without nitrogen doping as the substrate to investigate the effects of N-doped carbon on the electrocatalytic HER. The electrocatalytic HER performance of the as-prepared
catalysts was investigated by using a three-electrode setup system in 1 M KOH. As shown in Fig. S11, the Mo–Ni–2–1/CNT and Mo–Ni–2–1/CB require 295 and 273 mV versus RHE to obtain 10 mA cm$^{-2}$, and the corresponding Tafel slope are 135 and 86 mV dec$^{-1}$, respectively. For the Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs catalyst, it exhibits excellent HER activity with lower overpotentials of 183 mV (10 mA cm$^{-2}$) and Tafel slope of 71 mV dec$^{-1}$.

Durability is another critical criterion for the evaluation of electrocatalysts and therefore, the long-term stability of the Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs catalyst was investigated by LSV and i-t curves in 1 M KOH. As shown in Fig. S10, the LSV curve of Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs (750 °C) after 2000 cycles shows a slight change in overpotentials of 6 mV, when compared with the initial LSV curve, suggesting the excellent stability of the electrocatalysts. To evaluate the excellent structural stability of the Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs, the Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs after 2000 cycles CV tests was characterized by TEM, XRD and XPS. As shown in Fig. S12, TEM image of Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs after 2000 cycles CV exhibit few changes. XRD patterns reveal that the Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs retain the original crystal phase (Fig. S13). The Mo 3d XPS spectra (Fig. S14) displays three distinct doublets, and the results reveal that Mo$^{2+}$ peaks of Mo$_2$C disappear. The intensities of the Mo$^{2+}$ peaks in Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs increased significantly, indicating the oxidation of surface Mo after 2000 cycles CV tests. The Ni 2p XPS spectra of Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs display little change before and after 2000 cycles CV tests. The above results confirmed the extraordinary stability of Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs.

The i-t curve of Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs (750 °C) was measured at current density of 50 mA cm$^{-2}$ for 10 h (Fig. 9b). After continuous 10 h, the current density remains 80%, further indicating the good stability in alkaline. The Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs prepared at 750 °C display the best HER performance than the Ni/CNFs, Mo$_2$C/NCNFs. The superfine carbon nanofibers derived from chitin nanofibers prevented the formation Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C NPs without aggregation even at high carbonization temperature. The formation of Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C heterostructures using chitin nanofibers as hosts and nanoreactors. After the carbonization process, the Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C heterostructures nanoparticles were in situ synthesized on the chitin nanofibers derived N-doped carbon nanofibers. The 3D nanofibers networks exhibit large surface area and the nanoparticles distributed uniformly on the N-doped carbon nanofibers. The as-prepared catalysts exhibit excellent HER activity in alkaline solution. The Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs obtain the good HER activity with low overpotential of 183 mV at 10 mA cm$^{-2}$ and Tafel slope of 71 mV dec$^{-1}$ in 1 M KOH, which is smaller than that of Ni/CNFs and Mo$_2$C/NCNFs. The Mo$_{0.84}$Ni$_{0.16}$–Mo$_2$C/NCNFs displays temperature-dependent HER activity and the 750 °C is the best carbonization temperature. In addition, the as-synthesized catalyst exhibits outstanding stability during continuous HER electrolysis. This work provides a simple strategy to fabricate bimetal alloy metal carbide heterostructures on ultra-fine chitin derived N-doped carbon nanofibers, opening a new avenue to take advantage of earth-abundant biomass in energy conversion application.

Author contribution

Liangri Ying and Shuhui Sun contributed equally to this work. Han Zhu and Mingliang Du supervised the research. Han Zhu designed and engineered this work. Liangri Ying and Shuhui Sun performed the experiments with support from Wenjie Liu, Zhenfeng Zhu, Ao Liu, Lijing Yang, Shuanglong Lu, Fang Duan and Chongling Yang. Liangri Ying, Wenjie Liu and Shuhui Sun wrote the manuscript and Han Zhu revised the manuscript. All authors contributed to the general discussion.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Appendix A. Supplementary data

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References


