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Bimetal-decorated Nanocarbon as A Superior Electrocatalyst for Overall Water Splitting

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Abstract

Heteroatom and monometal decorated carbons (e.g., Fe-N/C or Co-N/C) are reported as effective oxygen reduction catalysts. However, they are seldom investigated for overall water splitting. Additionally, it is a significant challenge to increase the heteroatom content in carbon and achieve performance comparable or superior to precious metal-based catalysts. Here, NiFe-decorated, nitrogen, phosphorus, sulfur tri-doped nanocarbon with oxygen-containing groups, i.e., NiFe-N, P, S/C is reported as a highly-active electrocatalyst for overall water splitting. The carbons are prepared by one-step template-free pyrolysis. Alfalfa, one of the natural biomass with highest N : C ratio and significant P and S, works as the sole carbon and heteroatom source. During preparation, crucial factors including total amount of added transition metals, Ni to Fe molar ratio, and pyrolysis temperature, are optimized. Ni_{0.75}Fe_{0.25}-N, P, S/C prepared at 900 °C exhibits the best oxygen evolution reaction, hydrogen evolution reaction, and overall water splitting activity and stability. This material even exceeds the benchmark RuO₂ in catalysing oxygen evolution reaction. Its overall water splitting activity is comparable to Pt/C-RuO₂, making it one of the best water splitting electrocatalysts. This exciting performance is attributed to the high heteroatom level ((N+P+S+O) : C =27.6 at.%), as well as the bimetal decoration.

Key words: Nanocarbon; Water Splitting; Electrocatalyst; Bimetal; Biomass

Introduction

The heavy reliance of our society on fossil fuels has triggered serious environmental concerns and intense research on sustainable energy technologies. Among such technologies, electrochemical water splitting is considered as an efficient and clean technology for the production of high-purity H_2 . [1-9] However, the sluggish kinetics of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), the two half reactions of water splitting, require large overpotentials in excess of their theoretical thermodynamic value, i.e., 1.23 V. In the light of this sluggishness, typical state-of-the-art catalysts are precious metal-based, i.e., Ru, Ir and their oxides for OER and Pt for HER. It is important to note that those catalysts lack bifunctionality. In fact, Pt is not active towards OER since it is prone to surface oxidation in OER potential regions. Similarly, IrO_2 and RuO_2 have limited HER catalytic activity. In addition, the disadvantages of precious metal catalysts include durability issues and prohibitive cost, hindering their practical use. As a result, developing cost-effective, highly-active, and durable OER and HER catalysts is critical to accelerate the commercialization of the water splitting technology. [10]

Carbon-based materials exhibit a great promise as non-precious metal catalysts (NPMCs), due to their low cost, high conductivity, and large surface areas. Various strategies have been proposed to enhance the catalytic performance of carbon materials, including multi-heteroatom doping, [11] surface functionalization, [3] defect engineering (void, vacancies, and edges), [12,

13] and the construction of porous and 3D morphologies.[10] For example, Qiao *et al.* found that, compared with single N doping, which has limited impact on improving HER, coupling N with S doping contributes to a much faster HER catalytic kinetics.[14] Dai *et al.* reported that 2D N/S co-doped graphitic sheets with hierarchical stereoscopic holes that can catalyze ORR, OER, and HER.[15] Even though dual doping can effectively enhance the activity, the catalytic performance of metal-free carbons is still far from satisfactory and usually inferior to their metallic counterparts, especially in terms of overall water splitting activity.[16] One of the primary reasons is the low heteroatom content, limiting the number of active sites. Chen and coworkers have reported an innovative “superdoping” method (i.e. fluorination followed by thermal annealing), which significantly enhanced the doping level of B, N, or S.[11] However, it should be noted that, to date, this strategy has only been successfully applied to single-heteroatom doped carbon materials. It remains a significant challenge to increase the level of various heteroatoms in carbon. Another concern for the use of carbon-based materials for water splitting is that they are apt to oxidation (in an alkaline electrolyte: $C + 4OH^- - 4e^- = CO_3^{2-} + H_2O$) in the OER potential regions, resulting in electrolyte poisoning and a significant activity drop.[17] As a consequence, developing highly active and robust carbon materials with superior OER and HER bifunctional activity and excellent durability remains a significant challenge.

Incorporating active species (metallic or non-metallic moieties) into carbon is a promising method to improve the performance.[18] In recent years, there is an increasing interest in N and

transition metal (e.g. Fe, Co, Mn) co-decorated carbon materials (M-N/C) as enhanced oxygen catalysts.[19] The addition of transition metals, even in trace amounts, could remarkably enhance the ORR activity.[20-22] In fact, it is widely believed that the transition metal could coordinate with the heteroatom to form M-N_x moieties serving as the active sites.[23, 24] In addition to providing more active sites, the metal added during the synthesis is expected to catalyze the graphitization of the heteroatom-doped carbon.[25] In general, a higher graphitization degree contributes to enhanced stability.[25] A number of previous reports have demonstrated in contrast to monometal-decorated carbon, by combining different monometals, synergistic benefits can be obtained.[26-28] For example, by using *ab initio* calculation, the Goddard group found that monometallic catalysts have different catalytic efficiencies towards the nucleation and growth of carbon tubes, and that bimetallic catalysts can synergistically contribute to boosting the growth rate and increasing the size of the tubes.[29] This finding was further validated by subsequent experiments.[25, 30] In our own work, we compared different combinations of four common transition metals, i.e., FeCo, NiFe, FeMn, CoNi, MnCo, and NiMn, and found that NiFe contributes to the largest-size carbon tubes in comparison to the other materials.[30] However, the heteroatom content remained in the obtained carbons is quite low (< 6 at.%), and the prepared carbons have never been investigated yet for overall water splitting.[30]

The overwhelming majority of previously published works on transition metal and

heteroatom co-decorated carbon have focused on monometal decoration, single heteroatom doping, and ORR catalysis.[19-22] In contrast, here we report a novel bimetal-decorated and multi-heteroatom doped nanocarbon with oxygen-containing functional groups, i.e., $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$, as a superior electrocatalyst for overall water splitting. Alfalfa, the most cultivated forage legume in the world,[31] is selected as the sole carbon and heteroatom precursor. According to the nutrient database provided by the United States Department of Agriculture: in addition to ~93 g of water, 100 g of alfalfa contain ~4 g of protein (N and S source), ~2.1 g of carbohydrate (C source) as well as ~0.07 g of P. This makes alfalfa one of the natural materials with the highest N : C ratio (~ 1: 13) and significant P and S. During the preparation, we adjusted various factors including the total amount of added transition metals, the Ni to Fe molar ratio, and the pyrolysis temperatures. $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ prepared at 900 °C exceeds the benchmark RuO_2 in terms of OER activity. When assembling it as the symmetrical electrode for a homemade H-type cell, it requires only 1.59 V to deliver a current density of 10 mA cm^{-2} and shows negligible degradation for 50 h. This exciting performance is attributed to the high heteroatom level ((N+P+S+O) : C =27.6 at.%), as well as the bimetal decoration.

2. Experimental

2.1 Sample preparation

The reagents and chemicals in this work were utilized as-received without further purification. Alfalfa, which served as the carbon source and heteroatom doping precursor, was bought from Kaytee Products, Inc. Analytical grade Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ethanol were purchased from Sigma Aldrich. In a typical synthesis, alfalfa was washed in DI-water and thoroughly dried. After that, 2g of alfalfa was mixed with nickel and iron nitrates in ethanol. The obtained mixture was then treated ultrasonically for 2 h to achieve an evenly distributed slurry, which was then dried in a vacuum oven at 60 °C for 24 h. Following that, the thoroughly dried mixture was ground, transferred into a ceramic crucible, and then calcined in a tube furnace (GSL 1100X, MTI).[32, 33] The annealing was performed for 2 h with a ramping rate of 5 °C min⁻¹ in N₂ at a gas flow rate of 50 sccm. After heat treatment, the obtained product was washed in ethanol and deionized water, and then dried. The factors including the total amount (m) of transition metal nitrates, Ni to Fe molar ratio ($X_{\text{Ni}} : X_{\text{Fe}}$), as well as the annealing temperature T were optimized: m varies from 0, 0.002 mol, to 0.005 mol; different $X_{\text{Ni}} : X_{\text{Fe}}$ includes 0 : 4, 1 : 3, 2 : 2, 3 : 1, and 4 : 0; T ranged from 800 °C to 1000 °C with steps of 100 °C.

2.2 Basic Characterizations

The X-ray diffraction patterns were recorded by a diffractometer (Empyrean PANalytical) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA). Raman spectroscopy was scanned via a Renishaw inVia Raman microscope. The elemental compositions and chemical environments

of as-prepared samples were examined by X-ray photoelectron spectroscopy (XPS, PHI5600) with a monochromatic Al-source X-ray. The functional groups were detected by a Fourier transform infrared spectrometer (FTIR, Perkin Elmer Spectrum 100 model). N₂ adsorption and desorption isotherms were tested by an analyzer (Beckman Coulter, SA3100 model) at the temperature of 77 K. Particle surface area and corresponding pore size distribution were calculated with Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) formula, respectively. The morphologies of the samples were surveyed by scanning electron microscopy (SEM, JEOL, 6390). Transmission electron microscopy (TEM, JEM-2010F) equipped with energy dispersive X-ray (EDX) spectroscopy was applied to characterize the nanostructures.

2.3 Electrochemical Test

By resorting to a rotating ring-disk electrode device (RRDE-3A, BAS Inc.), we evaluated the OER and HER electrochemical characteristics of the materials. The tests were conducted in ambient temperature, with a three-electrode cell configuration (catalyst modified glassy carbon (GC, 4 mm in diameter), and Ag/AgCl (filled with 3 M NaCl) performed as the working electrode and reference electrode, respectively).[34, 35] For the counter electrode, a Pt wire was used in the OER potential regions while a graphite rod was applied in the HER potential ranges. The catalyst ink was obtained through drop-casting: for each sample, 10 mg of the as-prepared material was dispersed into the mixture of ethanol (1.9 mL) and 5 wt.% Nafion (0.1

mL). Next, the suspension was placed in an ultrasonic bath for 1 h to reduce agglomeration. Finally, the homogenously dispersed sample (10 μL) was dropped onto the surface of the freshly polished glassy carbon electrode to achieve a catalyst ink ($\sim 0.4 \text{ mg cm}_{\text{disk}}^{-2}$) with a uniform thickness. In addition to the materials we prepared, the benchmark catalysts, i.e., Pt/C (20 wt.% load, Sigma Aldrich) and RuO_2 (Sigma Aldrich) were tested for comparison. The electrolyte was 1 M KOH. During electrolysis, the polarization potential was controlled by an ALS2325E bipotentiostat. The linear sweep voltammetry (LSV) were scanned in oxygen (OER) or hydrogen (HER) saturated electrolyte at a scan rate of 5 mV s^{-1} . The potential correction was conducted by compensating the Ohmic drop of the electrolyte, whose resistance was determined to be $\approx 30 \Omega$ by electrochemical impedance spectroscopy (EIS).

To gain insight into the electrochemical active surface area (ECSA) of the prepared catalysts, cyclic voltammograms (CV) was scanned between 1.1 and 1.2 V vs. RHE, in which potential range the effect of Faradaic current is negligible and the measured current i could be attributed to double-layer capacitive charging.[30, 36] The double-layer capacitance C_{DL} and i are linearly dependent:

$$i = \dot{v} C_{DL} \quad (1)$$

where $\dot{v}$ represents the potential scan rate, and here we set at 0.005 V s^{-1} , 0.01 V s^{-1} , 0.02 V s^{-1} , 0.05 V s^{-1} , 0.1 V s^{-1} , and 0.2 V s^{-1} . Half of the anodic and cathodic current difference ($\Delta i/2 = (i_a - i_c)/2$) at 1.15 V vs. RHE was used to determine the capacitance, whose value is linearly

proportional to ECSA.[30, 36]

The EIS spectra were measured by a VSP (BioLogic) electrochemical workstation,[37] to gain insight into the charge transfer resistance during water electrolysis. The AC voltage amplitude was set at 10 mV. The impedance data were recorded within the frequency range from 100 kHz to 0.1 Hz.[38] During the EIS tests, the potential of the working electrode was set as 1.7 V vs. RHE for OER and -0.3 V vs. RHE for HER.[4]

We built a H-type cell to assess the overall water splitting performance, where the two electrodes were separated by an anion exchange membrane (AMI-7001). The anion exchange membrane helps ensure that the current generated is due to water splitting only rather than possible fuel crossover.[39] The electrode was prepared by dropping a catalyst suspension on the surface of nickel foam followed by air drying. The catalyst loading was determined to be $\sim 0.13 \text{ mg cm}^{-2}$. During water electrolysis, the generated H_2 and O_2 were collected by graded volumetric cylinders and their volume was determined by the water drainage method.[40] The generated gases will move water from the cylinders to a container, and the volumes can then be read from the graded marks on the cylinders. A constant current density of 10 mA cm^{-2} was then passed for 4250 s.

3. Results and Discussion

3.1. Preparation and characterization

We prepared the NiFe-decorated, N, P, S doped nanocarbon by a one-step template-free

pyrolysis of 2 g of washed and thoroughly dried alfalfa, mixed with quantitative amounts of nickel and iron nitrate salts. The detailed procedures are described in the experimental part and illustrated in **Scheme 1**. The transition metal works as the catalyst for the graphitization and growth of the carbon, and provide the precursor of residual metal decorated into carbon configuration.[25, 41] We note that the preparation conditions including the total amount of added transition metals (m), Ni to Fe molar ratio ($X_{\text{Ni}} : X_{\text{Fe}}$), and the pyrolysis temperatures (T) could play a significant role in determining the structure, composition, and activity of the as-prepared samples. Different values of m including 0, 0.002 mol and 0.005 mol were screened. A representative example can be found in **Figure S1**, which compares the nanostructure (**Figure S1(a)-(c)**) and BET surface areas (**Figure S1(d)-(e)**) of the carbons prepared with different m . When the total amount of Ni and Fe salt reached 0.005 mol, we observed an aggregation of the metal particles, which led to significantly reduced surface areas. Therefore, $m = 0.002$ mol is selected. On the other hand, we compared various pyrolysis temperatures including 800, 900, and 1000 °C. While the XRD patterns of such samples were similar (see **Figure S2 (a)**), the material annealed at 900 °C displayed the highest OER and HER activity (see **Figure S2(b) and (c)**). The BET surface area (S_{BET}) of the sample annealed at 900 °C is not the highest among the three (see **Table S1**), however, the heteroatom content ((N+P+S+O):C) in the carbon prepared at 900 °C is the largest (see **Table S1**). Heteroatoms within the carbon framework could alter the electronic structure of the adjacent carbon atoms, change the charge distribution,

and facilitate the adsorption of reaction intermediates, potentially boosting the water electrolysis.[3, 15, 42] That may be the reason to account for the highest activity of the carbon prepared at 900 °C. Among various $X_{Ni} : X_{Fe}$, we screened 0 : 4 (Fe-N, P, S/C), 1 : 3 ($Ni_{0.25}Fe_{0.75}$ -N, P, S/C), 2 : 2 ($Ni_{0.5}Fe_{0.5}$ -N, P, S/C), 3 : 1 ($Ni_{0.75}Fe_{0.25}$ -N, P, S/C), and 4 : 0 (Ni-N, P, S/C). From **Figure 1(a)**, the distinct peaks located at around 44.7° and 65.2° are attributed to the (110) and (200) crystal plane of the cubic metallic Fe phase (Im-3m, ICOD 01-089-7194), while the diffraction reflections centered around 44.2°, 51.5°, and 75.8°, are assigned to (111), (200), and (220) planes of the cubic metallic Ni or NiFe alloy phase (Pm-3m, ICOD 01-088-1715) respectively. No diffraction peaks of metal oxides or other composites are detected in the XRD patterns. In addition, a characteristic diffraction peak of carbon, located at around 26.4° and indexed to the (002) plane of the graphitic carbon (ICOD 00-008-0415), was also detected.

Scheme 1: In-situ synthesis of NiFe-decorated, nitrogen, phosphorus, sulfur tri-doped nanocarbon with rich oxygen-containing groups and structural defects.

Figure 1. Structural and compositional characterizations for NiFe-decorated, N, P, S doped carbons: **(a)** XRD, **(b)** Raman, and **(c)** XPS. XPS fitting of the $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ material: **(d)** C 1s; **(e)** N 1s; **(f)** P 2p; **(g)** S 2p; **(h)** O 1s, where the experimental data is represented with black circles and the simulated spectrum is outlined with a red line, **(i)** FTIR spectrum for N, P, S/C and $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$; **(j)** N_2 adsorption–desorption isotherm curves, and **(k)**

corresponding Barrett–Joyner–Halenda (BJH) pore size distribution.

The Raman spectra of as-prepared carbons are shown in **Figure 1(b)**. For the metal decorated carbons, three obvious peaks located at around 1582, 1352 and 2686 cm^{-1} are assigned to the G band, D band, and 2D band, respectively.[43] The G band is caused by the bond-stretching motion of sp^2 C, the D band is linked to the presence of defects, and the 2D band is sensitive to the number of the carbon layers.[43] By comparison, Ni-N, P, S/C ($I_D/I_G=0.92$) and Fe-N, P, S/C ($I_D/I_G=0.89$) are characterized by a larger I_D/I_G ratio than N, P, S/C ($I_D/I_G=0.85$), reflecting a higher disorder degree present in metal-decorated carbons, likely caused by the addition of transition metals. We also note that the bimetal-decorated carbon, i.e., $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -N, P, S/C, has an I_D/I_G identical to that of metal-free N, P, S/C. Even though the residual transition metals in carbon may increase the structural disorder, the bimetal addition can contribute to a higher degree of graphitization of the carbon materials.[25] This aspect was also validated by the direct imaging (see the TEM micrographs in **Figure 2(a)-(d)**). As a result, two factors including increased disorder concentration and enhanced degree of graphitization are likely counteracted, leading to the identical I_D/I_G of $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -N, P, S/C and N, P, S/C. In addition, compared with the monometal-decorated carbon materials (i.e. Ni-N, P, S/C ($I_{2D}/I_G = 0.39$) and Fe-N, P, S/C ($I_{2D}/I_G = 0.48$)), $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -N, P, S/C ($I_{2D}/I_G = 0.30$) has a lower I_{2D}/I_G ratio, reflecting an increased number of carbon layers.[25] This finding is in agreement with the TEM images reported in **Figure 2(f)-(h)**.

The XPS survey spectrum in **Figure 1(c)** detects C, N, P, S, and O as well as transition metals of the metal-decorated carbons. Compared with metal-free N, P, S/C and monometal-decorated carbon (Ni-N, P, S/C and Fe-N, P, S/C), the heteroatom levels ((N+P+S+O) : C) of the bimetal-decorated Ni_{0.75}Fe_{0.25}-N, P, S/C are similar, see **Table S2**. We should note that a high level of heteroatoms ((N+P+S+O) : C = 27.6 at.%) is present in Ni_{0.75}Fe_{0.25}-N, P, S/C, which is attributed to the precursor used, i.e., alfalfa. In addition, from **Table S2**, the amount of remained metal (~15 wt.% with (Ni+Fe) : C ≈ 2 at.%) is similar among those metal-decorated carbons. The deconvolution of the C 1s, N 1s, P 2p, S 2p, and O 1s spectrum of Ni_{0.75}Fe_{0.25}-N, P, S/C is presented in **Figure 1(d) - (h)**. The high-resolution C 1s spectrum has contributions from C-C (284.8 eV), C-S/C-P/C-N (285.8 eV), and C-O (287.0 eV).[44] It is difficult to separate the C-S, C-P or C-N from each other due to their similar binding energies. Consequently, only a single peak is used to represent this region.[45] The N 1s peak (**Figure 1(e)**) results from 3 contributions centered at 398.7, 400.7, and 401.6 eV, which correspond to pyridinic N (42.6 at%), pyrrolic N (27.9 at%), and graphitic N (29.5 at%), respectively.[46] The P 2p can be divided into P-C (132.9 eV) and P-O (133.8 eV).[47] For the S 2p shown in **Figure 2(g)**, the two peaks centered at 163.3 and 164.9 eV are assigned to S 2p 3/2 and S 2p 1/2 of C-S-C. Another peak located at about 169.1 eV is attributed to C-SO_x-C.[44] The O 1s peaks centered around 533.2, 532.0, and 530.9 eV are assigned to C-O, P-O/S-O, and C=O, respectively, [48] indicating oxygen-containing functional groups exist on the surface of Ni_{0.75}Fe_{0.25}-N, P, S/C. The

presence of such functional groups is further confirmed by FTIR, see **Figure 1(i)**. Fittings of Fe 2p and Ni 2p XPS spectrum in **Figure S3** suggest the metallic state of Fe and Ni in Ni_{0.75}Fe_{0.25}-N, P, S/C, which agrees with the XRD result in **Figure 1(a)**.

Compared with metal-free N, P, S/C ($S_{\text{BET}}=537.5 \text{ m}^2/\text{g}$), the addition of transition metals greatly reduces the BET surface area, see **Figure 1(j)**, and adjusting the Ni to Fe molar ratio fails to change S_{BET} significantly: for metal-decorated carbon, the S_{BET} ranges from 120 to 150 m^2/g . As shown in **Figure 1(k)**, the pore size distributions are similar among the carbon materials with a dominant contribution in the size range from 3.1 to 3.9 nm.

Figure 2. Nanostructural characterizations: TEM and high-resolution TEM images for (a) and (e) N, P, S/C; (b) and (f) Ni-N, P, S/C; (c) and (g) Fe-N, P, S/C; (d) and (h) $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -N, P, S/C; (i) TEM and corresponding EDX mapping of $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -N,P,S/C; (j) High-resolution TEM images of $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -N,P,S/C.

From the SEM micrographs in **Figure S4**, metal-free and transition metal-decorated carbons have similar microstructures: a generally porous structure is revealed, with no obvious particle size difference. However, the addition of the transition metal and the adjustment of the $X_{\text{Ni}} : X_{\text{Fe}}$

ratio lead to nanostructural differences among the materials. As shown in **Figure 2(a)** and **2(e)**, N, P, S/C is generally amorphous, where graphite ribbons with limited length are randomly distributed. Instead, Ni-N, P, S/C (**Figure 2(b)** and **2(f)**) and Fe-N, P, S/C (**Figure 2(c)** and **(g)**) display longer and more continuous carbon ribbons. As a comparison, large-size cage-like nanocarbons with a hollow nanostructure are observed for Ni_{0.75}Fe_{0.25}-N, P, S/C (see **Figure 2(d)**). The special hollow nanostructure not only can improve the mass transport and the accessibility of active sites during water electrolysis, but can also make nanocarbon flexible and stretchable to buffer the volume changes of the encapsulated bimetal nanoparticles during cycling.[13] The carbon shell sizes are also compared as a function of the transition metal decoration in **Figure S5**, where Ni_{0.75}Fe_{0.25}-N, P, S/C has a much larger shell size than monometal-decorated Ni-N, P, S/C and Fe-N, P, S/C. In addition, we should also note that the number of carbon layers of Ni_{0.75}Fe_{0.25}-N, P, S/C in the outside carbon shell is greater than that of Ni-N, P, S/C and Fe-N, P, S/C, see **Figure 2(f)-(h)** and **Figure S6**. This finding is in agreement with the lowered I_{2D}/I_G ratio in the Raman data shown in **Figure 1(b)**, and is consistent with the previous reports that bimetals could contribute to the growth of graphitized carbon.[25, 30] From **Figure 2(i)**, the Ni_{0.75}Fe_{0.25} nanoparticle is embedded into the nanocarbon. In addition, EDX mapping detects the target elements in the carbon framework, supporting the XPS results. Upon closer examination, the unique morphology endows Ni_{0.75}Fe_{0.25}-N, P, S/C with structural defects, including topological disclinations at the corner and broken fringes on

the surface,[49] as shown in **Figure 2(j)**. The defect characteristics could be attributed to the precursor used (a biomass instead of well-defined chemicals), high level of heteroatom doping, and surface functionalization, as well as the removal of inorganic ingredients during preparation.[13, 50] Those structural and edge defects are considered capable of changing the local electron density distribution and strengthening the affinity of carbon to reaction intermediates.[51]

3.2. Catalytic activity

All the electrocatalytic tests were conducted in 1 M KOH. The potentials were corrected against RHE with the relationship $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 1.02 \text{ V}$, see the details in **Figure S7**. The OER activities of the as-prepared samples were firstly investigated by LSV, as shown in **Figure 3(a)**. Compared with metal-free N, P, S/C, the OER activity was significantly improved by transition metal-decoration, as shown by the larger current densities and more negative onset potentials. In addition, bimetal-decorated carbons ($\text{Ni}_{0.25}\text{Fe}_{0.75}\text{-N, P, S/C}$, $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{-N, P, S/C}$, and $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$) have higher OER activities compared to monometal-decorated carbons (Ni-N, P, S/C and Fe-N, P, S/C), suggesting that bimetal addition is beneficial for this reaction. We should also note that the OER activity of $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ is the best among the synthesized samples, requiring an overpotential of only 0.28 V to deliver 10 mA cm^{-2} . Its activity even exceeds that of commercial RuO_2 , suggesting the great promise of $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ as an OER catalyst. The superior OER activity of $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$

is also reflected by its smaller Tafel slope (52 mV dec⁻¹) compared to RuO₂ (87 mV dec⁻¹). A smaller value of Tafel slope contributes to an increased production of O₂ at only slightly increased overpotentials. **Table S3** compares the tested samples against state-of-the-art catalysts. It is clear that Ni_{0.75}Fe_{0.25}-N, P, S/C exceeds most reported carbon materials and is comparable to, or even better than, many state-of-the-art OER catalysts. Further, the activity for RuO₂ we measured is consistent with other literature reports. In order to explore the origin of the high anodic current on Ni_{0.75}Fe_{0.25}-N, P, S/C catalyst, we carried out a rotating ring-disk electrode (RRDE) test, see **Figure 3(c)**. The ring potential was held at 0.4 V vs. RHE to reduce the oxygen evolved from the disk electrode. Similarly, to monitor the potentially generated H₂O₂, the Pt ring was kept at 1.5 V vs. RHE, a potential high enough to oxidize H₂O₂.^[52] It is clear that the ORR current on the ring is increased with the OER current on the disk, and the Faradaic efficiency is larger than 92 % (the OER Faradaic efficiency is calculated by $I_{\text{ring}}/I_{\text{disk}} \times N$, where N is the collection efficiency^[52]). In addition, no obvious H₂O₂ oxidation current is detected. The last two results suggest that the observed high current density is mainly due to efficient 4e⁻ OER pathway ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$) rather than the undesirable 2e⁻ peroxide formation ($2\text{OH}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{e}^-$) or carbon oxidation.

Figure 3: Catalytic performance assessment: (a) OER LSV polarization curves and (b) corresponding Tafel plots; (c) Detecting the generated O_2 and potential H_2O_2 through a RRDE

setup, which is schemed in the inset. The tests were conducted in N₂-saturated 1 M KOH. (d) HER polarization curves and (e) corresponding Tafel plots for the investigated samples: Pt/C (violet line), Ni_{0.75}Fe_{0.25}-N, P, S/C (black line), Ni_{0.5}Fe_{0.5}-N, P, S/C (red line), Ni_{0.25}Fe_{0.75}-N, P, S/C (orange line), Fe-N, P, S/C (green line), Ni-N, P, S/C (blue line), N, P, S/C (magenta line), GC (olive line). The polarization curves were measured at a scan rate of 5 mV s⁻¹ and a rotation of 1600 rpm. (f) OER and (g) HER stability: the horizontal axis is the overpotential (η) required to deliver a current density of 10 mA cm⁻² before cycling, and the vertical axis is the corresponding value after CV scans for 1000 cycles. If a catalyst lies on the dashed line, the catalyst is stable; if it is above the line, the catalyst deteriorates with testing.

The HER polarization curves are shown in **Figure 3(d)**. For the as-prepared samples, the HER activity of the materials can be ordered in a similar manner as the OER activity: bimetal-decoreated carbon, i.e., Ni_{0.75}Fe_{0.25}-N, P, S/C is still the most active in catalyzing HER, followed by the monometal-decorated carbons including Ni-N, P, S/C and Fe-N, P, S/C. Metal-free N, P, S/C is the least active. Ni_{0.75}Fe_{0.25}-N, P, S/C only requires an overpotential of 0.25 and 0.29 V to deliver a current density of 10 and 50 mA cm⁻², respectively. From **Figure 3(e)**, Ni_{0.75}Fe_{0.25}-N, P, S/C has a smaller HER Tafel slope (84 mV dec⁻¹) than Ni-N, P, S/C (94 mV dec⁻¹), Fe-N, P, S/C (96 mV dec⁻¹) and N, P, S/C (128 mV dec⁻¹). While the HER activity of Ni_{0.25}Fe_{0.75}-N, P, S/C is still inferior to commercial Pt/C, however, it is comparable to many state-of-the-art HER catalysts, see **Table S4**.

Accelerated aging test was used to evaluate the stability of the synthesized materials.[53] The results are displayed in Figure 3(f) and 3(g). From Figure S8(a) and (b), there is no obvious change of OER and HER polarization curves for Ni_{0.75}Fe_{0.25}-N, P, S/C after 1000 cycles, suggesting an excellent stability. In contrast, for monometal-decorated Ni-N, P, S/C and Fe-N, P, S/C, the overpotential needed to deliver a current density of 10 mA cm⁻² increased after cycling (see Figure 3(f) and 3(g)), implying performance degradation. The improved durability of Ni_{0.75}Fe_{0.25}-N, P, S/C in comparison to Ni-N, P, S/C and Fe-N, P, S/C could be attributed to the increased number of graphitic layers in the outside shell (see Figure 2(f)-(h) and Figure S6), which enhances the corrosion tolerance during cycling.[30, 41] From the TEM images in Figure S9, after CV scans, the carbon shell of Ni-N, P, S/C was damaged and its surface become amorphous. In contrast, there is no obvious change for Ni_{0.75}Fe_{0.25}-N, P, S/C. The stability of Ni_{0.75}Fe_{0.25}-N, P, S/C is further confirmed by the chronopotentiometric test, see Figure S8(c) and (d).

A H-type cell with an anion exchange membrane (AMI-7001), which helps prevent crossover, was built to assess the overall water splitting performance,[39] see Figure 4(a). Ni foam has the advantages of low cost, high conductivity, and the three-dimensional framework. Consequently, the investigated materials are loaded on the Ni foam (denoted as @Ni foam) serving as electrodes for water splitting.^[1, 39, 54-56] The contribution of the Ni foam to the overall water splitting current is negligible, see Figure 4b, where its low measured activity agrees well with previously

published data (see **Table S5**). $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ requires a voltage of 1.60 V to deliver the current density of 10 mA cm^{-2} . From **Figure 4b**, the overall water splitting activity of $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ is very close to Pt/C-RuO_2 , and at voltages larger than 1.67 V it exceeds Pt/C-RuO_2 . In addition, $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ is comparable to and even better than many state-of-the-art water splitting catalysts (see **Table S5**). The produced H_2 and O_2 are collected using the water drainage method.[40] From **Figure 4(c)**, for $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$, the amounts of collected gases are very close to those calculated, reflecting a faradaic efficiency reaching $\sim 100\%$. In addition, as evidenced by chronopotentiometric curves, see **Figure 4(d)**, $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ achieves a better catalytic durability than Pt/C-RuO_2 . The overall voltage necessary for $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ to reach a 10 mA cm^{-2} current density is virtually constant for 50 h. In contrast, Pt/C-RuO_2 degrade over the same time span,[4] with the corresponding voltages increased by 30 mV. The bare Ni foam displays no obvious voltage decrease at the current density of 10 mA cm^{-2} , consistent with previous reports,[57] implying that the influence of Ni foam on the stability is limited. **Figure S10** reports the TEM micrographs of $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-N, P, S/C}$ after the durability test. We can observe that the nanocarbon morphology does not change. This finding further provides evidence of its excellent stability.

Figure 4: (a) Photo of the water splitting cell, where the two electrodes are separated by an anion exchange membrane; (b) Overall water splitting polarization curves for the investigated samples; (c) Faradaic efficiency measurement; (d) Chronopotentiometry test of Ni_{0.75}Fe_{0.25}-N, P, S/C@Ni foam, Pt/C-RuO₂@Ni foam, and bare Ni foam at a constant current density of 10 mA cm⁻².

3.3. Discussion

From the above experimental results, Ni_{0.75}Fe_{0.25}-N, P, S/C has proven to be an excellent water splitting electrocatalyst with significantly improved activity and stability towards both OER and HER. OER in alkaline electrolyte is widely recognized to proceed with 4 elementary steps, involving the adsorption of OH⁻, *OH, *O as well as *OOH (**Figure 5(a)**). [58, 59] Differently, there are two possible mechanisms for HER in basic media, i.e., Volmer-Heyrovsky

and Volmer-Tafel process,[60, 61] see **Figure 5(b)**. Both reaction pathways include the adsorption of H₂O on the active site, the decomposition of H₂O giving H and OH⁻, the desorption of OH⁻, and the production of H* for H₂ generation. From above, charge transfer between catalyst surface and the adsorbed intermediates plays a significant role in both OER and HER. As shown in **Figure S11**, the CV was scanned to acquire the electrochemical active surface area (ECSA) of the catalysts. From the results, Ni_{0.75}Fe_{0.25}-N, P, S/C achieves a much larger capacitive current than Ni-N, P, S/C and Fe-N, P, S/C. For Ni_{0.75}Fe_{0.25}-N, P, S/C (4.4 mF cm⁻²), its double layer capacitance (the ECSA at the same loading mass) is approximately 1.8 - 2.8 times larger than that of monometal-decorated carbons, see **Figure 5(c)**, reflecting a substantially enlarged electrochemically active area. The much larger-size carbon shells of Ni_{0.75}Fe_{0.25}-N, P, S/C (see **Figure 2(b)-(d)** and **Figure S5**) are expected to facilitate ion exchange and favor charge transport, efficiently extending the active sites into the internal parts and contributing to a larger ECSA.[13, 62] On the other hand, from the EIS and the fitting results, see **Figure 5(d)** and **Table S6**, the OER and HER charge transfer resistances of Ni_{0.75}Fe_{0.25}-N, P, S/C are much smaller than those of monometal-decorated Ni-N, P, S/C and Fe-N, P, S/C. This lowered resistance suggests a significantly improved charge transfer kinetics. Bimetal addition results in a less disorder degree of carbon materials than monometal does, supported by the lower I_D/I_G in the Raman spectroscopy in **Figure 1(b)**, which favors not only a higher electrical conductivity but also reduced charge transfer resistance. In addition, alloying

bimetal could potentially contribute to a number of additional synergistic benefits, even though the detailed mechanism remained debated.[63-65] It has been reported that Fe doping into Ni can improve the conductivity of NiFe-based electrocatalyst,[64] and there are also other studies demonstrating that Fe doping can induce structural transformations of Ni-based catalysts leading to more OER-active species.[65] Moreover, alloy Fe and Ni can result in a ligand effect by forming heteroatom bonds, together with a strain effect caused by the change of the average metal-metal bond length.[66] Both effects could modify the electronic and electrochemical properties of the catalyst, potentially leading to an optimal binding strength between the catalyst surface and the reaction intermediates such as $*H$, as well as a faster charge transfer kinetics.[67]

Figure 5 (a) OER and (b) HER elementary steps in alkaline electrolyte. (c) Dependence of capacitive current densities (measured at 1.15 V vs. RHE) on potential scan rates. (d) EIS for

Ni_{0.75}Fe_{0.25}-N, P, S/C (black), Fe-N, P, S/C (green line), Ni-N, P, S/C (blue line).

Acid leaching was performed to assess role of bimetal addition. After washing Ni_{0.75}Fe_{0.25}-N, P, S/C in 3 M HCl for 24 h, the reflection intensity attributed to NiFe alloy in XRD has been significantly lowered, see **Figure S12(a)**. However, the TEM image in **Figure S12(b)** reveals the presence of residual metal nanoparticles encapsulated within the carbon layers, suggesting its higher tolerance to a harsh environment. From **Figure S12(c)-(d)**, the reduced amount of NiFe alloy definitely reduces OER and HER activity, which could be attributed to the reduced ECSA, see **Figure S12(e)-(f)**. The above results support that bimetal themselves can provide additional active species for water electrolysis.

Based on the above analysis, we attribute the excellent activity and stability of Ni_{0.75}Fe_{0.25}-N, P, S/C to two factors. The first one is the high heteroatom level ((N+P+S+O) : C =27.6 at.%). Those doped heteroatoms (N, P, S) and surface oxygen-containing functional groups could alter the electronic structure of the adjacent carbon atoms, change the charge distribution, and facilitate the adsorption of reaction intermediates, thus facilitating the water electrolysis.[3, 15, 42] However, we cannot separate one specific heteroatom out from the others to investigate its individual role, since we used a sole carbon and heteroatom precursor, i.e., alfalfa, to prepare all the carbons. By controlling the pyrolysis temperature, we are able to modify the heteroatom content, and observe that higher heteroatom level contributes to an enhanced OER and HER activity (see **Figure S2** and **Table S1**). The other beneficial factor is the bimetal decoration.

Bimetal addition reduces the disorder degree of carbon materials than monometal does (see **Figure 1(b)**), favoring a smaller charge transfer resistance (**Figure 5(d)**), and it also contributes to an increased number of graphitic layers in the outside shell (see **Figure 2(f)-(h)** and **Figure S6**), improving the corrosion tolerance during cycling (**Figure 3(f)** and **(g)**). In addition, bimetal alloy themselves can provide additional active species for water electrolysis, evidenced by the above acid leaching experiments.

Finally, we prepared another 3 samples of Ni_{0.75}Fe_{0.25}-N, P, S/C, and tested their OER and HER activity. From **Figure S13**, there is no obvious difference among the tested activities, suggesting the reproducibility of this excellent water splitting electrocatalyst prepared from alfalfa.

4. Conclusions

In this contribution, we developed a bimetal-decorated nanocarbon with a high heteroatom level from a sole carbon and heteroatom precursor, i.e., Alfalfa. In comparison to monometal, bimetal addition reduces the disorder degree in carbon, and contributes to larger-size and more robust carbon shells, leading to improved OER and HER activity and stability. Ni_{0.75}Fe_{0.25}-N, P, S/C is superior to commercial RuO₂ in catalyzing OER. Furthermore, its overall water splitting activity is comparable to that of Pt/C-RuO₂, making it one of the best carbon-based water splitting electrocatalysts. The exciting performance can be attributed to the high heteroatom level ((N+P+S+O) : C =27.6 at.%), as well as the bimetal decoration.

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