



Bimetal-decorated nanocarbon as a superior electrocatalyst for overall water splitting



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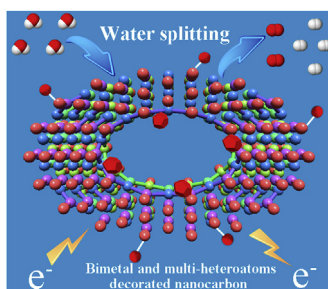
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HIGHLIGHTS

- Alfalfa works as the sole carbon and heteroatom source to prepare N,P,S tri-doped carbon.
- NiFe addition reduces disorder degree of the carbon, and introduces more active species.
- Ni_{0.75}Fe_{0.25}-N, P, S/C exceeds RuO₂ in catalyzing oxygen evolution reaction.
- The overall water splitting activity of Ni_{0.75}Fe_{0.25}-N, P, S/C is comparable to Pt/C-RuO₂.

GRAPHICAL ABSTRACT



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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.

1. 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 H₂ [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

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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, IrO₂ and RuO₂ 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 “super-doping” 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., Ni_{0.75}Fe_{0.25}-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. Ni_{0.75}Fe_{0.25}-N, P, S/C prepared at 900 °C exceeds the benchmark RuO₂ 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 (Fe(NO₃)₃·9H₂O), nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) 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_{Ni}: X_{Fe}), as well as the annealing temperature T were optimized: m varies from 0, 0.002 mol, to 0.005 mol; different X_{Ni}:X_{Fe} includes 0: 4, 1: 3, 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 Kα radiation (λ = 1.5406 Å, 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.

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