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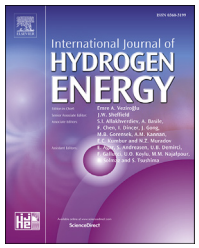

Nitrogen-doped oxidized carbon fiber as metal-free electrode towards highly efficient water oxidation

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ABSTRACT

Highly efficient and metal-free electrocatalysts hold promising in industrial water electrolysis with low cost, environmental friendliness and structural stability in wide pH electrolyte. Herein, N and O dual-doped carbon fiber (CF-O-N) has been hydrothermally synthesized as a three-dimensional (3D) electrocatalyst for oxygen evolution reaction (OER). The co-doping of N and O atoms acts as dual-active-site to improve OER properties, while the rough surface and large pores in CF-O-N electrode may expose abundant active sites and sufficient contacting in catalyst/electrolyte interfaces. CF-O-N electrode behaves excellently for OER with only 130 and 590 mV to generate 10 mA cm^{-2} and 100 mA cm^{-2}, respectively. The superior OER property of CF-O-N electrode than single N- or O-doped CF implies the synergistic effect between N and O dopants that may further enhance OER activities. More importantly, dual-doped CF-O-N electrode displays roust stability in 10,000 cycles of cyclic voltammogram (CV) and 12 h chronoamperometry test with unchangeable structures proved by post physical characterizations. It may provide a facile and rational design of self-supported and metal-free materials with excellent activities for water oxidation and holds promising for further industrialization.

Introduction

Electrochemical water splitting holds promising for efficient conversion of renewable energy into hydrogen fuel to resolve ever-increasing energy crisis caused by fossil fuels [1–6]. However, the efficiency of electrochemical water splitting is greatly restricted by intrinsically sluggish reaction of oxygen evolution reaction (OER) with considerable overpotential loss [7,8]. At present, noble Ir- or Ru-based materials exhibit highly active catalysts to overcome large overpotential, whereas their commercial applications are hampered by expensiveness and scarcity [9,10]. Therefore, cost-effective and earth-abundant materials are greatly desired to replace noble metal catalysts.

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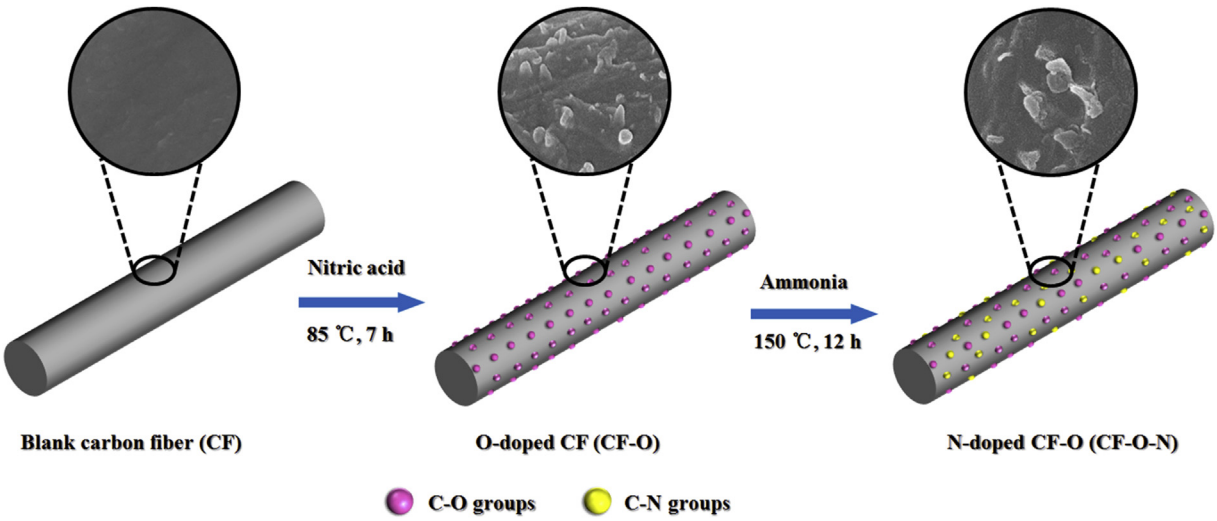
Currently, most of the reported efficient electrocatalysts for OER are usually transition metal-based composites, such as metal oxides (or hydroxides/oxyhydroxides) [11–16] and metal chalcogenides (sulfides or selenides) [17–22]. These electrocatalytically active species are usually attached on electrode surfaces with a polymer binder, which brings deducted impact on conductivity and exposure of active sites. Alternatively, conductive substrates like three-dimensional (3D) nickel foam [22–24] or two-dimensional (2D) Ti foil [21,25,26] are utilized to load the active species to further enhance the electron transfer efficiencies. However, metal-based catalysts often suffer from the tendency of corrosion in strong acid or alkaline, or dropping off the substrates, which lead to inevitable loss of active sites and unstable lifetime [12,27,28]. What is worse, the complicated synthesis with severe pollution, the releasing of metal ions from electrodes may bring harm to the environment and introduce cost problems for large-scale production [29]. Therefore, it is highly desired to develop metal-free catalyst with low cost, self-supporting features and excellent activities.

As typical metal-free element, carbon-based materials appear as earth-abundant, cheap, chemically inert to acid and alkaline electrolyte and environmentally friendly, which has been widely used as catalysts for many reactions [27,30–32]. Many carbon-based materials have been successfully developed for water electrolysis such as graphene [33,34], carbon black [35], nanotube [36,37] or graphitic carbon nitride (g-C_3N_4) [38,39]. In recent years, carbon cloth emerges as an attractive 3D carbon-based material with excellent mechanical stability, flexibility and high conductivity [40–42]. The unique 3D skeleton framework with large surface area enables fast mass and electron transport and facile dissipation for oxygen gas [14,43–46]. On the other hand, although pristine carbon nanomaterials are proved to have excellent conductivity, their intrinsic OER activities are poor [37]. One efficient approach to enhance the catalytic property of carbon-based materials is elemental doping with heteroatoms or hybridization, especially nitrogen element [34,37,47]. Many literature have proved that incorporation of nitrogen atoms into carbon matrix can effectively tune the electronic structure of the surrounding carbon atoms and modulate the local charge density distribution, leading to the improvement of the chemical reactivity and catalytic performance [36,48–50]. To further enhance the electrocatalytic activities of carbon materials, dual-doping of nitrogen and other elements is a rational routine [37,51–54]. Especially, the dual-doping of nitrogen and oxygen can create a synergistic coupling effect for enhanced catalytic properties [34,55]. Therefore, it is highly attractive to design dual-doped carbon fiber as metal-free electrode and explore its electrocatalytic performance for OER.

Herein, we have developed a facile two-step hydrothermal access to 3D self-supported carbon fiber electrode dual-doped by N and O heteroatoms (CF-O-N), which is schematically illustrated in Scheme 1. The first step of hydrothermal oxidization not only leads to surface roughing for improving contacting interface and charge transfer, but also introduces oxygen functional groups as catalytic centers. The secondary hydrothermal N-doping in ammonia can introduce N-containing groups (C-N groups) which are also electrocatalytically active for OER. Therefore, the N and O dual-doped CF-O-N loads abundant dual-active site with synergistic effect to further improve OER performance. In addition, as the whole electrode in water oxidation process, the metal-free CF-O-N electrode can avoid metal ion leaching and pollution to the environment, with advantages of high conductivity, excellent flexibility and structural strength. The CF-O-N electrode shows excellent OER activity requiring only 130 and 590 mV to deliver 10 mA cm^{-2} and 100 mA cm^{-2}, respectively, which is superior to single N- or O-doped CF (CF-N and CF-O). More importantly, CF-O-N possesses excellent durability with unchangeable structures in 10,000 cycles of stability test and 12 h long-term operation of water electrolysis. It may provide a facile and rational strategy for designing self-supported and metal-free materials towards excellent electrochemical performances and robust durability for water oxidation.



Scheme 1 – Schematic synthesis of CF-O-N electrode.

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