



Bottom-up fabrication of nitrogen-doped mesoporous carbon nanosheets as high performance oxygen reduction catalysts



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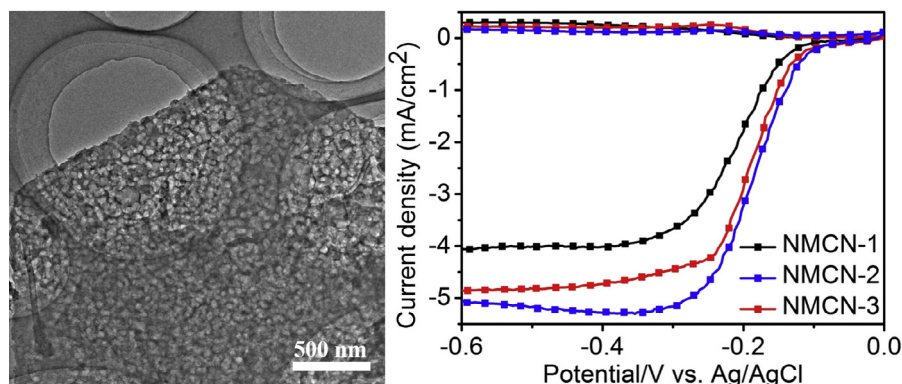
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GRAPHICAL ABSTRACT

Obtained by a bottom-up fabrication strategy, nitrogen-doped mesoporous carbon nanosheets with ordered hexagonal structures exhibit outstanding electrocatalytic activities towards oxygen reduction reaction.



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ABSTRACT

Nitrogen-doped mesoporous carbon nanosheets (NMCNs) with uniform hexagonal structures are fabricated via the thermal treatment of polyaniline wrapped cobalt hydroxide ($\text{Co}(\text{OH})_2$) nanosheets and the subsequent acid etching of the resulting composites. It is found that the morphologies, porosities and compositions of the NMCNs are greatly dependent on the ratio of the added aniline and $\text{Co}(\text{OH})_2$ nanosheets, which can in turn affect the electrochemical behavior of the NMCNs. As the electrocatalyst for oxygen reduction reaction in alkaline media, the NMCNs obtained with the aniline/ $\text{Co}(\text{OH})_2$ ratio of ~ 1.2 manifest excellent performance with the onset potential of -0.119 V, the half-wave potential of -0.182 V and the limiting current density of 5.06 mA cm^{-2} , which are superior to most of the previously reported N-doped porous carbon nanosheets.

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1. Introduction

Recently, porous carbon nanosheets have aroused intensive attentions due to their potential applications in energy devices

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such as lithium ion batteries, supercapacitors and fuel cells [1–6]. Generally, their unique two-dimensional (2D) morphology with thin thickness and high aspect ratio allows the sufficient exposure of the pores, which thus leads to good electrolyte accessibility and short diffusion distances for both mass and charge carriers [7–9]. On the other hand, the doping of nitrogen (N) atoms in the carbon frameworks of the nanosheets will boost their surface wettability and electronic conductivity [10,11]. Serving as the active sites for various electrochemical reactions, these N atoms can render the resulting N-doped porous nanosheets appealing candidates for electrocatalysis and energy storage [12–14].

Due to the above reasons, diversified approaches have been developed to fabricate N-doped porous carbon nanosheets in the last few years [15–20]. Among them, the carbonization of polymers loaded on a 2D template is one of the most appealing strategies since the structures and compositions of the resulting N-doped porous carbon nanosheets can be tuned in a molecular level by the delicate selection of precursor and reaction conditions [21,22]. For this purpose, graphene oxide (GO) is often used as the substrate because the large amount of oxygen containing functional groups on its surface can both render the good solution processability for GO and serve as the anchor points for the binding of various polymers [23–25]. Nevertheless, the introduction of porous structures in the carbon sheets from these methods generally requires additional templates or activation processes [3,23], which inevitably increase the complexity of the fabrication strategies. Moreover, the sizes, shapes and the oxidization degrees of GO are largely depended on their preparation conditions, which also hamper the application of GO as the 2D template for N-doped porous carbon nanosheets [26,27].

Herein, we report an unprecedented bottom-up strategy towards N-doped mesoporous carbon nanosheets (NMCNs) with ordered hexagonal structures by the thermal treatment of polyaniline (PANI) wrapped cobalt hydroxide ($\text{Co}(\text{OH})_2$) nanosheets and the following acid etching process. Compared with GO, $\text{Co}(\text{OH})_2$ nanosheets possess more uniform size and shape, which thus make them ideal templates to construct porous carbon nanosheets with ordered morphologies. On the other hand, the existence of cobalt species can facilitate the formation of graphitic carbon frameworks in the resulting nanosheets [28]. And the cobalt nanoparticles from $\text{Co}(\text{OH})_2$ can serve as the template for the creation of mesopores [29]. By modifying the loading ratio of aniline and $\text{Co}(\text{OH})_2$, the morphology, porosity, and compositions of the obtained NMCNs can be easily adjusted, which can further influence their performances as the electrocatalyst for oxygen reduction reaction (ORR). As the result, outstanding ORR activities with the onset potential of -0.119 V, the half-wave potential of -0.182 V and the limiting current density of 5.06 mA cm^{-2} are archived by NMCNs in alkaline media, which are superior to most of the previously reported N-doped porous carbon sheets (Table S1).

2. Experimental section

2.1. Preparation of $\text{Co}(\text{OH})_2$ nanosheets

Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Acros, 2.5 mmol) and hexamethylenetetramine (HMT, 99%, Sigma-Aldrich, 45 mmol) were dissolved in deionized water (500 ml). The solution was refluxed at 95 °C for 5 h under N_2 atmosphere. Brucite $\text{Co}(\text{OH})_2$ was obtained as pink powder by centrifuging the reaction mixture at 3000 r.p.m for 10 min and washing the resulting solid with deionized water [30].

2.2. Preparation of NMCNs

$\text{Co}(\text{OH})_2$ nanosheets (50 mg) were firstly dispersed in deionized water (25 ml). Ammonium hydroxide (250 μl) was added in the suspension and the mixture was stirred for 0.5 h. Subsequently, aniline (Aldrich, 40, 60, or 80 μl) was then added and the dispersion was stirred for 1 h. Ammonium persulfate (APS, Aldrich, 125 mg) dissolved in deionized water (25 ml) was then added dropwise and the mixture was stirred at 0 °C for 24 h. Polyaniline coated $\text{Co}(\text{OH})_2$ (PANI/ $\text{Co}(\text{OH})_2$) was obtained by centrifuging the reaction mixture at 5000 r.p.m for 10 min and washed the resulting powder with deionized water. Based on the amount of aniline added in the polymerization process, the samples were named as PANI/ $\text{Co}(\text{OH})_2$ -1 (40 μl), PANI/ $\text{Co}(\text{OH})_2$ -2 (60 μl), and PANI/ $\text{Co}(\text{OH})_2$ -3 (80 μl), respectively. These obtained composites were then thermally treated at 800 °C in N_2 for 3 h and the resulting solids were treated with H_2SO_4 (0.5 M) at 35 °C for 1 h to produce NMCNs as black powders.

2.3. Characterizations

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, Sirion 200, 25 kV). TEM measurement was conducted on a JEOL-1400 electron microscope at an operating voltage of 120 kV. The sample was dissolved in water and the suspension was dropped onto a copper grid covered with carbon film. X-ray photoelectron spectra (XPS) were determined by X-ray photoelectron spectrometer (AXIS Ultra^{PLD} Kratos, Japan). N_2 sorption analysis was conducted on a TriSta 3020 accelerated surface area and porosimetry instrument, equipped with automated surface area, at 77 K using Barrett-Emmett-Teller (BET) calculations for the surface area. XRD analysis was performed on a Rigaku D/Max 2500 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54$ Å) at a generator voltage of 40 kV and a generator current of 50 mA with a scanning speed of $5^\circ/\text{min}$ from 5° to 90° .

2.4. Electrochemical measurements

All the electrochemical measurements were carried out in a conventional three-electrode cell using the PINE electrochemical workstation (Pine Research Instrumentation, USA) at room temperature. Ag/AgCl and platinum wire were used as reference and counter electrodes, respectively. A RRDE electrode with a Pt ring (5.52 mm inner-diameter and 7.16 mm outer-diameter) and a glassy carbon disk (5.0 mm diameter) served as the substrate for the working electrode for evaluating the ORR activity and selectivity of various catalysts. The electrochemical experiments were conducted in O_2 saturated 0.1 M KOH electrolyte for oxygen reduction reaction. The RDE and RRDE measurements were conducted at a rotating speed of 1600 rpm with a sweep rate of 10 mV/s. The catalyst ink was prepared by blending the catalyst powder (10 mg) with 1 mL Nafion solution (0.5 wt%) in an ultrasonic bath. 6 μL of catalyst ink was then pipetted onto the GC surface, leading to a catalyst loading of 60 μg for alkaline. Commercial 20 wt% platinum on Vulcan carbon black (Pt/C) was measured for comparison. The working electrode was prepared as follows. 5 mg Pt/C was dispersed in 1 mL Nafion solution (0.25 wt%) by sonication for 1 h to obtain a well-dispersed ink. 4 μL of catalyst ink was then pipetted onto the GC surface, leading to a Pt/C loading of 20 μg . Other experimental conditions were the same as for the NMCN catalysts, except that 0.1 M HClO₄ was used as electrolyte. The scan rate of LSV curves was 10 mV s^{-1} and the scan rate of CV curves was 100 mV s^{-1} .

The four-electron selectivity of catalysts was evaluated based on the H_2O_2 yield, calculated from the following equation:

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