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Nitrogen-doped mesoporous network-like carbon as an efficient metal-free electrocatalyst for oxygen reduction reaction

Congxiu Guo ^{a,b}, Xili Tong ^{a,*}, Xiang-Yun Guo ^{a,**}^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China^b University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Nitrogen-doped mesoporous network-like carbon (NMNC) as a high-performance oxygen reduction reaction (ORR) catalyst was synthesized via hydrothermal reaction of glucose solution followed by pyrolysis under ammonia atmosphere. The obtained NMNC sample at 1000 °C (NMNC-1000) exhibits extremely high specific surface area (2588 m² g⁻¹), large pore volume and mesoporous structure, which facilitates mass transport and exposes more active sites. As a result, NMNC-1000 shows excellent electrocatalytic activity in alkaline media with high half-wave potential (0.759 V vs. RHE) for ORR via a four-electron pathway, which is only 32 mV more negative than that of 20% Pt/C, and stability with noticeable methanol-tolerance and CO anti-poisoning.

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Introduction

Efficient catalysts for oxygen reduction reaction (ORR) are extensively envisioned as the key to achieve excellent performance for fuel cells or metal-air batteries [1,2]. To date, Platinum and its alloys are still the most frequently used electrocatalysts for four-electron transfer ORR process. However, their intrinsic drawbacks including high cost, poor durability, susceptibility to fuel crossover and CO deactivation, severely impede the large-scale application of fuel cells [2–4]. Therefore, considerable efforts have been dedicated to develop low-cost, sufficiently efficient and durable ORR

catalysts based on non-precious metal or even metal-free materials. Recently, N-doped carbon materials have attracted intensive interest as promising alternatives to Pt-based ORR catalysts due to their high electrocatalytic activity, environmental friendliness, long-term operational stability and low cost [5–8]. N-doped carbon materials including carbon nanotube [3,9], carbon nanocages [10], mesoporous carbon spheres [11] and graphene [12] have been reported to show high catalytic activity for ORR. In particular, the 3-dimensional mesoporous network-like structures have exhibited the excellent ORR activity [13–19], because they can provide more exposure of active sites, fast channels

* Corresponding author.

** Corresponding author.

E-mail address: tongxili@sxicc.ac.cn (X. Tong).<http://dx.doi.org/10.1016/j.ijhydene.2016.10.043>

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for electron conduction and reactant diffusion [20,21]. Recently, various techniques were developed to fabricate 3-dimensional mesoporous network-like structure, including hard templates [19–23], soft templates [11,24], nano-casting [25,26], and so on. However, sacrificial templates will lead to impurities, high cost and complicated preparation steps [20]. Besides, most of carbon materials including graphene prepared by the Hummers oxidation method and carbon nanotubes, will be unavoidably induced metal impurities via preparation processes and original materials [27]. The trace levels of metal in carbon materials will limit the identification of the active sites in nitrogen-doped carbon materials.

Herein, we developed N-doped mesoporous network-like carbon (NMNC) as an efficient metal-free electrocatalyst for ORR in alkaline media. A large quantity of mesopores existed in NMNC materials are helpful for enhancing ORR performance. There are no any metallic species involved in the preparation of the NMNC materials, which can intrinsically avoid residual of trace metals and favor to explore the origin of ORR activity of N-doped carbon materials. In addition, the obtained NMNC-1000 shows excellent ORR performance, which is comparable to the commercial 20% Pt/C.

Experimental section

Materials

All chemicals were analytic grade and directly used as received without further purification. D-(+)-glucose monohydrate and potassium hydroxide were obtained from Sino-pharm Chemical Reagent Co. Ltd.

Synthesis of NMNC materials

Nitrogen-doped mesoporous network-like carbon (NMNC) materials were synthesized according to our disclosed patent [28]. In a typical synthesis, a glucose solution was transferred into a teflon-lined autoclave. Then, the autoclave was sealed and heated to 200 °C. This process produced a brown carbonaceous precursor. To obtain the nitrogen-doped mesoporous carbon, 500 mg dried carbonaceous precursor was heated at a heating rate of 5 °C min⁻¹ to 800, 900 and 1000 °C, and annealed at the temperature in NH₃ atmosphere for 3 h. The heating and cooling steps were performed in Ar atmosphere. The products obtained from different annealing temperatures were denoted as NMNC-800, NMNC-900 and NMNC-1000, respectively. For comparison, carbon without N-doping was also prepared by the same method but annealed in Ar atmosphere at 1000 °C for 3 h, denoted as C-1000. Besides, the sample NP-1000 was prepared via hydrothermal reaction of glucose solution at 180 °C and annealed at the temperature in NH₃ atmosphere at 1000 °C for 3 h.

Characterization

The X-ray diffraction (XRD) measurements were carried out using Mini Flex II diffractometer equipped with Cu K α radiation. The surface morphology and structure were examined by

field emission scanning electron microscopy (FESEM, JSM-7100F) and high-resolution transition electron microscopy (HRTEM, Tecnai G2 F20 S-Twin) coupled with energy dispersion spectroscopy (EDS). The surface elements were analyzed by X-ray photoelectron spectra (XPS, AXIS ULTRA DLD). The total C, H and N contents of the samples were measured by an elementary analysis system (Vario EL cube). The N₂ adsorption–desorption isotherms were measured on Micromeritics ASAP 2020 analyzer at 77 K. The specific surface area was calculated by applying the Brunauer–Emmett–Teller (BET) method. The pore volumes and pore size distributions were obtained according to the Barrett–Joyner–Halenda (BJH) model from the adsorption branches of isotherms. The total pore volumes were obtained from the adsorbed amount at a relative pressure (P/P_0) of 0.994. Raman spectra were collected with a LabRAM HR800 spectrometer (HORIBA Jobin Yvon) with 514.5 nm Ar laser as the excitation source. The contents of Ni, Co, and Fe in the samples were measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo iCAP 6300).

Electrochemical measurements

The electrochemical experiments of the catalysts for ORR were carried out in a conventional three-electrode cell with a CHI 760 D electrochemical workstation (CH Instruments, China). The platinum wire and saturated Ag/AgCl electrode (PINE RFOZZ1-30) were used as the counter and reference electrodes, respectively. All the potential were corrected to reversible hydrogen electrode according to the equation, $E_{vs\ RHE} = E_{vs\ Ag/AgCl} + E_{\phi\ Ag/AgCl} (0.197\ V) + 0.059\ pH$ [29,30]. A glassy carbon electrode (GCE) (PINE, 5 mm diameter, 0.196 cm² geometric area) was used as the substrate for the working electrode. Prior to surface coating, the GCE was polished in sequence with 1.0 and 0.05 μm alumina powders and rinsed with deionized water and ethanol to get a mirrorlike surface. To prepare the working electrodes, 5.0 mg catalyst powder was dispersed by sonication into 1.0 mL ethanol for 20 min to form a uniform catalyst ink (5 mg mL⁻¹). Then, 5 μL of catalyst ink was dropped onto the surface of GCE, followed by dropping 5 μL of Nafion solution in ethanol (0.1 wt%) as a binder, and dried at ambient temperature. For comparison, commercial 20 wt% Pt/C catalyst (Johnson Matthey) was also loaded onto the electrode surface in the same way. As the electrolyte for ORR, 0.1 M aqueous KOH was purged with high-purity O₂ or Ar for at least 30 min prior to electrochemical measurements. The cyclic voltammetry (CV) tests were run in Ar-saturated solution and O₂-saturated solution from 0.165 to 1.165 V with a sweep rate of 50 mV s⁻¹. The linear sweep voltammetry (LSV) on a rotating disk electrode (RDE) were carried out at a scan rate of 10 mV s⁻¹ at various rotation rates from 400 to 2000 rpm in O₂-saturated 0.1 M KOH solutions. Methanol crossover and CO poisoning tests were performed by a chronoamperometric technique at the bias potential of 0.665 V in O₂-saturated 0.1 M KOH solutions with a rotation rate of 1600 rpm. The rotating ring-disk electrodes (RRDE) (PINE, 5.61 mm diameter, 0.247 cm² geometric area) were conducted in O₂-saturated 0.1 M KOH solution at the rotation rate of 1600 rpm. The collection efficiency of the Pt ring electrode is 0.37.

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