Energy 152 (2018) 333–340

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Combustion reaction-derived nitrogen-doped porous carbon as an effective metal-Free catalyst for the oxygen reduction reaction

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ARTICLE INFO

Article history:
Received 2 February 2018
Received in revised form
24 March 2018
Accepted 30 March 2018
Available online 31 March 2018

Keywords:
Combustion reaction
Porous carbon foam
Nitrogen-doping
Oxygen reduction reaction

ABSTRACT

Finding an effective approach to prepare low-cost metal-free catalysts with excellent catalytic performance for the oxygen reduction reaction (ORR) is a crucial challenge for the commercialization of fuel cells. Herein, a novel and effective combustion approach was designed in order to construct the three-dimensional porous carbon foam and followed by heat treatment in an NH_3 atmosphere. In the combustion process, sucrose was used as the carbon source to produce the carbon framework, sodium bicarbonate as the pore-foaming agent to form the porous structure. This synthetic route is novel, cost-effective and without using any templates, expensive equipment as well as highly toxic chemical reagents. Compared with the control samples, the typical product exhibits the excellent catalytic activity in terms of not only a positive onset potential and high current density, but also low H_2O_2 yield and approximate four-electron reaction pathway in alkaline media. The reason may be attributed to the synergistic effect of the three-dimensional porous structure, high BET surface area (up to 1216 $m^2 g^{-1}$) and effective nitrogen-doping of the product. In addition, the novel method is of great importance, which may guide future efforts for the development of other porous carbon-based materials for applications in multi-fields.

1. Introduction

Oxygen reduction reaction (ORR) as an important process has attracted great attention because of its importance to some of the energy conversion applications, which is related to fuel cells, metal-air batteries, and so on [1–5]. In general, Pt-based materials have long been considered the high performance oxygen reduction catalyst to overcome the sluggish kinetics for the ORR [6–9]. However, the intrinsical scarcity and high cost of Pt have hindered the widespread use of this metal [10–13]. In response to these shortcomings, researchers have made many positive attempts to construct new catalysts in order to replace the precious Pt. These include N-CoTi@$CoTiO_3$/C [14], $MnWO_4$ [15], Fe@C_2N [16] and Fe_3O_4/$CoSe_2$ [17] as non-precious metal catalysts or nitrogen-doped graphene [18], carbon nano-onions [19], carbon sheets [20], porous graphdiyne [21], carbon nanoleaf networks [22] and N, S co-doped porous carbon [23] as metal-free catalysts by different raw materials and synthesis methods, which exhibited great catalytic activity for the ORR. Therefore, developing effective non-precious metal or metal-free catalysts is a promising exploration to replace Pt-based materials [24].

Nitrogen-doping as an effective way to improve catalytic performance of carbon material has attracted significant interest recently [25,26]. For example, Song et al. used the high-temperature pyrolysis approach to synthesize the nitrogen-doped carbon nanoribbons, which exhibited satisfactory catalytic activity in the ORR process [27]. Ashokkumar et al. reported a facile strategy for preparation of nitrogen-rich carbon nano-onions that presented excellent catalytic activity and stability for the ORR [19]. Yu et al. prepared the nitrogen-doped carbon nanofiber aerogel by direct carbonization of bacterial cellulose and followed by NH_3 activation; this product showed outstanding ORR activity and electrochemical stability, respectively [24]. Based on the above literatures, we can conclude that doping nitrogen into carbon to improve the catalytic activity of carbon materials has great potential in the development of oxygen reduction catalyst. Furthermore, some other favorable characteristics of carbon materials, such as large BET surface area and porous structure, play important roles in the creation of active sites on the surface and mass transfer for enhancing the catalytic performance in the ORR [28]. For instance,

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https://doi.org/10.1016/j.energy.2018.03.175
0360-5442/

Hu et al. reported the nitrogen-doped nanoporous carbon nanocables as an efficient ORR catalyst, which exhibited outstanding electrocatalytic activity for the ORR attributed to the synergistic effect of the high surface area, three-dimensional conductive network structure and nitrogen-doping [29]. Therefore, finding an effective approach for low-cost and large-scale preparation of nitrogen-doped porous carbon catalyst with high BET surface area and three-dimensional porous structure towards the ORR is worth exploring, which remains a great challenge.

Combustion as a kind of important chemical reaction can cause thermal decomposition of some chemical reagents and accompanied with gas generation, which could be well applied to synthesize porous materials. Therefore, there is an increasing interest and motivation for the use of combustion reaction to prepare the porous carbon material by reasonable design. For this to happen, the mixture of sucrose, sodium bicarbonate and ethanol has attracted our attention due to its great potential to construct the ideal porous carbon material by the improved combustion reaction. The synthesis process of porous carbon foam is illustrated in Fig. 1. Experiment principle is that sodium bicarbonate can be decomposed easily when it is heated, along with the production of large amounts of CO_2, which make the formed carbon expanded rapidly to form the three-dimensional porous structure, and then grown into snakelike carbon foam. Compared with the traditional methods for the preparation of porous carbon materials, such as soft and hard templates [30,31], as well as chemical vapor deposition method [32], this synthetic route has not used any templates and expensive equipment. The method is simple, rapid, low-cost and effective for the mass production of porous carbon-based materials, possessing potential commercial application in fuel cells. Therefore, we used this method for large-scale preparation of porous carbon materials and followed by NH_3 activation for the generation of nitrogen-doped porous carbon materials. We also investigated the relationship between structure and catalytic ORR activity, and analyzed the influence of nitrogen-doping, BET surface area, temperature and different media on the catalytic performance of samples for the ORR. At last, the mechanism of enhanced catalytic ORR activity for the typical product (NPCM1000) was explored.

Herein, we successfully prepared the nitrogen-doped porous carbon material that the typical product (NPCM1000) presents excellent catalytic activity in terms of positive onset potential, large current density, low H_2O_2 yield and approximate four-electron reaction pathway in alkaline media, suggesting its a promising ORR catalyst in fuel cells. In addition, this study will contribute concurrently to the guidance for preparation of other functional materials applied in energy fields, which are related to lithium-ion batteries, supercapacitors, and so on. Therefore, the research direction might be to extend the application of the method in the future.

2. Experimental section

2.1. Materials

Sucrose ($C_{12}H_{22}O_{11}$) and sodium bicarbonate ($NaHCO_3$) were purchased from Aladdin Industrial Corporation. Ethanol (CH_3CH_2OH) was purchased from Shanghai Titan Scientific Co., Ltd. Hydrochloric Acid (HCl, 36.0–38.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis process of porous carbon foam

Typically, 100 g of sucrose and 24 g of sodium bicarbonate were transferred to a 250 mL beaker and stirred at room temperature. Subsequently, 40 mL of ethanol was added into the beaker and stirred for some minutes to form mixture, which was transferred to another 100 mL beaker (Fig. 1a). Then, the mixture was ignited by a lighter (Fig. 1b). The combustion temperature is estimated to be about 500 °C during the process based on the combustion of ethanol. An interesting combustion phenomenon, black snake-like porous carbon foam with three-dimensional structure (Fig. 1c and d) appeared in front of our eyes a few minutes later.

2.3. Synthesis process of nitrogen-doped porous carbon material

Typically, the porous carbon foam was transferred to a 3000 mL beaker, which washed with distilled water several times. Then, hydrochloric acid (36.0–38.0%) was added into the porous carbon foam, stirred and soaked for two days to remove the residual sodium bicarbonate and sodium carbonate. Finally, the precursor was gained by washing with distilled water and freeze-drying for two days. To obtain the nitrogen-doped porous carbon material, the precursor was annealed in a tube furnace at 1000 °C for 2 h under flowing NH_3 atmosphere. The typical product was obtained and denoted as NPCM1000. For comparison, NPCM800 and NPCM900 were prepared according to the same procedure only different heat-treatment temperatures (800 °C or 900 °C for 2 h). PCM1000 was also prepared by the same procedure but in Ar atmosphere at 1000 °C for 2 h.

2.4. Characterization

Scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopic (XPS), X-ray diffraction (XRD) patterns and Brunauer–Emmett–Teller (BET) surface areas measurements were taken with a S-4800 (Hitachi, Japan), JEM-2100 (JEOL, Japan), X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo, USA), DX-2700 X-ray diffractometer and Micromeritics Tristar 3020 instrument, respectively.

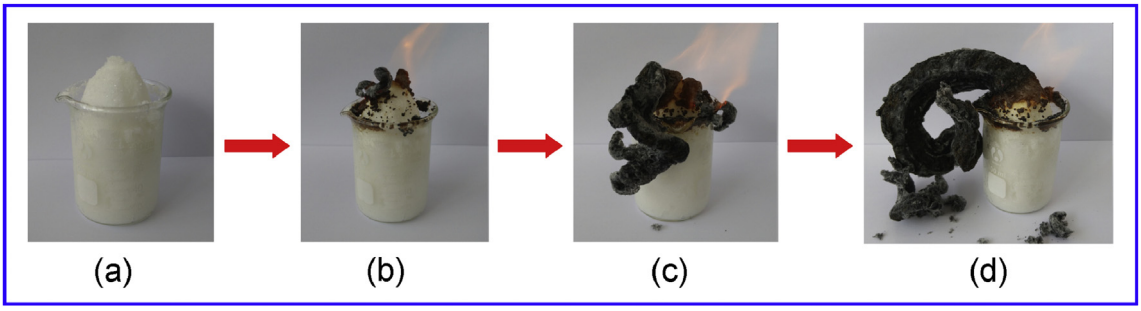

Fig. 1. Synthesis process of porous carbon foam by combustion reaction.