



Short communication

Covalent triazine-based frameworks as efficient metal-free electrocatalysts for oxygen reduction reaction in alkaline media

Jingliang Liu, Yaojuan Hu^{*}, Jingjing Cao

School of Environmental Science, Nanjing Xiaozhuang University, Nanjing 211171, PR China

ARTICLE INFO

Article history:

Received 25 January 2015

Received in revised form 17 March 2015

Accepted 19 March 2015

Available online 21 March 2015

Keywords:

Covalent triazine-based frameworks

Electrocatalytic

Oxygen reduction reaction

ABSTRACT

Covalent triazine-based frameworks (CTFs) were synthesized using an ionothermal method. The resultant CTFs were demonstrated as a metal-free electrocatalyst with superior electrocatalytic activity for oxygen reduction reaction (ORR) due to their high atomic percentage of pyridinic nitrogen, which is the most catalytically active site for ORR.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Energy is one of the biggest challenges for the 21st century. There is also increasing global demand for environmentally friendly energy sources. Fuel cells appear to be one of the alternative energy sources due to their high energy density, high conversion efficiency, and low pollution. For low temperature fuel cells, the kinetically sluggish oxygen reduction reaction (ORR) at the cathode is the foremost limitation to obtain the expected performance [1,2]. Nowadays, the best materials for catalysis of ORR are the Pt-based precious metal catalysts. However, Pt-based catalysts usually suffer from several disadvantages, such as high cost, poor durability, and sluggish electron-transfer kinetics for ORR, blocking the development and commercialization of fuel cells [3,4]. Therefore, extensive research efforts have been devoted to searching for metal-free or precious metal-free electrocatalysts that can facilitate the ORR [5–8].

Among these various metal-free electrocatalysts, nitrogen-doped carbon materials have been investigated extensively to substitute Pt-based electrocatalysts for ORR [9–12]. The introduction of heteroatoms in carbon materials has been reported to enhance the performance of ORR electrocatalysts. When a heteroatom is bonded with a carbon framework, it introduces a defect in the nearby sites due to difference in bond length and atomic size, and thereby can induce uneven charge distribution [13]. Clearly, the inclusion of nitrogen in the carbon structure induces active sites which can lead to the break of O–O bonds of oxygen molecules [14]. Moreover, it has been reported that the nitrogen-doped carbon materials are highly selective toward ORR and more tolerant to species such as methanol, CO, glucose, formaldehyde, etc. [15].

Nitrogen-doped carbon nanotubes [16,17], nanofibers [18,19], microporous carbon [20], graphene sheets [21], and graphene quantum dots [22,23] have been shown to exhibit high electrocatalytic activities for ORR. Even though various nitrogen-doped carbon materials have been developed as metal-free catalyst for ORR, the development of novel materials with high catalytic activity and strong durability is still highly desired.

It is reported that the atomic percentage of nitrogen and the structure of nitrogen species (pyridinic, graphitic, or pyrrolic) in the carbon lattice are crucial for optimizing the electrocatalytic performance for ORR [24]. Furthermore, because of their high surface area, tunable pore size, and large pore volume allowing facile molecular transport of reactants and products, microporous carbons have been a popular choice as electrocatalyst for fuel cells [25]. Therefore, the nitrogen-rich microporous carbon framework can be expected to dramatically enhance ORR electrocatalytic activity. In this communication, we report an effective ORR electrocatalyst, the covalent triazine-based frameworks (CTFs), which were synthesized by ionothermal method using 1,4-dicyanobenzene as precursors [26], and their superior electrocatalytic performance toward ORR. CTFs have high nitrogen atomic percentage, large surface area, and large pore volume which facilitate the transport of reactants and products.

2. Materials and methods

See detail in electronic Supplementary information.

3. Results and discussion

CTFs were synthesized by ionothermal method (see detail in Supplementary information 1.2) using 1,4-dicyanobenzene as precursors [26]. The FT-IR spectrum of CTFs is shown in Supplementary information (SI)

^{*} Corresponding author.

E-mail address: huyaojuan@njxzc.edu.cn (Y. Hu).

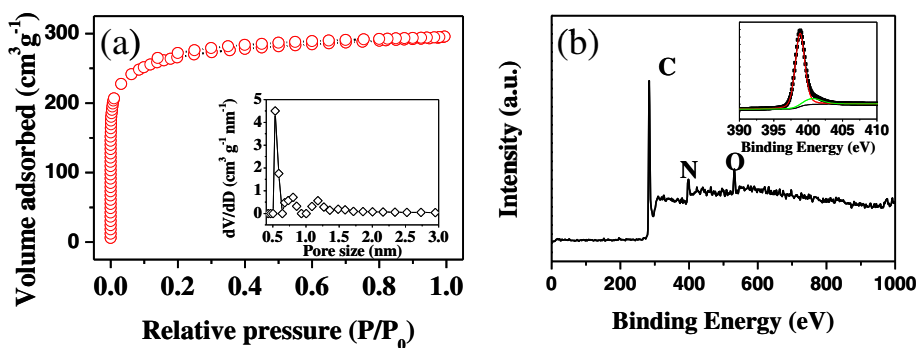


Fig. 1. (a) N_2 adsorption/desorption isotherms with an inset showing the pore size distribution. (b) XPS survey spectrum and N1s spectrum of CTFs.

Figure S1. The strong bands around 1507 and 1352 cm^{-1} are characteristic of the stretching and breathing vibrations of the triazine structure, respectively, and the weak band around 2228 cm^{-1} is assigned to the stretching vibration of $C\equiv N$ [27]. Powder XRD pattern of CTFs is presented in SI Figure S2. The diffraction peaks with 2θ at 7.2° and 15.1° are indexed to the carbon (100) and (200) diffractions, respectively, reflecting the crystalline triazine-based organic framework with hexagonal pores [26]. The broad diffraction peak at 26.2° is assigned to the (001) diffraction, characteristic of the interlayer aromatic sheets. The SEM and TEM of CTFs are displayed in SI Figure S3.

The surface area and pore size of the synthesized CTFs were determined by N_2 adsorption–desorption isotherms. The results of elemental analysis, specific surface area and pore volume of MCFs are listed in Table S1. Brunauer–Emmett–Teller (BET) analysis reveals a high specific surface area of $782.44\text{ m}^2\text{ g}^{-1}$, and a total pore volume of $0.42\text{ cm}^3\text{ g}^{-1}$. The isotherms and pore size distributions of CTFs are shown in Fig. 1(a). The isotherms exhibit the prominent characteristic of type-I isotherms with rapid adsorption of N_2 in very low pressure (P/P_0), reflecting the presence of micropores in the frameworks. Moreover, the pore size distribution (inset in Fig. 1(a)) displayed that MCFs consisted of micropore structure with a narrow distribution.

Elemental analysis indicated that the resulted CTFs have a N/C atom ratio of 0.259 (see Table S1). The amount of nitrogen doping and its nature of bonding with the carbon framework were investigated by XPS measurements. The XPS survey spectrum of CTFs given in Fig. 1(b) shows a predominant peak at 284.6 eV corresponding to C, and peak at 400.0 eV and 532.0 eV corresponding to N and O, respectively [13]. Quantitative XPS analysis shows that nitrogen is present with 17.58 at.% in the framework, which is in agreement with the result of elemental analysis. The high-resolution N1s XPS spectrum (inset in Fig. 1(b)) reveals two N1s peaks corresponding to different binding energies. The large peak at 398.8 eV is attributed to pyridinic nitrogen in the carbon framework, and a small peak at 401.0 eV is assigned to quaternary nitrogen, respectively, revealing that nitrogen atoms incorporated into the graphitic structure are mainly in pyridinic type, which is the most catalytically active site for ORR and can lower the ORR onset potential [17,28,29].

To investigate the electrocatalytic activity of the CTFs for the ORR, the cyclic voltammetry (CV) experiments in N_2 -saturated and O_2 -saturated 0.1 M KOH solutions were performed. The corresponding voltammograms can be seen in Fig. 2(a). As can be seen, a well-defined reduction peak occurs at around -0.25 V (vs. SCE) in the O_2 -saturated solution, whereas there is no such a peak in the N_2 -saturated one, indicating that the CTFs exhibit electrocatalytic activity toward the reduction of O_2 .

To better understand the electrocatalytic performance of the CTF catalysts during the ORR process, we compared its electrocatalytic performances with commercial Pt/C and CMK-3 as carbon framework

without nitrogen by linear sweep voltammetry (LSV) using a rotating disk electrode (RDE). The LSV was performed in an O_2 -saturated 0.1 M KOH solution at a rotation rate of 1600 rpm and a scan rate of 10 mV s^{-1} (Fig. 2(b)). At the applied potential lower than -0.4 V , the ORR is under a diffusion-controlled regime where mass transfer of O_2 to the electrode determines the ultimate current density. The ORR falls into the kinetics-controlled regime at the potential at or above -0.4 V . The onset potential for ORR at CTFs is approximately 0.0 V , relative to that for the commercial Pt/C catalyst and negative than that for CMK-3. Moreover, the onset potential for ORR at CTFs is negative than that for other nitrogen-doped carbon material (50 mV for nitrogen-doped carbon nanotube [16], 40 mV for graphene quantum dots [22], 80 mV for nanofibers [19]), which due to the pyridinic sites in the carbon frameworks lowers the ORR onset potential. The kinetic currents for CTFs and the Pt/C are similar, indicating the similar adsorption/reduction processes on both catalysts. The good ORR activity of the CTFs catalyst is ascribed to the presence of defect-induced active sites for O_2 adsorption, which are generated by changes in the bond length and the bond angle of the C–N bond. In addition, the lone-pair electrons in nitrogen may lead to an increase in the electrical conductivity, and the density of states at the Fermi level [25].

It is common knowledge that the ORR may process different pathways on different catalyst surfaces. One is that the indirect or peroxide pathway of oxygen reduction involves the formation of peroxide (H_2O_2) as an intermediate, where oxygen is first reduced to H_2O_2 and then further reduction of the H_2O_2 to water via a two-electron process. Another is the direct reduction to water via the four-electron process. For further insight into electron transfer parameters of the CTF catalysts, the RDE measurements that were performed at various rotating speeds are shown in Fig. 2(c), showing increasing catalytic current at increasing rotating speed due to improved mass transport at the electrode surface. The overall current density (j) in the reaction via RDE is the resultant of contributions from the kinetic current density (j_k) and diffusion-limiting current density through the solution boundary layer (j_d) according to the equation: $\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$. The value for j_d can be represented as $j_d = 0.62nFAcD^{2/3}\nu^{-1/6}\omega^{1/2}$, where n is the number of electrons transferred in the reaction, F is the Faraday constant, A is the geometric area of electrode, c is the concentration of oxygen in the solution at atmospheric pressure ($1.26 \times 10^{-3}\text{ M}$), D is the diffusion coefficient ($1.9 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($0.01\text{ cm}^2\text{ s}^{-1}$), and ω is the electrode rotation rate. According to this equation, a plot of the inverse of the current density at constant potential vs. $\omega^{-1/2}$ ought to result in a straight line with an intercept corresponding to the inverse of the purely kinetic current density (j_k) and a slope (B , Levich constant) defined by $0.62nFAcD^{2/3}\nu^{-1/6}$. To determine the number of electrons transferred in the reaction, the overall current density (j^{-1}) was plotted against the square root of angular velocity ($\omega^{-1/2}$). The corresponding Koutecky–Levich (K–L) plots are shown in

Download English Version:

<https://daneshyari.com/en/article/49720>

Download Persian Version:

<https://daneshyari.com/article/49720>

[Daneshyari.com](https://daneshyari.com)