



Polystyrene Microspheres-Templated Nitrogen-Doped Graphene Hollow Spheres as Metal-Free Catalyst for Oxygen Reduction Reaction



Wei Yan^{a,b}, Ling Wang^a, Chang Chen^a, Dan Zhang^{b,c}, Ai-Jun Li^{d,*}, Zheng Yao^a, Li-Yi Shi^{a,*}

^a Nano Science and Technology Research Center, Shanghai University, Shanghai 200444, PR China

^b Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai 200072, PR China

^c Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200444, PR China

^d Research Center for Composite Materials, Shanghai University, Shanghai 200444, PR China

ARTICLE INFO

Article history:

Received 12 October 2015

Received in revised form 14 November 2015

Accepted 30 November 2015

Available online 2 December 2015

Keywords:

Nitrogen-doped graphene

Polystyrene microsphere

Electrocatalytic activity

Oxygen reduction reaction

ABSTRACT

Nitrogen-doped graphene hollow microspheres (NGHMs) were constructed, using polystyrene microspheres (PSMs) as the sacrificial template. Negatively charged graphene oxide nanosheets (GONs) were assembled onto sulfonated PSMs with the aid of poly(ethyleneimine) through electrostatic interaction. NGHMs were obtained by pyrolysis the mixture of melamine and GON-wrapped PSMs under a nitrogen atmosphere. During the pyrolysis, the removal of PSMs and reduction of GONs and incorporation of heteroatoms were realized simultaneously. The nitrogen atomic percentage in NGHMs reached 7.13%, and sulfur content was also detected. The prepared NGHMs exhibited high catalytic activity toward oxygen reduction reaction (ORR) in alkaline solution with a comparable limiting current density to JM 40 wt% Pt/C. The ORR on NGHMs electrode was dominated by the four-electron pathway in a wide potential range with long-term stability and high fuel selectivity. The enhanced electrocatalytic performance of NGHMs could be ascribed not only to the high nitrogen content, but also to the hollow sphere architecture. Moreover, the nitrogen precursor, melamine, increased the percentage of graphitic-N and prevented hollow spheres from aggregation, which also helped to improve the catalytic activity of NGHMs.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Energy demand is expected to increase considerably in the coming years as a result of population growth and economic development. Currently, over 80% of the energy demand is met by fossil fuels [1]. Due to the limited reserves and the environmental problems of fossil fuels, exploring alternative energy sources and technologies becomes the issue of most concern. As electrochemical energy devices can transform chemical energy to electricity, they are considered as the alternative energy sources to fossil fuel. Various electrochemical energy devices, including fuel cells and metal-air batteries, are developed [2]. Oxygen reduction reaction (ORR) plays an important role in fuel cells and metal-air batteries. Currently, Pt and Pt-based alloys are the most efficient catalysts for ORR [3]. However, the scarcity and high cost of Pt preclude the large-commercialization of fuel cells intrinsically. In addition, Pt-based catalysts are susceptible to sluggish ORR kinetics, time-dependent drift, methanol crossover and CO poisoning. Thus,

extensive studies have been conducted to find alternative efficient ORR catalysts without Pt [4].

Nitrogen-doped carbon materials, such as carbon nanotube [5,6], carbon nanofiber [7,8], porous carbon [9,10] and graphene [11–20] have shown excellent catalytic activities toward ORR. In addition, compared with Pt-based catalysts, nitrogen-doped carbon materials exhibited long-term durability and tolerance to poisoning, which reveals the possibility to replace expensive Pt-based ORR catalysts with nitrogen-doped carbon materials. Graphene, one-atom-thick planar sheet of sp^2 -bonded carbon atoms, has attracted much attention due to its outstanding intrinsic properties [21]. Nitrogen-doped graphene (NG) shows different properties compared with pristine graphene [22]. Although pristine graphene is catalytically inactive toward ORR, NG exhibits high electrocatalytic activity for oxygen reduction. There have been reviews published on the nitrogen-doped graphene as efficient electrocatalysts towards ORR [23,24]. The doped nitrogen atoms break the distribution balance of the electron spin density and atomic charge density on the plane of graphene, facilitating oxygen adsorption and electron transfer, thus changing the electrocatalytic activity [24].

However, graphene nanosheets tend to agglomerate due to strong π - π stacking and Van der Waals interactions. The

* Corresponding authors. Fax: +86 21 66135392.

E-mail addresses: ajun.li@shu.edu.cn (A.-J. Li), shiliyi@shu.edu.cn (L.-Y. Shi).

agglomeration will block the catalytic sites on NG, decreasing the catalytic activity of NG towards ORR. Designing hollow spheres with ultrathin-shells is an effective strategy to overcome the agglomeration of nanosheets [25]. In addition, the interconnected network and porous architecture of hollow spheres provide a highway for fast electron transfer, and shorten the transport length of mass and thus reduce the overpotential of ORR originated from mass transport limitation [26]. Wu et al. and Jiang et al. constructed NG hollow spheres using silica microspheres as the template, followed by removing the silica microspheres with HF solution [26,27]. The constructed NG hollow spheres exhibited high current density, large electron transfer number and low overpotential toward ORR. The high ORR catalytic activities could be attributed not only to the N dopants, but also to the spherical hollow structure.

Besides silica microspheres, polystyrene microspheres (PSMs) can also be used as the sacrificial templates to construct graphene hollow spheres and three-dimensional macroporous graphene frameworks, and the constructed graphene architectures exhibited enhanced performance for supercapacitors [28–31], and for lithium and lithium ion batteries [32,33]. Herein, we report the preparation of NG hollow microspheres (NGHMs) with high catalytic activity toward ORR, using PSMs as the sacrificial template. Negatively charged graphene oxide nanosheets (GONs) were assembled onto the sulfonated PSMs with the aid of poly(ethyleneimine) (PEI), a cationic polyelectrolyte, through electrostatic interaction. The obtained GON-wrapped PSMs were mixed with melamine, and subsequently calcined in a nitrogen atmosphere to remove PSMs and realize GONs' reduction and heteroatoms incorporation simultaneously. The nitrogen content in NGHMs reached 7.13%, and low sulfur content was also detected. The synthesized NGHMs exhibited high catalytic activity toward ORR in alkaline solution with superb durability and good tolerance to poisoning. The electron transfer number was close to 4 and was almost independent of potential from -0.2 to -0.7 V (vs. Hg/HgO). The limiting current density was comparable to commercial JM 40 wt% Pt/C. The high electrocatalytic activity of NGHMs could be attributed not only to the high nitrogen content, but also to the hollow sphere architecture. Moreover, due to the structural similarity between melamine and graphitic-N, the graphitic-N percentage in NGHMs was greatly increased, which also contributed to the high catalytic activity of NGHMs toward ORR.

2. Experimental

2.1. Materials

Graphite flake (325 mesh) was purchased from Nanjing XFNANO Materials TECH Co., Ltd., China. Pt/C catalyst (40 wt% Pt on Vulcan carbon XC-72, HiSPEC 4000) was supplied by Johnson Matthey. Nafion solution (5 wt%) and PEI (average molecular weight of 1300) aqueous solution (50 wt%) were obtained from Sigma-Aldrich. Other chemicals such as styrene (St), methacrylic acid (MAA), melamine, potassium persulfate ($K_2S_2O_8$), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4 , 98%), sodium hydrogen carbonate ($NaHCO_3$) and hydrogen peroxide (H_2O_2 , 30%), bought from Sinopharm Chemical Reagents Co. Ltd. (Shanghai, China), were all of analytical grade. St and MAA were distilled by reduced pressure before use, and $K_2S_2O_8$ was refined by recrystallization. Other reagents were used as received without further purification. Deionized water was used throughout.

2.2. Preparation of PEI-coated PSMs

Monodispersed PSMs with the diameter about 195 nm, were used as the sacrificial template for the construction of NGHMs. PSMs were

prepared by soap-free emulsion polymerization according to the reference [34]. PSMs were collected and washed by centrifugation, and then suspended in water. Sulfonated PSMs were synthesized by mixing PSM suspension with H_2SO_4 . The mixture was stirred at $40^\circ C$ for 24 h, and sulfonated PSMs were collected and washed by centrifugation, and then suspended in water. PEI-coated PSMs were prepared by adding the sulfonated PSMs suspension and PEI solution into 10 mM phosphor buffer solution (PBS) of pH 7.4. The mixture was stirred for 2 h at room temperature. Excess PEI was removed by centrifugation, and PEI-coated PSMs were suspended in water with a solid content of 2 mg/mL.

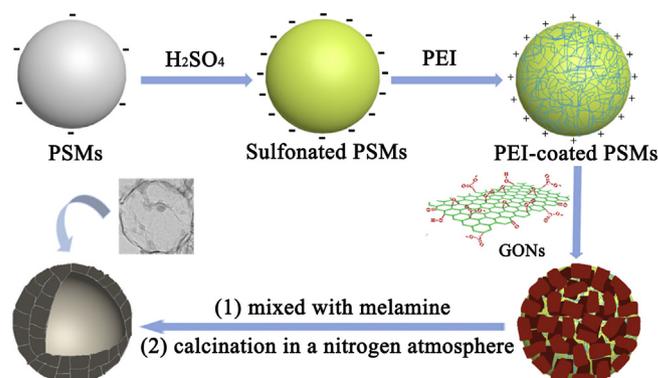
2.3. Construction of NGHMs

GO was prepared from graphite flake according to the Hummers' method [35]. GON aqueous dispersion (0.2 mg/mL) was obtained by ultrasonication for 6 hours, using a Sonifier (KQ 100 E, 100 W, Kunshan, China). 100 mL GON dispersion was mixed with 100 mL PEI-coated PSM suspension, which was stirred at room temperature for 2 h. Negatively-charged GONs were assembled onto the positively-charged microspheres through electrostatic interaction, leading to the formation of GON-wrapped PSMs. 0.3 g melamine was then added, and the mixture was stirred at room temperature for another 12 h. After that, the mixture was freeze-dried, and then air dried at $60^\circ C$ for 12 h. The obtained solid mixture was placed in a tubular furnace under a nitrogen atmosphere, heated to $800^\circ C$ at a heating rate of $5^\circ C/min$. NGHMs were obtained after the temperature was held at $800^\circ C$ for 2 h. The construction process of NGHMs is illustrated in Scheme 1.

For comparison, graphene hollow microspheres (GHMs) and reduced graphene nanosheets (rGONs) were prepared by placing GON-wrapped PSMs and GONs in a tubular furnace under a nitrogen atmosphere for calcination, respectively.

2.4. Characterization

Transmission electron microscopy (TEM) images were acquired using a JEM-200CX transmission electron microscope operated at an acceleration voltage of 120 KeV. Fourier transform infrared spectroscopic (FTIR) measurements were performed on a Nicolet Avatar370 FTIR instrument (Thermo Nicolet, USA) using KBr pellets. Powder X-ray diffraction (XRD) measurements were performed on a 18KW D/MAX2500V+/PC instrument using a graphite monochromator with Cu K α radiation ($k = 1.5406 \text{ \AA}$). The Raman spectra were measured with a Jobin-Yvon LabRam HR with a liquid nitrogen-cooled CCD multichannel detector at room temperature using conventional back scattering geometry. An argon ion laser at a wavelength of 633 nm served as the laser light source. The zeta-potential (ζ -potential) of materials were



Scheme 1. Schematic illustration of the construction process of NGHMs.

Download English Version:

<https://daneshyari.com/en/article/183351>

Download Persian Version:

<https://daneshyari.com/article/183351>

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