Preparation of nitrogen-doped graphene by solvothermal process as supporting material for fuel cell catalysts

Hosna Ghanbarlou[1,2], Soosan Rowshanzamir[1,2*], Mohammad Javad Parnian[1,2] , Bagher Kazeminasab[3]

[1] School of Chemical Engineering, Iran University of Science and Technology.
[2] Fuel Cell Laboratory, Green Research Center, Iran University of Science and Technology.
[3] Department of Energy Engineering, Science and Research Branch, Islamic Azad University, Tehran.

Article Information

Keywords

Abstract

Development of efficient electrocatalysts for oxygen reduction reaction is one of the most important issues for optimizing the performance of fuel cells and metal-air batteries. The introduction of nitrogen into carbon nanostructures has created new pathways for the development of non-precious electrocatalysts in fuel cells. In this work, nitrogen-doped graphene was synthesized by a low temperature solvothermal process to use as catalyst supports for oxygen reduction reactions. The morphology of the NG was studied using scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy showed that graphitic (Quaternary), pyridinic and pyridinic oxidized nitrogen formed by designed reaction and these types of nitrogen configurations has been found to be responsible for oxygen reduction reaction catalytic activity of N-doped carbon material. Cyclic voltammetry and linear sweep voltammetry were used to measure electrocatalytic activity. Electrochemical characterization reveal that the produced nitrogen-doped graphene not only as support but also as catalyst has good catalytic activity for oxygen reduction reaction in alkaline media.

1. Introduction

Fuel cell devices are considered as the most promising energy conversion technologies being developed for transport application. One of the most challenging issues facing fuel cells is the development of low cost, highly active and durable electrocatalyst for the cathode electrode where oxygen reduction reaction (ORR) take place [1, 2].

Carbon-supported platinum-based nanomaterials have been regarded as the best electrocatalysts for ORR in these electrochemical energy devices [3]. The cost of Pt catalyst, which is a limited natural resource, will gradually increase over time, Pt-based electrocatalysts also have shown low durability. In addition, during fuel cell operation, platinum nanoparticles usually agglomerate, detach from the carbon support, and can suffer CO poisoning [4].

*Corresponding author: Iran University of Science and Technology, P.O. Box: 16846-13114, Tehran, Iran. Tel. /fax:+98 2177491242
Email address: rowshanzamir@iust.ac.ir (S. Rowshanzamir)

Accordingly there is strong motivation to replace platinum with a low cost material, such as platinum alloys [5], metal porphyrins [6] or nitrogen doped carbon nanostructures [7, 8].

N-doped carbon materials such as vertically aligned N-doped carbon nanotubes [9], nitrogen doped carbon nanocapsules [8], nitrogen-containing porous carbons [10], and nitrogen-doped graphene (NG) [11, 12] have been considered as alternative electrocatalysts for ORR. Some of these nitrogen-containing nanocomposites have shown enhanced activity for ORR that is comparable to that of commercial platinum catalyst under alkaline conditions [13-15].

Graphene is a new 2-dimentional carbon material with intriguing properties, such as high surface area, high electrical conductivity, thermal stability, great electron mobility, and a unique graphitic basal plane that guarantees durability. The catalytic performance of graphene can be improved by doping it with heteroatoms such as nitrogen [15]. Nitrogen atoms in the matrix of the carbon withdraw electrons from adjacent carbon atoms because of the higher electronegativity of nitrogen and the resultant positive carbon atoms facilitate activation of ORR [16]. These active sites can also act as anchoring sites for metal nanoparticle deposition [17-19]. NG has more structural defects that lead to more uniform dispersion of metal nanoparticles compared to pristine graphene [20, 21].

When a nitrogen atom is doped into graphene lattice, it usually has three common bonding configurations within the carbon lattice, including quaternary N (or graphitic N), pyridinic N and pyrrolic N [22]. According to the pervious reports several researchers claimed that the graphitic and pyridinic nitrogen content in graphene sheets increase ORR activity in a system [23-25] Previous studies also have found that quaternary and pyridinic nitrogen are the most important species for catalyzing ORR due to the matching relationship between activity and nitrogen content [11, 25]. However this issue remain challenging that which types of nitrogen was responsible for ORR activity and it is still under debate.

So far several methods have been developed to synthesize N-doped graphene including arc discharge, chemical vapor deposition [26], thermal annealing of graphite oxide [27] and hydrothermal reaction [12]. All of these methods resulting in uncontrollable N-doping which produces mixture of pyridine-like, quaternery-like and pyrrole-like NG. Recently some of the researchers report more suitable method for synthesis of N-doped graphene which called solvothermal reaction [28].

In this work a novel solvothermal route is reported for NG synthesis using pentachloropyridine as both the carbon source and the nitrogen source. Due to the specific nitrogen configuration of pentachloropyridine only graphitic and pyridinic nitrogen were formed in resultant NG. This solvothermal reaction was used perviously by Geng. D. et al. [29] and synthesized NG was used as supporting material for Pt nanoparticles to investigate its durability. However by changing the reaction conditions such as temperature in present work graphene sheets with smaller sizes were synthesized. On the other hand the catalytic activity of synthesized NG was evaluated for ORR in alkalin media.

2. Experimental

2.1. Synthesis of N-doped graphene

The reaction of pentachloropyridine (1 g) and metallic potassium was carried out at about 160° C for 10 h in a 25 mL stainless steel autoclave. After the reaction was complete the autoclave was cooled to room temprature naturally. The salty-dark precipitate product was washed sequentially with acetone, absolute ethanol and water followed by drying in a vacuum at 80°C for 4 h.

2.2. Physical characterizations

2.2.1. Scanning electron microscopy

The morphology of the NG samples was obtained using scanning electron microscopy (SEM, Hitachi S-4160) operated at an accelerating voltage of 20 kV.

2.2.2. Transmission electron microscopy

The nanostructure of the NG was studied using transmission electron microscopy (TEM; ZEISS 900) with an accelerating voltage of 50-80 kV.

2.2.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data were recorded using an 8025-BesTec twin anode XR3E2 x-ray source system with monochromatic Al kα radiation.

2.3. Electrochemical measurements

Electrochemical measurements were carried out at room temperature in a conventional three-electrode cell connected to an electrochemical analyzer. Glassy carbon coated with catalyst ink was used as the working electrode. A saturated calomel electrode and a Pt plate were used as reference and counter electrodes, respectively. All potentials were relative to the saturated calomel electrode. Prior to surface coating, the glassy carbon electrode (GCE) was sequentially polished and then washed with deionized water for a few minutes.

For electrode preparation, 1 mg of total electrocatalyst was dispersed in a 1 mL mixture of 5 wt.% nafion solution and deionized water (volume ratio=1:9) by sonication. Catalyst dispersion (6 μl) was transferred onto a GCE (2 mm in diameter, 0.031415 cm^2 geometric area) and dried at 80°C for 15 min. ORR

activity can be evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). With CV, ORR was measured in oxygen-saturated 0.1 M KOH solution at 25°C with the scan rate of 100 mV/s in potential range from -1.2 to 0.2 V. Electrochemical impedance spectroscopy (EIS) was carried out with potentiostat/galvanostat/EIS (Biologic SP-150). The impedance spectra were measured by sweeping the frequency between the 1 MHz and 10 mHz in an oxygen-saturated 0.10 M KOH solution.

3. Results and Discussion

The morphological features of synthesized NG were identified with SEM and TEM. Fig. 1(a) represents SEM image of NG synthesized by solvothermal process. The sample contains the large number of nano-spheres that each one consist of many loose NG sheets. NG sheets wrapped around each other until formed these spherical shapes. Fig. 1(b) shows a TEM image of NG, it can be observed from the image that graphene forms small circle-like structures which are 100-200 nm in diameter.

X-ray photoelectron spectroscopy of the sample is shown in Fig.2a. The survey spectrum of NG reveals the peresence of C, N and O in the produced samples. The presence of N1s peak around 400 eV in NG material spectra in Fig.2a demonstrates the successful incorporation of nitrogen into graphene sheets.

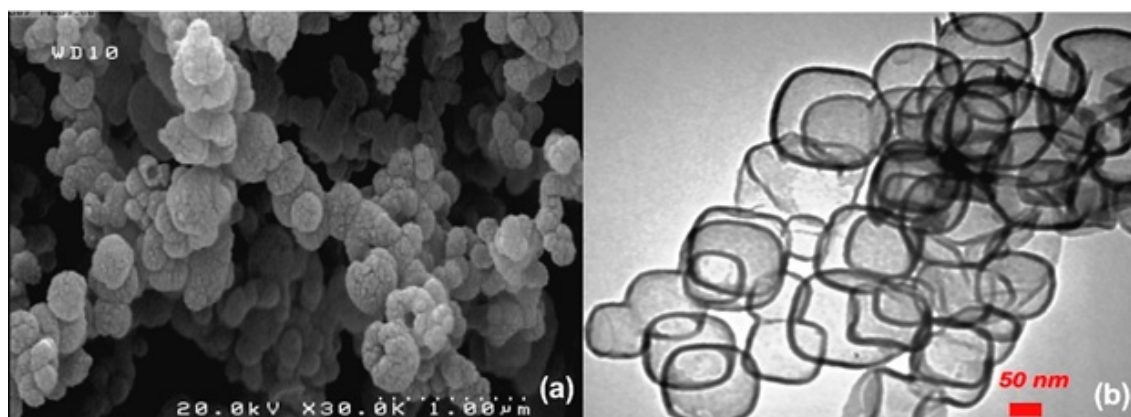The nitrogen configurations of NG samples were
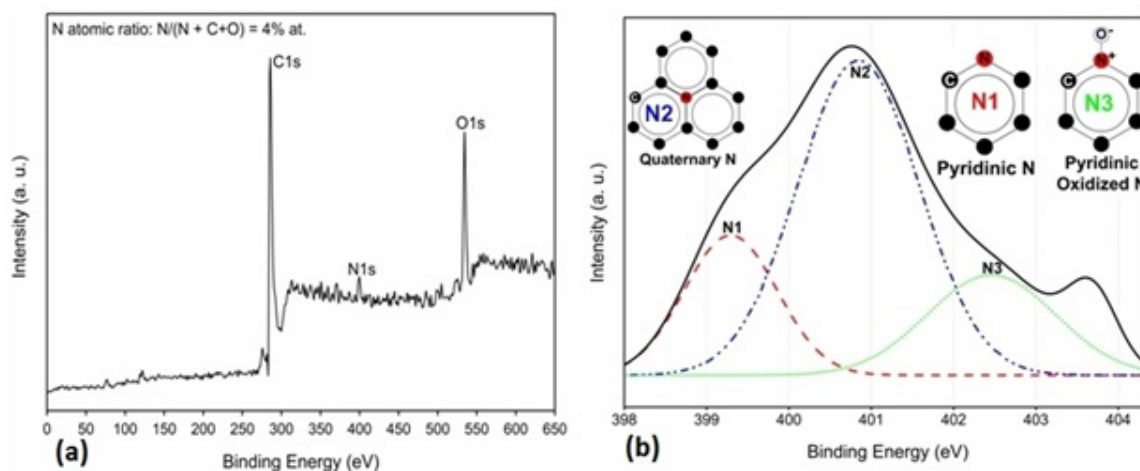

Fig. 1. (a) SEM and (b) TEM images of synthesized NG

Fig. 2. a) XPS survey spectrum of NG b) the de-convoluted N1s region for NG

analyzed by the curve fitting procedure. Fig.2b shows the deconvoluted N1s region of NG. From a curve deconvolution, the spectrum can be well-fitted to three peaks with binding energies centered at 399.2 eV, 400.9 eV and 402.5 eV, which are assigned to pyridinic-N, graphitic-N and pyridinic-N oxide species respectively. It is clear that synthesized NG has more proportion of pyridinic and graphitic nitrogen which shows that we can successfully controll the configuration of nitrogen in synthesis process.

The electrocatalytic activity of NG were determined in a conventional three-electrode system in alkaline solution. In nitrogen-saturated KOH solution, a clean capacitive CV background was seen (Fig. 3), while in the presence of oxygen, a prominent cathodic current appeared with a peak centered at ~-0.35 V vs. SCE indicating the pronounced catalytic activity of synthesized NG alone for ORR. This result is in good agreement with previous reports of other researchers that examine the catalytic activity of N-doped graphene with cyclic voltammetry in 0.1 M KOH solution and in presence of nitrogen and oxygen
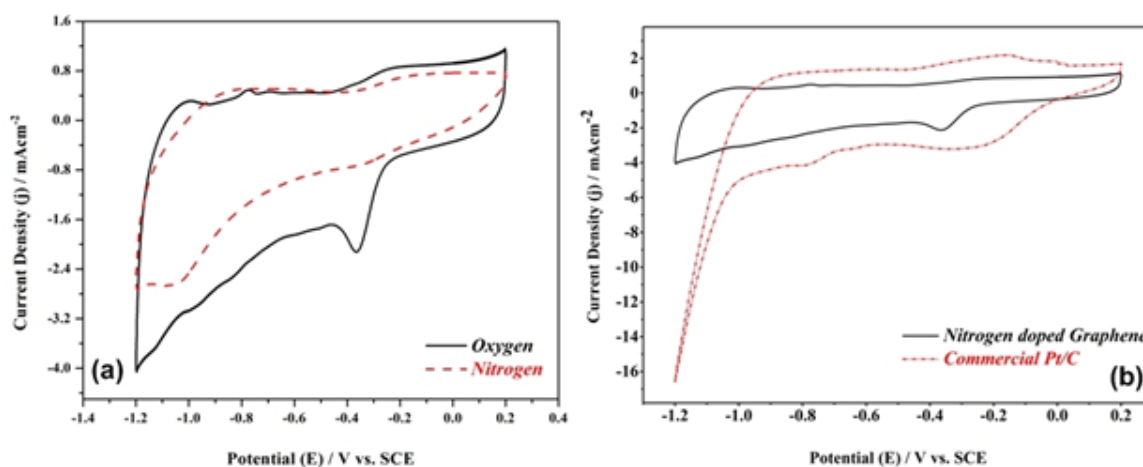

Fig. 3. Electrocatalytic activity of NG toward ORR (a) CV curves of NG in nitrogen and oxygen saturated 0.1 M KOH with a scanning rate of 100 mV/s. (b) CV curves of NG and commercial Pt/C electrode in 0.1 M KOH with a scanning rate of 100 mV/s.

[11, 14, 30]. The enhanced electrocatalytic activity of NG toward ORR suggests fast reaction kinetics with a high transferred electron density for oxygen molecules. The catalytic properties of N-doped graphene have also been explained by the charge rearrangement in its basal plane. The carbon atoms adjacent to a nitrogen atom held a substantially higher positive charge density to counterbalance the strong electronic affinity of nitrogen, which enhanced the adsorption of O_2, H_2O_2 or reactive intermediates which consequently facilitates the ORR.

Pyridinic-like and quaternary-like nitrogen atoms within carbon structures may boost the absorption of oxygen on graphene surface. Moreover, the formation of pentagons and defects in N-doped graphene structure furnishes more reaction sites for the ORR. Cyclic voltammograms of synthesized NG in comparison with commercial Pt/C are also shown in Fig. 3b. Existence of cathodic peak with peak current density of -2.11 mAcm^{-2} shows that NG alone has acceptable activity for ORR in alkaline media, which could be attributed to the presence of pyridinic and graphitic (quaternary) nitrogen types in graphene matrix, these types of nitrogen play an important role in electrocatalysis toward ORR.

Theoretical calculation shows that energy barriers for oxygen molecule dissociation can be reduced efficiently by all types of nitrogen doping in both carbon nanotubes and graphene [31] and the decrease in energy barrier is more significant by the graphite-like and pyridine-like nitrogen [29].

The oxygen reduction activity of NG were further investigated using linear sweep voltammetry. Fig. 4 shows LSV curves of synthesized NG and commercial platinum measured in O_2-saturated 0.1 M KOH at a sweep rate of 10 mVs^{-1}. It is clear that the value of limiting current density for NG is around -0.331 (mA cm^{-2}) which is almost 65% lower than that of Pt/C (-0.965 (mA cm^{-2})).

comparison of LSV curves also indicates that the performance of NG is still far from Pt/C in terms of onset potential and half wave potential. However the activity of NG material could be further improved by precipitation of non-precious metal nanoparticles on it
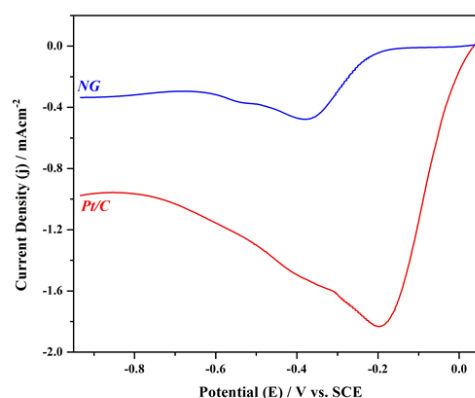

Fig 4. LSVs for ORR obtained at NG alone and commercial Pt/C electrodes at a scanning rate of 10 mV/s.

which is a great approach to produce active and non-precious electrocatalysts.

The stability of catalysts is one of the major concerns in current fuel cell technology. Stability of synthesized NG and commercial Pt/C was tested at a constant voltage of -0.25V (vs. SCE) for 15000 s in oxygen-saturated 0.1 M KOH solution. As shown in Fig. 5, the chronoamperometric response for NG exhibits slower attenuation and higher relative current than commercial Pt/C. After 15000 s, NG maintained a relative current of 82% in comparison to 59% for Pt/C. The results above demonstrate that NG has a desirable durability for the ORR in alkaline solution and has the potential to be a promising catalyst and catalyst support in alkaline fuel cells.
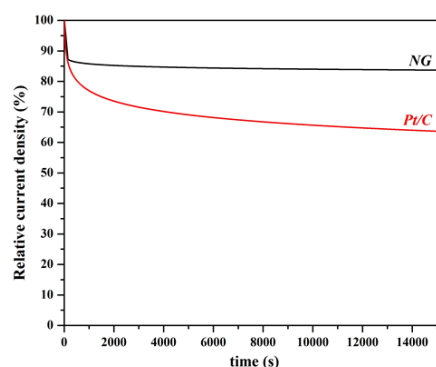

Fig. 5. Chronoamperometric responses for ORR for catalysts in O_2-saturated 0.1 M KOH solution at -0.3 V vs. SCE.

4. Conclusions

In summary, we developed an easily synthetic approach for large-scale preparation of NG via a simple solvothermal process. The doped nitrogen exists mainly as "pyridine" and "quaternary"-like bonding configurations in NG. This may facilitates new ways to design doped graphene materials with the controllable doping. Electron accepting ability of the nitrogen atoms create net positive charge on adjacent carbon atoms in hexagonal carbon plane of graphene, these carbon atoms can readily atrract electrons from anode and can act as active sites for ORR and also act as anchoring sites for metal nanoparticle deposition. Our experiment demonstrates that N-doped graphene offers desirable electrocatalytic characteristics as both support and catalyst in alkaline solution.

5. References

1. Bing Y, Liu H, Zhang L, Ghosh D, Zhang J. "Nanostructured Pt-alloy electrocatalysts for PEM fuel cell oxygen reduction reaction". Chem. Soc. Rev., 2010, 39: 2184.

2. Serov A, Kwak C. "Direct hydrazine fuel cells: A review". Applied Catalysis B: Environmental, 2010, 98: 1.

3. Zhang S, Shao Y, Yin G, Lin Y. "Stabilization of platinum nanoparticle electrocatalysts for oxygen reduction using poly(diallyldimethylammonium chloride)". J. Mater. Chem., 2009, 19: 7995.

4. Shao Y, Yin G, Gao Y. "Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell". J. Power Sources, 2007, 171: 558.

5. Wu H, Wexler D, Liu H. "Pt–Ni/C catalysts using different carbon supports for the cathode of the proton exchange membrane fuel cell (PEMFC)". Mater. Chem. Phys., 2012, 136: 845.

6. Chen Z, Higgins D, Yu A, Zhang L, Zhang J. "A review on non-precious metal electrocatalysts for PEM fuel cells". Energy & Environmental Science, 2011, 4: 3167.

7. Shao Y, Sui J, Yin G, Gao Y. "Nitrogen-doped carbon nanostructures and their composites as catalytic materials for proton exchange membrane fuel cell". Applied Catalysis B: Environmental, 2008, 79: 89.

8. Shanmugam S, Osaka T. "Efficient electrocatalytic oxygen reduction over metal free-nitrogen doped carbon nanocapsules". Chem. Commun., 2011, 47: 4463.

9. Mo Z, Liao S, Zheng Y, Fu Z. "Preparation of nitrogen-doped carbon nanotube arrays and their catalysis towards cathodic oxygen reduction in acidic and alkaline media". Carbon, 2012, 50: 2620.

10. Shen W, Fan W. "Nitrogen-containing porous carbons: synthesis and application". Journal of Materials Chemistry A, 2013, 1: 999.

11. Lin Z, Waller G H, Liu Y, Liu M, Wong C-p. "Simple preparation of nanoporous few-layer nitrogen-doped graphene for use as an efficient electrocatalyst for oxygen reduction and oxygen evolution reactions". Carbon, 2013, 53: 130.

12. Wu J, Zhang D, Wang Y, Hou B. "Electrocatalytic activity of nitrogen-doped graphene synthesized via a one-pot hydrothermal process towards oxygen reduction reaction". J. Power Sources, 2013, 227: 185.

13. Li H, Liu H, Jong Z, Qu W, Geng D, Sun X, Wang H. "Nitrogen-doped carbon nanotubes with high activity for oxygen reduction in alkaline media". Int. J. Hydrogen Energy, 2011, 36: 2258.

14. He C, Li Z, Cai M, Cai M, Wang J-Q, Tian Z, Zhang X, Shen P K. "A strategy for mass production of self-assembled nitrogen-doped graphene as catalytic materials". Journal of Materials Chemistry A, 2013, 1: 1401.

15. Geng D, Chen Y, Chen Y, Li Y, Li R, Sun X, Ye S, Knights S. "High oxygen-reduction activity and durability

of nitrogen-doped graphene". Energy & Environmental Science, 2011, 4: 760.

16. Zahoor A, Christy M, Hwang Y J, Lim Y R, Kim P, Nahm K S. "Improved electrocatalytic activity of carbon materials by nitrogen doping". Applied Catalysis B: Environmental, 2014, 147: 633.

17. Lu Z-J, Bao S-J, Gou Y-T, Cai C-J, Ji C-C, Xu M-W, Song J, Wang R. "Nitrogen-doped reduced-graphene oxide as an efficient metal-free electrocatalyst for oxygen reduction in fuel cells". RSC Advances, 2013, 3: 3990.

18. Huang C, Li C, Shi G. "Graphene based catalysts". Energy & Environmental Science, 2012, 5: 8848.

19. Zhang L-S, Liang X-Q, Song W-G, Wu Z-Y. "Identification of the nitrogen species on N-doped graphene layers and Pt/NG composite catalyst for direct methanol fuel cell". PCCP, 2010, 12: 12055.

20. Xiong B, Zhou Y, Zhao Y, Wang J, Chen X, O'Hayre R, Shao Z. "The use of nitrogen-doped graphene supporting Pt nanoparticles as a catalyst for methanol electrocatalytic oxidation". Carbon, 2013, 52: 181.

21. Imran Jafri R, Rajalakshmi N, Ramaprabhu S. "Nitrogen doped graphene nanoplatelets as catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell". J. Mater. Chem., 2010, 20: 7114.

22. Wang H, Maiyalagan T, Wang X. "Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, and Its Potential Applications". ACS Catalysis, 2012, 2: 781.

23. Liu G, Li X, Lee J-W, Popov B N. "A review of the development of nitrogen-modified carbon-based catalysts for oxygen reduction at USC". Catalysis Science & Technology, 2011, 1: 207.

24. Liu Q, Zhang H, Zhong H, Zhang S, Chen S. "N-doped graphene/carbon composite as non-precious metal electrocatalyst for oxygen reduction reaction". Electrochim. Acta, 2012, 81: 313.

25. Subramanian N P, Li X, Nallathambi V, Kumaraguru S P, Colon-Mercado H, Wu G, Lee J-W, Popov B N. "Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells". J. Power Sources, 2009, 188: 38.

26. Zhang M, Dai L. "Carbon nanomaterials as metal-free catalysts in next generation fuel cells". Nano Energy, 2012, 1: 514.

27. Lin Z, Song M-k, Ding Y, Liu Y, Liu M, Wong C-p. "Facile preparation of nitrogen-doped graphene as a metal-free catalyst for oxygen reduction reaction". PCCP, 2012, 14: 3381.

28. Deng D, Pan X, Yu L, Cui Y, Jiang Y, Qi J, Li W-X, Fu Q, Ma X, Xue Q, Sun G, Bao X. "Toward N-Doped Graphene via Solvothermal Synthesis". Chem. Mater., 2011, 23: 1188.

29. Geng D, Hu Y, Li Y, Li R, Sun X. "One-pot solvothermal synthesis of doped graphene with the designed nitrogen type used as a Pt support for fuel cells". Electrochem. Commun., 2012, 22: 65.

30. Bai J, Zhu Q, Lv Z, Dong H, Yu J, Dong L. "Nitrogen-doped graphene as catalysts and catalyst supports for oxygen reduction in both acidic and alkaline solutions". Int. J. Hydrogen Energy, 2013, 38: 1413.

31. Zheng B, Wang J, Wang F-B, Xia X-H. "Synthesis of nitrogen doped graphene with high electrocatalytic activity toward oxygen reduction reaction". Electrochem. Commun., 2013, 28: 24.