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Graphene based non-noble metal catalyst for oxygen reduction reaction

Yunhan Chuai*

College of Chemical Engineering and Environment, China University of Petroleum-Beijing (CUPB), Beijing, China

*Corresponding author e-mail: 15611818166@163.com

Abstract. The current noble-metal Pt based oxygen reduction reaction electrocatalysts suffer from high cost and poor operational durability. It is an urgent demand to developing alternative catalysts that are cost effective, readily available, and have the comparable catalytic activity than Pt for oxygen reduction reaction. Recently, graphene-based non-noble metal catalysts have been investigated and shown desirable activity and stability toward oxygen reduction reaction. Here, we offer a timely review paper to illustrate the recent progresses of graphene based electrocatalyst, including heteroatom doped graphene and graphene-inorganic nanoparticle composite. We hope this article can provide a guideline for rational design of highly active graphene-based non-noble metal catalysts toward oxygen reduction reaction.

1. Introduction

The increasing environmental influence and global energy demand brings about serious challenges to energy security, human health, and environmental protection. One potential strategy is designing and developing new-type energy conversion devices, such as fuel cells (FCs) or metal–air batteries (MABs). [1] These energy technologies have received intensive focus thanks to the high conversion efficiency, environmental-friendly feature, and prospective large-scale applications. The similarity between various of FCs and MABs is that the oxygen reduction reaction (ORR) is a basic constitution of their operation. The currently implementations are high cost and poor operational durability that stem from the traditional noble-metal Pt based ORR electrocatalysts. [2] Therefore, great efforts are needed to be devoted to preparation of alternative catalysts that are cost effective, readily available, and have the comparable catalytic activity than Pt for ORR. [3]

Along with the tremendous progresses in studying nonprecious metal electrocatalysts for ORR, a new type of graphene-based non-noble metal catalysts (NMCs) have been developed and investigated. [4] As one of most promising alternative electrocatalysts, which can dramatically decline the cost and improve the energy conversion efficiency of FCs and MABs. The aim of this article is to provide a comprehensive review of the topic by summarizing all the important developments in this emerging field of active research on carbon-based metal-free catalysts for ORR and presenting critical issues, challenges, and perspectives. We highlighted the significance of ORR to FCs and MABs and illustrate the characteristics and advantages of graphene material. Then, the recent progresses in the development of graphene based NMCs for ORR were reviewed, including heteroatom doped graphene and graphene-

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1 inorganic nanoparticle composite. Finally, we gave the summary on challenges and perspectives of graphene based NMCs for ORR.

2. Oxygen reduction electrocatalysis

The electrolytes of FCs and MABs can be divided into two groups, alkaline or acidic.

The alkaline electrolyte is often used in alkaline exchange membrane FCs or MABs, the hydroxide anions transport from the cathode and move to the anode. The ORR proceeds with two-electron reduction to form hydrogen peroxide products (eqn (1)) or four-electron reduction process forming hydroxide species (eqn (2)).

 $O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$ (1)

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-}$$
⁽²⁾

As for acidic electrolyte, the membranes enables the fast transport of protons from the anode to the cathode. Analogous to alkaline system, the ORR carries on by the two-electron (eqn (3)) or four-electron reduction (eqn (4)).

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$$
(3)

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \tag{4}$$

The four-electron reduction process is favourable for ORR because of the obvious efficiency superiority and the restriction of forming the H_2O_2 product on the electrode material surface that can result in the degradation of ionomer and membrane. In addition, the hydrogen peroxide in ORR can be indirectly or directly reduced to water, in which the reaction can happen by two steps of two-electron reduction process. Generally, the alkaline condition is more conducive to ORR kinetics, which provides the probability to use non-noble metal catalysts, such as: metal-oxides, gold, silver, and carbon nanostructures. Recent researches have proved that graphene-based NMCs shown outstanding catalytic property and cycling stability in alkaline electrolyte.

3. Graphene

Since the first inception in 2004, [5] graphene has emerged as the star material for its outstanding electronic and thermal, chemical and physical, surface and mechanical merits. From the basic structure level, graphene is made up of the two dimensional (2D) nanosheets with carbon atoms chemically bonded to form monolayer of the hexagonal pattern, which is one of the typical characteristics of graphite material. By the modified synthetic method or structure tailing strategies, researchers are able to adjust and improve the intrinsic properties of graphene based materials. In this regard, the graphene has been considered as ideal material for electrocatalysis application. As the surface-specific processes and reaction rates are governed by the catalyst properties that can be modulated. Rational design of graphene enables it to act as an electrocatalyst itself or interacting with catalytic nanoparticles decorated on the surface, which is favourable for improving the ORR kinetics.

4. Graphene based NMCs for ORR

4.1. Heteroatom doped graphene

According to the previous researches, graphene material itself demonstrated very limited ORR activity and shown the selectivity towards the two-electron reduction process. Hence, the heteroatom-doping strategy have been adapted for increasing the catalytic performance toward ORR, and nitrogen is the most commonly studied dopant atom.

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4.1.1. Nitrogen doped graphene. Qu et al. [6] first reported the nitrogen doped graphene (NG) had the great potential to use as electrocatalyst for ORR, the NG was synthesized by chemical vapour deposition (CVD) method, which possesses various advantages such as: cost effectiveness, easy preparation, and satisfied conservation of environment. Soon afterwards Geng et al. [7] fabricated NG by thermal treatment of GO in the argon/ammonia system at 900°. The ammonia can not only reduce graphene, but also promote the nitrogen doping in the framework of graphene. The as-prepared NG with the high nitrogen content (up to 2.8 %) displayed a high onset potential (OP) of 0.26 V in 0.1 M KOH solution, which is much higher than that of the undoped graphene.

To further improve the ORR activity of NG electrocatalysts, it's of great significance to obtain the deep understanding about the structure and mechanism of the NG material toward ORR process. Gong et al. [8] have predicted that nitrogen species can induce an enhanced adsorptive ability of neighbouring carbon atoms for oxygen molecules due to the charge shift. In 2014, Xing et al. [9] proved this prophesy through the indirect experimental characterization of the structure for active sites. The XPS measurements based on the synchrotron were conducted for NG catalysts both before and after the electrochemical test. It was observed that the NG electrocatalyst undergoes the obvious changes after ORR tests in 0.1M KOH by analyzing the high resolution C1s, O1s, and N1s. Especially, the authors established the correlation between the amount of –OH groups toward the activity of NG catalyst. The result suggests that that –OH groups can be chemisorbed by the carbon adjacent to pyridinic N. Thus, it was proposed that the adsorbed -OH species are intermediate materials of ORR, indicating the carbon adjacent to pyridinic N acts as the ORR active sites.

A great number of progresses have been achieved on the exploration and development of M–N–C electrocatalysts derived from metal organic framework (MOF) derived for ORR in acidic solution. MOFs have abundant pores and ligand structures that can provide both carbon sources and nitrogen to gain the porous catalyst during the annealing process. For example, Zhong et al. [10] firstly prepared the graphene oxide (GO) by the Hummers' method and then uniformly disperse the zeolitic imidazolate frameworks (ZIF) nanoparticles on GO surface. The ZIF precursors can coordinate with the surface species of GO by the functionalization with PVP. The zinc is generally regarded as inactive species for ORR and always removed during the heating processor after acid leaching treatment. After pyrolysis, the obtained graphene supported nitrogen doped carbon nanosheets (GNCNs) have the high surface area up to 911 m² g⁻¹. The improved OP and well-defined limited current density (LCS) were realized for GNCN catalyst, and the production yield of HO₂⁻ was less than 10%. The ORR activity of GNCN catalyst is more excellent than the sample obtained by the mechanical mixture of ZIF and GO, or the annealing of ZIF without the presence of GO. These performance metrics were also competitive to the commercial Pt/C electrode, indicating the superior intrinsic ORR activity of the GNCN catalyst.

4.1.2. Dual doped graphene. Apart from the nitrogen doping, there are numerous reportes about the graphene-based nanostructures doped with other dopant species, such as: boron, phosphorus, and sulfur. It has been investigated that the ORR kinetic could be enhanced by incorporating additional heteroatoms into nitrogen-doped graphene framework, which can further tailor the surface structure and electronic property of the catalysts.

Boron and nitrogen dual doped graphene-based materials (B, N-G) had been prepared and used as electrocatalysts for ORR. Xue et al. [11] constructed the three-dimensional (3D) boron and nitrogen doped graphene foams using CVD system by decomposing the melamine diborate species on the nickel foam surface. The authors have confirmed the successful doping of boron and nitrogen atoms into the planar framework of graphene. In addition, it was observed quite a part of hexagonal boron nitride (h-BN), however, which exhibited undesirable ORR activity due to the electronic resistivity and chemical inertness. To obtain the ORR-inactive and highly conductive h-BN with graphene, Zheng et al. [12] reported unique B,N-G catalyst by the thermally treating of GO accompanied with ammonia at 500 °C for 5h, followed by the annealing at 900 °C for 1h with boric acid, the as-prepared NG was then doped with biron. The doping of boron and nitrogen within the graphene structure was proved by XPS analysis. The B, N-G catalyst demonstrated high ORR activity in 0.1 M KOH in terms of OP, half-wave potential

($E_{1/2}$), LSC and four electron reduction mechanism compared with h-BN-graphene or individually doped graphene materials. Rotating Ring-Disk electrode (RRDE) tests and Koutecky–Levich analysis revealed the four-electron selectivity. The $E_{1/2}$ and OP for the B, N-G catalyst calculated to be -0.25 and -0.06 V vs. Ag/AgCl, respectively. Further more, the density functional theory (DFT) calculations were also employed to give a deep understanding of the chemical interactions between boron, nitrogen dopant atoms and graphene material. The authors found the ORR activity of B, N-G catalyst can be tuned by the beneficial synergistic effect, varying the microstructure of the active sites or tailing the identity of the doping species can achieve this and result in the improved catalytic activity.

The combination of both sulfur and nitrogen as dual dopants into graphene structure (S, N-G) has also been reported, more edge sites can be gained due to the morphological effects and adjusted charge distributions of carbon. Liang et al. [13] fabricated mesoporous S, N-G through physical mixing of GO, benzyl disulfide and melamine, which was then heated at 900 °C in Ar for 1h by adding the colloidal silica particles (12 nm). After reaction, the silica particles were removed by hydrofluoric acid. The S, N-G products displays high content of sulfur and nitrogen up to 2.0 and 4.5 %, respectively, accompanied with the massive mesopores ranging from 10 nm to 40 nm. The electrochemical measurements suggested that S, N-G has higher ORR activity than sulfur doped graphene (SG) and NG, highlighting the beneficial interactions of the dual-doping of graphene. Particularly, it demonstrated the high OP of -0.06 V vs. Ag/AgCl with the transferred electrons number of near 4.0, which is determined by Koutecky–Levich analysis. DFT calculations were performed and confirmed that the improved activity was attributed to the dual-doping with nitrogen and sulfur. When sulfur and nitrogen are simultaneously doped with graphene, plenty of carbon atoms have an electronic modification. In addition, the spin and charge densities of the S and N atoms are increased, leading to the enhanced catalytic activity providing higher intrinsic ORR activity.

4.2. Graphene/ inorganic nanoparticle composite

The function of graphene in ORR electrocatalysis can also be serve as the substrate for supporting the catalyst nanoparticle, which plays a vital role in avoiding the agglomerating or dissolving of metal oxide/sulfide nanoparticles.

As one class of NMCs, cobalt sulfides have attracted enormous attention thanks to their striking catalytic property, high electronic conductivity, and remarkable phase-dependant magnetic structures. Wang et al. [14] fabricated the graphene supported cobalt sulfide nanoparticles composite catalyst via a solution-phase reaction at low temperature and a pyrolysis at high-temperature. According to electrochemical tests, the current density increases with decreasing the applied potential, accompanied with an enhanced selectivity for the overall four-electron reduction process for ORR. After this, Higgins et al. [15] reported shape-controlled cobalt disulfide located on the surface of N, S-GO/CNT via a unique one-step solvothermal method. The GO in the composite can not only increase the surface area to restrict the CoS₂ from agglomerating, but also easy to dope with nitrogen and sulfur in solvothermal process. In 0.1 M HClO₄, such N, S-GO/CNT- CoS₂ catalyst exhibited the high OP and $E_{1/2}$ of 0.78 and 0.66 V vs. RHE, respectively. The ORR activity of N, S-GO/CNT- CoS₂ is the highest among the NMCs reported to date.

There were wide ranges of metal oxide nanoparticles, including Co_xO_y , Fe_xO_y , Mn_xO_y , and Cu_xO_y supported on graphene have been investigated to display promising activity tpward ORR. The $MnCo_2O_4$ particles with the diameter of ca. 5 nm were gained on the surface of nitrogen-doped reduced graphene oxide ($MnCo_2O_4/N$ -rGO) via a mild aqueous reaction by mixing GO, ethanol, NH_4OH , $Co(OAC)_2$ and $Mn(OAC)_2$ at 80 °C for 20h, and then a hydrothermal process at 150 °C for 3h. [16] The $E_{1/2}$ of 0.87 V vs. RHE was achieved in 1 M KOH solution, which is the highest value among the reported results for metal-oxide based ORR electrocatalysts. The electrons transfer number was calculated was determined as 3.9 by RRDE voltammetry with the potential ranging from 0.9 to 0.5 V vs. RHE, suggesting high selectivity of the four-electron ORR mechanism. Despite the great progresses have been made in the preparation of graphene–inorganic nanoparticle composites, some vital challenges still need to be overcame. Future studies should focus on advanced synthetic strategies and not just rely on the current techniques. Material engineering and the deep understanding of structure-activity relation based on the synergetic effects should be concerned.

5. Conclusion

In summary, we have reviewed the recent progresses of graphene based NMCs for ORR, including heteroatom doped graphene and graphene-inorganic nanoparticle composite. The heteroatom doped graphene based electrocatalysts have been extensively studied, and nitrogen doping has demonstrated the highest catalytic performance toward ORR. The 2D structure and tunable surface of graphene has made it promising as a suitable substrate to support inorganic nanoparticles that have displayed high ORR activity in alkaline or acidic electrolyte. Intensive progresses have been made over past few years in acquaintance the physicochemical features, structure-tailing, and surface-tuning of graphene material, which has played the vital role in the field of developing ORR active catalysts. Thus, it is of great aspiration for further investigating how the structural features and surface chemistry of the graphene based catalyst affect the ORR activity and stability. Further attention can be devoted to this for deeper understanding of graphene based NMCs, along with adapting advanced strategies to effectively synthesize the nanoarchitectures and controllable tune the surface structures. It is highly desired that strategically research will seize new opportunity to improve the ORR activity of graphene based NMCs.

References

- Li H, Li Q, Wen P, et al. Colloidal cobalt phosphide nanocrystals as trifunctional electrocatalysts for overall water splitting powered by a zinc–air battery[J]. Advanced Materials, 2018, 30(9): 1705796.
- [2] Kulkarni A, Siahrostami S, Patel A, et al. Understanding catalytic activity trends in the oxygen reduction reaction[J]. Chemical Reviews, 2018, 118(5): 2302-2312.
- [3] Chatterjee K, Ashokkumar M, Gullapalli H, et al. Nitrogen-rich carbon nano-onions for oxygen reduction reaction[J]. Carbon, 2018, 130: 645-651.
- [4] Foster S L, Bakovic S I P, Duda R D, et al. Catalysts for nitrogen reduction to ammonia[J]. Nature Catalysis, 2018, 1(7): 490.
- [5] Novoselov K S, Geim A K, Morozov S V, et al. Electric field effect in atomically thin carbon films[J]. Science, 2004, 306(5696): 666-669.
- [6] Qu L, Liu Y, Baek J B, et al. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells[J]. ACS Nano, 2010, 4(3): 1321-1326.
- [7] Geng D, Chen Y, Chen Y, et al. High oxygen-reduction activity and durability of nitrogen-doped graphene[J]. Energy & Environmental Science, 2011, 4(3): 760-764.
- [8] Gong K, Du F, Xia Z, et al. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction[J]. Science, 2009, 323(5915): 760-764.
- [9] Xing T, Zheng Y, Li L H, et al. Observation of active sites for oxygen reduction reaction on nitrogen-doped multilayer graphene[J]. ACS Nano, 2014, 8(7): 6856-6862.
- [10] Zhong H, Wang J, Zhang Y, et al. ZIF-8 derived graphene-based nitrogen-doped porous carbon sheets as highly efficient and durable oxygen reduction electrocatalysts[J]. Angewandte Chemie International Edition, 2014, 53(51): 14235-14239.
- [11] Xue Y, Yu D, Dai L, et al. Three-dimensional B, N-doped graphene foam as a metal-free catalyst for oxygen reduction reaction[J]. Physical Chemistry Chemical Physics, 2013, 15(29): 12220-12226.
- [12] Zheng Y, Jiao Y, Ge L, et al. Two-step boron and nitrogen doping in graphene for enhanced synergistic catalysis[J]. Angewandte Chemie International Edition, 2013, 52(11): 3110-3116.
- [13] Liang J, Jiao Y, Jaroniec M, et al. Sulfur and nitrogen dual-doped mesoporous graphene electrocatalyst for oxygen reduction with synergistically enhanced performance[J]. Angewandte Chemie International Edition, 2012, 51(46): 11496-11500.
- [14] Wang H, Liang Y, Li Y, et al. Co1-xS–Graphene Hybrid: A High-Performance Metal Chalcogenide Electrocatalyst for Oxygen Reduction[J]. Angewandte Chemie International

Edition, 2011, 50(46): 10969-10972.

- [15] Higgins D C, Hassan F M, Seo M H, et al. Shape-controlled octahedral cobalt disulfide nanoparticles supported on nitrogen and sulfur-doped graphene/carbon nanotube composites for oxygen reduction in acidic electrolyte[J]. Journal of Materials Chemistry A, 2015, 3(12): 6340-6350.
- [16] Liang Y, Wang H, Zhou J, et al. Covalent hybrid of spinel manganese-cobalt oxide and graphene as advanced oxygen reduction electrocatalysts[J]. Journal of the American Chemical Society, 2012, 134(7): 3517-3523.