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RESEARCH ARTICLE

FUNCTIONALIZED GRAPHENE-MnO₂ NANOCOMPOSITE IN FUEL CELL APPLICATIONS

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ABSTRACT

Functionalized Graphene-MnO₂ composites have been established to be a very proficient and promising electro-catalyst for oxygen reduction reaction (ORR), an essential step, in fuel cells applications. The composite has several advantages of easy fabrication, low production cost, superior charge transport and electrocatalytic properties that would ideally meet the urgent demands of green energy. This brief overview categorically narrates the basic requirements, recent progresses and achievements on the fabrication and performances of the composite as ORR catalyst. A concise outline on the challenges and future prospects of this research field has also been highlighted.

INTRODUCTION

Ever rising demands for renewable and sustainable energy has highly encouraged extensive research on energy conversion and storage systems that are efficient, cost effective and environmentally friendly. Among the various promising energy conversion technologies currently available, "fuel cell", owing to its eco-friendliness, production-economy, promising efficiency, has drawn a great deal of attention in the recent past in terms of both fundamentals as well as applications (Carrette *et al.*, 2000; Sharaf, 2014). In a fuel cell device, generally a substrate, (such as, di-hydrogen, methanol, and ethanol, alcohols, easily oxidizable organic compounds, etc) used as fuel, is electrochemically oxidized at the anode, and the released electrons are transferred to cathode where oxygen is electro-chemically reduced to water/ hydroxide ion. The oxygen reduction reaction (ORR) consisting of 4-e transfer process at the cathode has very sluggish reaction kinetics; which limits the cell performance to great extent. Accordingly, superior materials for electrocatalyses are required to facilitate the ORR (Song, 2008). Consequently, the electrocatalyst material for the ORR is a vital component for fuel cell and plays a key role in determining the performance of fuel cells, such as power output, open circuit, energy efficiency, and longevity (Wang, 2005; Shui *et al.*, 2015). Advanced ORR kinetics urges for electrode materials possessing outstanding

features, that include - resourceful storage, abundant mesoporous variety, long durability, attractive as well as facial chemistry, wide potential window and eco-friendliness, are the crucial points required to achieve improved fuel cell performances (Dai *et al.*, 2015). Till date, electrode materials for ORR embrace a variety of metals like platinum, silver, cobalt, iridium, rhodium, etc (Nie *et al.*, 2015; Wu *et al.*, 2014; Yasuda *et al.*, 2006); metal oxides like iron oxides, cobalt oxides and sulfides (Gasteiger *et al.*, 2005; Singh *et al.*, 2012; Suntivich *et al.* 2013; Liang *et al.*, 2011) with specific shapes, bimetallic/ intermetallic compositions (Wang *et al.*, 2010; Kuttiyiel *et al.*, 2012), and core-shell nanostructures (Zhang *et al.*, 2012; Chaudhuri and Paria, 2012), all of which have acquired some achievements in optimizing catalytic activity for ORR. Nonetheless serious limitations, such as high production cost, crossover effects and CO poisoning, side reactions and useless biproducts, are unavoidable in present cases which certainly lead to electrode material modifications to attain higher electrocatalytic efficiencies (Du *et al.*, 2007; Birry *et al.*, 2010). In the recent past, graphene-based-materials have been extensively fabricated to investigate their efficiencies as electrocatalysts for ORRs (Sun *et al.*, 2015; Wu *et al.*, 2012; Navaee and Salimi, 2015). Graphene-based nanocomposites are used as electrode materials for ORR, owing to the following advantages, namely:

- Flexible graphene nanosheets provide large surface area for accommodation and support to the anchored materials-metals/metal oxides, preventing their agglomeration;

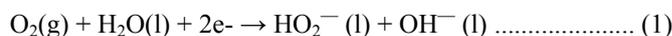
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- Better superficial characteristics of graphene owing to large surface area increase the solid-air contact efficiency, resulting in a large amount of oxygen adsorption on graphene layers;
- Superior electronic structure of graphene reinforcing faster electron transfer rate
- Structural defects on surfaces provide larger number of active sites for the functionalization of active groups promoting electrocatalytic ORR (Wang *et al.*, 2014; Li, 2008; Zhu *et al.*, 2014).

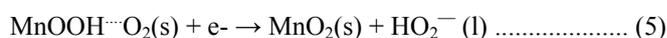
Recent reports on this research field include use of various transition metal oxides anchored onto graphene surface. Various morphologies such as one dimensional nanorods/tubes/fibres, two dimensional nanosheets/ nanoplates as well as three dimensional hollow nanostructures of the supported metal oxides on graphene have also been found to exhibit impressive results (Wang, *et al.*, 2009; Changyuan Hu *et al.*, 2013; Zhang *et al.*, 2011). Among the several transition metal oxides, oxides of manganese are particularly more popular due to its easy availability, low production cost and superior redox behavior. The family of oxides of manganese includes complex members such as MnO₂, Mn₂O₃, and Mn₃O₄ (Lee *et al.*, 2011). Each of these oxides display an extensive range of crystallographic structures and morphologies (Lee *et al.*, 2011; Cheng *et al.*, 2006; Chen, 2012; Tang *et al.*, 2014; Zhang *et al.*, 2013; Sun *et al.*, 2013). They have different extent of contributions to various catalytic activities. As far as ORR is concerned, MnO₂, amongst these various manganese oxides, has been found to exhibit impressive and improved catalytic activity in ORR. It is well known that MnO₂ can form many polymorphs such as α , β , γ , δ - types, offering characteristic properties and extensive applications. It acts as a promising material for due to its easy preparation, superior electrochemical performance, environmental friendliness, and lower production cost (Ali *et al.*, 2014; Zhang *et al.* 2013; Cheng *et al.*, 2006; Hu *et al.*, 2015). Over the past, various nanostructured MnO₂, including dendritic clusters, nanocrystals with different morphologies including nanospheres, nanowires/fibres, nanotubes/rods, nanobelts, and nanoflowers, have been successfully synthesized and characterized in details (Tang *et al.*, 2014; Sun *et al.*, 2013; Ali *et al.*, 2014; Zhang *et al.*, 2013). Lately, our group also experienced superior ORR as well as OER activities from microwave-synthesized Mn₂O₃ nano-balls (Ghosh *et al.*, 2013) Nevertheless, pure transition metal oxide electrodes have suffered largely from poor recyclability, low conductivity leading to questionable performances - mainly attributed to large morphological breakdown/ degradation during the repeated cycles. These problems have been successfully addressed to appreciable extent by anchoring them to conducting 2D substrates like graphene.

Graphene-MnO₂ composite has the potential to act as an effective ORR catalyst. This is ensured based on the following rationales: firstly, low price, ecofriendliness and intrinsic activity towards ORR. Secondly, high conducting graphene sheets facilitate rapid electron transport for ORR. Thirdly, greater dispersion of MnO₂ clusters on graphene sheets providing better electro catalytic performance. Finally, direct growth of MnO₂ nanostructures on graphene sheets without disrupting the conductive network would significantly reduce the contact resistance usually caused by conventional carbon-supported catalysts via simple absorption and/or mixing.

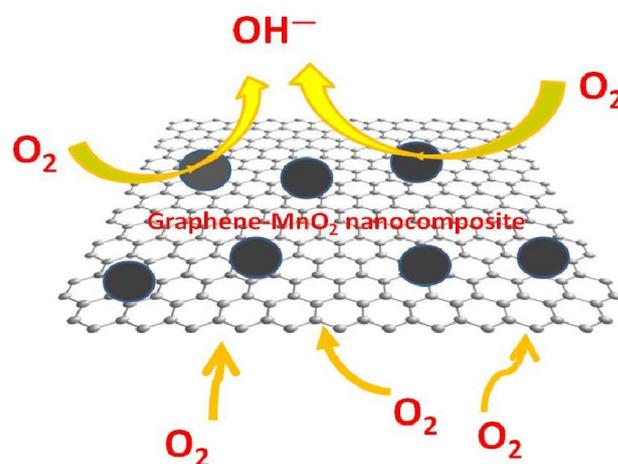
Therefore, the synergistic effect of MnO₂ clusters and graphene sheets is expected to offer superior catalytic activities in comparison with the pristine/physical mixing of the components (Sun *et al.*, 2015; Zhang *et al.*, 2013). As far as the chemistry of ORR mechanism is concerned, the electrode material catalyzes reduction of O₂ to HO₂⁻ as described in equation (1), the latter ultimately undergoes electrochemical transition to OH⁻ (equation (2)) (Verma *et al.* 2005; Cheng *et al.*, 2010).



It is reported that manganese dioxide adsorbs di-oxygen which is then reduced to HO₂⁻ as shown in the following equations: (Gao *et al.*, 2014),



Initially, Mn(IV) gets electrochemically reduced to Mn(III) in alkaline medium and becomes active to adsorb di-oxygen molecule. The adsorbed di-oxygen molecule acts as electron acceptor and accepts an electron from Mn(III) to form Mn(IV) and HO₂⁻ respectively, the later ultimately converted to hydroxyl ion following equation (2). The exfoliated functionalized graphene sheets offer more exposure to such active sites for reduction and thus exhibit superior ORR activity. This is shown schematically in Figure-1.



Literature survey shows that few years back, microwave-irradiated synthesis process of MnO₂ particles (size of 5-10 nm) were uniformly coated on the surface of graphene nanosheets, displayed a distinctive oxygen reduction peak at -0.43 V in alkaline solution, which is more positive than that of pristine-MnO₂ (-0.71 V) and even better than that of Pt/C (-0.44 V), representing that the nanohybrid acts as a significant ORR accelerator (Wen *et al.*, 2012). Yang *et al.* used MnO₂-graphene nanosheets as the air cathode in lithium-air cells and obtained a discharge capacity much higher than pure graphene nanosheets (GNS) catalyst (Yang *et al.*, 2012). G.kumar *et al.* used nanotubular MnO₂-GO composites as the air cathode in MFC and obtained a power density higher than the pure MnO₂ nanorods and MnO₂ nanotubes (Gnanakumar *et al.*, 2014).

The growth of hollow structured tunnels of α -MnO₂ nanotubes preferentially occurred along the [001] direction with increased surface area showing greater accommodating capability for molecular oxygen, attributing to outstanding catalytic activity towards the oxygen reduction reaction over the other solid structures. Qian et al. also obtained larger voltammetric currents for ORR with MnO₂/reduced graphene oxide (RGO) composites compared to pure RGO in alkaline solution and also showed that the MnO₂-RGO composite proceeds with a 4-electron reduction pathway for the ORR with higher activity (Qian and Lu, 2011). Basirun group reported graphene oxide electrocatalyst on MnO₂ air cathode as an efficient electron pump for enhanced oxygen reduction in alkaline solution where GO and ERGO accelerate the process of electron donation to the MnO₂ as well as to adsorbed oxygen atoms (Basirun *et al.*, 2015). To increase the solubility of graphene for processing purposes as well as improve the charge transfer rate, many researchers proposed the usage of graphene oxide or/and reduced graphene oxide as supporting substrate instead of pure graphene. Current reports show that MnO₂/reduced graphene oxide (MnO₂/rGO) composites were synthesized by a facile chemical reduction method assisted by poly(sodium 4-styrene sulfonate) (Sun *et al.*, 2015). There are two functional aspects used in this synthesis. Firstly to increase the solubility of graphene in aqueous solutions thereby using the modification- reduced graphene oxide (rGO); and secondly, to tether Mn²⁺ precursor onto graphene. Polymer-assisted synthetic strategy was also adopted to fabricate 3D MnO₂/rGO nanocomposites, which displayed good electrocatalytic activity towards four-electron reduction of oxygen.

Recently, the influence of different shapes of MnO₂ decorated on functionalized graphene on ORR in a systematic approach has been explored (D Majumdar, 2016). Lately, three-dimensional flower-like manganese oxide was directly grown on reduced graphene oxide (RGO) sheets via a chelation-mediated method, exhibiting appreciable catalytic activity, higher selectivity and better stability towards oxygen reduction reaction (Zhang *et al.*, 2013) They showed that hierarchical structure generated from 3D MnO₂ clusters and RGO thin sheets facilitate mass transfer of oxygen molecules that improves oxygen reduction synergistically. Moreover, RGO-MnO₂ composite is unable to catalyze the oxidation of the crossover methanol that otherwise, reduces the oxygen reduction current, leading to higher selectivity toward ORR. Few years back, S. Khilari group developed graphene supported α -MnO₂ nanotubes with minimum charge transfer resistance values facilitating enhanced charge transport, which in turn increases the oxygen reduction rate (Khilari *et al.*, 2013). Another group reported a new electrocatalyst based on a graphene oxide-intercalated layered manganese oxide, prepared by inserting graphene oxide sheets within the interlayers of protonated layered manganese oxides. They stated that the aforesaid electro-catalyst had more accessible Mn(III)/Mn(IV) sites which eventually resulted in superior ORR activity in alkaline medium (Park *et al.*, 2014). MnO₂ nanotubes are often mixed with metal like Ag, Pt with graphene is applied as the ORR catalyst in proton exchange membrane fuel cell, shown in Figure 2. (Liu *et al.*, 2015) The introduction of metal nanoparticles between the MnO₂ nanoparticles on graphene sheets can significantly improve the catalytic activation, through increase in charge transportation, creating abundant active sites through defects

for di-oxygen adsorption as well as HO₂⁻ reduction during the ORR process (Divya and Ramaprabhu, 2013; Liu, 2015). MnO₂ nanostructures grown directly onto Nitrogen-Doped

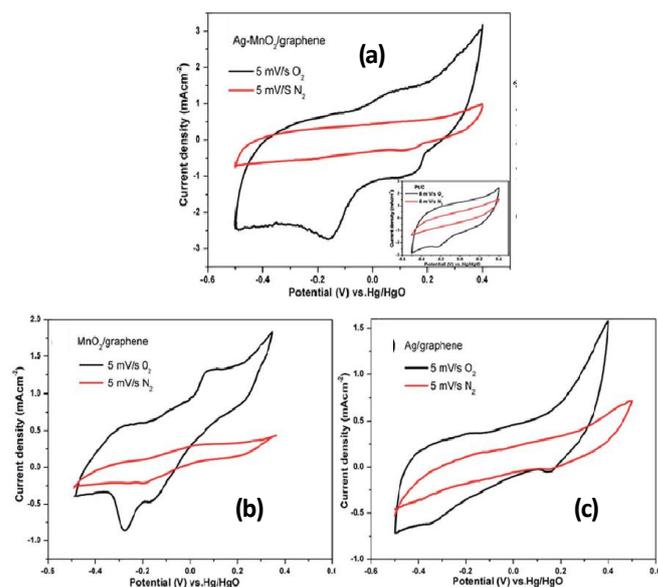


Figure 2. (a) CV of the Ag-MnO₂/graphene and Pt/C (the inset of figure a) electrode at scan rate of 5 mV s⁻¹ with the rotation rate at 1200 rpm in a 0.1 M KOH solution saturated with N₂ and O₂ respectively (b) and (c) CVs of the different electrode at scan rate of 5 mV s⁻¹ with the rotation rate at 1200 rpm in a 0.1 M KOH solution saturated with N₂ and O₂ of MnO₂/graphene and Ag/graphene composites respectively. [Ref: RSC Adv., 2015, 5, 15627–15633]

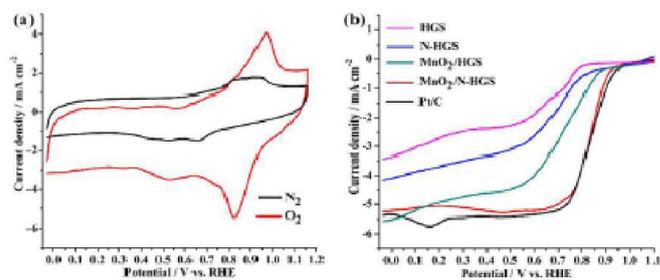


Figure 3. (a) CV curves of the MnO₂/N-HGS electrode at 50 mV s⁻¹ in 0.1 M KOH solutions saturated with N₂ or O₂. (b) LSV curves of the HGS, N-HGS, MnO₂/HGS, MnO₂/N-HGS, and Pt/C catalysts in 0.1 M KOH saturated with O₂ at 10 mV s⁻¹ at 1600 rpm. [Ref: ACS Appl. Mater. Interfaces 2016, 8, 35264–35269]

Graphene displayed high ORR activity with more positive onset potential, larger current density and ideal stability, owing to synergistic interactions between MnO₂ and the doped carbon nanomaterials, Figure 3 (Yu *et al.*, 2016). Nitrogen-doped thermally exfoliated graphene synthesized combined with α -MnO₂ nanotubes having larger surface area and higher electrical conductivity demonstrated excellent activity in aprotic non-aqueous electrolyte (Gautam *et al.*, 2016; Park *et al.*, 2013). Thus, above studies infer that the role of Graphene-MnO₂ composites in ORR is still in a very promising stage and the challenges still remain to be realized in a scientific and technical way. The fundamental mechanism of the kinetic process in these graphene-based nanocomposites is yet to be fully understood/explored, especially with respect to their surface functionalities/defects and hierarchical electrode structures. More systematic exploration and deeper understanding of the different catalytic mechanisms of these

types of graphene-based materials for ORR are required for optimum material design and device performance optimization. The durability and stability of these nanocomposites, too, of course, are of crucial importance for their practical application in real fuel cells. Obviously, the development of facile, green, cost-effectiveness, and controllable preparation method is still a significant issue, because the current assembly process requires rigorous reaction conditions (such as high temperature or pressure) and/or involves tedious procedures, which complicates its synthetic methodology. Consequently, much further research is necessary to understand the ultimate objective of final industrial implementation, with special priority to large scale, low cost, and simple production of these graphene-based materials with high catalytic activity and practical durability for ORR. This short review, nonetheless, is anticipated to encourage more future opportunities to achieve the aim and promote sustainability in this field of research.

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