A three-dimensional Mn$_3$O$_4$ network supported on a nitrogenated graphene electrocatalyst for efficient oxygen reduction reaction in alkaline media†

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Developing low cost oxygen reduction catalysts that perform with high efficiency is highly desirable for the commercial success of environmentally friendly energy conversion devices such as fuel cells and metal–air batteries. In this work a three-dimensional, 3D, self-assembled Mn$_3$O$_4$ hierarchical network has been grown on nitrogen doped reduced graphene oxide (NrGO), by a facile and controllable electrodeposition process and its electrocatalytic performance for oxygen reduction reaction (ORR) has been assessed. The directly electrodeposited MnO$_2$ on a glassy carbon electrode (GCE) exhibits little electrocatalytic activity, whereas the integrated Mn$_3$O$_4$/NrGO catalyst is more ORR active than the NrGO. The resulting electrode architecture exhibits an ‘apparent’ four-electron oxygen reduction pathway involving a dual site reduction mechanism due to the synergetic effect between Mn$_3$O$_4$ and NrGO. The 3D Mn$_3$O$_4$/NrGO hierarchical architecture exhibits improved durability and methanol tolerance, far exceeding the commercial Pt/C. The enhanced ORR performance of the room temperature electrodeposited Mn$_3$O$_4$ nanoflake network integrated with NrGO reported here offers a new pathway for designing advanced catalysts for energy conversion and storage.

Introduction

The development of catalytic materials for the oxygen reduction reaction (ORR) is one of the major challenges in electrochemical energy conversion and storage technologies such as fuel cells and metal–air batteries. The ORR reaction at the cathode proceeds through multistep electron transfer, leading to sluggish kinetics and a large overpotential. This large overpotential is related to the difficulty in O$_2$ adsorption on the electrode surface and O=O bond cleavage. An effective electrocatalyst such as platinum is needed to reduce the overpotential and expedite the reaction, through a single step four electron transfer process. However, the high use of platinum needed for achieving efficient ORR and its high cost due to its rarity are some of the most important factors that hinder the applicability of these devices to broad commercialization. An added reason is that Pt catalysts are vulnerable to poisoning by adsorption of the reaction intermediates and to the fuel crossover effect, which limits substantially their performance. To date, there have been notable improvements towards developing highly active and durable alternatives based on low cost earth abundant metal catalysts, such as the first-row transition metal oxides, spinels and perovskites. However, most non-precious metal catalysts developed so far still underperform the Pt benchmark.

Among the non-precious metal alternatives, manganese oxides have received intensive attention because of their high elemental abundance, low cost and toxicity and appreciable activity, when integrated with a conductive based support material such as graphene, carbon nanotubes or Ketjenblack. The ORR activity is dependent on the particle size and morphology as well as on the phase of the Mn oxide in the following order: MnOOH > Mn$_3$O$_4$ > Mn$_5$O$_8$ > Mn$_6$O$_{13}$. Manganese oxides with higher valence show better catalytic activity towards ORR and the surface Mn valance can be tuned with simple electrochemical cycling or heat treatment. Nevertheless, irrespective of their phase, manganese oxides, when used on their own, show mediocre electrocatalytic activity due to their low conductivity. Strategies to enhance their conductivity and hence facilitate electron transport for ORR include doping with cations, coating with metals and...
coupling with conductive nanostructures.\textsuperscript{16-27} Currently, intricate synthesis routes and medium performance disfavour their use as inexpensive and robust ORR catalysts in technological systems. Manganese oxides directly electrodeposited on conductive electrodes represent an attractive option, however deposition routes on standard electrodes such as the GCE resulted in oxides of comparatively low catalytic activity in the as-deposited state requiring high temperature annealing to create an active crystalline phase.\textsuperscript{31,32}

Bearing in mind that nitrogenated reduced graphene oxide is both ORR active and highly conductive, it is intuitive to use NrGO as a support electrode for the electrochemical deposition of manganese oxides and study their synergetic coupling effect. The ORR activity in nitrogen doped graphene has been rationalized using density functional calculations, where it was found that nitrogen doping alters the local spin or charge density thus promoting oxygen adsorption.\textsuperscript{33,34} So far only a few studies have explored Mn\textsubscript{3}O\textsubscript{4}/N-doped graphene hybrids as ORR catalysts, with the Mn\textsubscript{3}O\textsubscript{4} in the form of various shapes (spheres, cubes and ellipsoids)\textsuperscript{16,18,22,23,25} or Mn\textsubscript{3}O\textsubscript{4} nanoparticles encapsulated in nitrogen doped graphene.\textsuperscript{19} However their synthesis is based on solvothermal or reflux methods requiring low or high temperature steps to induce a highly crystalline Mn\textsubscript{3}O\textsubscript{4} phase for providing ORR catalytic sites. The ORR performance of Mn\textsubscript{3}O\textsubscript{4} catalysts in the form of nanoflakes, integrated on NrGO has never been investigated before.

Herein, direct growth of a three-dimensional poorly crystalline Mn\textsubscript{3}O\textsubscript{4} network on conductive NrGO was achieved by simple electrodeposition at room temperature. The integrated Mn\textsubscript{3}O\textsubscript{4}/NrGO structure displays high electrocatalytic activity with an apparent four-electron ORR in alkaline solutions. The improved performance of the Mn\textsubscript{3}O\textsubscript{4}/NrGO hierarchical nanostructure is attributed to the following factors: (i) the direct growth of the Mn\textsubscript{3}O\textsubscript{4} network on the underlying conductive NrGO provides strong coupling between the two catalysts, which affords coupling reactions leading to improved performance. In addition the strong coupling also reduces the interfacial resistance and improves electron transport; (ii) the highly porous Mn\textsubscript{3}O\textsubscript{4} network with moderate long range order affords a high density of surface defects, which potentially act as active sites for oxygen adsorption, contributing to the ORR activity. Our study is distinctively different from previous ones that examine Mn\textsubscript{3}O\textsubscript{4}/N-doped graphene hybrids based on temperature dependent solvothermal or reflux methods. In contrast to previous studies that concentrate on well crystallized Mn\textsubscript{3}O\textsubscript{4}, we have found that due to the absence of any high temperature step the Mn\textsubscript{3}O\textsubscript{4} nanoflakes are not highly crystalline but possess a moderate long range order, which contributes to the efficient ORR activity by providing ample defect sites for oxygen adsorption.

**Experimental section**

**Chemicals**

Graphite powder (particle size < 20 μm) was purchased from Alfa Aesar. Sodium nitrate (NaNO\textsubscript{3}), potassium permanganate (K\textsubscript{2}MnO\textsubscript{4}), ammonia hydroxide (30 wt% in H\textsubscript{2}O), hydrazine solution (35 wt% in H\textsubscript{2}O), N,N-dimethylformamide (DMF), manganese acetate (Mn(CH\textsubscript{3}COO)\textsubscript{2}), sodium sulphate (Na\textsubscript{2}SO\textsubscript{4}), and alumina (particle size 0.05 μm) were purchased from Sigma Aldrich. All solutions used in electrochemical experiments were freshly prepared with Millipore water of resistivity 15 MΩ.

**Synthesis of graphene oxide**

Graphene oxide was produced by using a modified Hummer’s method.\textsuperscript{35} Graphite powder of particle size 20 μm was used as the starting material. 2.5 g of graphite, 2 g of NaNO\textsubscript{3} and 85 ml of H\textsubscript{2}SO\textsubscript{4} were mixed together in a 250 ml round bottom flask in an ice bath to form a homogenous mixture. A solution of 11.25 g of K\textsubscript{2}MnO\textsubscript{4} in distilled water was gradually added to the solution. After 2 h the solution was removed from the ice bath and stirred at room temperature for five days. The brown color slurry was added to 500 ml of 5 wt% H\textsubscript{2}SO\textsubscript{4} and gradually 10 ml of H\textsubscript{2}O\textsubscript{2} (30 wt% in H\textsubscript{2}O) was added to the mixture and stirred for 24 h. The mixture was centrifuged and the residue was further purified by dispersing in 500 ml of aqueous solution of 3 wt% H\textsubscript{2}SO\textsubscript{4} and 0.5 wt% H\textsubscript{2}O\textsubscript{2}. After 24 h of stirring the supernatant was removed. The process was repeated five times. The solid product obtained after the rigorous cleaning process was rinsed with copious amounts of water and dried in an oven.

**Synthesis of nitrogen doped graphene**

GO was exfoliated in water by ultrasonication for 2 h. GO dispersion is centrifuged at 1000 rpm for 5 min to remove any thicker graphite oxide and the supernatant is centrifuged at 3000 rpm for 30 min. The obtained graphene oxide pellet is dried in an oven at 60 °C for 48 h. NrGO is synthesized through hydrothermal reaction of graphene oxide with ammonia and hydrazine.\textsuperscript{36} In a typical experiment as-synthesized graphite oxide is suspended in water to give a concentration of 1 mg ml\textsuperscript{-1} followed by sonication of 2 h. 70 ml of above solution pH is adjusted to 10 by ammonia hydroxide and 1 ml of hydrazine (35 wt% in H\textsubscript{2}O) is added to the solution and stirred for 15 min. The solution was transferred to a 100 ml Teflon lined vessel to carry out the hydrothermal reaction at 160 °C for three hours. The resultant product is cleaned with plenty of DI water and collected by centrifugation at 3000 rpm for 45 min. The pellet is dried under vacuum at 60 °C for 48 h.

**Electrodeposition of Mn\textsubscript{3}O\textsubscript{4} nanoflakes on NrGO**

5 mg of NrGO is dispersed in 1 ml of DMF with 50 μl of Nafion through one hour sonication to form a homogenous ink. 6 μl (30 μg) of NrGO suspension is spread on a 3 mm GCE and dried under an infrared lamp, which results in a final loading of 0.425 mg cm\textsuperscript{-2}. First NrGO ORR performance is measured in O\textsubscript{2} saturated 0.1 M KOH solution and then Mn\textsubscript{3}O\textsubscript{4} nanoflakes were electrodeposited on NrGO. The fabrication process is shown in Fig. 1. The electrochemical deposition is carried out in 0.1 M Na\textsubscript{2}SO\textsubscript{4} + 0.05 M Mn(CH\textsubscript{3}COO)\textsubscript{2} in the potential range of 0 to −1.5 V (vs. Ag/AgCl) at a scan rate of 50 mV s\textsuperscript{-1} under two consecutive scans. To determine the density of the Mn\textsubscript{3}O\textsubscript{4}/NrGO, NrGO is drop dried on both sides of a large glassy carbon substrate (2.5 cm × 2.5 cm) and weighed before and after
Electrodeposition by a microbalance and the density of the Mn$_3$O$_4$/NrGO is estimated to be 0.45 mg cm$^{-2}$. Mn$_3$O$_4$ nanoflakes were electrodeposited on the GCE for 2–10 CVs and one microliter of Na$_2$SO$_4$ + 0.05 M Mn(CH$_3$COO)$_2$ solution. For XRD measurement the material is scrapped off the GCE substrate and dispersed in 90% ethanol and drop dried on the Si substrate.

**Electrochemical measurements**

A rotating disk electrode with a glassy carbon disk of 3 mm diameter is used in this study. Prior to surface modification the electrode is polished with alumina powder of particle size 0.05 µm and then cleaned by sonication in water for 2 min. A Pt wire and Ag/AgCl electrode were used as collector and reference electrodes. The electrolyte is freshly prepared 0.1 M KOH and experiments were carried out at room temperature. The electrolyte is saturated with O$_2$/Ar by bubbling O$_2$/Ar for 15 min. A flow of O$_2$/Ar is maintained over the electrolyte during the measurements. Cyclic voltammograms were collected at a scan rate of 0.1 V s$^{-1}$ after preconditioning the electrode through 25 CVs. RDE measurements were performed at a scan rate of 10 mV s$^{-1}$ and the base line in the Ar saturated electrolyte is subtracted.

The electron transfer numbers are calculated by the Kou-Tecky–Levich equation as given below.

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{nFkC_0} + \frac{1}{0.62nFD\omega^{-1/2}C_{O_2}^{-1/2}}$$

Where $J$ is the measured current density, $J_L$ and $J_K$ are kinetic and limiting diffusion current densities. $n$ is the electron transfer number in the ORR process. $F$ is the Faraday constant (96 500 C mol$^{-1}$), $C_0$ is the bulk concentration of O$_2$ (1.2 × 10$^{-6}$ mol cm$^{-3}$), $D$ is the diffusion constant of O$_2$ in 0.1 M KOH (1.9 × 10$^{-5}$ cm$^2$ s$^{-1}$), $v$ is the kinematic viscosity of the electrolyte (0.01 cm$^2$ s$^{-1}$) and $\omega$ is the angular frequency of the disk (=2πN, $N$ is the linear frequency) and $k$ is the electron transfer rate constant.

**Results and discussion**

The synthesis of the Mn$_3$O$_4$/NrGO nanostructure is illustrated in Fig. 1. First NrGO was produced through hydrothermal treatment of graphene oxide in the presence of ammonia and hydrazine. Mn$_3$O$_4$ nanoflakes were electrodeposited onto a pre-coated NrGO glassy carbon electrode through a voltage cycling protocol in the voltage range of 0 to −1.5 V vs. Ag/AgCl in a solution of manganese acetate and sodium sulphate. The morphological and microstructural changes were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It can be seen from the SEM images of Fig. 2a and b that the nitrogenated reduced graphene oxide demonstrated a 3D flame like appearance possessing an interconnected three-dimensional porous network. Low magnification TEM images exhibited a wrinkled morphology, which is characteristic of graphene produced via harsh oxidative and reduction treatments and is indicative of the defective structure. The selected area electron diffraction (SAED) yielded a ring-shaped pattern indicative of a random overlay of NrGO layers. Each set of layers provides a well-defined set of diffraction spots, which make regular hexagons (e.g., the one inserted in Fig. 2c), with different rotational angles. The edge-on views at a high magnification confirm a crystalline interior and are composed of a stack of 5–7 layers. The average interlayer distance is 0.37 nm. Compared to the graphite interspacing of 0.34 nm, this enlarged interspacing indicates a moderate oxidation level present in the NrGO, which is in agreement with the XPS results, presented later.
Fig. 3a and b show low and high magnification SEM images of the hierarchical structure of the Mn₃O₄ nanostructure. The Mn₃O₄ nanoflakes are interconnected with each other, forming a highly porous surface morphology. The formation of the nanoflakes is initiated by strong electrostatic interactions between the oxygen functional groups of the NrGO and the Mn cations, providing the nucleation sites. After only two deposition cycles, nanoflakes appeared and were assembled to form a

hierarchical structure. Fig. 3c and d show TEM and high resolution TEM (HRTEM) images of Mn₃O₄ nanoflakes on NrGO. These TEM samples were prepared by carefully removing the material from the GCE, followed by ultrasonication in isopropanol and coating the TEM grids (lacey carbon coated copper grids) with a few drops. From Fig. 3c it can be seen that the Mn₃O₄ nanoflakes are firmly anchored on NrGO even after ultrasonic dispersion, indicating a strong linkage between NrGO sheets and Mn₃O₄ nanoflakes. The arrows mark the edges of Mn₃O₄ nanoflakes on NrGO. The high-resolution TEM image of Mn₃O₄ nanoflakes in Fig. 3d (and S8†) shows the presence of polycrystalline subunits with various grain boundaries and growth directions. Crystal lattice fringes with d-spacings of 0.25 nm and 0.24 nm can be assigned to the (211) and (202) planes respectively of Hausmannite Mn₃O₄. The selected area diffraction (SAED) pattern taken from a Mn₃O₄ nanoflake also confirms the polycrystalline nature. The marked diffraction circles correspond to (200), (211), (204) and (116) planes of Mn₃O₄.

The polycrystalline phase of the hierarchical structure was confirmed by XRD (Fig. 4a). The XRD pattern of NrGO shows two distinctive peaks at 24.5° and 43.0° corresponding to the (002) and (100) reflections of graphitic carbon. The average interlayer distance was calculated to be 3.62 Å, similar to that obtained from HRTEM measurements. The pattern of the hierarchical structure, in addition to characteristic peaks associated with NrGO and NaF, displays weak and significantly broadened diffraction peaks at 32.6°, 36.2° and 38.5° revealing poor crystallinity. The peaks are indexed to (103), (211), and (004) crystal planes of the tetragonal Hausmannite Mn₃O₄ structure (a = 5.65 Å and c = 9.44 Å, JCPD card no: 80-0382). The results reveal that the room temperature electrochemical synthesis process leads to a poorly crystalline form of manganese oxide with a moderate
degree of long range order, which may offer more active sites for ORR.

Interestingly, the $I_D/I_G$ intensity ratio increases from 1.05 for GO to 1.4 for NrGO and Mn$_3$O$_4$/NrGO as shown in Fig. 4b. Naturally, one would expect a decrease in the $I_D/I_G$ ratio upon hydrothermal treatment of GO since the disorder associated with the semi-amorphous graphene oxide diminishes. It is well documented that the ratio of the D to G peak is a measure of the size of sp$^2$ ring clusters in a network of sp$^2$ and sp$^3$ carbon.

Therefore the observed increase in $I_D/I_G$ is indicative of a decrease in the size of sp$^2$ domains upon reduction. The origin of this reduction is not well understood, however various suggestions have been proposed.\textsuperscript{37,38} One hypothesis is that the hydrothermal reduction process decreases the spatial dimensions of the sp$^2$ regions in the graphene, but increases their overall presence in the material. This is possible if the sp$^2$ sites generated by reduction are isolated from the originally present sp$^3$ clusters by defects such as vacancies or residual sp$^3$ carbon. Various trends in the $I_D/I_G$ ratio have been reported in the literature upon reduction of GO. The $I_D/I_G$ ratio has been reported to increase,\textsuperscript{39–41} decrease,\textsuperscript{42,43} remain nearly constant,\textsuperscript{44,45} or decrease following an increase.\textsuperscript{46} In all cases, an appreciable D-peak signal has been observed, indicating that significant disorder remains in the reduced sample. It should be noted that in our study an additional factor which contributes to the enhancement of the D band intensity upon hydrothermal reduction is the incorporation of N dopants.\textsuperscript{47,48} The Mn$_3$O$_4$/NrGO architecture shows an additional peak at 650 cm$^{-1}$, which is characteristic of the Hausmannite Mn$_3$O$_4$ phase, confirming further its presence. It is assigned to the A$_{1g}$ mode, which corresponds to the Mn–O breathing vibration of divalent manganese ions in tetrahedral coordination.\textsuperscript{52,49–51}

X-ray photoemission spectroscopy provided further evidence on the oxidation state of Mn and determined the elemental composition of NrGO. The oxygen and nitrogen contents in the NrGO were estimated as 9.0 at% and 4.1 at% respectively. The carbon to oxygen ratio was 9.6 indicating a moderate level of reduction. The N 1s in NrGO can be divided into four components pyridinic N (398.8 eV), pyrrolic N (400.0 eV) substitutional (401.54 eV) and pyridine N-oxide (403.4 eV) as shown in Fig. 4c and these assignments are in agreement with the literature.\textsuperscript{36}

As shown in Fig. 4d, the Mn 2p core level spectrum displays two peaks at binding energies of 653.50 eV and 641.70 eV, corresponding to the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ spin-orbit states of manganese oxide respectively. The spin-energy separation is an acceptable way for determining the oxidation phase of Mn and in this case the observed separation of 11.8 eV is in agreement with the literature values for the Mn$_3$O$_4$.\textsuperscript{57,53} The peak separation between Mn 2p$_{3/2}$ and the lowest component of O 1s (Fig. S2†) is 111.8 eV is also consistent with the reported value of Mn–O for the Mn$_3$O$_4$.\textsuperscript{54,55} Additionally the Mn 3s (Fig. S3†) peak separation is 5.5 eV, which is consistent with the reported literature for Mn$_3$O$_4$.\textsuperscript{55–58}

The ORR catalytic activity of the Mn$_3$O$_4$/NrGO architecture was studied in a conventional three electrode system in both O$_2$ saturated and Ar saturated 0.1 M KOH electrolyte solutions. Fig. 5a presents the steady state cyclic voltammograms of NrGO and Mn$_3$O$_4$/NrGO deposited on glassy carbon electrodes, referring to the Ag/AgCl electrode. For NrGO a featureless voltammogram was obtained in the absence of oxygen. The development of a quasi rectangular shape is indicative of the co-existence of a high surface area and relatively high conduc-
tance.\textsuperscript{64,65} When oxygen is introduced a clear oxygen reduction peak is observed at $–0.29$ V vs. Ag/AgCl. Mn$_3$O$_4$/NrGO displayed two distinctive peaks in the absence of oxygen; an oxidation peak at $–15$ mV and a reduction peak at $–0.59$ V. When oxygen was introduced an additional reduction peak located at $–0.29$ V was observed due to oxygen reduction. The results indicate that the presence of redox peaks at $–15$ mV and $–0.59$ V is due to oxidation and reduction of Mn$_3$O$_4$.\textsuperscript{52,56,57} Remarkably, for the Mn$_3$O$_4$/NrGO architecture the onset potential shifted to more positive direction and the reduction reaction current density was increased compared to the NrGO, indicating that the performance enhancement is brought by the introduction of Mn$_3$O$_4$ nanoflakes in the integrated structure.
To gain a better insight into the beneficial role of NrGO as a support for the Mn$_3$O$_4$ nanoflakes we investigated the morphology, structure and ORR performance of electro-deposited MnO$_x$ directly on the GCE under a sequence of 2, 5, and 10 cycles (CVs) (see ESI Fig. S4 and S5†). There is a progressive growth of MnO$_x$ nanoflakes between 2 and 10 cycles on the GCE, which is getting more dense and uniform at 10 cycles. Overall MnO$_x$ nanoflakes grow at a higher rate on NrGO than on GCE. Raman spectra (Fig. S4†) from the electro-deposited MnO$_x$/GCE under 10 cycles show a distinct broad peak centered around 650 cm$^{-1}$, which is indicative of the Mn$_3$O$_4$ phase. The broadness and low intensity of the peak indicate a high degree of disorder. From the CVs the ORR reduction current at $-0.45$ V increases with the deposition cycles. Similarly linear sweep voltammograms (LSVs) show an increase in the current in the diffusion controlled limited region, which is related to an increase in active sites due to the enhanced surface area. However the onset potential does not move appreciably.

Rotating disk electrode analysis of the Mn$_3$O$_4$/NrGO catalyst together with that of NrGO, MnO$_x$ and the bare GCE and state of the art commercial Pt/C catalyst (20 wt% Pt on Vulcan XC-72) is presented in Fig. 5. The half-wave potentials of NrGO, Mn$_3$O$_4$/NrGO are located at $-0.26$ V and $-0.2$ V respectively, confirming that Mn$_3$O$_4$/NrGO has better electrocatalytic activity towards oxygen reduction reaction than NrGO. The Mn$_3$O$_4$/NrGO displays a limiting current density of 4.4 mA cm$^{-2}$ at $-0.4$ V, which is higher than that of NrGO (3.2 mA cm$^{-2}$) and comparable with that of Pt/C (4.7 mA cm$^{-2}$).

To evaluate the electron transfer numbers linear sweeps were measured at different rotation rates for NrGO and Mn$_3$O$_4$/NrGO as shown in Fig. 6a and c. The transferred electrons were calculated by the Koutecky–Levich (K–L) eqn (1) and the K–L plots for NrGO and Mn$_3$O$_4$/NrGO are shown in Fig. 6b and d. The electron transfer numbers for NrGO vary between 2.7 and 3.3 throughout the voltage range of $-0.4$ V to $-0.8$ V. In Fig. 6c which presents LSVs for Mn$_3$O$_4$/NrGO at different rotating speeds, three separate potential regions can be observed. At low potentials $E < -0.2$ V, the ORR is under kinetic control. The potential range of $-0.2$ V to $-0.4$ V is the mixed kinetic-diffusion region. At high potentials ($E > -0.4$ V), the ORR is controlled by O$_2$ diffusion. In Fig. 6d, good linear fitting can be seen for each potential with identical slopes and the calculated electron transfer numbers at the Mn$_3$O$_4$/NrGO electrode are close to 3.7. The ORR performance of the Mn$_3$O$_4$/NrGO deposited on carbon fiber paper deteriorated upon annealing at low temperatures up to 300 °C (Fig. S11 and S12†) and no improvement in the crystallinity Mn$_3$O$_4$ phase was observed (Fig. S13†).

It is well known that in alkaline electrolytes, oxygen may be reduced through a direct four electron reduction process to OH$^-$ following reaction (2), or through a series ($2e^- \times 2e^-$) pathway involving a peroxide HO$_2^-$ intermediate, via reactions (3) and (4). Alternatively, the HO$_2^-$ formed in reaction (3) may disproportionate to OH$^-$ and O$_2$ according to reaction (5). Reactions (4) and (5) may proceed concurrently so that the O$_2$ formed in (5) is subsequently reduced back to peroxide through reaction (3) with eqn (4) and (5) cycled repeatedly until all the O$_2$ is converted to OH$^-$. If reactions (4) and (5) are very fast, it would then appear as if oxygen is reduced directly to OH$^-$ through the four electron transfer process.

$$\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- \quad (2) \\
\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{HO}_2^- + \text{OH}^- \quad (3) \\
\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- & \rightarrow 3\text{OH}^- \quad (4) \\
\text{HO}_2^- & \rightarrow \frac{1}{2}\text{O}_2 + \text{OH}^- \quad (5)
\end{align*}$$

In an effort to understand the ORR process occurring on Mn$_3$O$_4$/NrGO, the H$_2$O$_2$ reduction reaction (HORR) and oxygen reduction reaction (ORR) was measured over Mn$_3$O$_4$/NrGO, NrGO and MnO$_x$ electrodes as shown in Fig. S7†. An H$_2$O$_2$ concentration of 1.3 mM was used, which is the same as O$_2$ concentration in O$_2$ saturated 0.1 M KOH solution. The HORR current on MnO$_x$ is rather significant when compared to the ORR current in the higher voltage region, which indicates that the MnO$_x$ is active for both ORR and HORR when electro-deposited on the GC electrode. In the case of both NrGO and Mn$_3$O$_4$/NrGO the HORR current is far less than the ORR current. This indicates that both NrGO and Mn$_3$O$_4$/NrGO are rather inactive towards the HORR. These observations suggest that the likely mechanism on the Mn$_3$O$_4$/NrGO for overall 4e ORR takes place by a series pathway via peroxide disproportionation reaction as exemplified by eqn (3) and (5). First a two-electron reduction to hydrogen peroxide at low overpotential occurs at NrGO (low $n$ numbers) and subsequently Mn$_3$O$_4$ catalyzes the disproportionation of HO$_2^-$ intermediates. Several groups have also proposed that reactions (3) and (5) are the likely mechanism to take place on MnO$_x$/carbon catalysts. The morphology of the integrated Mn$_3$O$_4$/NrGO electrode could also play a critical role in producing the exceptional catalytic activity by the suggested disproportionation intermediate mechanism. For example, the porous structure of the electrode may trap peroxide intermediates and thus facilitate the disproportionation pathway. Fig. 6f presents the mass-corrected Tafel plots of the logarithm of kinetic current density, log $J_k$ (mA cm$^{-2}$), vs. the electrode potential $E$ for the ORR on the NrGO, Mn$_3$O$_4$/NrGO and Pt/C electrodes in an O$_2$ saturated 0.1 M KOH solution. Kinetic current densities were extracted from the steady-state polarization according to the Koutecky–Levich equation.

$$J_k = \frac{J_D \times J}{(J - J_D)} \quad (6)$$

where $J_D$ is the diffusion-limiting current density. These Tafel curves were derived from the polarization curves of Fig. 5b with a rotation rate of 1600 rpm. Two distinct Tafel slopes in low and high potential regions are observed for each catalyst, which indicate that oxygen reduction occurred by different mechanisms in these two regions. At low overpotentials, the Tafel slopes for NrGO, Mn$_3$O$_4$/NrGO and Pt/C are $-48$, $-62$ and $-58$ mV dec$^{-1}$, while at high overpotentials the corresponding
slopes are −207, −129 and −114 mV dec⁻¹. The two different Tafel slopes for each catalyst result from different adsorbed oxygen coverage, which follows a Temkin isotherm (high coverage) at low overpotentials and a Langmuir isotherm (low coverage) at higher overpotentials. Theoretically, a Tafel slope of −60 mV dec⁻¹ at low overpotentials is associated with an intermediate oxide coverage arising from ORR, whereby the first electron transfer step involving an adsorbed product is the rate-determining step (Temkin isotherm). On the other hand a Tafel slope of −120 mV dec⁻¹ at high overpotentials can be explained by a migration of adsorbed oxygen intermediates, which is commonly the case when a two-electron transfer reaction is the rate-determining step (Langmuir isotherm). The Tafel slopes of Mn₃O₄/NrGO in low and high potential regions are very close to the values of the Pt/C catalyst. This demonstrates that the oxygen adsorption mechanism of Mn₃O₄/NrGO is similar to that of the Pt/C catalyst. For NrGO, the Tafel slope values of −48 mV dec⁻¹ and −207 mV dec⁻¹ in low and high current density regions were significantly different and account for the lower activity of the NrGO catalysts. Detailed comparisons of the ORR...
activity of our MnO₂/NrGO catalyst with other representative manganese oxide catalysts⁹,16–27,31 are presented in Table S2.† The MnO₂/NrGO is among the most active MnO₂ based catalysts in terms of half-wave potential and limiting current density.

Other important performance metrics for an ORR catalyst include cyclic stability and tolerance to fuel molecules such as methanol, which is of importance to direct methanol fuel cells. The stability of NrGO, MnO₂/NrGO and Pt/C was evaluated by monitoring the chronoamperometric response at the half-wave potential of each electrode rotated at 1600 rpm in oxygen saturated 0.1 M KOH solution. As shown in Fig. 7a, the MnO₂/NrGO showed a higher stability than the Pt/C, retaining 63% of its initial current after 8 h of testing. The smallest attenuation in the catalytic activity for all three electrodes was observed for the NrGO, which lost only 15% of its initial activity. The electrodes were further tested for possible crossover in the presence of 3 M methanol at 0.26 V and 0.18 V for NrGO and MnO₂/NrGO (Fig. 7b). After the addition of methanol the ORR current for NrGO and MnO₂/NrGO decreased by 4.2% and 6.5% respectively, while that for Pt/C suffered a major shift from cathodic to anodic as a result of methanol oxidation reaction (see ESI Fig. S10†). The results indicate that both MnO₂/NrGO and NrGO have excellent immunity towards methanol crossover which overcomes a main challenge faced by precious metal catalysts in fuel cells.

Electrochemical impedance spectroscopy (EIS) is a useful technique to characterize interface reactions and electrode kinetics in ORR. Fig. 8 shows representative Nyquist plots of the EIS response of MnO₂/NrGO and NrGO electrodes at an overpotential of −140 mV where ORR is taking place. The data were fit using the equivalent circuit illustrated in the inset of Fig. 8, and the resultant fitting parameters are summarized in Table S1 (ESI†). The MnO₂/NrGO exhibits a smaller semicircle when compared to NrGO, which clearly demonstrates that the MnO₂/NrGO electrode possesses a lower charge transfer resistance and thus allows much faster shuttling of electrons during ORR. The results further reflect the electrocatalytic activity of both electrodes for ORR.

Conclusions

In conclusion, a 3D hierarchical structure of MnO₂ nanoflakes supported on nitrogenated reduced graphene oxide, exhibiting high performance for the ORR in alkaline medium, was successfully prepared by room temperature electrodeposition. The oxygen reduction of the integrated catalyst followed the apparent four-electron transfer pathway due to the synergetic effects between MnO₂ nanoflakes and NrGO. The high surface area network and moderate long range crystalline order of MnO₂ nanoflakes provided ample defects sites for oxygen adsorption, whereas the immediate coupling between the MnO₂ nanoflakes and the conductive NrGO guaranteed efficient electron transport. In addition to high ORR activity, the as-prepared MnO₂/NrGO catalyst shows superior methanol tolerance and stability when compared to commercial Pt/C for ORR. Thus MnO₂/NrGO represents a low cost and highly active catalyst which can be used as a cathode in fuel cells or metal–air batteries in alkaline solutions.

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Notes and references