



Design and synthesis of conductive carbon polyhedrons enriched with Mn-Oxide active-centres for oxygen reduction reaction

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ABSTRACT

The development of efficient, low-cost and stable electrocatalysts as the alternative to platinum for the oxygen reduction reaction (ORR) is of significance for many important electrochemical devices, such as fuel cells and metal–air batteries. Herein we discuss the design and synthesis of a $Mn_xO_y/N-C$ hybrid catalyst that can address both the activity and durability issues caused by the high productivity of peroxide (H_2O_2) in nitrogen-doped carbon (N-C). The high activity and stability of the $Mn_xO_y/N-C-3$ catalyst is ascribed to its novel hybrid structure, in which Mn_xO_y is a good catalyst for decomposition of peroxide, while N-C not only catalyses the ORR but also prevents Mn_xO_y agglomeration. RRDE study indicates a typical 4-electron ORR pathway with very low peroxide production (~1.9%) and considerable stability. In light of the low cost and high earth abundance of Mn, the highly active $Mn_xO_y/N-C$ is a promising candidate to be used as a cathode material in metal–air batteries and alkaline fuel cells.

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1. Introduction

The most important issue of the modern energy-related electrochemistry is the use of cheap and eventually eco-friendly materials for solar cells, batteries, fuel cells and supercapacitors to replace Pt and other costly components with valid alternative [1–7]. As an indispensable component of fuel cells and metal-air batteries, the electrocatalyst for oxygen reduction reaction (ORR) plays a dominant role in determining their performances [8]. Currently, the prevailing catalysts are mainly Pt-based materials, which are costly and unstable [9–12]. Durability improvements and cost reductions must be achieved to render these electrochemical devices commercially competitive with conventional technologies. As such, intensive efforts to explore platinum-free catalysts for ORR to replace the precious platinum have been going on for several decades to bring this efficient technology into real applications [13–15]. In this respect, nitrogen-doped carbon (N-C) materials represent important candidates as metal-free

catalysts for ORR because of their unique electronic properties and structural features [16,17]. In spite of some significant achievements, the ORR performance and stability of most reported N-C catalysts is still much inferior to that of commercial Pt/C catalyst [18,19]. As theoretically expected for the complete reduction of O_2 to H_2O ; mechanistic analysis of electrochemical process catalysed by N-C shows that the number of transferred electrons is not always four, in some cases; lower, uneven values are calculated [20–26]. These typical numbers of electron being between two and four thereby responsible for hydrogen peroxide (H_2O_2) formation through two electron transfer mechanism (Scheme S1) [20–24,27–30]. The H_2O_2 can oxidise N-C and makes N-C become very hydrophilic, and finally causes the porous N-C electrode water-flooded, thus interrupt oxygen transport to the active sites. Hence, the presence of hydrogen peroxide in N-C based porous electrodes not only damages the porous structure but also shortens the lifetime of the electrodes made of the N-C catalysts [19,27,28]. Therefore, to design a catalyst that can accelerate O_2 reduction to H_2O via the $4e^-$ pathway but inhibit O_2 reduction to H_2O_2 via the $2e^-$ pathway is highly required to substitute Pt/C.

Herein, we develop a $Mn_xO_y/N-C$ hybrid catalyst that can address both the activity and durability issues caused by the high productivity of H_2O_2 in N-C catalysis of ORR. In this perspective, zeolitic imidazole framework (ZIF-8) polyhedrons were selected as

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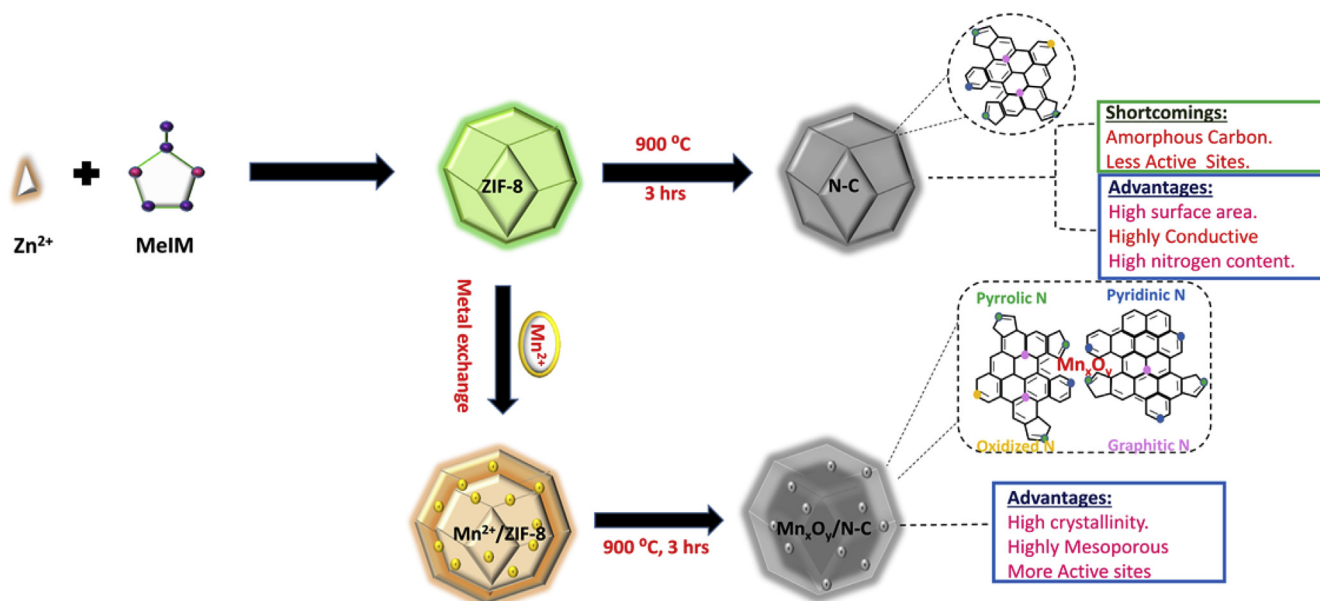
a perfect platform to synergistically immobilize the Mn^{2+} ions in the structures of ZIF-8 through Mn-N coordination with imidazole (Scheme 1) via post-synthetic exchange (PSE) method [31]. At high temperature pyrolysis, Mn^{2+} and ZIF-8 can transform into Mn_xO_y (MnO_2/Mn_3O_4) and N-C respectively. The presence of Zn species leads to spatial isolation for Mn to suppress its sintering during pyrolysis. For such a hybrid $Mn_xO_y/N-C$ catalyst, the high ORR activity [32,33] and hydrogen peroxide disproportionation ability of Mn_xO_y can enhance the ORR activity and stability; preventing the N-C oxidation by H_2O_2 [34–38]. Furthermore, the high conductivity, high surface area and porous structures of N-C not only provide many active-sites for ORR but also facilitate the electron transportation. The resultant $Mn_xO_y/N-C$ catalyst show excellent ORR activity in alkaline media, superior stability (8000 cycles) and stronger methanol tolerance compared to those of Pt/C. To the best of our knowledge, this is the first report of such a hybrid $Mn_xO_y/N-C$ catalyst with excellent durability and methanol tolerance. Our findings highlight the importance of post-synthetic exchange strategy and intensity-dependent catalytic active-sites for controlling the electron transfer heterogeneity and production of H_2O_2 in N-C nanostructures, offering a radically different approach to the fabrication of non-precious electrocatalyst.

2. Results and discussion

The ZIF-8 polyhedrons with a uniform particle size of ~150 nm were prepared by a facile synthetic route in methanol at room temperature (Fig. 1a and synthesis details shown in the experimental section). Interestingly, post-synthetic cation exchange of the zinc ions in ZIF-8 polyhedrons by Mn(II) could be achieved by simply soaking ZIF-8 in a methanolic solution of $Mn(NO_3)_2$ (Fig. 1b). The $Mn^{2+}/ZIF-8$ was prepared deliberately as a self-sacrificing template and a precursor to synthesize $Mn_xO_y/N-C$, as illustrated in Scheme 1. The SEM-EDX analysis showed that ~13% of Zn(II) centres has been successfully exchanged by Mn(II) in ZIF-8 (Mn:Zn/3:1) (Fig. S1). The XRD (Fig. S2 a) and BET (Fig. S3 a,b) results before and after Mn(II) exchange confirmed that the partial exchange of Zn(II) by Mn(II) in ZIF-8, did not affect the crystal structure and the BET surface area value of ZIF-8. The as-prepared $Mn^{2+}/ZIF-8$

precursors were further annealed at $900^\circ C$ under N_2 atmosphere (experimental section) to transform $Mn^{2+}/ZIF-8$ into $Mn_xO_y/N-C-x$ ($x = 1,3,5$ the molar ratio of Mn to Zn). As shown in Fig. 1 c, the as-prepared $Mn_xO_y/N-C-3$ after thermal treatments well inherited the overall polyhedral morphology but the surface of N-C underwent slight shrinkage and became concave, (Fig. 1d). As observed in the magnified SEM image, many white dots were appeared on $Mn_xO_y/N-C-3$ surface. It was very likely that Mn_xO_y species were captured at N-C surface during the pyrolysis. The high-resolution TEM (HR-TEM) images revealed the d-spacing of 0.272 nm and 0.307 nm (Fig. 1f) for adjacent lattice fringes matched well with that of the (103) and (112) planes of (hausmannite) Mn_3O_4 nanoparticle, suggesting that the Mn^{2+} has been successfully transformed into Mn_xO_y ($MnO_2 + Mn_3O_4$) [39]. The formation of the Mn_xO_y was also confirmed by powder X-ray diffraction (XRD). As shown in figure S2b, $Mn_xO_y/N-C-3$ exhibited the characteristic peaks of MnO_2 and Mn_3O_4 (Mn_xO_y) diffraction indexed faces (112), (103), (211), (220), (105) and graphitic carbon diffraction index (222), which confirms the synthesis of $Mn_xO_y/N-C-3$ with multi sorts of Mn valence. As compared to the reference sample (N-C) (Fig. S2 c), the relatively same intensity ratio (1.192) of the I_D/I_G for $Mn_xO_y/N-C-3$ in Raman spectra with additional Mn–O band (650 cm^{-1}) further confirmed its high degree of graphitization, which is favorable for improving the electrical conductivity for ORR [39].

The porous nature of $Mn_xO_y/N-C-3$ was further carried out by N_2 adsorption–desorption experiment. The Brunauer–Emmett–Teller analysis (Fig. S3 d) demonstrated that the $Mn_xO_y/N-C-3$ showed a high surface area of $1497\text{ m}^2\text{ g}^{-1}$, which was almost equal to that of N-C ($1504\text{ m}^2\text{ g}^{-1}$, Fig. S3 c). This result indicated that Mn_xO_y NPs did not affect the entire surface area. The nitrogen adsorption-desorption isotherms reveal the existence of mesopores with relative pressures (P/P_0) from 0.45 to 1.0, having distinct hysteresis loop of type-IV (Fig. S3 d). The corresponding pore-size distribution analysis of $Mn_xO_y/N-C-3$ (Fig. S3 d inset) clearly revealed the existence of a great quantity of mesopores. The diameter of most pores fell in a range from 2.0 to 10.5 nm, which should be large enough for free diffusion of oxygen molecule with a kinetic diameter of 0.346 nm [40]. Hence, the ORR process became more facilitated due to the faster oxygen adsorption and molecular transport



Scheme 1. Synthetic Illustration of $Mn_xO_y/N-C$ Electrocatalyst.

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