Encapsulated MnO in N-doping carbon nanofibers as efficient ORR electrocatalysts

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ABSTRACT Development of cheap, abundant and noble-metal-free materials as high efficient oxygen reduction electrocatalysts is crucial for future energy storage system. Here, one-dimensional (1D) MnO N-doped carbon nanofibers (MnO-NCNFs) were successfully developed by electrospinning combined with high temperature pyrolysis. The MnO-NCNFs exhibit promising electrochemical performance, methanol tolerance, and durability in alkaline medium. The outstanding electrocatalytic activity is mainly attributed to several issues. First of all, the uniform 1D fiber structure and the conductive network could facilitate the electron transport. Besides, the introduction of Mn into the precursor can catalyze the transformation of amorphous carbon to graphite carbon, while the improved graphitization means better conductivity, beneficial for the enhancement of catalytic activity for oxygen reduction reaction (ORR). Furthermore, the porous structure and high surface area can effectively decrease the mass transport resistance and increase the exposed ORR active sites, thus improve utilization efficiency and raise the quantity of exposed ORR active sites. The synergistic effect of MnO and NCNFs matrix, which enhances charge transfer, adsorbent transport, and delivers efficiency in the electrolyte solution, ensures the high ORR performance of MnO-NCNFs.

Keywords: electrospinning, MnO, N-doping carbon nanofibers, graphitization, oxygen reduction electrocatalysts

INTRODUCTION

The development of catalysts for oxygen reduction reaction (ORR) is one of the major challenges in energy conversion and storage systems such as metal-air batteries and fuel cells [1–4]. However, the multistep electron

transfer of ORR leads to sluggish kinetics and a large overpotential, which is related to O₂ adsorption on the electrode surface and the O–O bond cleavage [5–7]. Pt-based materials are effective electrocatalysts, which can promote the reaction and reduce the overpotential through a one-step four electron transfer process [8–12]. The high cost of Pt-based materials hinders the applications in broad commercialization [13–15]. Another issue is that the Pt-based electrocatalysts are vulnerable to the fuel crossover effect and poisoning by the adsorption of reaction intermediates, which restricts their tolerance performance [16,17]. Consequently, an amount of alternative non-precious catalysts have been explored to facilitate the ORR performance and replace Pt-based materials [18,19].

Nowadays, transition metal oxides, metal nitrogen carbon compounds, and metal macrocyclic compounds are considered to have good performances for ORR catalytic activity in alkaline solutions [20–22]. Among the non-precious metal alternatives, manganese oxides have received tremendous attentions owing to their low cost and nontoxicity, high elemental abundance, and appreciable ORR catalytic activity, when combined with a conductive support such as one dimensional (1D) carbon nanotubes, 2D graphene or 3D carbon frameworks [23–26]. As well known the decomposition of hydrogen peroxide formed during the electrochemical reduction of oxygen could be accelerated by manganese oxides [27,28]. However, manganese oxides decompose at low potential when they are directly exposed to harsh alkaline condition [29]. Besides, the poor electrical conductivity of manganese oxides further hinders their ORR perfor-

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mance [30–32]. Therefore, improvement of electrical conductivity and protection from corrosion is essential to manganese oxides during the ORR process [32–34]. Besides, the synergistic effect between manganese oxides and carbon matrix can enhance the charge transfer, adsorbent transport, which has attracted tremendous attentions to explore the superior ORR performance based on manganese based materials [35].

Encapsulating manganese oxide in few layer carbons may be an attractive way to overcome of poor corrosion tolerance and enhance the electrical conductivity of the carbonaceous materials. As a conventional precursor for electrospinning, polyacrylonitrile (PAN) could be graphitized during heating treatment, which renders it a potential candidate to prepare graphitic carbon encapsulating manganese oxide. In this study, we demonstrate the fabrication of manganese oxide encapsulated in graphitic carbon nanofibers by electrospinning PAN and polyvinyl pyrrolidone (PVP) precursors combined with high temperature pyrolysis. The obtained nanofibers possess typical mesoporous structure, which is attributed to the pyrolysis of organics and gas release at high temperature. The fibers exhibit promising electrochemical performance, methanol tolerance, and durability in alkaline medium.

EXPERIMENT SECTION

Synthesis of MnO-based nanofibers

All the chemicals were directly used without further purification. In a typical process, 0.8 g of manganese acetylacetonate, 0.4 g of PAN ($M_w \sim 150,000$), and 0.4 g of PVP ($M_w \sim 1,300,000$) were added into 10 mL dimethylformamide (DMF) and the resulting solution was stirred vigorously for 10 h at 70°C with water bath. Then, the as-prepared solution was placed in a 20 mL syringe with a stainless steel needle (22G). The feed rate of the mixture solution maintained at 1.5 mL h⁻¹. A rotating drum wrapped by aluminum foil was used as the collector. The applied voltage and the distance were varied between 0–20 kV and 0–15 cm, respectively. In order to obtain MnO-based carbon fibers, the as-spun fibers were heated from room temperature to 280°C for 2 h at a heating rate of 5°C min⁻¹. Then, the as-stabilized fibers were heated to 800°C for 2 h at a rate of 1°C min⁻¹ under an argon atmosphere. As a reference, MnO-NCNFs without PVP were prepared by the same procedure with equal weight of PAN in the precursors. Moreover, the NCNFs were obtained with the same procedure without the addition of manganese acetylacetonate.

Catalyst characterization

Field emission scanning electron microscopy (FESEM, JEOL 7001F) and high-resolution transmission electron microscopy (JEOL, JEM-2010F at 200 kV) were performed to characterize the morphologies of the prepared materials. X-ray diffraction (XRD) pattern was recorded in a Bruker-AXS Micro-diffractometer (D8 Advance X-ray diffractometer, Cu K α , $\lambda = 1.5046$ Å, 40 kV and 40 mA) from 10° to 80° to investigate the crystalline structure. Graphitized degree of these samples was also detected by Raman spectroscopy using Jobin-Yvon T6400 confocal Raman spectrometer with 532 nm diode laser excitation on 1800-line grating. Nitrogen adsorption/desorption isotherms were measured on a Micromeritics, ASAP2020 gas sorption analyzer at 77 K. All samples were firstly degassed at 200°C on a vacuum line following a standard protocol before measurement. The specific surface area was determined from N₂ adsorption isotherm by applying Brunauer-Emmett-Teller (BET) theory and the pore size distributions were obtained from the adsorption branch by means of Barrette-Joynere-Halenda (BJH). X-ray photoelectron spectroscopy (XPS) was investigated using a VG scientific ESCALAB 220iXL spectrometer with an Al K α ($h\nu = 1486.69$ eV) X-ray source. All binding energies were carefully aligned by reference to the C 1s peak (284.6 eV) arising from surface hydrocarbons or possible adventitious hydrocarbon.

Electrochemical measurement

All the electrochemical properties of samples were evaluated using a three-electrode system connected to electrochemical workstation (Biologic VMP3). The catalyst coated on glassy carbon (GC) rotating disk electrode (RDE) with a diameter of 5.0 mm was used as the working electrode, while Pt wire was the counter electrode and Hg/HgO was the reference electrode. The electrolyte was 0.1 mol L⁻¹ KOH solution. The GC electrode was polished carefully with 0.3 μ m alumina and then ultrasonically cleaned in absolute ethanol to remove the residues. The electrocatalyst ink was prepared by dispersing 10 mg catalysts into 1 mL 0.5% Nafion solution (a mixture of water and isopropanol with volume ratio of 3:1) by ultrasonication for 30 min. After that, 8 μ L of dispersion (the corresponding weight of the catalyst was 80 μ g) was loaded onto the GC electrode and dried under room temperature. As a reference, 20 wt.% commercial Pt/C and MnO-NCNFs catalysts without PVP modification were prepared with the same procedure. The electrochemical experiments were carried out in O₂-saturated 0.1 mol L⁻¹ KOH electrolyte for the ORR per-

formance. The potential range was cyclically scanned from 0.2 V to -0.8 V with a scan rate of 10 mV s^{-1} . The cyclic voltammetry (CV) results were obtained at ambient temperature after purging N_2 or O_2 gas for 30 min. RDE measurements were carried out at rotating rates from 400 to 2500 rpm at a scan rate of 10 mV s^{-1} .

RESULTS AND DISCUSSION

Electrocatalyst characterization

The MnO-based N-doping carbon nanofibers (MnO-NCNFs) were prepared by electrospinning technology combined with post-pyrolysis. As shown in Fig. S1 (Supplementary information), a single-needle apparatus was used, which was consisted of an aluminum foil collector, a syringe pump, and a high voltage power supply connected to a spinnerette. The as-electrospun nanofibers were stabilized at 280°C and then were carbonized at 800°C to form MnO-CNFs in argon atmosphere. The detailed structure information and morphology of the as-obtained nanofibers were investigated by FESEM. As illustrated in Fig. 1a, the as-electrospun sample consists of ultra-long nanofibers, the smooth surface with fairly uniform diameter ($\sim 500 \text{ nm}$). After annealing at 800°C for 2 h in argon atmosphere, the smooth, ultra-long nanofibers transform to short nanofibers with an amount of nanoparticles on the surface. The diameter of the MnO-NCNFs is 250–350 nm. The shrinkage of nanofibers is likely a result of the decomposition of precursors or carbonization during high temperature pyrolysis. Furthermore, the pyrolysis treatment also leads to the porosity throughout the nanofiber structure as exhibited in the typical TEM image (Fig. 1c). This unique pore structure is favorable for the penetration of electrolyte. Obviously, there are plenty of cubic particles on the surface of the nanofibers, rather than only appearing in the nanofibers, which provide more active sites, thus enhance the electrocatalytic activity. Moreover, the distributions of C, N, Mn, and O are clearly presented in the energy dispersive spectroscopy (EDS) elemental mappings (inset of Fig. 1c), which suggest that N and MnO are distributed in the carbon nanofibers. The interior structure of the cubic nanoparticles was further studied by HRTEM measurements. As shown in Fig. 1d, a typical MnO particle is covered by layers of graphitic shells. The lattice spacing of 0.36 nm originates from graphitic carbon. It confirms that the presence of transition metal Mn may catalyze the transformation of amorphous carbon to graphitized carbon. The lattice fringe of MnO is calculated to be 0.221 nm , which matches well with the spacing of

Figure 1 (a) SEM image of the as-electrospun nanofibers; (b) SEM image of the MnO-NCNFs; (c) TEM image of the MnO-NCNFs and corresponding EDS mappings (inset); (d) HRTEM image of the MnO nanoparticle covered by carbon shells.

(200) plane of cubic MnO. The selected-area electron diffraction (SAED) pattern (inset in Fig. 1d) demonstrates that the MnO nanoparticles are polycrystalline.

XRD measurements were investigated to confirm the crystalline structure of the MnO-NCNFs (Fig. 2a). The samples exhibit five peaks at 34.9° , 40.5° , 58.7° , 70.2° , and 73.8° , which are assigned to (111), (200), (220), (311), and (222), respectively, of cubic $Fm-3m$ MnO (JCPDF#07-0230). The XRD pattern of MnO-NCNFs shows a broad XRD peak at 26° , which is attributed to the (002) plane of graphitic carbon. It is in good agreement with the HRTEM results. The improved graphitization of carbon might be beneficial in enhancing electrical conductivity and effectively forming ORR-active N-C species. The spectrum shown in Fig. 2b also demonstrates the graphitic carbon resonances (G band) at about 1600 cm^{-1} and defect band (D band) at about 1350 cm^{-1} for MnO-NCNFs. These results suggest that, the MnO-based nanofibers have a graphitic structure with a certain amount of disorder carbon [21,36]. An estimation of the total order related to the carbon structures can be given by I_D/I_G . The I_D/I_G of MnO-NCNFs is 1.38, most likely due to the decomposition of PVP at high temperature treatment, which will be further discussed below. BET analyses were performed to study the specific surface area and pore size of the fibers. Fig. 2c exhibits the N_2 adsorption/desorption isotherm of MnO-NCNFs, from which the corresponding specific surface area is approximately $305 \text{ m}^2 \text{ g}^{-1}$. The distinct hysteresis loop at medium and high relative pressures regions (0.46–0.96) indicates the presence of mesopores. The pore size distribution (inset of Fig. 2c) suggests the formation of mesopores with the pore dia-

Figure 2 (a) XRD pattern; (b) Raman spectrum; (c) nitrogen adsorption/desorption isotherm and corresponding pore size distribution (inset); and (d) XPS survey spectrum of the MnO-NCNFs.

meter in the range of 2 to 15 nm. These mesopores are helpful for the ORR activity, which can efficiently decrease the mass transport resistance and increase the exposed ORR active sites.

The elemental composition of the MnO-NCNFs was determined by XPS measurements (Fig. 2d). One can see that the C 1s, N 1s, Mn 2p, and O 1s are clearly defined in the as-prepared catalysts, in accordance with the EDS mapping results. As shown in Fig. 3a, the Mn 2p core level spectrum displays two peaks at 653.5 and 641.7 eV, corresponding to the Mn $2p_{1/2}$ and Mn $2p_{3/2}$ spin orbit states of MnO, where the binding energy could be attributed to the characteristic of Mn^{2+} . Besides, a splitting satellite peak at 646.3 eV further indicates the existence of MnO [37]. The high-resolution spectrum for the O 1s region (Fig. 3b) shows three oxygen contributions, denoted as O1, O2, and O3, respectively. Specifically, the component O1 at 530.0 eV is typical of metal-oxygen bonds belonging to Mn–O bond [38]. The well-resolved O2 component at 532.1 eV corresponds to a higher number of defect sites with low oxygen coordination

usually observed in materials with small particles [39]. The component O3 can be attributed to multiplicity of physic- or chemi-sorbed water on or near the surface in accordance with the large surface area of as-electrospun MnO-NCNFs [29,39]. The C 1s spectrum of MnO-NCNFs illustrated in Fig. 3c shows large peaks at 284.8 eV, indicating that the nanofibers contain large quantities of sp^2 -hybridized carbon, followed by the next highest peak at 285.4 eV, revealing nitrogen-carbon binding types. Moreover, the resultant peaks at 286.5 and 288.8 eV belong to C–O and –COOH respectively, which are derived from partial surface oxidation [40]. As well known, nitrogen species play a key role for ORR activity that nitrogen has a higher electronegativity than carbon and its incorporation results in a relatively high positive charge density on neighbor carbon atoms where O_2 molecular is adsorbed in ORR [2,41]. The fitted high-resolution N 1s spectrum, as displayed in Fig. 3d, shows four types of N species, oxidized-N (403.5 eV), graphitic-N (401 eV), pyrrolic-N (400 eV), and pyridinic-N (398.4 eV) [42,43]. Moreover, the peak at a binding en-

Figure 3 High-resolution XPS scans of Mn 2p (a), O 1s (b), C 1s (c), and N 1s (d) in the MnO-NCNFs.

ergy of 398.4 eV should contain the contribution from nitrogen bound to the metal (Mn-N_x), owing to the small binding energies difference between the metal-N and pyridinic-N [43]. Generally, pyridinic-N and graphitic N are believed to present in active sites. These kinds of ORR active nitrogen species in MnO-NCNFs possess a high content, which may lead to high catalytic activity.

Electrochemical performance

The resulting MnO-NCNFs exhibit remarkable electrocatalytic activity for ORR. Fig. 4a depicts the RDE voltammograms for the MnO-NCNFs prepared with different PVP contents in precursor solution, as well as carbon nanofibers without the addition of Mn-based precursor. Obviously, the MnO-NCNFs with PVP modification exhibit the best ORR catalytic performance, which shows positive onset potential (+0.03 V vs. Hg/HgO) and high limiting current density (−4.79 mA cm^{−2}). Besides, the NCNFs without MnO or PVP exhibit poor electrocatalytic activity, which confirms the critical role of MnO incorporation and PVP modification. Herein, we choose MnO-NCNFs with PVP modification with the

best ORR catalytic performance for further investigation. To examine the electrocatalytic activity of the MnO-NCNFs, CV measurements were carried out for commercial Pt/C and MnO-NCNFs in oxygen- and nitrogen-saturated 0.1 mol L^{−1} KOH (Fig. 4b). The MnO-NCNFs display quasi-rectangular double-layer capacity current in nitrogen, and a well-defined ORR peak in oxygen with a peak potential of −0.118 V is observed, which is a little negative compared to that of Pt/C (−0.032 V). Additionally, a small oxidation peak appears at −0.043 V for MnO-NCNFs in alkaline solution, suggesting MnO incorporation in the carbon material plays the role of a mediator in the electron transfer processes during the ORR occurring in alkaline conditions.

To better characterize the ORR activities for MnO-NCNFs, linear sweep voltammetry (LSV) measurements at different rotation rates were further conducted with a RDE setup (Fig. 4c). The MnO-NCNFs show significantly enhanced current density with increased rotation rate (from 400 to 2500 rpm), which can be ascribed to the increased diffusion rate at high speeds. The corresponding Koutecky-Levich (K-L) plots at various potentials

Figure 4 (a) LSV curves of MnO-NCNFs with different PVP concentration in an oxygen-saturated 0.1 mol L⁻¹ KOH solution at a rotation speed of 1600 rpm; (b) CV curves of MnO-NCNFs and Pt/C catalysts in oxygen-saturated and nitrogen-saturated with a scan rate of 10 mV s⁻¹, respectively; (c) LSV curves of MnO-NCNFs with various rotation rates and corresponding K-L plot at different potentials (inset); (d) RRDE polarization of MnO-NCNFs at a rotating speed of 1600 rpm; (e) CV curves of MnO and Pt/C in oxygen-saturated 0.1 mol L⁻¹ KOH with and without 0.1 mol L⁻¹ CH₃OH; (f) chronoamperometric curves of MnO-NCNFs and Pt/C at -0.35 V (vs. Hg/HgO) in an O₂-saturated 0.1 mol L⁻¹ KOH solution. The rotation speed is 1600 rpm.

(inset of Fig. 3c) are obtained from LSVs and all plots show good linearity, which suggests first-order reaction kinetics with respect to the concentration of dissolved oxygen. The transferred electron numbers per oxygen molecule involved in an ORR process are determined by the K-L equation as follows [42,44]:

$$1/J = 1/J_k + 1/(B\omega^{1/2}), \quad (1)$$

$$B = 0.2nFC_0D_0^{2/3}\nu^{-1/6}, \quad (2)$$

$$J_k = nFkC_o, \quad (3)$$

here, J is the measured current density, J_k is the kinetic current densities, ω is the rotation speed, n is the trans-

ferred electron number, F is the Faraday constant, C_o is the saturated concentration of O_2 in the electrolyte, D_o is the diffusion coefficient of O_2 in the solution, ν is the kinetic viscosity of the electrolyte, and k is the electron-transfer rate constant. The number of electrons transferred is calculated to be 3.75 at all potentials investigated, demonstrating high selectivity towards overall 4 electron reduction mechanism occurring on the MnO-NCNFs. Moreover, the mass activity of MnO-NCNFs is 19.8 A g^{-1} at the peak potential ($-0.115 \text{ V vs. Hg/HgO}$), which is higher than that of MnO-NCNFs without PVP modification (9.5 A g^{-1}) and comparable to that of commercial Pt/C (21.5 A g^{-1}), further confirming the favorable kinetics and high intrinsic ORR activity of MnO-NCNFs.

In general, the 4e process corresponding to the complete reduction of oxygen into water is believed to be more efficient than the 2e process that produces H_2O_2 , additionally, H_2O_2 formed during the 2e process is poisonous to catalysts. To further validate the four-electron-transfer pathway of MnO-NCNFs, rotating-ring disc electrode (RRDE) measurements were performed to determine the four-electron selectivity. Fig. 4d depicts the ring and disk currents measured at 1600 rpm in $0.1 \text{ mol L}^{-1} \text{ KOH}$. The electron transfer number and the yield of H_2O_2 from RRDE are performed on the basis of the following equations [45]:

$$n = 4I_{\text{disk}} / (I_{\text{disk}} + I_{\text{ring}} / N), \quad (4)$$

$$H_2O_2\% = 200(I_{\text{ring}} / N) / (I_{\text{disk}} + I_{\text{ring}} / N), \quad (5)$$

where I_{disk} is the disk current, I_{ring} is the ring current, and N is the current collection efficiency of Pt ring electrode (37%). The number of electrons transferred is calculated to be about 3.73, which is in good agreement with the results from K-L analysis. Accordingly, the H_2O_2 yield of MnO-NCNFs is about 13.4%, indicating good selectivity toward the 4e ORR to generate H_2O .

Besides catalytic activity, the methanol tolerance and the durability of the electrocatalyst are regarded as the most important issues for ORR catalysts. In practice, the fuel molecules such as methanol in the anode occasionally permeate through the polymer membrane to cathode, which seriously affects the whole cell performance. Therefore, to evaluate the crossover effect, the CV scanning for MnO-NCNFs was measured in O_2 -saturated $0.1 \text{ mol L}^{-1} \text{ KOH}$ with 0.1 mol L^{-1} methanol. As shown in Fig. 4e, almost no change of CV curves can be observed, while commercial Pt/C displays typical crossover, because the electro-oxidation of methanol is much easier than the reduction of oxygen. Furthermore, the long-term stability

of MnO-NCNFs and commercial Pt/C catalysts are investigated at -0.35 V for 10,000 s in O_2 -saturated $0.1 \text{ mol L}^{-1} \text{ KOH}$ solution with a rotation speed of 1600 rpm. As displayed in Fig. 4f, about 92.85% of the original current density is retained for MnO-NCNFs, whereas the Pt/C shows a much higher current loss of $\sim 12.66\%$, demonstrating the superior stability of MnO-NCNFs. All these results indicate that the MnO-NCNFs exhibit strong tolerance toward methanol and high durability, which makes it a potential electrocatalyst for ORR.

Mechanism on electrocatalyst activity

According to the above results, we believe that the excellent catalytic performance of the MnO-NCNFs may be attributed to several aspects as follows. First, the uniform 1D fiber structure and the conductive network could facilitate the electron transport [45]. Second, the introduction of Mn in precursor can catalyze the transformation of amorphous carbon to graphitic carbon, while the improved degree of graphitization means better conductivity, which might be beneficial for the enhancement of catalytic activity for ORR [1]. Third, the porous structure and high surface area can effectively decrease the mass transport resistance and increase the exposed ORR active sites, thus improving utilization efficiency and raising quantity of exposed ORR active sites [5,43]. The last but not the least, the synergistic effect between MnO and NCNFs carbon matrix also plays an important role in the high ORR catalytic performance, which enhances the charge transfer, absorbents transport during the ORR process [32,34,35].

Compared to MnO-NCNFs without PVP introduction, the MnO-NCNFs exhibit superior ORR activity (Fig. 4a, Fig. S2, and Table S1), which means that PVP modification plays an important role in the improvement of ORR activity. As shown in Fig. S2, the MnO-NCNFs without PVP modification display lower limit currents and half-wave potential at various rotation speeds than that of MnO-NCNFs. To gain insight into the ORR activity enhancement of MnO-NCNFs, HRTEM, Raman, BET, and XPS were conducted to analyze the content and chemical state of the MnO-NCNFs without PVP modification (Fig. S3). Without PVP, the obtained fibers display more graphitic structure with uniformly stacked graphite-like planes (inset of Fig. S3a). The Raman analysis confirms that the I_D/I_G is 0.79, which represents the higher degree of graphitization for MnO-NCNFs without PVP modification. However, the MnO-NCNFs with randomly stacked graphite-like planes (Fig. 1d) that abundant edges rather than the basal plane are exposed on the

surface of the fibers would be beneficial to enhance the electrocatalytic properties. This random graphitic structure could be attributed the decomposition of PVP at lower temperature during pyrolysis process. As shown in Fig. S3b, the BET surface area of the MnO-NCNFs without PVP is only $156 \text{ m}^2 \text{ g}^{-1}$, which is lower than that of MnO-NCNFs ($305 \text{ m}^2 \text{ g}^{-1}$). The higher surface area means more exposed active sites, which could facilitate the catalytic performance dramatically. The high resolution C 1s spectrum of MnO-NCNFs without PVP can be de-convolved into three bands, where the dominant C=C at 284.5 eV further demonstrates the higher graphitic degree. The fitted N 1s spectra of MnO-NCNFs without PVP modification are shown in Fig. S3d, which also displays four types of N species, pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N. It should be noting that the content of N species in the MnO-NCNFs without PVP modification is higher than that of MnO-NCNFs (Fig. S4), which is mainly due to the reduction of PAN content in the precursor during preparation process. However, the relative contents of pyrrolic-N and oxidized-N in the MnO-NCNFs without PVP modification are higher than that of MnO-NCNFs (Figs. 3d and S4), which is not beneficial to the catalytic activity on ORR process. The relative high graphitic-N and pyridinic-N contents in MnO-NCNFs are likely play dominant role in the determination of ORR activity.

CONCLUSIONS

In summary, MnO-NCNFs were synthesized *via* electrospinning with PVP and PAN modification and pyrolysis, which were employed as ORR catalysts in alkaline solution. PAN is employed to fabricate the nanofibers and provides carbon and nitrogen sources during pyrolysis. The synergistic effect between Mn species and carbon matrix can enhance the charge transfer, absorbents transport, and further improve the catalytic activity. Furthermore, the PVP modification plays a conspicuous role in improving the electrochemical performance of catalysts. The obtained MnO-NCNFs exhibit prominent ORR activity mainly attributed to their chemical composition and structure with high specific surface area, 1D framework structure, as well as the synergistic effect between Mn species and carbon matrix. The preparation of MnO-NCNFs with high ORR catalytic activity provides a unique synthetic approach to fabricate 1D non-noble catalyst by electrospinning.

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- 1 Aijaz A, Masa J, Rösler C, *et al.* Co@Co₃O₄ encapsulated in carbon nanotube-grafted nitrogen-doped carbon polyhedra as an advanced bifunctional oxygen electrode. *Angew Chem Int Ed*, 2016, 55: 4087–4091
- 2 Liu R, Zhang H, Liu S, *et al.* Shrimp-shell derived carbon nanodots as carbon and nitrogen sources to fabricate three-dimensional N-doped porous carbon electrocatalysts for the oxygen reduction reaction. *Phys Chem Chem Phys*, 2016, 18: 4095–4101
- 3 Wu G, More KL, Johnston CM, *et al.* High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt. *Science*, 2011, 332: 443–447
- 4 Koh K, Meng Y, Huang X, *et al.* N- and O-doped mesoporous carbons derived from rice grains: efficient metal-free electrocatalysts for hydrazine oxidation. *Chem Commun*, 2016, 52: 13588–13591
- 5 Meng Y, Voiry D, Goswami A, *et al.* N-, O-, and S-tridoped nanoporous carbons as selective catalysts for oxygen reduction and alcohol oxidation reactions. *J Am Chem Soc*, 2014, 136: 13554–13557
- 6 Chen Z, Zhao H, Zhang J, *et al.* IrNi nanoparticle-decorated flower-shaped NiCo₂O₄ nanostructures: controllable synthesis and enhanced electrochemical activity for oxygen evolution reaction. *Sci China Mater*, 2016, 60: 119–130
- 7 Lu S, Zhuang Z. Electrocatalysts for hydrogen oxidation and evolution reactions. *Sci China Mater*, 2016, 59: 217–238
- 8 Bu L, Zhang N, Guo S, *et al.* Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis. *Science*, 2016, 354: 1410–1414
- 9 Shen K, Chen X, Chen J, *et al.* Development of MOF-derived carbon-based nanomaterials for efficient catalysis. *ACS Catal*, 2016, 6: 5887–5903
- 10 Huang H, Du C, Wu S, *et al.* Thermolytical entrapment of ultra-small MoC nanoparticles into 3D frameworks of nitrogen-rich graphene for efficient oxygen reduction. *J Phys Chem C*, 2016, 120: 15707–15713
- 11 Meng Y, Zou X, Huang X, *et al.* Polypyrrole-derived nitrogen and oxygen Co-doped mesoporous carbons as efficient metal-free electrocatalyst for hydrazine oxidation. *Adv Mater*, 2014, 26: 6510–6516
- 12 Fu QQ, Li HH, Ma SY, *et al.* A mixed-solvent route to unique PtAuCu ternary nanotubes templated from Cu nanowires as efficient dual electrocatalysts. *Sci China Mater*, 2016, 59: 112–121
- 13 Yin P, Yao T, Wu Y, *et al.* Single cobalt atoms with precise N-coordination as superior oxygen reduction reaction catalysts. *Angew Chem Int Ed*, 2016, 55: 10800–10805
- 14 Xia BY, Yan Y, Li N, *et al.* A metal-organic framework-derived bifunctional oxygen electrocatalyst. *Nat Energy*, 2016, 1: 15006
- 15 Wei J, Liang Y, Hu Y, *et al.* Hydrothermal synthesis of metal-polyphenol coordination crystals and their derived metal/N-doped carbon composites for oxygen electrocatalysis. *Angew Chem Int Ed*, 2016, 55: 12470–12474
- 16 Zhou T, Du Y, Yin S, *et al.* Nitrogen-doped cobalt phosphate@nanocarbon hybrids for efficient electrocatalytic oxygen reduction. *Energy Environ Sci*, 2016, 9: 2563–2570
- 17 Wang MQ, Ye C, Bao SJ, *et al.* Platanus hispanica-inspired design of Co-carbon nanotube frameworks through chemical vapor deposition: a highly integrated hierarchical electrocatalyst for oxygen reduction reactions. *Chem Commun*, 2016, 52: 12992–12995
- 18 Wu ZY, Xu XX, Hu BC, *et al.* Iron carbide nanoparticles encapsulated in mesoporous Fe-N-doped carbon nanofibers for ef-

- cient electrocatalysis. *Angew Chem Int Ed*, 2015, 54: 8179–8183
- 19 Singh KP, Bae EJ, Yu JS. Fe-P: a new class of electroactive catalyst for oxygen reduction reaction. *J Am Chem Soc*, 2015, 137: 3165–3168
- 20 Li W, Yu A, Higgins DC, *et al.* Biologically inspired highly durable iron phthalocyanine catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells. *J Am Chem Soc*, 2010, 132: 17056–17058
- 21 Wang S, Cui Z, Cao M. A template-free method for preparation of cobalt nanoparticles embedded in N-doped carbon nanofibers with a hierarchical pore structure for oxygen reduction. *Chem Eur J*, 2015, 21: 2165–2172
- 22 Tao L, Wang Q, Dou S, *et al.* Edge-rich and dopant-free graphene as a highly efficient metal-free electrocatalyst for the oxygen reduction reaction. *Chem Commun*, 2016, 52: 2764–2767
- 23 Li PC, Hu CC, You TH, *et al.* Development and characterization of bi-functional air electrodes for rechargeable zinc-air batteries: effects of carbons. *Carbon*, 2017, 111: 813–821
- 24 Delmondo L, Salvador GP, Muñoz-Tabares JA, *et al.* Nanostructured Mn_2O_3 for oxygen reduction reaction (ORR) catalysts. *Appl Surf Sci*, 2016, 388: 631–639
- 25 Sumboja A, Ge X, Zheng G, *et al.* Durable rechargeable zinc-air batteries with neutral electrolyte and manganese oxide catalyst. *J Power Sources*, 2016, 332: 330–336
- 26 Zhang F, Shi Y, Xue T, *et al.* *In situ* electrochemically converting $\text{Fe}_2\text{O}_3\text{-Ni(OH)}_2$ to $\text{NiFe}_2\text{O}_4\text{-NiOOH}$: a highly efficient electrocatalyst towards water oxidation. *Sci China Mater*, 2017, 60: 324–334
- 27 Calegario ML, Lima FHB, Ticianelli EA. Oxygen reduction reaction on nanosized manganese oxide particles dispersed on carbon in alkaline solutions. *J Power Sources*, 2006, 158: 735–739
- 28 Mao L. Mechanistic study of the reduction of oxygen in air electrode with manganese oxides as electrocatalysts. *Electrochim Acta*, 2003, 48: 1015–1021
- 29 Cheng H, Xu K, Xing L, *et al.* Manganous oxide nanoparticles encapsulated in few-layer carbon as an efficient electrocatalyst for oxygen reduction in alkaline media. *J Mater Chem A*, 2016, 4: 11775–11781
- 30 Yuan H, He Z. Graphene-modified electrodes for enhancing the performance of microbial fuel cells. *Nanoscale*, 2015, 7: 7022–7029
- 31 Chen G, Sunarso J, Zhu Y, *et al.* Highly active carbon/ $\alpha\text{-MnO}_2$ hybrid oxygen reduction reaction electrocatalysts. *ChemElectroChem*, 2016, 3: 1760–1767
- 32 Cao S, Han N, Han J, *et al.* Mesoporous hybrid shells of carbonized polyaniline/ Mn_2O_3 as non-precious efficient oxygen reduction reaction catalyst. *ACS Appl Mater Interfaces*, 2016, 8: 6040–6050
- 33 Aricò AS, Bruce P, Scrosati B, *et al.* Nanostructured materials for advanced energy conversion and storage devices. *Nat Mater*, 2005, 4: 366–377
- 34 Tang Q, Jiang L, Liu J, *et al.* Effect of surface manganese valence of manganese oxides on the activity of the oxygen reduction reaction in alkaline media. *ACS Catal*, 2014, 4: 457–463
- 35 Chen R, Yan J, Liu Y, *et al.* Three-dimensional nitrogen-doped graphene/ MnO nanoparticle hybrids as a high-performance catalyst for oxygen reduction reaction. *J Phys Chem C*, 2015, 119: 8032–8037
- 36 Dou S, Tao L, Huo J, *et al.* Etched and doped Co_9S_8 /graphene hybrid for oxygen electrocatalysis. *Energy Environ Sci*, 2016, 9: 1320–1326
- 37 Zhao X, Du Y, Jin L, *et al.* Membranes of MnO beading in carbon nanofibers as flexible anodes for high-performance lithium-ion batteries. *Sci Rep*, 2015, 5: 14146
- 38 Liu B, Hu X, Xu H, *et al.* Encapsulation of MnO nanocrystals in electrospun carbon nanofibers as high-performance anode materials for lithium-ion batteries. *Sci Rep*, 2014, 4: 4229
- 39 Yuan C, Li J, Hou L, *et al.* Ultrathin Mesoporous NiCo_2O_4 nanosheets supported on Ni foam as advanced electrodes for supercapacitors. *Adv Funct Mater*, 2012, 22: 4592–4597
- 40 Wu J, Park HW, Yu A, *et al.* Facile synthesis and evaluation of nanofibrous iron-carbon based non-precious oxygen reduction reaction catalysts for Li-O_2 battery applications. *J Phys Chem C*, 2012, 116: 9427–9432
- 41 Wu TX, Wang GZ, Zhang X, *et al.* Transforming chitosan into N-doped graphitic carbon electrocatalysts. *Chem Commun*, 2015, 51: 1334–1337
- 42 Xie S, Huang S, Wei W, *et al.* Chitosan waste-derived Co and N Co-doped carbon electrocatalyst for efficient oxygen reduction reaction. *ChemElectroChem*, 2015, 2: 1806–1812
- 43 Lin L, Zhu Q, Xu AW. Noble-metal-free Fe-N/C catalyst for highly efficient oxygen reduction reaction under both alkaline and acidic conditions. *J Am Chem Soc*, 2014, 136: 11027–11033
- 44 Yin J, Qiu Y, Yu J. Onion-like graphitic nanoshell structured Fe-N/C nanofibers derived from electrospinning for oxygen reduction reaction in acid media. *Electrochem Commun*, 2013, 30: 1–4
- 45 Zamani P, Higgins D, Hassan F, *et al.* Electrospun iron-polyaniline-polyacrylonitrile derived nanofibers as non-precious oxygen reduction reaction catalysts for PEM fuel cells. *Electrochim Acta*, 2014, 139: 111–116

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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氮掺杂碳纤维包覆一氧化锰作为高效氧还原电催化剂

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摘要 廉价、储量丰富的非贵金属材料作为高效氧还原电催化剂是未来能量存储系统实际应用的关键。基于此, 我们通过静电纺丝法并结合相应热处理制备了一维氮掺杂碳纳米纤维包覆一氧化锰(MnO-NCNFs)。该材料在碱性体系中表现出良好的电化学性能, 耐甲醇腐蚀性和稳定性。其优异的电催化活性主要归结于以下几点: (1) 均一的一维纤维结构和导电网络能够促进反应过程中快速的电子转移; (2) 过渡金属锰的引入能够促进无定型碳向石墨碳的转变, 同时石墨化程度的提高意味着更好的导电性, 有利于氧还原活性的提高; (3) 多孔结构和高比表面积能够有效降低传质阻力并提高暴露的氧还原活性位点数量, 进而提高物质利用效率。