Ultrasonic synthesis of Mn-Ni-Fe tri-metallic oxide anchored on polymer-grafted conductive carbon for rechargeable zinc-air battery

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As a promising electrochemical energy device, a rechargeable zinc-air battery (RZAB) requires cost-effective cathode catalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Some earth-abundant transition metal oxides have certain levels of bi-functional ORR/OER catalytic activities yet low electronic conductivities. The addition of high-electronic-conductivity material such as carbon black could result in another problem because there is low compatibility between metal oxide and carbon. In this work, polymer chains are ultrasonically prepared to act as binders to anchor metal-oxide active sites to porous domains of carbon black. The monomer N-isopropyl acrylamide is polymerized under ultrasonication instead of using conventional radical initiators which are dangerous and harmful. Reactive free radicals produced by ultrasonic irradiation can also help to form the Mn-Ni-Fe tri-metallic oxide. Thus, aided by the amide-type polymer as an adhesive, the tri-metallic oxide anchored on polymer-grafted carbon black prepared by ultrasonication possess a large number of metal-oxide active sites and hierarchical pores, contributing substantially to the enhanced ORR/OER electrocatalytic performance in the RZABs. Accordingly, this work provides interesting insight into the effective combination of inherently incompatible components for the fabrication of composite materials from an ultrasonic standpoint.

1. Introduction

Over the past decades, the global environment has been rapidly deteriorated due to the increasing use of fossil fuels [1]. In the current age, it is highly anticipated to develop green energy devices. Rechargeable metal-air batteries are the environmental-friendly energy conversion devices with high performance and practical feasibility [2–4]. Among them, the rechargeable zinc-air battery (RZAB) is particularly attractive [5], with several advantages such as intrinsic safety, high specific capacity, and high theoretical energy (1086 Wh kg⁻¹, including O₂) [6,7]. The air–cathode of RZAB needs a bi-functional catalyst having activities for both using O₂ (when discharging) and producing O₂ (when charging) efficiently, that is, oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [8]. Commercially available catalysts are usually platinum on carbon (Pt/C) for ORR and iridium dioxide or ruthenium dioxide for OER, which all involve noble metals and exhibit mono-functional catalytic performance [4,5]. Such disadvantages limit the wide use of RZAB.

As alternatives to noble metallic elements, first-row transition metal oxides and their derivatives are considered as good ORR/OER catalysts [9–11]. However, simple metal oxides often exhibit relatively low electrical conductivity [12] and small specific surface area (<400 m² g⁻¹) [13]. Hence metal oxides should be integrated with conductive materials for the improved performance. It is known that conductive carbon black (CB) is commercially mature activated carbon having high electrical conductivity and plentiful pores, which provide large surface areas for chemical modifications [12,14,15]. In this sense, the combination of conductive carbon with metal oxides can enhance the ORR/OER electrochemical performance [16].

In general terms, nevertheless, the degree of combination of metal oxides and carbon is relatively low, leading to the easily leaching of metal oxides from carbon and the resultant unstable performance. That being so, it is reasonable to look for a binder that helps to anchor metal oxides to the carbon surface, and such binder can be polymers. In this scheme, monomers are first anchored within a porous carbon matrix followed by the polymerization of them, forming the polymer-grafted carbon, and then heteroatom groups in polymer chains are able to act as ligand donors to bind metallic ions in a coordination mode, making...
possible the subsequent formation of metal-oxide active sites anchored on polymer-grafted carbon.

Unfortunately, a substantial number of polymers are prepared using radical initiators that include organic/inorganic peroxide and azo compounds, which are either dangerously explosive or toxic to human health and the environment [17]. On the other hand, acoustic cavitation generated by ultrasonic irradiation can produce numerous micro-bubbles and cause violent collisions of particles, thereby leading to high temperatures locally (>5000 K) and a large number of free radicals [18]. It has been demonstrated that free radicals produced by ultrasound are able to induce the polymerization of monomers [19–21]. Moreover, the ultrasonic environments are favourable for the formation of metal oxides without using extra chemical reagents or apparatus [22,23]. From the green chemistry perspective, ultrasonication is an environmentally friendly and highly energy efficient method for the preparation of polymers and metal oxides.

In this work we introduce the convenient route to the effective combination of earth-abundant tri-metallic oxide and conductive CB using an amide-type polymer induced by ultrasonic cavitation. The monomer Ni-isopropyl acrylamide (NIPAm) undergoes the polymerization using ultrasonication instead of any radical initiator. The polymer chains formed are grafted on the surface of CB, and the amide groups in the polymer can bind three types of metal ions (i.e., Mn$^{2+}$, Ni$^{2+}$ and Fe$^{2+}$) through the efficient coordination, resulting in the production of metal oxide by the second round of ultrasonic irradiation. Thanks to the amide-type polymer as a binder, the Mn-Ni-Fe tri-metallic oxide anchored on polymer-grafted CB has both the appropriate amount of metal-oxide active sites and a sufficient number of hierarchical pores, leading to the enhanced ORR/OER electrocatalytic performance compared to its ultrasonication-free counterpart and commercial catalysts, which proves to be suited as a redox bi-functional catalyst in the RZAB. Accordingly, this work provides appealing insight into the effective combination of the two inherently incompatible parts for the construction of composite materials.

2. Experimental section

2.1. Materials and instruments

N-isopropyl acrylamide (NIPAm, 98%, Adamas-beta), ferrous sulfate heptahydrate (FeSO$_4$•7H$_2$O, Adamas-beta), manganese (II) chloride (MnCl$_2$, 99%, Adamas-beta), nickel (II) chloride hexahydrate (NiCl$_2$•6H$_2$O, 99%, Adamas-beta), isopropyl alcohol (C$_3$H$_6$O, 99.7%, Sinopharm Chemical), Ketjenblack® CB (EC300J conductive carbon black, Japan Lion), Nafion® perfluorinated resin solution (5 wt%, Sigma-Aldrich), α-Al$_2$O$_3$ with diameter of 50 mm (99%, Tianjin Aida), platinum on carbon (Pt/C, 10 wt%, Sigma-Aldrich), ruthenium oxide (RuO$_2$, 99.95%, Adamas-beta), potassium hydroxide (KOH, >90%, General reagent), zinc acetate (Zn(ac)$_2$, 99.5%, Adamas-beta), high-purity nitrogen and oxygen gases (99.999%, Xuzhou Special Gases), and ultrapure water (18.2 MΩ cm, Sartorius arium).

Field-emission scanning electron microscopy (FESEM) images were acquired using Quanta FEG 250. Transmission electron microscopy (TEM) as well as high-resolution TEM (HRTEM) images were obtained on FEI Tecnai TF30. Nitrogen adsorption–desorption isotherms were obtained by Quantachrome Autosorb iQ. Pore width distributions were gained based on the quenched solid density functional theory (DFT) model. X-ray diffraction (XRD) patterns were acquired by PANalytical X’Pert3 Powder using the Cu Kα radiation ($\lambda = 1.54178$ Å). X-ray photoelectron spectroscopy (XPS) measurements were conducted on Thermo Fisher ESCALAB 250Xi using the Al Kα radiation (1486.6 eV) and binding energies were calibrated according to the C 1 s peak (284.8 eV). An ultrasonic exfoliation instrument with six-sided distributed ultrasonic transducers (Scientz-CHF-5B, Ningbo Scientz) was used to intensify the dispersion of CB. An ultrasonic instrument equipped with a microwave generator (Scientz-IIDM, Ningbo Scientz) was employed to synthesize catalysts.

2.2. Catalyst synthesis

From the beginning, 0.5 g of CB was dispersed in 100 mL of ethanol in a 250 mL sealed beaker and ultrasonically treated using the ultrasonic exfoliation instrument for half an hour (20 kHz, 576 W). Then, 1.5 g of NIPAm was dissolved in 100 mL of ultrapure water, which was added to the black suspension of the dispersed CB. After that, the mixture was degassed by high-purity N$_2$ using a capillary glass-made gas inlet for 10 min at a flow rate of 50 scm. Further, the degassed mixture was transferred to a three-neck flask and placed in the ultrasound/micro-wave instrument. The ultrasonic horn was inserted 5 cm below the liquid level through the centre neck of the three-neck flask. As for the other two necks, one was linked to a reflux condensation maintained at 0 ºC, and the other was sealed using a polytetrafluoroethylene (PTFE) cap. The mixture was then treated under a 500 W ultrasound for half an hour with the assistance of microwave (200 W) at the initial 500 s for rapid warming. Subsequently, 10 mL of 0.05 M NiCl$_2$, 10 mL of 0.05 M FeSO$_4$ and 10 mL of 0.05 M MnCl$_2$ solutions were added to the mixture, followed by the second round of ultrasonic irradiation for another half an hour (20 kHz, 500 W). Finally, the ultrasonically treated mixture was centrifuged and dried at 80 ºC overnight. The obtained material was denoted U-MnNiFe@NCB. To investigate the ultrasonic effect, a sample was prepared using stirring (at 80 ºC) to replace the ultrasonic treatments mentioned above, leaving the other conditions unchanged. This control sample was denoted MnNiFe@NCB.

2.3. Electrochemical measurements

Electrochemical tests were conducted using an electrochemical workstation (Iviumstat.h, Ivium Technologies) at 25 ºC. In a three-electrode configuration, a rotating disc electrode with glassy carbon surface (GC-RDE) connected with a rotator (AFM-ERCE, Pine Research) was employed to load a catalyst, acting as a working electrode. Additionally, a Ag/AgCl electrode (3.5 M KCl) connected to the main cell through a Luggin capillary was employed as a reference electrode, and a platinum foil was used as a counter electrode. All the potentials measured in this paper were converted to the reversible hydrogen electrode (RHE) based on the following equation: E(RHE) = E(Ag/AgCl) + 0.2046 + 0.059•pH. The catalyst ink was made by mixing 3.0 mg of the catalyst, 70 µL of isopropl alcohol, 170 µL of ultrapure water as well as 10 µL of 5 wt% Nafion® perfluorinated resin solution together under ultrasonication for half an hour to form a homogenized mixture. Meanwhile, the GC-RDE (6 mm in diameter for GC) was polished with α-Al$_2$O$_3$ and washed thoroughly with ultrapure water and ethanol. Afterwards, 8 µL of the catalyst ink was transferred onto the polished surface of GC-RDE using a pipette and dried naturally. The catalyst loading was 0.49 mg cm$^{-2}$. Regarding the inks of the commercial catalysts, 1 mg of 10 wt% Pt/C or 2 mg of RuO$_2$ was mixed with 10 µL of Nafion® perfluorinated resin solution, 170 µL of isopropyl alcohol and 70 µL of ultrapure water under ultrasonic irradiation for half an hour. The loadings of Pt/C or RuO$_2$ were 0.16 mg cm$^{-2}$ and 0.32 mg cm$^{-2}$, respectively.

Regarding ORR experiments, the gas (O$_2$ or N$_2$) with a flow rate of 80 scm was first fed into the electrolyte (0.1 M KOH) for half an hour and then through the headspace above the electrolyte solution during measurements. Cyclic voltammery (CV) measurements were undertaken to activate catalysts with a scan rate of 50 mV s$^{-1}$ for 50 cycles prior to electrocatalytic measurements. Linear sweep voltammery (LSV) experiments at different rotating rates (400–2025 rpm) with a scan rate of 10 mV s$^{-1}$ were conducted. As for LSV curves, the currents obtained in the N$_2$-saturated solution were subtracted from those in the O$_2$-saturated solution in order to eliminate strong capacitative currents from porous carbon. The Koutecky-Levich (K-L) equation shown below was employed to obtain the electron-transfer number [24]:

\[
\frac{i}{i_0} = \frac{1}{2} \left( \frac{1}{\alpha} + \frac{1}{\beta} \right)
\]
where $\omega$ is rotating rate (rpm), $j_k$ is kinetic current density (m Ach cm$^{-2}$), $j$ is total current density (m Ach cm$^{-2}$), and $B$ is the K-L slope, which can be expressed as [24, 25]:

\[
B = 0.2aF_{C_{0}}D_{0}^{2/3}v^{-1/6}
\]

where $F$ is the Faraday constant (96485 C mol$^{-1}$), $n$ is the electron-transfer number, $C_{0}$ is the saturated $O_2$ concentration ($1.2 \times 10^{-3}$ mol L$^{-1}$), $D_0$ is the diffusion coefficient of $O_2$ ($1.9 \times 10^{-5}$ cm$^{2}$ s$^{-1}$), and $v$ is the kinematic viscosity in 0.1 M KOH (0.01 cm$^{2}$ s$^{-1}$). For the OER measurements, the LSV curves were recorded with a scan rate of 10 mV s$^{-1}$ at a rotating rate of 1,600 rpm after the electrolyte (0.1 M KOH) was saturated with $N_2$ with a flow rate of 80 sccm. The $iR$-drop compensation was made to minimize the ohmic potential loss of electrodes due to the solution resistance.

2.4. RZAB measurements

Custom-made RZABs comprising air-cathodes and zinc-plate anodes were assembled, each with three poly(methyl methacrylate) (PMMA) plates. The air-cathode was made by pressing catalyst-loaded carbon paper, air-breathable water-proof layer (placed in the middle), and nickel foam at 10 MPa. The catalyst ink for the RZAB measurements was prepared by mixing 3 mg of U-MnNiFe@NCB, 70 $\mu$L of isopropyl alcohol, 140 $\mu$L of ultrapure water and 10 $\mu$L of 5 wt% Nafion® perfluorinated resin solution together under ultrasonication for half an hour. As for the Pt/C-RuO$_2$ catalyst, 1 mg of 10 wt% Pt/C and 2 mg of RuO$_2$ were mixed in 70 $\mu$L of ultrapure water, 170 $\mu$L of isopropyl alcohol and 10 $\mu$L of 5 wt % Nafion® perfluorinated resin solution under ultrasonication for half an hour. For either of these catalysts, the catalyst area on the electrode is 1.77 cm$^2$, and the mass loading of catalyst is 1.69 mg cm$^{-2}$ in each battery. The electrolyte comprising 0.2 M Zn(ac)$_2$ and 6.0 M KOH was circulated by a peristaltic pump. The specific capacity was calculated by the following equation [26]:

\[
\frac{1}{j} - \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}
\]

Fig. 1. A schematic illustration of preparing U-MnNiFe@NCB by the ultrasonic routes (a). FESEM images of CB and U-MnNiFe@NCB at different magnifications: 50,000× (b,e), 100,000× (c,f), and 150,000× (d,g).
\[ C_s = \frac{I \Delta t}{m_{Zn}} \]  

where \( I \) is current (mA), \( C_s \) is specific capacity (mAh g\(^{-1}\)), \( \Delta t \) is time from the beginning until zinc was totally consumed (s), \( m_{Zn} \) is the consumed zinc mass (g).

3. Results and discussion

The pristine CB undergoes the two-round ultrasonic treatments, being converted to the polymer/metal oxide-modified material U-MnNiFe@NCB, as shown in Fig. 1a. The FESEM images of CB and U-MnNiFe@NCB at different magnifications (Fig. 1b-g and Fig. S1) show that the two samples have the similar morphology of nanosized carbon granules, suggesting that the ultrasonic modification does not change the basic structure of the CB. Free radicals generated by the ultrasonic cavitation are able to induce the polymerization of NIPAm, resulting in the formation of PNIPAm that is grafted onto the carbon granules. The grafted polymer chains contain the structural units terminated by amide groups, which can act as good donor groups bonded to metal ions. To determine whether PNIPAm was successfully grafted and its content, U-MnNiFe@NCB, MnNiFe@NCB and CB were vacuum heated at 250 °C for 6 h with a ramp rate of 10 °C min\(^{-1}\) separately. As shown in Table S1, the grafting proportion of U-MnNiFe@NCB is ca. 23.0%, revealing that its surface is indeed modified with sufficient quantities of PNIPAm by the ultrasonication. By comparison, the grafting proportion of MnNiFe@NCB is only 6.7% (Table S1), showing the low content of volatile organic components in the material without undergoing the ultrasonication. This difference in the grafting proportions can be explained by the fact that the polymer PNIPAm with the network of carbon skeletons formed using the ultrasound favour the adherence to the surface of porous carbon compared to the monomers.

The TEM images of U-MnNiFe@NCB at different magnifications (Fig. 2a and b) also exhibit its typically granular morphology, consistent with the FESEM observations. Further, the HRTEM image of U-MnNiFe@NCB (Fig. 2c) shows its overwhelmingly amorphous feature, together with a few lattice fringes. A magnified view of the lattice fringes by the inverse fast Fourier transform (IFFT) of the circled region is shown in the inset of Fig. 2c. The d-spacing is 0.34 nm, which can be ascribed to the (002) surface of graphitized carbon [27]. Also, another two types of lattice fringes are found in the HRTEM image of U-MnNiFe@NCB (Fig. 2d). As magnified in the insets of Fig. 2d, the d-spacings of these lattice fringes include 0.21 nm and 0.30 nm, which should be ascribed to the metal oxide formed by the ultrasonication. Fig. 2e-k exhibit the high-angle annular dark-field (HAADF)-TEM and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of U-MnNiFe@NCB.
MnNiFe@NCB. The three metallic elements Fe, Mn, and Ni coexist with O, indicating the formation of the tri-metallic oxide on the CB.

The XRD patterns of U-MnNiFe@NCB, MnNiFe@NCB, and CB are exhibited in Fig. 3. The widened bands centred at 24.0° are seen from all the three patterns, corresponding to the (002) plane of graphitized carbon [28] and consistent with the HRTEM observation (Fig. 2c). The widened characteristics of diffraction peaks also confirm the three materials possess the amorphous carbon matrices. By comparison with MnNiFe@NCB and CB, U-MnNiFe@NCB has the two additional small yet sharp peaks centred at 30.3° and 43.4° observable from its XRD pattern, which can be ascribed to the (220) and (400) planes of Mn-doped NiFeO$_4$, respectively [29,30]. The d-spacings of the (220) and (400) planes of Mn-doped NiFeO$_4$ are 0.30 nm and 0.21 nm, respectively [29,30], which are consistent with the HRTEM data (Fig. 2d). Thus, it can be inferred that the metal ions Ni$^{2+}$, Fe$^{3+}$ and Mn$^{2+}$ attached to the polymer-grafted carbon granules by the amide groups are converted to Mn-doped NiFeO$_4$ under the ultrasonication.

The elemental compositions of Mn-doped NiFeO$_4$ anchored on the polymer-grafted CB, along with the control samples MnNiFe@NCB and CB, are evaluated using the XPS technique. The wide-scan XPS spectra of the three materials are shown in Fig. S2a and the corresponding elemental information is summarized in Table S2. The pristine CB contains only two elements C and O, whereas U-MnNiFe@NCB possesses the largest quantities of N, O, Mn, Ni, and Fe among the three materials, and MnNiFe@NCB prepared without using the ultrasonication has the intermediate amounts of these elements, indicating that the grafted polymer chains produced by the ultrasonic cavitation, acting as adhesives, allow the CB to bind with the metallic elements effectively. Without the ultrasonication or any radical initiator, the polymerization of NIPAm could not be triggered spontaneously. Because the polymer NiPNiAm formed in U-MnNiFe@NCB binds more tightly to the carbon surface than its monomer NIPAm as mentioned above, MnNiFe@NCB contains the lower amounts of potential N-/O-donor groups anchored on the surface of CB and thus the reduced number of the coordinated metal ions. For the non-metallic elements, the narrow-scan C 1 s spectrum of U-MnNiFe@NCB (Fig. 4a) can be split into the four subpeaks C=C (284.7 eV) [31,32], C=C/C=O/C=N (285.4 eV) [31], C=O (286.4 eV) [31] and O=C=O (289.2 eV) [32]. Likewise, the narrow-scan N 1 s spectrum of U-MnNiFe@NCB (Fig. 4b) can be split into the three peaks N–Q (quaternary nitrogen, 401.5 eV) [33], HNC=O (400.2 eV) [34] and metal-N (399.2 eV) [35], and its O 1 s counterpart (Fig. 4c) can also be decomposed into the three subpeaks O=C=O (533.5 eV) [31], N=C=O (532.0 eV) [36] and O$^-$ (530.5 eV) [37]. By contrast, the C 1 s spectrum of CB that lacks nitrogen or metallic elements (Fig. S2b) can be split into the three subpeaks C=C (284.8 eV) [31], C=C/C=O (285.4 eV) [31] and O=C=O (289.2 eV) [32], whereas its O 1 s counterpart (Fig. S2c) can also be split into the two peaks O=C=O (533.5 eV) and C-OH (532.3 eV) [31]. Indeed, the chemical bonding of the non-metallic elements is different between U-MnNiFe@NCB and CB, because of the existence of the grafted polymer and metal oxide in the former. Evidently, the existence of the metal-N bonding on the surface of U-MnNiFe@NCB shows that the metal ions are coordinated to the amide groups of the grafted NiPNiAm. Additionally, the existence of the lattice oxygen O$^-$ indicates the formation of transition metal oxide [37,38]. In other words, the metal ions bind to the N and O donor atoms of the amide groups that are part of the grafted polymer in the coordination mode, forming the metal oxide under the ultrasonication. Regarding the metallic elements, on the other hand, the high-resolution Mn 2p, Fe 2p and Ni 2p XPS spectra of U-MnNiFe@NCB (Fig. 4d–f) show the typical characteristics of 2p$_3/2$ Fe$^{3+}$ (711.7 eV), 2p$_1/2$ Fe$^{3+}$ (724.9 eV), 2p$_3/2$ Mn$^{2+}$ (642.4 eV) and 2p$_3/2$ Ni$^{2+}$ (855.8 eV) [39,40]. The surface contents of Mn, Ni and Fe in U-MnNiFe@NCB are 0.28 at%, 0.23 at% and 0.91 at%, respectively, as summarized in Table S2; that is, the atomic ratio of Mn to Ni to Fe is 1:0.82:3.25. Thus, the chemical formula of Mn-doped NiFeO$_4$ anchored on the polymer-grafted CB synthesized by the ultrasonication can be written as Mn$_{0.6}$Ni$_{0.5}$Fe$_2$O$_4$, the formation of which should involve the following steps under the ultrasonic irradiation [41]:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \\
2\text{H}_2\text{O} & \rightarrow 2\text{H}_2 + 2\text{O}_2 \\
2\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow 2\text{Fe}^{2+} + 2\text{OH}^- \\
2\text{Fe}^{3+} + 2\text{OH}^- & \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O} \\
\text{Ni}^{2+} + 2\text{H}_2\text{O} + 2\text{OH}^- & \rightarrow \text{Ni}^{3+} + 2\text{H}_2\text{O} + \text{O}_2 \\
3\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 6\text{OH}^- & \rightarrow 2\text{Mn}_2\text{O}_4 + 4\text{H}_2\text{O} \\
4\text{Fe}^{3+}\text{O}_4 + 3\text{NiO} + 1.2\text{Mn}_2\text{O}_4 & \rightarrow 6\text{Mn}_{0.6}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4
\end{align*}
\]

It can be seen that ultrasound plays important roles in the generation of the tri-metallic oxide: the ultrasonic cavitation induces the formation of free radicals that can produce peroxide, which reacts with the metal ions in a series of steps until the formation of Mn$_{0.6}$Ni$_{0.5}$Fe$_2$O$_4$. Without the ultrasound, metal oxide could hardly be obtained under the given conditions. This can also explain why the diffraction peaks of Mn$_{0.2}$Ni$_{0.8}$Fe$_2$O$_4$ or any other metal oxide are absent in the XRD pattern of MnNiFe@NCB obtained without employing the ultrasound (Fig. 3). Accordingly, the ultrasonication helps to induce not only the polymerization of NiPNiAm but also the formation of the tri-metallic oxide Mn$_{0.6}$Ni$_{0.5}$Fe$_2$O$_4$, and the grafted polymer chains act as binders to anchor the active sites (i.e. the metal oxide) to the porous electrode (i.e. the CB).

In addition to active sites, porous properties have significant effects on the catalytic performance, and in this case the CB provides the porous domains for mass transport. N$_2$ adsorption–desorption isothermal experiments were conducted to investigate pore structures of the three materials. The isotherms of U-MnNiFe@NCB, MnNiFe@NCB, and CB (Fig. 5a) can be classified as Type I/II [42,43]. Specifically, the largely increased adsorption volumes at p/p$_0 \sim 0$ indicate the existence of micropores [44,45], the hysteresis loops at p/p$_0 = 0.45 \sim 0.95$ are caused by mesopores [46,47], and the large uptakes at p/p$_0 > 0.95$ imply the presence of macropores [48]. Both U-MnNiFe@NCB and MnNiFe@NCB are characteristic of hierarchical pores originating from the CB. The surface areas of U-MnNiFe@NCB, MnNiFe@NCB and CB are 414 m$^2$g$^{-1}$, 615 m$^2$g$^{-1}$, and 725 m$^2$g$^{-1}$, respectively. The change of surface areas
reflects the degree of pore blockage by the grafted polymer chains, that is, the more the polymer on the surface, the higher the degree of pore blockage and the smaller the surface area, which is consistent with the corresponding grafting proportions of the materials mentioned above (Table S1). Moreover, the pore width distributions of U-MnNiFe@NCB, MnNiFe@NCB and CB based on the DFT method are shown in Fig. 5b. Overall, the three curves look similar to each other, confirming the pore structures of U-MnNiFe@NCB and MnNiFe@NCB stem from the characteristics of the CB and that no major changes are made to the pore width distributions after the surface modifications either with or without the ultrasonication. On the other hand, there is a noticeable difference between U-MnNiFe@NCB and CB in the micropore domains. U-MnNiFe@NCB has the two lower peaks centred at 0.8 nm and 1.4 nm than the CB, whereas their mesopore counterparts are comparatively close to each other, indicating that the ultrasonic modification has the stronger effect on micropores. This can also be quantitatively demonstrated according to the data from Table S3. The CB has the surface area and pore volume of micropores roughly three times greater than U-MnNiFe@NCB, whereas the differences between CB and U-MnNiFe@NCB in surface areas and pore volumes of mesopores are very little. It can then be inferred that the grafted polymer tends to ‘bury’ the micropore sites. In other words, the ultrasonic modification does not lead to a significant loss of mesopores that are responsible for mass transport, whereas micropores act as effective anchor points for the ultrasonically-induced polymer chains that capture the metal-oxide active sites, therefore achieving the fine balance between active sites and mass transport in this material design.

Next, the electrochemical measurements were conducted to evaluate the catalytic activities towards ORR and OER for U-MnNiFe@NCB, MnNiFe@NCB and CB. The ORR performance, Fig. 6a shows the LSVs of the three samples alongside commercial 10 wt% Pt/C. U-MnNiFe@NCB achieves an acceptable level of ORR catalytic activity, having the onset potential ($E_{\text{onset, ORR}}$) of 0.92 V, the half-wave potential ($E_{1/2,\text{ORR}}$) of 0.73 V and the limiting current density of 5 mA cm$^{-2}$ at 1,600 rpm, superior to MnNiFe@NCB, CB and 10 wt% Pt/C. The inferior ORR performance of MnNiFe@NCB and CB can be ascribed to the lack of metal-oxide active sites in these two materials. The ORR electron-transfer numbers of U-MnNiFe@NCB, MnNiFe@NCB, CB and 10 wt% Pt/C are 3.7, 3.2, 2.3 and 3.6, respectively, according to the corresponding K-L plots (Fig. 6b and Fig. S3), showing the ORR by U-MnNiFe@NCB is predominantly the 4-electron process that is energetically favourable for electrochemical devices. Moreover, the OER catalytic performance of MnNiFe@NCB is compared with that of MnNiFe@NCB, CB and RuO$_2$. The LSVs of the four materials concerning their OER behaviours are exhibited in Fig. 6c. U-MnNiFe@NCB shows the onset potential ($E_{\text{onset, OER}}$) of 1.64 V at 10 mA cm$^{-2}$, more negative than MnNiFe@NCB (1.79 V), CB (1.89 V) and RuO$_2$ (1.67 V), which indicates the better OER performance of U-MnNiFe@NCB than the other three...
samples [49]. This can also be confirmed by its minimal overpotential requirement for OER. The OER overpotential of U-MnNiFe@NCB (at 10 mA cm$^{-2}$) is 410 mV, the smallest value among the samples (MnNiFe@NCB: 560 mV; CB: 660 mV; RuO$_2$: 440 mV). Furthermore, considering the ORR/OER activities holistically (Fig. 6d), U-MnNiFe@NCB exhibits the superior bi-functional performance to the commercial Pt/C and RuO$_2$. The $\Delta E$ gap ($E_{\text{onset ORR}} - E_{1/2 \text{ORR}}$) can reflect the ORR/OER performance of electrocatalysts: the wider the $\Delta E$ gap, the less efficient the bi-functional catalyst [50]. As shown in Fig. 6d, the $\Delta E$ gap of U-MnNiFe@NCB is the narrowest among the catalysts studied, showing its

![Figure 6](image6.png)

**Fig. 6.** The LSVs of U-MnNiFe@NCB, MnNiFe@NCB, CB and 10 wt% Pt/C at 1,600 rpm for ORR (a); the K-L plots of U-MnNiFe@NCB (b); the LSVs of U-MnNiFe@NCB, MnNiFe@NCB, CB and RuO$_2$ for OER at 1,600 rpm (c); the LSV curves of U-MnNiFe@NCB, RuO$_2$ and Pt/C at 1,600 rpm for ORR/OER (d).

![Figure 7](image7.png)

**Fig. 7.** A schematic illustration of the two RZABs connected in series (a); the OCV curves (b), charging/discharging polarization curves (c), and battery performance (d) of the U-MnNiFe@NCB and Pt/C-RuO$_2$ batteries; the stability test of the U-MnNiFe@NCB battery (e); a photograph of the two U-MnNiFe@NCB batteries connected in series powering one white LED (f).
reasonable performance towards ORR/OER. Clearly, the major reason why U-MnNiFe@NCB exhibits the much improved bi-functional ORR/OER performance compared to MnNiFe@NCB is the much larger amount of metal-oxide active sites (produced by the ultrasonication) anchored on the surface of CB by the grafted polymer chains (also produced by the ultrasonication) for U-MnNiFe@NCB compared to its non-ultrasonically treated counterpart.

Custom-made RZABs were designed to evaluate the bi-functional ORR/OER electrocatalytic performance of U-MnNiFe@NCB in real electrochemical devices. Fig. 7a shows the schematic illustration of the two zinc-air batteries connected in series, each made of two electrodes—a zinc-plate anode and an air-cathode. The electrolyte that contains 0.2 M Zn(ac)2 and 6.0 M KOH flows in each battery by an external peristaltic pump. The air-cathode is composed of nickel foam, air-breathable water-proof layer and carbon paper loaded with a catalyst. Fig. 7b presents the open-circuit voltage (OCV) performance of the two RZABs using U-MnNiFe@NCB and the mixture of 10 wt% Pt/C and RuO2 as the cathode catalysts (abbreviated as the U-MnNiFe@NCB battery and the Pt/C-RuO2 battery respectively). It can be seen that the U-MnNiFe@NCB battery exhibits an OCV of 1.47 V, the voltage being slightly larger than the Pt/C-RuO2 battery (1.43 V). Additionally, Fig. 7c shows the charging/discharging polarization curves of the U-MnNiFe@NCB and Pt/C-RuO2 batteries. There is a larger voltage gap between the charging and discharging data of the Pt/C-RuO2 battery compared to its U-MnNiFe@NCB counterpart, indicating the enhanced performance of the latter [31]. As exhibited in Fig. 7d, the power density of the U-MnNiFe@NCB battery achieves the maximum (96 mW cm−2), the value being much larger than for the Pt/C-RuO2 battery (45 mW cm−2). Furthermore, the specific capacity of the U-MnNiFe@NCB battery was measured to be 746.6 mAh gZn−1 (Fig. 54), which is larger compared to the Pt/C-RuO2 battery (630.2 mAh gZn−1). Indeed, U-MnNiFe@NCB proves to be the fine bi-functional electrocatalyst for RZABs. Finally, the stability test of the U-MnNiFe@NCB battery was undertaken at a current density of 5 mA cm-2 with repeatedly 5-min charging and 5-min discharging for 160 cycles (96,000 s in total). The result in Fig. 7e shows that the voltage gap between charging and discharging undergoes almost no obvious change (from 0.73 V at the beginning to 0.76 V in the end), revealing the good stability of U-MnNiFe@NCB. Fig. 7f shows the demonstration of a white LED light powered by the two U-MnNiFe@NCB batteries connected in series. Though still in the infancy, these gadgets are instructive as the non-noble metallic oxides produced ultrasonically have the comparable bi-functional catalytic activities to the noble metal counterparts.

4. Conclusions

To summarize, this work demonstrates the important roles of ultrasonication in the fabrication of metal-oxide/porous carbon composite materials in which polymer chains act as binders. Reactive free radicals generated by ultrasonic cavitation not only help to polymerize monomers without using dangerous radical initiators but also favour the formation of the Mn-Ni-Fe tri-metallic oxide that is otherwise impossible to obtain without ultrasonication. Our investigations have also shown that ultrasonically induced polymers are inclined to anchor within micropore domains instead of mesopores, which would not block mesopore pathways. This is particularly important, because the increase in the number of active sites (metal oxide) does not come into conflict with the enhancement in mass transport (relevant to mesopores) in this material design. With numerous active sites and fast mass transport, U-MnNiFe@NCB possesses the superior bi-functional ORR/OER electrocatalytic performance to its ultrasonication-free counterpart and commercial catalysts. Moreover, two in-series connected RZABs using U-MnNiFe@NCB as air-cathodes are capable of powering small electronics, demonstrating its potential to work well in a real device. As a consequence, this work provides useful frameworks of ideas for understanding multiple effects of ultrasonication on the assembly of composite materials that comprise inherently incompatible components.

CRediT authorship contribution statement

Bolin Jin: Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing.

Peiyao Bai: Formal analysis, Investigation, Validation, Visualization, Writing – original draft. Qiang Ru: Formal analysis, Investigation, Validation. Weiqi Liu: Formal analysis, Validation. Huifen Wang: Formal analysis, Visualization. Lang Xu: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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