Preparation of a MnO$_2$@C@MnO Core-shell Heterojunction as a Highly Efficient Electrocatalyst for the Oxygen Evolution Reaction

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Manganese-based cocatalyst decoration is an effective strategy for constructing an efficient electrocatalyst for the OER. A novel MnO$_2$ nanowires@C@MnO nanosheet core-shell heterojunction with a unique interfacial microstructure was successfully constructed in this study. The structure and morphology of the as-prepared one-dimensional MnO$_2$ nanowires and MnO$_2$@C@MnO electrocatalyst were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform-infrared (FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The results clearly revealed that the MnO$_2$ nanowires@C@MnO nanosheet core-shell heterojunction was a mixture of one-dimensional MnO$_2$ nanowires and 2D MnO nanosheets. Electrochemical performance tests showed that the electrochemical activity of the MnO$_2$@20%C@MnO core-shell heterojunction for the OER was considerably enhanced over those of pristine one-dimensional MnO$_2$ nanowires, MnO$_2$@15%C@MnO and MnO$_2$@30%C@MnO. MnO$_2$@20%C@MnO had a lower overpotential (520 mV at 10 mA/cm$^2$) and Tafel slope (66 mV/dec) than the one-dimensional MnO$_2$ nanowires (650 mV at 10 mA/cm$^2$ and 133 mV/dec, respectively). Electrochemical analyses showed superior OER performance for MnO$_2$@20%C@MnO, which was mainly attributed to the introduction of C and the coexistence of MnO$_2$ nanowires and MnO nanosheets. In addition, the MnO$_2$ nanowires@C@MnO nanosheet core-shell heterojunction provided abundant transport channels for electrons, ions and electrolyte penetration, accelerating the separation of bubbles at the electrode surface.

Keywords: MnO$_2$, C, Core-shell heterojunction, OER activity.
1. INTRODUCTION

Increasing energy demand in modern society in recent years has motivated the wide study of renewable and sustainable energy development. As a clean and high-efficient energy carrier, hydrogen is regarded as one of the foremost energy candidates to replace fossil fuels [1-6]. Electrochemical technology is considered to be one of the most promising technologies for large-scale hydrogen production [7,8]. However, the limited efficiency of the water splitting process results in slow kinetics for the oxygen evolution reaction (OER) [9]. Therefore, efficient OER electrocatalysts have been developed to accelerate the reaction kinetics and water splitting process [5,10-15]. Extensive studies have shown IrO$_2$ and RuO$_2$ to be the best performing OER electrocatalysts to date. IrO$_2$ and RuO$_2$ are widely used, but have limitations of scarcity and high-cost [16-18].

Extensive studies have been performed in the last few years to develop OER electrocatalysts that are cost-effective, nontoxic, efficient, and stable. To this end, various electrode materials have been used as electrocatalysts for water splitting, including conducting perovskites [19-22], carbon-based materials [23,24], chalcogenides [25,26], hybrid composites [27,28], metal oxides [29-32] and transition metal oxides [33,34]. In particular, manganese oxide (MnO$_2$) remains a very attractive OER candidate due to its eco-friendliness, low cost, nontoxicity, high abundance, high activity/stability and promising OER activity [35]. MnO$_2$ occurs as various structural phases, including $\alpha$-MnO$_2$, $\beta$-MnO$_2$, $\gamma$-MnO$_2$ and $\lambda$-MnO$_2$, among which $\alpha$-MnO$_2$ has the best electrical properties and highest OER activity when used as an electrochemical catalyst for water splitting. However, to the best of our knowledge, the effect of the morphology of $\alpha$-MnO$_2$ on the OER activity and electrochemical performance has not been thoroughly investigated. Therefore, studies have been performed to synthesize $\alpha$-MnO$_2$ with various morphologies, including nanowires [36-38], nanotubes, nanoparticles, nanorods and nanosheets [39]. Among these morphologies, $\alpha$-MnO$_2$ nanowires exhibit the highest OER performance. The [MnO$_6$] octahedral units in $\alpha$-MnO$_2$ are regularly arranged into 2x2 channels, providing abundant pathways for ions and exposing numerous active sites [40,41]. However, the inherently metastable morphology and low electrical conductivity of MnO$_2$ necessitates the use of conductive additives to improve the electrical conductivity of MnO$_2$ for application as an electrode catalyst [42-46].

Carbon-based materials have been extensively studied as conductive additives because of their tunable surface chemistry, excellent electrical conductivity and corrosion resistance. In general, carbon-based materials have a lower electrochemical activity and higher conductivity and stability than metal oxides. Thus, carbon-based materials can be composited with metal oxide catalysts to enhance their electrocatalytic activity and stability. For instance, C nanorod arrays were loaded on CeO$_2$ derived from metal organic frameworks to prepare a CeO$_2$/C composite as a highly efficient OER electrocatalyst [47]. Carbon materials have superior electrical conductivity and oxygen mass transfer properties [48,49].

Therefore, the objective of this study was to hybridize C with Mn metal oxides to form electrocatalysts. Carbon-coated MnO$_2$ was successfully prepared by a liquid phase method and thermal treatment. XRD analysis showed that C reduced Mn$^{4+}$ to Mn$^{2+}$. SEM and TEM characterization showed that MnO$_2$-coated carbon existed both as one-dimensional MnO$_2$ nanowires and two-dimensional MnO nanosheets, resulting in the formation of MnO$_2$ nanowires@C@MnO nanosheet (MnO$_2$@C@MnO) core-shell heterojunctions. This novel structure promoted the OER activity of MnO$_2$. The carbon content of the catalyst was correlated with the OER activity. The results of electrochemical tests showed that among MnO$_2$@C@MnO heterojunctions with different C mass ratios, the MnO$_2$@20%C@MnO core-
shell heterojunction successfully decreased the overpotential and Tafel slope from those of the one-dimensional MnO_2 nanowires (650 mV and 133 mV/dec, respectively) to 520 mV at 10 mA/cm^2 and 66 mV/dec, respectively. There were two main reasons for the enhanced OER activity of MnO_2@20%C@MnO. First, the excellent OER performance and stability resulted from the high specific surface area and outstanding electrical conductivity of the electrocatalyst. Second, synergy between MnO_2 and carbon enabled C to reduce Mn^{4+} to Mn^{2+}, resulting in MnO_2 nanowires@C@MnO nanosheet core-shell heterojunctions with enhanced OER activity.

2. EXPERIMENTAL

2.1 Materials

All the chemicals used during the experiments were of analytical grade and did not require further purification.

2.2 Synthesis of MnO_2 nanowires

KMnO_4 and NH_4F were added to 150 ml of distilled water using the hydrothermal method; the resulting mixture was magnetically stirred for 30 min, transferred to a 200 ml stainless steel reactor, heated at 160 °C for 24 h, and washed several times with distilled water and an ethanol solution. The obtained product was freeze-dried to yield MnO_2 nanowires.

2.3 Synthesis of the MnO_2 Nanowire@C@MnO Nanosheet Core-shell Heterostructure

MnO_2@C core-shell heterojunctions were prepared by the liquid phase method and thermal treatment. MnO_2 nanowires (0.4 g) were dispersed in 160 ml of distilled water. The resulting solution was alternately stirred and ultrasonicated for 6 h to form a uniform suspension (A). Tris (hydroxymethyl) methyl aminomethane (THAM, 2.85 g) was dissolved in 177.5 ml of deionized water, and 73.5 mL of 0.1 M HCl were added to the resulting solution. Following the complete dissolution of THAM, 0.4 g of dopamine was added to the solution form a uniform suspension (B). Then, solution B was added to solution A, and the resulting mixture was stirred for 30 min. The surface of the MnO_2 nanowires was encased in dopamine hydrochloride (PDA). The obtained product was centrifuged and freeze-dried, followed by several washes with water and alcohol, to yield MnO_2@PDA nanowires. MnO_2@C@MnO was produced by annealing the MnO_2@PDA nanowires in an N_2 flow at 600 °C for 2 h at a heating rate of 2 °C/min. The prepared samples were labelled MnO_2@C_x@MnO, where x denotes the C mass ratio, that is, MnO_2@15%C@MnO, MnO_2@20%C@MnO and MnO_2@30%C@MnO.

2.4 Characterization

The crystal structures and phases of the as-prepared samples were investigated by X-ray diffractometry (XRD) using a Rigaku D/MAX2200 PC (Tokyo, Japan) with Cu Kα radiation at a
wavelength $\lambda=0.15418$ nm, an operating voltage of 40 kV and an operating current of 40 mA. The sample morphology was characterized by field emission scanning electron microscopy (FE-SEM, using a Hitachi S-4800 & Hiroba EDX electron microscope). The sample morphology was also characterized using a transmission electron microscope (TEM) operated at 200 kV (JEM 3010, JEOL, Tokyo, Japan). Fourier transform-infrared (FT-IR) spectra of the samples were obtained on a Bruker Vector 22 spectrometer. Raman spectroscopy was performed using a BRUKER RFS 27, and a standalone FT-Raman analyser with a resolution of 0.2 cm\(^{-1}\) was used to determine the basic dynamic response of the specimens. A specific surface area analyser (JW-BK100B) was used to evaluate the specific surface area and pore volume and size of the samples. The surface electronic states of the samples were measured by X-ray photoelectron spectroscopy (XPS, Kratos Axis Supra) using, an ultrahigh vacuum VG Scientific Corp MK-II electron spectrometer with a multichannel detector. All the binding energies were corrected using C1s at 284.6 eV as a reference.

2.5 Electrochemical measurements

Electrochemical tests were performed on a CHI660E (CHENHUA) electrochemical workstation. The three-electrode system consisted of an Hg/HgO reference electrode, a Pt wire counter electrode, and the prepared sample as the working electrode. All the electrochemical measurements were performed in a 0.066 M phosphate buffer (pH=7). The potential measured by the Hg/HgO electrode was transformed to the reversible hydrogen electrode (RHE) potential using $E_{\text{RHE}}=E_{\text{Hg/HgO}}+0.098+0.059pH$. Cyclic voltammogram and linear voltammogram curves were obtained over a range of 0.2 V to 1.3 V. Electrochemical impedance spectroscopy (EIS) was conducted over a range of 10 kHz to 0.01 Hz. The OER activity of the samples was evaluated at least three times for each electrocatalytic experiment to test the experimental reproducibility. Equivalent circuit fitting was performed on the EIS data using ZSimpWin 3.3 software.

The activity of the electrocatalyst was evaluated by applying CV and LSV techniques to determine the slope (mV/dec) and overpotential. Stability tests were conducted long-term chronoamperometry.

3. RESULTS AND DISCUSSION

3.1 XRD, SEM and TEM analysis

The XRD patterns of the synthesized 1D MnO\(_2\) nanowires and MnO\(_2\)@C@MnO core-shell heterojunction are shown in Figure 1a. The peaks at 12.85°, 18.35°, 25.74°, 28.94°, 36.63°, 37.75°, 39.11°, 41.18°, 42.08°, 46.79°, 49.88°, 56.33°, 60.36°, 65.38° and 69.66° in the pure MnO\(_2\) spectrum were indexed to the (110), (200), (220), (310), (400), (211), (330), (420), (301), (510), (411), (600), (521), (002) and (541) reflections of the $\alpha$-MnO\(_2\) phase, respectively, matching well with the standard profile of JCPDS No. 44-0141. The sharp intense diffraction peaks in the spectrum of the MnO\(_2\) nanowires indicated high crystallinity. The XRD patterns of the MnO\(_2\)@C@MnO core-shell heterojunction are shown in Figure 1b: the diffraction peaks of the $\alpha$-MnO\(_2\) phase do not appear in the spectrum of the MnO\(_2\)@C@MnO core-shell heterojunction produced after C coating using PDA, indicating that the +4 valence of manganese was reduced. The new diffraction peaks at $2\theta = 34.99^\circ$, $30.63^\circ$, and $34.49^\circ$ are attributed to the (002) and (101) reflections of the $\alpha$-MnO\(_2\) phase, respectively.
40.65°, 58.82°, 70.53° and 73.91° were indexed to face-centred cubic MnO (JCPDS No.07-0230). This result indicated that the final sample was a mixture of MnO2 and MnO. The absence of the diffraction peaks of MnO2 in the spectrum of the MnO2@C@MnO core-shell heterojunction resulted from the growth of the crystal plane of ultrathin MnO nanosheets in a preferential orientation. The absence of clear diffraction peaks for C in the spectrum of the MnO2@C@MnO core-shell heterojunction resulted from the small quantity and high dispersion of C in the samples. The presence of C was further confirmed by SEM, TEM, HRTEM, Raman shift and XPS analyses. The absence of additional diffraction peaks or other phases indicated the high purity of the one-dimensional MnO2 nanowires and MnO2@C@MnO core-shell heterojunction. A schematic of the synthesis process and formation of the MnO2@C@MnO core-shell heterojunction is shown in Figure 1b. The MnO2@C@MnO core-shell heterojunction was prepared by the liquid phase method and thermal treatment.

The morphologies of the one-dimensional MnO2 nanowires and MnO2@C@MnO core-shell heterojunctions were analysed using SEM. As shown in Figure 1c, MnO2 consisted of a large number of randomly oriented ultralong nanowires with diameters of approximately 50 nm and lengths ranging between 5 and 20 μm. The one-dimensional MnO2 nanowires were well-dispersed and entangled into a three-dimensional network, where some nanowires were slightly bent. The ultralong structure and high dispersion of the one-dimensional MnO2 nanowires resulted in excellent flexibility and mechanical stability that could be exploited for chemical separation. Figure 1d shows the corresponding SEM images of the MnO2@C@MnO core-shell heterojunction. The morphology of the carbon-coated MnO2@C@MnO core-shell heterojunction was similar to that of the MnO2 nanowires, showing that the carbon coating did not affect the micromorphology of the MnO2@C@MnO core-shell heterojunction. However, the diameter of the MnO2@C@MnO core-shell heterojunction increased, and MnO nanoplates grew on the surface of the MnO2@C nanowires. The carbon coating stabilized the framework structure and strengthened the electronic conductor. The MnO nanosheets also provided a large number of reaction sites and large specific surface area, promoting the efficient separation and transfer of electrons and holes and the OER performance.

Transmission electron microscopy (TEM) and high-performance transmission electron microscopy (HRTEM) images of the MnO2@C@MnO core-shell heterojunction are shown in Figure 1e and f for further analysis of the material microstructure. The TEM images of the MnO2@C@MnO core-shell heterojunction presented in Figure 1e show that the carbon coating did not destroy the nanostructure of MnO2@C nanowires. MnO2 nanowires with porous structures formed mainly due to the reduction of manganese dioxide during the carbonization process. An ultrathin C coating could clearly be observed on the surface of the MnO2 nanowires. MnO2@C@MnO exhibited an ideal core-shell heterostructure, in which the MnO nanosheets grew on the surface of the MnO2@C nanowires. The core-shell structure composed of nanowires (one-dimensional) and nanosheets (two-dimensional) facilitated the transfer and separation of electrons and holes and electrochemical reactions [50]. Figure 1f shows a HRTEM image of the MnO2@C@MnO core-shell heterojunction. The lattice fringes of MnO2 and MnO can be clearly seen, where the lattice spacings of 0.30 nm and 0.22 nm correspond to the (310) and (200) crystal planes, respectively, which is consistent with the XRD results.
Figure 1. XRD patterns (a) of one-dimensional MnO$_2$ nanowires and MnO$_2$@20%C@MnO core-shell heterojunction; The preparation diagram of MnO$_2$@C@MnO core-shell heterojunction (b); SEM images of one-dimensional MnO$_2$ nanowires (c) and MnO$_2$@20%C@MnO core-shell heterojunction (d); TEM images (e) and HRTEM images (f) of MnO$_2$@20%C@MnO core-shell heterojunction.

3.2 FT-IR and Raman spectra analysis

Figure 2a shows the FT-IR spectra that were obtained to investigate the surface functional groups of the as-synthesized samples. The spectrum of the pure one-dimensional MnO$_2$ nanowires exhibited the two main characteristic peaks of the Mn-O stretching vibration in the MnO$_6$ octahedral framework over the 800 to 400 cm$^{-1}$ range [51,52]. The peak at 1630 cm$^{-1}$ and the strong and broad peak at 3430 cm$^{-1}$, corresponded to the stretching vibration of the O-H bond in the adsorbed water during the compression of the sample and KBr, respectively. The intensity of the characteristic peak in the 400-800 cm$^{-1}$ range
of the FT-IR spectrum of the MnO₂ nanowires was reduced in the FT-IR spectrum of the MnO₂@C@MnO core-shell heterojunction because the introduction of C into the material increased the number of defects, inducing an internal stress that distorted the lattice.

The Raman spectra of the one-dimensional MnO₂ nanowire and MnO₂@C@MnO core-shell heterojunction are shown in Figure 2b. The three characteristic Raman peaks in the spectrum of the one-dimensional MnO₂ nanowire at 386, 576 and 624 cm⁻¹ correspond to Mn-O bonds, that is, the bending vibration of Mn-O-Mn, ν₃(Mn-O) stretching vibration of n₃(Mn-O) caused by Mn⁴⁺ at the bottom surface and symmetric telescopic vibration of ν₁(Mn-O) in the [MnO₆] octahedron, respectively [53]. Compared to the Raman spectrum of the MnO₂ nanowires, the characteristic peaks in the 550-700 cm⁻¹ range were reduced in intensity in the Raman spectrum of the MnO₂@C@MnO core-shell heterojunction, where the characteristic peak at 576 cm⁻¹ was redshifted and the characteristic peak of 624 cm⁻¹ was blueshifted because the introduction of C into the material increased the number of defects, inducing an internal stress that distorted the lattice. The peak in the 550-700 cm⁻¹ range of the Raman spectrum of the MnO₂@C@MnO core-shell heterojunction was wider than that in the Raman spectrum of MnO₂, because the introduction of C created a large number of metal vacancies that destroyed the symmetry of the crystal structure and the compression or stretching of the lattice generated a residual stress. Two other Raman bands appeared at 1347 cm⁻¹ (D band) and 1595 cm⁻¹ (G band) in the spectrum of the MnO₂@C@MnO core-shell heterojunction. The D band was a defect band, and the G band corresponded to the E₂g mode (graphitic carbon), indicating that C had been successfully loaded onto the MnO₂ nanowire surface.

Figure 2. FTIR spectra (a) and Raman spectra (b) of one-dimensional MnO₂ nanowires and MnO₂@20%C@MnO core-shell heterojunction.

3.3 N₂ adsorption-desorption isotherms and pore diameter distribution

As shown in Figure 3, the N₂ adsorption-desorption isotherms of the one-dimensional MnO₂ nanowires and MnO₂@20%C@MnO core-shell heterojunction contained a Type H3 hysteresis loop. MnO₂@20%C@MnO possessed a larger BET specific surface area (Figure 3b, 44.538 m²/g) than the one-dimensional MnO₂ nanowires (Figure 3a, 35.504 m²/g). This high specific surface area facilitated O₂ transport adsorption/desorption, exposed more accessible active sites for the OER, and increased the
catalytic capacity. The high specific surface area also provided sufficient space for the OER to occur, thereby enhancing the electrocatalytic activity of MnO$_2$@20%C@MnO. The reduction of manganese dioxide in the one-dimensional nanowires during carbonization resulted in pore formation in the MnO$_2$@20%C@MnO core-shell heterojunction. The pore size of MnO$_2$@20%C@MnO was 22.064 nm (Figure 3b), whereas that of the one-dimensional MnO$_2$ nanowires was 29.734 nm (Figure 3a). The specific surface area of the MnO$_2$@20%C@MnO core-shell heterojunction resulted in superior conductivity that facilitated electron transport.

![Figure 3. N$_2$ adsorption-desorption isotherms and pore diameter distribution (insert) of one-dimensional MnO$_2$ nanowires (a) and MnO$_2$@20%C@MnO core-shell heterojunction (b).](image)

### 3.4 XPS analysis

The chemical composition and state of the sample were further determined from the XPS spectra: peaks for C, O and Mn can be seen in Figure 4a. There are no discernible peaks of other impurities in Figure 4a, which is consistent with the XRD analysis. Four core-level signals of C 1s appeared at 292.6 eV, 288.4 eV, 285.8 eV and 284.8 eV corresponding to O=C-O, C=O, C-O and C=C/C=C bands, respectively (Figure 4b). As shown in Figure 4c, the O 1s spectrum contained two main characteristic peaks, corresponding to Mn-O-H (531.2 eV) and Mn-O-Mn (529.9 eV) [54,55]. The peaks in the Mn 2p XPS spectra at ~642.2 eV and 653.2 eV were assigned to Mn 2p1/2 and Mn 2p3/2, respectively (Figure 4d). The C-O and Mn-OH bonds were easily etherified, which promoted the C-O-Mn band transition and made the MnO$_2$@C@MnO core-shell heterojunction more robust. The low binding energy of MnO$_2$@20%C@MnO reflected the migration of electron clouds in the material.
3.5 Electrochemical measurements: OER studies

Figure 5a shows the polarization curves obtained for the 1D MnO$_2$ nanowires and MnO$_2$@C$_x$@MnO at a scan rate of 50 mV/s. At a current density of 10 mA/cm$^2$, MnO$_2$@20%C@MnO required an overpotential of only 520 mV, which was considerably smaller than that of MnO$_2$@15%C@MnO (620 mV), MnO$_2$@30%C@MnO (560 mV) and the MnO$_2$ nanowires (650 mV). The Tafel slopes of these catalysts reflected the reaction kinetics of the oxygen evolution process. As shown in Figure 5b, the Tafel slope of MnO$_2$@20%C@MnO was 66 mV/dec, which was superior to that of MnO$_2$@15%C@MnO (100 mV/dec), MnO$_2$@30%C@MnO (91 mV/dec) and the 1D MnO$_2$ nanowires (133 mV/dec). These results showed that the fastest OER kinetics were obtained using MnO$_2$@20%C@MnO.

These enhanced kinetics were further verified by the EIS spectrum. The EIS data were analysed using Nyquist plots, and the fitting results for the the equivalent circuits shown in Figure 5c. The Nyquist plots of all the prepared samples contained a semicircle in the high-frequency region, the diameter of which reflected the charge transfer in the sample. The MnO$_2$@20%C@MnO core-shell heterojunction had the smallest charge transfer resistance, indicating a rapid faradaic process. In the inset of Figure 5c, $R_s$, $R_{ct}$, $R_{OER}$, Q1 and Q2 denote the electrolyte resistance, charge transfer resistance, oxygen evolution reaction resistance, constant-phase element 1 and constant-phase element 2, respectively. The measurement data are shown in Table 1: MnO$_2$@20%C@MnO (11.77 KΩ) had a smaller $R_{ct}$ than the one-dimensional MnO$_2$ nanowires (99.32 KΩ). This result showed that modifying the one-dimensional MnO$_2$ nanowires with C nanoparticles significantly reduce the charge transfer resistance, resulting in
enhanced electrical conductivity for the MnO$_2$@20%C@MnO core-shell heterojunction. The R$_{\text{OER}}$ of MnO$_2$@20%C@MnO (129.4 Ω) was lower than that of the one-dimensional MnO$_2$ nanowires (166.2 Ω). This result provided strong evidence that MnO$_2$@20%C@MnO enhanced the OER performance. Figure 5d shows the results of a cyclic voltammetry (CV) test performed in a 0.066 M phosphate buffer (pH 7) at a scanning rate of 30 mV/s using a three-electrode setup. It is important to maintain a neutral pH in artificial photosynthetic systems involving multilayer metal oxides and process equipment. Hence, all the electrocatalytic properties of the samples were determined in a neutral pH system. Figure 5d displays the CVs of the one-dimensional MnO$_2$ nanowires and MnO$_2$@C$_x$@MnO core-shell heterojunctions. The MnO$_2$@20%C@MnO core-shell heterojunction exhibited a higher current density than the one-dimensional MnO$_2$ nanowires, MnO$_2$@15%C@MnO and MnO$_2$@30%C@MnO.

![Figure 5](image)

**Figure 5.** The OER polarization curves in 0.066 M phosphate buffer (pH 7) (a); Tafel plots (b); EIS Nyquist plots (c) and CV curves (d) of the 1D MnO$_2$ nanowires and different mole ratios of MnO$_2$@C$_x$@MnO core-shell heterojunction.

**Table 1.** Electrochemical impedance fitting data

<table>
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<th>Samples</th>
<th>$R_s$/Ω</th>
<th>$R_{ct}$/kΩ</th>
<th>$R_{\text{OER}}$/Ω</th>
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<td>83.87</td>
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<td>83.98</td>
<td>51.35</td>
<td>158.9</td>
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</table>

The double layer capacitance ($C_{dl}$) was used to evaluate the electrochemically active surface area (ECSA) and inherent electrocatalytic activity of the samples. As shown in Figure 6a,b, the CV curves of
the 1D MnO$_2$ nanowire and MnO$_2$@20%C@MnO obtained at scan rates ranging from 20 to 60 mV/s exhibited a rapid current response to voltage reversal at each end potential, reflecting ideal electrochemical capacitive behaviour. Figure 6c shows the $C_{dl}$ values calculated from the CV curves. The higher $C_{dl}$ (6.0 mF/cm$^2$) of the MnO$_2$@20%C@MnO core-shell heterojunction sample compared to that of the 1D MnO$_2$ nanowires (3.3 mF/cm$^2$) indicated that the abundant heterostructures, oxygen vacancies and unique porous structures of the nanowires and nanosheets increased the ECSA and created more active sites for the OER. As shown in Figure 6d, the MnO$_2$@20%C@MnO core-shell heterojunction easily maintained high activity over a long period of 6 h, reflecting the excellent durability of the catalyst.

![Figure 6](image-url)

Figure 6. CV curves of the one-dimensional MnO$_2$ nanowire (a) and MnO$_2$@20%C@MnO core-shell heterojunction (b) at scan rates of 20, 30, 40, 50 and 60 mV s$^{-1}$; $C_{dl}$ measurements of the one-dimensional MnO$_2$ nanowire and MnO$_2$@20%C@MnO core-shell heterojunction (c); Long-term durability test of the MnO$_2$@20%C@MnO core-shell heterojunction (d).

To comprehensively evaluate the OER activity of the MnO$_2$@C@MnO core-shell heterojunction, the OER activities of the MnO$_2$@C@MnO core-shell heterojunction and MnO$_x$ reported in the literature are compared in Table 2. The overpotential and Tafel slopes of the MnO$_2$@20%C@MnO core-shell heterojunction were as low as those for MnO$_x$, reported in the literature, such as $\alpha$-Mn$_{0.9}$Co$_{0.1}$O$_2$ ($\alpha$-Mn$_{0.9}$V$_{0.1}$O$_2$, $\alpha$-MnO$_2$) [56], MnO$_2$-NS/Cs$^+$/NS [57], $\beta$-MnO$_2$ (broken $\beta$-MnO$_2$) [58], $\alpha$-Mn$_2$O$_3$[59], MnO$_x$ NWs[60] and $\alpha$-MnO$_2$ (7.6 at% Co and 9.4 at% Ru) [61, 62-68], which was attributed to the good electrical conductivity of the novel core-shell heterojunction. For $\alpha$-MnO$_2$-NWN($\alpha$-MnO$_2$-NWs) [69], MnO@rGO [70] and the 1D MnO$_2$ nanowires (MnO$_2$@mpg-C$_3$N$_4$) [71], the lower overpotential but
higher Tafel slopes compared to those of the MnO$_2$@20%C@MnO core-shell heterojunction inhibited the OER activity. The comparative analysis presented above shows that the superiority of the MnO$_2$@20%C@MnO core-shell heterojunction to most MnO$_x$-based electrocatalysts.

Table 2. OER activities comparisons among MnO$_2$@C@MnO core-shell heterojunction and previously reported MnO$_x$ in the literatures

<table>
<thead>
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<th>Materials</th>
<th>Overpotential (mV) (at a current density of 10 mA/cm$^2$)</th>
<th>Tafel Slopes (mV/dec)</th>
<th>Double Layer Capacitance (C$_{dl}$) (mF/cm$^2$)</th>
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<td>MnO$_2$@30%C@MnO</td>
<td>560</td>
<td>91</td>
<td>/</td>
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<tr>
<td>α-Mn$<em>{0.9}$Co$</em>{0.1}$O$_2$</td>
<td>690V</td>
<td>120</td>
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<tr>
<td>α-Mn$<em>{0.9}$V$</em>{0.1}$O$_2$</td>
<td>720V</td>
<td>150</td>
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<td>740V</td>
<td>184</td>
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<td>MnO$_2$-NS/Cs$^+$/NS</td>
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<td>101.3</td>
<td>/</td>
<td>[57]</td>
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<tr>
<td>β-MnO$_2$</td>
<td>600</td>
<td>109.3</td>
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</tr>
<tr>
<td>Broken β-MnO$_2$</td>
<td>580</td>
<td>101.5</td>
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<td>α-Mn$_2$O$_3$</td>
<td>1740</td>
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<td>MnO$_3$ NWs</td>
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</tr>
<tr>
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<td>α-MnO$_2$ (9.4 at% Ru)</td>
<td>680</td>
<td>62</td>
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<td>[61]</td>
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<td>MnO@Co-N/C</td>
<td>530</td>
<td>112</td>
<td>/</td>
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<tr>
<td>Nascent δ-MnO$_2$</td>
<td>590</td>
<td>/</td>
<td>/</td>
<td>[63]</td>
</tr>
<tr>
<td>CaMnxOy-400/600</td>
<td>550</td>
<td>/</td>
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<td>[64]</td>
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<tr>
<td>MnO</td>
<td>610</td>
<td>/</td>
<td>/</td>
<td>[65]</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>580</td>
<td>/</td>
<td>/</td>
<td>[65]</td>
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<tr>
<td>Partially oxidized MnO NCs</td>
<td>530</td>
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<td>[66]</td>
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<tr>
<td>CaMn$_x$O$_y$</td>
<td>550</td>
<td>/</td>
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<tr>
<td>MnO$_2$-NWRs/CNTs350</td>
<td>1760</td>
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<td>α-MnO$_2$-NWN</td>
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<td>65.6</td>
<td>4.51</td>
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<td>α-MnO$_2$-NWs</td>
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<td>MnO@rGO</td>
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<td>97</td>
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<td>1D MnO$_2$ nanowires</td>
<td>460</td>
<td>105</td>
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<tr>
<td>MnO$_2$@mpg-C$_3$N$_4$</td>
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<td>90</td>
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4. CONCLUSIONS

A novel MnO$_2$ nanowires@C@MnO nanosheet core-shell heterojunction was successfully constructed by the liquid phase method and thermal treatment. During long-term electrocatalysis, the active sites in the MnO$_2$@C@MnO core-shell heterojunction were fully utilized and the integrity of the active area was maintained. The high specific surface area and mesoporous structure of the MnO$_2$@C@MnO core-shell heterojunction resulted in efficient electrolyte penetration and fast charge transfer, which enhanced the reaction kinetics. The MnO$_2$@20%C@MnO core-shell heterojunction exhibited excellent electrochemical performance for the OER. The optimized MnO$_2$@20%C@MnO had a low overpotential of 520 mV at a current density of 10 mA/cm$^2$ and a small Tafel slope of 66 mV/dec. MnO$_2$@20%C@MnO exhibited moderate stability over 6 h. MnO$_2$@20%C@MnO exhibited excellent OER activity because the introduction of C and the coexistence of nanowires and nanosheets created a large number of active sites and improved the conductivity.

ACKNOWLEDGEMENTS

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References


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