Enhanced Cycleability of Amorphous MnO$_2$ by Covering on $\alpha$-MnO$_2$ Needles in an Electrochemical Capacitor

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Abstract: An allomorph MnO$_2$@MnO$_2$ core-shell nanostructure was developed via a two-step aqueous reaction method. The data analysis of Scanning Electron Microscopy, Transmission Electron Microscopy, X-Ray Diffraction and N$_2$ adsorption-desorption isotherms experiments indicated that this unique architecture consisted of a porous layer of amorphous-MnO$_2$ nano-sheets which were well grown onto the surface of $\alpha$-MnO$_2$ nano-needles. Cyclic voltammetry experiments revealed that the double-layer charging and Faradaic pseudo-capacity of the MnO$_2$@MnO$_2$ capacitor electrode contributed to a specific capacitance of 150.3 F·g$^{-1}$ at a current density of 0.1 A·g$^{-1}$. Long cycle life experiments on the as-prepared MnO$_2$@MnO$_2$ sample showed nearly a 99.3% retention after 5000 cycles at a current density of 2 A·g$^{-1}$. This retention value was found to be significantly higher than those reported for amorphous MnO$_2$-based capacitor electrodes. It was also found that the remarkable cycleability of the MnO$_2$@MnO$_2$ was due to the supporting role of $\alpha$-MnO$_2$ nano-needle core and the outer amorphous MnO$_2$ layer.

Keywords: manganese dioxide; core-shell structure; porous; electrochemical capacitors; long stability

1. Introduction

Electrochemical Capacitors (ECs) have been considered as promising electrochemical Energy Storage Devices (ESDs) due to their inherent advantages, such as high power density, long cycle life, high safety factor and environmentally benign nature [1]. With features complementary to batteries and fuel cells, ECs have been widely used as ESDs in many areas, such as in Smart Grids, Electric Vehicles (EVs) and Fuel Cell power systems [2]. Various transition metal oxides have been studied for ECs because of high capacitance originated of solid-state pseudofaradaic reaction, abundance and environmentally friendly properties. Among them, manganese dioxide (MnO$_2$), a widely used cathode material in battery technologies, has been an attractive material in the area of ECs because of its advantageous properties [3–7]. In comparison to the multiple crystallographic MnO$_2$ forms, amorphous MnO$_2$ has been considered a predominant candidate as an EC electrode material due to its large initial capacity [8–10]. However, due to the poor cycleability of amorphous MnO$_2$, this material has not been extensively used in ECs [11].
On the other hand, core-shell nanostructured MnO₂@MnO₂ can significantly improve the long
cycling stability of MnO₂, i.e., 90% retention after 20,000 cycles at a current density of 5 A·g⁻¹.
The authors found that the superior cycleability of the MnO₂@MnO₂ material was due to the
core-shell nanostructure in which the wire-like ß-MnO₂ core provided a stable structural backbone [12].
Similar findings were recently reported by Ma and co-workers who showed that the α-MnO₂ nanowires
acted as the stable backbone for δ-MnO₂ nano-sheets to form a hierarchical structured composite which
exhibited excellent cycling stability values, e.g., 98.1% retention after 10,000 charge-discharge cycles [13].
Furthermore, the cycling stabilities of both core-shell nanostructured MnO₂@MnO₂ electrodes
are distinctly superior to those reported for other core-shell nanostructures composed of other
transition metal oxides and MnO₂ such as Co₃O₄@MnO₂ [14–16], SnO₂@MnO₂ [17], NiO-MnO₂ [18],
and NiCo₂O₄/MnO₂ [19].

Inspired and excited by the above findings in the literature, we produced a hierarchically
allomorph α-MnO₂@amorphous MnO₂ core-shell structure, in which α-MnO₂ needles were the core
and amorphous MnO₂ nano-sheets the shell. It was found that when the core-shell MnO₂@MnO₂
composite was used as an electrode, well-dispersed amorphous MnO₂ layers on α-MnO₂ needles
allowed a fast, reversible Faradic reaction and enabled ion diffusion (due to the porous nature of
the material). It was observed that a one-dimensional α-MnO₂ needles acted as the backbone which
maintained the structural integrity during the charge-discharge process, thus enhancing the cycling
life of the shell. In addition, its porous feature of amorphous MnO₂ (248.9 m²·g⁻¹) also provided more
contact area with the electrolyte, consequently the active surface was greatly improved. As expected,
our designed α-MnO₂@amorphous MnO₂ hierarchical electrode exhibited a long-term stability during
the cycling tests together with high specific capacitance and rate capability values.

2. Experimental

2.1. Synthesis of α-MnO₂@amorphous MnO₂

All chemical reagents were of high purity AR grade and used as received. The hierarchically
core–shell α-MnO₂@amorphous MnO₂ nanostructure material was synthesized in two steps. In the
first step, α-MnO₂ needles were prepared by a hydrothermal reaction. Twenty milliliters of 8 mmol·L⁻¹
KMnO₄ solution was added into 20 mL of 4 mmol·L⁻¹ MnSO₄ solution with vigorous stirring.
The above solution was topped up to 80 mL with ultra-pure water and then transferred to a 100 mL
Teflon-lined autoclave, and heated at 140 °C for 12 h. Thereafter, the autoclave was allowed to cool to
ambient temperature. The resulting solid product was collected by centrifugation, washed thoroughly
with distilled water and then dried overnight in air at 60 °C. In the second step, the as-synthesized
α-MnO₂ needles were dispersed in 30 mL of 0.41 mmol·L⁻¹ MnSO₄ solution with vigorous stirring.
Subsequently, 20 mL of 0.28 mmol·L⁻¹ KMnO₄ solution was added dropwise to the above solution.
The reaction was maintained for 12 h. After that, the resulting solid product denoted as “MnO₂@MnO₂”
was collected by centrifugation, washed thoroughly with distilled water and then dried overnight in
air at 60 °C. For comparison purposes, amorphous MnO₂ nano-sheets were also prepared in which the
second-step procedure and materials were used but without the addition of the α-MnO₂ needles.

2.2. Characterizations

X-ray diffraction (XRD) was carried out using a Shimadzu XD-3A (Shimadzu, Kyoto, Japan)
fitted with a filtered Cu-Kα radiation (λ = 0.15418 nm) generated at 40 kV and 30 mA. The sorption
isotherms were obtained on a Quantachrome Autosorb-1 volumetric analyzer. Specific surface area
was determined by the Brunauer-Emmett-Teller (BET) method and the Density Functional Theory
(DFT) was used for analyzing the full range of pore size distribution. Scanning Electron Microscopy
(SEM) images were obtained on Carl Zeiss Ultra Plus (Carl Zeiss Microscopy GmbH, Jena, Germany).
Fine structures were analyzed by Transmission Electron Microscopy (TEM) using a JEM-2010 (JEOL
Ltd, Tokyo, Japan) microscope.
2.3. Electrochemical Measurements

Cyclic voltammograms (CV) and galvanostatic charge/discharge experiments were performed to evaluate the electrochemical behaviour of $\alpha$-MnO$_2$@amorphous MnO$_2$ in a three-electrode cell configuration. The working electrode (WE) was fabricated by pasting a homogeneous slurry of $\alpha$-MnO$_2$@amorphous MnO$_2$, carbon black and poly(tetrafluoroethylene) with a mass ratio of 80:10:10 into ethylene glycol, and then the mixture was rolled out to form uniform slices, followed by drying at 80 °C for 6 h. Subsequently, the slices were pressed onto a stainless steel (1 cm $\times$ 1 cm) plate with a tablet press. The amount of electrode material on the electrode was approximately 10 mg.

A three-electrode cell was used for the electrochemical experiments, in which the reference electrode (RE) was an Hg/HgO (1 M KOH) electrode and active carbon is working electrode (WE). The electrolyte was a 1.0 mol·L$^{-1}$ LiOH. CV experiments were performed in the potential range (−0.14 V vs. Hg/HgO and +0.61 V vs. Hg/HgO) (0 to 0.75 V vs. SHE (standard hydrogen electrode)) at different scan rates of 2, 5, 10, 20 and 50 mV·s$^{-1}$ on a CHI 650D electrochemical workstation. Galvanostatic charge/discharge (from −0.14 to 0.61 V vs. Hg/HgO) and cycle life tests were carried out using a Neware Battery Tester (Shenzhen Neware Technology Company, Shenzhen, China). Electrochemical Impedance Spectroscopy (EIS) analyses (Metrohm, Utrecht, The Netherlands) were performed between 10 kHz and 0.01 Hz using a 5 mV RMS sinusoidal modulation at the Open Circuit Potential (OCP).

3. Results and Discussion

In this study, $\alpha$-MnO$_2$ was synthesized in the first step by a hydrothermal process via the following reaction:

$$2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

(1)

The XRD pattern of the material, shown as the black line in Figure 1, displays diffraction peaks characteristics for tetragonal $\alpha$-MnO$_2$ (JCPDS PDF 72-1982) [20]. The products obtained at the second step shown as the red line exhibit two broad diffraction peaks at around 37° and 66°, indicating the amorphous nature of the MnO$_2$ sample [9]. When the amorphous MnO$_2$ grew on the $\alpha$-MnO$_2$, the XRD pattern of MnO$_2$@MnO$_2$ (shown as the blue line) displays the characteristics of the two MnO$_2$ samples, suggesting that the presence of the $\alpha$-MnO$_2$ base did not affect the structure of the amorphous MnO$_2$.

![Figure 1. XRD patterns of MnO$_2$@MnO$_2$, $\alpha$-MnO$_2$ and amorphous MnO$_2$ samples.](image-url)

Figure 2 shows the morphologies of the three samples. It can be observed in Figure 2a that the as-prepared $\alpha$-MnO$_2$ needles have a width of 50–150 nm and a length extending from 1 to 5 μm. The inset of Figure 2a indicates that the needle-like $\alpha$-MnO$_2$ surface is smooth. The SEM image of
MnO$_2$@MnO$_2$ shown in Figure 2b reveals that the length of the needles was kept unchanged. The high resolution SEM image in Figure 2c clearly shows a cotton-like surface, resulting from the uniform growth of amorphous MnO$_2$. Meanwhile, no packed amorphous MnO$_2$ was observed in the space among the needles, indicating that the amorphous MnO$_2$ preferred to cover on the surface of the $\alpha$-MnO$_2$ needles. When the $\alpha$-MnO$_2$ needles were not present, the amorphous MnO$_2$ would aggregate into pompom-like clusters.

![Figure 2. SEM images of: (a) $\alpha$-MnO$_2$ needles; (b,c) MnO$_2$@MnO$_2$; and (d) amorphous MnO$_2$.](image)

Further structural characterizations of the MnO$_2$@MnO$_2$ were carried out by TEM. Figure 3a shows a typical TEM image of the MnO$_2$@MnO$_2$, revealing that the hierarchically nanostructure is constructed by numerous thin nano-sheet “shells” covered on the needle “core”, which is in very good agreement with the SEM observation. From Figure 3b, it was possible to determine a shell thickness of ca. 50 nm. The figure also shows that the shell layer had an open structure with the interconnected nano-sheets creating abundant space. High resolution TEM of the shell in Figure 3c did not display clear lattice fringe, indicating poor crystallinity of the shell, which is in agreement with the XRD results. The EDX pattern, shown in Figure 3d, indicates that MnO$_2$@MnO$_2$ consisted principally of the elements of manganese and oxygen.

![Figure 3. (a-c) TEM images with different magnification; and (d) EDX (Energy-dispersive X-ray) spectrum of MnO$_2$@MnO$_2$.](image)
N₂ adsorption-desorption isotherms of α-MnO₂, MnO₂@MnO₂ and amorphous MnO₂ are shown in Figure 4. From the figure, it can be observed that α-MnO₂ needles displayed type II isotherms according to the IUPAC classification. The isotherms of amorphous MnO₂ could be classified as type IV [21]. A distinct hysteresis loop can also be observed in the larger range of 0.4–1.0 P/P₀ indicating a relatively large pore size [22]. When composite α-MnO₂ needles and amorphous MnO₂ were both present, type III isotherms were observed for MnO₂@MnO₂, which could be the mix of type II and IV isotherms. Their pore size distributions are shown in Figure 4b. As observed, the three samples had micro- and mesopores; and the amount of the pores increased following the sequence of α-MnO₂ < MnO₂@MnO₂ < amorphous MnO₂. The BET specific surface areas of α-MnO₂, MnO₂@MnO₂ and amorphous MnO₂ were found to be 21.2, 54.4 and 248.9 m²·g⁻¹, respectively. The total pore volume values calculated from the total nitrogen adsorption were 0.15, 0.28 and 0.41 cm³·g⁻¹, respectively. The relatively low BET surface area and total pore volume of MnO₂@MnO₂ compared to amorphous MnO₂ can be attributed to the presence of α-MnO₂ in the hierarchical structure.

Figure 4. N₂ adsorption-desorption isotherms (a) and the pore size distribution (b) of α-MnO₂, MnO₂@MnO₂ and amorphous MnO₂.

Electrochemical performance of MnO₂@MnO₂ was firstly studied by Cyclic Voltammetry (CV) in the potential window of (−0.14; +0.61 V (vs. Hg/HgO)). Figure 5 shows cyclic voltammograms recorded at a scan rate of 5 mV·s⁻¹. The figure also shows that all CV curves are “roughly” of symmetric rectangular shapes, typical of pseudo-capacitive behavior, and the redox peak potentials of +0.49 V and +0.44 V vs. Hg/HgO correspond to the reversible Faradaic redox reaction, indicating that the electrode was charged and discharged through the intercalation/deintercalation of Li⁺ into the MnO₂ structure accompanied by the valence conversion of Mn⁴⁺ to Mn³⁺ [23]. This finding also indicates that the capacitance of the three capacitor electrodes consists of the double-layer charging and Faradaic pseudo-capacity. It was found that the voltammetric current response decreased in the following sequence: amorphous MnO₂ > MnO₂@MnO₂ > α-MnO₂, indicating that the capacitance decreased in a similar trend, which could be attributed to a decrease of the BET surface area, leading to a decrease of the double-layer charging.

To further investigate the cyclability of MnO₂@MnO₂, galvanostatic charge/discharge experiments were performed at constant current densities of 0.1 A·g⁻¹ as shown in Figure 6. The figure shows that the three samples exhibited linear variation in potential during the charging/discharging process and had quasi-symmetrical shapes, indicating a clear contribution from the pseudo-capacitive and double layer processes [24]. Based upon the galvanostatic discharge curves, the specific capacitance was calculated according to the following Equation (2):

\[ C = \frac{I\Delta t}{m\Delta V} \]  

(2)

where C (F·g⁻¹) is the specific capacitance, I (mA) is the charge-discharge current, Δt (s) is the discharge time, m (mg) represents the mass of the electrode (active material), and ΔV (V) is the potential drop...
during discharge. The specific capacitance of the $\alpha$-MnO$_2$, MnO$_2$@MnO$_2$ and amorphous MnO$_2$ electrodes were calculated to be 91.2, 150.3 and 247.0 F·g$^{-1}$ respectively. From the data, it can be observed that amorphous MnO$_2$ exhibited the highest specific capacitances, which resulted from the largest surface area among the three samples. This observation is in excellent agreement with other reported findings which state that the use of amorphous MnO$_2$ as EC electrode material exhibits large initial capacity compared to the multiple crystallographic MnO$_2$ forms, as shown in Table 1 [8–10]. It was also found that the specific capacitances of the as-prepared MnO$_2$@MnO$_2$ were larger than isomorphous MnO$_2$@MnO$_2$ electrode (108 F·g$^{-1}$ at 5 A·g$^{-1}$) [12], but smaller than the allomorph MnO$_2$@MnO$_2$ electrode (310.2 F·g$^{-1}$ at 0.5 A·g$^{-1}$) [13]. In addition, it was also observed that the presence of $\alpha$-MnO$_2$ is not favorable for the initial capacity of amorphous MnO$_2$.

**Figure 5.** CV curves of the $\alpha$-MnO$_2$, MnO$_2$@MnO$_2$ and amorphous MnO$_2$ electrodes at scan rate of 5 mV·s$^{-1}$.

**Figure 6.** Charge-discharge behavior of the $\alpha$-MnO$_2$, MnO$_2$@MnO$_2$ and amorphous MnO$_2$ electrodes at current density of 0.1 A·g$^{-1}$. 
Table 1. Comparison of the specific capacitance of as-prepared electrodes to other reported amorphous MnO2 and MnO2@MnO2 electrodes.

| Samples          | [Ref.] | The specific Capacitance (F·g⁻¹) | Electrolyte Type & Concentration | Scan Rate or Current Density |
|------------------|--------|---------------------------------|---------------------------------|-----------------------------|
| Amorphous MnO2   | herein | 247                             | 1.0 M LiOH                       | 0.1 A·g⁻¹                   |
| MnO2@MnO2        | herein | 150                             | 1.0 M LiOH                       | 0.1 A·g⁻¹                   |
| Amorphous MnO2   | [8]    | 242                             | 0.5 M Na₂SO₄                     | 2 mA·cm⁻²                   |
| Amorphous MnO2   | [9]    | 110                             | 2 M NaCl                         | 5 mV·s⁻¹                    |
| Amorphous MnO2   | [10]   | 242                             | 1.0 M Na₂SO₄                     | 2 mV·s⁻¹                    |
| Amorphous MnO2   | [25]   | 79                              | 1.0 M Na₂SO₄                     | 1 A·g⁻¹                     |
| MnO2@MnO2        | [12]   | 108                             | 0.5 M Na₂SO₄                     | 5 A·g⁻¹                     |
| MnO2@MnO2        | [13]   | 310                             | 6.0 M KOH                        | 0.5 A·g⁻¹                   |

To evaluate the cyclic stability of the MnO2@MnO2 electrode, galvanostatic charge/discharge tests were performed at a current density of 2 A·g⁻¹. As shown in Figure 7, after 5000 cycles, the specific capacitance retention of the α-MnO₂, MnO2@MnO2 and amorphous MnO2 electrode remained 99.1%, 99.3% and 77.4% of their initial capacity respectively, indicating a good cyclic stability for α-MnO₂ and MnO2@MnO2. As seen in the inset, the comparison of the charge-discharge curves of MnO2@MnO2 between the first (1st) and the eighth (8th) cycles indicates that the curves are very stable, further emphasizing the long-term stability of MnO2@MnO2. In addition, it was found that the retention of MnO2@MnO2 after 5000 cycles was higher than that of many MnO2-based composite electrodes [14,26–29]. This finding clearly demonstrates that the presence of α-MnO₂ needles can efficiently improve the cycleability of amorphous MnO₂.

![Figure 7. Cyclic stability of the three electrodes in a 1 mol·L⁻¹ LiOH electrolyte measured using the galvanostatic charge-discharge technique at a current density of 2 A·g⁻¹.](image)

Rate capability testing of MnO2@MnO2 was evaluated at current densities ranging from 0.1 A·g⁻¹ to 5 A·g⁻¹. Figure 8 shows that the specific capacitance decreased as the current density increased, standard finding which is in good agreement with reported literature on MnO₂-based hybrids. From 0.1 A·g⁻¹ to 5 A·g⁻¹, the specific capacitances of MnO2@MnO2 decreased from 150.3 F·g⁻¹ to 58.4 F·g⁻¹, corresponding to a 38.9% retention of its initial capacitance. The decreasing trend of the capacitance indicates that some parts of the MnO2@MnO2 structure are inaccessible for the intercalation
of Li\textsuperscript{+} ions at high current density. Compared to some reported MnO\textsubscript{2}-based capacitor electrodes [5,30], the rate capability of as-prepared MnO\textsubscript{2}@MnO\textsubscript{2} is comparable, which could be ascribed to its unique structure, namely the outer porous structure act as a continuous pathway for the diffusion of electrolyte, which can shorten solid state transport distances for ions into the MnO\textsubscript{2} structure.

![Graph](image_url)

**Figure 8.** (a) Galvanostatic charge-discharge curves of the MnO\textsubscript{2}@MnO\textsubscript{2} electrode at different current densities of 0.1, 0.5, 1 and 5 A·g\textsuperscript{-1}, respectively; and (b) variation in specific capacitance with current density obtained based on Figure 8a.

To elucidate the causes behind the difference in capacitance among the three electrodes, EIS experiments were performed. *Nyquist* plots of the three electrodes were generated. Figure 9 displays: (i) semicircles located at the high frequency region which could be related to the charge transfer process at the electrode/electrolyte interface; and (ii) straight lines at the low frequency region possibly ascribed to the ion diffusion process in the bulk of the active mass. It can also be seen in Figure 9 that the semicircles decrease in the sequence of: amorphous MnO\textsubscript{2}, MnO\textsubscript{2}@MnO\textsubscript{2}, and α-MnO\textsubscript{2}, suggesting that the charge transfer resistance decreases from amorphous MnO\textsubscript{2} to α-MnO\textsubscript{2}. It may be observed that the linear slope of amorphous MnO\textsubscript{2} is larger than that of MnO\textsubscript{2}@MnO\textsubscript{2} and α-MnO\textsubscript{2}, suggesting that the ion diffusion resistance for amorphous MnO\textsubscript{2} is lower than MnO\textsubscript{2}@MnO\textsubscript{2} and α-MnO\textsubscript{2}. These results indicate that the charge transfer resistance of amorphous MnO\textsubscript{2} can lead to improved capacitor by mixing with α-MnO\textsubscript{2} needles, but the ion diffusion resistance is increased, which could be attributed to the large different of the porous structure between the amorphous MnO\textsubscript{2} and the α-MnO\textsubscript{2} needles.

![Graph](image_url)

**Figure 9.** *Nyquist* plots of the electrochemical impedance spectroscopy for the three electrodes.
4. Conclusions

A hierarchical $\alpha$-MnO$_2$ nano-needles@amorphous MnO$_2$ thin nano-sheet core-shell nanostructure was fabricated by a two-step aqueous reaction method. As an electrode for pseudo-capacitors, at a current density of 0.1 A·g$^{-1}$, the constructed MnO$_2$@MnO$_2$ exhibited a promising specific capacitance of 150.3 F·g$^{-1}$, which consisted of the double-layer charging and Faradaic pseudo-capacity. Importantly, nearly 99.3% retention after 5000 cycles at a current density of 2 A·g$^{-1}$ was found. Such intriguing electrochemical properties may be attributed to the hierarchically allomorphs core-shell configuration, in which 1D MnO$_2$ nano-needle core acted as a stable structural backbone and 2D amorphous MnO$_2$ provided a large surface area and more active sites. Thus, the fabricated MnO$_2$@MnO$_2$ electrode material with a unique hierarchically allomorphs core-shell architecture are promising candidate material for high-cycleability in Energy Storage Devices.

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References

1. Jiang, R.; Huang, T.; Liu, J.; Zhuang, J.; Yu, A. A novel method to prepare nanostructured manganese dioxide and its electrochemical properties as a supercapacitor electrode. *Electrochim. Acta* **2009**, *54*, 3047–3052. [CrossRef]

2. Wang, J.-G.; Yang, Y.; Huang, Z.-H.; Kang, F. Interfacial synthesis of mesoporous MnO$_2$/polyaniline hollow spheres and their application in electrochemical capacitors. *J. Power Sources* **2012**, *204*, 236–243. [CrossRef]

3. Li, S.-H.; Liu, Q.-H.; Qi, L.; Lu, L.-H.; Wang, H.-Y. Progress in research on manganese dioxide electrode materials for electrochemical capacitors. *Chin. J. Anal. Chem.* **2012**, *40*, 339–346. [CrossRef]

4. Toupin, M.; Brousse, T.; Be’langer, D. Influence of microstucture on the charge storage properties of chemically synthesized manganese dioxide. *Chem. Mater.* **2002**, *14*, 3946–3952. [CrossRef]

5. Wang, R.; Ma, Y.; Wang, H.; Key, J.; Brett, D.; Ji, S.; Yin, S.; Shen, P.K. A cost effective, highly porous, manganese oxide/carbon supercapacitor material with high rate capability. *J. Mater. Chem. A* **2016**, *4*, 5390–5394. [CrossRef]

6. Minakshi, M.; Mitchell, D.R.G.; Prince, K. Incorporation of TiB$_2$ additive into MnO$_2$ cathode and its influence on rechargeability in an aqueous battery system. *Solid State Ion.* **2008**, *179*, 355–361. [CrossRef]

7. Minakshi, M. Examining manganese dioxide electrode in KOH electrolyte using TEM technique. *J. Electroanal. Chem.* **2008**, *616*, 99–106. [CrossRef]

8. Bao, S.-J.; He, B.-L.; Liang, Y.-Y.; Zhou, W.-J.; Li, H.-L. Synthesis and electrochemical characterization of amorphous MnO$_2$ for electrochemical capacitor. *Mater. Sci. Eng. A* **2005**, *397*, 305–309. [CrossRef]

9. Reddy, R.N.; Reddy, R.G. Synthesis and electrochemical characterization of amorphous MnO$_2$ electrochemical capacitor electrode material. *J. Power Sources* **2004**, *132*, 315–320. [CrossRef]

10. Xu, C.; Li, B.; Du, H.; Kang, F.; Zeng, Y. Supercapacitive studies on amorphous MnO$_2$ in mild solutions. *J. Power Sources* **2008**, *184*, 691–694. [CrossRef]

11. Zhan, H.; Zhou, Y.H.; Wang, C.G.; Guo, W.Y.; Peng, Z.H. Improved electrochemical performance of amorphous MnO$_2$ modified by a novel supermolecular compound. *Mater. Chem. Phys.* **2005**, *90*, 353–360. [CrossRef]

12. Shao, J.; Zhou, X.; Liu, Q.; Zou, R.; Li, W.; Yang, J.; Hu, J. Mechanism analysis of the capacitance contributions and ultralong cycling-stability of the isomorphous MnO$_2$@MnO$_2$ core/shell nanostructures for supercapacitors. *J. Mater. Chem. A* **2015**, *3*, 6168–6176. [CrossRef]

13. Ma, Z.; Shao, G.; Fan, Y.; Wang, G.; Song, J.; Shen, D. Construction of hierarchical $\alpha$-MnO$_2$ Nanowires@Ultradthin $\delta$-MnO$_2$ nanosheets core-shell nanostructure with excellent cycling stability for high-power asymmetric supercapacitor electrodes. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9050–9058. [CrossRef] [PubMed]
14. Huang, M.; Zhang, Y.; Li, F.; Zhang, L.; Wen, Z.; Liu, Q. Facile synthesis of hierarchical Co$_3$O$_4$@MnO$_2$ core-shell arrays on Ni foam for asymmetric supercapacitors. *J. Power Sources* 2014, 252, 98–106. [CrossRef]

15. Yang, W.; Gao, Z.; Ma, J.; Zhang, X.; Wang, J. Controlled synthesis of Co$_3$O$_4$ and Co$_3$O$_4$@MnO$_2$ nanoarchitectures and their electrochemical capacitor application. *J. Alloys Compd.* 2014, 611, 171–178. [CrossRef]

16. Wang, K.; Shi, Z.; Wang, Y.; Ye, Z.; Xia, H.; Liu, G.; Qiao, G. Co$_3$O$_4$ nanowires@MnO$_2$ nanolayer or nanoflakes core-shell arrays for high-performance supercapacitors: The influence of morphology on performance. *J. Alloys Compd.* 2015, 624, 85–93. [CrossRef]

17. Yan, J.; Khoo, E.; Sumboja, A.; Lee, P.S. Facile coating of manganese oxide on tin oxide nanowires with high-performance capacitive behavior. *ACS Nano* 2010, 4, 4247–4255. [CrossRef] [PubMed]

18. Liu, J.; Jiang, J.; Bosman, M.; Fan, H.J. Three-dimensional tubular arrays of MnO$_2$–NiO nanoflakes with high areal pseudocapacitance. *J. Mater. Chem.* 2012, 22, 2419–2426. [CrossRef]

19. Yu, L.; Zhang, G.; Yuan, C.; Lou, X.W.D. Hierarchical NiCo$_2$O$_4$@MnO$_2$ core-shell heterostructured nanowire arrays on Ni foam as high-performance supercapacitor electrodes. *Chem. Commun.* 2013, 49, 137–139. [CrossRef] [PubMed]

20. Ma, Y.; Wang, R.; Wang, H.; Key, J.; Ji, S. Control of MnO$_2$ nanocrystal shape from tremella to nanobelts for enhancement of the oxygen reduction reaction activity. *J. Power Sources* 2015, 280, 526–532. [CrossRef]

21. Brunauer, S.; Demine, L.S.; Deming, W.E.; Teller, E. On a theory of the van der Waals adsorption of gases. *J. Am. Chem. Soc.* 1940, 62, 1723–1732. [CrossRef]

22. Zhou, T.; Wang, H.; Ji, S.; Linkov, V.; Wang, R. Soybean-derived mesoporous carbon as an effective catalyst support for electrooxidation of methanol. *J. Power Sources* 2014, 248, 427–433. [CrossRef]

23. Qu, Q.; Zhang, P.; Wang, B.; Chen, Y.; Tian, S.; Wu, Y.; Holze, R. Electrochemical performance of MnO$_2$ nanorods in neutral aqueous electrolytes as a cathode for asymmetric supercapacitors. *J. Phys. Chem. C* 2009, 113, 14020–14027. [CrossRef]

24. Sodtipinta, J.; Pon-On, W.; Veerasai, W.; Smith, S.M.; Pakawatpanurut, P. Chelating agent- and surfactant-assisted synthesis of manganese oxide/carbon nanotube composite for electrochemical capacitors. *Mater. Res. Bull.* 2013, 48, 1204–1212. [CrossRef]

25. Pang, M.; Long, G.; Jiang, S.; Ji, Y.; Han, W.; Wang, B.; Liu, X.; Xi, Y. Rapid synthesis of graphene/amorphous α-MnO$_2$ composite with enhanced electrochemical performance for electrochemical capacitor. *Mater. Sci. Eng. B* 2015, 194, 41–47. [CrossRef]

26. Zhao, Y.; Meng, Y.; Jiang, P. Carbon@MnO$_2$ core-shell nanospheres for flexible high-performance supercapacitor electrode materials. *J. Power Sources* 2014, 259, 219–226. [CrossRef]

27. Han, D.; Jing, X.; Xu, P.; Ding, Y.; Liu, J. Facile synthesis of hierarchical hollow ε-MnO$_2$ spheres and their application in supercapacitor electrodes. *J. Solid State Chem.* 2014, 218, 178–183. [CrossRef]

28. Lee, T.T.; Hong, J.R.; Lin, W.C.; Hu, C.C.; Wu, P.W.; Li, Y.Y. Synthesis of petal-like carbon Nanocapsule@MnO$_2$ core-shell particles and their application in supercapacitors. *J. Electrochem. Soc.* 2014, 161, H598–H605. [CrossRef]

29. Min, S.; Zhao, C.; Zhang, Z.; Wang, K.; Chen, G.; Qian, X.; Guo, Z. Hydrothermal growth of MnO$_2$/RGO/Ni(OH)$_2$ on nickel foam with superior supercapacitor performance. *RSC Adv.* 2015, 5, 62571–62576. [CrossRef]

30. Ren, Q.; Wang, R.; Wang, H.; Key, J.; Brett, D.J.L.; Ji, S.; Yin, S.; Shen, P.K. Ranunculus flower-like Ni(OH)$_2$@Mn$_2$O$_3$ as a high specific capacitance cathode material for alkaline supercapacitors. *J. Mater. Chem. A* 2016, 4, 7591–7595. [CrossRef]