Three dimensional manganese oxide on carbon nanotube hydrogels for asymmetric supercapacitors†

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In this article, we report the development of manganese oxide (Mn$_3$O$_4$) on carbon nanotube (CNT) hydrogels as binder-free electrodes for asymmetric supercapacitors. The CNT hydrogels consisting of three dimensionally inter-connected nanotubes are prepared via a facile sol–gel method. Afterwards, flower-like Mn$_3$O$_4$ is incorporated into CNT hydrogels using a pulse electrochemical deposition. Satisfactory electrochemical performance with a high specific capacitance of 182 F g$^{-1}$ (473 mF cm$^{-2}$) is achieved. When employing activated carbon as negative electrodes, the assembled asymmetric supercapacitor exhibits a high potential window of 2 V to reach a specific energy of 26.6 W h kg$^{-1}$ and a specific power of 5.2 kW kg$^{-1}$. These results are much better compared with the results from pure Mn$_3$O$_4$. The remarkable performance of our composites can be ascribed to a highly conducting CNT micro-scaffold and pseudocapacitive Mn$_3$O$_4$.

1. Introduction

The current global economy heavily relies on the consumption of traditional fossil fuels such as coal and petroleum. However, these non-renewable sources are expected to be depleted by the end of this century. Besides that, the combustion of fossil fuels exacerbates global warming by emitting large amounts of greenhouse gases. To address these challenges, various renewable energy sources such as solar, wind and geothermal energy have been explored. Their power output, however, naturally fluctuates under diverse environmental situations, which increases the difficulty of an effective energy harvest. In the light of this, electrochemical energy storage (EES) units are essential for better energy balance and coordination. Among various storage devices such as batteries and fuel cells, supercapacitors have drawn great attentions due to their moderate power and energy density.

Supercapacitors can be categorized into electrochemical double layer capacitor (EDLC) and pseudocapacitor based on two different working mechanisms. The first one takes an advantage of an electrochemical double layer formed at the electrode/electrolyte interface to store energy, while the second one utilizes fast redox chemical reactions. For its resemblance to capacitors, the second category is named as ‘pseudocapacitors’. Various types of activated carbon (AC) have been extensively investigated as electrode materials for EDLC due to their high surface area. Regardless of possessing ultrahigh cycling stability, AC suffers from a low specific capacitance. On the other hand, metal oxides/hydroxides and conducting polymers are widely used as pseudocapacitive materials because of their large theoretical capacitances. Nevertheless, the poor cycling life and compromised power performance greatly limit their future development. Therefore, it is essential to develop versatile composites to combine the merits of EDLC and pseudocapacitive materials.

Carbon nanotubes (CNTs), being the one-dimensional carbon allotrope with fantastic intrinsic properties, are widely used as a conductivity strengthening phase in composite design. To date, Ni(OH)$_2$/CNT, MnO$_2$/CNT, Co$_3$O$_4$/CNT and NiCo$_2$O$_4$/CNT composite materials have been thoroughly investigated as supercapacitor electrode materials. Synthesized from the traditional routines, these composites exist in form of powders in which additional polymer binders have to be used for electrode fabrication. It is believed that the insulating nature of these polymer binders greatly hinders material performance. In order to overcome this problem, binder-free CNT composites with three-dimensional (3D) architectures have been proposed. Generally, nickel and copper metal foams are used as the macro-scaffolds to grow CNTs, followed by incorporating pseudocapacitive materials into their 3D structure.

Tang et al. grew CNT on the nickel foam via chemical vapor deposition (CVD) and then successively synthesized Ni(OH)$_2$ on the nanotubes using a chemical bath deposition. As a result, a core/shell structure with ultrahigh capacitance (3300 F g$^{-1}$).
has been achieved. Similar methods have been used by Wu et al. to prepare 3D nickel cobalt oxide NiCoO2/CNT nanostructure. However, these methods only form a thin CNT film on nickel scaffold, leading to a small mass loading. By proper coating of these empty macro-pores, electrochemical performance of the supercapacitors can be further improved. From this perspective, Bryning et al. applied a sol–gel method to grow 3D CNT gels without using any metal foams thereby reached high porosity and electrical conductivity. Unfortunately, these CNT gels suffered from low mechanical rigidity. Previously, we developed the Ni(OH)2/CNT gels in which CNTs were used as a micro-scaffold and the nickel foam was used as a macro-scaffold. Compared with the Ni(OH)2, Mn3O4 has a larger potential window, better cycling stability and higher natural abundance and, thus, can serve as an ideal candidate for supercapacitor applications.

In this work, we successfully developed Mn3O4/CNT hydrogels using a pulse electrochemical deposition method. The composite has achieved a balanced gravimetric capacitance of 182 F g\(^{-1}\) based on the total mass of the composite and areal capacitance of 473 mF cm\(^{-2}\) based on the geometric area of electrode. When using commercial AC as negative electrode material, the asymmetric supercapacitor can reach a stable potential as large as 2 V. It is found that a high specific energy of 26.6 Wh kg\(^{-1}\) and specific power of 5.2 kW kg\(^{-1}\) can be realized. To the best of our knowledge, it is the first application of the 3D CNT hydrogel with Mn3O4 for supercapacitors.

2. Experimental section

2.1 Materials

CNTs (single-walled) composed of one third metallic and two thirds of semiconducting nanotubes were obtained from Chengdu Organic Chemicals Co Ltd. Manganese acetate tetra-hydrate (Mn(CH\(_3\)COO)\(_2\)·4H\(_2\)O), sodium dodecylbenzene sulfonate (SDBS), activated carbon (AC) and sodium sulfate (Na\(_2\)SO\(_4\)) were purchased from Sigma-Aldrich. Absolute ethanol and hydrochloric acid (HCl 37%) were obtained from Merck Pte Ltd. Nickel foams with thickness of 1.2 mm were bought from MTI Co. CNTs were purified by immersing into diluted HCl solution before use. Other chemicals were directly used without further purification.

2.2 Synthesis

Firstly, homogeneous dispersion consisting of CNTs (3 mg mL\(^{-1}\)) and SDBS (15 mg mL\(^{-1}\)) was prepared using probe sonication (60 W) for 30 min followed by 30 min bath sonication. Afterwards, cleaned nickel foams with area of 1 × 1 cm\(^2\) were immersed in the as-prepared CNT dispersion under sonication for 10 min. Next, the CNT-coated nickel foams underwent aging for two days to form inter-connected CNT hydrogels (nanotube micro-scaffolds). The prepared hydrogels were subsequently washed using copious deionized (DI) water for a week to remove remaining surfactants. To obtain the Mn3O4/CNT hybrid hydrogels, plating solution consisting of 100 mM Na\(_2\)SO\(_4\) and 10 mM Mn(CH\(_3\)COO)\(_2\) was prepared in advance. The CNT hydrogels were immersed in the plating solution for 2 h to exchange the water inside with plating solutions. Next, pulse electrochemical deposition was carried out under a current of 2 mA cm\(^{-2}\) with an ON/OFF ratio of 10 s/20 s. After 150 cycles of deposition, the Mn\(_3\)O\(_4\)/CNT hydrogels were washed with DI water and stored in water overnight. For characterizations, the Mn3O4/CNT hydrogels were dried using critical carbon dioxide to maintain their original structure. Typically, the mass loadings of the CNT were 0.3–0.5 mg cm\(^{-2}\) and those of composites were in range of 2.2–2.6 mg cm\(^{-2}\). For comparison, pure Mn3O4 was also deposited directly on the nickel foam based on the same protocols in the absence of CNTs.

2.3 Characterizations

The crystal structure of the Mn3O4/CNTs aerogels was determined by the X-ray diffraclactometer (XRD Shimazu 6000) with Cu K\(_\alpha\) radiation. Sample morphology was investigated using the field emission scanning microscopy (FESEM Hitachi S4300). Transmission electron microscopy (TEM) analysis together with selected area electron diffraction (SAED) was performed on the JEOI 2010 transmission electron microscope for further investigation of the sample microstructures.

2.4 Electrochemical measurements

For electrochemical tests with three-electrode configuration, as-prepared Mn3O4/CNT composites were directly used as the working electrodes. Platinum (1 × 1 cm\(^2\) in area) and saturated calomel electrode (SCE) were selected as the counter and reference electrodes, respectively. For the assembly of asymmetric supercapacitor, AC was used as the negative electrodes and Mn3O4 or Mn3O4/CNT hydrogel was used as the positive electrodes. The mass ratio between AC and Mn3O4/CNT was 2 : 1 and the ratio between the AC and Mn3O4 was 3 : 2 based on charge balance. The asymmetric cells were assembled in swagelok cells with porous cellulose membrane as separators. All electrochemical measurements were carried out in 0.5 M Na\(_2\)SO\(_4\) electrolyte. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were conducted on the Solartron 1287 electrochemical workstation. Calculations of the specific capacitance, specific energy and specific power were based on followed equations:\(^{35}\)

\[ C_s = \frac{\int i dV}{2m \Delta V} \]  \hspace{1cm} (1)

\[ C_s = \frac{\int i \Delta t}{m \Delta V} \]  \hspace{1cm} (2)

\[ E = \frac{1}{2} C_s \Delta V^2 \times \frac{1000}{3600} \]  \hspace{1cm} (3)

\[ P = \frac{E}{\Delta t} \times 3600 \]  \hspace{1cm} (4)

where \( C_s \) is the specific capacitance (F g\(^{-1}\)), \( I \) is the current (A), \( V \) is the scan rate (V s\(^{-1}\)) in CV tests, \( \Delta V \) is the potential window...
(V), $\Delta t$ is the discharge time (s), $E$ is the specific energy (W h kg$^{-1}$) and $P$ is the specific power (W kg$^{-1}$). For asymmetric supercapacitor tests, $m$ is the total mass (g) of AC and composites on both electrodes.

3. Results and discussions

3.1 Structures and morphologies

The hydrogel composites are synthesized according to the procedure illustrated in Fig. 1. The CNT dispersion undergoes the stage of gelation in ambient atmosphere for two days to form the inter-connected structure, which is reported in our previous work.$^{31}$ The formation of the CNT 3D network is caused by the strong van der Waals interactions between nanotubes. When placing the CNT hydrogel at the anode for deposition, manganese ions dissolved in water were oxidized under the positive voltage to give Mn$_3$O$_4$ precipitation at the CNT hydrogels described by following equation:$^{34}$

$$4H_2O + 3Mn^{2+} = Mn_3O_4 + 2e^- + 8H^+ \quad (5)$$

Different from the galvanostatic or potentiostatic deposition, we apply a pulse deposition technique to tune Mn$_3$O$_4$ properties (Fig. S1†). During the “ON” period, the Mn$_3$O$_4$ are grown on the CNTs under a constant current. At the “OFF” stage, the current is set to zero to facilitate the ion diffusion from the central plating solution, considering the large thickness of the prepared hydrogels. As a result, morphology can be carefully controlled to avoid any unwanted agglomerations of active materials.

Fig. 2 presents morphology of the Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT composites. Without the 3D inter-connected CNT networks, Mn$_3$O$_4$ merely stay at the surface of nickel foam, leaving majority of the macro-pores in the nickel foams unoccupied (Fig. 2a). With high magnification shown in Fig. 2b, we can see that the Mn$_3$O$_4$ is composed of severely stacked nanoparticles. This kind of agglomerations will not only hinder the ion diffusion but also extend the electron pathways, leading to poor electrochemical performance.$^{35}$ For the pristine CNT hydrogels deposited inside the nickel foam, they presented a network consisting of bundled nanotubes (Fig. S2†), which also can be found in our previous report.$^{31}$ While for the Mn$_3$O$_4$/CNT, the hydrogel fully occupies the macro-pores inside the nickel foams (Fig. 2c). In this architecture, CNT hydrogel serves as a micro-scaffold for electron transport and Mn$_3$O$_4$ plays a role of capacitance enhancer. The CNT micro-scaffold and Mn$_3$O$_4$ with higher magnification can be seen in the Fig. 2d. The CNT micro-scaffold presents the three-dimensional (3D) random inter-connected structure with homogeneously deposited Mn$_3$O$_4$ nano-flowers with a typical size of 300–400 nm. The flower-like Mn$_3$O$_4$ morphology can be ascribed to a controlled pulse deposition method in which Mn$_3$O$_4$ replicates the CNT patterns. The high transparency of Mn$_3$O$_4$ also indicates their ultrathin nature. The mesopores woven from CNTs are believed to effectively facilitate the ion diffusion process and boost the device performance. It is also worth noting that the CNT hydrogel not only fill the macro pores inside the nickel foam but also cover the nickel foam backbones as thin layers (Fig. S3†). As a result, CNTs are inclined to grow on nanotubes both inside nickel foam and on nickel foam backbone surface.

More detailed micro-structure information of materials is investigated by TEM. For the nickel foam directly coated with Mn$_3$O$_4$ (Fig. 3a), manganese oxide phase consists of aggregated secondary particles with an average size around 50 nm. For the Mn$_3$O$_4$/CNT composite (Fig. 3b), we see that nanotubes form several bundles with a diameter around 10 nm, composing a micro-scaffold. The bundling of CNTs is probably caused by capillary force during the gelation period. This kind of micro-scaffold not only will improve the electrical conductivity of the electrode materials but also be effective in preventing Mn$_3$O$_4$ aggregation. Moreover, Mn$_3$O$_4$ is presented as the ultrathin flakes in the composite indicated by their curled peripheral edges. From the SAED images in Fig. 3c and d, the diffraction patterns can be ascribed to (103), (004), (224) crystal planes of Mn$_3$O$_4$ (JCPDS no. 18-0803). No diffraction pattern from CNTs is found due to their low content in the composite.

Typical XRD patterns of the pure Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT hydrogel composite are presented in Fig. S4† Three main peaks coming from the nickel foam can be easily identified. With a careful observation, peaks located at 34.7°, 39.1° can be ascribed to the tetragonal-phase Mn$_3$O$_4$. Compared with peaks from the nickel foam, the Mn$_3$O$_4$ peaks have much smaller intensity, which might be attributable to two aspects. One possible reason is that the hydrogels have a low density, making

![Fig. 1 Schematic illustration of preparation of the Mn$_3$O$_4$/CNT composite.](Image)
them highly transparent to the X-rays. The other possible reason is the poor crystallinity of Mn$_3$O$_4$, which is synthesized at room temperature. The composition of the samples are also confirmed by the energy-dispersive X-ray spectroscopy (EDX) in which the atomic ratios between manganese and oxygen are closed to 3 : 4 (Fig. S5 and S6†).

3.2 Electrochemical performances

Fig. 4 presents the electrochemical performance of the Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT composites tested with three-electrode configuration. Fig. 4a displays the CV curves of the Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT at 5 mV s$^{-1}$. Compared with the Mn$_3$O$_4$, our developed 3D hydrogel composite exhibits a larger enclosed area, suggesting a higher specific capacitance. A pair of anodic/cathodic peaks of Mn$_3$O$_4$/CNT is found at 0.62 and 0.47 V, respectively, due to the redox nature of Mn$_3$O$_4$. We interestingly find this pair of peak does not appear in the pure Mn$_3$O$_4$ because of a large resistance in the absence of the conductive CNTs. CV curves at different scan rates from 5 to 100 mV s$^{-1}$ of the Mn$_3$O$_4$/CNT are given in Fig. 4b. A mirror-image feature demonstrates a good reversibility of the electrode materials. Contributed to high electrical conductivity of the 3D CNT structure, the CV loop still maintains almost a rectangular shape at a high scan rate of 100 mV s$^{-1}$. The calculated specific capacitances are 182 at 2 mV s$^{-1}$ and 91 F g$^{-1}$ at 100 mV s$^{-1}$, respectively. It is worth noting that the specific capacitances of manganese oxides are strongly related to the thickness of the materials. Depositing thin layer material can dramatically improve the gravimetric capacitance. Unfortunately, this strategy usually results in an ultralow areal and volumetric capacitance, limiting the application of materials. For example, specific capacitances of more than 200 F g$^{-1}$ have been reported for Mn$_3$O$_4$ previously, they either calculated capacitance merely based on Mn$_3$O$_4$ or applied a strategy on a basis of ultralow mass loading (<1 mg cm$^{-2}$) of active materials, suffering a low areal capacitance. Nevertheless, for our composite, due to a large mass loading over ~2 mg cm$^{-2}$, high areal capacitance of 400 mF cm$^{-2}$ can be reached (Fig. S7†). For our composites, the main roles of the CNTs in this composite are to enhance the conductivity and prevent Mn$_3$O$_4$ agglomeration, instead of the capacitance provider. GCD curves above of Mn$_3$O$_4$/CNT with different specific currents from 0.38 to 19.22 A g$^{-1}$ are given in the Fig. 4c. The near-linear charge and discharge curves with negligible curvature reflect ideal capacitor behaviour. As seen in Fig. 4d, in contrast to pure Mn$_3$O$_4$ materials, the Mn$_3$O$_4$/CNT composite not only presents a higher capacitance at low discharge rate but also a good retention (71.6%) at high discharge rate.

The cycling performance of the Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT are shown in Fig. 4e. Mn$_3$O$_4$/CNT presents a gradual capacitance drop to 1000th cycles with a final retention of 68.9%. For Mn$_3$O$_4$, a sharp capacitance drop is found after the initial activation capacitance. Then the specific capacitance keeps stable at about 80 F g$^{-1}$. The final specific capacitance is only 61.7% of the stable capacitance. Fig. 4f shows the EIS results of the Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT composite. Based on the embedded equivalent circuit, the equivalent series resistances (ESR) of Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT are 1.95 and 1.41 ohm, which represent the internal resistance of electrode, electrolyte and connecting
wires. The smaller ESR of the Mn$_3$O$_4$ is attributable to the good host/guest materials interface between CNTs and Mn$_3$O$_4$, which effectively facilitates the electron transport process.

Considering a scalable production, AC is chosen as the negative electrode material to assemble an asymmetric supercapacitor. The CV curves at 30 mV s$^{-1}$ of negative (AC) and positive (Mn$_3$O$_4$/CNT) electrode are presented in Fig. 5a. The AC processes a working potential ranging from −1 to 0 V and at the same time the Mn$_3$O$_4$/CNT hydrogel can successfully work within a potential range of 0−1 V. Therefore, the potential window of the asymmetric supercapacitor should be around 2 V. In order to demonstrate this estimation, CV tests of Mn$_3$O$_4$/CNT based asymmetric supercapacitor are carried out as given in the Fig. 5b. Rectangular loops can be observed with a potential window extending from 1 to 2 V, suggesting a good stability under higher potential. The larger working potential range also increased specific capacitance, indicated by a current increasing. The improved electrochemical performance under higher potential is related to the deeper activated Mn$_3$O$_4$. The GCD profiles of asymmetric supercapacitors using Mn$_3$O$_4$/CNT composites are displayed in Fig. 5c. A potential as high as 2 V can be guaranteed at the discharge rate from 0.5 to 10 A g$^{-1}$. Higher specific capacitance of Mn$_3$O$_4$/CNT compared with Mn$_3$O$_4$ benefits from the better electrochemical performance of positive electrode (Fig. 5d).

The cycling stability of two kinds of the asymmetric supercapacitors is shown in Fig. 6a. Initial activations are found for both Mn$_3$O$_4$ and Mn$_3$O$_4$/CNT which are associated with the electrolyte infiltration. After the short activation process, the Mn$_3$O$_4$/CNT composite could reach a stable specific capacitance above 25 F g$^{-1}$ and achieved a good retention of 103.9% after 1000th cycling. While for Mn$_3$O$_4$, only 84.0% of original capacitance is reserved. It is interesting to find there is a discrepancy of cycling stability tested with two-electrode and three-electrode configuration. We propose there two reasons to explain. Firstly, in three-electrode configuration, the composite was connected to the electrical wire using a simple conducting alligator and there is no other external force between the testing material and outer circuit. As a result, the any kind of fracture of materials due to cycling will directly drop into the electrolyte, causing the capacitance degradation. While in two-electrode configuration, the negative electrode, separator and positive electrodes were assembled in a swagelok cell. Under a tightening force from screw thread, even the fractured material is still in contact with the nickel foam, leading to a better cycling stability. Secondly, though the three-electrode cell was sealed using paraffin during the cycling performance, the sealing capability is not as good as ones with swagelok cell. Thus the degradation of the electrolyte might cause the cycling drop. To understand the power and energy performance of the assembled asymmetric supercapacitors, Ragone plot is given in Fig. 6b. High specific energy of 26.6 W h kg$^{-1}$ and 5.6 kW kg$^{-1}$ are achieved for Mn$_3$O$_4$/CNT, which is better than the pure Mn$_3$O$_4$ and other related reports.

To further reveal the degradation mechanism of the electrode materials, we have characterized our sample using FESEM after cycling tests (Fig. 7). As can be seen in Fig. 7a, a large number of the tiny surface agglomerations have been observed for Mn$_3$O$_4$. The large surface changes compared to the pristine Mn$_3$O$_4$ can be attributed to the structural changes from surficial ion intercalation in the long term cycling test. For the Mn$_3$O$_4$/CNT composite (Fig. 7b), we can also observe morphology changes with bundled CNTs. This kind of morphology evolution is responsible for the capacitance degradation after activation period (~100th cycle). However, due to the electron pathways established by CNTs and the ultrathin nature of Mn$_3$O$_4$, the composite is still capable to maintain its majority of its original capacitance.

![Fig. 5](image_url)  
**Fig. 5** Electrochemical performance of the asymmetric supercapacitor: (a) comparative CV of AC (black) and the Mn$_3$O$_4$/CNT hydrogel (red) at 30 mV s$^{-1}$, (b) CV of the asymmetric supercapacitor measured at different potentials at 30 mV s$^{-1}$, (c) GCD curves of the asymmetric supercapacitor at different current densities, and (d) specific capacitances from GCD tests.

![Fig. 6](image_url)  
**Fig. 6** (a) Cycling stability and (b) Ragone plot of asymmetric supercapacitors.

![Fig. 7](image_url)  
**Fig. 7** FESEM images of (a) Mn$_3$O$_4$ and (b) the Mn$_3$O$_4$/CNT hydrogel after cycling.
4. Conclusions

In summary, we have successfully developed the Mn$_3$O$_4$/CNT hydrogels for supercapacitor applications. By utilizing a pulse electrochemical deposition, a high areal capacitance above 473 mF cm$^{-2}$ can be achieved. The assembled asymmetric supercapacitor can reach a potential as high as 2 V in the aqueous electrolyte. Compared with the single-component Mn$_3$O$_4$ electrodes and electrochemical catalysis. (1) serving as electron transport highway and (2) inhibiting serious aggregation of active materials. We believe our prepared composites may also have applications in the field of battery electrodes and electrochemical catalysis.

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Notes and references