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One-step Synthesis of Mesoporous MnO₂/carbon Sphere Composites for Asymmetric Electrochemical Capacitors

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Whisker-like MnO₂/carbon sphere (MnO₂/C) composites with a mesoporous structure are synthesized through an easy one-step hydrothermal method using glucose as carbon sources without any catalyst or template. Highly porous interconnected MnO₂ nanowhiskers are uniformly coated on the surface of the carbon sphere to construct a mesoporous architecture. A high-voltage asymmetric electrochemical capacitor (EC) is assembled with active carbon as the negative electrode and MnO₂/C spheres as the positive electrode in a neutral aqueous 5 M LiNO₃ solution as electrolyte. This aqueous electrolyte-based asymmetric EC is reversibly cycled within the wide-voltage region of 0-2.0 V. Moreover, a high specific capacitance of 307.6 F g⁻¹ and a superior long-term cyclic stability of nearly 96.6% retention after 1000 cycles are observed.

Introduction

Supercapacitors, also as known as electrochemical capacitors or ultracapacitors, are attracting considerable interest because of their combined merits, i.e., high energy density of batteries and high power density of conventional dielectric capacitors.1-3

Supercapacitors can be divided into two types based on energy storage mechanism, such as: electrical double-layer capacitors (EDLCs) that use carbon-active electrode materials and pseudocapacitors that employ metal oxides and conduct polymers electrode materials.4,5 Each type of electrode material has specific advantages and disadvantages.6-12 Carbon materials have high power density and long cycle life but low specific capacitance.8,10 The metal oxides have higher energy density compared to conventional carbon materials and better cycling stability than polymer materials, however, they have lower energy density than lithium ion battery immensely, which limit their application.11,12 The resolution of these problems inspires attempts in developing novel electrode materials by coupling carbon materials with high electrical conductivity and electrochemically active materials as electrode for the supercapacitor.

Manganese dioxides (MnO₂) is an attractive option among various metal oxides used as a supercapacitor electrode material because of its low cost, environmentally friendly, and high theoretical specific capacitance (1370 F g⁻¹).13,14 Furthermore, MnO₂-based materials are typically applied in neutral aqueous electrolytes, which fulfill the environmental requirements of “green electrolytes” in supercapacitors.15-17 However, its poor electrical conductivity limits its application. Thus, loading MnO₂ materials on carbon materials, such as carbon nanotubes, carbon fibers, graphene, and graphene aerogel, is essential.18-24

Jiang et al.18 designed and synthesized rGO/CNTs/MnO₂ nanocomposites with a high specific capacitance of up to 319 F g⁻¹ with enhanced rate capability (222 F g⁻¹ even at 60 A g⁻¹) in 1 M Na₂SO₄. Luo et al.21 proposed an easy method to prepare well-ordered whisker-like MnO₂ arrays with carbon fiber, which had excellent long cycle life property. Wu et al.22 developed a high-voltage (2.0 V) asymmetric electrochemical capacitor, where graphene served as a negative electrode and MnO₂ nanowire/graphene as a positive electrode in a neutral aqueous Na₂SO₄. Ji et al.24 anchored MnO₂ on graphene aerogel as the electrode material, which exhibited good electrochemical stability. Huang et al.25 synthesized MnO₂@C nanosheet array on a titanium foil via hydrothermal method, but through two hydrothermal steps. Zhu et al.26 incorporated MnO₂ inside the CMK-3 ordered pore channels, which was modified by using 1 M H₂SO₄ for 3 h in order to improve the accessibility of pore channels and surface reactivity. However, the achievement of these composite materials often requires complex or accurate control of the synthesis process.

Thus, we developed a novel method to fabricate mesoporous MnO₂/C composites for the supercapacitor using a one-step hydrothermal approach without any catalysts or templates.
Unlike conventional approaches, this method not only avoids the subsequent complicated procedure for the removal of the template, but also the hydrothermal process contains self-assemble process of MnO₂ and carbonization of glucose without any active pretreatment, which simplifying the preparation process of the mesoporous MnO₂/C composites. The whisker-like MnO₂ arrayed on carbon sphere surface with a mesoporous structure, a large surface area, and porosity facilitated the rapid transport of electrons and ions in the electrode. An asymmetric supercapacitor with MnO₂/C composites as the positive electrode and active carbon as the negative electrode in 5 M LiNO₃ electrolyte indicated high specific capacitance and energy density, as well as good cycling stability with a wide voltage region of 0 to 2.0 V.

**Experimental section**

**Synthesis of samples**

All reagents were of analytical grade and were used directly without further purification. Deionized (DI) water was used throughout the experiment. The typical synthesis process of MnO₂/C composites is described as follows: First, 0.1 g glucose was dispersed into 20 mL DI water through ultrasonic vibration for 30 min. Second, 1.35 g manganese sulfate monohydrate (MnSO₄·H₂O) was added in the suspension and the mixed solution was stirred by magnetic bar for 6 h. Third, 1.82g ammonium persulfate ((NH₄)₂S₂O₈) was added with further stirred for a short, after that the mixed solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and treated hydrothermally at 180 °C for 3 h. Finally, products were harvested by centrifugation upon cooling down to room temperature, rinsed several times with DI water and absolute ethanol, and then dried at 80 °C for 12 h.

**Material characterization**

The crystal structure of the products was characterized by X-ray diffraction (XRD) with a Rigaku D/max UltimaIII using Cu Kα radiation (λ = 1.50405 Å). The morphology and structure of the synthesized materials were investigated using field emission scanning electron microscopy (FESEM, Hitachi S4300). Specific surface area and pore size distribution (PSD) curves were determined by a Brunauer-Emmett-Teller (BET) measurement (ASAP 2020).

**Electrochemical measurement**

The electrochemical performance of the MnO₂/C composites and the MnO₂ was evaluated by the three-electrode cell method. The working electrode was prepared by mixing 80 wt% active material, 10 wt% acetylene black, and 10 wt% polytetrafluoroethylene (PTFE, 60 wt% dispersion in water). Afterwards, the slurry was spread onto a nickel foam current collector (1 × 1 cm). A platinum wire (1 mm in diameter) and Hg/HgCl₂ electrode (SCE, saturated KCl, 0.214 V vs. NHE at 25 °C) were used as the counter and reference electrodes, respectively. The active carbon electrode was measured within a potential window of -1.0 to 0.0 V, whereas MnO₂ and MnO₂/C spheres were measured within a potential window of 0.0 V to 1.0 V at a scan rate of 10 mV s⁻¹. The asymmetric supercapacitor was measured in a two-electrode system, which contained two slices of an electrode material with the same size. The MnO₂ and MnO₂/C composites in the two electrode system were the positive electrode, and the active carbon (AC) was mixed with 10 wt% acetylene black and 5 wt% PTFE (60 wt% dispersion in water) to fabricate the negative electrode. All other electrochemical characterization was performed using AUTOLAB (ECO CHEMIE, PGSTAT 100) in 5 M LiNO₃ aqueous solution as electrolyte at room temperature and normal pressure.

**Results and discussion**

Fig. 1(a) shows the XRD patterns of the prepared carbon sphere and MnO₂/C composites. The large peaks at 26° and 43° indicated the graphitic character of the carbon sphere, whereas the other three peaks at 20 = 12.8° (001), 36.8° (111) and 65.7° (311) in the MnO₂/C composite, correspond to the diffraction peaks of the birnessite-type MnO₂ (JCPDS 80-1098). The broadened and weakened peaks of the MnO₂ indicated poor crystallinity in the composite, which was favourable for the supercapacitor. Fig. 1(b) shows the SEM image of bare carbon sphere with diameter of 1 µm and plain surfaces which was glucose treated hydrothermally at 180 °C for 3 h. Figs. 1(c, d) show the images of the MnO₂ and MnO₂/C composites. MnO₂ arrays could be clearly seen from Fig. 2(e, f), in which each sphere was significantly rough-coated with MnO₂ nanowhiskers. This sphere-whisker structure, which was mesoporous and with a high specific surface area, was favourable for improving the main pseudocapacitance of MnO₂ and the electric double-layer (EDL) capacitance of the carbon sphere given that the hydrated ions in the electrolyte are easily accessible to the exterior and interior pore surfaces.
Fig. 2 shows the TEM images of MnO$_2$/C composite. The carbon sphere had a graphitic structure with a diameter of ~1 µm. When coated with MnO$_2$, the size of the sphere-whisker structure increased to ~1.5 µm with the length of MnO$_2$ whisker of 200 nm. Noted that MnO$_2$ whiskers grown on the carbon sphere, making the composite promising for higher energy storage capacity. HRTEM image further indicated that the interplanar spacing of birnessite-type MnO$_2$ whisker was ~0.69 nm (Fig. 2b), which was in accordance with the literature.\textsuperscript{32,33} The electron diffraction (ED) pattern (Fig. 2d, inset), taken from a randomly chosen area, showed MnO$_2$ with a polycrystalline nature.

![Fig. 2 TEM images of MnO$_2$/C composite](image)

**Fig. 2** (a) TEM and (b) HRTEM images of MnO$_2$/C composite, inset showed the corresponding SAED pattern.

Fig. 3 shows the nitrogen adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution curves of the carbon, MnO$_2$ and MnO$_2$/C composites. The hysteresis loop in relative pressure ($P/P_0$) range from 0.45 to 0.90, which might be ascribed to the presence of a mesoporous structure,\textsuperscript{34,35} and from 0.9 to 1.0 provided the interpolate space that primarily showed the mesoporous structure in the MnO$_2$/C composites (Fig. 3(a)). Owing to the adding of the carbon sphere, the surface area of the MnO$_2$/C composites (142.46 m$^2$ g$^{-1}$) was much higher than that of MnO$_2$ (64.59 m$^2$ g$^{-1}$), as well as the BJH pore size distribution curves (Fig. 3(b)), which exhibited the distribution of pore sizes between 3 nm and 4 nm. So the well-fined, pore-size mesoporous structure of MnO$_2$/C composites facilitated an effective electrolyte diffusion and rapid charge transfer, which can facilitate a high electrochemical performance.\textsuperscript{36} Detailed structural parameters are summarized in Table 1.

![Fig. 3 Nitrogen adsorption-desorption isotherms](image)

**Fig. 3** (a) N$_2$ adsorption-desorption isotherms and (b) corresponding pore size distribution of the as-prepared carbon, MnO$_2$ and MnO$_2$/C composite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET area / m$^2$ g$^{-1}$</th>
<th>Total pore volume / cm$^3$ g$^{-1}$</th>
<th>Average pore size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>353.82</td>
<td>0.34</td>
<td>26.98</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>64.59</td>
<td>0.16</td>
<td>3.81</td>
</tr>
<tr>
<td>MnO$_2$/C</td>
<td>142.46</td>
<td>0.27</td>
<td>4.32</td>
</tr>
</tbody>
</table>

We performed cyclic voltammograms (CV) of the ECs in a 5 M LiNO$_3$ aqueous solution using a three-electrode system to evaluate the electrochemical properties and quantify the specific capacitance of the as-prepared MnO$_2$ and MnO$_2$/C spheres. Fig. 5(a) shows that the CV curves of these electrodes had the nearly ideal rectangular shape, which indicated the efficient charge transfer and the almost ideal capacitive behaviours. Note that no apparent redox peaks were observed at the voltage of 0.0 V to 1.0 V, which due to MnO$_2$ electrode in mild aqueous electrolyte is a fast, reversible successive multiple surface redox reaction, whose shape is close to that of the EDLC.\textsuperscript{37} Based on these results, we could see that the stable voltage window between 0.0 V to 1.0 V was for MnO$_2$/C composites and between -1.0 V to 0 V was for active carbons with capacitive behaviour, relative to the SCE. Therefore, the operating cell voltage could be extended to about 2.0 V in a mild aqueous solution because of the existing MnO$_2$ with higher cutoff potential (1.0 V) in the electrode materials, and the active carbon with a lower cutoff potential window (-1.0 V), which were assembled into asymmetric ECs.\textsuperscript{42-44} The asymmetric EC was constructed by using MnO$_2$ and MnO$_2$/C as the positive electrode and AC as the negative electrode and characterized by using a 5 M LiNO$_3$ solution as electrolyte to evaluate the potential application in EC. Based on charge balance theory, the charge stored by each electrode will follow the relationship $q = q'$. Accordingly, the mass balancing will follow eqn. (1):\textsuperscript{45}

\[ m^+ = (C \times \Delta E); (C^+ \times \Delta E') \]

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Where $m$, $C$, and $\Delta E$ represent the mass, the specific capacitance, and the potential range for the charge-discharge process of electrode, respectively.

Fig. 5 (a) CV curves of AC and MnO$_2$/C composite electrodes performed in three-electrode; (b) CV curves of (b) CV curves of MnO$_2$/C/AC at different scan rates with a wide potential windows of 2.0 V; (c) galvanostatic charge-discharge curves of MnO$_2$/C//AC at different current densities; (d) Correlation of specific capacitances with discharge currents of MnO$_2$/C//AC and inset (d) Ragone plots of the power density versus energy density of MnO$_2$/C//AC.

Fig. 5(b) shows the typical CV curves of MnO$_2$ and MnO$_2$/C spheres measured at a scan rate of 10 mV s$^{-1}$, which exhibited a rectangular-like shape without obvious redox peaks, suggesting that the pseudocapacitive reactions that occurred between the MnO$_2$ and electrolyte was fast and reversible.$^{38}$ The current responses of the MnO$_2$/C//AC EC was larger than the MnO$_2$//AC EC, which implied higher specific capacitance value. The excellent specific capacitance of the MnO$_2$/C//AC EC was mainly attributed to the addition of the carbon sphere. Although the shapes of the CV curves deviated from ideal rectangular shape, the areas surrounded by the CV curves were not significantly influenced by the increasing scan rate, which indicated the desirable fast charge-discharge property of the sample. To further evaluate the electrochemical performance of the MnO$_2$ and MnO$_2$/C composites, galvanostatic charge/discharge tests were conducted at a current density of 1 A g$^{-1}$ as shown in Fig. 5(c) between 0 V and 2.0 V. The almost triangular shapes reversed the Faradic reaction for charge storage. Thus, the increased discharge time for MnO$_2$/C composites suggested a better capacitance performance because of the mesoporous structure and favourable pore connectivity. Furthermore, the specific capacitance ($C_\lambda$) of the two complete two-electrode system (Fig. 5(d)), as well as the energy and power densities ($E_D$, $P_D$) (inset Fig. 5(d)) were calculated on the basis of the galvanostatic charge-discharge result and using the relation provided below:

$$C_\lambda = C/m = (I \times \Delta t)/(\Delta V \times m)$$  \hspace{1cm} (2)

$$E_D = C\Delta V^2/2m$$  \hspace{1cm} (3)

$$P_D = 4V/2m$$  \hspace{1cm} (4)

Where $C$ is the total measured capacitance of the two-electrode system; $I$ is the constant current used during discharge; $\Delta t$ is the discharge time; $\Delta V$ is the voltage difference during time and $m$ is the mass of the active material on the electrode. A slight decrease in the capacitance of MnO$_2$/C was observed with increasing current density from 0.5 A g$^{-1}$ to 10 A g$^{-1}$. This result implied the fast charge transfer of the EC due to the mesoporous structure which reduced the internal resistance of the composite electrode. The MnO$_2$/C//AC delivered high energy and power densities because of the enhanced specific capacitance and the enlarged working voltage (from 1.0 V to 2.0 V). The energy density reached 19.9 Wh kg$^{-1}$ at a power density of 500 W kg$^{-1}$, and remained at 6.2 Wh kg$^{-1}$ with a power density of 8000 W kg$^{-1}$. The high performance of the asymmetric ECs could be ascribed to the following factors: (1) the wide operating cell voltage (2.0 V), in which the cell voltage was extended to 2.0 V resulting in a large increase in energy density; (2) MnO$_2$/C composites provided a porous structure with mesopores in addition to their high electrical conductivity, superior mechanical properties, and the surface area providing a fast interconnected network for the transport of electrons and ions.

The long-term cycling performance of the asymmetric supercapacitor was crucial for practical applications. Fig. 6 shows the capacitance fading over 1000 cycles between a maximum working voltage (2.0 V) for the two samples. The capacitance fading of capacitors with MnO$_2$/C and MnO$_2$ were able to retain about 96.6 and 90.1%, respectively. These results suggested the long-term electrochemical stability of the MnO$_2$/C composites at current density of 1 A g$^{-1}$ for consecutive 1000 cycles, which signified a good mechanical stability of the MnO$_2$/C composites. The cycling performance at progressively increased current density was recorded in Fig. 6(b) to further understand the stability for MnO$_2$/C and MnO$_2$. The mesoporous MnO$_2$/C composites 0 consistently demonstrated stable capacitance even when suffering from a change of the current delivery. After 300 cycles, a capacitance of 305.3 F g$^{-1}$ could be recovered without any decrease as the current density diminishes to 0.2 A g$^{-1}$ for another 50 cycles. This finding indicated that the MnO$_2$/C composites had excellent rate performance and cyclability assigned to the unique sphere-whisker structure of MnO$_2$/C composites (positive electrode), which could improve the stability by effectively preventing the aggregation of carbon sphere and provide a specific surface area with rich mesoporous structure of MnO$_2$ nanowhisker.

The impedances of MnO$_2$/C and MnO$_2$ electrodes were measured at frequencies from 100 kHz to 0.01 Hz to identify the relationship between electrochemical performance and electrode kinetics. Fig. 7 shows that both electrodes exhibited a liner spike at low frequency characterized capacitive behaviour, which demonstrated the common equivalent circuit descriptions of these features: the intercept on the real part at the high-frequency end was ohmic resistance ($R_s$), including the resistance of intrinsic resistance of substrate, contact resistance at the active material/current collector interface and ionic resistance of electrolyte, and was mainly controlled by the ionic resistance of the electrolyte. The $R_s$ of the two electrodes were almost the same value of 0.8 $\Omega$, because both the electrodes...
were tested in 5 M LiNO₃ electrolyte; with the size of the semicircular that encompasses the medium-frequency response, was an indication of the charge-transfer resistance (Rct) and a parallel constant phase element (CPE) in the electrode reaction; and the inclined line in the low-frequency region represented the Warburg impedance (Zw) relative to the ions' diffusion/transport throughout the electrode.⁵⁰⁻⁵² As shown in Fig. 7(a), a major difference was observe on the Rct, MnO₂/C composite electrode indicated a low value at 0.6 Ω and a linear vertical curve, which suggested better capacitive behaviour of the composite electrode compared to that of the MnO₂ electrode (1.5 Ω) in the low frequency region.⁴⁹ These results might be attributed to the fast electron transition and the good contact between the current-collector and whisker arrays associated with the sphere-whisker mesoporous structure of the MnO₂/C composites, which confirmed that the MnO₂/C composites was a promising supercapacitor electrode material.

![Nyquist plots](image)

**Fig. 7** (a) Nyquist plots of MnO₂/C and MnO₂ electrodes before and after cycles; (b) The electrical equivalent circuit used for fitting impedance spectra.

**Conclusions**

A simple, low-cost synthesis of nanowhisker MnO₂ anchored to carbon sphere was demonstrated. The mesoporous structure easily forms an efficient conducting network and serves as a favourable buffer in relieving the internal stress that occurs during Faradic processes, further, protecting the electrode from physical damage. Asymmetric EC based on the MnO₂/C composites as positive electrode and AC as negative electrode was assembled in a 5 M LiNO₃ aqueous. EC can be utilized in a wide voltage region of 0 V to 2.0 V, which enhanced the specific capacitance at 307.6 F g⁻¹ and indicated a good capacitance retention of 96.6% over 1000 cycles. Therefore, the present MnO₂/C nanocomposites can serve as an attractive candidate material for supercapacitor electrodes.

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**Notes and references**

The mesoporous MnO$_2$/C composites were simply synthesised using one-step hydrothermal approach that not only without any catalysts or templates, but also the carbon from carbonization of glucose without any active pretreatment.