Electrochemical Performance of MnO$_2$/Graphene Flower-like Microspheres Prepared by Thermally-Exfoliated Graphite

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To enhance the electrochemical performance of MnO$_2$/graphene composite, herein, thermally-exfoliated graphite (TE-G) is adopted as a raw material, and a hydrothermal reaction is conducted to achieve the exfoliation of TE-G and the loading of MnO$_2$ nanosheets. Through optimizing the TE-G/KMnO$_4$ ratio in the redox reaction between carbon and KMnO$_4$, flower-like MnO$_2$/G microspheres (MnO$_2$/G-10) are obtained with 83.2% MnO$_2$ and 16.8% residual graphene. Meanwhile, corresponding MnO$_2$/rGO composites are prepared by using rGO as raw materials. Serving as a working electrode in a three-electrode system, MnO$_2$/G-10 composite displays a specific capacitance of 500 F g$^{-1}$ at 1 A g$^{-1}$, outstanding rate performance, and capacitance retention of 85.3% for 5,000 cycles. The performance is much better than that of optimized MnO$_2$/rGO composite. We ascribe this to the high carbon fraction in TE-G resulting in a high fraction of MnO$_2$ in composite, and the oxygen-containing groups in rGO reduce the resulting MnO$_2$ fraction in the composite. The superior electrochemical performance of MnO$_2$/G-10 is dependent on the hierarchical porous structure constructed by MnO$_2$ nanosheet arrays and the residual graphene layer in the composite. In addition, a supercapacitor assembled by TE-G negative electrode and MnO$_2$/G positive electrode also exhibits superior performance. In consideration of the low cost of raw materials, the MnO$_2$/G composite exhibits great application potential in the field of supercapacitors.

Keywords: MnO$_2$, thermally-exfoliated graphite, supercapacitors, electrochemical performance, flower-like microspheres

INTRODUCTION

Among the existing energy storage devices, the supercapacitor is an important device for high power density, rapid charge/discharge, and long cycling life. The fabrication of electrode materials is a major task for developing high-performance supercapacitors (Raj et al., 2020; Oncu et al., 2021; Zhang et al., 2021). To achieve the rapid transport and transfer of ions/electrons, various carbon materials have been developed in the field of supercapacitors, including carbon nanotubes (Lei et al., 2020), graphene (Sha et al., 2021), carbon nanosheets (Sevilla and Fuertes, 2014), porous carbon (Zhao et al., 2020), carbon fibers (Srimuk et al., 2015), and so on. Nevertheless, the poor specific capacitance of these carbon materials affects their wide application in supercapacitors, due to the electrical double
layer capacitance (EDLC) feature (Sevilla and Fuertes, 2014; Ferrero et al., 2015). To enhance the specific capacitance, carbon materials have been hybridized with various metal oxides for introducing high pseudocapacitance (Yan et al., 2014, 2021). Among those transition metal oxides, MnO2 has been regarded as the most promising electrode material, due to the large theoretical specific capacitance of 1370 F g\(^{-1}\), natural abundance, and low price (Xu et al., 2007, 2018; Zhang et al., 2020c).

Lots of methods have been reported to prepare MnO2/rGO composites, such as the chemical precipitation method (Gong et al., 2021), alcohol infiltrated substrate method (Zhang et al., 2020b), and hydrothermal route (Liu et al., 2015). Among these methods, the hydrothermal method is the most convenient way for synthesizing MnO2/rGO composites. During a hydrothermal process, a redox reaction takes place between carbon and KMnO4, and MnO2 nanostructures are uniformly generated on graphene nanosheets, with the consumption of a certain amount of carbon (Ping et al., 2019; 2; Hong et al., 2021; Wang T. et al., 2021). In this respect, by using sulfur-reduced graphene oxide (RGO-S) as raw materials, Tarimo et al. (Tarimo et al., 2020) synthesized RGO-S/MnO2 composite via a hydrothermal method, and the optimized RGO-S/MnO2 composites had a low capacitance (180.4 F g\(^{-1}\)). Yang et al. (Yang et al., 2012) prepared rGO firstly by using graphene oxide (GO) and then synthesized urchin-like MnO2 on rGO nanosheet through a hydrothermal reaction under the presence of KMnO4. The optimized rGO/MnO2 composites exhibited a high capacitance of 263 F g\(^{-1}\). Moreover, Liu et al. (Liu et al., 2014) prepared GO firstly by Hummers method and then synthesized MnO2-GO composites via hydrothermal reaction. The MnO2-GO composite presented a capacitance of 213 F g\(^{-1}\) at 0.1 A g\(^{-1}\). From these works about MnO2/graphene composites, the graphene in composite is usually derived from GO prepared by Hummers method (Vimuna et al., 2020). In addition, the resulting MnO2/rGO composites deliver the specific capacitance of less than 300 F g\(^{-1}\), which further limits the development of high-performance supercapacitors. Up to now, there is no report about MnO2/graphene composites prepared by using expandable graphite as raw materials.

In view of the larger specific surface area, lower oxygen content, more complete lamellar structure, and low cost and easy preparation of thermally-exfoliated graphite (TE-G), herein, TE-G was adopted as raw materials, and a hydrothermal reaction was performed to fabricate MnO2/graphene composite through a redox reaction between KMnO4 and C. Most importantly, the hydrothermal reaction achieves the exfoliation of TE-G. As a result, flower-like MnO2/graphene microspheres were produced, in which, the residual graphene layer was wrapped by abundant thin MnO2 nanosheets. The optimized MnO2/graphene microspheres exhibited excellent electrochemical performance in supercapacitors. To verify the performance advantage of TE-G in preparing MnO2/graphene composite, various MnO2/rGO composites were fabricated by using GO as reactants, and corresponding electrochemical performance was investigated. Compared with rGO, the MnO2/G composite prepared with TE-G as raw material shows better performance and a more convenient method.

**EXPERIMENT**

**Materials**

Potassium chloride (KCl), Expandable graphite (EG, 80 mesh), and potassium permanganate (KMnO4) were obtained from Tianjin Damao Chemical Reagent Factory.

**Preparation of Thermally-Exfoliated Graphene**

Thermally-exfoliated graphite (TE-G) was synthesized according to our previous work (Liu et al., 2021). Specifically, EG was heated at 500°C for 100 min under N\(_2\) to obtain thermally-exfoliated graphene (TE-G).

**Preparation of MnO2/Graphene (MnO2/G) Composites**

In a typical synthesis, 1.0 g KMnO4 was put into deionized water (80 ml) and stirred for 30 min to produce a uniform solution. Meanwhile, different amounts of TE-G powders were put into the KMnO4 solution and stirred for 30 min, and then, the mixture was put into a stainless-steel autoclave. The hydrothermal reaction was conducted at 180°C for 15 h. The production was filtered, rinsed repeatedly by deionized water, and dried at 60°C for 12 h to obtain MnO2/G composites. The redox reaction equation of C and KMnO4 can be described as: 4MnO4\(^{-}\) + 3C + H\(_2\)O → 4MnO2 + CO\(_2\)\(^{2-}\) + 2HCO\(_3\)\(^{-}\). According to the equation, the theoretical mass ratio of KMnO4 and C can be calculated as 1/17.7. Therefore, to change the MnO2 fraction in the MnO2/G composite, the KMnO4/TE-G mass ratio was set as 5, 10, and 20, and the resulting composites were coded as MnO2/G-5, MnO2/G-10, and MnO2/G-20. In addition, the hydrothermal reaction of TE-G in deionized water and in KCl solution was carried out under the same condition, and the resulting samples were coded as TE-G-H\(_2\)O and TE-G-KCl, respectively. The rGO was used to prepare MnO2/rGO composites. The ratio of KMnO4/rGO was kept the same as the ratio of KMnO4/TE-G composites, and the sample was named MnO2/rGO-5, MnO2/rGO-10, and MnO2/rGO-20.

**Testing and Characterization**

The field-emission scanning electron microscopy (FE-SEM; SU8010) and transmission electron microscopy (TEM; JEM-2100) were used to observe the morphologies of samples. The crystallographic feature was performed by X-ray diffraction (XRD; D8-Advance) with Cu Ka radiation source. X-ray photoelectron spectra (XPS) were recorded by using a Thermo Scientific K-Alpha XPS spectrometer. The working voltage was 12 kV, and the X-Ray source was Al Ka. Pore size distribution and the specific surface area were tested by using the SSA-7000 device, according to the BJH model and BET method.

**Electrochemical Performance**

A three-electrode system was used to test the electrochemical performance of samples in an electrolyte of 6 M KOH. The poly
(vinylidene fluoride)/acetylene black/active materials were weighed at the ratio of 5:10:85, and dissolved in N-methyl-2-pyrrolidone (NMP) to prepare a slurry. Foam nickel (1 × 1 cm²) was used to support the slurry and served as the working electrode. The platinum sheet was acted as the counter electrode, and the saturated calomel electrode (SCE) was used as the reference electrode. A CHI 660E electrochemical workstation (Shanghai Chenhua Co. Ltd.) was used to test electrochemical impedance spectroscopy (EIS), galvanostatic charge/discharge curves (GCD), cycling stability, and cyclic voltammetry (CV) curves. Asymmetric supercapacitor (ASCs) devices were assembled by using TE-G as the negative electrode and MnO2/G composite as a positive electrode with 6 M KOH electrolyte. The separator was glass fiber filter paper. In the ASCs device, Formula I (Wang et al., 2018): \[ R = \frac{m^+}{m^-} = \frac{(C^- \times \Delta V^-)}{(C^+ \times \Delta V^+)} \] can be applied to obtain the ratio of positive/negative electrode material. Formula II (Brousse et al., 2007; Hong et al., 2021): \[ C = \frac{I \times \Delta t}{\Delta V} \] was employed in calculating the specific capacitance (C) in a three-electrode system. Formula III (Brousse et al., 2007): \[ C_S = 4C/M \] and Formula IV (Li et al., 2021): \[ P = \frac{E}{\Delta t} \] \[ (\Delta V)^2/3.6 \] and Formula V (Brousse et al., 2007): \[ E = 0.5C (\Delta V)^2/3.6 \] and Formula V (Brousse et al., 2007): \[ P = E/\Delta t \] can be applied to obtain specific capacitance (Cs), the energy density (E) and power density (P) of the ASCs, respectively.

RESULTS AND DISCUSSION

Preparation Process of MnO2/G Composite

Figure 1 exhibits the preparation process of flower-like MnO2/G microspheres. Firstly, under the presence of N2, the expandable graphite (EG) was heated at 500°C to prepare TE-G. Under a high temperature, the intercalation agent in EG expands and violently decomposes, resulting in a large amount of gas spilling and forming micropores, mesopores, and macropores. As shown in Figure 1, TE-G shows an accordion structure with a thick lamella. Moreover, abundant cavity structures can be observed on TE-G. Secondly, under a hydrothermal process, K2MnO4 reacts with C to generate MnO2, in which, each single-layer of graphene in TE-G reacts with K2MnO4 and is then wrapped by abundant MnO2 nanosheets. The loading of MnO2 thick nanosheets on graphene layers leads to the exfoliation of TE-G. From the inset SEM image, after the redox reaction, graphene nanosheets were wrapped by MnO2 nanosheet arrays in different directions to produce flower-like microspheres. Compared with rGO, the consumption of graphene nanosheets and the generation of thick MnO2 layers lead to the delamination of TE-G. In order to confirm the advantage of MnO2/G composite, corresponding MnO2/rGO composites were prepared, and the microstructure and electrochemical performance were investigated.

Microstructure of MnO2/G Composites

The morphologies of TE-G and different MnO2/G composites samples were characterized by using TEM and SEM. From Figure 2A,B, pure TE-G presents an accordion structure with a large number of holes, and Figure 2C indicates the stacking structure of abundant graphene nanosheets. From these MnO2/G samples, under a low ratio of K2MnO4/TE-G, a few graphene sheets in TE-G participate in the redox reaction with K2MnO4. Hence, a few MnO2 nanosheets are generated on the graphene surface (Figure 2D). When the ratio of K2MnO4/TE-G increases to 10, dense MnO2 nanosheet arrays are generated in all directions of graphene nanosheets, presenting a flower spherical structure (Figure 2D). When the ratio of K2MnO4/TE-G increases to 10, dense MnO2 nanosheet arrays are generated in all directions of graphene nanosheets, presenting a flower spherical structure (Figure 2D). From the high magnification SEM in Figure 2F, the resulting MnO2 nanosheets arrays exhibit a honeycomb-like structure. The results show that the redox reaction between carbon and K2MnO4 produces MnO2 nanosheets on graphene, which achieves the delamination of TE-G. From Figure 2G,H, there are dense MnO2 nanosheets arrays dispersed on the graphene surface. Moreover, the TEM image also shows the connection of different MnO2/G flower spheres, which may be resulted from the fracture of large graphene nanosheets during the high-temperature hydrothermal reaction process. As shown in Figure 2I, we can observe the diffraction fringes of MnO2 on the graphene surface. The fringe spacing of ~0.8 nm corresponds to the (001) facet of δ-MnO2 (Wang J. et al., 2021). When the ratio of K2MnO4/TE-G
reaches 20, excessive MnO$_2$ nanosheets are generated and piled up on the surface of the MnO$_2$/G composite (Figure 2E).

In order to prove that the exfoliating of TE-G is related to the KMnO$_4$-assisted hydrothermal reaction, two controls are designed by using only deionized water and KCl solution, respectively. In the absence of KMnO$_4$, the hydrothermal reaction cannot exfoliate the TE-G. As shown in Figure 3A, the accordion structure is kept the same as pure TE-G (Figure 2A). Under the presence of K$^+$ derived from KCl, the resulting TE-G also keeps the same structure with pure TE-G in Figure 2A. Therefore, the exfoliation of TE-G is dependent on KMnO$_4$-assisted hydrothermal reaction, and the *in-situ* reaction between graphene nanosheet and KMnO$_4$ consumes carbon and introduces MnO$_2$ nanosheet arrays, which effectively exfoliate TE-G. To disclose the advantage of TE-G in preparing MnO$_2$/G composites, rGO was used as reductants, and resulting MnO$_2$/rGO composites were shown in Figure 3C,D. The MnO$_2$/rGO composite shows the same flower spheres as MnO$_2$/G composite (Figure 2D–F). The result indicates that the reaction between rGO and KMnO$_4$ is the same as the reaction between TE-G and KMnO$_4$, that is, the redox reaction of graphene nanosheets and KMnO$_4$. However, the major difference between the two reactions is the carbon precursors. TE-G has condensed graphene nanosheets with no oxygen-containing groups, while rGO is the exfoliated graphene containing oxygen-containing groups. Compared with rGO, TE-G has a low cost and high carbon content, which would consume more KMnO$_4$ and introduce much more MnO$_2$, while some rGO nanosheets are not wrapped by MnO$_2$ nanosheets arrays (Figure 3C), and much more MnO$_2$ nanosheets would enhance the electrochemical performance of MnO$_2$/G composites, which will be discussed further.

**Elemental Distribution of MnO$_2$/G Composites**

Elemental mapping and EDS were conducted to verify residual graphene in MnO$_2$/G composite. MnO$_2$ nanosheets (Figure 4A) keep the same with the SEM morphology (Figure 2F). The distribution of O is in accordance with the Mn (Figure 4C), which reflects the generation of MnO$_2$. In addition, the dispersed C signals verify the residual graphene in the MnO$_2$/G composite. From Figure 4E, the C content is at 35.31%, further demonstrating the residual carbon derived from graphene. To detect the precise carbon content in composite, TG curves of TE-G, MnO$_2$/G-5, MnO$_2$/G-10, and MnO$_2$/G-20 are given in Figure 4F. When the temperature is higher than 600°C, TE-G begins to decompose, and no residual carbon remains at 800°C. Compared with TE-G, the residual fractions of three composites are 72.5, 75.5, and 81.0% at 800°C in air. Based on the principle in Ref. (Wang J. et al., 2021), the final product of MnO$_2$/G composite is Mn$_2$O$_3$ at 800°C. According to the same Mn content, we can calculate the fraction of MnO$_2$, that is, 80.0, 83.2, and 89.3%, respectively. The residual carbon fractions in
MnO₂/G-5, MnO₂/G-10, and MnO₂/G-20 are 20.0, 16.8, and 10.7%, respectively. Therefore, the TG result affirms the incomplete reaction of carbon (TE-G), and residual graphene nanosheet still exists in the MnO₂/G composite.

Fourier transform infra-red (FTIR) was provided in Supplementary Figure S1, the peak at ~3,425 cm⁻¹ is attributed to the O-H vibration of GO or rGO. The peaks of ~1,633 cm⁻¹ and 1,313 cm⁻¹ correspond to the stretching
and bending vibration of C-O, respectively. Compared with GO or rGO, there are a few oxygen-containing groups in TE-G, which is conducive to the redox reaction between TE-G and KMnO₄, and a high fraction of carbon would consume a large amount of KMnO₄ and generate many more MnO₂ nanosheets. To verify the high fraction of MnO₂ in MnO₂/G composites, the TG curves of MnO₂/rGO-5 and MnO₂/rGO-20 were measured to obtain the content of MnO₂ in MnO₂/G composites. As given in Supplementary Figure S2, the residual fractions of MnO₂/rGO-5 and MnO₂/rGO-20 are 57.7 and 67.0%, respectively. Therefore, the fraction of MnO₂ can be calculated as 63.6 and 73.8%, respectively. The result shows that the MnO₂ content of MnO₂/rGO is much lower than that of the corresponding MnO₂/G composite. The reason can be ascribed to the low C fraction in rGO, resulting in fewer MnO₂ nanosheets.

Crystal Structure and Surface Chemistry of TE-G and MnO₂/G

In order to analyze the crystal structure of samples, XRD testing was performed. As shown in Figure 5A sharp diffraction peak at 26.4° is attributed to the (002) crystal plane of TE-G (Thommes and Cychoz, 2014). According to the Bragg equation: 2dsinθ = nλ, the layer spacing d is calculated as 0.34 nm. After reacted with KMnO₄, four peaks can be observed at 12.2°, 24.7°, 36.6°, and 65.6°, these peaks correspond to the (001), (002), (100), and (110) facets of δ-MnO₂ (JCPDS # 80–1098) (Wei et al., 2012; Zhu et al., 2017). When the amount of KMnO₄ increased, the (002) peak of carbon (TE-G) at 26.4° disappears, which is assigned to the loading of MnO₂ thick nanosheets on graphene layers leads to the exfoliation of TE-G. This phenomenon indicates the consumption of TE-G and results in a low fraction of carbon in MnO₂/G composites. Compared with MnO₂/G composite, hydrothermally-treated TE-G samples under deionized water or KCl both show a sharp diffraction peak at 26.4° (as shown in Supplementary Figure S3), which confirms that the TE-G cannot be exfoliated by H₂O or KCl under hydrothermal reaction. Therefore, the exfoliation of TE-G is dependent on KMnO₄. In addition, the chemical bonds and valance state of TE-G and MnO₂/G-10 samples were characterized by XPS. From the general spectra in Figure 5B. The TE-G spectrum shows the peaks of C and O elements. After reacting with KMnO₄, the peak of C weakens, and the peaks of O and Mn elements are stronger obviously, due to the generation of MnO₂ and the consumption of TE-G nanosheets. Figure 5C–E shows the magnified C, O, and Mn spectrum. From Figure 5C, the magnified C 1s spectrum can be divided into two peaks at 284.3 and 285.9 eV, which are attributed to the C-C/C=C bond and C=O bond (Yang et al., 2020), respectively. The high-resolution O 1s can be convoluted into two main peaks at 532.0 and 529.5 eV (Figure 5D) corresponding to the bond of C-O-Mn generated between graphene and MnO₂, and the bond of Mn-O-Mn in MnO₂ (Yang and Park, 2018; Yang et al., 2020). From the magnified Mn 2p spectrum (Figure 5E), the 2p orbital of Mn has two major peaks at 642.1 and 653.8 eV, corresponding to Mn 2p₃/₂ and Mn 2p₁/₂. The distance of the two peaks is around 11.7 eV, which reflects the +4 valence of the Mn element (Yang and Park, 2018; Li et al., 2020). Hence, the MnO₂ in the composite is further proved by XPS.

BET Analysis

Figure 6 shows the N₂ adsorption-desorption isotherms curves and pore distribution of different samples according to the BJH model and BET method. TE-G exhibits a high adsorption capacity and a big specific surface area at low pressure. The
specific surface area of TE-G is 1055.7 m² g⁻¹, and a big specific surface area facilitates the infiltration and stripping of TE-G. When increased the amount of KMnO₄, abundant MnO₂ nanosheets loading on graphene surface decreases the specific surface area. The specific surfaces of MnO₂/G-5, MnO₂/G-10, and MnO₂/G-20 are 252.3 m² g⁻¹, 76.1 m² g⁻¹, and 39.4 m² g⁻¹. From Figure 6B, TE-G has much more micropores and mesopores. The loading of MnO₂ on graphene decreases the fraction of micropores and mesopores. However, the macroporous structure of MnO₂/G composite would accelerate the charge transfer and ion diffusion, further improving the electrochemical performance.

**Electrochemical Performance**

A three-electrode system was used to investigate the electrochemical performance of different samples, by using 6 M KOH electrolyte. Figure 7A presents the CV curves of TE-G and different MnO₂/G composites at 20 mV s⁻¹. The CV curve of TE-G displays a quasi-rectangular shape, reflecting the EDLC characteristic of TE-G. When introducing MnO₂, the resulting MnO₂/G composites show two pseudocapacitive peaks of MnO₂ corresponding to the faradic redox reaction of MnO₂. The faradic redox reaction mechanism of MnO₂ is verified as the valence shift between Mn⁴⁺/Mn³⁺ and Mn³⁺/Mn²⁺ (Zhou et al., 2015; Xie et al., 2019). The redox peaks centered at ~0.1 and


~0.4 V (vs Hg/HgO) can be assigned to the reversible redox reaction: \( \text{Mn}^{4+} \leftrightarrow \text{Mn}^{3+} + e^- \), while the other pair of redox peaks around ~0.3 and ~0.6 V (vs Hg/HgO) originate from the faradic redox reactions related to \( \text{Mn}^{4+} \leftrightarrow \text{Mn}^{3+} + e^- \) (Toupin et al., 2004; Zhou et al., 2015; Xie et al., 2019), corresponding to the two faradic redox peaks in CV curve further reflecting the pseudocapacitance characteristics from MnO₂. In addition, the CV curve of the MnO₂/G-10 sample has the largest area among these samples, revealing the maximum specific capacitance. Figure 7B exhibits the GCD curves of TE-G and different MnO₂/G samples. TE-G shows a linear symmetrical triangle, reflecting a typical EDLCs feature related to the adsorption and desorption of ions. When increased the amount of KMnO₄, the pseudocapacitive feature can be verified by the shape of GCD curves. The MnO₂/G-10 composite exhibits the longest discharge time of 250.0 s, much longer than that of pure TE-G (53.8 s). On the basis of the equation of SC = IΔt/(mV), the specific capacitance would be obtained. From Figure 7C, TE-G has a specific capacitance of 107.6 F g⁻¹ at 1 A g⁻¹. When hybridizing with MnO₂, MnO₂/G composites show high specific capacitances. Among these composites, the MnO₂/G-10 sample has the maximum specific capacitance of 500 F g⁻¹ at 1 A g⁻¹. Even operated at 10 A g⁻¹, the capacitance is 314 F g⁻¹, which is assigned to a large number of MnO₂ nanosheets with high capacitance content loaded to the surface of graphene. In comparison with MnO₂/G-10, the MnO₂/G-20 composite has a capacitance of 158 F g⁻¹, because of the stacked MnO₂ aggregation on graphene (Figure 2E). The MnO₂ aggregations obstruct the fast transfer of charges/ions, further decreasing the capacitance. Therefore, the MnO₂/G-20 composite exhibit a lower specific capacitance and poor electrochemical performance.

Figure 7D shows the EIS plots of different samples. Each EIS curve consists of an oblique line in the low-frequency range and a hemisphere in the high-frequency range. The Warburg impedance (W1) can be reflected by an oblique line, which reflects the diffusive resistance of the electrode in the electrolyte. The intercept in the X-axis and the diameter of the hemisphere reflect the internal resistance (R1) and charge transfer resistance (R2), respectively. ZView software was used to obtain the fitting curves (solid line) in Figure 7D. The fitting data were listed in Supplementary Table S1. The R1 values of TE-G, MnO₂/G-5, MnO₂/G-10, and MnO₂/G-20 are 0.484, 0.480, 0.213, and 0.217 Ω, respectively. In addition, the R2 values are 0.341, 0.669, 0.332 and 0.379 Ω, respectively. Therefore, the MnO₂/G-10 composite exhibits the minimum value of R1 and R2 among these samples, which indicates the minimum internal resistance and charge transfer resistance. The reason can be explained as the residual graphene in composite enhances the electronic conductivity. Moreover, hierarchical porous flower spheres of MnO₂ promote the fast transfer of charges/ions, which facilitate the pseudocapacitive reaction of MnO₂ in the electrolyte. Unfortunately, abundant MnO₂ aggregated clusters impede the rapid transfer of charges/ions, increase the internal resistance, which leads to the poor electrochemical performance of KMnO₄/G-20 composite.

To further verify the performance advantage of MnO₂/G composite, the electrochemical performance of MnO₂/rGO composites are given in Supplementary Figure S4. Both CV curves and GCD curves of different MnO₂/rGO composites show the pseudocapacitive feature of MnO₂, the area of MnO₂/rGO composites enclosed by the CV curve is much smaller than that of the MnO₂/G-10 composite. In addition, the maximum discharge time of MnO₂/rGO-20 is 64.7 s, the specific capacitance can be calculated as 129.4 F g⁻¹, much lower than that of the MnO₂/G composite. The reason is the less carbon fraction in rGO limits the redox reaction with KMnO₄, resulting in less MnO₂ nanosheets loading on rGO (in Supplementary Figure S2). Therefore, TE-G shows an obvious performance advantage to high-cost rGO.

The cycling stability of TE-G, MnO₂/G-10, and MnO₂/rGO-20 composite was tested at a current density of 5 A g⁻¹. As given in Figure 8, the specific capacitance of TE-G increases and then decreases during the first 500 cycles, which is assigned to poor wettability between TE-G and the electrolyte. As TE-G only contains a small amount of oxygen-containing groups, the wettability between TE-G and the electrolyte is poor. With the progress of the charge-discharge cycle, the wettability between TE-G and the electrolyte is improved, and the specific capacitance gradually increases. However, due to the limitation of the material itself, the specific capacitance content of TE-G decreases gradually with the increase of the cycle numbers. The specific capacitance of TE-G declines from the original 87.0 F g⁻¹ to 78.6 F g⁻¹ after 5,000 cycles. The capacitance retention rate is 90.4%, for the EDLC feature. The capacitance of MnO₂/rGO composites decreases from an initial 108.6 F g⁻¹~94.1 F g⁻¹, and the capacitance retention rate is 86.6%, which was attributed to the lower content of MnO₂ and more graphene lamellar residues (as shown in Supplementary Figure S2). In comparison with MnO₂/rGO, the MnO₂/G-10 composite has a low capacitance retention rate of 85.3%, and the capacitance decreases to 307.0 F g⁻¹ from 340.1 F g⁻¹. The low capacitance retention of the MnO₂/G-10 sample is attributed to a high fraction of MnO₂ nanosheets in the composite. However, considering the high specific capacitance, MnO₂/G-10 composite still presents...
outstanding cycling stability, which is attributed to the residual graphene layer remaining in the flower spherical structure.

To testify the outstanding performance of MnO2/G composite with a flower spherical structure, we list the capacitance and long-term cycling performance of reported MnO2/graphene in Table 1. Considering the difference in testing conditions, the MnO2/C electrode material has the largest specific capacitance of 480.3 F g\(^{-1}\) (Jeong et al., 2021). The maximum capacitance retention is 99.4% for 5,000 cycles (Vimuna et al., 2020). Although our MnO2/G composite (MnO2/G-10) has a low capacitance retention rate of 85.3%. Particularly, the specific capacitance of our MnO2/G composite is 500 F g\(^{-1}\), much higher than reported samples. Therefore, the MnO2/G composite with flower spheres structure displays an excellent electrochemical performance, which can be ascribed to two aspects. First of all, a large amount of MnO2 nanosheets arrays loading on graphene constructs a homogeneous hierarchical porous structure, which promotes the transport of electrons and ions, and reduces the charge transfer resistance. Moreover, the special microstructure facilitates the interface contact between MnO2 nanosheets and electrolyte and releases a high specific capacitance. Secondly, TE-G is composed of stacking graphene layers, which facilitates the redox reaction between KMnO4 and C, resulting in a high fraction of MnO2 in composite, which increases the pseudocapacitance. Moreover, the residual graphene layer in composite improves the conductivity of electrode material and decreases the internal resistance, which enables an outstanding rate capability and cycling performance.

In addition, we assembled an asymmetric supercapacitor (ASC) with TE-G negative electrode and MnO2/G-10 positive electrode. From Figure 9A, the CV curves show quasi-rectangular shapes. With an increase of scan rate, the area of the CV curve increases, with a shape of quasi-rectangular, further indicating the EDLC feature. The ASC can be operated stably under a broad voltage window of 0–1.0 V (Figure 9B).
**Figure 9C**, the longest discharge time reaches 201.6 s, corresponding to the maximum specific capacitance of 100.8 F g\(^{-1}\) at 0.5 A g\(^{-1}\). The capacitance reduces to 78.8 F g\(^{-1}\) at a large current density of 5 A g\(^{-1}\), indicating an excellent rate capability. **Figure 9E** provides the energy density (E) and power density (P) at different current densities. The energy density is 14.0 Wh kg\(^{-1}\) at the power density of 250.0 W kg\(^{-1}\). With an increase of power density, the energy density drops to 10.94 Wh kg\(^{-1}\) (2500 W kg\(^{-1}\)), further reflecting the excellent power/energy combination. **Figure 9F** shows the cycling stability of ASC. When measured at 5 A g\(^{-1}\), the capacitance retention rate is 98.6% after 5000 cycles, reflecting the superior cycling stability. Therefore, flower-like MnO\(_2\)/G microspheres exhibit outstanding performance in ASC.

**CONCLUSION**

To hybridize thermally-exfoliated graphite (TE-G) and MnO\(_2\), a KMnO\(_4\)-assisted hydrothermal method was adopted to achieve the exfoliation of TE-G and the loading of MnO\(_2\) nanosheets. Through changing the ratio of TE-G and KMnO\(_4\), flower-like MnO\(_2\)/G microspheres (MnO\(_2\)/G-10) were fabricated containing 83.2% MnO\(_2\) and 16.8% residual graphene layer. To confirm the advantage of TE-G reactants, corresponding MnO\(_2\)/rGO composites were prepared by using rGO as raw materials. When tested in a three-electrode system, the MnO\(_2\)/G-10 sample displays a maximum specific capacitance of 500 F g\(^{-1}\), an outstanding rate of performance, and a high capacitance retention rate (85.3% for 5000 cycles). The performance is much better than that of the optimized MnO\(_2\)/rGO composite. The reason can be explained as the high carbon fraction in TE-G resulting in a high fraction of MnO\(_2\) in flower-like MnO\(_2\)/G microspheres, and the oxygen-containing groups in rGO reduce the effective redox reaction between KMnO\(_4\) and carbon. The superior electrochemical performance of MnO\(_2\)/G-10 is related to the hierarchical porous structure constructed by MnO\(_2\) nanosheet arrays and conductive graphene in the composite. Moreover, the ASC consisted of MnO\(_2\)/G positive electrode and TE-G negative electrode has a capacitance of 100.8 F g\(^{-1}\) at 0.5 A g\(^{-1}\), with a high capacitance retention of 98.6% for 5000 cycles. The energy density is 14.0 Wh kg\(^{-1}\) at the power density of 250.0 W kg\(^{-1}\). In consideration of the low cost of raw materials, the MnO\(_2\)/G composite shows great application potential in the supercapacitors field.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

**AUTHOR CONTRIBUTIONS**

XL: Conceptualization, Methodology, Experiment, Original draft preparation. BL: Conceptualization, Supervision, Reviewing and Editing. XH: Writing- Reviewing and Editing, Software JL: Investigation, Data curation.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.870541/full#supplementary-material

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