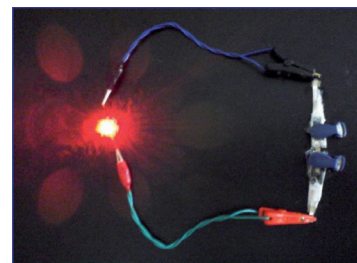


Conducting graphite/MnO₂ nanoflower hybrid electrode-based symmetric high-performance supercapacitors



Supercondensadores simétricos de alto rendimiento basados en electrodos híbridos de nano-flores conductoras de grafito/MnO₂



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RESUMEN

Este artículo desarrolla un sencillo y económico medio de baño de agua hirviendo con simultánea agitación magnética para sintetizar nanomateriales con MnO₂. En él, informamos sobre una nueva estructura de electrodos con nano-flores (NF) conductoras de grafito (G)/MnO₂, en la que una solución híbrida de nanomateriales de grafito conductor y MnO₂ fue regular y naturalmente depositada sobre papel carbón. Tales estructuras de nano-flores disminuyen eficazmente la resistencia al transporte de cargas y facilitan la transmisión de iones o electrones en el electrodo. Los electrodos híbridos de NF de G/MnO₂ muestran una alta capacitancia específica (Cs) de 506 F/g, altas densidades energía/potencia y excelente estabilidad de ciclo, reteniendo un 94% de la capacitancia tras más de 2.000 ciclos. Además, fueron fabricados con éxito supercondensadores simétricos (SSCs) con materiales híbridos de NF de G/MnO₂ como electrodos, que mostraban características prometedoras con una densidad de energía máxima de 11,72 Wh/kg y una densidad de potencia de 16,88 kW/kg. Tales electrodos híbridos de alto rendimiento de base papel carbón con NF de G/MnO₂ pueden suponer el futuro para supercondensadores de rendimientos superiores.

• **Palabras clave:** Grafito, Nano-flores de MnO₂, Deposición natural, Supercondensadores.

paper-based G/MnO₂ NF hybrid electrodes can hold promise for superior performance supercapacitors.

Keywords: Graphite, MnO₂ nanoflower, Natural deposition, Supercapacitor.

1. INTRODUCTION

Recently, renewable and sustainable energy has received intensive attention owing to the increase of energy and power consumption coupled with the critical issue of global climate change. To realize the full-scale applications of renewable, intermittent solar and wind energy, the development of low-cost, high-performance, and environmentally friendly energy storage devices remains a challenge [1–4]. Among the various energy storage devices, supercapacitors (SCs) have been considered a promising candidate for featuring high power density, excellent cycling performance, and rapid charge and discharge rates [5–10]. However, the energy density of SCs is limited, which can generally achieve values of 4 to 5 Wh/kg lower than those of batteries (on the order of 20 to 150 Wh/kg) [11,12]. Consequently, enhancing the energy density values while maintaining the superior performance of high power density and excellent cycling stability for SCs remains a major challenge [13]. Exploring novel electrode materials is an effective approach for improving the energy density of supercapacitors.

Currently, carbon nanofibers [14], metal oxide [15], transition metal oxides [16], and nanocomposite based on carbon nanotubes and nanosized-manganese oxide [17] have been extensively studied as possible supercapacitor electrode materials. Among these materials, MnO₂ is generally regarded as the one with the highest potential for SCs due to its ideal capacitor performance, great abundance, superior cycle lifetime, low cost, and environmental benignity [18,19]. However, poor electrical conductivity (10⁻⁵–10⁻⁶ S/cm) and densely packed structure limit rate capability in the development of high-power supercapacitors [20–22]. To effectively use MnO₂, considerable efforts have been made to explore novel hybrid electrodes via the coupling of various conductive materials, such as metal nanostructures [23], carbon (C) [24], and conducting polymers (CPs) [25]. Among these materials, C/MnO₂ nanostructure-based supercapacitor electrodes hold particular promise for SCs because carbon is light and characterized by high conductivity and good capacitive property. C/MnO₂ nanostructure-based

ABSTRACT

This paper developed a simple and inexpensive approach of boiling water-bath with simultaneous magnetic stirring to synthesize MnO₂ nanomaterials. In this paper, we proposed a novel structure of conducting graphite (G)/MnO₂ nanoflower (NF) hybrid electrodes, in which conducting graphite and MnO₂ nanomaterials hybrid solution were uniformly naturally deposited onto carbon paper. Such NF structures effectively decrease the charge transport resistance and facilitate ion or electron transmission in the electrode. G/MnO₂ NF hybrid electrodes exhibit a high specific capacitance (Cs) of 506 F/g, high energy/power density, and excellent cycling stability with 94% capacitance retained over 2000 cycles. Furthermore, symmetric supercapacitors (SSCs) with G/MnO₂ NF hybrid materials as electrodes were successfully fabricated, which achieved promising characteristics with a maximum energy density of 11.72 Wh/kg and a power density of 16.88 kW/kg. Such low-cost, high-performance carbon

supercapacitor electrodes show excellent properties. However, exploring novel hybrid electrode materials with superior performance are still necessary to realize large-scale energy storage applications.

In this study, a unique architecture of conducting G/MnO₂ NF hybrid electrodes was successfully fabricated. In the architecture, conducting graphite demonstrated superior electrical conductivity and high chemical stability. Moreover, MnO₂ NF structures not only effectively decreased the charge transport resistance and facilitated ion and electron transmission in the electrode, but also eased the access of electrolytes to the electrodes. The results proved that the fabricated G/MnO₂ NF hybrid electrodes exhibited high specific capacitance, large energy density, and potential as electrode materials for high-performance supercapacitors. G/MnO₂ NF hybrid electrode-based SSCs were successfully fabricated, which also achieved superior performance.

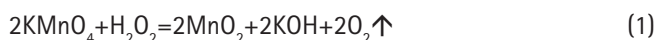
2. MATERIALS AND METHODS

2.1. MATERIALS

Potassium permanganate (KMnO₄), nitric acid (HNO₃), sodium sulfate (Na₂SO₄), ethanol (CH₃CH₂OH), hydrogen peroxide (H₂O₂), and polyethylene glycol-200 ([CH₂-O-CH₂]_n) are commercially available. In this study, these reagents of analytical grade were used as received. Conducting graphite, poly(tetrafluoroethylene) (PTFE), and separator were all purchased and used as received without further purification. Carbon paper was used as a substrate for supercapacitor. The surfactant removal of carbon paper was performed by washing with ethanol and double-distilled water, and the carbon paper was subsequently placed into 3 M nitric acid solution at 120 °C oil-bath reflux for 2 h. Double-distilled water was used for all solutions, which was purified with a labpure water system to a specific resistance of over 18.25 MΩ·cm.

2.2. SYNTHESIS OF MnO₂ NANOMATERIALS

First, the heat treatment process of 150 ml of 9.2 mM KMnO₄ solution was carried out with magnetically stirring until it boils within a water bath. Subsequently, 1.5 ml of 8.8 M H₂O₂ and 5 ml PEG200 were added drop-by-drop into the mixture, respectively. After heating at 100 °C for 30 min with constant whisking, the mixture was allowed to cool down slowly in the air. After the reaction, the sample was separated by centrifugation, washed three times with double-distilled water and ethanol, and dried at 50 °C for 10 h. Subsequently, MnO₂ nanomaterials were obtained. The reactions can be formulated as follows.



2.3. SAMPLE CHARACTERIZATION

The surface morphologies of the obtained samples were characterized using scanning electron microscopy (SEM, HITACHI S-4800, Japan). The fabricated hybrid electrodes were also analyzed by X-ray energy dispersive spectroscopy (EDS, Thermo Scientific, United States); Fourier transform infrared (FTIR, Bruker Tensor 27, Germany) spectra were used to study the chemical compositions and chemical bonding of the samples.

2.4. HALF-CELL (G/ MnO₂ NF HYBRID ELECTRODES) FABRICATION

To evaluate the electrochemical properties of MnO₂ nanomaterials, G/MnO₂ NF hybrid electrodes were fabricated. MnO₂ nanomaterials, conducting graphite, and PTFE binder were mixed in a

weight ratio of 75:20:5 [23] using 70% (v/v) ethanol as the solvent to yield a paste. The addition of conducting graphite could enhance the conductivity of active MnO₂ nanomaterials and increase the utilization ratio of high electrode nanomaterials. Typically, with the aid of ultrasonication for 30 min, the paste was incorporated into carbon paper (1.0 cm×2.0 cm) using a simple natural deposition process (dip and dry). Finally, the fabricated electrode was dried under a vacuum oven at 50 °C for 2 h.

2.5. FABRICATION OF SUPERCAPACITORS

To demonstrate the superior performance of G/MnO₂ NF hybrid electrodes for energy storage devices, we successfully assembled symmetric supercapacitors (SSCs) using two identical G/MnO₂ NF hybrid materials as electrodes that were separated with an ion-porous separator and an aqueous electrolyte of 1.0 M Na₂SO₄. Before the fabrication, the ion-porous separator and the two electrodes were impregnated with electrolyte for 30 min to drench them thoroughly.

2.6. ELECTROCHEMICAL MEASUREMENT

All of the electrochemical characterizations were carried out using a CHI 660E electrochemical workstation (Shanghai Chenhua Instruments Co.). In the half-cell test, a conventional three-electrode configuration was used to measure the cyclic voltammetry, galvanostatic charge-discharge behavior, and electrochemical impedance spectroscopy (EIS), where G/MnO₂ NF hybrid electrode was used as a working electrode, and a Pt foil (1.0 cm×2.0 cm) and a SCE Saturated Calomel Electrode (Sat'd KCL) were used as counter and reference electrode, respectively. Cyclic voltammeteries (CVs) were performed in the potential range of 0 V to 0.82 V under a sweep rate of 5~100 mV/s. The stabilities of G/MnO₂ NF hybrid electrodes were also tested by CV measurements for 2000 cycles, at a scan rate of 50 mV/s. Galvanostatic charge-discharge tests were performed at different current densities (0.15~5.00 A/g). EIS was measured to study the conductivity of G/MnO₂ NF hybrid electrodes in 0.5 M Na₂SO₄ solution over a wide range of frequencies (1 to 10 kHz). To determine the electrochemical performance of fabricated SSCs, cyclic voltammeteries and galvanostatic charge-discharge curves were measured by a two-electrode system. In addition to EIS, the electrolyte used in all of the measurements was 1 M Na₂SO₄ aqueous solution at pH 8.

2.7. CALCULATIONS

The gravimetric specific capacitance (C_s) of each device was measured from the cyclic voltammometric curves at different scan rates using the formula given in Eq. (2):

$$C_s = \frac{1}{s \cdot m \cdot \Delta V} \int_{V_0}^{V_0 + \Delta V} i dV \quad (2)$$

where *m*, *i*, Δ*V*, and *s* refer to the active mass of hybrid electrodes, the current (mA), the voltage range of one scanning segment (V), and the scan rate value, respectively.

The specific capacitance (C_s), energy density (E), internal resistance, (iR) and power density (P) of a supercapacitor cell were also obtained from the galvanostatic charge-discharge curves at different current densities according to Eqs. (3) to (6):

$$C_s = \frac{I_d \cdot T_d}{m \cdot \Delta V} \quad (3)$$

$$E = 0.5 C_s \Delta V^2 \quad (4)$$

$$iR = \frac{\Delta V_{iR}}{2I_d} \quad (5)$$

$$P = \frac{\Delta V^2}{4iRm} \quad (6)$$

where I_d is the constant discharge current, T_d is the discharge time, m is the total mass of active material in both electrodes, ΔV is the potential drop during discharge, and ΔV_{iR} is the potential sudden drop during discharge.

In two symmetric tandem supercapacitors, the specific capacitance (C_{se}) of the electrode (G/MnO₂ NF) was calculated using the following equation:

$$C_{se} = 4C_s \quad (7)$$

3. RESULTS AND DISCUSSION

Fig.1 illustrates the two key steps for preparing SSCs, namely, (i) conformal coating of G/MnO₂ NF hybrid materials onto highly

porous carbon paper fibers, and (ii) fabricating a symmetric SSC with two identical G/MnO₂ NF hybrid electrodes, ion-porous separator, and aqueous electrolyte. These steps are described at length in the section on experimental procedure.

In this work, we employed a facile approach of synthesizing MnO₂ nanomaterials. Figures 2(a), and 2(b) depict the representative SEM images of MnO₂ NP, graphite flakes, and MnO₂ NF-coated carbon paper microfiber, respectively. Figure 2(c) shows that MnO₂ NF are uniformly coated onto the carbon paper microfiber. Figures 2(a) and 2(c) demonstrate that the surface morphologies of MnO₂ materials change from MnO₂ nanoparticles (MnO₂ NP) to MnO₂ nanoflowers (MnO₂ NF) as the scan rate is increased after 100 cycles.

Figures 3(a) and 3(b) show the EDS results of MnO₂ NP and MnO₂ NF, respectively. The K element sharply decreased in Fig. 3(b) parallel with Fig. 3(a), this decrease could be attributed to K⁺ dissolution into electrolyte. Thus, the results of EDS confirmed the formation of the MnO₂ NF structure. The MnO₂ NF structures could offer large accessible surface areas to facilitate effective electrolyte ion and electron transport during SC operations.

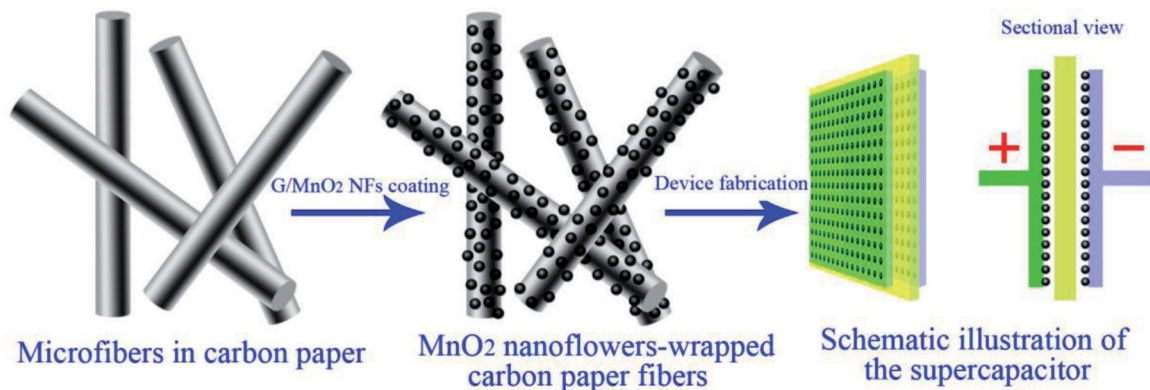


Fig. 1: Schematic illustration for the fabrication of conducting graphite/MnO₂ nanoflower (G/MnO₂ NF) hybrid electrode-based symmetric supercapacitors (SSCs)

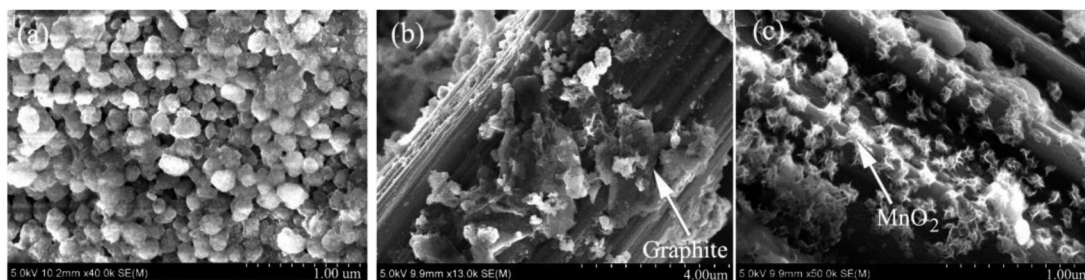


Fig. 2: Coating conducting graphite/MnO₂-nanostructured hybrid materials onto porous carbon paper fibers, the carbon paper used as SSC electrodes. SEM images of (a) MnO₂ nanoparticles (MnO₂ NP), (b) a typical microfiber with coating of graphite flakes, and (c) a representative microfiber with conformal coating of MnO₂ nanoflowers (MnO₂ NF).

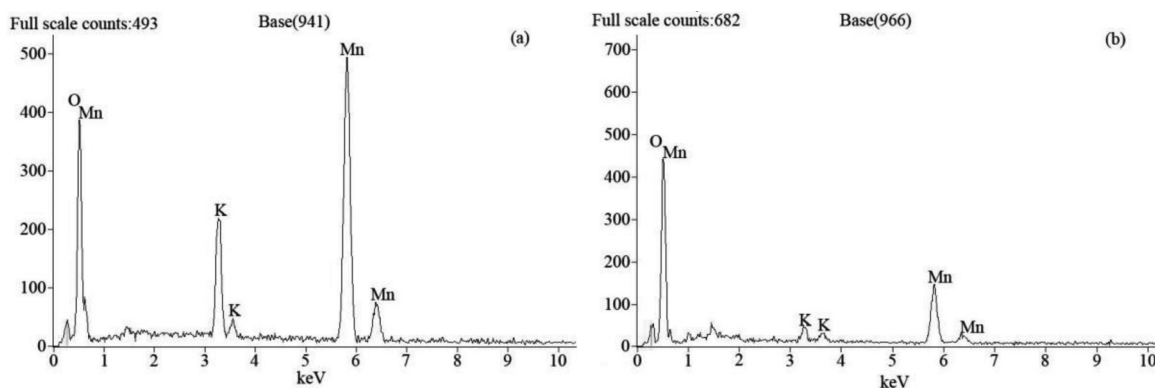


Fig. 3: EDS spectrum of (a) MnO₂ NPs and (b) MnO₂ NFs

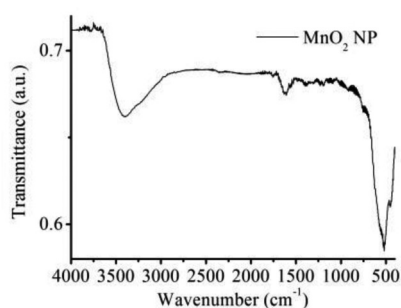


Fig. 4: FTIR spectra of MnO₂ NP

We studied the chemical bonding of MnO₂ NP. Fig. 4 shows the FTIR spectrum of the MnO₂ NP synthesized materials in the range of 4000–400 cm⁻¹. The FTIR spectra display three strong absorption peaks located at 3419 cm⁻¹ and 1635 cm⁻¹, which correspond to O–H

stretching and bending vibration, and 1557 cm⁻¹ may be ascribed to C–C stretching vibration, respectively. Furthermore, the two narrow absorption bands observed at 518 and 448 cm⁻¹ may be ascribed to Mn–O stretching vibrations. These characteristic bands are inconsistent with a normal MnO₂ structure owing to the contribution of PEG 200, thus confirming the formation of MnO₂ NP synthesized materials.

Specific capacitance (C_s) is one of the most key factors for high-performance supercapacitor. Achieving the highest C_s with regard to MnO₂ NF mass entails infinitesimal thickness and scan rate to facilitate the transport of ions and electrons in MnO₂ NF

hybrid electrode materials. However, high power and energy performance for the supercapacitor depends on the total mass. Therefore, optimizing the MnO₂ mass percentage with regard to the total mass is essential. We have performed a detailed research of varying scan rates and mass loadings across a wide range to confirm a trend, which will be useful for fabricating practical supercapacitors based on conductive carbon papers.

To demonstrate the superior performance of the half-cell of G/MnO₂ NF as an active SC electrode, we have examined their electrochemical performance by implementing cyclic voltammetry (CV) and galvanostatic charge/discharge (CP) measurements on a three-electrode system, as shown in Fig. 5.

Fig. 5(a) shows the CVs of 1.29 mg/cm² sample at different scan rates. CVs evidently exhibit a nearly rectangular shape at a scan rate of 20 mV/s, which indicate ideal capacitive behavior. As the scan rate increases (5 to 100 mV/s), the peak current increases but the shape deviates from that of an ideal supercapacitor, possibly due to the increasing over potentials lead to large RC time constant and resistance. The electrochemical properties of the half-cell of G/MnO₂ NF were performed with two different scan rates of 5 mV/s and 50 mV/s. The active MnO₂ mass changes from 0.06 mg/cm² to 3.32 mg/cm² accordingly. At the same scan rate, the total capacitance increases as the MnO₂ mass increases, as indicated by the increased current (see Figs. 5(b) and 5(c)). This

outcome may be attributed to the synergistic effects arising from each component of hybrid electrodes, which further enhances the electrical conductivity and contributes the ion transport between the electrolyte and MnO₂ NF. In addition, as the scan rate increases from 5 mV/s to 50 mV/s, the CV curves shape shows some distortions from an ideal capacitor. The improved electrochemical properties are also confirmed by the galvanostatic charging/discharging test performed with various current densities.

According to the galvanostatic charge/discharge curves for the half-cell of G/MnO₂ NF as shown in Fig. 5(d), the nearly triangular shape indicates that the sample exhibits superior reversible redox process and ideal supercapacitive performance, which are essentially in accordance with the result of the CV curves. These CP curves also display only a small voltage drop at the beginning of each discharge curve, which is indicative of the sample with low internal resistance (iR). The specific capacitance of the sample is calculated from the CV curves over a wide range of scan rates. Fig. 5(e) illustrates

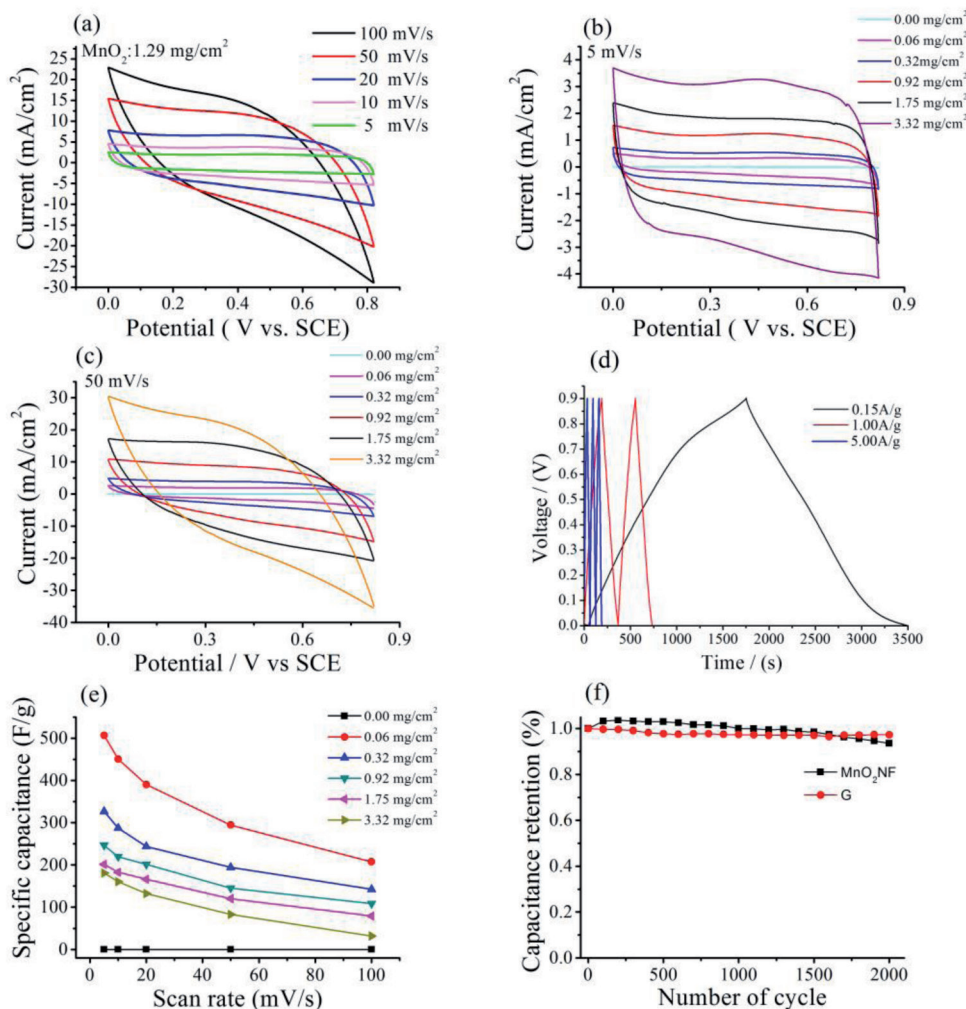


Fig. 5: Evaluation of the performance of a half-cell of G/MnO₂ NFs. (a) Cyclic voltammetry (CV) curves of a half-cell of G/MnO₂ NFs at various scan rates. The areal mass for MnO₂ NFs is 1.29 mg/cm². (b, c) CV curves of G/MnO₂ NF-based electrodes with diverse areal mass densities for MnO₂ NFs collected at scan rates of 5 mV/s (b) and 50 mV/s (c), respectively. (d) Galvanostatic charge/discharge curves of a half-cell of G/MnO₂ NFs at various current densities. (e) Specific capacitance versus scan rate for the half-cells of G/MnO₂ NFs based on various areal mass densities for MnO₂ NFs. (f) Cycling performance of the half-cell of G and G/MnO₂ NFs for 2000 cycles at a scan rate of 50 mV/s

the summary plot of C_s vs. scan rate with respect to the MnO₂ NF mass. As the scan rate decreases, C_s dramatically increases for the half-cell of G/MnO₂ NF. The highest C_s vs. a scan rate of 5 mV/s is 506 F/g for a sample with 0.06 mg/cm² MnO₂ NF, indicating that G/MnO₂ NF exhibit superior supercapacitive performance. As the thickness decreases, C_s increases because the infinitely small thickness of MnO₂ NF facilitates the transport of ions and electrons. The high electrical conductivity and diffusion constant contribute to the superior supercapacitive behavior. The active areal mass loading for practical devices merits further confirmation in future research.

Cyclic stability is another key factor in supercapacitor operations. Fig. 5(f) depicts the excellent cycling performance of the sample with 94% capacitance retained after 2000 cycles, which nearly approaches the level of graphite. Although graphite materials exhibit high cycle stability, the low C_s significantly limits their application, as shown in Fig. 5(f). The novel G/MnO₂ NF electrodes could possibly help keep them bound together and retain the mechanical stabilization of MnO₂ NF during the cycling tests to avoid MnO₂ nanomaterial loss, which are responsible for the high cyclic performance.

To evaluate the conductivity of G/MnO₂ NF electrode, we performed EIS measurement in a three-electrode system. EIS con-

high frequency (100 kHz) of the G/MnO₂ NF-based electrodes is estimated to be ~4.8 ohms in contrast to ~5.7 ohms for G/MnO₂-based electrodes, which reflects the higher conductivity achieved in the G/MnO₂ NF-based electrodes. This value is contributed from the contact resistance of the system with the external circuit. At lower frequencies, the increased vertical shape for G/MnO₂ NFs indicates an improved supercapacitive behavior [6]. Fig. 6(b) clearly demonstrates the improved supercapacitive performance due to the contribution of graphite. The higher conductivity of G/MnO₂ NF than MnO₂ NFs will enhance rate capability for high power and rapid charge-discharge. These EIS data concur with the equivalent circuit (see Fig. 7), in which C denotes a double-layer capacitance, R_p represents the charge transfer resistance, and R_s refers to the solution resistance.

To evaluate the feasibility of G/MnO₂ NF hybrid materials for SCs, a simple symmetric supercapacitor based on two identical G/MnO₂ NF hybrid electrodes was successfully fabricated, as shown in Fig. 8. After charging at 1.5 mA/cm² for 10 s, the device lit up a red LED for approximately 15 min.

The galvanostatic charge-discharge measurements of SSC based on G/MnO₂ NFs were also performed in 1 M Na₂SO₄ solution on a two-electrode system, as shown in Fig.9. Portable equipment has become increasingly prevalent nowadays, which often requires

cells packaged in series of the two or more to meet energy and power requirements. For example, laptop batteries normally have four 3.6 V lithium ion battery cells connected in series to achieve a voltage of 14.4 V. Thus, using tandem serial assemblies to develop SCs that could regulate over the operating voltage would be of great interest. Herein, we connected two SSC units in series, compared with a single SSC. Fig. 9 shows the galvanostatic charge-dis-

charge curves for two tandem SSCs connected in series. The tandem series SSCs exhibit an enhanced working potential of 1.8 V compared with a single device, which operates at 0.9 V. Both the single device and the tandem devices collect at the same current density. As with the single SSC, the two tandem SSCs devices exhibit nearly perfect triangular charge/discharge curves with a minimal voltage drop, which indicates predominant capacitive properties with a miniscule internal resistance. Thus, when used in tandem,

the SSCs exhibit with minimal energy losses, which would increase voltages and energy densities.

Power and energy densities are key parameters for a supercapacitor. To show the overall performance of SSC based on

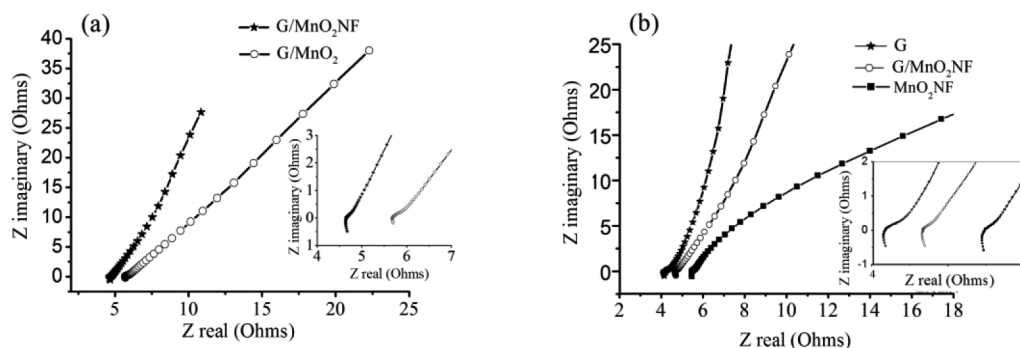


Fig. 6: (a) Nyquist plots of G/MnO₂ NFs and G/MnO₂ over a frequency range of 100 kHz to 1 Hz. Inset: enlargement of the Nyquist plots in the high-frequency region. (b) Nyquist plots for G, G/MnO₂ NFs, and MnO₂ NFs, the inset representing a magnification for the high-frequency region

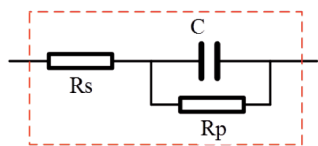


Fig. 7: The equivalent circuit of G/MnO₂ NF electrodes

firmed the rapid ion transport within the G/MnO₂ NF electrodes. Fig. 6(a) shows the Nyquist plots of G/MnO₂ NFs and G/MnO₂ between 1 Hz and 10 kHz. The series resistance at

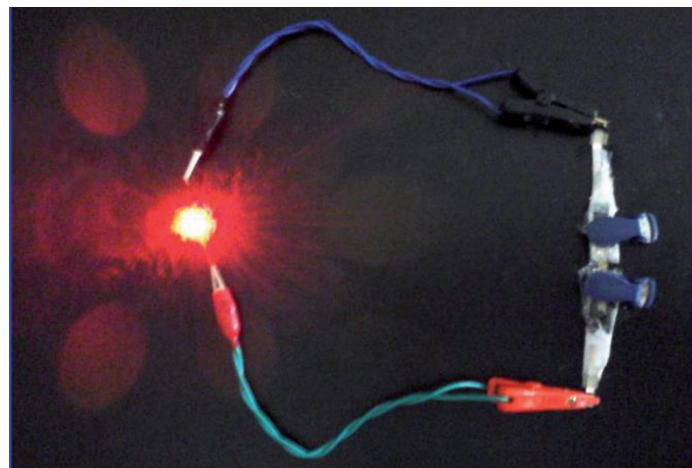


Fig. 8: This charged simple fabricated symmetric supercapacitor is used to power a red light-emitting diode (LED)

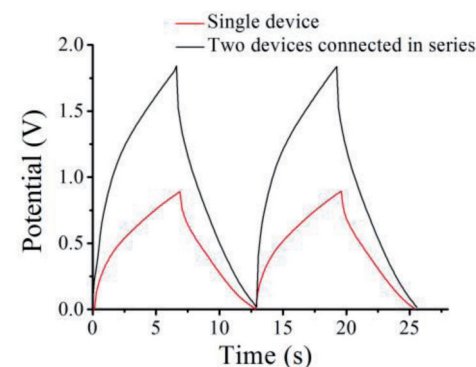


Fig. 9: Galvanostatic charge-discharge curves for a single SSC and two tandem SSCs connected in series

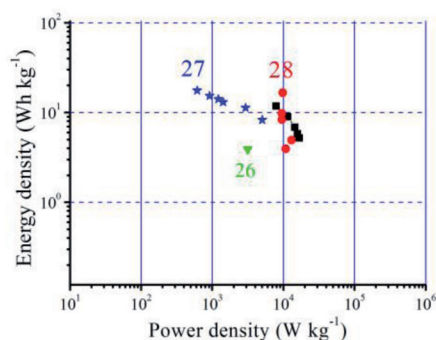


Fig. 10: Ragone plot of power density versus energy density for our G/MnO₂ NF hybrid electrodes (black points) and others using similar electrodes reported in literatures (refs 26, 27 and 28) for comparison

G/MnO₂ NF hybrid electrodes, a Ragone plot is illustrated in Fig. 10. The plot compares power and energy densities of G/MnO₂ NF hybrid electrodes to other reported similar supercapacitors. SSC can provide energy densities of up to 11.72

Wh/kg and can deliver the highest power density of 16.88 kW/kg, which is higher than the reported MnO₂/MnO₂-based SCs [26], polyaniline/MnO₂ nanotube-based SCs [27] and slightly lower than the MnO₂/carbon nanotube-based SCs [28].

4. CONCLUSION

In conclusion, a symmetric high performance supercapacitors based on lowcost conducting graphite/MnO₂ nanoflower hybrid electrode was designed and fabricated through a facile method. The G/MnO₂ NF hybrid electrodes retains 94% of its initial capacitance after 2000 cycles. The SSC achieved an excellent specific capacitance of 506 F/g and an energy

density of 11.72 Wh/kg. The high electrical conductivity and facilitated electron and ion transmission of the novel G/MnO₂ NF hybrid electrodes are responsible for the high supercapacitive performance of SSCs. Further improvement in energy and power densities can be achieved with developed novel MnO₂ nanomaterials, increased mass loading of MnO₂ nanomaterials, and optimized mass balance of both electrodes for hybrid SSCs. These SSCs may create new opportunities for energy storage devices due to the facility of the device architecture and the availability of conducting graphite.

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APPRECIATION

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