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## High mass loading flower-like $\text{MnO}_2$ on $\text{NiCo}_2\text{O}_4$ deposited graphene/nickel foam as high-performance electrodes for asymmetric supercapacitors<sup>†</sup>

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The implementation of high mass loading  $\text{MnO}_2$  on electrochemical electrodes of supercapacitors is currently challenging due to the poor electrical conductivity and elongated electron/ion transport distance. In this paper, a  $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  heterostructure was built on the surface of three-dimensional graphene/nickel foam (GNF) by a hydrothermal method. The petal structured  $\text{NiCo}_2\text{O}_4$  loaded on graphene played a wonderful role as a supporting framework, which provided more space for the growth of high mass loading  $\text{MnO}_2$  microflowers, thereby increasing the utilization rate of the active material  $\text{MnO}_2$ . The GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  composite was used as a positive electrode and achieved a high areal capacitance of  $1630.5\text{ mF cm}^{-2}$  at  $2\text{ mA cm}^{-2}$  in the neutral  $\text{Na}_2\text{SO}_4$  solution. The asymmetric supercapacitor assembled with the GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  positive electrode and activated carbon negative electrode possessed a wide voltage window (2.1 V) and splendid energy density ( $45.9\text{ Wh kg}^{-1}$ ), which was attributed to the satisfactory electroactive area, low resistance, quick mass diffusion and ion transport caused by high mass loading  $\text{MnO}_2$ .

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### Introduction

The research on portable supercapacitors has been given great attention owing to the high power density, fast charging and discharging, excellent cycling performance, indefinite lifespan, nonvulnerability to temperature change, nontoxicity in nature, and their being more reliable than batteries. According to the different charge-storage mechanisms, supercapacitors are divided into electric double-layer capacitors (EDLCs) and pseudocapacitors.<sup>1–3</sup> Compared with the carbon-based active materials for EDLCs, the pseudocapacitive electrode materials can provide higher specific capacitance and energy density which is related to specific capacitance and voltage window. Therefore, there are usually two strategies for increasing energy

density, namely increasing specific capacitance and expanding the voltage window. Rational design of the nanostructure of the composites to increase the content and utilization of high-capacitance active materials per unit area of the electrode material is a feasible method.<sup>4,5</sup> Many composites of different pseudocapacitive materials and carbon materials with high specific capacitances have been researched, such as  $\text{MnO}_2$ /graphene/NF (NF, nickel foam),<sup>6</sup>  $\text{RuO}_2$ /graphene,<sup>7</sup>  $\text{RuO}_2$ /graphene/CNT (CNT, carbon nanotubes),<sup>8</sup> and  $\text{V}_2\text{O}_5$ -CNTs/GF (GF, graphene form)<sup>9</sup> with different morphologies.<sup>10,11</sup> Numerous studies have shown that combining  $\text{MnO}_2$  with a highly conductive material to form a composite material can significantly enhance its electrical conductivity and electrochemical performance.<sup>12–14</sup> For example, Garakani *et al.* used GF substrates to grow  $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  arrays as a freestanding supercapacitor electrode with great enhancement in both gravimetric and areal capacitances.<sup>15</sup> Lu *et al.* obtained supercapacitors with good cycling performance using  $\text{WO}_{3-x}@\text{Au}@\text{MnO}_2$  core–shell structure nanocomposites as electrodes.<sup>16</sup> Wang's group prepared composites of hierarchical  $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  nanosheets on carbo cloth which used as positive electrodes and achieved excellent electrochemical performance.<sup>17</sup> However, the specific capacitance mostly reported so far could be obtained just by loading a low mass  $\text{MnO}_2$  ( $<1\text{ mg cm}^{-2}$ ). Therefore, it's still urgent to load higher mass  $\text{MnO}_2$  to acquire higher specific capacitance, higher energy density and wide

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voltage window in practical application.<sup>18–22</sup> In this paper, we designed heterogeneous  $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  materials on a graphene modified NF (GNF) substrate. The conductive petal-like  $\text{NiCo}_2\text{O}_4$  arrays constructed on NF provided additional space to allow higher mass loading of  $\text{MnO}_2$  micro-flowers. With GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  composite material as the positive electrode and GNF@AC (AC, activated carbon) as the negative electrode, an asymmetric supercapacitor (ASC) was fabricated in a neutral  $\text{Na}_2\text{SO}_4$  aqueous electrolyte. The electrode with high mass loading provides outstanding specific capacitance of  $1630.5 \text{ mF cm}^{-2}$  at  $2 \text{ mA cm}^{-2}$ . The assembled ASC shows excellent cycling performance, with its voltage window of  $2.1 \text{ V}$ , and the energy density of  $505.2 \mu\text{Wh cm}^{-2}$  ( $45.9 \text{ Wh kg}^{-1}$ ,  $5.1 \text{ mWh cm}^{-3}$ ), demonstrating its application potential in the field of energy storage.

## Experimental section

### Growth of graphene on Ni foam (GNF)

Fig. 1 shows the synthesis process of GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  electrode. First, graphene layer was deposited on the surface of NF by radio-frequency plasma enhanced chemical vapor deposition system (RF-PECVD).<sup>23–27</sup> Three pieces of NF with the area of  $1 \times 2 \text{ cm}^2$  and the thickness of  $0.5 \text{ mm}$  were ultrasonically cleaned in acetone,  $1 \text{ M HCl}$  and ethanol, and blown dried with moisture-free air. The quartz boat with NF substrates was then placed in the heating zone of RF-PECVD. The chamber was evacuated to a pressure less than  $300 \text{ mTorr}$  and then hydrogen gas was introduced at a rate of  $6 \text{ sccm}$ . Plasma was generated for  $10 \text{ min}$  with the RF power of  $300 \text{ W}$  to further remove contaminants on the substrates. When heating the chamber to  $750 \text{ }^\circ\text{C}$ , graphene layer was grown by introducing  $\text{CH}_4$ , Ar and  $\text{H}_2$  at flow rates of  $10 \text{ sccm}$  for  $30 \text{ min}$  under a plasma power of  $250 \text{ W}$  and a total pressure of  $\sim 400 \text{ mTorr}$ . After the temperature was lowered to room temperature at a frequency of  $10 \text{ }^\circ\text{C min}^{-1}$ , the GNF was obtained.

### Preparation of GNF@ $\text{NiCo}_2\text{O}_4$ and GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$

Petal shaped  $\text{NiCo}_2\text{O}_4$  nanoarrays were deposited on GNF by using hydrothermal method. Typically,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $1 \text{ mmol}$ ),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $2 \text{ mmol}$ ) and urea ( $12 \text{ mmol}$ ) were added into  $100 \text{ mL}$  deionized (D.I.) water and stirred for  $30 \text{ minutes}$  to obtain a homogenous mixed solution. GNF was treated with plasma for  $100 \text{ s}$  to make it hydrophilic and ready for use. Subsequently, a piece of treated GNF and  $10 \text{ mL}$  of the mixed solution were put into a Teflon-lined stainless-steel autoclave. The autoclave was heated to  $160 \text{ }^\circ\text{C}$  in the oven and

kept it for  $10 \text{ h}$ ,  $15 \text{ h}$ ,  $20 \text{ h}$  and  $25 \text{ h}$ , respectively, followed by naturally cooled to room temperature. The obtained precursors were washed repeatedly with D.I. water and ethanol, thereafter desiccated in the oven at  $60 \text{ }^\circ\text{C}$  for  $12 \text{ h}$ . Lastly, the precursors were annealed in atmosphere at  $300 \text{ }^\circ\text{C}$  for two hours to obtain petal-like GNF@ $\text{NiCo}_2\text{O}_4$ . By weighing the GNF before and after  $\text{NiCo}_2\text{O}_4$  deposition, the mass loading of  $\text{NiCo}_2\text{O}_4$  obtained under different reaction time was obtained. Furthermore, GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  was prepared by the second hydrothermal treatment. The  $\text{KMnO}_4$  ( $0.45 \text{ g}$ ) was added into D.I. water ( $10 \text{ mL}$ ), and was stirred for  $30 \text{ minutes}$  to obtain purple solution. The solution was placed in an autoclave simultaneously with as-synthesized GNF@ $\text{NiCo}_2\text{O}_4$ , heated to  $160 \text{ }^\circ\text{C}$  and maintained for  $10 \text{ hours}$ , then freely cooled to ambient temperature. After that, the resulting compound was washed repeatedly to remove the residue and desiccated in oven at  $60 \text{ }^\circ\text{C}$  for  $12 \text{ hours}$ , then GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  was obtained. As a control, we also synthesized GNF@ $\text{MnO}_2$  (without  $\text{NiCo}_2\text{O}_4$ ) and NF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  (without graphene) under the same conditions.

### Fabrication of GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2/\text{AC}$ asymmetric pseudocapacitor

The formula for balancing the charge between the positive and negative electrodes is as follows:<sup>28,29</sup>

$$q = C \times \Delta V \times m \quad (1)$$

$$q^+ = q^- \quad (2)$$

where  $C$  and  $\Delta V$  are the specific capacitance and charge/discharge potential range of each electrode, respectively. AC, acetylene black and polyvinylidene fluoride (PVDF) binder were mixed evenly into a slurry according to the weight ratio of  $8 : 1 : 1$ , and then pressed on NF to construct the negative electrode. Next, it was dried in an oven at  $60 \text{ }^\circ\text{C}$  for  $10 \text{ hours}$ . The positive electrode, negative electrode and separator were cut into  $1 \times 1 \text{ cm}^2$  size and  $1 \text{ M Na}_2\text{SO}_4$  was used as the electrolyte to assemble the CR2018 coin cell.

### Materials characterization

To determine the morphology and microstructural characteristic of the products, Hitachi S-4800 field emission scanning electron microscope (FE-SEM) was employed. The crystalline structures of samples were examined by a Bruker D8 Discover X-ray powder diffractometer (XRD,  $\text{Cu K}_\alpha$ ,  $\lambda = 0.15418 \text{ nm}$ ). The valence state of the composite was measured by X-ray

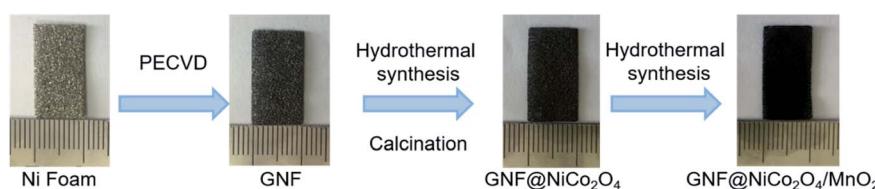


Fig. 1 Schematic of the synthesis process of GNF@ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ .



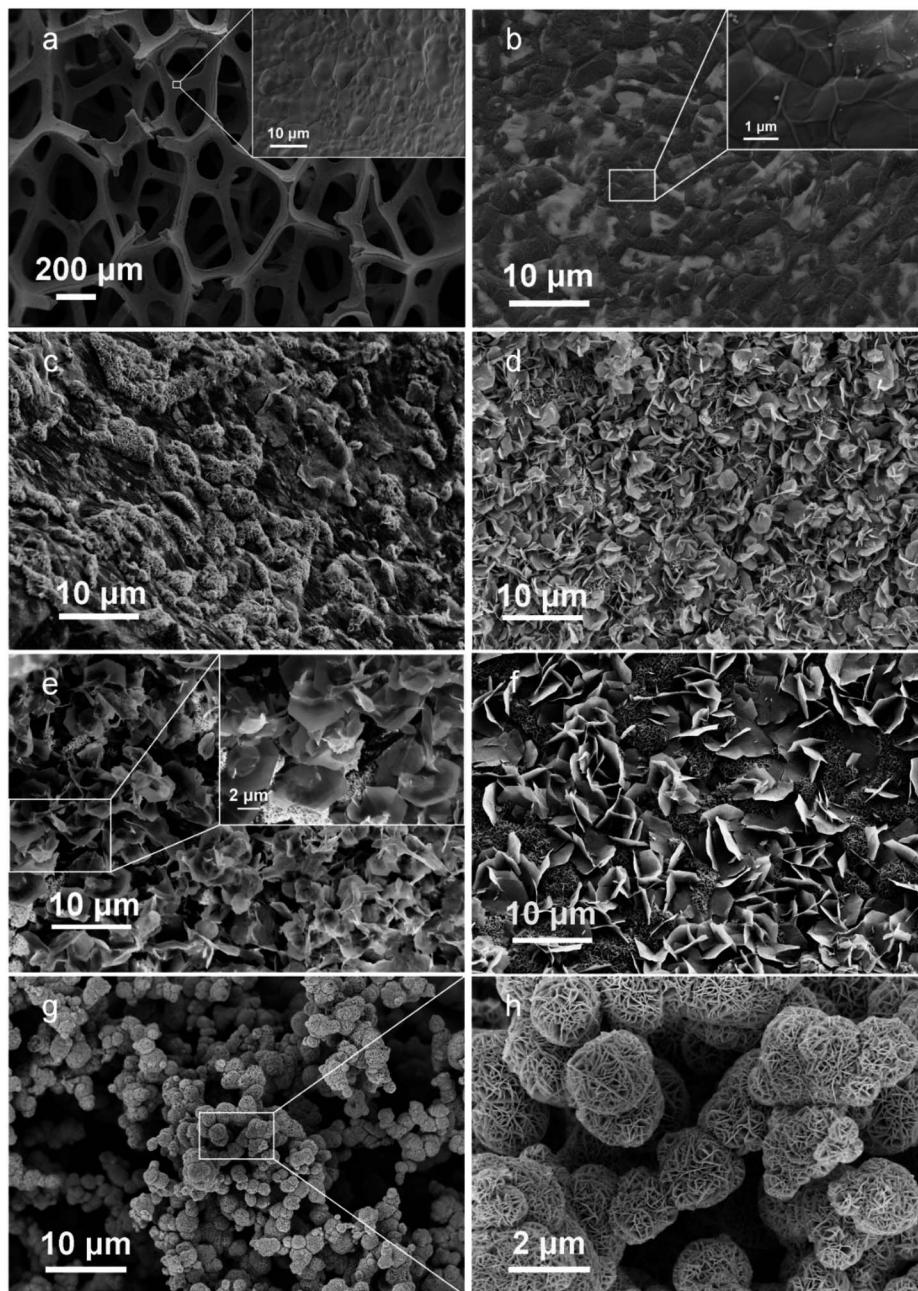


Fig. 2 SEM images of (a) bare Ni foam, (b) GNF, (c) GNF@NiCo<sub>2</sub>O<sub>4</sub>-10 h, (d) GNF@NiCo<sub>2</sub>O<sub>4</sub>-15 h, (e) GNF@NiCo<sub>2</sub>O<sub>4</sub>-20 h, (f) GNF@NiCo<sub>2</sub>O<sub>4</sub>-25 h, (g and h) GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>.

photoelectron spectrometer (XPS, Thermo Scientific ESCALAB 250Xi). Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore-size distribution analysis were carried out by a surface area analyzer (Autosorb-iQ). Lab RAM HR-Evolution (Horiba, 532 nm laser excitation) Raman spectrometer was utilized to investigate the Raman spectra of graphene. The mass loading was obtained by measuring the mass change of the sample before and after the reaction with a microbalance. Specially, the mass loading of graphene was  $0.1 \text{ mg cm}^{-2}$  in the obtained GNF; it was determined to be about  $1.4 \text{ mg cm}^{-2}$  of NiCo<sub>2</sub>O<sub>4</sub> for the obtained GNF@NiCo<sub>2</sub>O<sub>4</sub> (hydrothermal reaction time was 20 hours); the mass loadings

of MnO<sub>2</sub> for GNF@MnO<sub>2</sub> and GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> were  $3.0 \text{ mg cm}^{-2}$  and  $3.5 \text{ mg cm}^{-2}$ , respectively. Hence, the total mass loading of active materials for GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> achieved  $5.0 \text{ mg cm}^{-2}$ . The mass loading of negative electrode was  $6.0 \text{ mg cm}^{-2}$ .

### Electrochemical measurements

The electrochemical test was performed using 760E electrochemical workstation (CH instrument, China). The electrochemical property of single electrode was examined under three-electrode configuration in 1 M Na<sub>2</sub>SO<sub>4</sub> solution. A Pt foil was applied as counter electrode and saturated calomel



electrode (SCE) electrode was employed as reference electrode. The electrochemical impedance spectroscopy (EIS) was analyzed at the open circuit potential in frequency range from 0.01 Hz to 100 kHz. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were performed in the operating potential range of 0–0.8 V. The specific capacitance ( $C_s$ ,  $C_m$ ) is calculated by the following formulas (3) and (4) using GCD data.<sup>30–32</sup>

$$C_s = \frac{I \times \Delta t}{s \times \Delta V} \quad (3)$$

$$C_m = \frac{I \times \Delta t}{m \times \Delta V} \quad (4)$$

where  $I$  (mA),  $\Delta t$  (s),  $s$  ( $\text{cm}^2$ ),  $m$  (g), and  $\Delta V$  (V) represent the discharge current, discharge time, area, loading mass, and voltage window, respectively. The cycling capacity retention rate was the ratio between the final capacity and the initial one. The energy density  $E$  of the ASC was calculated by eqn (5), and (6) was used to calculate the power density:<sup>33–35</sup>

$$E = \frac{1}{2} C V^2 \quad (5)$$

$$P = \frac{E}{\Delta t} \quad (6)$$

where  $C$  represented the specific capacitance obtained from above equations, and  $V$  and  $t$  were the voltage window and discharge time, respectively.

## Results and discussion

### Morphologies and structures of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>

High-quality graphene was obtained by adjusting the gas flow rate, the reaction gas ratio, the reaction time, and the radio frequency power during the reaction *via* RF-PECVD system. Fig. 2a and b show the morphology of the bare NF surface before and after the deposition of graphene. Clear graphene wrinkles are uniformly covered on the 3D NF network. From the SEM images of GNF@NiCo<sub>2</sub>O<sub>4</sub> in Fig. 2c–f, it is found that the GNF is covered by NiCo<sub>2</sub>O<sub>4</sub> sheet arrays through hydrothermal treatment. As the reaction time increases, the surface morphology of GNF@NiCo<sub>2</sub>O<sub>4</sub> changes significantly. When the reaction is carried out for 10 hours, some scattered flaky networks are overlaid on GNF. After 15 hours, large sheets begin to grow between the flaky networks, and form new network arrays. When the time reaches 20 hours, the large petal-like micro-sheets form a 3D layered framework, which is beneficial for further deposition of new materials. After 25 hours of reaction, the larger sheets are scattered on the top of the network formed by the smaller sheets and do not form an orderly network. When MnO<sub>2</sub> is deposited on the surface of GNF@NiCo<sub>2</sub>O<sub>4</sub> (reaction time of 20 hours), the flower-like MnO<sub>2</sub> microspheres are evenly dispersed on the NiCo<sub>2</sub>O<sub>4</sub> nanosheet arrays, as shown in Fig. 2g and h. The microspheres are also formed by many sheets, which provides a 3D structure and is beneficial for electron transmission and ion diffusion. The microstructures were also characterized by the Raman spectrum and XRD pattern. From

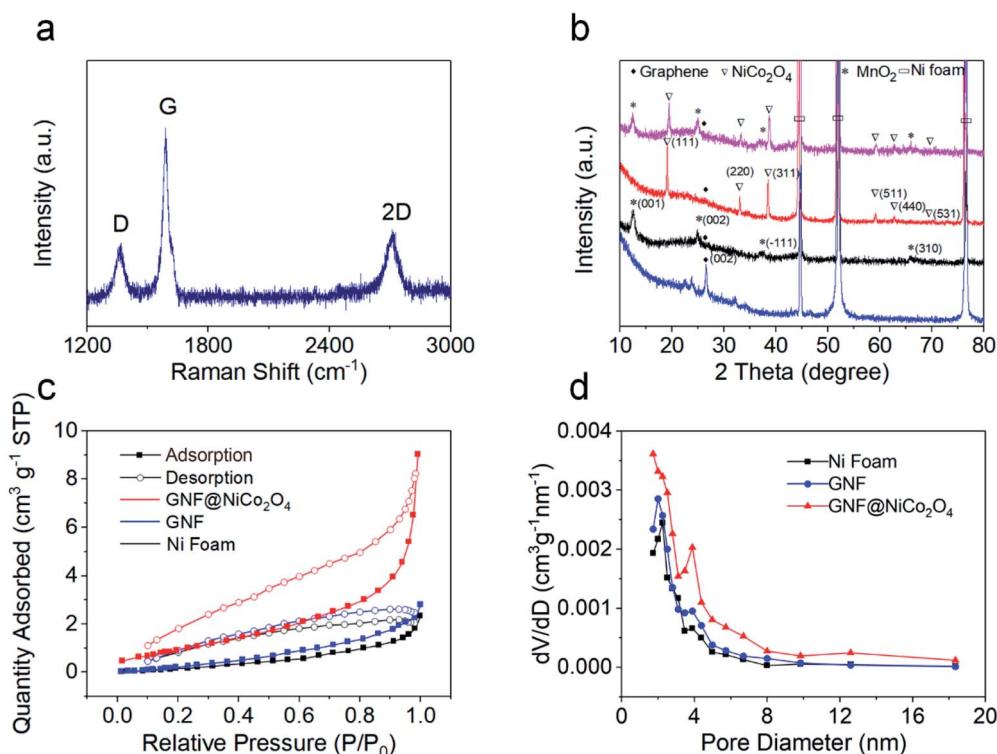


Fig. 3 (a) Raman spectra of GNF, (b) XRD patterns of GNF (blue line), GNF@MnO<sub>2</sub> (black line), GNF@NiCo<sub>2</sub>O<sub>4</sub> (red line), and GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> (pink line). (c and d) The nitrogen adsorption/desorption isotherms and the corresponding BJH pore size distribution of Ni foam (black line), GNF (red line), and GNF@NiCo<sub>2</sub>O<sub>4</sub> (blue line).



the Raman spectrum of GNF in Fig. 3a, it shows the characteristic D, G, and 2D peaks located at  $1353\text{ cm}^{-1}$ ,  $1580\text{ cm}^{-1}$ , and  $2702\text{ cm}^{-1}$ , respectively. The position of Raman peak and the intensity ratio of graphene will be affected by defects and the number of graphene layers.<sup>36</sup> The D band is disordered  $\text{sp}^2\text{ C}$  in graphene.<sup>37</sup> The intensity ratio of the D band to the G band ( $I_{\text{D}}/I_{\text{G}} = 0.27$ ) indicates the graphene with few defects.<sup>38</sup> The peak at  $1580\text{ cm}^{-1}$  (G band) stands for  $\text{sp}^2\text{ C}$  in graphene, and the  $I_{\text{G}}/I_{\text{2D}}$  ratio of 2.05 represents its multi-layer structure.<sup>39,40</sup> The XRD pattern of GNF (Fig. 3b blue line) presents a sharp peak at  $2\theta \approx 26.4^\circ$ , which corresponds to (002) reflection of graphene (JCPDS 75-1621).<sup>41</sup> For GNF@NiCo<sub>2</sub>O<sub>4</sub>-20 h samples, in addition to the three typical peaks of Ni, another six well-defined diffraction peaks are shown at  $2\theta$  equalling to  $\sim 19.0^\circ$  (111),  $32.9^\circ$  (220),  $38.4^\circ$  (311),  $59.1^\circ$  (511),  $62.7^\circ$  (440) and  $69.4^\circ$  (531), which represent the spinel crystalline structure of

NiCo<sub>2</sub>O<sub>4</sub> (JCPDS file no. 20-0781).<sup>42</sup> The XRD pattern of GNF@MnO<sub>2</sub> (black line in Fig. 3b) shows that the diffraction peaks near to  $12.3^\circ$ ,  $24.8^\circ$ ,  $37.3^\circ$ , and  $65.9^\circ$  can well match (001), (002), (-111), and (310) planes of monoclinic birnessite-type MnO<sub>2</sub> (JCPDS 42-1317).<sup>43,44</sup> The XRD pattern of the GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> (the pink line in Fig. 3b) shows a small peak at  $2\theta \approx 26.4^\circ$  corresponding to the graphene and other characteristic peaks related to crystallographic planes of NiCo<sub>2</sub>O<sub>4</sub> (JCPDS 020-0781) and MnO<sub>2</sub> (JCPDS 42-1317). The surface areas and pore size of the samples were measured by nitrogen adsorption/desorption tests. The specific surface area of GNF@NiCo<sub>2</sub>O<sub>4</sub> is  $13.02\text{ m}^2\text{ g}^{-1}$  calculated by Brunauer–Emmett–Teller (BET) method, which is two times higher than that of GNF (Fig. 3c). It indicates that the presence of NiCo<sub>2</sub>O<sub>4</sub> effectively increases the specific surface area of the composite. Barrett–Joyner–Halenda (BJH) pore size distribution shows the

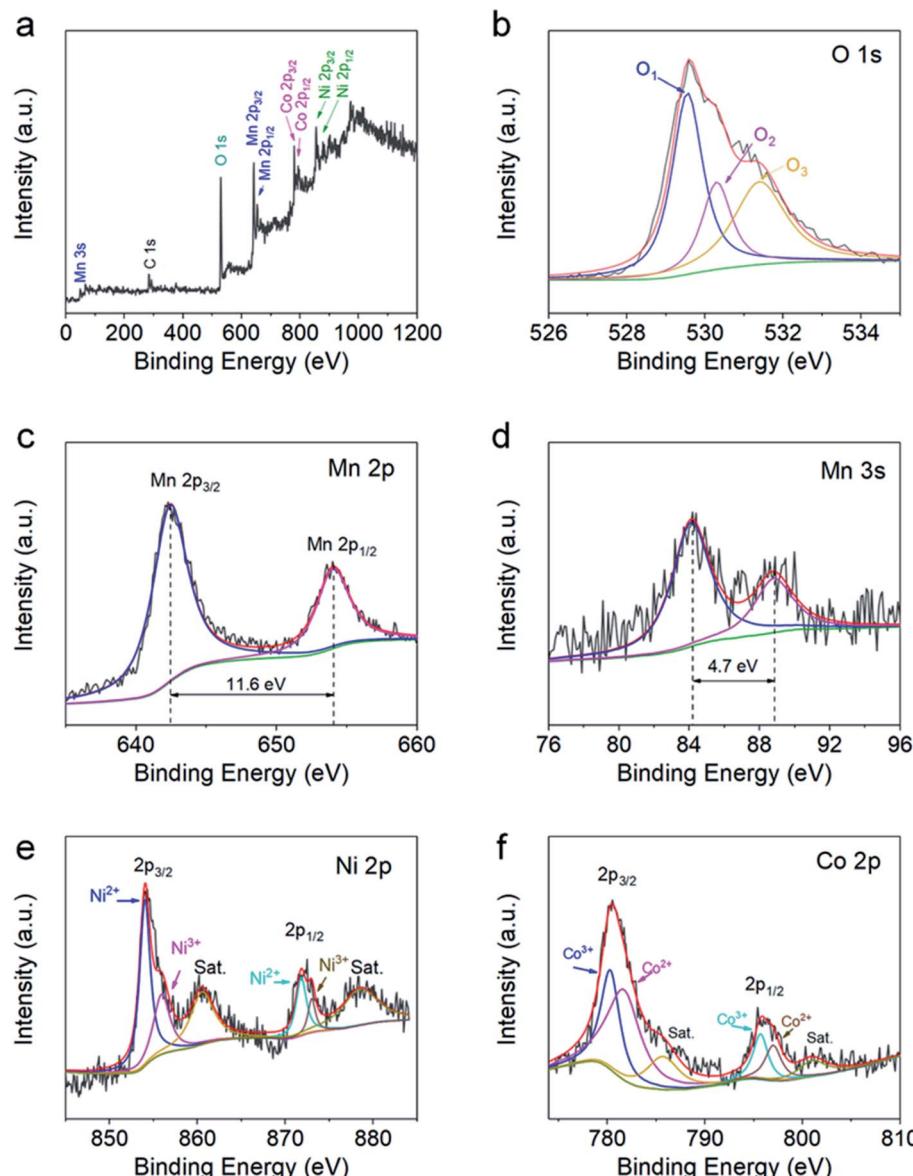


Fig. 4 XPS spectra of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>. (a) Survey scan, (b) O 1s, (c) Mn 2p, (d) Mn 3s, (e) Ni 2p, and (f) Co 2p core level spectra.



microporous and mesoporous of GNF@NiCo<sub>2</sub>O<sub>4</sub> are distributed in 1.7–8.0 nm range (Fig. 3d).<sup>45–47</sup> The 3D structure of GNF@NiCo<sub>2</sub>O<sub>4</sub> increases the distribution space of MnO<sub>2</sub>, thereby increasing the surface area of MnO<sub>2</sub> in contact with the electrolyte, providing more electron transport channels and shortening the electron/ion transport distance.

The chemical composition of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> was also investigated by XPS measurement. Fig. 4a shows the survey spectrum, indicating the presence of C, Mn, O, Ni, and Co elements. Fig. 4b shows that the O 1s core level spectrum of the prepared GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> and can be divided into three characteristic peaks, namely O<sub>1</sub>, O<sub>2</sub> and O<sub>3</sub> located at 529.5 eV, 530.3 eV and 531.4 eV, respectively. The fitted peak O<sub>1</sub> can be attributed to the lattice O<sup>2-</sup>, which corresponds to a typical metal–oxygen bond.<sup>48</sup> The peak of O<sub>2</sub> is associated with the surface oxygen in OH<sup>-</sup>.<sup>49</sup> The O<sub>3</sub> peak is related to oxygen ions with low coordination on the surface of metal oxides, and formally these oxide ions are O<sup>-</sup> species with lower electron density than the classical O<sup>2-</sup> ions.<sup>50</sup> Fig. 4c is the scanning spectrum of Mn 2p.

Two distinct characteristic peaks located at 642.4 eV and 654.0 eV correspond to Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub>, respectively. The distance between the two peaks is about 11.6 eV, which confirms the formation of MnO<sub>2</sub>.<sup>51</sup> In the Mn 3s spectrum (Fig. 4d), the peaks are observed near 84.1 eV and 88.8 eV, the energy separation of 4.7 eV further indicates that the Mn

element in the sample mainly exists in the form of +4 valence.<sup>52</sup> Fig. 4e shows the scanning spectrum of the Ni 2p energy level, showing two distinct main peaks corresponding to Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub>. The two fitted peaks placed at 854.0 eV and 871.8 V correspond to Ni<sup>2+</sup>, and the two peaks at 855.9 eV and 873 eV correspond to Ni<sup>3+</sup>. The satellite peaks located at 860.5 eV and 878.5 eV are indicators of the two shake-type peaks of Ni.<sup>53,54</sup> The Co 2p spectrum (Fig. 4f) similarly shows two spin-orbit double peaks and two satellite peaks. The two main peaks are attributed to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>. Among them, the two fitted peaks at 781.7 V and 797 eV are attributed to Co<sup>2+</sup>, while the other two at 780.3 eV and 797.0 eV belong to Co.<sup>3</sup> The two satellite peaks are located at 785.7 eV and 801.0 eV.<sup>55</sup>

### Supercapacitive performance of electrodes

To investigate the electrochemical properties of the materials, the composites were immersed in a three-electrode configuration by adopting it as the working electrode. Fig. S1† provides the CV curves of pure NF at different scan rates. The areas of the CV curves are very small, which indicates that pure NF has a low capacity. The effect of hydrothermal reaction time on the electrochemical performance of GNF@NiCo<sub>2</sub>O<sub>4</sub> was explored at the same scanning frequency. As shown in Fig. 5a, the current response of GNF@NiCo<sub>2</sub>O<sub>4</sub> with 20 hours hydrothermal reaction is the largest, showing that the sample may possess the highest specific capacitance. This is verified by the GCD curves

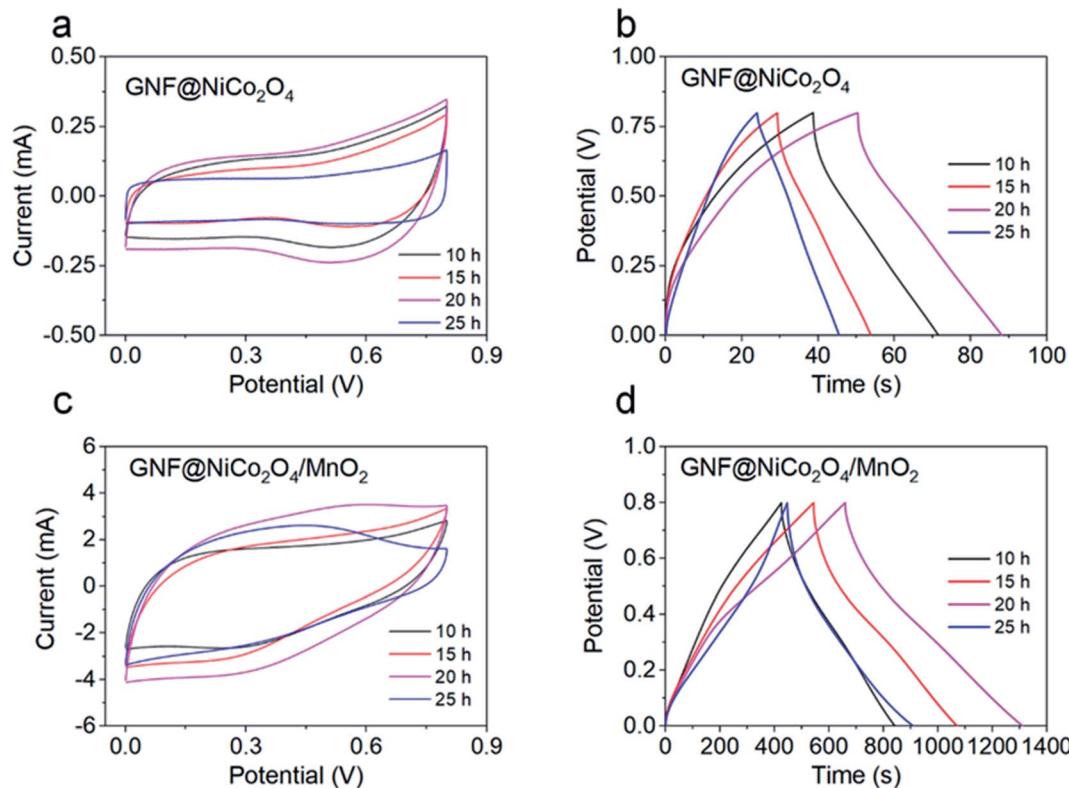


Fig. 5 (a) The CV curves of GNF@NiCo<sub>2</sub>O<sub>4</sub> electrodes with different reaction time at 5 mV s<sup>-1</sup>, (b) the GCD curves of GNF@NiCo<sub>2</sub>O<sub>4</sub> electrodes with different reaction time at 2 mA cm<sup>-2</sup>, (c) the CV curves of different GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> electrodes at 10 mV s<sup>-1</sup>, (d) the GCD curves of different GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> electrodes at 2 mA cm<sup>-2</sup>.



which shows the relationship between the discharge time of different GNF@NiCo<sub>2</sub>O<sub>4</sub> samples and hydrothermal reaction time (Fig. 5b). The longest discharge time of the GNF@NiCo<sub>2</sub>O<sub>4</sub>-20 h proves its highest area specific capacitance. But the CV curve of GNF@NiCo<sub>2</sub>O<sub>4</sub> does not show a clear redox peak, and the GCD curve has no sloping plateau, indicating that its redox-active is suppressed in salt solutions, and its short charge and discharge time also prove this result.

When MnO<sub>2</sub> was deposited on the GNF@NiCo<sub>2</sub>O<sub>4</sub> with different reaction time for 10 hours to obtain different

GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> composites, the CV curve (Fig. 5c) and GCD curve (Fig. 5d) of the sample with GNF@NiCo<sub>2</sub>O<sub>4</sub>-20 h are more symmetrical rectangular and triangular than other samples, indicating the pseudocapacitive properties of the electrode are primarily attributed to the two electron-transferred charge storage mechanism of MnO<sub>2</sub> in the mild Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. This involves surface adsorption/desorption and the reversible redox transition, the exchange of protons and/or cations with the electrolyte and different oxidation states, and can be expressed as follows

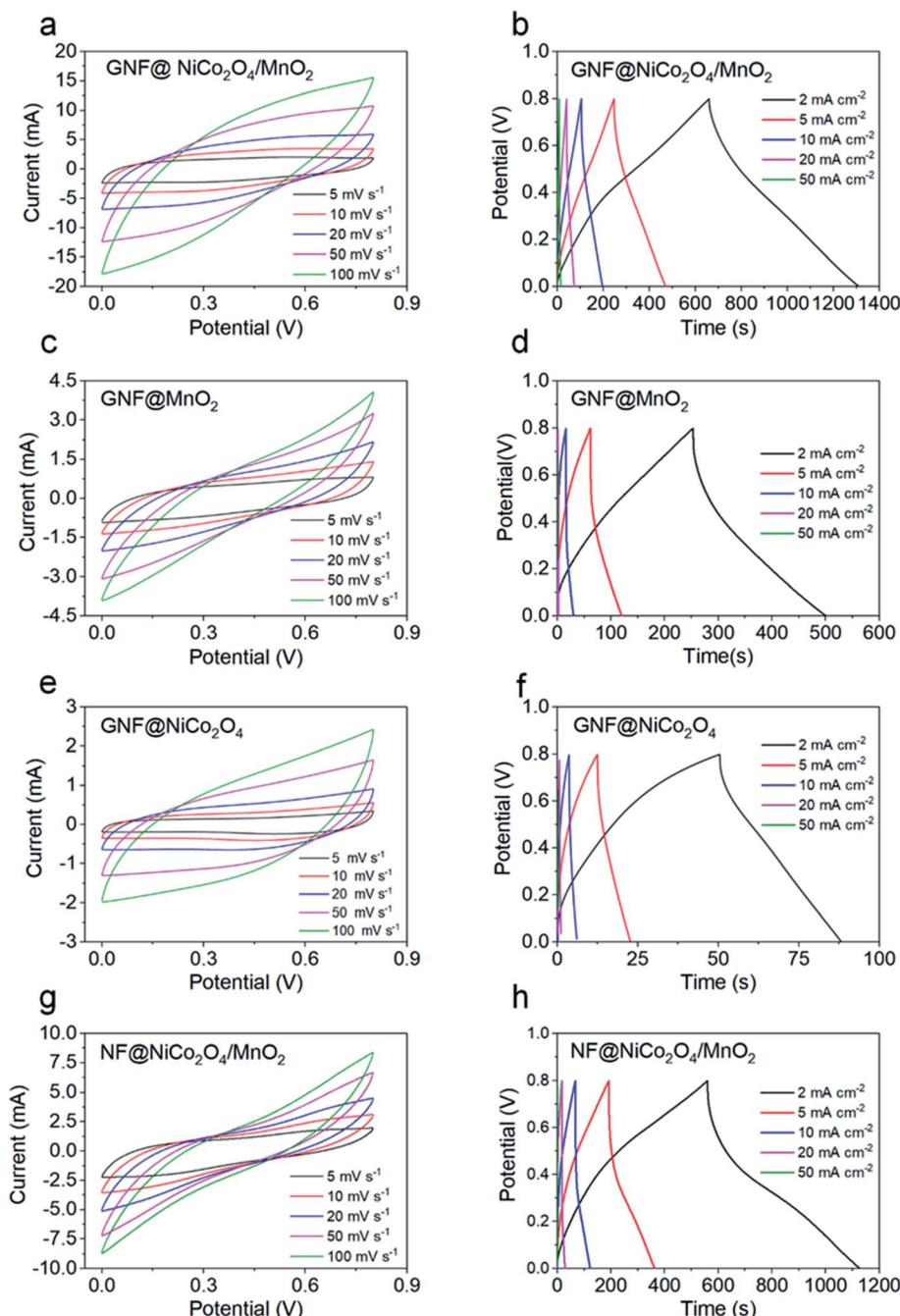
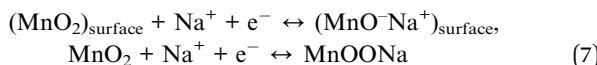


Fig. 6 (a, c, e and g) CV curves of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>, GNF@MnO<sub>2</sub>, GNF@NiCo<sub>2</sub>O<sub>4</sub> and NF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> samples at different scan rates, (b, d, f and h) GCD curves of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>, GNF@MnO<sub>2</sub>, GNF@NiCo<sub>2</sub>O<sub>4</sub> and NF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> samples at different current densities.





The composite material with GNF@NiCo<sub>2</sub>O<sub>4</sub>-20 h has the largest CV curve area and the longest discharge time among all composites, revealing that it has the highest specific capacitance. Therefore, it is used in the following study.

The electrochemical properties of the GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>, GNF@NiCo<sub>2</sub>O<sub>4</sub>, GNF@MnO<sub>2</sub> and NF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> were studied in detail. Fig. 6 shows the CV and GCD curves of these electrodes. A largest integrated area in CV and longest discharging time in GCD curves of the GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> electrode demonstrate its best electrochemical performance in comparison with GNF@NiCo<sub>2</sub>O<sub>4</sub>, GNF@MnO<sub>2</sub> and NF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>. Rectangular-like CV shapes of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> reveal good capacitive reversibility, and the triangular symmetry of GCD curves hints its excellent pseudocapacitive properties. Meanwhile, its nearly symmetric GCD profiles and the lower IR drop than other samples suggest favourable conductivity. Fig. 7a illustrates the specific capacitances of these samples obtained by the GCD data. It can be observed that the GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> delivers higher specific capacitance of 1630.5, 1402.5, 1150.0, 832.5, and 387.5 mF cm<sup>-2</sup>, compared to only 94.5, 63.75, 30.0, 12.5 and 10.0 mF cm<sup>-2</sup> for the GNF@NiCo<sub>2</sub>O<sub>4</sub>, 619.3, 366.3, 172.5, 25.0 and 11.1 mF cm<sup>-2</sup> for the GNF@MnO<sub>2</sub>, and 1422.3, 1067.5, 690.0, 292.5, and 18.8 mF cm<sup>-2</sup> for the NF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> at current densities of 2, 5, 10, 20 and 50 mA cm<sup>-2</sup>, respectively. Note that the areal capacitance of GNF@NiCo<sub>2</sub>O<sub>4</sub> is almost negligible. The areal specific capacitance of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> is 17.3 and 2.6 times higher than those of GNF@NiCo<sub>2</sub>O<sub>4</sub> and GNF@MnO<sub>2</sub> at 2 mA cm<sup>-2</sup>, respectively. The mass loading of MnO<sub>2</sub> has increased from 3 mg cm<sup>-2</sup> of GNF@MnO<sub>2</sub> to 3.5 mg cm<sup>-2</sup> of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>. The increase in mass loading is very small, but the areal capacitance of the composite has increased by 2.6 times than GNF@MnO<sub>2</sub>. It can be seen that the increase in capacitance is not caused by the increase in the mass loading of MnO<sub>2</sub>, but the structure of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> effectively improves the utilization of the active MnO<sub>2</sub>. The petal structured NiCo<sub>2</sub>O<sub>4</sub> provides large surface area for the high mass loading of MnO<sub>2</sub> and more electron transmission channels to MnO<sub>2</sub>, and reduces the accumulation of MnO<sub>2</sub>. As a result, the capacitance utilization of MnO<sub>2</sub> is improved

and the areal capacitance of the composite material increases.<sup>56</sup> In addition, it is observed that when the current density increases from 2 mA cm<sup>-2</sup> to 20 mA cm<sup>-2</sup>, the original surface capacitance of the GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> loses 48.9%, demonstrating its outstanding rate capability. The specific capacitance of NF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> is only 208.3 mF cm<sup>-2</sup> lower than that of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> at 2 mA cm<sup>-2</sup>. However, its areal capacitance drops by nearly 80% from 2 to 20 mA cm<sup>-2</sup>, illustrating its poor rate performance. This demonstrates that the graphene effectively improves the rate performance of the electrodes. The EIS test was conducted to estimate charge transfer kinetics of the hybrid materials and the obtained Nyquist plots are given in Fig. 7b. In general, the equivalent series resistance (ESR, R<sub>s</sub>) of an electrode can be determined by observing the EIS spectrum in the high frequency region. It includes the inherent resistance of the electrode material (both current collector and active material), the contact resistance of the electrode/electrolyte interface and the bulk resistance of the electrolyte, and its value depends on the intercept of the spectrum on the transverse axis. That is, the R<sub>s</sub> of the electrode can be seen at the intersection of the transverse axis.<sup>57</sup> The semicircle in the Nyquist plot can be used to determine the charge transfer resistance R<sub>ct</sub>, the larger the diameter of the semicircle, the larger R<sub>ct</sub> of the electrode.<sup>58</sup> The GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> electrode reveals a smaller equivalent series resistance R<sub>s</sub> (5.3 Ω) and charge transfer resistance R<sub>ct</sub> (10.4 Ω) compared to that of GNF@MnO<sub>2</sub> (R<sub>s</sub> 5.7 Ω, R<sub>ct</sub> 55.7), suggesting its better electrical conductivity and rapid charge mobility. Low frequency range is related to the Warburg impedance which reflects the ion diffusion/transport in the electrolyte.<sup>59</sup> The slope of GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> is higher than that of GNF@MnO<sub>2</sub>, indicating its lower diffusion resistance. These results further convincingly prove that the existence of petal structured NiCo<sub>2</sub>O<sub>4</sub> as skeleton for the depositing of MnO<sub>2</sub> can effectively decrease the internal resistance and facilitate the electron transfer, which is beneficial to promote the areal capacitance of the hybrid GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub>.<sup>60</sup>

### Electrochemical performance of the asymmetric supercapacitor

In order to further evaluate the potential of the GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> electrode in practical applications, ASC was fabricated with GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> composite and GNF@AC composite

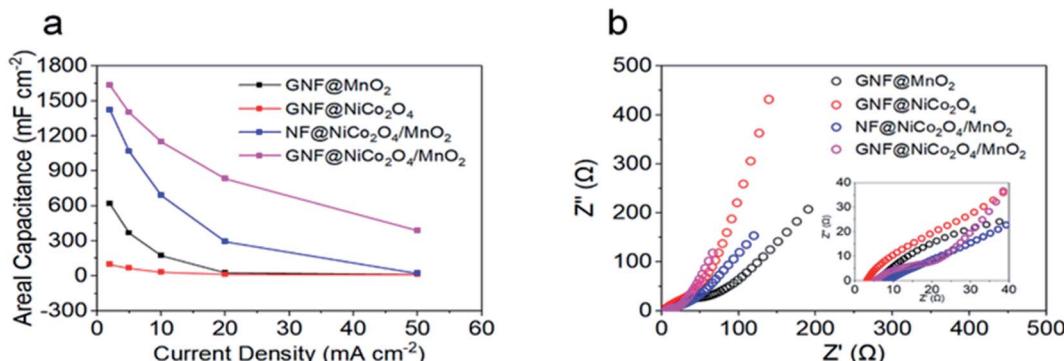


Fig. 7 (a) Areal capacitances of different electrodes at different current densities, (b) Nyquist plots of different samples over a frequency range of 0.01 Hz to 100 kHz.



as the positive and negative, respectively. The electrochemical test of the assembled supercapacitor shows that its large voltage window is 2.1 V, which is beneficial for the promotion of energy density. Fig. 8a shows the CV curve with a voltage window of 1.8 V–2.4 V. Fig. 8b exhibits the CV curves of supercapacitors at different scan rates. The CV curves maintain a good symmetry and are almost rectangular, showing its typical capacitive performance and stable electrochemical performance. The GCD curves of the device at various current densities are depicted in Fig. 8c. Its triangular-like shapes manifest a reversible capacitive behavior. The areal capacitance based on GCD test is calculated to be  $824.8 \text{ mF cm}^{-2}$  at  $2 \text{ mA cm}^{-2}$  (Fig. 8d). The reason for the excellent capacitance of the device is mainly due to the heterostructure of the GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> composite

material. The MnO<sub>2</sub> is a petal-like nanosheet with a small thickness. This microstructure ensures high electrochemical utilization of active materials and provides a large surface area and more channels for the enhancement of the electrolyte permeation. NiCo<sub>2</sub>O<sub>4</sub> is used as a conductive scaffold and its large surface area and rich pore structure provide more growth space for MnO<sub>2</sub>, increasing the number of active sites for pseudo-active MnO<sub>2</sub> species, and providing more electron transmission path, thereby realizing a high utilization rate of MnO<sub>2</sub>.<sup>61,62</sup> At a high current density of  $20 \text{ mA cm}^{-2}$ , the fabricated ASC achieves an excellent capacitance retention rate of 80.7% even after 5000 cycles (Fig. 8e). In addition, the capacitance of the supercapacitor shows an increasing trend in the first 500 cycles due to an activation process of the electrode.<sup>63</sup>

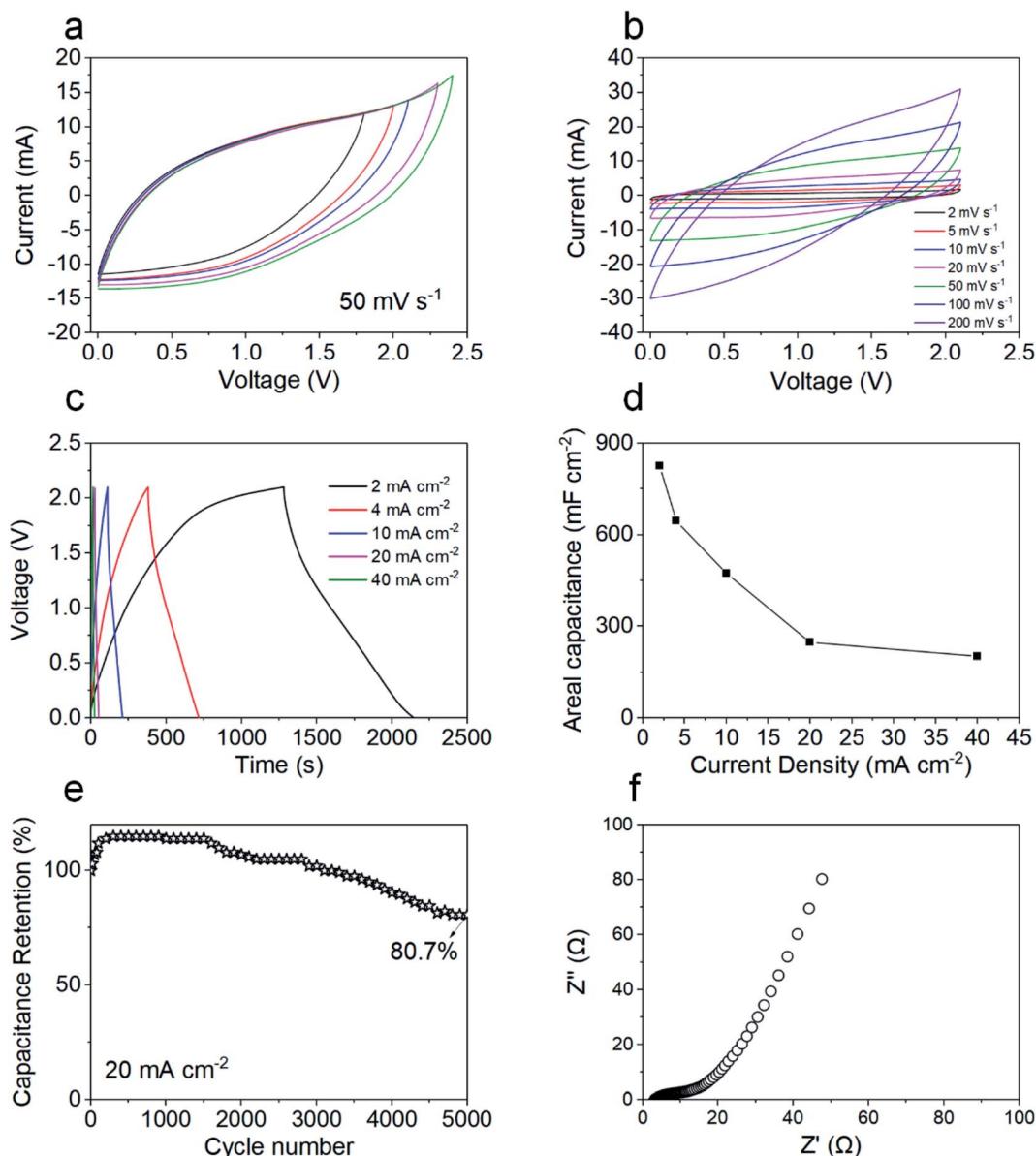


Fig. 8 (a) The CV curves of ASC with different voltage windows, (b) the CV curves of ASC at different scan rates, (c) the GCD curves of ASC at different current densities, (d) GCD profiles of the composite electrodes at different current densities, (e) cyclic stability of the ASC for 2000 cycles at  $20 \text{ mA cm}^{-2}$ , (f) Nyquist plots of the ASC over a frequency range of 0.01 Hz to 100 kHz.



EIS was performed to test the electrochemical properties of ASC, and the Nyquist plots of the ASC are summarized in Fig. 8f. The Nyquist plots show the impedance  $R_s$  of the device is  $3.2\ \Omega$  and the charge transfer resistance  $R_{ct}$  of the device is  $13.6\ \Omega$ . The high slope in the low frequency region suggests that the supercapacitor possesses low diffusion resistance and excellent capacitive behavior.<sup>64</sup> When its power density is  $2100.0\ \mu\text{W cm}^{-2}$  ( $190.9\ \text{W kg}^{-1}$ ,  $21.0\ \text{mW cm}^{-3}$ ), the ASC delivers a good specific energy density of  $2100.0\ \mu\text{W cm}^{-2}$  ( $190.9\ \text{W kg}^{-1}$ ,  $21.0\ \text{mW cm}^{-3}$ ). It possesses better performance than numerous energy storage devices previously reported (Table 1), such as  $\text{MnO}_2/\text{graphene}/\text{graphene}$  ( $30.4\ \text{Wh kg}^{-1}$  at  $100\ \text{W kg}^{-1}$ ),<sup>65</sup>  $\text{NF}/\text{NiCo}_2\text{O}_4/\text{MnO}_2/\text{AC}$  ( $35\ \text{Wh kg}^{-1}$  at  $163\ \text{W kg}^{-1}$ ),<sup>66</sup>  $\text{MnO}_2/\text{C}/\text{N-doped carbon}$  ( $39.5\ \text{Wh kg}^{-1}$  at  $200\ \text{W kg}^{-1}$ ),<sup>28</sup> *et al.*

Accelerated aging tests were also performed under floating conditions after 5000 charge-discharge cycles. The leakage current was recorded during each 2 hours period of constant voltages (1 V–2.1 V) and then the device was permitted to self-discharge for 2 h. As shown in the Fig. S2,† during the leakage current measurements, once the device is fully charged, the leakage current decreases rapidly within seconds and quickly reaches equilibrium. At higher voltages (2 V and 2.1 V), it takes a little longer to reach a plateau. In all cases, however, the leakage current drops sharply to values as low as  $250\ \mu\text{A cm}^{-2}$  within a period of 5 minutes. This illustrates the good stability of the cell electrodes. It can be found from Table S1† that the values of leakage currents at different voltages are very small, only  $0.007\ \mu\text{A cm}^{-2}$  at 1 V. And as the voltage decreases, the value of leakage current also becomes smaller, which shows that the rate of leakage current depends on the voltage.<sup>67,68</sup> Self-discharge is a spontaneous voltage drop of the energy storage device for a certain storage time, which is detrimental to the voltage and energy retention of the supercapacitor. The self-discharge characteristics can be straightforwardly captured by the time-related voltage retention. Fig. S3† shows the decay of the voltage within 2 h at different starting voltages, and it can be found that the voltage of the supercapacitor decreases gradually with time. It quickly stabilizes at low voltages, and as the voltage increases, it takes longer to reach a stable value. However, at

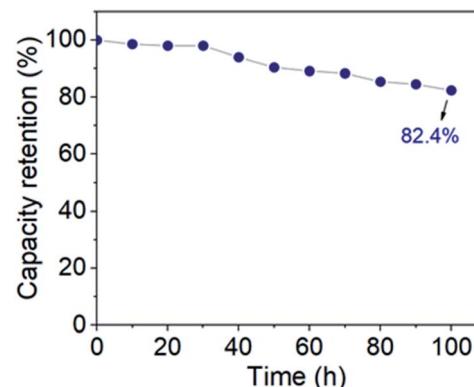


Fig. 9 Floating test of ASC at a constant voltage of 2.1 V for 100 h.

high voltages (1.8 V–2.1 V), the voltage value over 2 h is higher than 1.5 V, which is a generally suitable voltage for supplying power to electronic devices.<sup>72</sup> This proves the potential of the supercapacitor for practical applications. Floating test is a dependable technique for stability analysis of supercapacitor electrode. After the leakage current and self-discharge tests, a float test was performed for 100 hours to further evaluate the stability of the ASC. The voltage was kept at 2.1 V and five GCD cycles were performed at  $4\ \text{mA cm}^{-2}$  at 10 h intervals. As shown in Fig. 9, the capacity retention value after 100 h of voltage hold is 82.4%, which indicates that the ASC voltage is stable over this voltage window and time. The outstanding performance of the ASC indicates its potential in practical application.

## Conclusions

In summary, heterogeneous structured  $\text{NiCo}_2\text{O}_4/\text{MnO}_2$  was designed on GNF *via* a convenient two-step hydrothermal method. The petal structured  $\text{NiCo}_2\text{O}_4$  provided large surface area for the growth of high mass loading  $\text{MnO}_2$  micro-flowers, which effectively avoided the excessive stacking of high mass-loading  $\text{MnO}_2$  and increased the electron transmission channel with  $\text{MnO}_2$ . The addition of graphene buffer layer also effectively improved the rate performance of the electrode

Table 1 Performance comparison between our ASC and other similar supercapacitors

Positive electrode	Electrolyte	Voltage window	Energy density	Power density	Ref.
GNF/ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$	KOH	1.6 V	$27.8\ \text{Wh kg}^{-1}$	$400.3\ \text{W kg}^{-1}$	69
$\text{MnO}_2/\text{G}$	$\text{Na}_2\text{SO}_4$	2.0 V	$30.4\ \text{Wh kg}^{-1}$	$100\ \text{W kg}^{-1}$	65
$\text{NF}/\text{NiCo}_2\text{O}_4/\text{MnO}_2$	NaOH	1.5 V	$35\ \text{Wh kg}^{-1}$	$163\ \text{W kg}^{-1}$	66
$\text{MnO}_2/\text{C}$	$\text{Na}_2\text{SO}_4$	2.0 V	$39.5\ \text{Wh kg}^{-1}$	$200\ \text{W kg}^{-1}$	28
$\text{G}/\text{MnO}_2$	$\text{Na}_2\text{SO}_4$	1.8 V	$51.1\ \text{Wh kg}^{-1}$	$102.2\ \text{W kg}^{-1}$	43
$\delta\text{-MnO}_2$	$\text{Na}_2\text{SO}_4$	2.0 V	$52.22\ \text{Wh kg}^{-1}$	$100\ \text{W kg}^{-1}$	61
$\text{NiCo}_2\text{O}_4/\text{MnO}_2/\text{G}$	KOH	1.5 V	$55.1\ \text{Wh kg}^{-1}$	$187.5\ \text{W kg}^{-1}$	15
$\text{Na-MnO}_2/\text{CNTF}/\text{MoS}_2/\text{CNTF}$	$\text{Na}_2\text{SO}_4$	2.2 V	$178.4\ \mu\text{Wh cm}^{-2}$	$1100.9\ \mu\text{W cm}^{-2}$	70
$\text{MnO}_2/\text{NiCo}_2\text{O}_4$	KOH	1.5 V	$0.715\ \text{mWh cm}^{-3}$	$353.7\ \text{mW cm}^{-3}$	71
$\text{NiCo}_2\text{O}_4/\text{MnO}_2$	KOH	1.6 V	$2.55\ \text{mWh cm}^{-3}$	$22\ \text{mW cm}^{-3}$	17
$\text{CNT}/\text{MnO}_2/\text{G}/\text{CC}$	$\text{Na}_2\text{SO}_4$	2.2 V	$10.18\ \text{mWh cm}^{-3}$	$20\ \text{mW cm}^{-3}$	18
GNF/ $\text{NiCo}_2\text{O}_4/\text{MnO}_2$	$\text{Na}_2\text{SO}_4$	2.1 V	$45.9\ \text{Wh kg}^{-1}$ , $505.2\ \mu\text{Wh cm}^{-2}$ , $5.1\ \text{mWh cm}^{-3}$	$190.9\ \text{W kg}^{-1}$ , $2100.0\ \mu\text{W cm}^{-2}$ , $21.0\ \text{mW cm}^{-3}$	This work



materials, presenting a high areal capacitance of 1630.5 mF cm<sup>-2</sup> at 2 mA cm<sup>-2</sup>. The asymmetric supercapacitor was fabricated by using GNF@NiCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> as the positive electrode, GNF@AC as the negative electrode, and an environmentally friendly Na<sub>2</sub>SO<sub>4</sub> solution as the electrolyte. The ASC reached a wide voltage window of 2.1 V and a high specific energy density of 505.2 µWh cm<sup>-2</sup> (45.9 Wh kg<sup>-1</sup>, 5.1 mWh cm<sup>-3</sup>) at a specific power of 2100.0 µW cm<sup>-2</sup> (190.9 W kg<sup>-1</sup>, 21.0 mW cm<sup>-3</sup>). The superior performance of the asymmetric supercapacitor indicates its practical application for the design of high mass loading supercapacitors.

## Conflicts of interest

There are no conflicts to declare.

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