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Article

Flexible Asymmetric Supercapacitors Constructed by Reduced Graphene oxide/MoO₃ and MnO₂ Electrochemically Deposited on Carbon Cloth

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Abstract: A flexible asymmetric supercapacitor (ASCs) is successfully developed by using the composite of MoO₃ and graphene oxide (GO) electrochemically deposited on carbon cloth (CC) (MoO₃/rGO/CC) as the negative electrode, the MnO₂ deposited on CC (MnO₂/CC) as the positive electrode and Na₂SO₄/polyvinyl alcohol (PVA) as gel electrolyte. The results show that the introduction of GO layer can remarkably increase the specific capacitance of MoO₃ from 282.7 F g⁻¹ to 341.0 F g⁻¹. Furthermore, the combination of such good electrode materials and a neutral gel electrolyte renders the fabrication of high-performance ASC with a large operating potential difference of 1.6 V in 0.5 mol L⁻¹ Na₂SO₄ solution of water. Furthermore, the ASCs exhibit excellent cycle ability and the capacitance can maintain 87 % of its initial value after 6000 cycles. The fact that a light-emitting diode can be lighted up by the ASCs indicates the device's potential applications as energy storage devices. The encouraging results demonstrate a promising application of the composite of MoO₃ and GO in energy storage devices.

Keywords: Carbon cloth; reduced graphene oxide; MoO₃; MnO₂; asymmetric supercapacitors

1. Introduction

Supercapacitors (SCs) are potential energy storage devices and have been extensively studied owing to their characteristics such as high energy density, fast charge/discharge rates and long cyclic life [1,2]. They have been widely applied in hybrid electric vehicles, backup energy systems and mobile electronic devices, etc. [3]. With the increasing requirement for personal electronics in modern society, to make electronic devices flexible and portable has become the research hotspot at present. Correspondingly, flexible and portable electronic devices need a new type of energy storage equipment different from traditional ones to be designed [4–8]. Therefore flexible energy storage devices, especially flexible asymmetric SCs (ASCs) have received extensive attention because they can provide higher energy density compared with symmetric SCs [9–15].

To fabricate flexible ASCs (FASCs), it is necessary and crucial to select the current collector and active materials because they directly affect the performance of FASCs [19–21]. As a new flexible conductor, carbon cloth (CC) has attracted widespread attention in recent years for preparing SCs' electrodes due to its three-dimensional (3D) network structure and reasonable electrochemical stability [16]. By using CC as a substrate, conducting polymers deposited on it has shown high energy density and power density. For example, Horng et al. have successfully fabricated polyaniline (PANI) nanowire/CC nanocomposite electrodes by employing electrochemical deposition, and the PANI has displayed an excellent specific capacitance of (C_s) 1079 F g⁻¹ [17]. A flexible electrode of CC/MoS₂/PANI has been prepared via combining the facile hydrothermal method and in situ polymerization method, the PANI of this electrode shows a C_s value of 972 F g⁻¹ at a current density of 1 A g⁻¹ which is significantly higher than that of CC/MoS₂ (425 F g⁻¹) [18].

Transition metal oxides are the other commonly used electrode materials for SCs, at first the noble metal oxides such as RuO_2 [22] and RhO_x [23], etc. are extensively studied because of their high faradic capacitance and good conductivity. Despite the excellent capacitive performances, the practical application of the noble metal oxides is limited by their scarcity and high price. Therefore numerous researches have focused on the replacement of precious metal oxides with cheap transition metal oxides [24] due to their comparative theoretical C_s , availability and relatively reversible characteristics. Up to date, the hierarchical porous MnO_2 nanoflakes have been prepared by a rapid hydrothermal method without any templates and show the maximum C_s of 268 F g^{-1} [25]. Transition metal oxides are the other commonly used electrode materials for SCs, at first the noble metal oxides such as RuO_2 [22] and RhO_x [23], etc. are extensively studied because of their high faradic capacitance and good conductivity. Despite the excellent capacitive performances, the practical application of the noble metal oxides is limited by their scarcity and high price. Therefore numerous researches have focused on the replacement of precious metal oxides with cheap transition metal oxides [24] due to their comparative theoretical C_s , availability and relatively reversible characteristics. Up to date, the hierarchical porous MnO_2 nanoflakes have been prepared by a rapid hydrothermal method without any templates and show the maximum C_s of 268 F g^{-1} [25]. Different from the usually used electrode material of MnO_2 which possesses capacitive property at positive potential range, MoO_3 exhibits capacitance at negative potential range and has attracted much attention [26,27,65]. Furthermore, the other attractive nature of MoO_3 is its particular 2D layered structure, which is conducive to provide high power density for capacitor applications because of the adequate intercalation between the layers and electrolyte ions [28]. In fact, the capacitive property of MoO_3 is strongly affected by its, for example, MoO_3 exhibits C_s value of about 280, 110 and 30 F g^{-1} when it shows nanoplate, nanowire and nanorod morphologies respectively [29]. Recently, Pujari et al. have found that hexagonal MoO_3 micro rods display a C_s of 194 F g^{-1} [30]. Despite the efforts on MoO_3 , the C_s values are still not very high due to its low conductivity. Therefore, it is necessary to develop a strategy to prepare the composites with relatively high conductivity by adding some highly conductive materials [30–35]. Among the various methods for composites, co-electrochemically depositing active materials and carbon materials is proved to be effective approach; as precursor of graphene, graphene oxide (GO) has attracted great interest for fabricating composites recently because of GO's easy manipulation in the aqueous medium, and high specific area [36,37].

In this work, we choose CC as a flexible substrate to deposit MoO_3 as negative electrode, during which the graphene oxide (GO) is added to form the composite of MoO_3 and reduced GO (rGO) through electrochemical co-deposition. It is expected that the introduction of rGO not only improves the conductivity of the composite but also increase the C_s of MoO_3 . The electrode prepared by electrochemically depositing MnO_2 on CC is used as positive electrode, $\text{MoO}_3/\text{rGO}/\text{CC}$ as negative electrode and $\text{NaSO}_4/\text{polyvinylene oxide}$ as gel electrolyte and separator to assembly ASCs. By using this strategy, we hope that the FASCs can possess the high operating potential differences, energy density and power density.

Therefore, metal oxide and conductive polymer composites with CC as the substrate are promising electrode materials for SCs.

For instance, conductive polymers can be designed as flexible electrodes due to their high energy storage, low cost, and easy preparation. Conductive polymers are able to form composites with carbon materials or metal oxides, which improves their electrochemical properties. In particular, conductive polymers decorated on CC exhibit improved specific capacitance and power capacity when used as composite electrodes.

2. Experimental

2.1. Reagents and Materials

Manganese (II) acetate ($\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$), ammonium molybdate $[(\text{NH}_4)_2\text{MoO}_4]$, ammonium chloride, polyvinyl alcohol (PVA, Mw 85000), and sodium sulfate (Na_2SO_4) were purchased from

Aladdin Chemical Co. and used without further purification. Conductive CC substrate was obtained from Shanghai Chuxi Industrial Co. Ltd.

2.2. Preparation of the Negative Electrodes

Pretreatment of the CC: The commercial CC was first immersed in concentrated nitric acid (HNO_3 , 68 wt. %) and then heated at 60 °C for about 6 hours in a water bath to make the surface hydrophilic. Subsequently, the CC was washed with distilled water thoroughly and then soaked in distilled water for use.

Electrochemically depositing MoO_3 on CC: The used electrolyte here (30.0 mL) was an aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ (0.05 mol L^{-1}) and NH_4Cl (0.05 mol L^{-1}) and its pH value were adjusted to 2.0 by acetic acid. The pretreated CC slices (1×1 cm^2) were used as working electrode, a Pt sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode; by using a constant current density of 4 mA cm^{-2} , different amounts of MoO_3 were deposited on CC by controlling the depositing time (700-1300 s). According to the capacitance measured by using a three-electrode system in 0.5 M Na_2SO_4 electrolyte, the MoO_3/CC prepared from 1000 s was used to assemble the ASCs.

Electrochemically depositing MoO_3/rGO on CC: First, GO was prepared by oxidizing 300 mesh graphite powder according to the modified hummer method [38]. The sample of $\text{MoO}_3/\text{rGO}/\text{CC}$ prepared by using electrochemical deposition method according to 2.2 was used as a work electrode here to deposit GO on the surface of MoO_3/CC by cyclic voltammetry (CV) method in different concentrations of GO solution, and the obtained electrode was defined as $\text{MoO}_3/\text{rGO}/\text{CC}$. The appropriate GO in the electrolyte is selected by optimizing the deposition time and the CV number. Place $\text{MoO}_3/\text{rGO}/\text{CC}$ in a vacuum oven overnight. The electrochemical performance test was carried out in a three-electrode system after drying.

2.3. Fabrication of the Electrode of MnO_2/CC

By using a three-electrode system, MnO_2/CC was also prepared via an electro-deposition method. In the mixing solution of $\text{Mn}(\text{Ac})_2$ (0.05 mol L^{-1}) and Na_2SO_4 (0.05 mol L^{-1}), the MnO_2 was deposited on the pre-treated CC at a constant current of 4.0 mA cm^{-2} when the CC was used as working electrode, a Pt plate as counter electrode and a saturated calomel electrode (SCE) as reference electrode, and the amount of MnO_2 was controlled by depositing time (600-1400 s). After the deposition process was completed, the electrode of MnO_2/CC was washed by deionized water and dried in a vacuum oven at 70 °C overnight. The electrode of MnO_2/CC prepared from different depositing time was defined as $\text{MnO}_2/\text{CC}-t$ (t was the depositing time).

2.4. Fabrication of the FASC Devices

Gel electrolyte: 1.0 g PVA powders were slowly added into 10.0 mL solution of Na_2SO_4 (0.5 mol L^{-1}) under stirring, then the mixture was heated to 85 °C until the mixture became transparent, then the solution was naturally cooled to room temperature for utilization.

Assemble of FASC device: Firstly, the CC was first pretreated with HNO_3 at 60 °C to remove the sizing agent on the surface of the fibers. Then, MnO_2/CC and $\text{MoO}_3/\text{rGO}/\text{CC}$ were fabricated using a facile electrodeposition method. MnO_2 or MoO_3 or rGO was grown on the CC substrate using three-electrode configuration with CC as the working electrode, Pt piece as the counter electrode, and Hg/HgCl_2 as the reference electrode. Finally, $\text{MoO}_3/\text{rGO}/\text{CC}$ as negative electrode and MnO_2/CC as positive electrode. According to the capacitance measured by using the three-electrode system, it was clear that the capacitances of the $\text{MoO}_3/\text{rGO}/\text{CC}$ negative electrode and MnO_2/CC positive electrode can be balanced when geometric area of the two electrodes was the same. When the FASC device was assembled, the $\text{Na}_2\text{SO}_4/\text{PVA}$ gel electrolyte was uniformly covered on one electrode such as MnO_2/CC , then the other electrode ($\text{MoO}_3/\text{rGO}/\text{CC}$) was placed on the face of MnO_2/CC which was covered by $\text{Na}_2\text{SO}_4/\text{PVA}$ gel electrolyte and followed by pressure to make the two electrodes together, subsequently, the assembled devices were frozen in refrigerator for 30 min. Finally, the fabrication of FASC was completed after the frozen device was placed at room temperature to unfreeze.

2.5. Characterization and Electrochemical Measurements

The electrodes' morphologies were observed by using a scanning electron microscope (SEM, JEOL 6701) operating at accelerating voltage of 10 kV. Attenuated total reflection-Fourier transforming infrared spectra (ATR-FTIR) were collected on a Nicolet iS50R (USA) instrument in a range of 400-4000 cm^{-1} with a resolution of 2 cm^{-1} . X-ray photoelectron spectroscopy (XPS ESCAL-ab 220i-XL, VG Scientific, England) was performed by using a monochromic Al K α as source.

The capacitive measurements of the electrode materials and the ASCs were carried out on a CHI 660E electrochemical work station. Three-electrode system was used to test the electrodes' capacitive performance, the prepared positive and negative electrodes were used as the working electrode, a Pt sheet as the counter electrode and a SCE as reference electrode. Aqueous solution of Na_2SO_4 (0.5 M) was used as electrolyte for testing MnO_2 and MoO_3 capacitive properties, respectively. The potential windows were set to 0-1.0 V for positive electrode (MnO_2) and -1.0-0 V for negative electrode (MoO_3) during the cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests. Using the two-electrode system, the performances of the FASCs were evaluated. The CV measurements were carried out in a voltage range of 0.0-1.6 V and the scan rates were varied from 2 to 100 mV s^{-1} . The GCD tests were performed at various current densities from 1.0 to 12.0 mA cm^{-2} with cut off voltage of 0.0-1.6 V. In the frequency range of 0.01-100000 Hz, the electrochemical impedance spectra (EIS) were measured by employing a disturbance with 5 mV potential amplitude. The cyclic stabilities were estimated on the same instrument by successive CV scan at 100 mV s^{-1} .

3. Results and Discussion

3.1. Structural Properties Characterization of All Samples

Figure 1 depicts a schematic illustration of the procedure for the preparation of electrodes and the device. Based on the flexibility and conductivity of CC, and the potential ranges of electrochemical activity for MoO_3 and MnO_2 [39,40], the FASCs can be fabricated by using $\text{MoO}_3/\text{rGO}/\text{CC}$ as negative electrode and MnO_2/CC as positive electrode in $\text{Na}_2\text{SO}_4/\text{PVA}$ gel electrolyte.

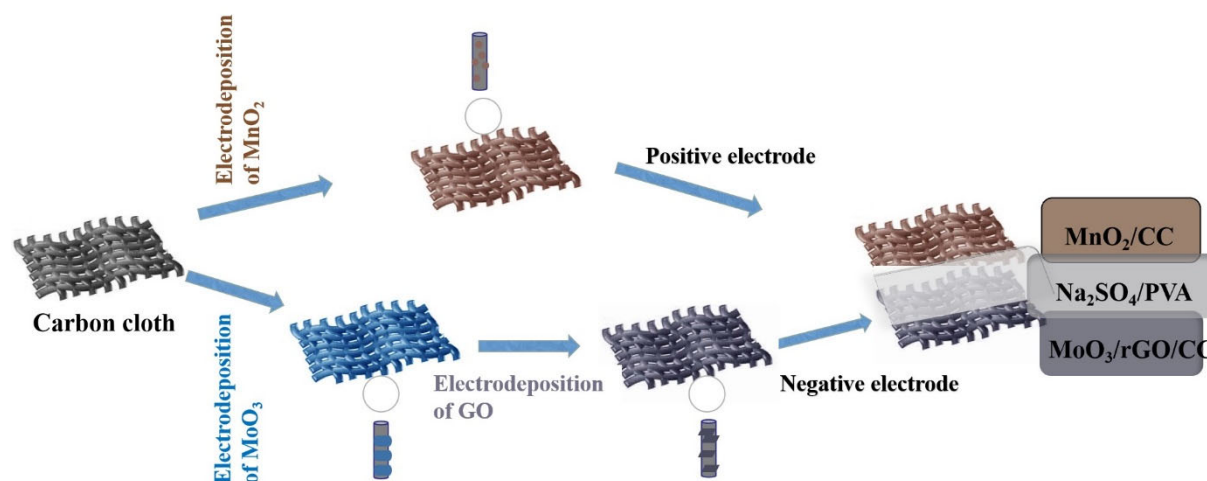


Figure 1. Schematic diagram for preparing $\text{MoO}_3/\text{rGO}/\text{CC}$ and MnO_2/CC electrodes and the assembled ASC.

From the SEM image shown in Figure 2, it is found that fibers contained in CC have the clean surface with some grooves (Figure 2A), the diameter of the fibers is relatively uniform and many accumulated pores are observed among the fibers (Figure 2B). When the molybdenum oxide has been electrochemically deposited, the surface of the fiber will be covered by a layer of molybdenum oxide, it can be seen from the image of MoO_3/CC (Figure 2C) the fiber is uniformly wrapped by a layer of molybdenum oxide, but the film has many cracks which are caused during the drying process. Under

the large magnification, the corrugated morphology is observed (Figure 2D), this rough surface structure is favorable to increase the surface area of MoO_3 . Notably, the film thickness and mass loading can be well controlled by changing the deposition time. When the deposition time is 1000 s, the well “skeleton/skin” architecture with the carbon fiber as the skeleton and MoO_3 as the skin can be obtained [41,42].

As shown in Figure 2E and F, the surface of CC is decorated with flaked rGO, and the embedded enlarged image (Figure 2G) clearly shows that GO makes the smooth surface of carbon smooth. In addition, uniform rGO nanosheets form 2D layered structure on the surface of $\text{MoO}_3/\text{rGO}/\text{CC}$, which increases the surface area and improves the electrical conductivity compared with the blank CC. SEM results showed that the surface of MoO_3/CC composite was successfully coated with a layer of rGO.

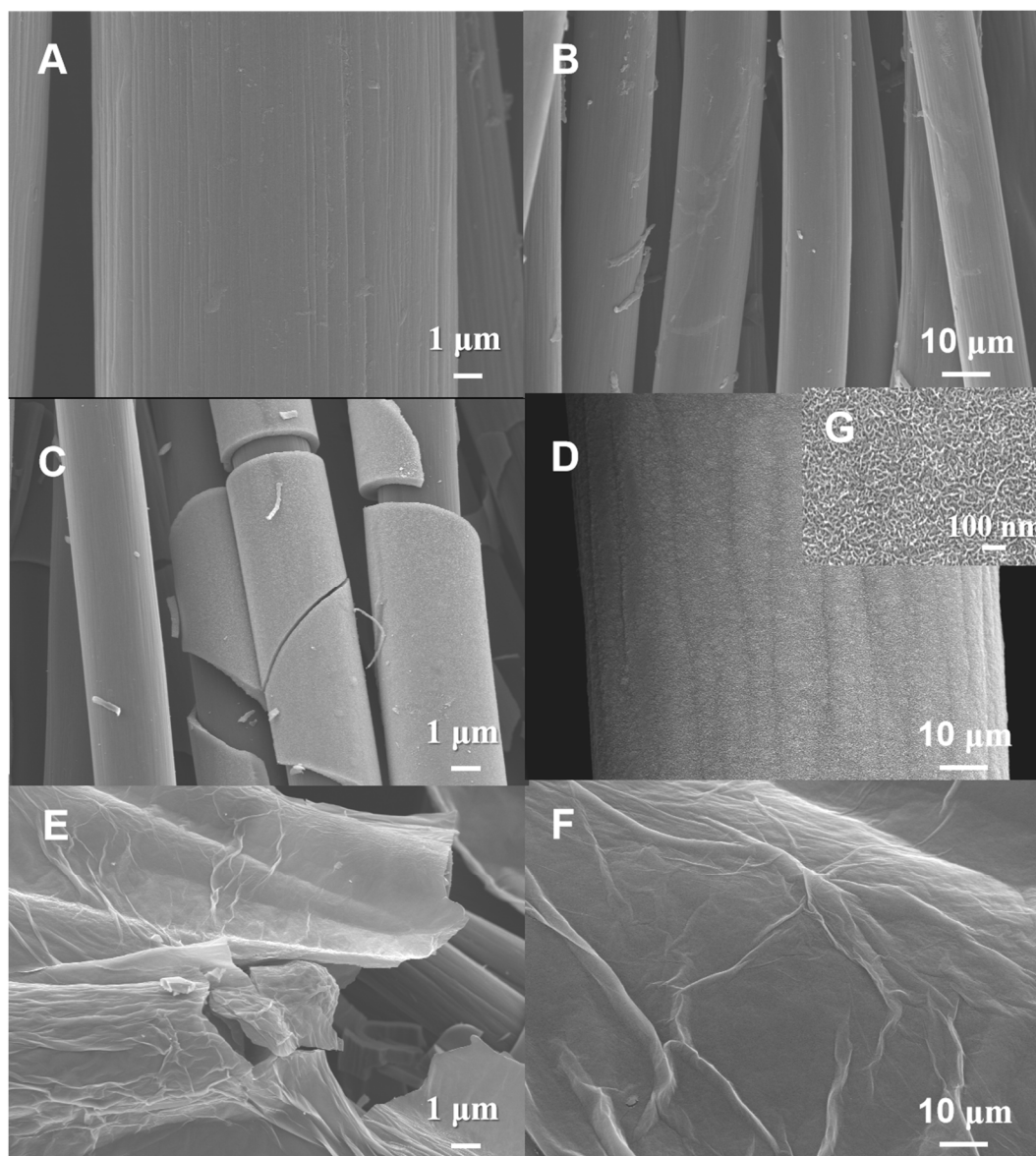


Figure 2. The SEM images in different magnification for CC (A, B), MoO_3/CC (C, D), $\text{MoO}_3/\text{rGO}/\text{CC}$ (E, F).

To confirm the nature of the product, the as-prepared materials have been characterized by X-ray diffraction. From the Figure 3, it can be found all the samples show the obvious peaks related to the substrate of CC or rGO, but no distinguishable peaks can be seen for the components of MoO_3 and MnO_2 , which may be attributed to the fact that the formed MoO_3 and MnO_2 are amorphous or the crystalline is too small, or the weak diffraction peaks related to MoO_3 and MnO_2 are covered up by the diffraction peak of C due to the small amount of the active materials [16,43–45]. FTIR

spectroscopy provides details of the band characteristics of the components of composites. As shown in Figure S3, no strong characteristic peaks are seen in the wave number ranged from 400 to 2000 cm^{-1} . The spectrum of MoO_3/CC exhibits three major peaks located at 955, 826 and 753 cm^{-1} , which are attributed to the $\text{Mo}=\text{O}$ stretching vibration of the terminal oxygen, and the symmetric and asymmetric stretching vibration of the bridging oxygen in $\text{Mo}-\text{O}-\text{Mo}$, respectively [46]. However, the IR spectrum for $\text{GO}/\text{MoO}_3/\text{CC}$ exhibit the characteristic of rGO [16] besides the MoO_3 's characteristics, confirming that rGO has successfully loaded on the surface of MoO_3/CC .

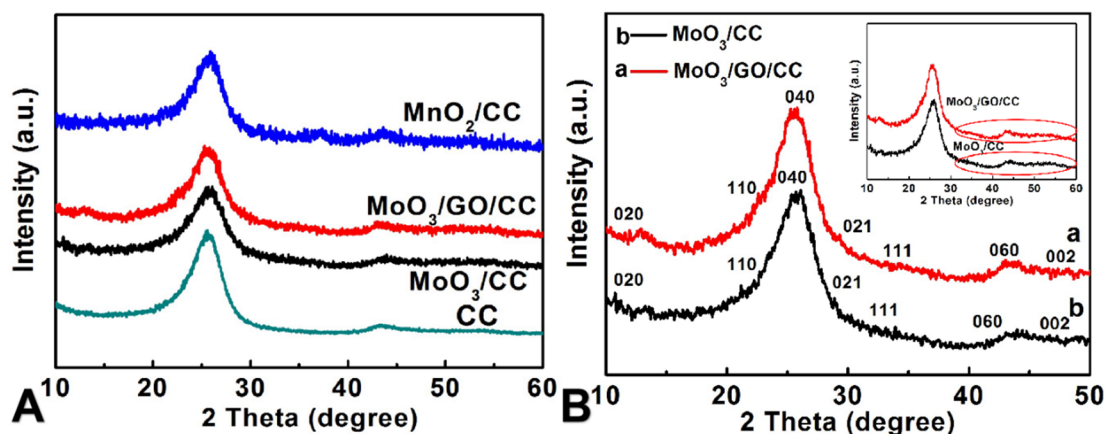


Figure 3. The XRD patterns of CC, MnO_2/CC , MoO_3/CC and $\text{MoO}_3/\text{rGO}/\text{CC}$ (A), the magnified XRD patterns for MoO_3/CC and $\text{MoO}_3/\text{rGO}/\text{CC}$ in the range of 10-50 ° (B).

Analysis of the XPS can reveal the chemical states of the samples of MnO_2/CC (a), $\text{MoO}_3/\text{rGO}/\text{CC}$ (b), MoO_3/CC (c) and CC (d) (Figure 4A). All the spectra show the XPS peaks related to the element of Mn or Mo together with that of C and O. In particular, the characteristic doublet of $\text{Mn}2\text{p}$ (Figure 4B) $2\text{p}_{1/2}$ (654.1 eV) and $\text{Mn}2\text{p } 2\text{p}_{3/2}$ (642.4 eV) from MnO_2/CC identify the formation of MnO_2 due to the difference between the two peaks of 11.7 eV [48]. Similarly, the double peaks observed at 233.0 and 236.2 eV in $\text{MoO}_3/\text{rGO}/\text{CC}$ can be contributed to $\text{Mo } 3\text{d}_{5/2}$ and $\text{Mo } 3\text{d}_{3/2}$ respectively due to spin-orbit splitting (Figure 4D) [45]. According to the fitted results, it can find that the components of MoO_2 and MoO_x exhibit in the sample besides the component of MoO_3 [47]. By comparison, in the $\text{Mo } 3\text{d}$ spectrum of the $\text{MoO}_3/\text{rGO}/\text{CC}$ composite, the aforementioned peaks shift to 232.8 and 236.0 eV, respectively, where such 0.2 eV offset results from the interaction between rGO and MoO_3 . The peak intensity in the MoO_3/CC spectrum is higher than that in the $\text{MoO}_3/\text{rGO}/\text{CC}$ spectrum, indicating that the experimental molybdenum content in MoO_3/CC is higher than that in $\text{MoO}_3/\text{rGO}/\text{CC}$ [16].

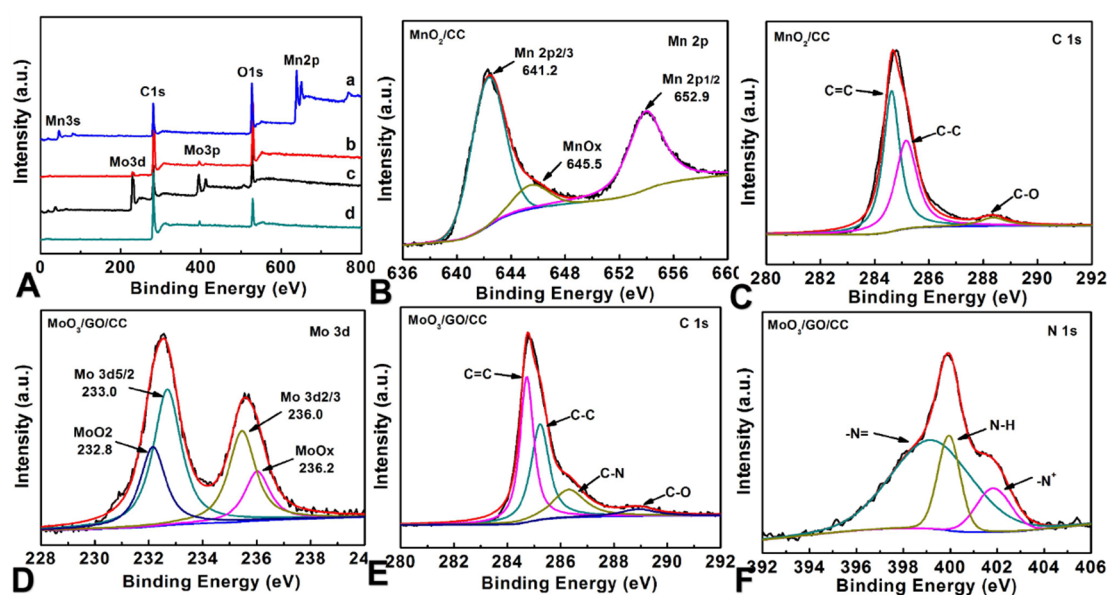


Figure 4. (A) The whole XPS spectra for MnO₂/CC (a), MoO₃/CC (b), MoO₃/rGO/CC (c) and CC (d), (B) the high-resolution XPS for Mn2p in MnO₂/CC, (C) the C1s XPS for MnO₂/CC, (D) the high-resolution XPS for Mo3d in MoO₃/rGO/CC, (E) the C1s XPS and (F) N1s XPS for MoO₃/rGO/CC.

3.2. The Electrochemical Properties of MoO₃/rGO/CC

The galvanostatic method is used to deposit MoO₃ on the pretreated CC, and the depositing current and depositing time are optimized by changing the current and depositing time. Firstly, the deposition current is optimized in the same deposition solution by changing the current keeping the depositing charge amount constant. The obtained electrodes' CV curves are tested by employing three-electrode system, according to the formulae shown in the supporting information, the specific capacitances are calculated and the plot of C_m value versus the currents is drawn in Figure S1. It can be seen that the C_m value reaches a maximum value of 282.8 F g⁻¹ at a current of 6 mA. Subsequently, the current is fixed at 6 mA to changing the deposition time to optimize the time. It can be found in Figure S1B, the maximal C_m value of 283.5 F g⁻¹ achieves when the depositing time is 1000 s. Therefore, we use the condition of 6 mA constant current and depositing time of 1000 s to prepare the electrode at following experiments. In order to improve the performance, the electrodes of MoO₃/CC are used as working electrode to electrochemically deposit the rGO in different GO solution, from Figure S1C, we can find when the concentration of GO solution is about 7.0 mg mL⁻¹, the modified electrode shows largest C_m value. Therefore, the electrode prepared at above mentioned condition will be evaluated in detail.

It is clear from Figure 5A that the electrode of MoO₃/rGO/CC exhibit far larger surrounded CV area than MoO₃/CC at the same scan rate, while the capacitance contribution from CC can be completely neglected. The CV curves of the MoO₃/rGO/CC electrode exhibit a similar shape at different potential scan rates from 5 to 100 mV s⁻¹, based on the curves, the C_m values of MoO₃/rGO/CC are calculated and shown in Figure 5C, it is clear that the C_m values of MoO₃/rGO/CC decrease with the increase of the scan rates because the limited diffusion time for ions when the scan rate is large, and has the largest C_m value of 341.0 F g⁻¹ which is much higher than that of MoO₃/CC electrode (282.8 F g⁻¹) at 1 mV s⁻¹ scan rate, which can be attributed to the conductive rGO sheets on the MoO₃ surface provide a shorter transmission path for the electrons and the electrolyte ions. The C_m values for the MoO₃/rGO/CC show a downward trend with the increase of the scan rates. The GCD curves of the MoO₃/rGO/CC electrode in potential range of -1.0-0 V (Figure 5D) display almost symmetric shapes at different current densities, the iR drop is small at low current density and increases with the increment of the current densities, the C_m values obtained from the GCD curves are similar to those from CV profiles. The good capacitive performance of MoO₃/rGO/CC can be attributed to the close contact between the carbon fiber and the MoO₃ layer, the more transporting route for electrons

provided by the coated rGO sheets on the MoO₃ besides the fast and efficient charge transport originated from the 3D CC framework.

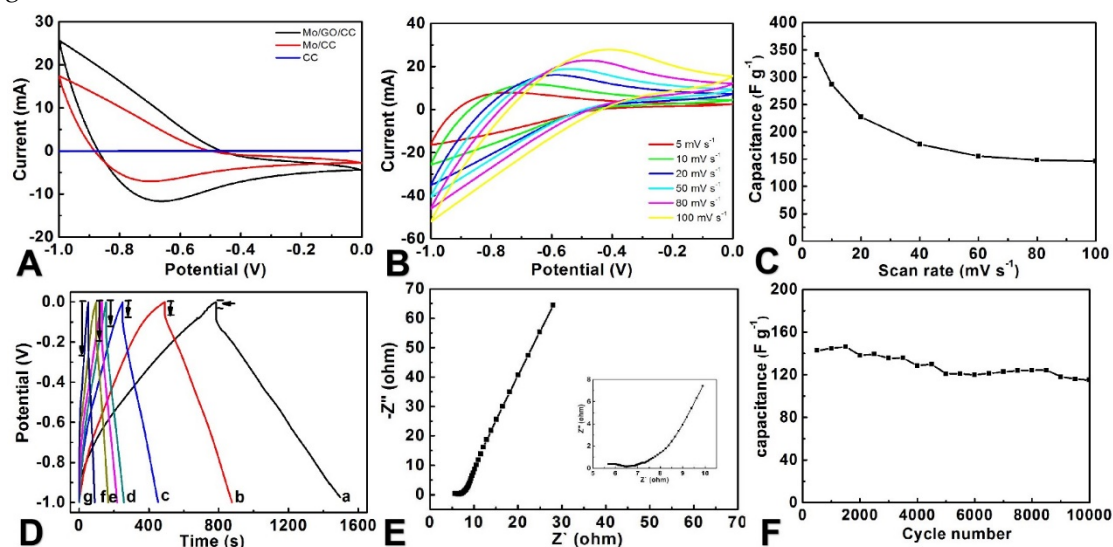


Figure 5. Electrochemical behaviors of MoO₃/rGO/CC electrode: (A) CV curves of CC, MoO₃/CC and MoO₃/rGO/CC, (B) CV curves for the MoO₃/rGO/CC electrode at different scan rates, (C) the plot of the C_m values versus scan rate for MoO₃/rGO/CC, (D) GCD curves of the MoO₃/rGO/CC electrode at different current densities (a, b, c, d, e, f and g represent GCD curves with current density of 1-7 mA cm⁻² respectively), (E) EIS spectra for the MoO₃/rGO/CC electrode, (F) the plot of capacitance versus the cyclic number for MoO₃/rGO/CC. Electrolyte is 0.5 mol L⁻¹ Na₂SO₄ aqueous solution.

At an open circuit potential, the EIS spectrum has been recorded within the frequency range from 100 kHz to 0.01 Hz to reveal the kinetic property of MoO₃/rGO/CC. It is clear that a semicircle in the high frequency region and a linear spike in the low frequency region are appeared in the Nyquist plots (Figure 5E) [49]. The typical small semicircle in the high frequency region is related to the Faradaic charge transfer resistance (R_{ct}) of the electrode material, which is associated with electrical conductivity and the charge transfer path between the electrode material and the electrolyte [50]. The profile can be fitted by using the Zview software, from the fitted Nyquist plots, the R_{ct} value of GO/MoO₃/CC electrode is 1.824 Ω, indicating the enhanced the charge transportation provided by the decorated rGO on the surface. The electrochemical stability of the electrodes has been also investigated by successive CV scanning at a scan rate of 100 mV s⁻¹ (Figure 5F), it is found that MoO₃/rGO/CC can retain 88.6 % of its initial capacitance, indicating good cycling stability.

3.3. Electrochemical Performance of the FASC

To prepare ASC device, the capacitance of negative electrode must match that of positive electrode. The matching of the two electrodes' capacitance can be determined by the charge balance relationship of Q₊ = Q₋, where Q₊ is the charge stored in positive electrode and Q₋ the charge in negative electrode. To the flexible devices, the charge storage at each electrode relies on the C_a, operating voltage window (ΔV), and geometric surface area (S), the charge storage can be given by equation (1):

$$Q = C_a \times \Delta V \times S \quad (1)$$

To satisfy Q₊ = Q₋, the areal balance can be expressed by using the relationship as (2) [70]:

$$\frac{S_+}{S_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (2)$$

The positive electrode has been prepared by using CC as substrate via electrochemical depositing method. The conditions for depositing MnO₂ have been optimized and the results are shown in the supporting information (Figure S2). It can be seen that the electrode prepared at a

current of 4 mA for 1000 s exhibits the optimal C_m value (343.3 F g^{-1}), and the electrodes prepared under this condition are further investigated and used to assemble the devices. In $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution, the MnO_2/CC electrodes exhibit CV curves with quasi rectangle shape when the sweep rates are low, indicating fairly good performances of MnO_2/CC (Figure 6A). From the plot of the C_m versus the scan rates, it is easy to find that the C_m values decrease with the increment of scan rates, and the C_m value can still remain 45.1% of its largest C_m value at scan rate of 100 mV s^{-1} (Figure 6B), indicating a fairly good rate capability. Based on the results obtained from CV tests in three-electrode system, the area ratio of $\text{MoO}_3/\text{rGO}/\text{CC}$ to MnO_2/CC and is set to 1:1 for the ASC device. Therefore, the devices are constructed by using the $\text{Na}_2\text{SO}_4/\text{PVA}$ gel electrolyte to separate the negative electrode of $\text{MoO}_3/\text{rGO}/\text{CC}$ and positive electrode of MnO_2/CC . By employing the two-electrode system, the CV profiles of the device are recorded within different voltage windows at scan rate of 20 mV s^{-1} (Figure 6C and D) to determine the operating potential difference. It is clear that the operating potential difference of the device can be expanded to 1.6 V since the potential window for $\text{MoO}_3/\text{rGO}/\text{CC}$ electrode is -1.0 – 0 V , while MnO_2/CC electrode is 0 – 1.0 V which are determined by three-electrode system [51–53]. Notably, the CV curves of the ASC device resemble those observed for MnO_2/CC electrode measured in the three-electrode system, the redox couples stably maintain from scan rate of 2 to 100 mV s^{-1} (Figure 6E). The C_m values for the ASC (Figure 6F) also show a downward trend with the increase of the scan rates. At the scan rate of 2 mV s^{-1} , the device shows a C_m value of about 98.3 F g^{-1} (C_a of 226.4 mF cm^{-2}).

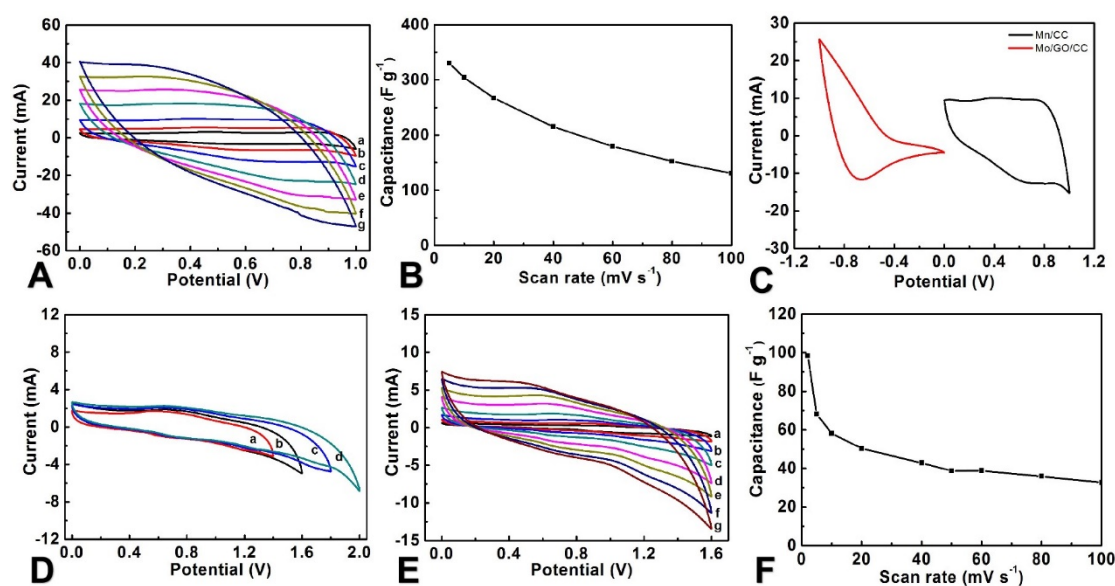


Figure 6. (A) CV curves for MnO_2/CC at different scan rates (a-g represent scan rates of 5, 10, 20, 40, 60, 80 and 100 mV s^{-1} , respectively), (B) the plot of C_m of MnO_2/CC versus the scan rates, (C) the CV curves of the positive and negative electrodes in three-electrode system at a scan rate of 20 mV s^{-1} , (D) the FASC's CV curves recorded at various potential difference windows at 20 mV s^{-1} (a, b, c, and d represent of 0–1.4, 1.6, 1.8 and 2.0 V respectively), (E) the FASC's CV curves recorded at different scan rates (a-g represent scan rates of 2, 5, 10, 20, 50, 80 and 100 mV s^{-1} , respectively), (F) the plot of the FASC's C_m based on active material versus scan rates.

The GCD curves of the ASC device (Figure 7A) show quasi-linear and symmetrical shapes, which suggest a rapid voltage-current response and fairly good electrochemical reversibility. The slight deviation from straight line can be attributed to the pseudo capacitance existed in the devices. Under the low current density, the GCD curves display a small iR drops, but with the increase of the current density, the iR drops increase obviously, which are mainly originated from the internal resistance of the devices. At current density of 1.0 mA cm^{-2} , the C_m of the device can reach to about 112.8 F g^{-1} and C_a of 193.5 mF cm^{-2} . It is expected that the C_m values of the ASC decrease gradually

with the increment of the current density due to ions diffusion limitation (Figure 7B), which is similar to CV results.

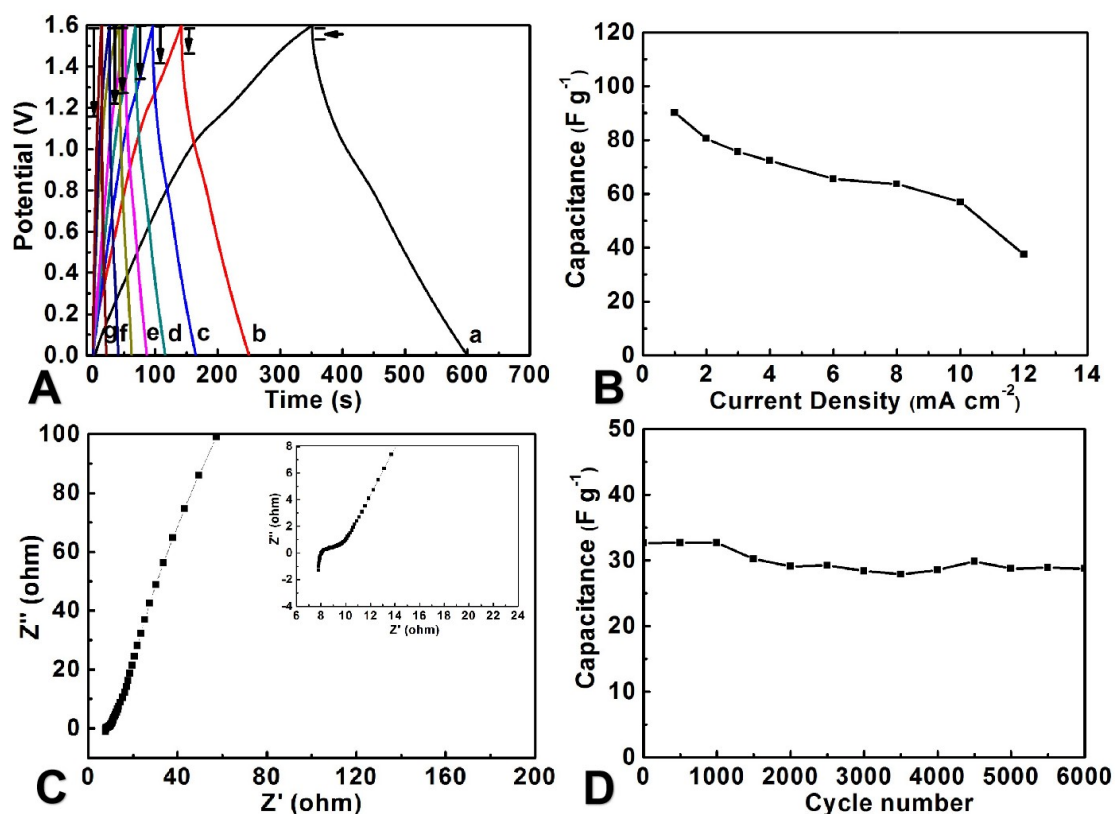


Figure 7. (A) GCD curves of ASC recorded at different current densities (a-g represent current densities of 1.0, 2.0, 3.0, 4.0, 7.0, 10.0 and $12.0 mA cm^{-2}$), (B) the plot of specific capacitances versus current densities, (C) Nyquist plots for the ASC of $MoO_3/rGO/CC/MnO_2/CC$, (H) the plot of the capacitance of ASC versus the cyclic number.

EIS experiment is conducted to further examine the detailed electrochemical properties of the ASC device (Figure 7C). In the high-frequency region, the small intercept between the semicircle and Z' axis indicates a low equivalent series resistance [54,55]. In the medium frequency range, the radius of the semicircle [56] is related to the R_{ct} which represents the resistance produced by the Faradaic reaction of the electrode with the electrolyte. At the low frequencies, a line nearly perpendicular to the Z' axis reveals the fairly good capacitive feature because vertical line usually indicates ideal capacitance. The cyclic stability of the ASC device has also been evaluated by successive CV scan within the potential difference range of 0-1.6 V. After 6000 cycles, the capacitance of ASC device can retain 88.1 % of its initial value, indicating good cycling stability, expressing relatively proper electrochemical stability of this kind of ASC device (Figure 7D).

To evaluate the device's practical properties, the energy and power densities have been calculated based on the discharging branch of GCD curves are by using the formulae of supplementary materials and shown in the Ragone plots (Figure 8A). It's obvious that the ASC shows an energy density of $32.1 Wh kg^{-1}$ at $533.3 W kg^{-1}$; more remarkably, even when the power density of device reaches $5333.3 W kg^{-1}$, the energy density still remains $20.2 Wh kg^{-1}$, which is better than other devices previously reported (Table 1) due to the electrode's high electrochemical capacitance and good rate capability, demonstrating the potential application of these kind of electrode materials. Furthermore, a LED can be driven by the fully charged tandem cells (Figure 8B), demonstrating the potentially practical application. The combination of good pseudo capacitive materials supported on CC substrate and a mild gel electrolyte provides an efficient approach to fabricate high-performance ASCs with good cycling.

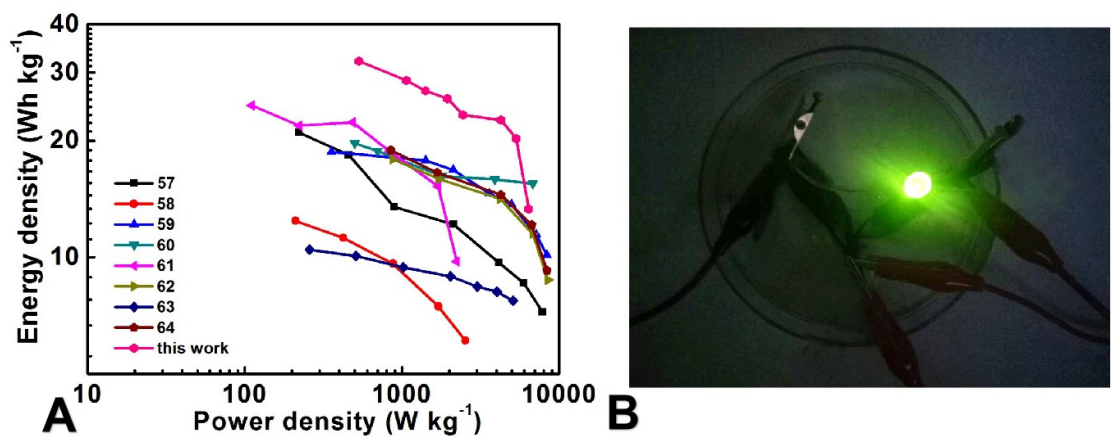


Figure 8. (A) the Ragone plots for ASC of MoO₃/rGO/CC//MnO₂/CC and some other devices from previous literature for comparison [57–64], (B) the photograph of a LED lighted by two cells connected in series.

Table 1. Comparison of the energy density and cyclic stability of the ASCs.

Electrode materials	Electrolyte	Energy density (Wh kg ⁻¹)	Stability (capacitance retention %, cycles)	Ref.
MoO ₃ -PPy//CNTs-MnO ₂	Na ₂ SO ₄ /PVA gel	21.0	76.0, 10000 cycles	[57]
MnO ₂ @PEDOT//PEDOT	LiClO ₄ /PMMA gel	9.8	86.0, 1250 cycles	[58]
Fe ₃ O ₄ embedded in Carbon nanosheet//porous carbon	KOH/PVA gel	18.3	70.8, 5000 cycles	[59]
Graphene (IL-CMG) //RuO ₂ -IL-CMG	H ₂ SO ₄ /PVA gel	19.7	95.0, 2000 cycles	[60]
CNTs/MnO ₂ //CNTs/PANI	Na ₂ SO ₄ /PVP gel	24.8	-	[61]
Co ₃ O ₄ nanowires/Ni-foam //carbon aerogel	KOH/PVA gel	17.9	-	[62]
Mn ₃ O ₄ nanoparticle/graphene //CNT/graphene	KCl/PVA gel	32.7	86.0, 10000 cycles	[63]
Graphene/Ni(OH) ₂ // graphene/CNT	KOH/PVA gel	18	-	[64]
MoO ₃ /rGO/CC//MnO ₂ /CC	Na ₂ SO ₄ /PVA gel	32.1	88.1, 6000 cycles	This work

4. Conclusions

An easy and straightforward method for depositing high-active pseudo capacitive materials on carbon cloth hosts (MoO₃/rGO/CC and MnO₂/CC) has been developed. The conductive carbon cloth

with good mechanical flexibility not only provides efficient support for loading active materials to fabricate hybrid ASCs, but also facilitates fast ion and electron transport at the electrode/electrolyte interface. The introduction of rGO layer can remarkably improve the specific capacitance of the MoO₃ layer on the carbon fibers from 282.7 to 341.0 F g⁻¹. Furthermore, the assembled ASC by using the electrochemically deposited electrodes and a neutral gel electrolyte Na₂SO₄/PVA possesses a large operation potential of 1.6 V, exhibits a high energy density of 32.08 Wh kg⁻¹ at the power density of 0.53 kW kg⁻¹, and 5.33 Wh kg⁻¹ at 20.2 kW kg⁻¹. Furthermore, the ASC exhibits good cycle ability and the capacitance can maintain 87.1 % of its initial value after 6000 cycles. The ability of that two ASC devices connected in series are able to light up a LED that indicates its potential applications as energy storage devices.

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