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Communication

Laser processed micro-supercapacitors based on carbon nanotubes/manganese dioxide nanosheets composite with excellent electrochemical performance and aesthetic property

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ABSTRACT

Micro-supercapacitors with excellent electrochemical performance and aesthetic property are realized using the carbon nanotubes/manganese dioxide nanosheets (CNTs/δ-MnO_2) composite as electrodes. This CNTs/δ-MnO_2 nanocomposite is excellently compatible with the slurry dispensing process for electrode fabrication, and thus is conducive for preparing thick electrode films, which exhibits a specific capacitance of 257 F/g with an electrode thickness of 13 μm. By involving laser-scribing technique, the electrode film can be patterned with a high resolution and fabricated into a planar micro-supercapacitor, showing the maximum energy density of 6.83 mWh/cm^3 at the power density of 154.3 mW/cm^3, and maintained a value of 2.71 mWh/cm^3 at the maximum power density of 2557.5 mW/cm^3. Considering the versatility of the laser-scribing technical platform, the micro-supercapacitors fabricated in this way exhibit excellent aesthetic property and can cater to various miniaturized wearable electronic applications. This technology opens up opportunities for facile and scalable fabrication of high performance energy devices with shape diversity and a meaning of art.

With the rapid development of wearable/portable electronics, there is considerable demand in developing energy storage systems [1–3] having superior functionity and shape versatility. Among all the power sources, micro-supercapacitors [4–9] exhibit ultrahigh power densities and superior cycling lifetime, which could be several times higher than those of traditional batteries and supercapacitors. However, most state-of-the-art micro-supercapacitors are still limited with monotonous layout and a low mass loading of active material, which could hardly meet the need of mini- power sources with a high capacitive level.

The exploration of active materials in micro-supercapacitors mainly concerns highly reversible capacitance, environmental friendliness, mechanical flexibility and compositional stability [10–12]. Recently, carbon-based micro-supercapacitors utilizing graphene [13], carbon nanotubes [14], carbide-derived carbon [15] and onion-like carbon [16] has been widely used. These advanced electrochemical double layer capacitors (EDLCs) present a high power density, but generally exhibit low volumetric capacitance. To overcome this constraint, a series of pseudocapacitive electrode materials, such as MnO_2 [17,18], VS_2 [19], CuO [20] and PEDOT:PSS [21] have been used. These achievements have provided elaborate insights into the technological development of micro-supercapacitors. Among them, manganese oxides have been proven an excellent pseudocapactive electrode material for high-performance micro-supercapacitors [17], owing to their high theoretical specific capacity (1380 F/g) [22], large operating potential window, low material cost, and environmental friendliness. Recently, the ultrathin δ-MnO_2 nanosheets with large surface areas and porous structure have been proven as a competitive active material for energy storage application. While the intrinsic flaws of manganese oxides still exist. Especially, the poor electrical conductivity (10^{-5}–10^{-6} S/cm) would deteriorate rate capability and shorten the cycle life of the electrodes, which limits the electrochemical performance. To solve this problem, conductive additives, for example carbon nanotubes, with the properties of high surface area, remarkable conductivity and mechanical stability [23,24], have been explored to incorporate with MnO_2 to enhance the performance of electrode materials. However, how to further increase the mass loading of the active material, so as to improve the specific capacitance per area, still remains a challenge.

With the rise of wearable electronics, demands not only concern about energy storage functionality, but also include

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cultural and fashion aspects. Shi *et al.* recently presented a visual and aesthetic property (*i.e.*, letter, word, pattern or picture) of supercapacitors through screen printing method [25]. Lin *et al.* demonstrated a high performance planar supercapacitor, in which the pattern of interdigitated metal finger arrays was inkjet printed on flexible substrates [26]. These works pioneered the energy storage devices to meet the specific demand of the consumer electronics [27]. Apart from the aesthetical pleasure, consumers also expect the portable devices to be physically small. For example, devices with amazing patterns can be attached to necklaces or fingernails while maintaining the function of energy storage. However, screen printing with relatively low precision and inkjet printing with the limitation of thicker electrode films pose challenges for high-performance aesthetic micro-devices. In recent years, the laser scribing technique, which enables practicable and meticulous fabrication [13,28], has prompted increasing research interests on graphical fabrication of various functional electronic devices [29].

Herein, we introduce a laser processed micro-supercapacitors (LPMS) based on carbon nanotubes/manganese dioxide nanosheets (CNTs/δ-MnO_2) composite electrode. This composite with excellent electrochemical performance was synthesized through facile and scalable method. In such a device, the pattern of interdigitated active material finger arrays was finely fabricated through laser scribing technique. Most interestingly, this LPMS can be designed to show desirably aesthetic property and shape diversity. For example, a device with a vivid pattern can stick on a necklace while maintaining the function of energy storage. Overall, our technology reported here opens up opportunities for facile and meticulous fabrication of energy devices with shape diversity and a meaning of art. These energy devices can be broadly used in future wearable components.

Typically, 200 mL aqueous suspension of CNTs (NTP2021, ShenZhen Nanotech Port) with different concentrations (1 mg/mL, 2.5 mg/mL, 6 mg/mL, 12 mg/mL, 18 mg/mL) was added into a three-necked flask and heated to 90 °C with magnetic stirring. Pumping through a multi-channel peristaltic pump (Longerpump, BT100-1L) at a speed of 0.5 mL/min, $KMnO_4$ (0.05 mol/L, 100 mL) and $Mn(Ac)_2$ (0.05 mol/L, 100 mL) solutions were added into the flask simultaneously. With this method, the δ-MnO_2 nanosheets can grow on the surface of CNTs and thus form a composite in the flask with a high surface area. After reaction, the flask was cooled down to room temperature, and the as-obtained solution was then centrifuged (Bioridge, DD–5 M) at the speed of 5000 r/min and washed several times by deionized water. Finally, the precipitate was freeze-dried (BMH Instruments, Alpha 1-2 LD plus). In this way, different CNTs/δ-MnO_2 composite samples with the MnO_2 mass percentages of 21.5%, 27.3%, 41.5%, 66.5%, and 81.4% can be obtained.

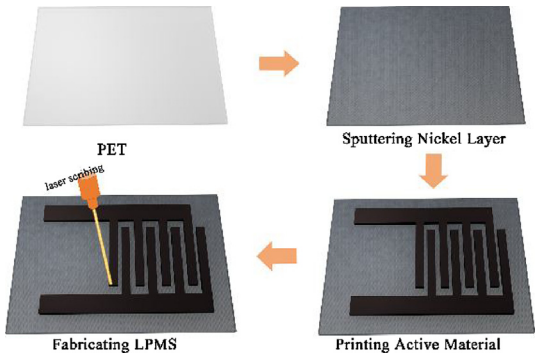

Fig. 1. Schematic of the electrode fabrication process.

Then the CNTs/δ-MnO_2 powder (1.28 g) was mixed with 0.16 g PVDF binder, 0.16 g superP conductive agent and NMP solvent (8 mL) in a planetary rotator mixer (Hasai 300, China) for preparing the electrode slurry.

The fabrication process of the LPMS is shown in Fig. 1. A typical LPMS was fabricated in the following steps. Firstly, polyethylene terephthalate (PET) was chosen as the flexible substrate; then a thin layer of nickel was magnetron-sputtered at ambient temperature with 1 μm in thickness. Then the electrode slurry was bladed onto the substrate and dried in vacuum oven at 120 °C for 12 h. The thickness of the electrode was 13 μm in this work and can be tunable. Afterwards, the laser beam (wavelength: 355 nm, model: Han's Laser EP-15-DW) was used to ablate redundant parts of the CNTs/δ-MnO_2 film and nickel layer to form an interdigital-electrode-structure LPMS array. In this work, the area of a single LPMS unit was controlled to be 60 mm^2. The width of the interdigital fingers and the interspace between them were 300 μm and 250 μm, respectively, and these configurations can be conveniently modified.

The detailed characterization and electrochemical measurements were provided in the Supporting information.

The CNTs/δ-MnO_2 composite was prepared by a redox reaction, where $KMnO_4$ was used as the oxidizing agent and $Mn(Ac)_2$ as the reducing agent. CNTs functioned as a nucleation site for the formation the MnO_2 nanosheets [30]. To evaluate the electrochemical performance of CNTs/δ-MnO_2 composite electrode, CV, GCD and EIS studies were conducted using a three-electrode configuration. 0.5 mol/L aqueous Na_2SO_4 electrolyte was used and the working potential window was selected between 0 V and 0.8 V (*vs.* Ag/AgCl). As is shown in Fig. S1 (Supporting information), the dramatic enhanced electrochemical performance of CNTs/δ-MnO_2 composite compared with pure CNTs film is attributed to the good synergetic effect between two components. CV curves of CNTs/δ-MnO_2 with varying MnO_2 ratios (21.5%, 27.3%, 46.5%, 66.5%, and 81.4%) at the scan rate of 20 mV/s are presented in Fig. S2 (Supporting information). As the CNTs/δ-MnO_2-41.5% showed a much better capacitance performance, the following results are presented based on this ratio. We take CNTs/δ-MnO_2 as the abbreviation for the CNTs/δ-MnO_2-41.5% in the following results for brief expression.

Fig. 2a illustrates the typical CV performance of the electrode with various scan rates ranging from 5 mV/s to 200 mV/s. It shows that the CV curves were relatively rectangular in shape at low scan rate, and exhibited a near mirror-image current response on voltage reversal. When the scan rate got faster, there were no significant differences in the shape of the curves, indicating a fast charge/discharge capability and effective diffusion of electrolyte in the electrode material. As is presented in Fig. 2b, the GCD curves of the CNTs/δ-MnO_2 electrode at various current densities of 0.5, 1.0, 2.0, 5.0 and 10.0 A/g suggest excellent reversibility of charge storage and small voltage drop (0.05 V), which could be attributed to the high electrical conductivity of the CNTs/δ-MnO_2 composite electrode, further demonstrating the excellent capacitive behaviour of the composite electrode. The calculated C_m of the CNTs/δ-MnO_2 electrode as a function of current density, calculated from the GCD tests based on equation S1 (Supporting information), exhibited a maximum value of 257 F/g at the current density of 0.5 A/g.

While in most cases, a high C_m value (~700 F/g) could be obtained when the film of the electrode material is very thin and the material needs to be loaded onto a current collector with high surface area, which is not included when calculating the specific capacitance value. With the increase of the current density, the C_m value decreased correspondingly, but still exhibited a value of 163 F/g at the scan rate of 2 A/g, which confirmed relatively excellent rate performance of the CNTs/δ-MnO_2 composite electrode.

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