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Optimization of coplanar high rate supercapacitors

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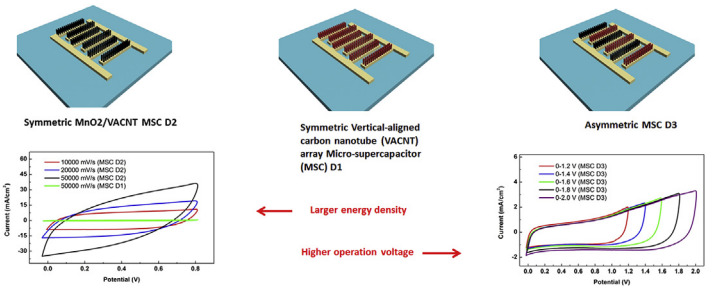
HIGHLIGHTS

- Low density VACNT array are applied as matrix of high power micro-supercapacitor.
- Through introducing MnO_2, the capacitance exhibit tremendous improvement.
- Energy density has been increased from 0.017 to 0.426 mWh cm^{-3} at 50000 mV s^{-1}.
- Due to asymmetric design of the MSC, potential window is increased to 1.2 V.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we describe two efficient methods to enhance the electrochemical performance of high-rate coplanar micro-supercapacitors (MSCs). Through introducing MnO_2 nanosheets on vertical-aligned carbon nanotube (VACNT) array, the areal capacitance and volumetric energy density exhibit tremendous improvements which have been increased from 0.011 mF cm^{-2} to 0.017 mWh cm^{-3} to 0.479 mF cm^{-2} and 0.426 mWh cm^{-3} respectively at an ultrahigh scan rate of 50000 mV s^{-1}. Subsequently, by fabricating an asymmetric MSC, the energy density could be increased to 0.167 mWh cm^{-3} as well. Moreover, as a result of applying MnO_2/VACNT as the positive electrode and VACNT as the negative electrode, the cell operating voltage in aqueous electrolyte could be increased to as high as 2.0 V. Our advanced planar MSCs could operate well at different high scan rates and offer a promising integration potential with other in-plane devices on the same substrate.

1. Introduction

Due to the rapid development of miniaturized electronic devices, micro-scale systems integrated with high rate performance power sources are in high demand for future applications [1–3]. However, to integrate the traditional energy storage devices, such as lithium-ion batteries and sandwiched supercapacitors, etc. directly with on-chip devices or integrated circuits is challenging, because these devices are difficult to downscale in size and unsuited to the planar geometric design as well as the fabrication processes [4,5].

Planar micro-supercapacitors (MSCs), as a novel type of micro-scale energy storage devices, have attracted significant attentions due to their special structure in which ion transporting pathways are much shorter than conventional LIBs and supercapacitors [6,7]. Compared with commercial batteries and supercapacitors, planar MSCs theoretically could deliver higher energy densities and exhibit larger rate capabilities [8–10]. In addition, wafer process technologies have been employed to manufacture the planar MSCs, making this newly developed power source environmental friendly

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and present the potential of integration with various on-chip devices, like energy harvesting devices, nanostructured sensors and radio frequency identification tags, etc. [11–13].

Recently lots of efforts have been made on developing electrochemical performance of planar MSCs via two approaches: (1) utilization of nanostructured based active materials, including onion-like carbon [14], reduced graphene oxide [15], graphene quantum dots [16] and graphene oxide/CNT composite [17], etc. and (2) employment of advanced thin film manufacture technologies, like inject printing [18], in-situ photoresist-derived [19] and layer-by-layer assembling [20], etc. These approaches have successfully increased the energy densities and enhance the rate performance of planar MSCs in different degrees. However, to meet the practical integration requirements of different micro-systems, the power delivery capability still needs to be enhanced, especially for some applications that ultrafast rate performance [21] and sufficient peak power [22] are highly required. Therefore, some groups have fabricated high performance planar MSCs with ultrafast energy deliver capabilities, in which the charge/discharge time was able to reach milliseconds level. A graphene-based in-plane MSC [23] demonstrated an ultrafast rate of 3.6 ms, satisfying the requirements of high frequency filtering devices. Nevertheless, although graphene, as a robust two-dimensional (2D) material, presents an outstanding electrical conductivity and high double layer capacitance property, the architecture nature of graphene constraints the areal specific capacitance of the MSC as the thickness of thin graphene film is always limited within nanometers scale. A 3D nanostructured planar MSC basing on the high density vertical-aligned CNT array [24] did increase the areal energy density of capacitor, reaching a maximum power density of 0.115 W cm^{-2} in aqueous electrolyte due to the carpet-like 3D structure largely enriching the electrode thickness up to micrometers level. An obvious drawback of pure CNT based MSCs is the low theoretical specific capacitance of 120 F g^{-1} [25] when compared with other active materials like manganese dioxide (MnO_2), vanadium disulfide (VS_2) and nickel oxide (NiO) et al. [26–28] Besides, most of the planar MSCs were fabricated with the same materials for both electrodes which means the potential window of these symmetric structure MSCs would be restricted by the decomposition of water in neutral liquid electrolyte. Thus how to enhance the performance of ultrafast rate planar MSCs is still a challenging issue.

To optimize the electrochemical performance of high-rate planar MSCs, we have designed three types of nanostructured based MSCs through employing a low density vertical-aligned carbon nanotube (VACNT) array and MnO_2 nanosheets: (1) symmetric bare VACNT arrays based MSC (D1); (2) symmetric MnO_2 nanosheets deposited onto VACNT arrays based MSC (D2); (3) asymmetric hybrid MSC (D3) where a MnO_2/VACNT array is used as the positive electrode and a bare VACNT array is employed as the negative electrode. In-situ growth of low density VACNT array on the current collector could directly reduce the interfacial resistance and the unique one-dimensional nanostructure could offer a short charge transporting pathway further increasing the conductivity between the active material and current collector. Moreover the straight morphology and low density VACNT array synthesized in our device [29] not only tremendously enlarge the surface to volume ratio of electrode, also make the liquid electrolyte easily penetrating inside the VACNT array. According to the volumetric energy density E (mWh cm^{-3}) relationship ($E = C_s\ \Delta V^2/7200$), where C_s refers to stack capacitance (mF cm^{-3}) and ΔV (V) refers to operating potential window, this electrode is supposed to show a large enhancement in the specific capacitance C_s [30] for MSC (D2) and due to the asymmetric structure of MSC (D3). The working potential range ΔV would be correspondingly broadened in 0.5 M Na_2SO_4 aqueous electrolyte. So both approaches are expected to present superior high-rate electrochemical performance.

Here, we have successfully prepared the three types of MSCs and conducted related electrochemical characterizations. Interestingly, the low density VACNT arrays MSC (D1) reveals an excellent capacitive property at high rate conditions. A significant enhancement in energy density of MnO_2 nanosheets decorated VACNT arrays based MSC (D2) has been proved as well. Additionally, an asymmetric capacitor (D3) exhibits an outstanding electrochemical behavior in aqueous medium with a high potential window.

2. Experimental

Quartz slides were used as the substrates for all MSCs. The interdigital electrodes were patterned with a conventional photolithography technique. Subsequently, a four-layer-metal of Ti/Au/Al_2O_3/Ni thin film was deposited on the quartz plates as both current collectors and catalysts through an electron beam evaporator system. After a lift-off process, VACNT arrays was grown in a mixture of ammonia/acetylene (240/60 sccm) gas atmosphere under 120 W (plasma-enhanced CVD) at 800 °C [29] to form MSC D1. The sample was carefully treated by oxygen plasma to remove carbon residual (SEM image of substrate surface is presented in Fig. S1) and then MnO_2 nanosheet was electrodeposited on the VACNT array according to the relative reference [36]. Simply speaking, the electrodes with VACNT on the substrate were immersed in an aqueous solution of 20 mM $Mn(NO_3)_2$ and 100 mM $NaNO_3$, a constant current density of 66.7 μA cm^{-2} was continuously applied for 10 min in a two-electrode setup. For MSC D2, both electrodes were decorated with MnO_2 nanosheet. Only one electrode was coated for MSC D3. The deposited specific mass loading of MnO_2 nanosheet was approximately 1.1 mg cm^{-2}.

The morphology characterizations of pure VACNT array and MnO_2 nanosheet coated VACNT array were studied using an ordinary optical microscope, a field-emission scanning electron microscopy (SEM, LEO 1550 Gemini) and a Raman system (WITec) under a 532 nm wavelength excitation, respectively. Electrochemical characterizations of all the MSCs were carried out through an electrochemical workstation (AUTOLAB, M 101) in a 0.5 M Na_2SO_4 aqueous electrolyte under a two-electrode measurement setup. All electrochemical impedance spectroscopy (EIS) plots were tested in the frequency ranging from 100 kHz to 1 Hz at open circuit potential.

3. Results and discussion

Fabrication processes of the three planar MSCs are shown in Fig. 1. Quartz slides were applied as transparent substrates for all devices. After conventional micro-fabrication processes (photolithography, electron-beam evaporation deposition and lift-off), multi-layer electrodes with the catalysts for VACNT growth were patterned on all the substrates and the corresponding photograph is presented in Fig. 2a. Well-spaced VACNT arrays of all samples were grown through a plasma-enhancement chemical vapor deposition (PECVD) system. Subsequently selective coating MnO_2 nanosheets onto VANCT arrays via electrochemical deposition processes on one electrode and both electrodes were carried out.

The dimensions of the interdigitated electrodes (detailed information is included in Fig. S2) are presented in the microscope images Fig. 2b (edge area of MSC) and Fig. 2c (middle fingers area of MSC). In this work, the width of interdigitated electrodes and the interspacing between them are preciously controlled to be 100 μm Fig. 2d, e and 2f are the optical microscope images of the middle parts for MSC D1, D2 and D3 respectively, in which the light color areas correspond to the quartz substrate between the electrodes of