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Electrochemically synthesized and vertically aligned carbon nanotube–polypyrrole nanolayers for high energy storage devices

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ABSTRACT

In this work, we successfully demonstrate the fabrication of vertically aligned carbon nanotube (VACNT)-polypyrrole (PPY) nanocomposites as a "hybrid supercapacitor" material directly integrated on silicon-based electrodes. In contrast to previous works, three distinctive achievements have been accomplished: (1) a "hybrid supercapacitor" using VACNT forest with electroplated PPY and dodecylbenzenesulfonate (DBS) as a dopant in acetonitrile, (2) realizing 500% higher capacitance as compared to the capacitance of electrodes made of VACNT or DBS-doped PPY alone, and (3) highly reversible cycling between −1 V and +1 V with improved knee frequency at 797 Hz. As such this hybrid nanocomposite could become a new class of material for future supercapacitors. We also demonstrate the life-cycle stability of the VACNT-PPY nanocomposite supercapacitor, as well as its rapid charge-discharge capabilities and low leakage current. Electrochemical impedance modeling results suggest that the VACNT-PPY supercapacitor has higher electric double layer capacitance in addition to higher pseudocapacitance compared to uncoated VACNTs.

1. Introduction

Power sources for portable 3D micro-systems including distributed sensor networks are critical for their operational life, performance, and reliability [1]. With the increasing presence of MEMS devices in a wide range of technologies, there is a growing need to develop high-performance electrical energy storage technologies with high power density and ease of fabrication [2]. The two major power sources for portable devices are batteries and capacitors, which have historically lagged behind the development of micro-electronic circuits, in areas such as system integration density [3]. As supercapacitors store electrical energy by either fast ion absorption at the electrode/electrolyte interface as in electric double layer capacitor (EDLC) [4] or quick and reversible surface redox reactions as in pseudo supercapacitor (PSC) [5], they bridge the power density gap between dielectric capacitors and batteries. Supercapacitors find myriad commercial successes in high power applications, such as backup power supplies, camera flash units, electric cars, or power load-leveling of heavy machinery [6].

It is desirable to enhance the energy density of supercapacitors by increasing either their specific capacitance or their operating voltage [7]. Fan et al. developed an asymmetric supercapacitor with different anode/cathode materials in order to maximize the operating voltage [8]. PSCs based on metal oxides such as RuO_2 and MnO_2 or conducting polymers including polypyrrole (PPY) and polyaniline (PANI) have been under extensive investigations over the past decades because their specific energy density is higher than that of their EDLC counterparts [9]. Organic electrodes based on electronically conducting polymers have many benefits in PSC formation, including environmental stability, low-cost, and high-energy density [10]. Specifically, PPY offers unique properties as a PSC material with the ease of process compatibility, redox-tunable conductivity as p-doped or undoped polymer, and biocompatibility [11].

Previously, An et al. presented a high-capacitance supercapacitor based on a mixture of single-walled carbon nanotubes (SWNT) and PPY using polytetrafluoroethylene (PTFE) as the binding material and KOH as the electrolyte [12]. In order to overcome the large variations due to CNT/PPY composition, Fang et al. electrodeposited PPY on a pre-assembled CNT membrane using short potential pulses and tested the fabricated supercapacitor in the electrolyte

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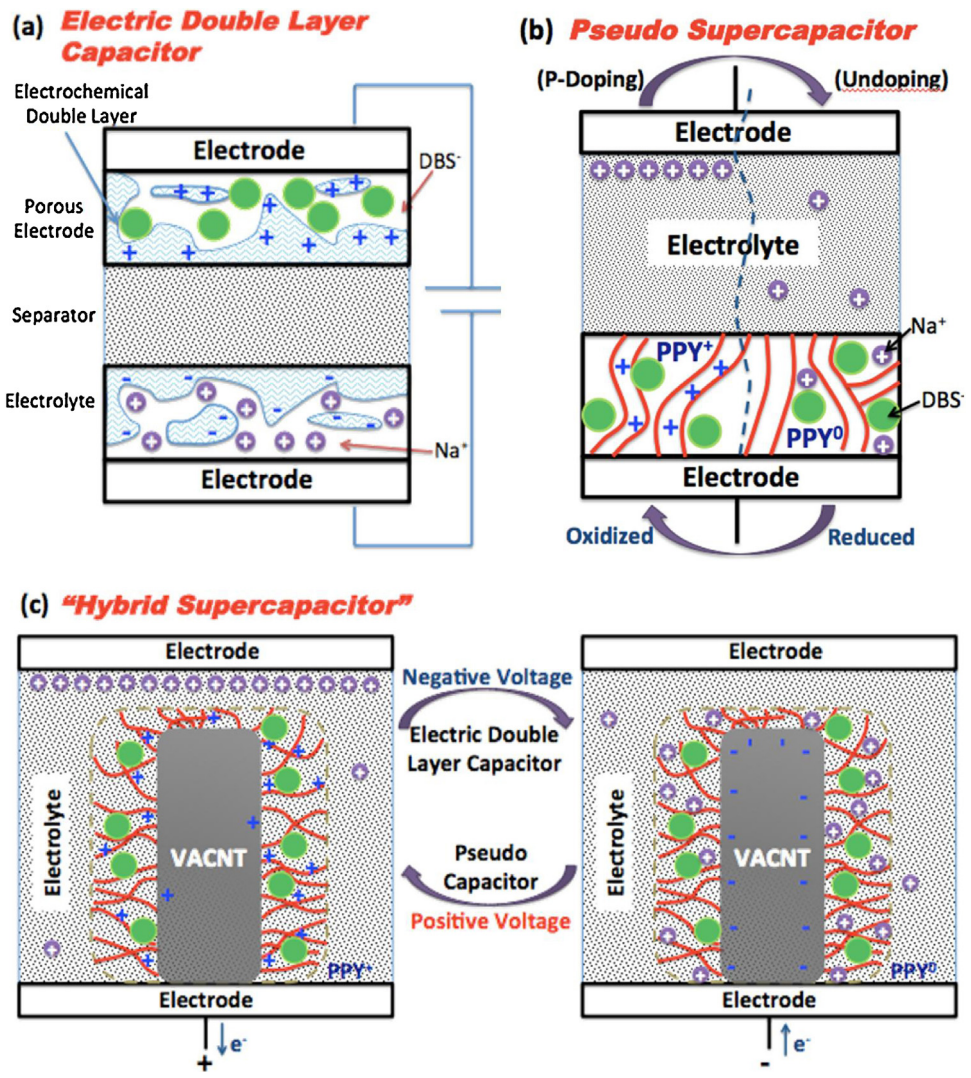

Fig. 1. A schematic diagram illustrating the operation principles of: (a) Electric Double Layer Capacitor (EDLC), where charge is stored in the electrochemical double layer; (b) Pseudo Supercapacitor (PSC), where PPY changes between oxidized (p-doped) and reduced (undoped) states during charging and discharging, respectively; and (c) Hybrid Supercapacitor with vertically aligned CNT (VACNT) coated with PPY as the nanocomposite material. For a positive input voltage, DBS^- ions are stored in the polymer mesh as dopants. Under a negative input voltage, Na^+ ions move into the VACNT-PPY composite, storing charge in an electrochemical double layer. Due to their large size, DBS^- ions remain in the PPY matrix in (b) and (c) even with a negative input voltage.

solution of Na_2SO_4 [13]. Frackowiak et al. prepared the electroconducting PPY using a simple chemical polymerization technique on an entangled CNT mesh, where H_2SO_4 was later used as the electrolyte [14]. It is worth mentioning that the PPY/CNT supercapacitors demonstrated in the literature works were not optimized by mass or volume because of the requirement of a binding material during their construction and they suffered from a large contact resistance between CNT/PPY nanocomposite and the metal electrode. In addition, the operational voltage was limited to 0–0.8 V range due to the selected negative doping ion and the nature of the aqueous electrolyte, which was either basic or acidic.

Recently, we have demonstrated nano-textured electrodes with enhanced specific energy density using vertically aligned carbon nanotubes (VACNT) as an EDLC [15], and VACNT with electroplated nickel nanoparticles as a PSC using vacuum infiltration technique [16]. In addition to the high specific surface area, VACNT offer other advantages including low contact resistance to the metal electrode, high conductivity, and binder-free integration. In order to overcome the drawbacks of the previous works, this paper presents a hybrid supercapacitor combining EDLC and PSC on the same electrode using VACNT forests as the cores and electroplated conductive polymer PPY as the shells with dodecylbenzenesulfonate (DBS^-) as a dopant ion in acetonitrile for high energy density and large voltage window of operation.

2. Operation principle

The operation principle of an EDLC is illustrated in Fig. 1(a), where charge is stored electrostatically in the electrochemical double layer at the interface between the VACNT electrode and the electrolyte. When an electric potential is applied, the Na^+ and DBS^- ions within the electrolyte separate and are drawn to their respective electric double layers. The separator prevents the opposite electrodes from shorting and the capacitance is proportional to the electrode area. Fig. 1(b) explains the operation principle of a PPY-based PSC, where the PPY transforms from the reduced (undoped) state to the oxidized (p-doped) state during charging and discharging, respectively. Due to their large size, the DBS^- ions remain within the PPY matrix, while Na^+ ions move in and out of the PPY based on the applied voltage [17]. The operation principle of a VACNT-PPY supercapacitor as an EDLC/PSC hybrid supercapacitor is demonstrated in Fig. 1(c). For positive input voltages, the