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Fabrication and characterization of flexible and high capacitance supercapacitors based on MnO_2/CNT/papers

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ABSTRACT

Flexible paper-based supercapacitors were fabricated using carbon nanotubes (CNTs) and manganese oxides (MnO_2), and their electrochemical properties were characterized in a three-electrode system. CNTs were synthesized via water-assisted chemical vapor deposition (CVD) and dispersed in water using the surfactant sodium dodecylbenzenesulfonate (SDBS). The solution containing dispersed CNTs was simply coated on papers by drop-dry method. MnO_2 was then electrochemically deposited on the CNT-coated papers. The MnO_2/CNT/paper supercapacitors showed high specific capacitance of 540 F/g. Specific energy and specific power were 20 Wh/kg and 1.5 kW/kg, respectively, at current density of 5 A/g in 0.1 M sodium sulfate (Na_2SO_4) aqueous solution. Demonstrated high capacitance of the paper-based electrochemical capacitor makes it a promising candidate for flexible and low-cost energy storage device applications.

1. Introduction

For efficient use of sustainable and renewable resources, it is important to develop energy storage devices that can efficiently store electricity generated from energy conversion devices such as solar cells and fuel cells [1,2]. While batteries have been extensively studied due to their high energy density, electrochemical capacitors, also called supercapacitors or ultracapacitors, have recently attracted considerable attention owing to their higher power density than that of batteries [3,4]. The supercapacitors also have longer cycle life, are safer during high rate charge and discharge processes, and consist of materials that have lower environmental impact [5]. Owing to these advantages, the supercapacitors may find practical applications such as portable electronics, hybrid electrical vehicles, and large industrial equipments by replacing or complementing batteries [6].

Combination of different kinds of capacitive materials could lead to enhanced supercapacitor performance. There are two kinds of supercapacitors depending on charge storage mechanism and active materials: (i) electrochemical double layer capacitors (EDLC) and (ii) redox supercapacitors or pseudo-capacitors [1,5]. In EDLCs, carbon-based materials with high specific surface area are most widely used and energy storage mechanism is based on simple physical movement of ions to and from the carbon electrode surface. In redox supercapacitors, metal oxides or conducting polymers are commonly employed and energy is stored through fast and reversible electrochemical charge transfer process. Since pseudocapacitive materials usually have high capacitance, conformal coating of them onto the carbon-based materials with large specific surface area and high conductivity could significantly improve supercapacitor performance [1]. For example, it has been shown that combining manganese oxides (MnO_2) and carbon nanotubes (CNTs) can lead to the enhancement of supercapacitor performance [7,8].

On the other hand, flexible devices have also received increasing attention owing to the development of a wide range of flexible and wearable electronics [9–11]. Papers have been recognized as one of the flexible and low-cost substrates that are potentially useful for various applications such as microfluidic devices, portable bioassay devices, organic electronics, and active matrix displays [12–16]. Very recently, it has been demonstrated that papers also can be used as an excellent substrate for the fabrication of high performance energy storage devices [17]. The papers were coated with CNTs to provide electrical properties to them. CNTs have not only high conductivity but also other excellent properties for supercapacitor applications such as high mechanical strength, large specific surface area, and chemical stability [18]. Moreover, coating process is very simple, inexpensive, and scalable. Specific capacitance of 200 F/g was obtained from the CNT-coated paper supercapacitors [17]. However, to replace or complement batteries, improvement in energy density is highly desirable, and this could be achieved

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by coating pseudocapacitive materials onto the papers coated with carbon nanotubes.

In this report, we demonstrate that flexible paper-based supercapacitors with increased specific capacitance and specific energy can be fabricated by depositing MnO_2 on CNT-coated papers. Regular office papers were coated with aqueous CNT ink prepared using CVD-grown CNTs and surfactants. MnO_2 was subsequently deposited electrochemically on the CNT-coated papers. The MnO_2/CNT/paper supercapacitors were mechanically flexible and showed high specific capacitance (~540 F/g) and specific energy (up to ~45 Wh/kg) in 0.1 M sodium sulfate (Na_2SO_4) aqueous solution.

2. Experimental

CNTs were synthesized via water-assisted CVD. 10 nm of aluminum (Al) and 1 nm of iron (Fe) were e-beam evaporated on silicon (Si) substrates with silicon oxide (SiO_2) layer on top. The substrate was placed in the middle of a quartz tube in a furnace (Lindberg, TF55030A). Ethylene (C_2H_4), hydrogen (H_2) and argon (Ar) were introduced to the quartz tube at the flow rate of 50, 100 and 125 sccm, respectively. Simultaneously, small amount of water was introduced by flowing Ar through a bubbler containing de-ionized (DI) water at the flow rate of 0.75 sccm. The reaction typically lasted for 5–10 min at 800 °C.

CNT ink was fabricated by adding 20 mg of CNTs grown by the water-assisted CVD and 20 mg of sodium dodecylbenzenesulfonate (SDBS) surfactant in 20 mL of DI water. The CNT solution was bath-sonicated for 5 min and then bar-sonicated for 20 min. The solution was centrifuged at 3000 rpm for 5 min to remove surfactant in supernatant. The CNT precipitates were placed on a poly(tetrafluoroethylene) (PTFE, Millipore, pore size ~1 μm) filter paper and rinsed with DI water. The CNTs were re-dispersed in 20 mL of DI water by sonication. CNT coated papers were fabricated by dropping the CNT solution (0.2 mL) onto a piece of paper (Hankuk paper, Hiper CC A4) with an area of 1 cm × 1 cm and drying them at 80 °C in an oven for 2 h. MnO_2 were deposited on the CNT/paper by sweeping voltage in the range of 0–1.2 V in aqueous solution of 0.1 M Na_2SO_4 and 0.1 M $Mn(CH_3COO)_2$ for 100 cycles. The electrodes were oven-dried at 80 °C for an hour.

Deposited CNTs and MnO_2 were characterized by scanning electron microscopy (SEM, Hitachi S4700 or JEOL JSM 7500F) and energy dispersive X-ray spectroscopy (EDS). The properties of CNTs were characterized by transmission electron microscopy (TEM, Philips Tecnai 20) and Raman spectroscopy (Horiba HR 800). Supercapacitor properties were measured using a three electrode system. A MnO_2/CNT/paper, an Ag/AgCl (CH Instruments, CHI111, 3 M KCl), and a Pt gauze were used as a working, a reference, and a counter electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charge/discharge measurement were carried out in the voltage range of 0–0.8 V in 0.1 M Na_2SO_4 aqueous solution (Ivium Technologies, CompactStat). Electrochemical impedance spectroscopy (EIS) was performed to measure equivalent series resistance (ESR).

3. Results and discussion

A forest form of aligned CNTs was synthesized on a SiO_2/Si substrate via water-assisted CVD as shown in Fig. 1. In supercapacitor applications, the CNTs with small diameter are preferred to those with large diameter due to the higher surface area. The CNTs with small diameters can be preferentially produced using Al/Fe bilayer catalyst during CVD [19–21]. The diameter of CNTs is generally determined by catalyst-particle size [22]. The small size of the Fe catalyst nanoparticles can be retained by the presence of underlying Al layer even at high CVD temperature because the Al layer supposedly prevents aggregation of Fe nanoparticles [21]. In addition, small amount of water was introduced during the CVD process to maximize the yield of CNTs. Introduction of small amount of water is known to extend catalyst life time by protecting catalyst surface from deposition of unwanted carbon species [23]. Under these growth conditions, a dense film of aligned CNTs with a length of up to ~1 mm was grown (Fig. 1a). The estimated growth rate was ~160 μm/min. Vertical alignment of the CNTs was clearly observed by SEM (Fig. 1b). TEM characterization revealed that the average number of walls and diameter of the CNTs were

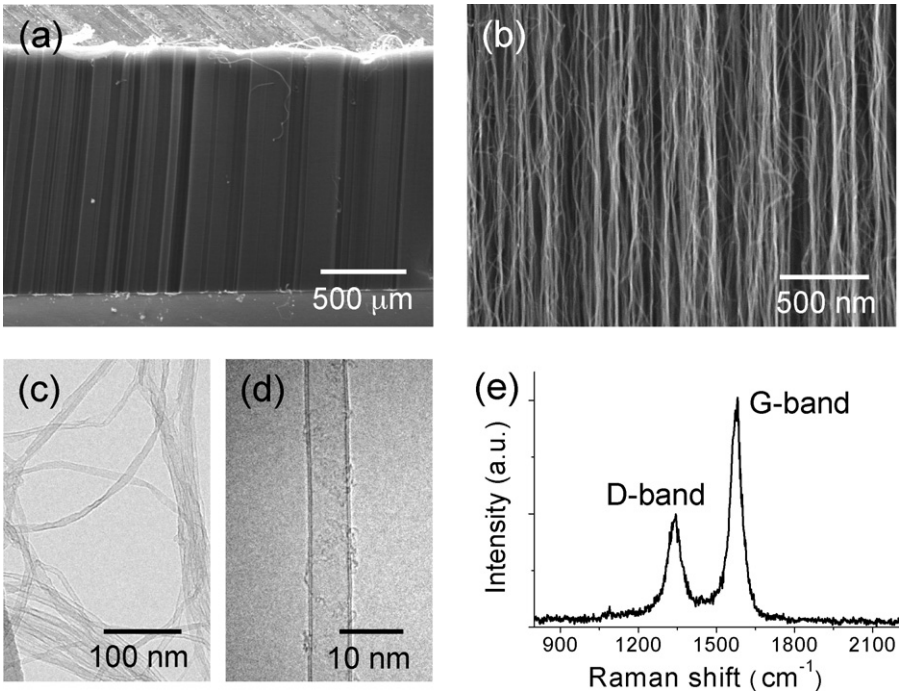

Fig. 1. (a) A scanning electron microscopy (SEM) image of carbon nanotubes (CNTs) vertically grown on a SiO_2/Si substrate. (b) An SEM image showing the alignment of CNTs. (c) A transmission electron microscopy (TEM) image of CNTs. (d) A TEM image showing double walls of CNTs. (e) Raman spectrum of CNTs.