Fabrication and Characterization of an All-Solid-State Stretchable Supercapacitor using Polypyrrole-CNT Hybrid Partially Embedded in PDMS

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ABSTRACT

We present a supercapacitor with polypyrrole-dodecylbenzenesulfonate (PPy(DBS))-vertically aligned carbon nanotube (VACNT) hybrid partially embedded into PDMS. The facile technique enables the partial-embedding of vertically aligned carbon nanotubes in PDMS, which facilitates a stable charge/discharge under varied strains. The measured capacitance was 2 mF/cm² at a scan rate of 1000 mV/s with a gel electrolyte. The structure was seamlessly stretched up to 160% with a capacitance attenuation by 30% at 160% stretching. The measured capacitance value were very well maintained under bending with its angles varying from 0 to 180 degrees.

Keywords: flexible supercapacitors; vertically aligned carbon nanotubes; polypyrrole-dodecylbenzenesulfonate; PDMS; fabrication process

1 INTRODUCTION

Energy storage technologies can be categorized, based on the form of energy stored in the system, into mechanical (pumped hydroelectric storage, compressed air energy storage and flywheels), electrochemical (conventional rechargeable batteries and flow batteries), electrical (capacitors, supercapacitors and superconducting magnetic energy storage), thermochemical (solar fuels), chemical (hydrogen storage with fuel cells), and thermal (sensible heat storage and latent heat storage) energy storage.

Supercapacitors can be categorized as electric double layer capacitors, pseudocapacitors, hybrid capacitors (including electric double layer capacitors and pseudocapacitors). Applying these supercapacitors into flexible electronics would benefit a wide range of applications in wearable and multifunctional electronics, including flexible displays, curved smart phones, electronic skins, and implantable medical devices. More specifically, flexible supercapacitors can meet the demand of lightweight, flexible, and portable electronic devices. Consequently technologies for flexible energy storage have to be developed for such flexible electronic devices [1,4,5], and efforts have been made to improve the performance of the flexible supercapacitors. Among several candidates for supercapacitor materials, vertically aligned carbon nanotube (VACNT) and polypyrrole-dodecylbenzenesulfonate (PPy(DBS)) are promising materials for electrodes of flexible supercapacitors owing to their excellent electrical, and mechanical properties [6–10].

In this work, we present a supercapacitor composed of PPy(DBS)-VACNT hybrid, partially embedded into PDMS. The device is facilely fabricated by the partial-embedding of PPy(DBS)-VACNTs in PDMS, permitting a strong hold of PPy(DBS)-VACNT hybrid into Polydimethylsiloxane (PDMS), which facilitates a stable charge/discharge under varied strains.

2 EXPERIMENTAL SECTION

We synthesized VACNTs using atmospheric-pressure chemical vapor deposition (APCVD) into carpet-like structures. The catalyst layer consisting of 5 nm Al and 3 nm Fe was deposited on the Si/SiO₂ substrate prepared using physical vapor deposition (PVD). Then the substrate was placed in the atmosphere pressure chemical vapor deposition (APCVD) chamber. The furnace temperature was increased to 750°C with a constant 500 sccm Ar flow. VACNTs were grown at 750°C for 15 minutes with 60 sccm H₂ and 100 sccm C₂H₄. Then the chamber was cooled down to the room temperature while maintaining the same Ar flow rate. The structure of the grown CNTs is vertically aligned in general, while the individual carbon nanotubes are entangled with each other. The morphology of the...
VACNTs were characterized using scanning electron microscopy (SEM).

To fabricate flexible substrates with embedded VACNTs, we transferred the grown VACNTs onto partially cured PDMS. First, we used a liquid mixture of PDMS base and curing agent (Sylgard 184 Silicone Elastomer, Dow Corning) which were mixed with a ratio of 10:1 to form a PDMS substrate. After degasing under reduced pressure in a vacuum pump, the bubbles were all removed while PDMS was still liquid. Then the liquid PDMS was placed on a hot plate at 65°C for about 30 minutes before it was fully cured. We optimized the curing condition of PDMS, where the partially cured PDMS was tacky but not fully wet. The grown VACNTs were then placed onto partially cured PDMS. Then the tips of CNTs were partially immersed into PDMS slowly. During the curing process, the embedded CNTs were eventually wetted by PDMS. Then after PDMS was fully cured, the VACNT-PDMS structure was successfully peeled off from the Si/SiO₂ substrate owing to the strong adhesion between PDMS and VACNTs. The entire fabrication process is rapid and facile, which permits the integration of VACNT-PDMS substrate.

After VACNT embedding, PPy(DBS) film was electropolymerized atop the VACNT-covered substrate. First, 1mL pyrrole monomer (reagent grade, 98%, Sigma-Aldrich, St. Louis, MO) was thoroughly mixed with 150mL 0.1mol/L sodium dodecylbenzenesulfonate (NaDBS, technical grade, Sigma-Aldrich, St. Louis, MO) solution. Then, VACNT-covered substrate, a saturated calomel electrode (SCE, Fisher Scientific Inc., Pittsburgh, PA), and stainless steel mesh (5 cm × 5 cm) were submerged in the solution as the working, reference, and counter electrode, respectively. The coating of PPy(DBS) surface was carried out using a potentiostat (263A, Princeton Applied Research, Oak Ridge, TN) by applying 0.8V to the working electrode (vs. SCE) and stopped once surface charge density reached 300 mC/cm². After fabrication, PPy(DBS) surface was rinsed and dried in air overnight before any further characterizations.

PVA-KOH gel electrolyte was fabricated by mixing 1g poly(vinyl alcohol) (PVA) powder with 1g KOH powder in 10 ml DI water. After mixing at 60’ for around 1 hour and continuously stirring, it took on a homogeneous viscous and clear appearance. Then PVA-KOH gel electrolyte was dripped onto the surface of the VACNT-PDMS structures. The all-solid-state flexible supercapacitor was fabricated by stacking two PPy-VACNT-PDMS structures face-to-face with PVA-KOH gel electrolyte in the middle. The electrochemical property of the flexible supercapacitor was measured at different scan rates from 50 mV/s to 1000 mV/s using cyclic voltammetry.

The electrochemical behavior was characterized using cyclic voltammetry (CV) in a two electrode configuration. CV measurements were performed within the potential range of 0.0V-0.5V as scan rates of 50-1000 mV/s by using a potentiostat. The capacitances of the electrodes were calculated as a capacitance per area (F/cm²). The average capacitance was normalized per area of the samples and was estimated according to the following equation [11–13]:

\[ C = \frac{\int_{E_1}^{E_2} I \, dV}{\Delta V \times V \times A} \]  

where I is the current, A is the area of the supercapacitor, \( \Delta V \) is the scanning rate, \( E_1 \) and \( E_2 \) are the voltage and \( V = E_2 - E_1 \).

We performed both the tensile strain measurements and the bending strain measurements by using a stretching stage manually to evaluate the flexibility and durability.

### 3 RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammetry (CV) curve recorded at a scanning rate of 1000 mV/s with PVA-KOH gel electrolyte. As can be seen, the structure showed good electrochemical stability and capacitive behaviors at scanning rate of 1000 mV/s. The capacitance can be calculated to be 2 mF/cm² at 1000 mV/s.
4 CONCLUSION

We have demonstrated a flexible supercapacitor composed of PPy-VACNTs on PDMS substrate. The device was fabricated using a new, facile technique that enables the partial-embedding of vertically aligned carbon nanotubes in PDMS. As a result, the devices were reliable and stable under both stretching AND bending (flexibility) for a long-cyclic testing. The fabrication process was very reproducible and reliable. As next steps, the performance of this flexible supercapacitor will be fully characterized at various applied strain values (stretching, bending and twisting at different frequencies under different temperatures and humidity values). The cyclic behavior of supercapacitors will be investigated under such applied strains. The droplet behavior of the surface of PPy-VACNT-PDMS structure will be characterized under PPy redox and under different stretching strains at varying PPy thickness and surface morphology.

REFERENCES


