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Qiang Liu
Cleveland State University

Osama Nayfeh
University of Illinois at Urbana-Champaign

Munir H. Nayfeh
University of Illinois at Urbana-Champaign

Siu-Tung Yau
Cleveland State University, s.yau@csuohio.edu

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Flexible supercapacitor sheets based on hybrid nanocomposite materials

Qiang Liu^a, Osama Nayfeh^b, Munir H. Nayfeh^b, Siu-Tung Yau^{a,*}

^aDepartment of Electrical and Computer Engineering, Cleveland State University, Cleveland, OH 44115, USA

^bDepartment of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Introduction

The incorporation of inorganic nanomaterials into organic conducting polymers to form hybrid nanocomposite materials appears to be an effective approach for preparing electrochemical energy storage materials [1]. The capacitance of the hybrid materials consists of the pseudocapacitance produced by the polymers and, in most cases, the electric double-layer capacitance generated by the nanomaterials. The hybrid

nature of the materials, when used to construct supercapacitors, has resulted in enhanced energy and power capabilities [2]. To date, conducting polymers such as polyaniline (PANI), polypyrrole and polythiophene have been used to anchor inorganic nanomaterials such as carbon nanotubes (CNT) and nanoparticles for the construction of supercapacitors [3,4] and for studying the properties of the composite materials. Previously, this group has reported the preparation of a composite material consisting PANI and silicon nanoparticles [5]. The material was characterized by depositing the material on single electrodes. In a subsequent work, this group has described a simple approach for constructing flexible sheets of supercapacitors using a composite material made of PANI and carbon nanotubes. Carbon nanotubes were used to

*Corresponding author. Tel.: +1 216 875 9783;
fax: +1 216 687 5405.

E-mail address: s.yau@csuohio.edu

reduce the internal resistance of the conducting polymer. The capacitor sheets show a specific capacitance of 16 F/g. Stacks of capacitor sheets were used to light up three light-emitting diodes [6].

In this article, we report the construction and characterization of flexible supercapacitor sheets, whose active electrode material was a nanocomposite material consisting of the conducting polymer, polyaniline, and nanomaterials with quasi-zero, one and two dimensionalities, including carbon nanotubes, silicon nanoparticles, titanium oxide particles and graphene flakes. The capacitor sheets show a high specific capacitance of 477.1 F/g. Stacks of capacitor sheets have been used for the first time to power a LED lamp consisting of 12 LEDs to demonstrate the potential of the nanocomposite-based capacitor sheet in illumination applications.

Experimental

Silicon nanoparticles were made by electrochemical etching of a silicon wafer in hydrofluoric acid and hydrogen peroxide followed by shaking off the particles from the etched wafer using ultrasound in water or organic solvents as described previously [7]. This etching technique can be used to prepare 1-nanometer particles (Si1) and 2.8-nanometer particles (Si2.8), depending on etching conditions. A water-based Si2.8 suspension (10 μ M) was used in the present work. Single-walled carbon nanotubes (CNT) were purchased from Carbon Solutions. The 50 nm titanium dioxide particles (TiO₂) in the form of powder were purchased from Nanostructured & Amorphous Materials. The 12 nm flakes of graphene (GR) were purchased from Graphene Supermarket. Polyaniline (PANI) dispersed in xylene was purchased from Sigma-Aldrich.

Flexible capacitor sheets were fabricated using a two-step method described previously [6]. Polyvinyl alcohol (PVA) powder (Sigma-Aldrich) was mixed with water with a ratio of 1:9 by weight. The PVA mixture was then mixed with phosphoric acid (H₃PO₄, 85%) with a ratio of 9:1 by volume. Films of PVA were formed by first casting the final mixture on a glass surface and then peeling the cast off from the surface after water had evaporated. Free-standing films with a thickness of about 0.3 mm were used as flexible electrolyte. To prepare the nanocomposite materials, initially 0.4 ml of PANI and 0.003 g of single-walled CNT were mixed in 99% N-dimethylformamide (final volume was 1 ml) to form the base mixture. Then three individual

nanomaterials (0.6 ml of Si2.8, 0.02 g of GR or 0.02 g of TiO₂) were mixed with 1 ml of the base mixture to form composite mixture, i.e. PANI/CNT/Si2.8, PANI/CNT/GP and PANI/CNT/TiO₂. A painting brush was used to transfer the composite material to both sides of a PVA sheet to form and define the shape of a capacitor. Painted sheets were put in an oven at 40 C for the water content in to evaporate. The two-dimensional size of the capacitor was about 5 mm \times 5 mm. Electrical contacts to the nanocomposite materials were made by either using metallic clips or copper sheets. Figure 1(a) shows a supercapacitor sheet.

Cyclic voltammetry of the nanocomposite materials deposited on single electrodes and galvanostatic charging-discharging measurements of capacitor sheets were performed using a commercial potentiostat (CH Instrument 660C). The electrochemical cell used was a conventional three-electrode cell with a commercial Ag/AgCl (3 M KCl) electrode as the reference electrode and a platinum wire as the counter electrode. For voltammetry measurements, the cell potential was scanned at 50 mV/s. Charging-discharging measurements were made at different current densities with cutoff voltages of 0 and up to 2.0 V. Voltammetry measurements were made with electrodes immersed in 0.5 M H₂SO₄ aqueous electrolyte. Deionized water (σ =18.2 M Ω cm, Direct Q3, Millipore) was used to prepare solutions. Phosphate buffer solution (PBS, 100 mM) was prepared for general use. Highly oriented pyrolytic graphite (HOPG) was used as electrodes to support the nanocomposite materials. Scanning electron microscopy was performed using an Amray 1820 instrument.

Results and discussion

Scanning electron microscopy (SEM) has been used to study the structures of the nanocomposite materials. The SEM images of the PANI/GR and PANI/CNT/GR nanocomposite materials are shown in Figure 1(b) and (c), respectively. Figure 1(b) shows that nanoscale flakes of GR are incorporated into a matrix of PANI. A limited amount of pores are present in the material. Figure 1(c) shows that the incorporation of CNT into the material has created pores with sizes ranging from micrometer to nanometer. The SEM resolution was not high enough to resolve the nanoparticles.

The charge-storing properties of the nanocomposite materials were first characterized qualitatively by performing cyclic voltammetry with single HOPG electrodes, on which equal weights of the nanocomposite materials had

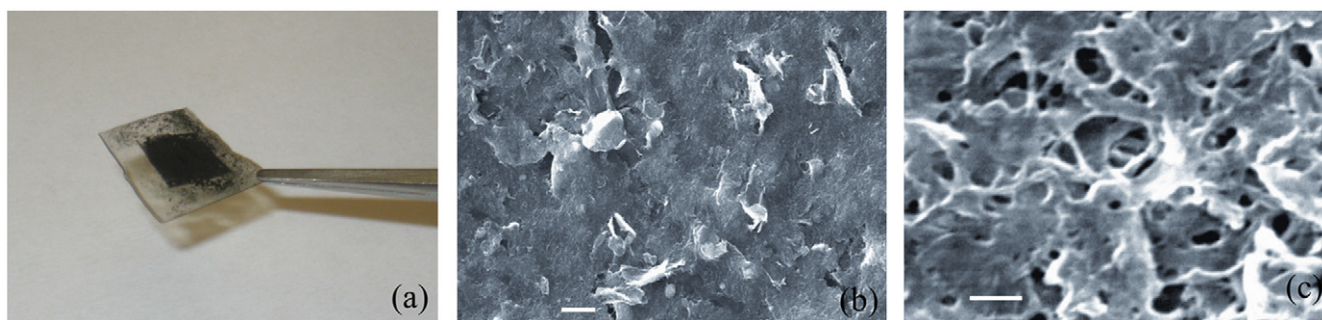


Figure 1 (a) The flexible supercapacitor sheet. (b) SEM image of PANI/GR nanocomposite material. The horizontal bar indicates 10 μ m. (c) SEM image of PANI/CNT/GR nanocomposite material. The horizontal bar indicates 1 μ m.

been deposited individually on only one side of the electrodes. For comparison purposes, cyclic voltammetry was also performed with single HOPG electrodes, which were coated with the same weight of PANI or the PANI/CNT composite as the three nanocomposite materials. Figure 2(a) shows the voltammograms (CVs) of the single PANI electrode and the PANI/CNT electrode. CV1 was obtained with the PANI electrode immersed in 1 M H₂SO₄. CV1 shows three pairs of redox peaks, namely, A₁/C₁, A₂/C₂ and A₃/C₃. A₁/C₁ and A₃/C₃ indicate respectively the transition between leucoemeraldine and emeraldine salt and the transition between emeraldine salt and pernigraniline [8]. A₂/C₂ has been attributed to the presence of ortho-coupled polymers [9]. The appearance of the redox peaks indicates that the purchased PANI was functional as conducting polymer and therefore the redox processes of PANI gave rise to pseudocapacitance of the electrode [10]. CV2 was obtained with the PANI/CNT electrode. The three pairs of redox peaks still appear in CV2 with a positive 100 mV shift in potential. Comparing the two CVs indicates that the total current level of the PANI/CNT electrode is increased due to the presence of CNT, which is used in supercapacitors mainly as an electrical conductivity enhancer while contributing an electrical double-layer capacitance [11] component to the total capacitance of the electrode.

The CVs obtained with single electrodes, on which the three nanocomposite materials have been deposited individually, are shown in Figure 2(b). The three CVs, when compared to

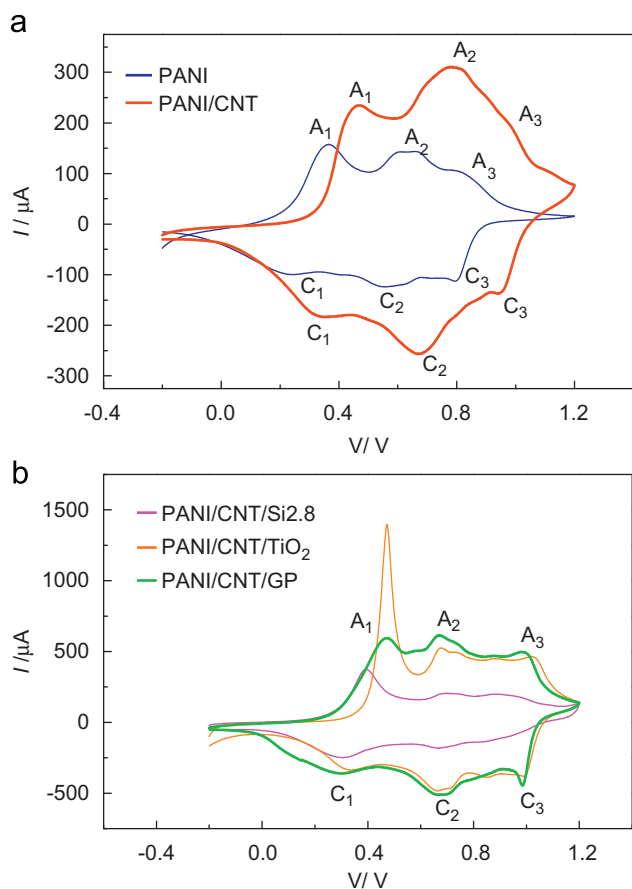


Figure 2 (a) CVs of PANI and PANI/CNT single electrodes. (b) CVs of the three single nanocomposite electrodes.

the CVs in Figure 2(a), show enhanced current levels, which are caused by the presence of the nanomaterials. The enhanced current levels indicate enhanced electrode capacitances. Therefore, Figure 2(b) qualitatively indicates the enhanced electrode capacitances produced by the presence of the nanomaterials in the conducting polymer. The change in the peak heights and the shift in the peak potentials as the result of adding the nanomaterials in PANI suggest a possible faradic process associated with the nanomaterials, which is believed to produce only the double-layer capacitance.

The capacitances of the nanocomposite capacitor sheets constructed as described above have been characterized by performing the charging-discharging process of the sheets. The charging-discharging characteristics are presented as Trace 1 in Figure 3(a), (b) and (c) for the PANI/CNT/Si₂.8, PANI/CNT/GP and PANI/CNT/TiO₂ composites, respectively. For comparison purposes, capacitor sheets constructed without CNT have been also characterized and the results are displayed as Trace 2 in Figure 3(a), (b) and (c). Trace 2 of Figure 3 indicates a large equivalent series resistance (ESR) of the charge-storing material (the vertical drop in voltage), which in principle reduces the power output of the capacitor sheet [12]. Trace 1, however, shows that the inclusion of CNT in the composite materials effectively reduces ESR due to the increased conductivity provided by CNT. This effect is clearly reflected in the insets of Figure 3, where Trace 1 and Trace 2 are brought together so that the discharging processes occur at the same time for comparison purposes.

The performance of the composite materials as the active material for supercapacitors has been characterized quantitatively. The specific capacitances C_s of the capacitor sheets have been evaluated using Trace 1 of Figure 3 according to $C_s = I / (m \times dV/dt)$, where I is the discharging current, m is the mass of the electrode material and dV/dt is the rate of change in the discharging potential obtained from the charging-discharging trace. The estimated values of C_s of the PANI/CNT/Si₂.8, PANI/CNT/GP and PANI/CNT/TiO₂ capacitor sheets are 77.18 F/g, 136.84 F/g and 477.1 F/g, respectively. Note that the high value 477.1 F/g for the PANI/CNT/TiO₂ capacitor sheet reflects the fact that transition metal oxides such as TiO₂ provide high capacitance [2]. All discharge curves for sheets were obtained at 0.4 $\mu\text{A}/\text{mm}^2$.

Another quantitative method for assessing the performance of capacitors is the Ragone plot. The Ragone plot of a capacitor shows the relation between the energy-storage and power capabilities of the capacitor. The Ragone plots of capacitor sheets made with and without CNT are shown in Figure 3(d). The plots show a general trend that the energy-storage and power capabilities of capacitor sheets made with CNT are significantly larger than those made without CNT. In particular, the energy-storage capabilities show a 5-9 times increase as the result of the inclusion of CNT. Previously, the Ragone plot of PANI/CNT composite capacitor sheets [6] shows a maximum specific energy of 0.6 Wh kg⁻¹ and a maximum power capability of 0.2 kW kg⁻¹, which are to be compared to the respective maximum values of 17 Wh kg⁻¹ and 5 kW kg⁻¹ obtained in the present work. The results obtained in the present work indicate the effect of the nanomaterials on improving the energy and power capabilities for supercapacitor applications.

To probe the charging/discharging processes occurring in the nanocomposite materials, ac impedance spectroscopy

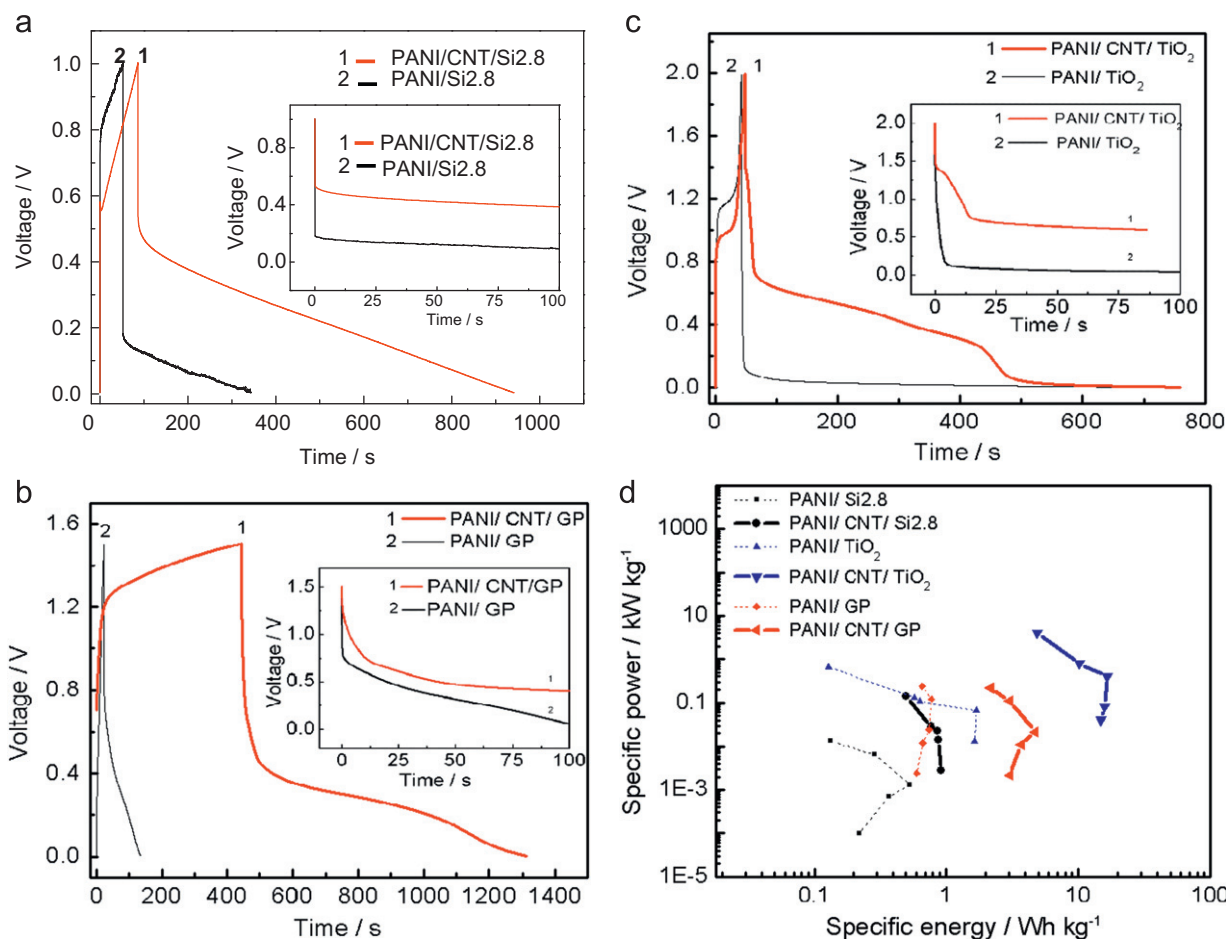


Figure 3 (a)-(c) Charging/discharging characteristics of nanocomposite-based capacitor sheets with and without CNT. (d) Ragone plots of capacitor sheets with and without CNT.

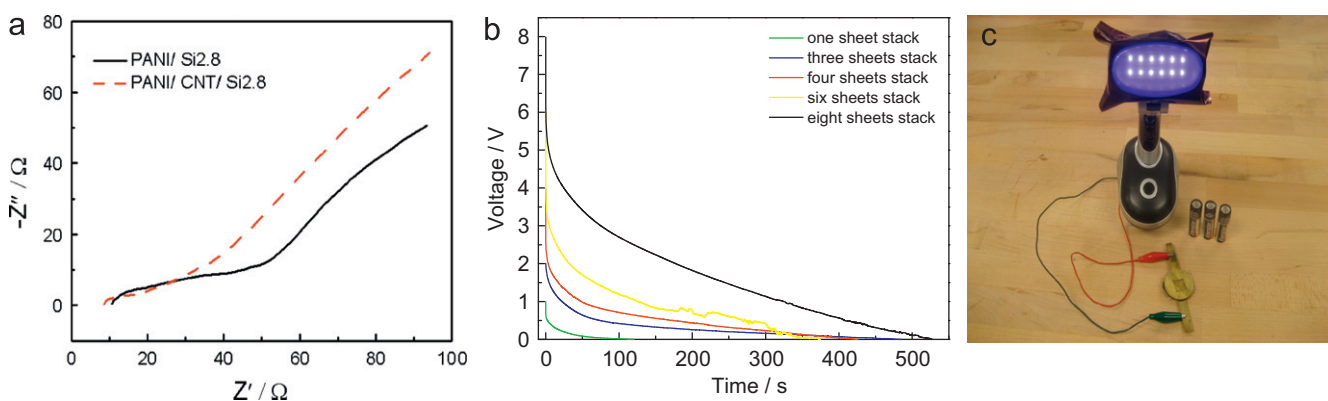


Figure 4 (a) AC impedance spectra of the PANI/Si_{2.8} and PANI/CNT/Si_{2.8} capacitor sheets. (b) Discharging characteristics of a stack of PANI/CNT/Si_{2.8} capacitor sheets. (c) A portable LED lamp powered by a stack of 8 capacitor sheets.

[13] has been performed with the capacitor sheets between 5 mHz and 100 kHz. The impedance spectra of a PANI/Si_{2.8} capacitor sheet and a PANI/CNT/Si_{2.8} capacitor sheet are shown in Figure 4(a). The spectra reveal weak semi-circle structures in the high frequency parts of the spectra, indicating that the polarization resistance of the PANI/Si_{2.8} capacitor sheet is about 40 Ω while that of the PANI/CNT/Si_{2.8} is about 10 Ω. The other two types of capacitor sheets show similar effect. The reduced polarization

resistances as the result of the inclusion of CNT could be due to the increased porosity in the nanocomposite materials created by the presence of CNT.

The potential of the nanocomposite-based supercapacitor sheets in illumination applications has been demonstrated with a portable light-emitting diodes (LEDs) lamp, which requires three AA batteries to provide 4.5 V to drive an assembly of 12 white LEDs for its operation. Since a single capacitor sheet provides only about 0.8 V, stacks of

capacitor sheets were used in order to achieve high operating voltage. Figure 4(b) shows the discharging characteristics of PANI/CNT/Si₂.8 capacitor stacks of up to 8 sheets. The operating voltage appears to increase from 0.8 V to 6 V (where discharging starts) as the number of sheet is increased from 1 to 8. Figure 4(c) shows the operation of the LED lamp.

Conclusions

Nanomaterials such as carbon nanotubes, silicon and titanium oxide particles and grapheme flakes have been incorporated into the conducting polymer polyaniline to form nanocomposite materials. Electrochemical characterizations of the nanocomposite materials that were deposited on single electrodes indicated significantly improved electrode capacitance for supercapacitor applications. The nanocomposite materials have been used to construct flexible supercapacitor sheets, which showed enhanced charge-storage and power capabilities as the result of the presence of the nanomaterials. The inclusion of carbon nanotubes in the nanocomposite materials was observed to reduce the equivalent series resistance of the materials due to its high conductivity. Stacks of capacitor sheets were used to power an LED lamp. The experimental results of the present work indicate the potential of the nanocomposite materials and the capacitor sheet in portable illumination applications.

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