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Functionalized Single Wall Carbon Nanotubes Treated with Pyrrole for Electrochemical Supercapacitor Membranes

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Supercapacitor electrodes based on pyrrole treated-functionalized single wall carbon nanotubes (SWNTs) were developed. High values of capacitance (350 F/g), power density (4.8 kW/kg), and energy density (3.3 kJ/kg) were obtained in 6 M KOH, and the capacitance is almost 7 times that of the control buckypaper. Specific capacitance of these materials has a strong dependence on the macropore surface area. The double layer capacity of pyrrole treated-functionalized SWNT electrodes is 154 μF/cm^2 based on the BET model, and even higher based on the DFT model.

Introduction

Carbon nanotubes (CNTs) are being widely studied for electrochemical supercapacitor electrodes due to their unique properties and structure, which include high surface area,[1] high conductivity,[2,3] and chemical stability. Capacitance values from 20 to 180 F/g have been reported and depend on CNT purity and electrolyte,[4−9] as well as on specimen treatment such as CO_2 physical activation,[10] KOH chemical activation,[11,12] or exposure to nitric acid,[13−17] fluorine,[18] or ammonia plasma.[19] On the other hand, conducting polymers, such as polyacetylene, polypyrrole, polyaniline, polythiophene, and their derivatives, are also common electrode materials for supercapacitors.[20−22] The modification of CNTs with conducting polymers is one way to increase the capacitance of the composite resulting from redox contribution of the conducting polymers.[23] In the CNT/conducting polymer composite, CNTs are electron acceptors, while the conducting polymer serves as an electron donor. A charge-transfer complex is formed between CNTs in their ground state and aniline monomer.[24] A number of CNT/conducting polymer composite studies in electrochemical capacitor application have been reported.[25−33]

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The CNT/conducting polymer composite prepared by polymerization of pyrrole on the nanotubes with ammonium persulfate as an oxidant exhibited a capacitance value up to 180 F/g,[25] while a single wall carbon nanotube (SWNT)/polypyrrole composite exhibited a capacitance value up to 260 F/g.[26] In two separate studies, it was shown that the capacitance of an unoriented multiwall carbon nanotube (MWNT)/polypyrrole composite was at least 2 times higher than that of either component.[27,28] Supercapacitor behavior of aligned arrays of NTs coated with polypyrrole has also been reported.[29] Negatively charged MWNTs/polypyrrole layers were further investigated by co-deposition via electrochemical oxidation of pyrrole. Electrochemical quartz crystal microbalance (EQCM) confirmed the redox pseudocapacitance response of the polypyrrole with a mechanism involving rigid intercalation/deintercalation of counterions into the polymer layer.[30] The capacitance of the layer composite was reported to be more than 200 F/g in potassium chloride and tetrabutylammonium bromide solutions.[30] CNT matrices can provide a mesoporous scaffold, on which a porous layer of polypyrrole can be electrodeposited; hence a high charge dynamics during supercapacitor performance can be achieved.[31] A MWNT/poly(3-methylthylthiophene) composite-based supercapacitor was evaluated in 1 M $LiClO_4$ acetonitrile solution, and its specific capacitance was about 80 F/g.[32] A MWNT/poly(3,4-ethylenedioxythiophene) composite, prepared by chemical or electrochemical polymerization, when evaluated in 1 M H_2SO_4, 6 M KOH, or 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in acetonitrile, exhibited good cycling performance, and moderate capacitance values in the range from 60 to 160 F/g.[22] The capacitance of SWNT/polyaniline (PANI) composite fabricated by in-situ electrochemical polymerization was 310 F/g, higher than that of pure PANI, because the complex structure in this composite offered more active sites for Faradaic reactions.[33] In this paper, we describe methodology for the fabrication of nanoscale-enhanced electrochemical capacitor electrodes that can achieve very high capacitance. The electrodes were based on a composite of water-soluble arylsulfonic acid-functionalized SWNTs that had been treated with pyrrole. This is the first correlation of capacitance with the pore size and surface area for carbon nanotube/pyrrole treated composite electrodes.

Experimental Section

In a typical SWNT functionalization procedure,[34] 175 mg of purified SWNT (HiPco produced SWNTs were purified by heating in a water-rich atmosphere at 220 °C followed by HCl extraction to give purified SWNTs (p-SWNTs)) dispersed in 200 mL of 20% oleum via magnetic stirring (3 h) was treated with sulfanilic acid (10.08 g, 0.0582 mol), sodium nitrite (4.02 g, 0.0583 mol), and 2,2′-azobisisobutyronitrile (0.96 g, 0.0058 mol) at 80 °C for 1 h to give a mixture that was carefully poured into water. The resulting suspension was filtered through a polycarbonate membrane (0.22 μm), and the filter cake was washed with water, acetone, and filtered, then resuspended in DMF, filtered, and dried[34] to give a product in which 1 in 54 carbons of the SWNT were functionalized by an arylsulfonic acid group according to thermogravimetric analysis (TGA). Although sulfonated aromatic pyrolysates can be carbonaceous, thereby complicating the TGA data, Raman D- to G-band intensities were similar to those of known material of that degree of functionalization. In a typical pyrrole treatment, 28 mg of the functionalized SWNT was mixed in 300 mL of deionized water with Fe(II)Cl_2 (50 mg, 0.39 mmol) and pyrrole (4.84 g, 72.1 mmol). After mixing overnight on an orbital shaker, the suspension was filtered using a PTFE filter and the solid was washed with water. Various samples and sample designations are given in Table 1, and the general structure is given in Figure 1.

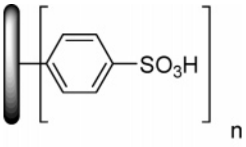

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Figure 1. The general structure of the arylsulfonic acid-functionalized SWNTs in samples **1**−**4**.

Table 1. Sample Treatments and Designations

sample name	chemical treatment
buckypaper	untreated HiPco SWNTs
1	p-SWNT[a] heavily functionalized with arylsulfonic acid moieties (mainly individual tubes) and then treated with pyrrole
2	raw SWNT functionalized with arylsulfonic acid moieties and then treated with pyrrole
3	p-SWNT[a] functionalized with arylsulfonic acid moieties and then treated with pyrrole; approximately 1 in 33 carbons functionalized by TGA
4	p-SWNT[a] functionalized with arylsulfonic acid moieties and then treated with pyrrole; approximately 1 in 54 carbons functionalized by TGA

[a] p-SWNT= oxidatively purified material.

The scanning electron microscopy (SEM) was performed on LEO 1530 at 10 kV on gold-coated samples. X-ray photoelectron spectra (XPS) were collected on a SSX-100 ESCAE spectrometer using Al Kα radiation ($h\nu = 1486.6$ eV) operating at 10 kV as an excitation source. The pass energy was 150 eV. The vacuum in the analysis chamber was about 5×10^{-9} Torr. The spectra analysis was accomplished using ESCA 2000.

The isothermal N_2 gas adsorption and desorption at 77 K were carried out on ASAP 2020 (Micromeritics Inc.), on samples degassed at 90 °C for 16 h at 1×10^{-4} Pa. The specific surface area, pore size, and pore size distribution were determined using Brunauer, Emmet, Teller (BET) and density functional theory (DFT) methods.[35] The double layer capacitance of the samples was evaluated via a two-electrode cell. Two film electrodes (diameter = 0.8 cm) separated by a thin microporous membrane (Celgard 3400) were sandwiched between nickel current collectors, and 6 M KOH aqueous solution was used as the electrolyte. Constant current charging and discharging (CC) and cyclic voltammetry measurements (CV) were carried out on Solartron 1470 Cell Test at room temperature for capacitance evaluation. In CC measurements, the cell was charged and discharged in 0−0.8 V range at a current of 0.5, 1, 5, and 10 mA. In CV measurements, scanning rates were 10, 20, and 50 mV/s. The capacitance, power density, and energy density were calculated as described previously.[36]

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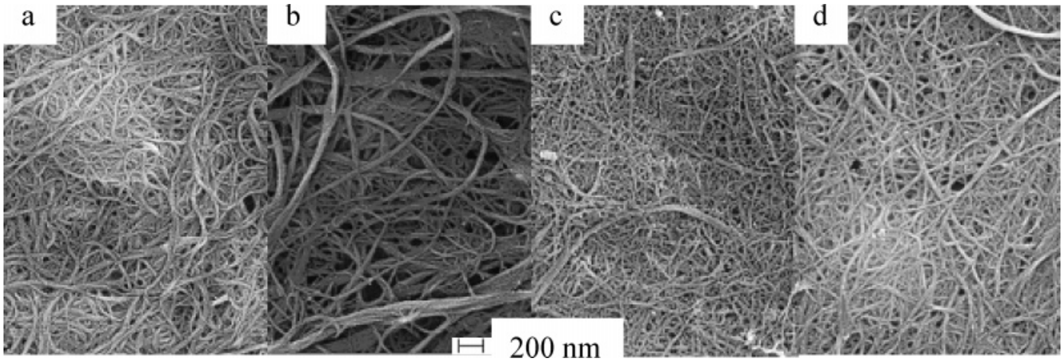

Figure 2. SEM images of SWNT and pyrrole treated-functionalized SWNT electrode surface. (a) Buckypaper; (b) **2**; (c) **3**; (d) **4**.

Table 2. Capacitance, Surface Area, and Pore Volume of Buckypaper and Pyrrole Treated SWNT Electrodes

		buckypaper	**1**	**2**	**3**	**4**
capacitance (F/g)[a]	0.1 V	55	176	151	114	305
	0.7 V	41	28	41	36	45
	mean value	49	102	93	80	183
BET surface area (m^2/g)		546	148	205	113	198
total pore volume (cm^3/g)		0.76	0.47	0.47	0.34	0.51
DFT surface area (m^2/g)	total	297	95	122	66	125
	micro[b]	167	12	40	32	24
	meso	128	27	46	27	25
	macro	2	56	36	7	76
DFT pore volume (cm^3/g)	total	0.69	0.28	0.32	0.30	0.25
	micro	0.11	0.01	0.03	0.02	0.02
	meso	0.52	0.21	0.25	0.22	0.18
	macro	0.06	0.06	0.05	0.06	0.05
C_{dl} (μF/cm^2) (0.1 V capacitance)	BET	10	119	74	101	154
	DFT-total	19	186	124	173	243
	DFT-meso&macro	43	214	183	330	302

[a] 1 mA discharge current. [b] Micro-, meso-, and macropore refer to the pore sizes of <2, 2−50, and >50 nm, respectively.

Results and Discussion

From SEM studies, the diameter of SWNT bundles in the buckypaper was measured to be 48 ± 16 nm, and these bundles appeared to be densely packed and form a SWNT rope network (Figure 2a). By comparison, SWNT bundle diameters in the pyrrole treated samples were measured to be 61 ± 18 (**2**), 43 ± 11 (**3**), and 51 ± 13 (**4**) nm. In comparison to buckypaper and pyrrole treated sample **2**, the SWNTs in **3** (Figure 2c) appear to be shorter and packed more densely. On the surface of these films, there are many pores among the abundant SWNT or SWNT/pyrrole treated rope networks. The difference in packing was apparently caused by the degree of arylsulfonic acid functionalization. Based on the TGA study, we conclude that 1 out of every 54 carbons were functionalized in **4**, while 1 out of every 33 carbons were functionalized in **3**.

Buckypaper as well as SWNT/pyrrole treated electrodes exhibit type IV nitrogen adsorption isotherm (Figure 3), which is indicative of samples having relatively large pores. Data in Table 2 show that the pyrrole treated samples have a lower surface area than the buckypaper. The ideal specific surface area can be as high as 1315 m^2/g for individual SWNT with 1 nm diameter and about 500 m^2/g for bundles.[1] KOH chemical activation can increase the surface area of CNTs,[12,37] while functionalization can diminish the surface area by destroying small-diameter CNTs.[38,39] Based on IUPAC classification, the pore size is divided into three groups: micropores (pore width $<$ 2 nm), mesopores (between 2 and 50 nm), and macropores ($>$50 nm). As compared to micropores, macropores have negligible contribution to the total surface area.[40,41] Based on the DFT

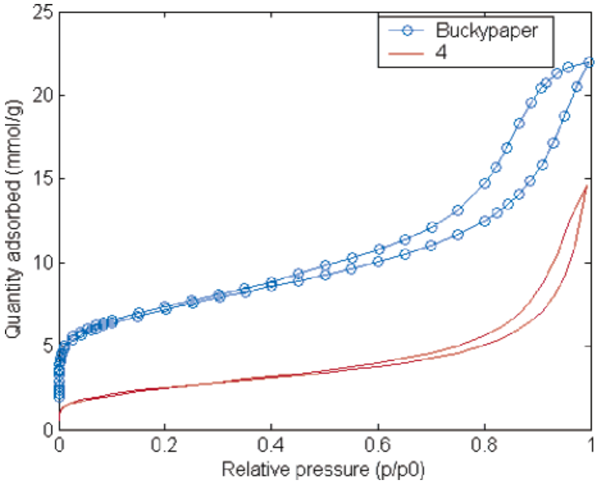

Figure 3. Adsorbed N_2 quantity versus relative pressure of isothermal N_2 adsorption (77 K) of SWNT and pyrrole treated-functionalized SWNT films.

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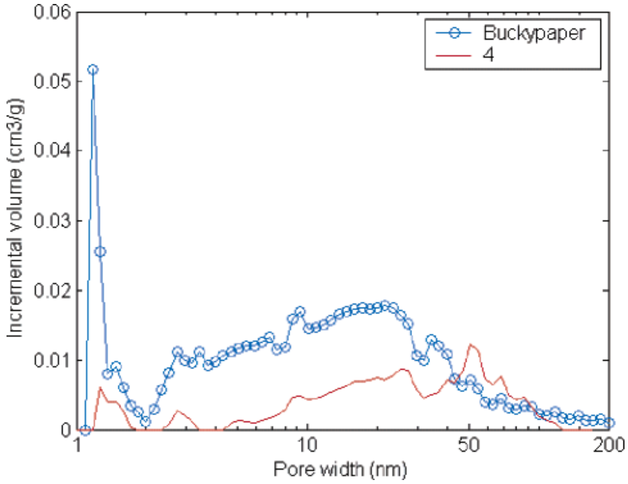

Figure 4. Pore size distribution determined by DFT model for SWNT and pyrrole treated-functionalized SWNT electrodes.

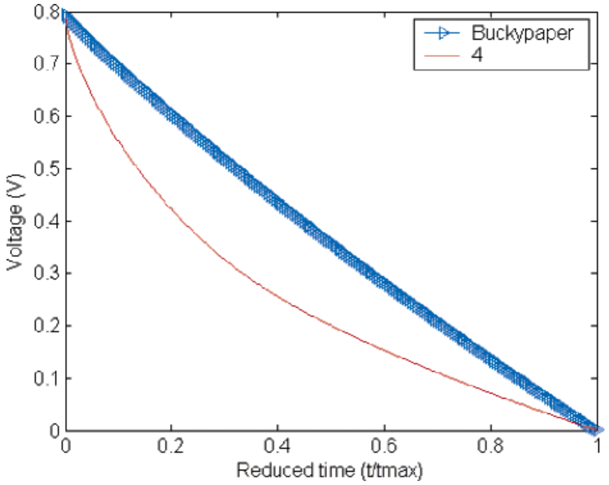

Figure 5. Constant current discharge behavior of buckypaper and pyrrole treated arylsulfonic acid-functionalized SWNTs. The current is 1 mA.

Table 3. Atomic Concentration on SWNT and Pyrrole Treated SWNT Electrode Surface Obtained from XPS

	C (%)	O (%)	N (%)	S (%)	Cl (%)
buckypaper	96	4			
3	70.9	18.9	8.1	1.8	0.3
4	74.5	12.3	10.3	2.4	0.5

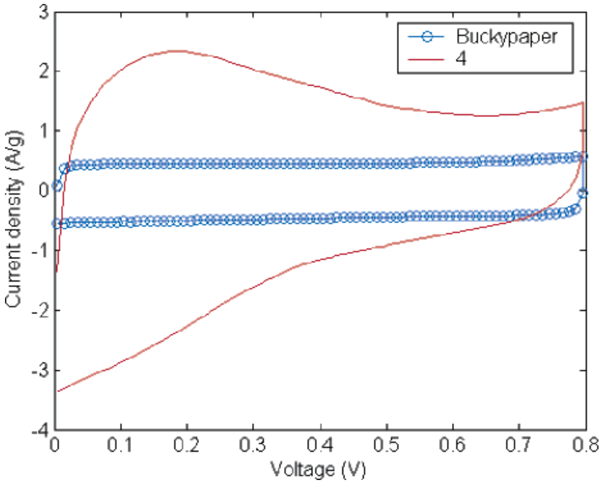

Figure 6. CV plots of SWNT and pyrrole treated arylsulfonic acid-functionalized SWNTs. The scan rate is 10 mV/s.

model, it is shown that buckypaper is predominantly composed of micropores, while pyrrole treated samples are mainly composed of meso- and macropores (Figure 4). The surface area contribution for the pyrrole treated samples from macropores is as high as 61% of total DFT surface area (Table 2). Atomic concentrations of the buckypaper and pyrrole treated SWNTs electrode surfaces as determined from XPS are given in Table 3, which shows that **4** contains more pyrrole than **3**. Because the ratio of N to S in **3** and **4** is 4.5 to 4.2:1 (respectively) by XPS, the majority of pyrrole is polymerized or otherwise associated with the functionalized SWNTs; if only sulfonic acid/pyrrole salt were present, the ratio of N to S would be about 0.4:1.0.

Constant current discharge behavior of buckypaper is almost linear with time, while for the pyrrole treated-functionalized SWNTs electrodes the discharge behavior is nonlinear (Figure 5). Figure 6 compares a typical CV for buckypaper and SWNT/pyrrole film electrodes. The buckypaper voltammetric curve is closer to an ideal parallelogram shape, exhibiting no pseudocapacitance or very little contribution from redox reaction. However, in the case of pyrrole treated-functionalized SWNTs film electrodes, a peak at 0.1−0.2 V was observed that may correspond to the oxidation and reduction of polypyrrole that might have been formed during the pyrrole treatment. The CV peak current of pyrrole treated films was double (**2** and **3**, not shown) and 4 times (**4**) the value obtained for the buckypaper. The capacitance of the buckypaper was about 55 F/g, which was comparable to the value reported in the literature.[36] The specific capacitance of polypyrrole is reported to be about 160 F/g.[42] In this study, pyrrole treated sample **4** exhibited a specific capacitance of 350 F/g, which is 7 times the value obtained for the buckypaper.

The discharging current density (A/g) is calculated by using $I\ (m_A + m_B)/(m_A m_B)$ in the CC measurement (m_A and m_B are electrode masses, respectively), and using s^*C_{sp} in the CV measurement (s is the scanning rate in cyclic voltammetry, and C_{sp} is the specific capacitance). Figure 7 shows the specific capacitance of buckypaper and pyrrole treated-functionalized SWNTs as a function of discharge current density. Except for buckypaper, the specific capacitances of the samples decreased rapidly at the relatively low discharge current density, and then tended to level off at higher current density. Sample **1** dropped faster than others from 205 F/g at 0.4 A/g to 50 F/g at 2.5 A/g. The decrease in specific capacitance of pyrrole treated-functionalized SWNT samples may be caused by some pores not being accessible efficiently at higher current density, and perhaps larger internal resistance of the pyrrole moieties in comparison to SWNT.

Frackowiak et al.[12] reported that micropores make the main contribution to the specific capacitance because micropores wetted by the electrolytic solution contribute extensively to the adsorption of ions on the electrochemically active surface of the electrodes. Micropores result in the higher surface area. However, higher surface area does not always result in higher specific capacitance (Figure 8a), as the specific capacitance

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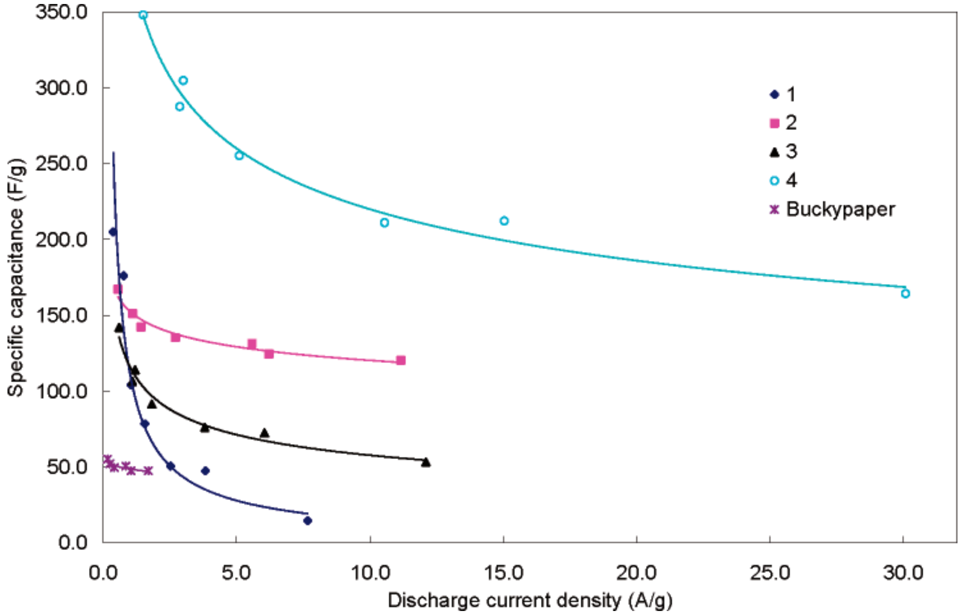

Figure 7. Specific capacitance of buckypaper and pyrrole treated SWNT electrodes as a function of discharge current density.

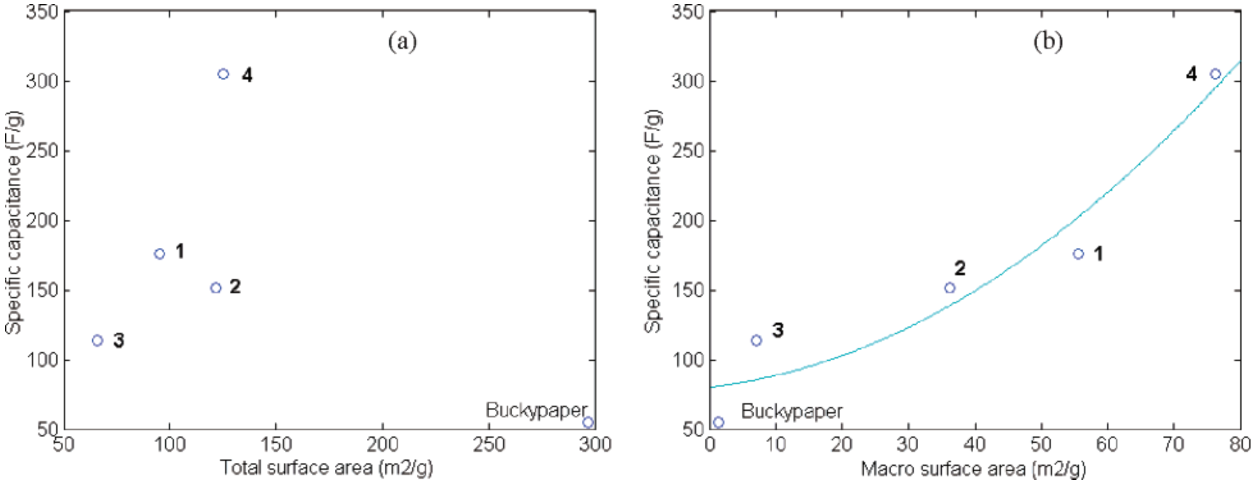

Figure 8. Specific capacitance (at 1 mA current) versus total surface area (a) and macro surface area (b) for SWNT buckypaper and pyrrole treated SWNT electrodes.

depends on the pore size and pore size distribution. The capacitance did show proportionality to the macropore surface area (Figure 8b). All pyrrole treated samples show significant macropore surface area, while macropore surface area in the buckypaper is negligible. It is exciting to note that, at 0.1 V, the capacitances increased from 114 to 305 F/g with the macrosurface area increasing from 7 to 76 m^2/g for the pyrrole treated samples. Extrapolation of Figure 8b suggests that a much higher capacitance value, above 800 F/g, can be expected if the macrosurface area can be doubled to about 150 m^2/g.

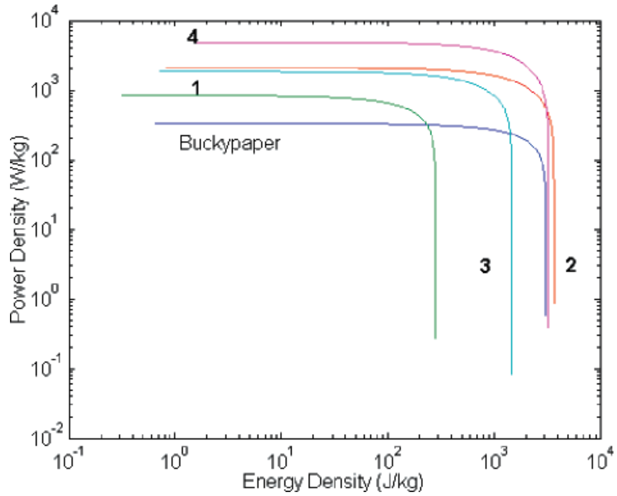

Figure 9. Ragone plots for various samples at 10 mA discharging current.

The double layer storage capacities of the SWNT and pyrrole treated SWNTs electrodes were calculated and are listed in Table 2. The double layer capacity of the buckypaper is 10 μF/cm^2, which is comparable to the value reported for activated carbon materials.[43] The double layer capacity of the pyrrole treated samples is up to 154 μF/cm^2 based on the BET model, while higher values were obtained based on the DFT model. The Ragone plot (Figure 9) shows that the pyrrole treated samples have higher power (up to 4.8

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kW/kg) and energy (3.3 kJ/kg) densities than the buckypaper. At 10 mA discharging current, the power density of **4** is almost 25 times that of the control buckypaper electrode.

Conclusions

The SWNTs were functionalized with arylsulfonic acid and treated with pyrrole. The capacitance, power density, and energy density were evaluated using galvanostatic constant current charge/discharge and cyclic voltammetry. The capacitance is up to 350 F/g, which is almost 7 times that of the untreated buckypaper. The surface area, pore size, and pore size distribution were determined by N_2 isothermal adsorption and desorption. Correlating the capacitance with surface area, pore size, and pore size distribution, we found that the macropores make a significant contribution to the capacitance performance of these materials. The double layer storage capacity can be as high as 154 μF/cm^2 based on the BET model, and even higher based on the DFT model.

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