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Freestanding, bendable thin film for supercapacitors using DNA-dispersed double walled carbon nanotubes

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Freestanding, thin, and bendable electrodes for supercapacitors are fabricated by filtering DNA-dispersed double walled carbon nanotubes (DWNTs) into a thin film and thermally treating the film in argon. We found that DNA has the ability to disperse the strongly bundled DWNTs and is converted to phosphorus-enriched carbons, which give rise to strong redox peaks at around 0.4 V. The combination of the large capacitance from the DNA-derived carbons and the high electrical conductivity of carbon nanotubes allow DWNT/DNA films to be used as a potential electrode material for supercapacitors. © *2009 American Institute of Physics*. [doi:10.1063/1.3271768]

Biomolecule-engineered nanosized active materials targeted for energy storage devices have attracted lots of attention because of their high charge rate capability and large storage capacity.[1,2] Supercapacitors have several advantages over lithium ion batteries, such as higher power density and higher efficiency, due to simple ion adsorption on their electrodes.[3] It is well known that the electrochemical performance of the supercapacitor strongly depends on the morphology, texture, and composition of the electrode material.[3] Among the many types of active materials, carbon nanotubes have been studied as a potential candidate for achieving a high performance supercapacitor due to both their intrinsically high electrical conductivity and their nanosized diameter.[4–6]

However, presently available carbon nanotube samples are in a bundled structure and contain metallic impurities that limit the capacitance of carbon nanotube-based supercapacitors. To solve these problems, we used high purity (99%) double walled carbon nanotubes (DWNTs) prepared by a catalytic chemical vapor deposition and subsequent oxidation process.[7] Their high purity relative to residual catalyst particles has been confirmed by diamagnetic susceptibility experiments.[8] In addition, we have chosen single stranded DNA (ssDNA) for dispersing the strongly bundled DWNTs, and we have confirmed the dispersion state of the tubes in an aqueous ssDNA solution using optical spectroscopy. Then, the filtered DWNT/DNA films were thermally treated at 600 °C in argon in order to convert the insulating ssDNA into porous carbon materials. We have found that the freestanding DWNT-derived thin electrodes thus prepared exhibited two times more capacitance than a pure DWNT film, due to the evolution of the pseudocapacitance from the phosphorous-containing functional groups. We also found that these films were mechanically strong enough to show flexibility. This is due to their intrinsic morphology, such as the small diameter and the long length of the nanotubes, which also made them easy to fabricate.

We used high purity and crystalline [shown by the absence of the Raman D band in Fig. 1(c)] DWNTs in which nanotubes with an outer diameter of approximately 1.6 nm were packed in hexagonal arrays [Fig. 1(a)] within larger-sized bundles [Fig. 1(b)]. By dispersing the DWNTs (approximately 20 mg) in an aqueous solution (10 ml) with the help of DNA (5 and 10 mg) under strong sonication (KUBOTA UP50H, approximately 470 $\mathrm{W/cm^2}$) for 1 h at 4 °C, we prepared a homogeneously dispersed opaque DWNT suspension [see inset in Fig. 1(c)]. In order to evaluate the dispersion state of the tubes in an aqueous DNA

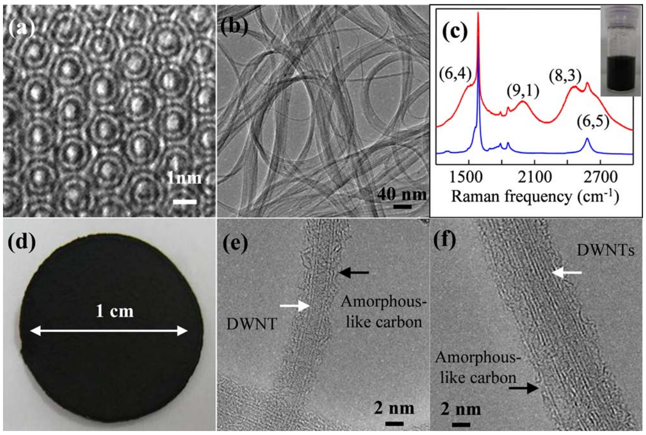

FIG. 1. (Color online) TEM images exhibiting (a) hexagonally packed and (b) strongly bundled DWNTs, (c) Raman/luminescent spectra of the pristine DWNT and DNA-dispersed DWNT suspensions using the 785 nm excitation laser line. The appearance of luminescence peaks (coming from the semiconducting inner tubes) indicates the generation of isolated DWNTs in an aqueous DNA solution (see inset). (d) Photograph of a freestanding, thin and bendable DWNT/DNA film prepared by filtering and subsequent thermal treatment in argon. TEM images exhibiting the formation of DNA-derived carbons on isolated (e) and thin-bundled (f) DWNTs.

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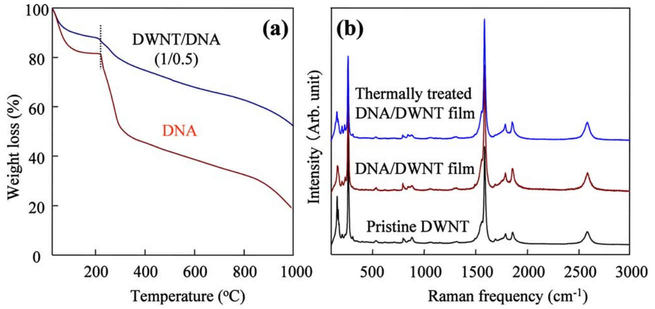

FIG. 2. (Color online) (a) TGA profile of a DNA and a DWNT/DNA sample with a heating rate of 5 °C/min in argon and (b) Raman spectra taken with laser excitation of 785 nm for pristine DWNT, DNA/DWNT and thermally treated DNA/DWNT film samples, respectively.

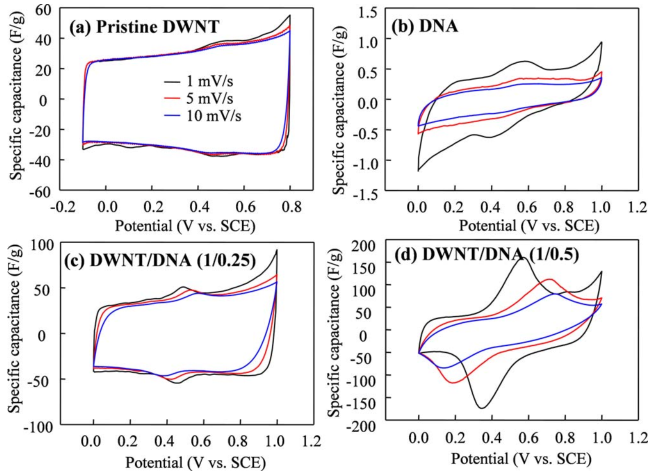

FIG. 3. (Color online) Cyclic voltammograms of (a) a pristine DWNT film, (b) a DNA-derived carbon film, and (c, d) DNA/DWNT films at different scan rates for the applied potential. Strong redox peaks are clearly seen at 0.4 V for DNA-containing samples.

solution, a Raman/fluorescence spectrum (laser excitation of 785 nm) was obtained for the centrifuged (20,000 g) DWNT suspension. Several strong luminescence peaks (coming from the semiconducting inner tubes) are clearly seen [Fig. 1(c)], indicating that individually dispersed DWNTs are partially generated through the interaction of the DWNTs with DNA, because we are not able to see luminescent signals from the bundled DWNT samples due to the presence of entrapped metallic tubes which quench the luminescence.[9] Then, by filtering the DWNT suspension, drying it for 24 h in vacuum, and then thermally treating the suspension at 600 °C in argon for structural conversion from an insulating DNA to a carbon material in argon, we obtained flexible, thin (10–30 μm) and self-supporting DWNT/DNA films [Fig. 1(d)] that could be used for supercapacitors. The porosity of the film could be controlled by changing either the amount of DNA added or the thermal treatment temperature, or changing both.

The DNA in DWNTs starts to show an abrupt weight loss in the temperature range of 200–300 °C and its carbonization yield at 600 °C is found to be approximately 40% [Fig. 2(a)]. In order to study the effect of the DNA on the vibrational properties of DWNTs, Raman spectra from a pristine DWNT film, and from filtered and thermally treated DWNT/DNA films were taken with 785 nm laser excitation. No noticeable change is seen in the Raman G band and the G′ band frequencies associated with the DNA wrapping. However, the decreased intensities of the radial breathing modes below 500 cm^{-1} with respect to the intensity of the G band [Fig. 2(b)] suggest that the wrapped DNA as well as the coated DNA-derived carbons on the individualized and thin bundled DWNTs partially suppresses the coherent vibration of carbon atoms normal to the nanotube axis. TEM observations on thermally treated DWNT/DNA films support our assumption that amorphous-like carbons are deposited on the isolated and thin bundled DWNTs [Figs. 1(e) and 1(f)].

Then, we carried out cyclic voltammetry (CV) measurements in an argon-purged 30% H_2SO_4 solution for the thermally treated DWNT/DNA films as compared with those of pure DWNTs and DNA-derived carbon, where a platinum wire electrode and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. The measured currents from the cyclic voltammograms (CVs) were converted into single electrode capacitance values with regard to the electrode mass (Table I). The pure DWNT film exhibited a CV with a rectangular shape, indicating that the charge storage process is a non-Faradic double layer reaction [Fig. 3(a)]. However, in the CVs of thermally treated DWNT/DNA films [Figs. 3(c) and 3(d)], redox peaks at 0.4 V are observed and become more intense by increasing the added amount of DNA. Thus, the enhancement of the capacitance by a factor of two caused by adding DNA (ca. 66.9 F/g) can be explained by the evolution of a pseudocapacitance. This is because we have clearly observed

TABLE I. Composition, pore structure, and capacitance of a pristine DWNT film and thermally treated DWNT/DNA films.

	Composition (at. %) [a]					Pore structure[b]			
Sample	Na	P	N	O	C	SSA (m^2/g) [c]	V_{micro} (cm^3/g) [d]	APD (nm)[e]	Capacitance (F/g)[f]
Pristine DWNT	⋯	⋯	⋯	2.07	97.93	574	0.256	12.16	28.4
Pure DNA	0.15	7.75	13.95	29.42	48.73	⋯	⋯	⋯	0.39
DWNT/DNA (1/0.25)	0.40	0.79	0.34	1.51	96.96	424	0.208	11.75	43.67
DWNT/DNA (1/0.5)	0.70	1.59	0.78	4.03	92.90	321	0.153	9.55	66.89

[a] Chemical compositions of each sample were obtained from x-ray photoemission spectroscopy.
[b] Pore parameters were obtained by N_2 adsorption.
[c] SSA indicates specific surface area.
[d] V_{micro} indicates micropore volume.
[e] APD indicates average pore diameter.
[f] Capacitance values were obtained at the rate of 1 mV/s.

a redox peak from DNA-derived carbon [Fig. 3(b)] and the volume and diameter of the micropores for storing charges is decreased by the presence of DNA-derived carbons (Table I). To determine the origin of the pseudocapacitance (faradic reaction), we carried out an x-ray photoelectron spectroscopy (MultiLab2000 spectrometer) (Table I) study on the DNA and DWNT/DNA films thermally treated at 600 °C in argon. Here we found that the phosphorus functional groups with a PO_x $(2 \leq x \leq 4)$ unit are a possible candidate for the redox peak, because DNA consists primarily of carbon and hydrogen, along with nitrogen, oxygen, and phosphorus. We are able to discard the effect of oxygen functional groups (such as quinone) on the pseudocapacitance[10,11] because they have been found not to produce large redox peaks at around 0.4 V which are seen in conventional carbons, including pristine DWNTs.

In summary, we have fabricated a freestanding, thin and bendable electrode for supercapacitors by filtering DNA-dispersed DWNTs in the form of a film and then thermally treating these films in argon.

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