DNA-DISPERSED SINGLE- AND DOUBLE-WALLED NANOTUBES-DERIVED FREESTANDING ELECTRODE FOR SUPERCAPACITORS

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In the past few decades, energy storage devices such as lithium ion secondary batteries (LIBs) and supercapacitors have attracted much attention because of their potential uses in environmentally friendly hybrid electric vehicles. The supercapacitor has several merits over LIBs, such as higher energy density, higher rate capability, and higher efficiency, due to its simple ion adsorption on electrodes. Therefore, the electrochemical performance of the supercapacitor strongly depends on the morphology and texture of electrode material. Among many types of materials, single- and double-walled carbon nanotubes (SWNTs and DWNTs) were selected as the possible candidate to fabricate freestanding, flexible and thin electrodes (without using a binder) for supercapacitors. However, carbon nanotubes are present in the form of bundles, so a method of dispersing carbon nanotubes must be developed in order to increase the accessible surface area of carbon nanotube-based electrode for supercapacitors. This study used single stranded DNA (ssDNA) as a dispersing agent and studied the dispersion state of SWNTs and DWNTs in an aqueous ssDNA solution with the help of optical spectroscopy. The filtered DNA/nanotube films were then thermally treated at 600^{o}C in argon in order to convert insulating ssDNA to porous carbon materials. Finally, we have carried out the structural characterization of the flexible and freestanding SWNTs and DWNTs-derived thin electrodes and then measured their electrochemical for supercapacitors.

DNA-Dispersed Double and Single Walled Carbon Nanotubes – Derived Freestanding Electrode for Supercapacitor

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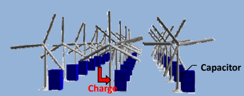
Background

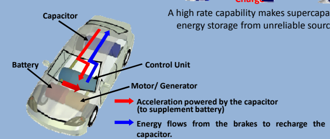
ENERGY STORAGE

Energy storage is one of the biggest hindrances to the current advances in alternative energy production technologies. Currently, the two main forms of energy storage are batteries and supercapacitors.

- Supercapacitors have a much higher rate capability
- Supercapacitors have a better power density



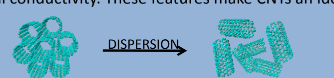
A high rate capability makes supercapacitors ideal for energy storage from unreliable sources like wind.



A car like this might be plausible in the future if supercapacitors and batteries improve enough.

CARBON NANOTUBES

Carbon nanotubes (CNT) are a unique allotrope of carbon, formed by rolling up single sheets of graphene into individual tubes. Their shape and nanostructure gives them an unusually high specific surface area (SSA), as well as a high electrical conductivity. These features make CNTs an ideal material for a supercapacitor electrode.



Bundled nanotubes limit the available surface area for the electrons.

Dispersed nanotubes have more surface area for ions to occupy.

Van der Waals forces cause bundling of nanotubes.

- Bundling decreases SSA

The purpose of this experiment was to find the best method of dispersing the nanotubes, and make a electrode for supercapacitor using the resulting material.

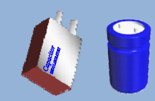
What is a Supercapacitor?

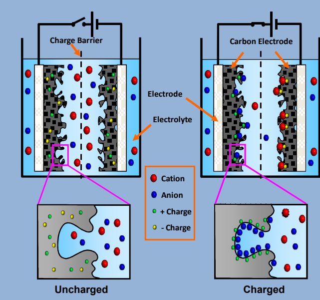
A supercapacitor is a specific type of capacitor, which is characterized by having a very high capacitance.

- Additional capacitance from high SSA carbon electrode.

Supercapacitors are unique because of:

- High rate capability.
- Long lifetime.



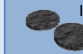


Experimental Procedure

In this experiment, single stranded DNA was used as dispersing agent for single and double walled carbon nanotubes (SWNTs and DWNTs) in an aqueous solution.

I. Fabrication of SWNTs and DWNTs-based electrode

- Sonicating DNA-CNT aqueous solution
- Filtering and drying to obtain a thin film
- Thermally treating a thin film at 600°C in argon



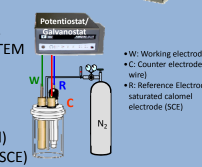
Thin films must be made flat for future testing.

II. Structural Characterizations

- SSA and electrical conductivity.
- Resonance Raman, SEM, and TEM
- ESCA

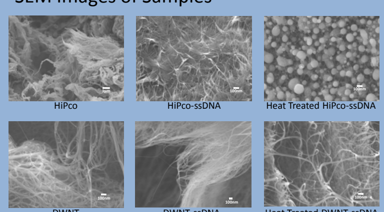
III. Capacitance test

- Electrolyte : 30 % H_2SO_4 (= 5.63 mol/L, N_2 gas saturated)
- Potential window : 0 ~ 1 V (vs. SCE)
- Electrochemical activity : 50mV/s – 20cycles
- Scan rate : 100 → 50 → 20 → 10 → 5 → 1 mV/s

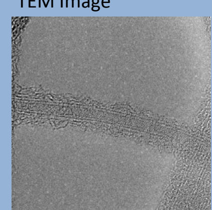


Results

SEM Images of Samples



TEM Image



TEM Image showing a DWNT covered with DNA-derived amorphous carbon

Results from ESCA

Atomic Percentages in Samples

Element	Single Walled 1-0.25	Single Walled 1-0.5	Double Walled 1-0.25	Double Walled 1-0.5
C 1s	89.14	76.84	96.96	92.9
O 1s	6.292	10.39	1.506	4.033
N 1s	1.085	1.445	0.3443	0.7849
P 2s	1.015	3.181	0.3527	0.7236
P 2p-	1.145	3.703	0.435	0.8639
Na 1s	0.3641	1.241	0.08719	0.1656
Na 2s	0.955	3.202	0.3146	0.5315

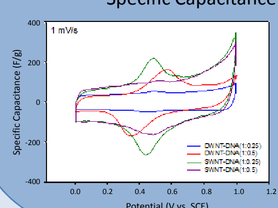
N_2 adsorption Data

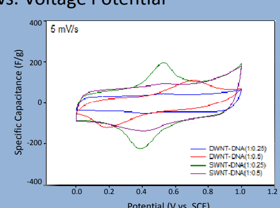
Sample	SSA (BET)[1)]	TPV[2)]	V_{micro}[3)]	f_{micro}[4)]	APD[5)]
Pristine SWNT	706	1.171	0.273	0.233	6.64
Pristine DWNT	574	1.747	0.256	0.146	12.16
SWNT:DNA=(1:0.5)	629	0.570	0.270	0.474	3.62
DWNT:DNA=(1:0.5)	321	0.766	0.153	0.200	9.55
SWNT:DNA=(1:0.25)	608	0.460	0.264	0.575	3.02
DWNT:DNA=(1:0.25)	424	1.245	0.208	0.167	11.75

1) Specific surface area, m^2/g
2) Total pore volume at 0.98 (P/P_0)
3) Micropore volume obtained by DA method, cm^3/g
4) Fraction of micropore in volume to TPV
5) Average pore diameter, nm

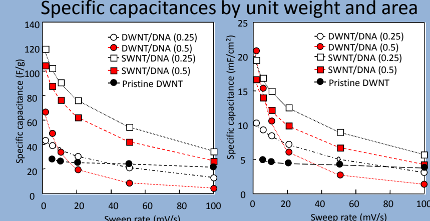
Electrochemical Tests

Specific Capacitance vs. Voltage Potential





Specific capacitances by unit weight and area



Analysis & Conclusions

ESCA RESULTS

Results from ESCA (XPS) showed that the primary element in each of the samples was carbon.

- Other elements present in varying amounts across the samples.
- Elements including nitrogen, phosphorous, oxygen and sodium.
- Heat treatment performed at low temperatures, so DNA carbonization was not as complete.

SSA CV RESULTS

Steep peaks around 0.4 V in the specific capacitance vs voltage graphs indicate the occurrence of a redox reaction.

-Electrode chemically interacts with electryolyte (H_2SO_4).
-Attributed to oxygen functional groups
-Increases the capacitance at this voltage.
-SWNT samples were better in capacitance and had higher SSA (from N_2 adsorption tests).

CONCLUSIONS

When compared with pristine HiPco (SWNT) samples, the specific capacitance of these samples is much higher, while the SSA is actually lower than the pristine tubes. While the reasons for this are currently unknown, one hypothesis is that some of the oxygen-containing functional groups surrounding the nanotubes interact with the ions in the electrolyte, allowing the samples to hold more charge as electrodes. In order to determine the reasons for this anomaly, further testing must be done. Tests will include increasing the amount of DNA used, as well as testing out different types and purities of DNA.

Future Work

Future experiments will be done on the electrochemical characteristics of this mixture. This work will include:

- Testing more variations of the amount of DNA present in the mixture.
- Testing other heat treatment temperatures.
- Performing electrochemical tests on the non-heat treated samples.

Due to the organic composition of the DNA-nanotube materials, there may also be applications in biological fields. Further research into these possible applications will also be tested in the future.

SUMMER NANOTECHNOLOGY STUDY PROGRAM IN JAPAN

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