Enhanced Electrochemical Ultracapacitor Using MnO_2 Nanoparticles on Vertically-Aligned Carbon Nanotubes

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Outline

- **Ultracapacitors (Supercapacitors, Electrochemical Capacitors)**
  - Fundamentals
  - State-of-the-art in comparison to other energy storage devices
- **Novel Innovation**
  - Nano-architectured Attachment
  - MnO_2/CNT based Ultracapacitors
- **Earlier Development at Vanderbilt**
  - Experiments/Characterization/Discussion of Results
    - CNT-Based Ultracapacitors by MPCVD and HFCVD
    - MnO_2/CNT Ultracapacitors
- **NASA/JSC STTR Phase I Results**

Ultracapacitor Fundamentals

Capacitance is given by, $C = \varepsilon A / d$

For ultracapacitor, charge is stored at the electrode-electrolyte interface, so call the electrochemical double layer EDL (the Helmholtz layer). Typically d= ~5 angstroms.

Conventional capacitor: nF/cm^2
Electrochemical ultracapacitor (EDL): uF/cm^2
Electrochemical ultracapacitor using Hybrid Nano-composite: mF/cm^2

The **energy** stored in an ultracapacitor, $W = (1/2)CV^2$

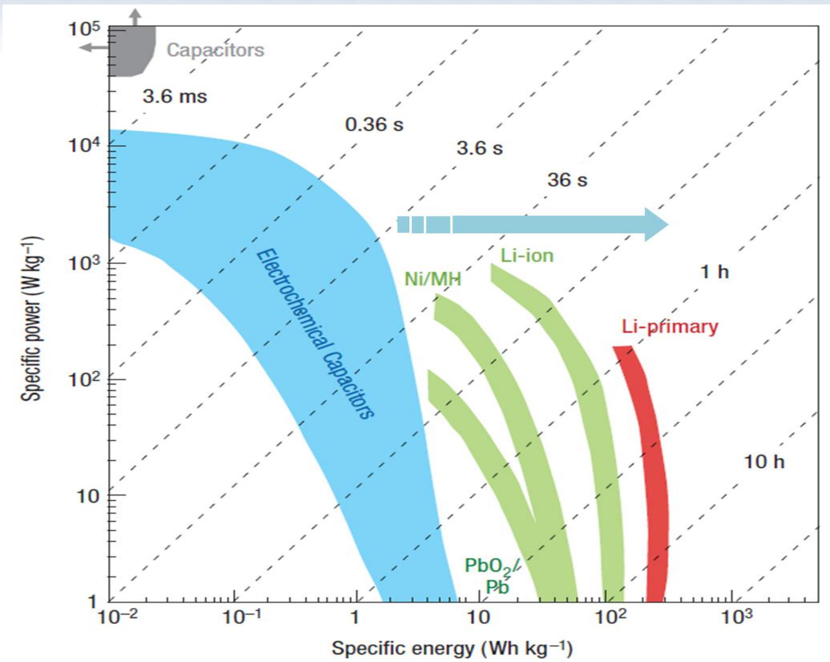
The **power** stored in an ultracapacitor, $P = V^2 / 4R$

where R is the total equivalent series resistance (ESR) of a cell.

Energy density, $Wh/kg = (1/8)(F/g)(V^2/3.6)$

where F/g is the specific capacitance of the electrode material and V is the cell voltage dependent primarily on the electrolyte used in the device.

State of the Art



	Battery	Electrostatic capacitor	EC
Discharge time	0.3–3 h	10^{-3} to 10^{-6} s	0.3–30 s
Charge time	1–5 h	10^{-3} to 10^{-6} s	0.3–30 s
Energy density (Wh/kg)	10–100	<0.1	1–10
Specific power (W/kg)	50–200	>10,000	≈1000
Charge-discharge efficiency	0.7–0.85	≈1	0.85–0.98
Cycle life	500–2000	>500,000	>100,000

Ragone plot (energy density vs. power density) for various energy-storage devices. Nature, Vol. 7, 845-854 (2008)

Strengths of Electrochemical Capacitors ECs (ultracapacitors):

- **Energy density is 10-100 times higher than that of electrostatic capacitors**
- **Higher power density, shorter charge/discharge time, longer cycle- and shelve-life compared with batteries**
- **Probably the most important next generation energy storage device (need to reduce cost and improve energy density)**
- **Potential applications: Electric vehicles/transportations, portable electronic devices/equipments/MEMS, GRIDS, etc**

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Competing Technologies of ECs

- **Electrical double-layer capacitors (EDLCs)**
  (low cost, low capacitance)
  Carbon-based materials

- **Pseudocapacitors** (usually high cost, high capacitance)
  Transition metal oxides & Conducting polymers

  RuO_2 presents the highest specific capacitance while it is expensive.

  MnO_2 is low cost, natural abundance, and environmental safety.

- **Nanocomposites** (moderate cost, high capacitance)
  Carbon-based materials + Transition metal oxides

Novel Innovation

Concept:
Nano-architectured attachment pseudocapacitive nanoparticles

Nano-architecture:
CNT/MnO_2 nanocomposite electrodes

Implementation:
Close-packed vertically-aligned CNTs as well-structured conductors to maximize area
Attachment of dispersed MnO_2 pseudocapacitive nanoparticles for optimum specific capacitance

Energy Storage Mechanisms

- Electrical double-layer capacitors

Surface dissociation, Ion adsorption from solution

$$C = \varepsilon \frac{A}{d}$$

ε : dielectric constant

A : surface area

d : thickness of the double layer

- Pseudocapacitors

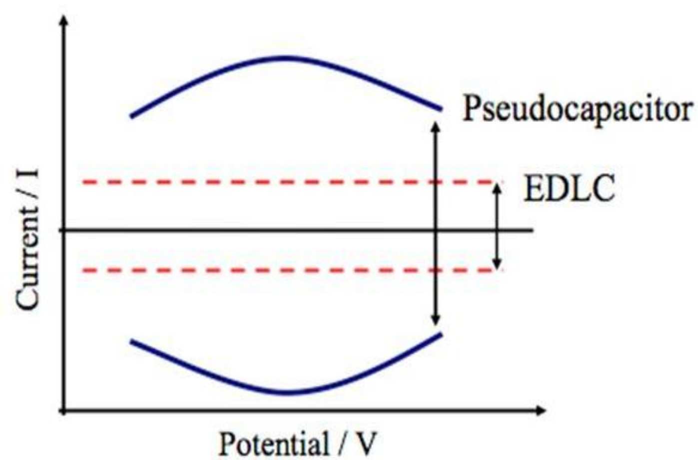
Faradic current from electrosorption and an oxidation-reduction reaction.

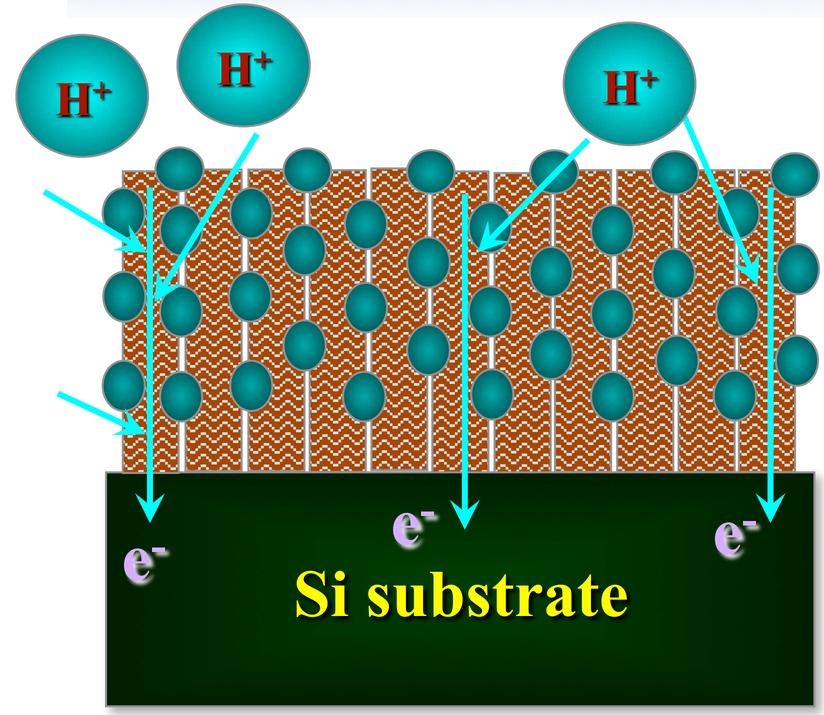
$$M + A^{-} \leftrightarrow MA^{(1-\delta)-} + \delta e^{-}$$

$$O + ne^{-} \leftrightarrow R$$

Energy Storage Mechanisms

- Hybrid electrochemical capacitors





- The pseudocapacitance of MnO_2 can be attributed to the following redox reaction:

$$MnO_2 + H^+ + e^- \leftrightarrow MnOOH$$

Shorter diffusion distance

& lower contact resistance

➔ High efficiency current

Electrodes Materials for ECs

- The key factors of electrode materials for ECs:
  - High specific capacitance
  - High specific surface area
  - Low internal electric resistance
  - Low price
  - Environmentally friendly material

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Electrode Materials for ECs

- Carbon-based materials

  Such as : **CNTs**, Active carbon, Graphite, Carbon fibers

  High chemical stability

  High specific surface area

  High electric conductivity

- Transition metal oxides

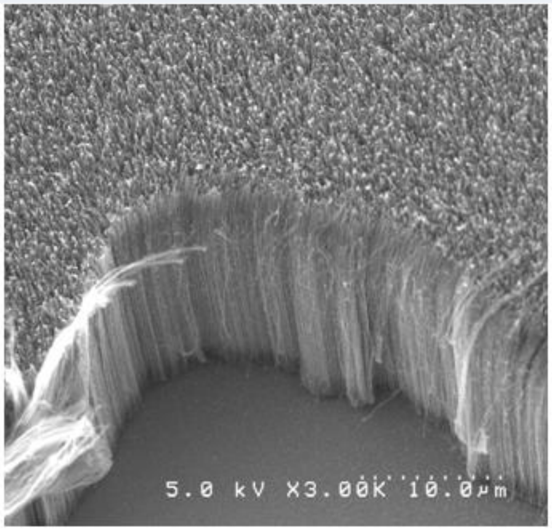
  Such as : $\mathbf{MnO_2}$, RuO_2, NiO_x, CoO_x, V_2O_5

  Low cost

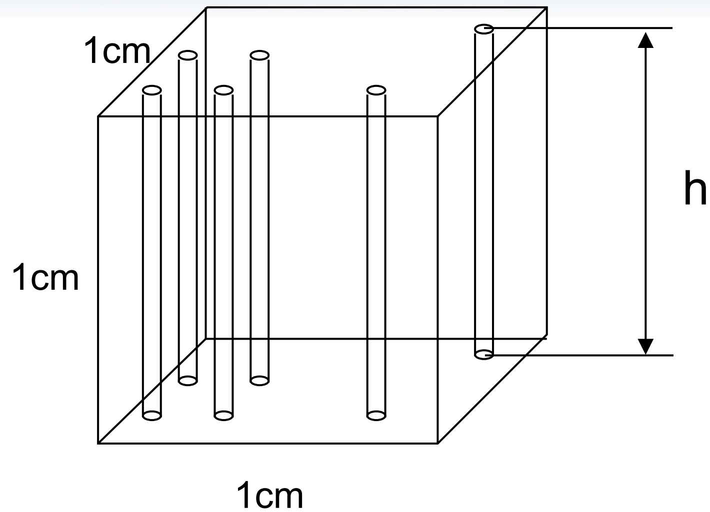
  Natural abundance

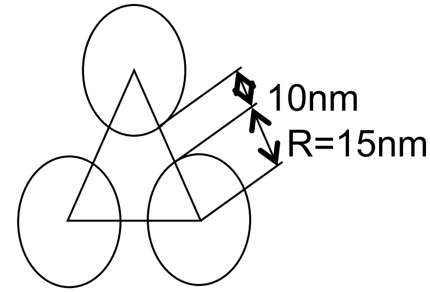
  Environmentally friendly

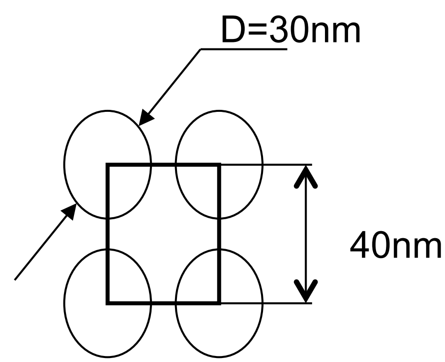
Novel Innovation



SEM of vertically aligned CNTs







1 tube per 40nmx40nm=1600nm^2
1cm^2=10^{14}nm^2 (can accommodate 6.25x10^{10} tubes/cm^2
Surface area of 1 tube=pi*30nm*1cm=9.42x10^{-6}cm^2
Total surface area of all tubes on 1cm^2 area
=(6.25x10^{10} tubes/cm^2)*(9.42x10^{-6}cm^2)=58.9m^2

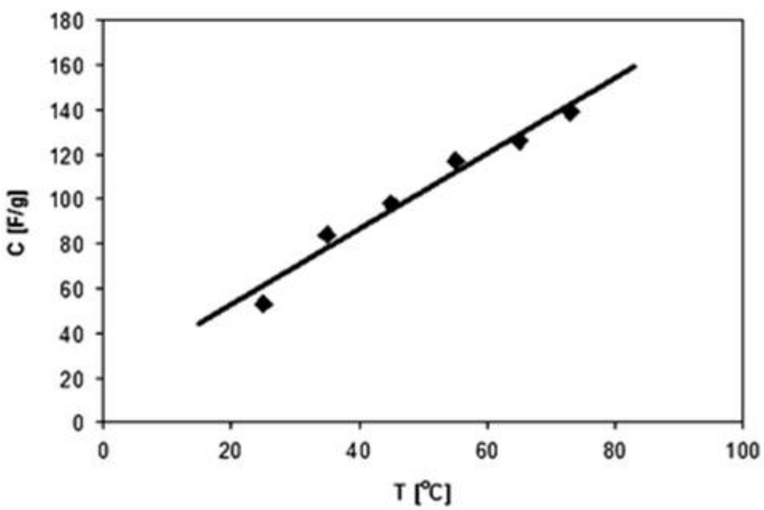
An area of 5 cm^2 with 1cm tall CNT Ξ area 1 football field (360ft x160ft (5351m^2))

One sheet of 8.5”x11” paper with 1.5mm tall CNTs Ξ 1 football field !!!

Novel Innovation

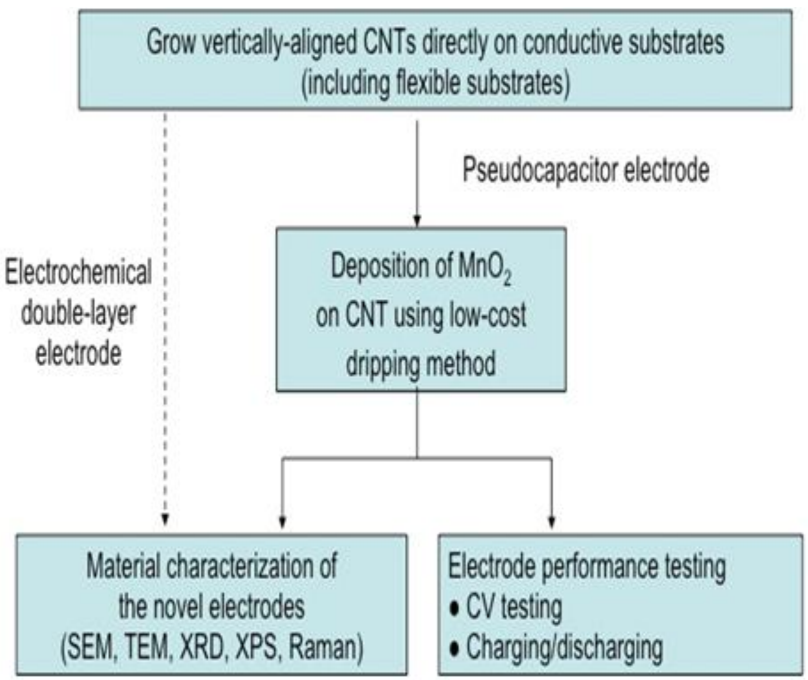
Electrolytes used for supercapacitors:

- Aqueous (H_2SO_4, KOH, NaOH)
- Organic (acetonitrile-dissolved tetraethyl ammonium tetrafluoroborate)
- Ionic liquids (trigeminal tricationic)

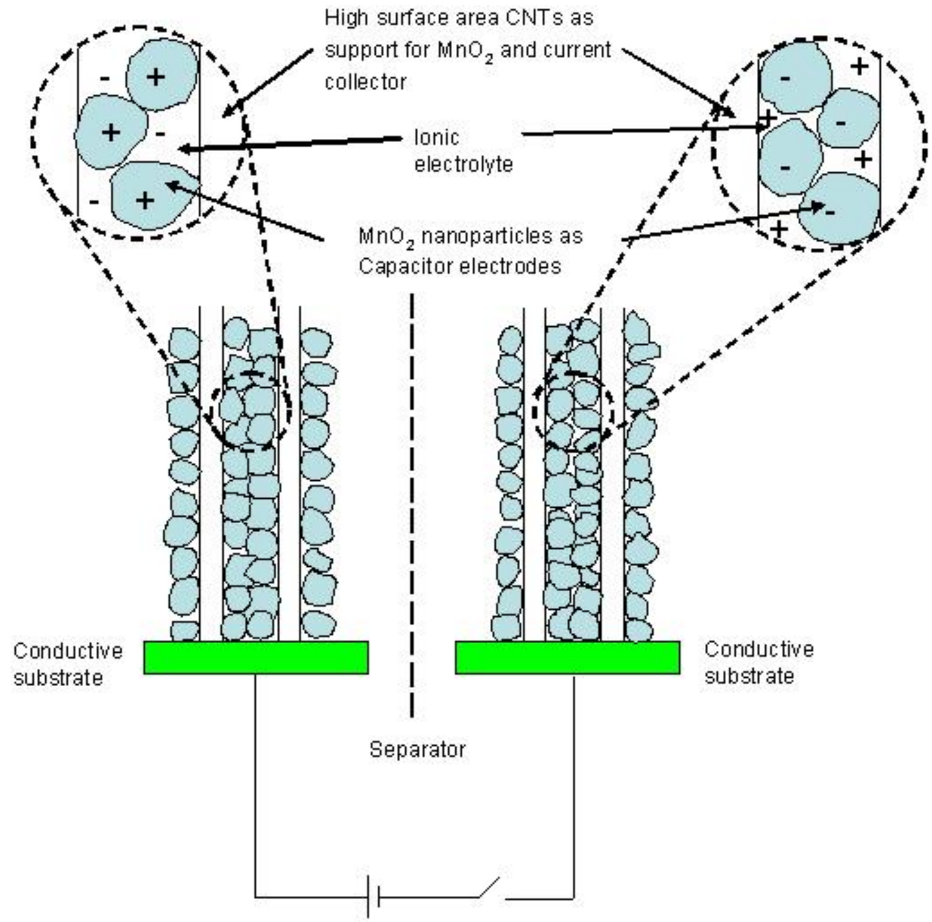


Temperature dependence of specific capacitance for activated carbon electrode in trigeminal tricationic electrolyte.

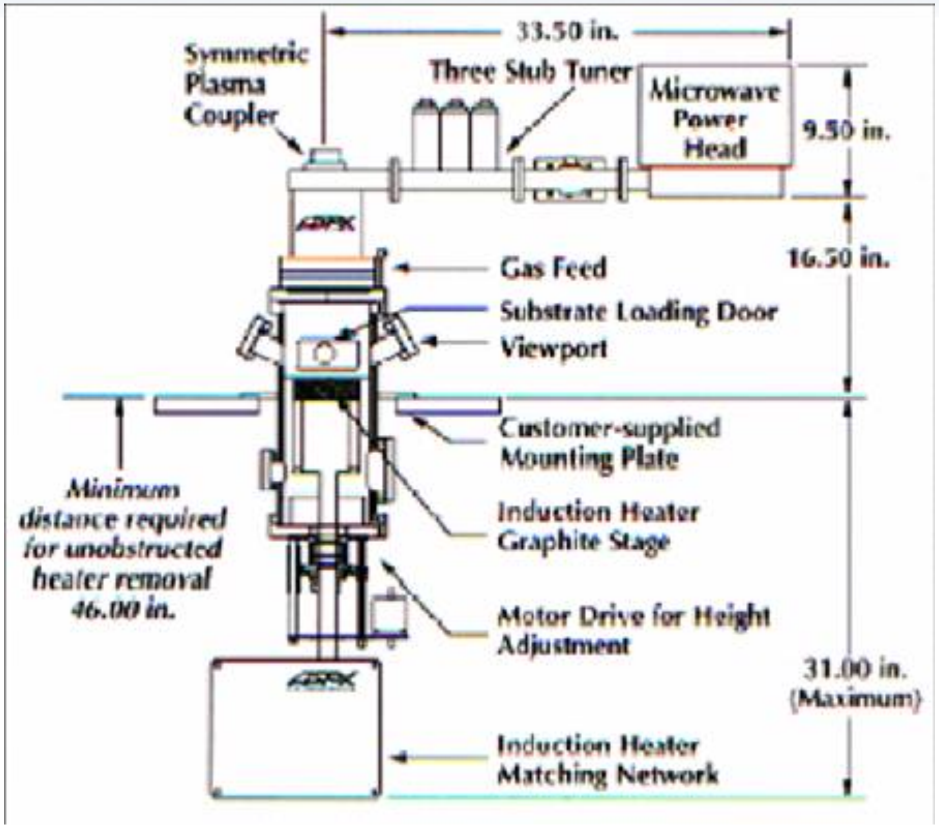
Experimental Methods



Experimental Methods and Procedures



MPCVD CNTs with Ni Catalyst



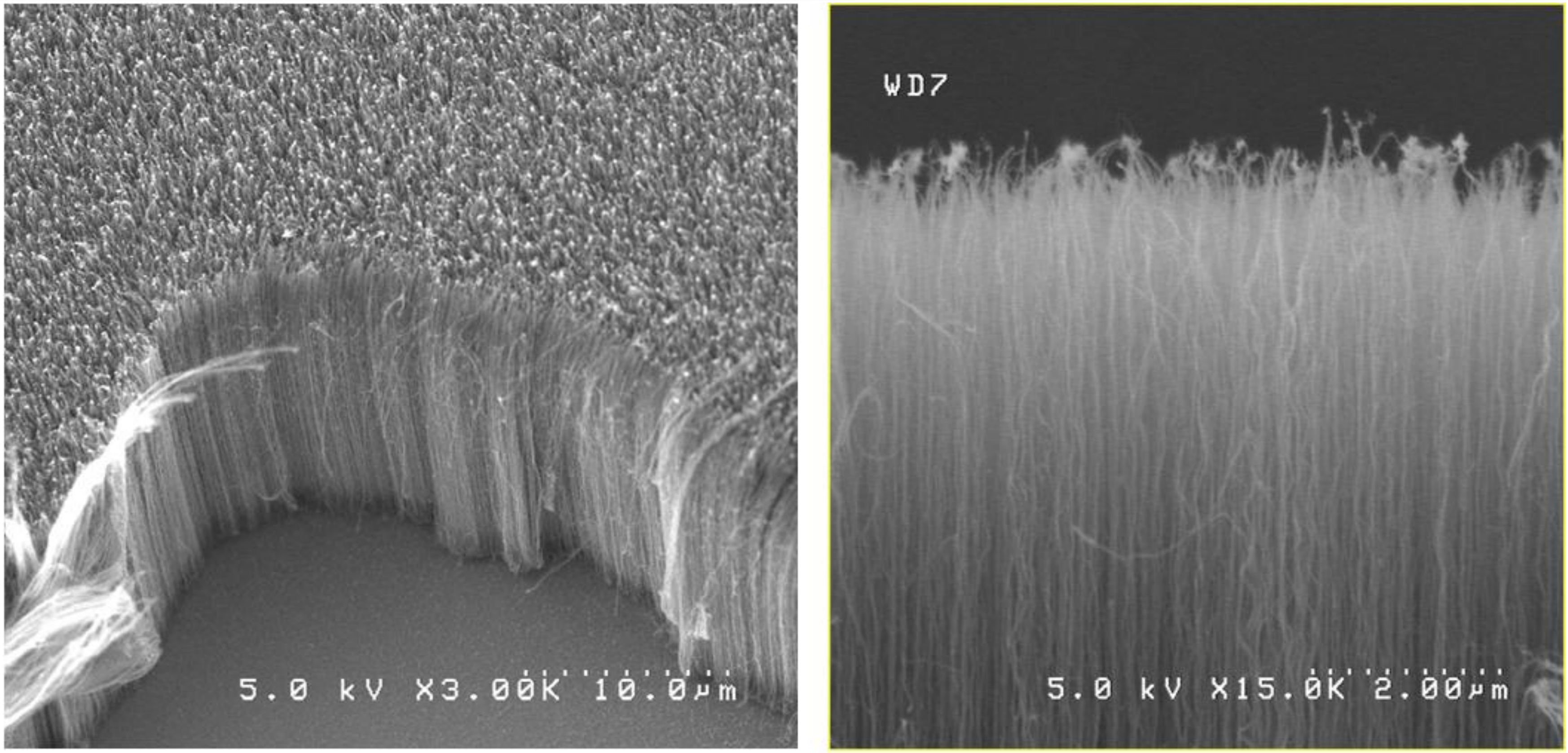
MPCVD Synthesis of CNTs

- **Method: Microwave plasma enhanced CVD process**
- **Substrates: N^{++} Si wafer deposited with 4nm Ti as buffer layer**
- **Catalyst: Nickel (2-4nm), cobalt (2-4nm)**
- **Gases: CH_4 (15 sccm), H_2 (120 sccm)**
- **Temperature for synthesis: 650 ^{o}C**
- **Pressure for synthesis: 20 Torr**
- **Growth time: 1-2 minutes**

We also have other methods of CNT synthesis experiences

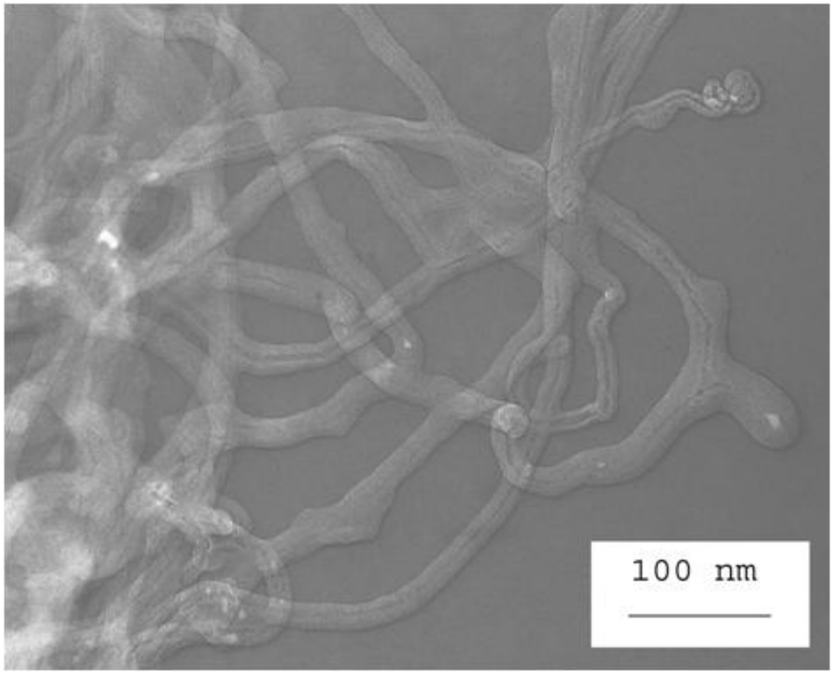
- **Thermal CVD (good for wafer scale)**
- **HFCVD (good for extremely tall CNTs)**

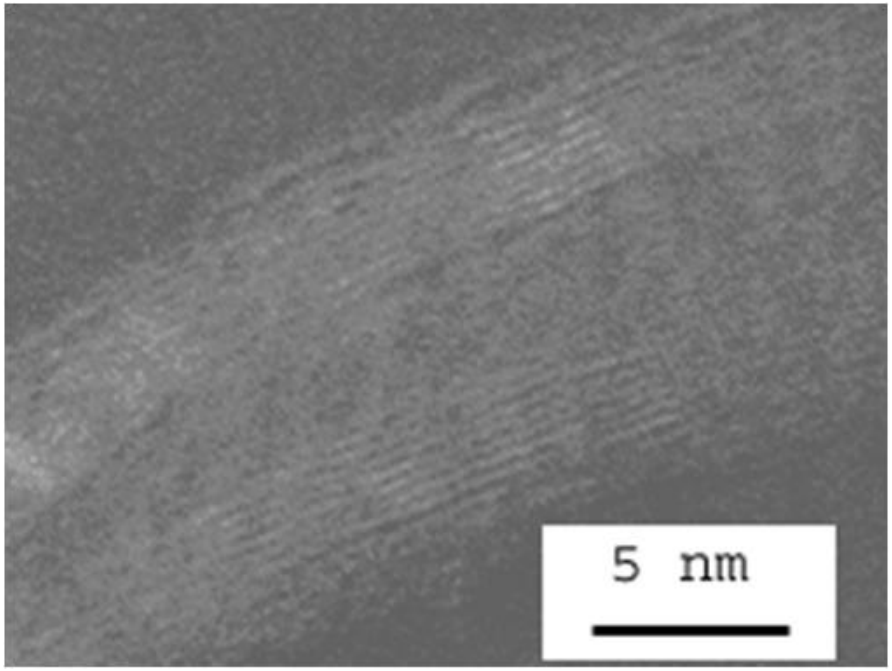
Results & Discussion



SEM of vertically aligned CNTs mat. Right is the high mag. cross section of CNTs

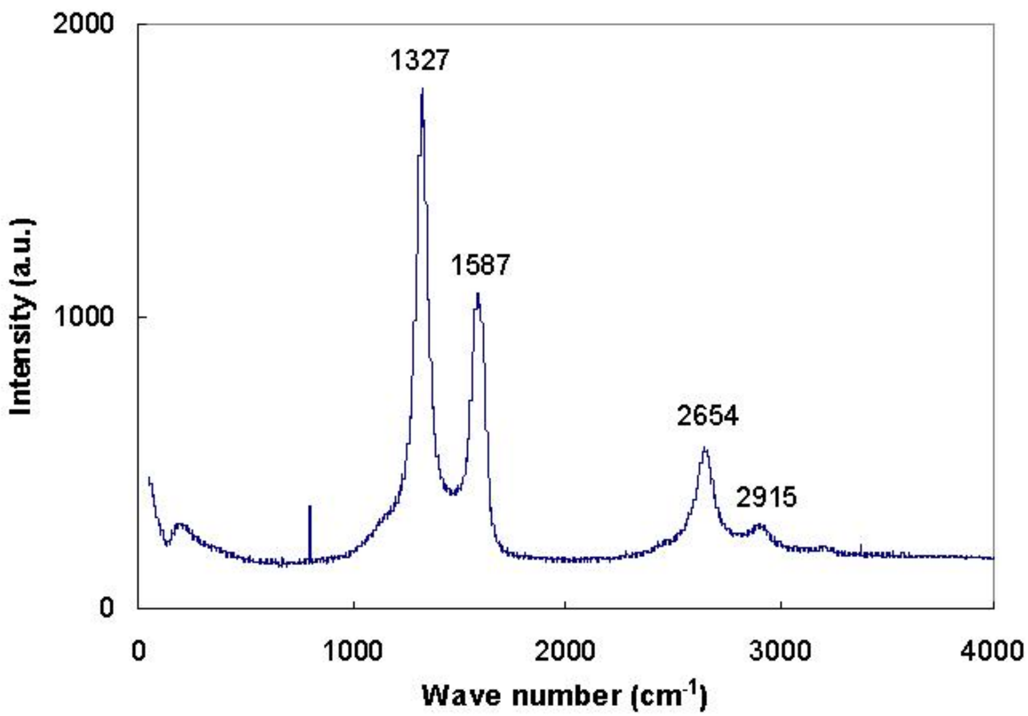
Results & Discussion





The hollow tube structure of as-grown CNTs is readily seen even in low magnification TEM image (a). Some catalyst particles are trapped at the ends of nanotubes, suggesting tip growth mode. The nanotube shown in high magnification TEM picture (b) has about 10 walls and the inter-wall spacing is ~ 0.34 nm. Note: MPCVD CNTs have less amorphous carbon coating than thermal CVD grown CNTs.

Results & Discussion



Raman spectrum of as-grown CNT thin films.

- The strongest peak at 1327 cm^{-1} is assigned to the D-band indicating the presence of disorder or defects in the nanotube structures.
- The second strongest band at 1587 cm^{-1} corresponds to G-band graphite mode.
- The other bands located at 2654 and 2915 cm^{-1} are due to the second-order combinations of 2D and D + G, respectively.

Experiment

Cost-effective drip coating of MnO_2

► Preparation of MnO_2 from $KMnO_4$

► Collection of MnO_2 nanoparticles precipitate

► MnO_2 powder is added into acetone and ultra-sonicated to form a uniform suspension.

► MnO_2/acetone suspension is dripped onto CNT thin film drop-wise and dried.

Other methods of attaching MnO_2 on CNTs are in progress at Vanderbilt

Results & Discussion

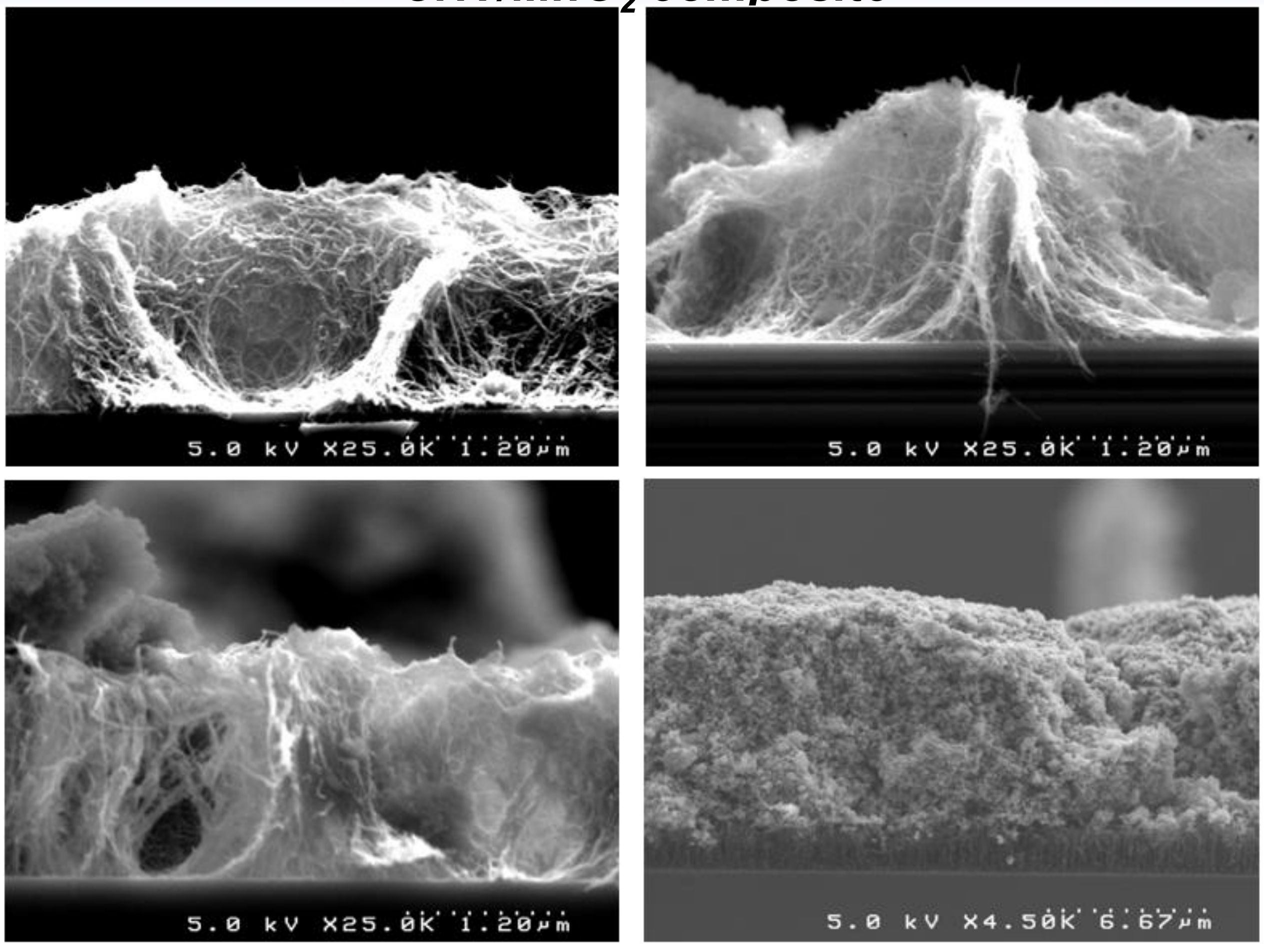
CNT/MnO_2 composite

5 drops

10 drops

15 drops

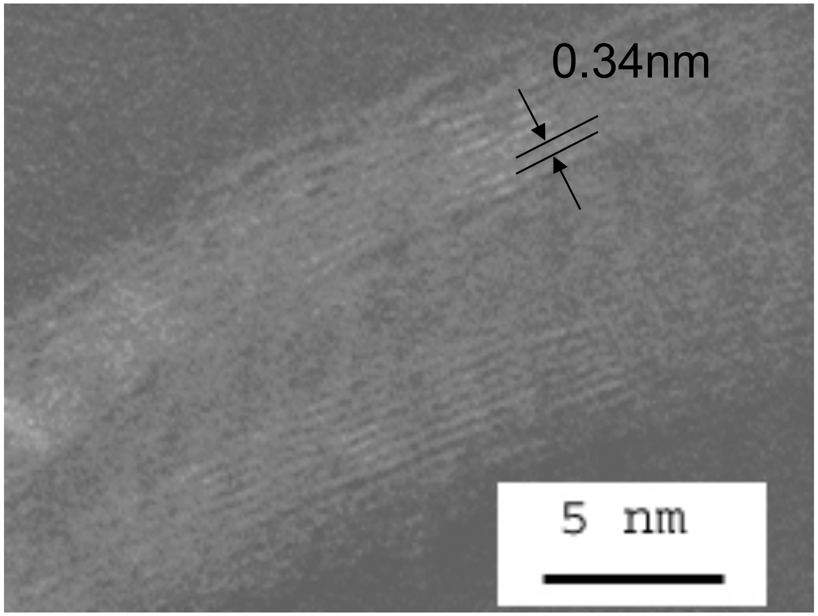
30 drops

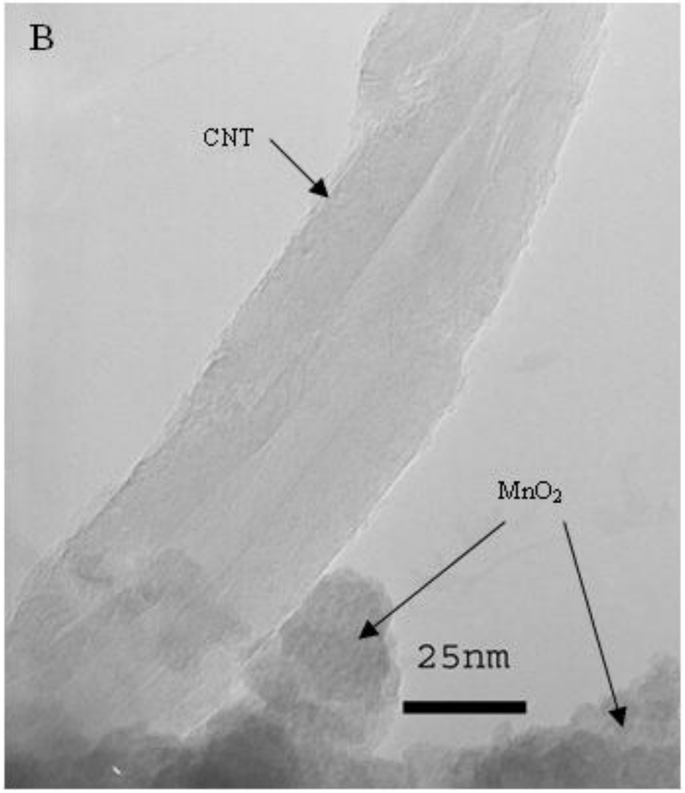


MnO_2 less than 15 drops can be fully absorbed into CNT film. Higher quantity of MnO_2 builds up on top of CNT arrays.

Results & Discussion

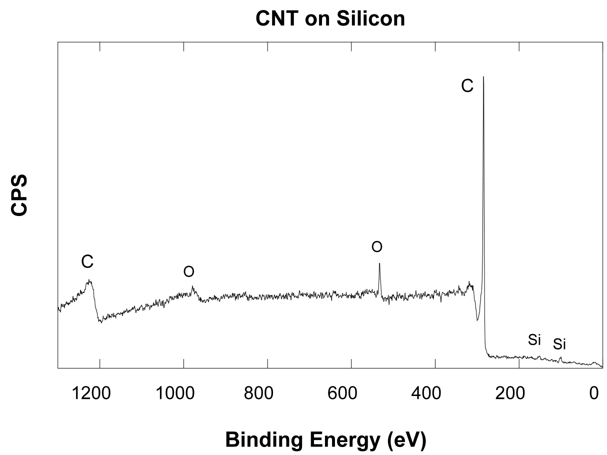
CNT/MnO_2 composite

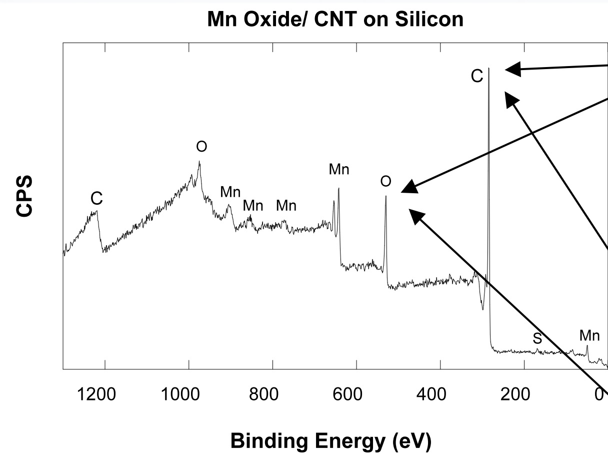




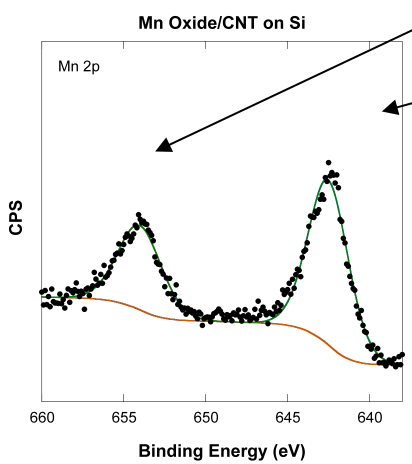
TEM images showing MnO_2 particles attached to CNTs.

MnO_2 Binding Energies



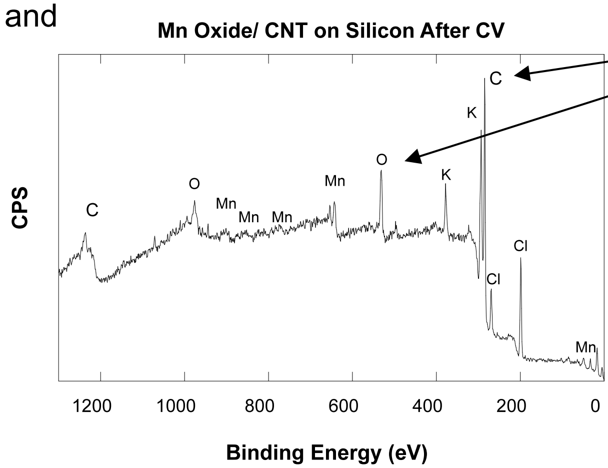


Higher O1s to C1s ratio is caused by addition of MnO_2 to the CNT film.



Mn 2p1/2 (653.6eV) and

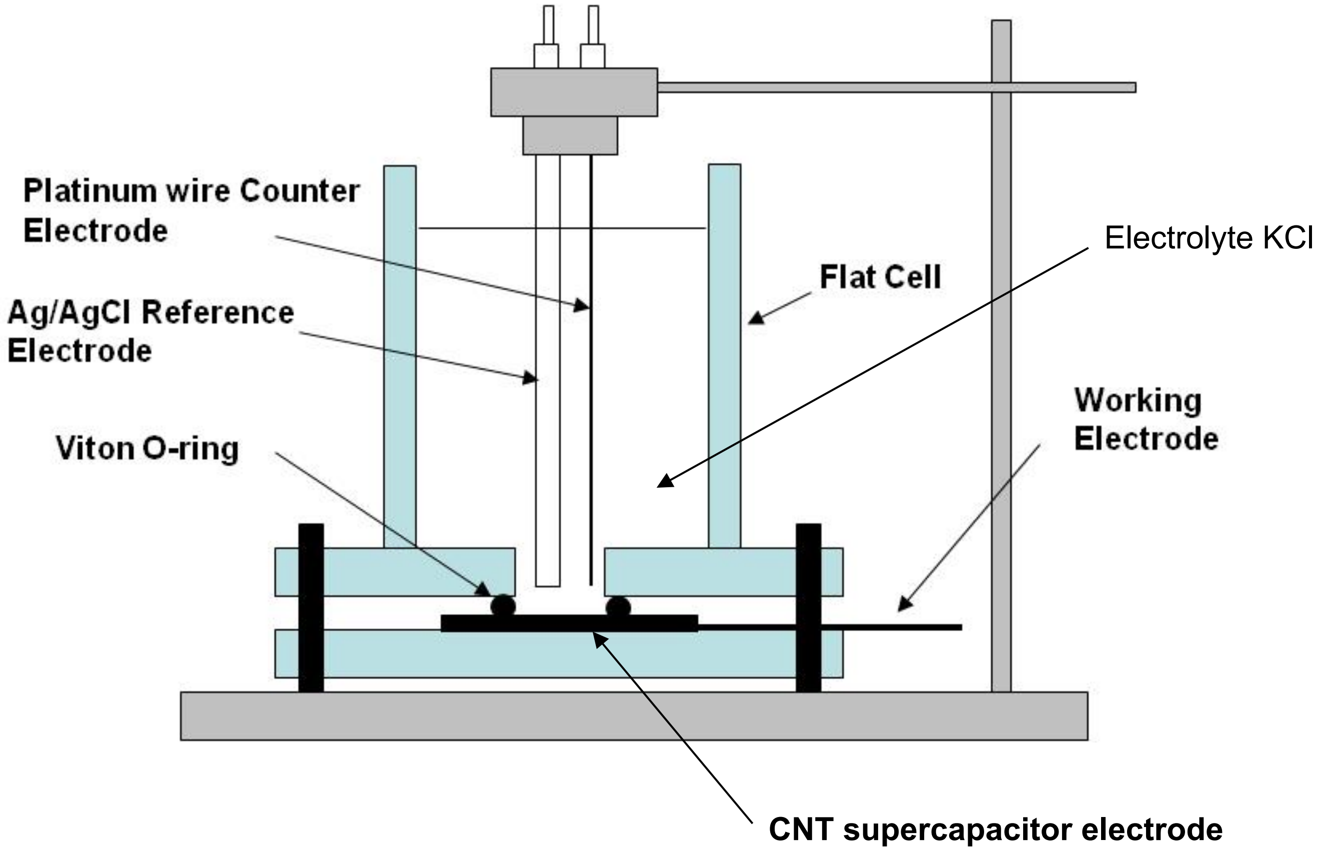
Mn 2p3/2 (642.2eV) correspond to MnO2 binding energy



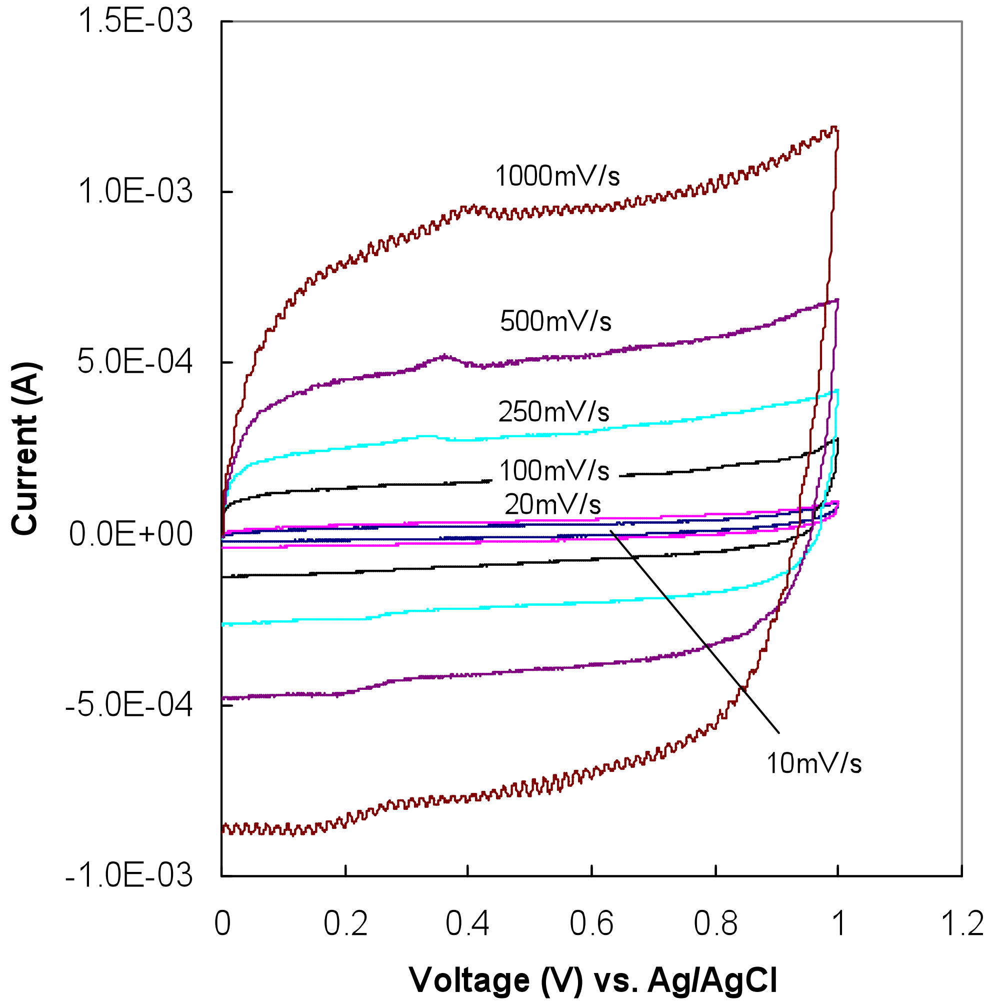
O1s to C1s ratio does not change after cyclic voltammetry testing indicating the chemical stability of MnO_2 nanoparticles.

Experiment: Supercapacitors

Test cell for electrochemical supercapacitor characterization



Results & Discussion

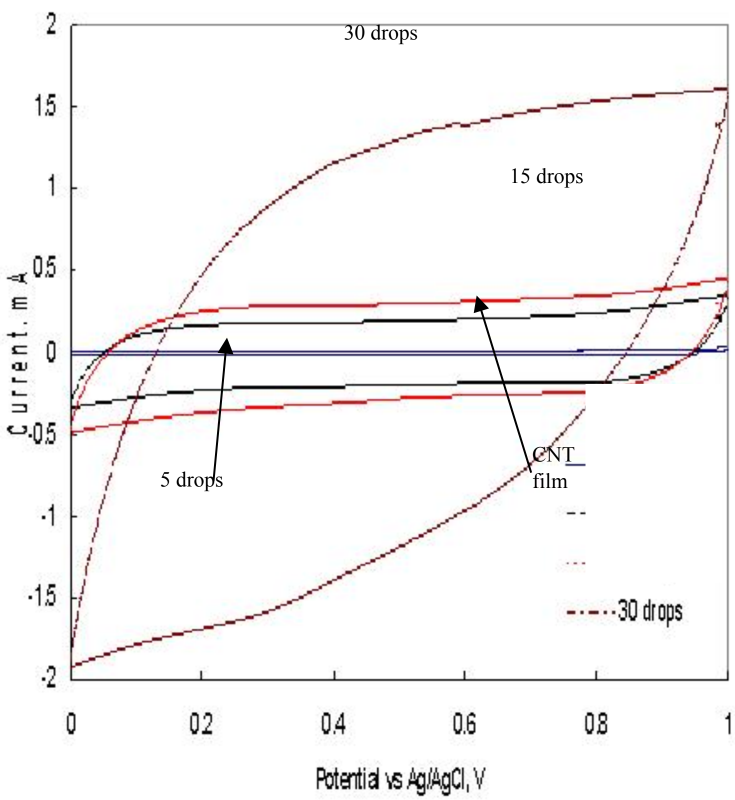


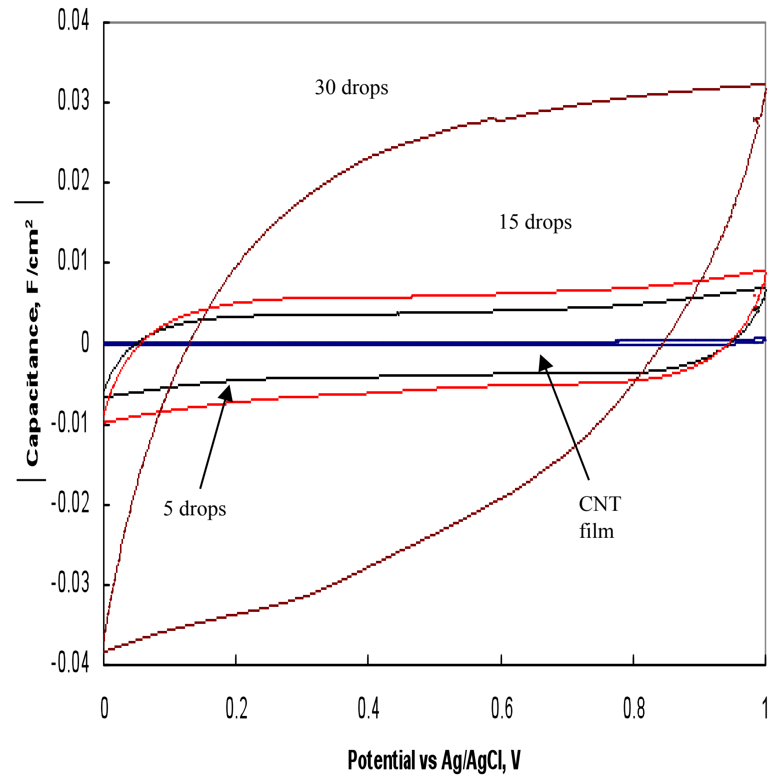
* Nearly rectangular shaped I-V curve is maintained while the scan rate varies from 10 to 1000mV/s.

C=I/[(dv/dt)A]

Cyclic voltammograms of CNT electrode based on 3 nm Ni film with three minutes of pretreatment.

Results & Discussion



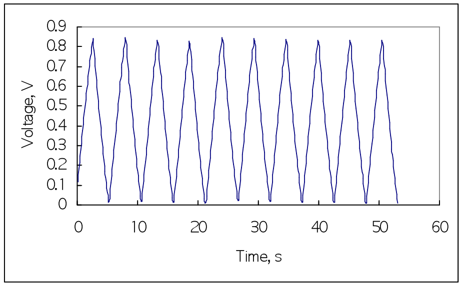


Cyclic Voltammetry

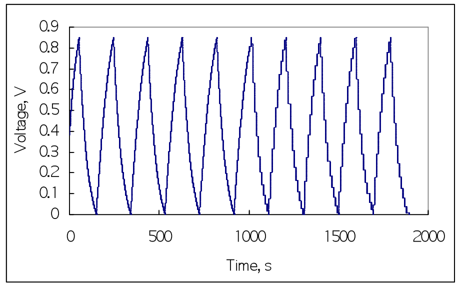
* CNT/MnO_2 can achieve capacitance more than 400 times higher than as-grown CNTs.

Results & Discussion

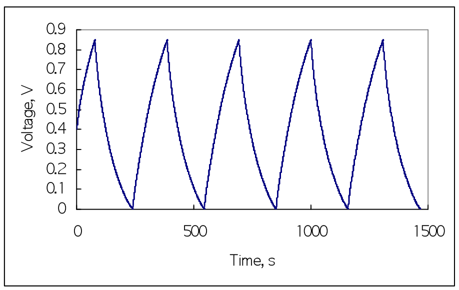
Galvanostatic charging-discharging



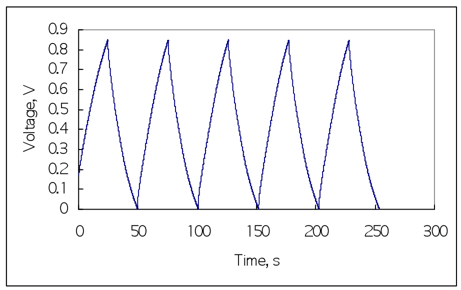
A



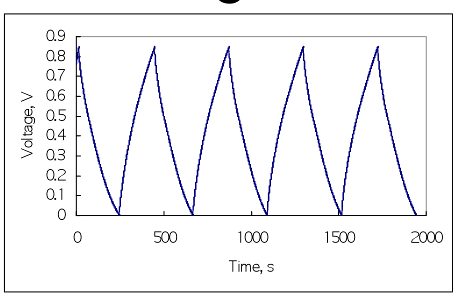
B



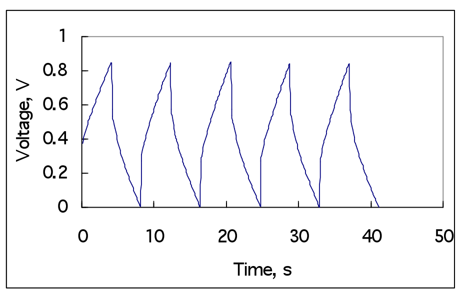
C



D



E



F

* Capacitances can be calculated based on the galvanostatic charging-discharging time and current.

A: CNT film at 30uA;

B: 5D at 30uA;

C: 15D at 30uA;

D: 15D at 120uA;

E: 30D at 120 uA;

F: 30D at 1920uA.

* Specific capacitance ~650 F/g.

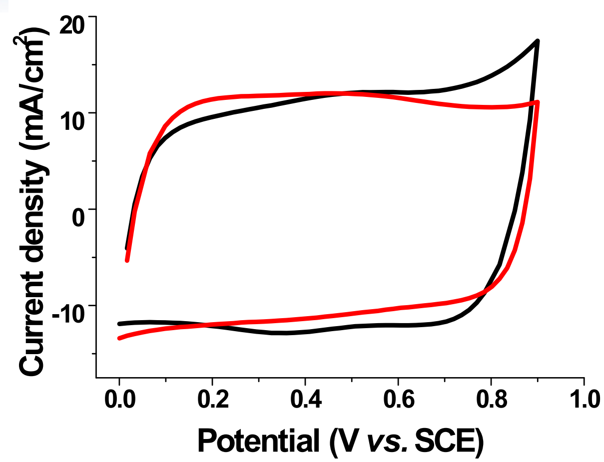
* Charging/discharging current ~17A/g.

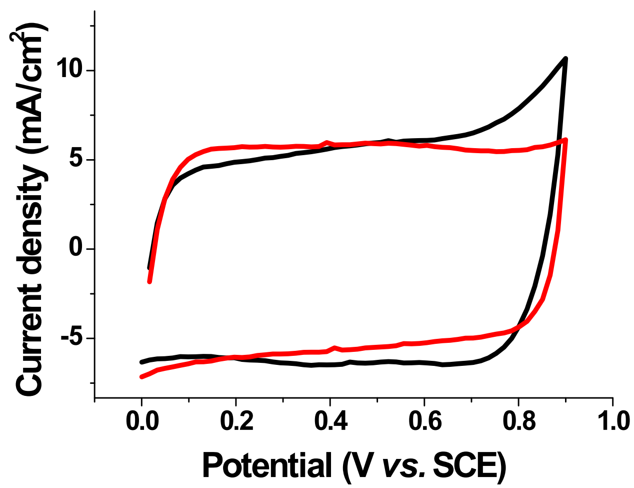
Stability of MnO_2-MWCNTs

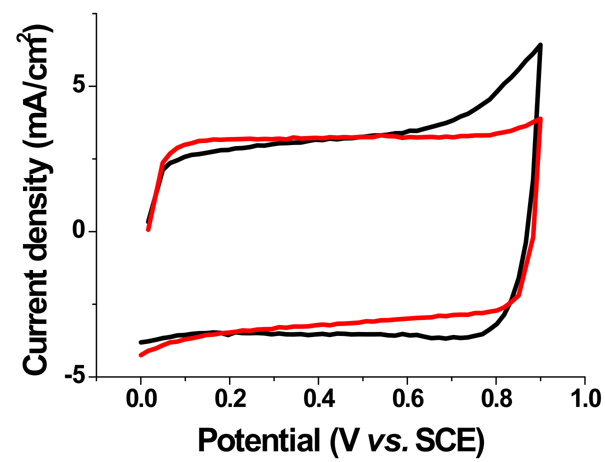
1st cycle

1080th cycle

Retain 96% after 1080 cycles





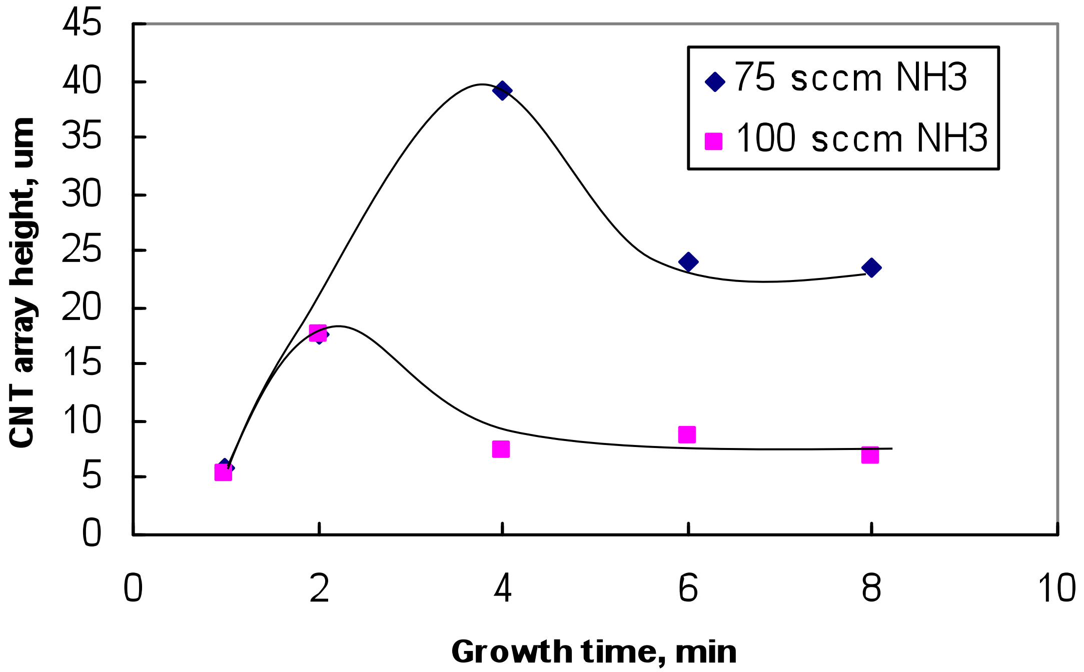


Major Advances During Phase I Effort

- Better CNT growth by a factor of ~10. CNT heights were ~5 microns and are now 40 to 50 microns with further improvements to come.
- Better control over catalyst (Ni or Co) deposition. (*The catalyst sites are where the CNTs begin their growth.*) Our advances here (1) help with CNT growth, (2) can facilitate the application of the MnO2 particles, and (3) impact our choice of large-scale fabrication techniques.
- We have achieved **~700F/g and are on track to achieve >2000F/g** upon completion of Phase II.

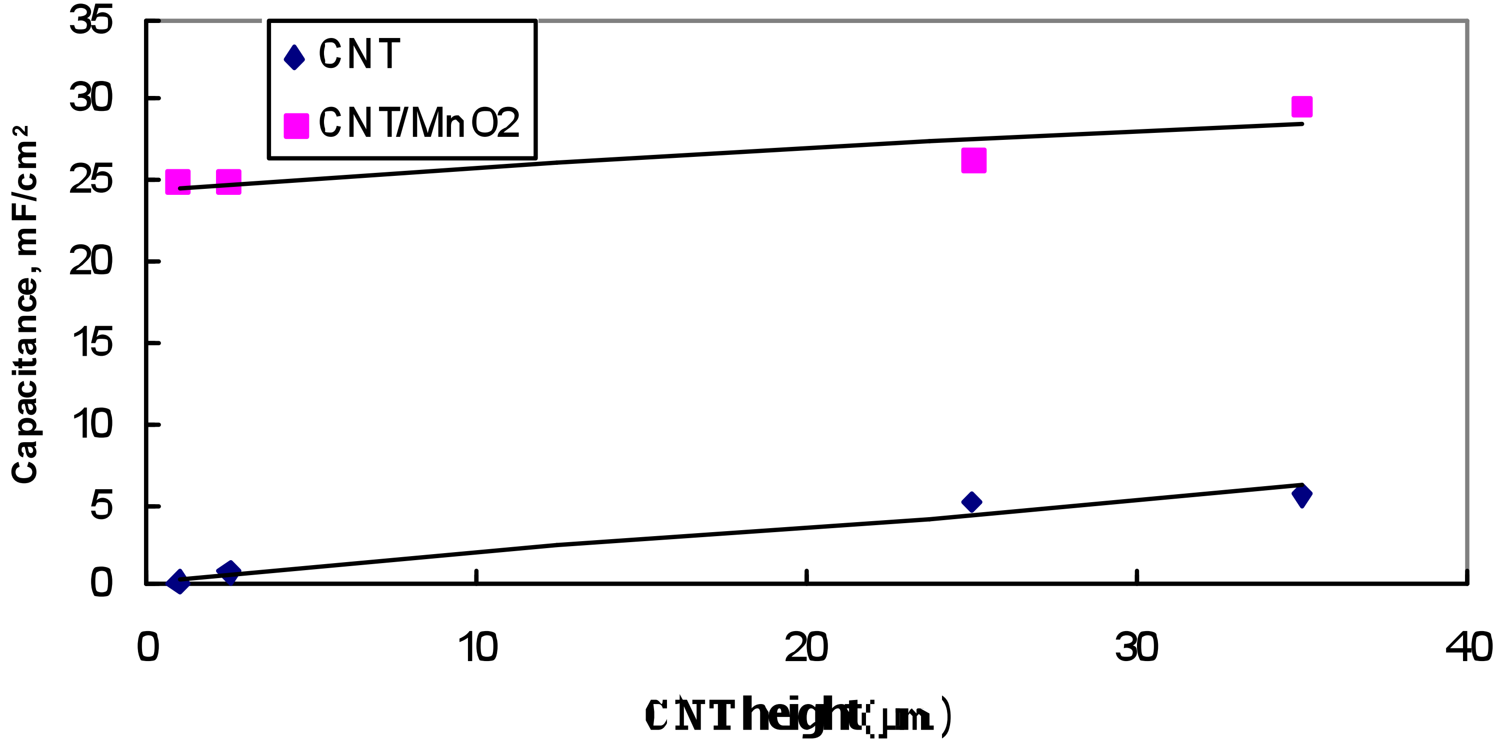
Control Over CNT Growth

- We have optimized our catalyst deposition and also our ammonia pre-treatment.



Summary and comparison of the height of CNTs versus growth time between two groups of samples: samples pretreated and grown with 75 sccm and 100 sccm of ammonia, respectively.

Capacitance Measurements



Capacitance (at scan rate of 100 mV/s) of CNT electrodes and CNT/ MnO_2 hybrid electrodes versus CNT height.

Conclusions

MnO_2 coated CNT electrodes for high-performance electrochemical capacitors

► Direct growth of vertically aligned CNTs on conductive Si substrates provides a great platform for attachment of pseudocapacitor material such as MnO_2.

► A new, efficient, and low-cost process has been developed for fabrication of MnO_2/CNT composite electrode. The resulting structure demonstrates outstanding capacitance behavior with power density more than 400 times of as-grown CNT thin film and excellent long-term chemical stability.

► High specific capacitance of 700F/g and high charging-discharging current have been achieved.

► Both electrode materials and electrolyte utilized in the newly developed electrochemical capacitor system do not present a hazard to the environment.