Carbon Nanostructured for Energy Storage

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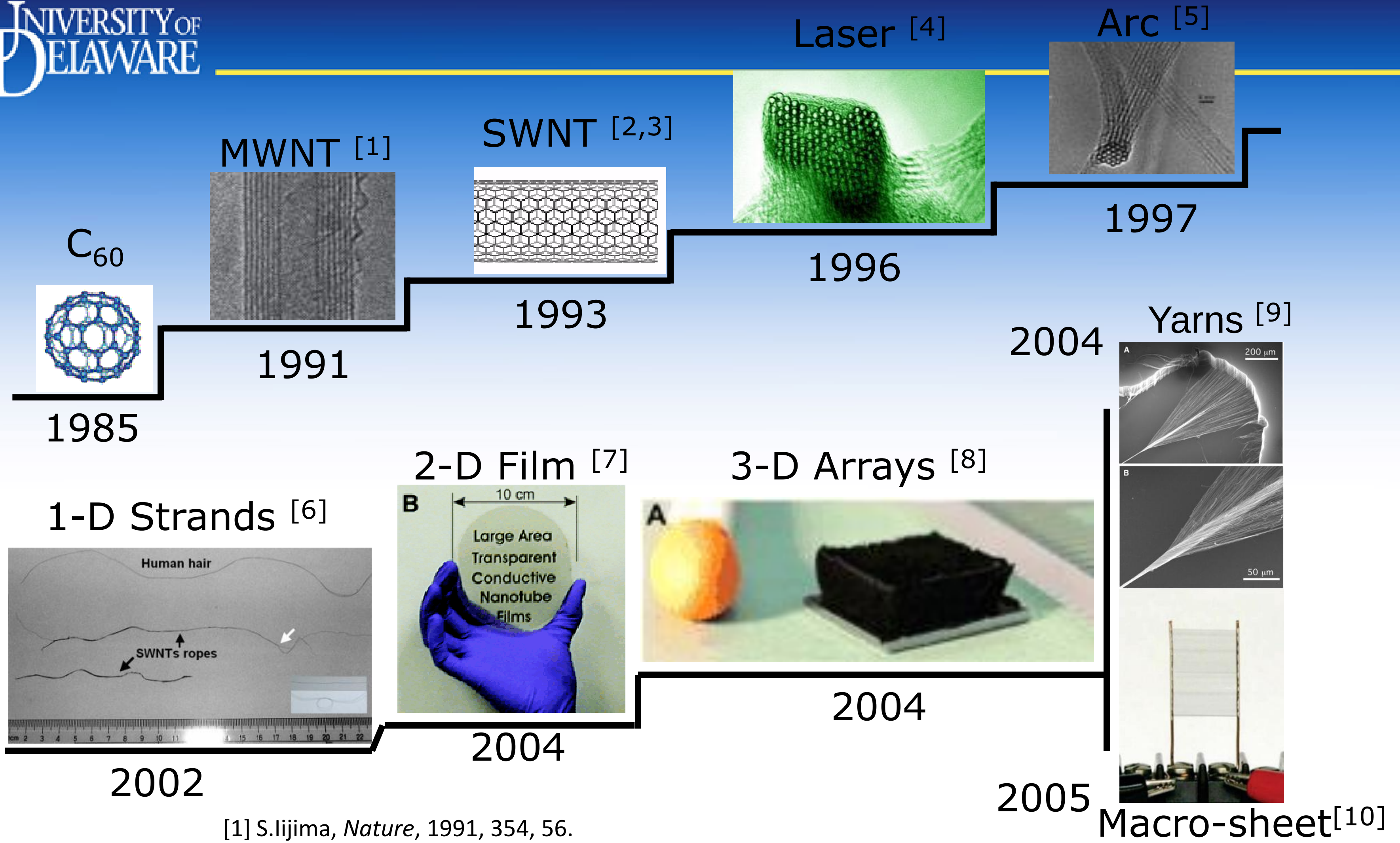
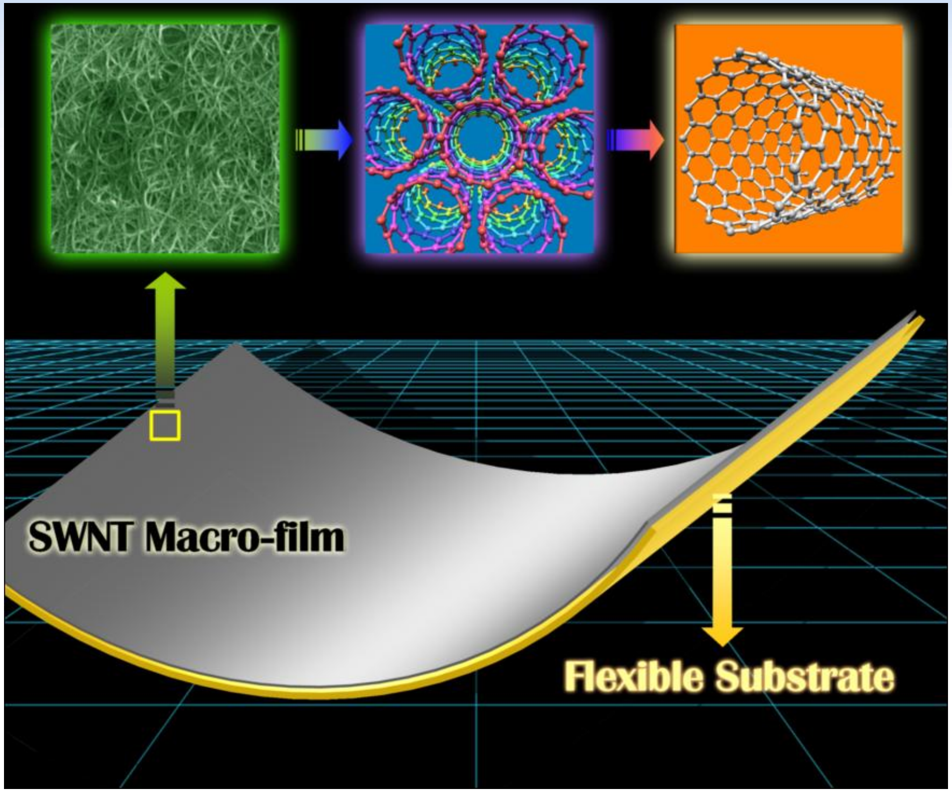


[1] S.Iijima, *Nature*, 1991, 354, 56.
[2] S.Iijima et al., *Nature*, 1993, 363, 603.
[3] D.S.Bethune et al., *Nature*, 1993, 363, 605.
[4] A.Thess et al., *Science*, 1996, 273, 483.
[5] C.Journet et al., *Nature*, 1997, 388, 756.
[6] H.Zhu et al., *Science*, 2002, 296, 884.
[7] Z. Wu et al., *Science*, 2004, 305, 1273.
[8] K. Hata et al., *Science*, 2004, 306, 1362.
[9] M. Zhang et al. *Science,* 2004, 306, 1358.
[10] M. Zhang et al., *Science*, 2005, 309, 1217.

Why CNT Films for Supercapacitors?

Assembly of nanoscale building blocks (CNTs) into controlled 2-D multifunctional macroscopic structures for various applications

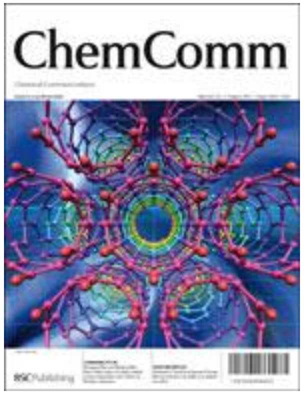


Properties:

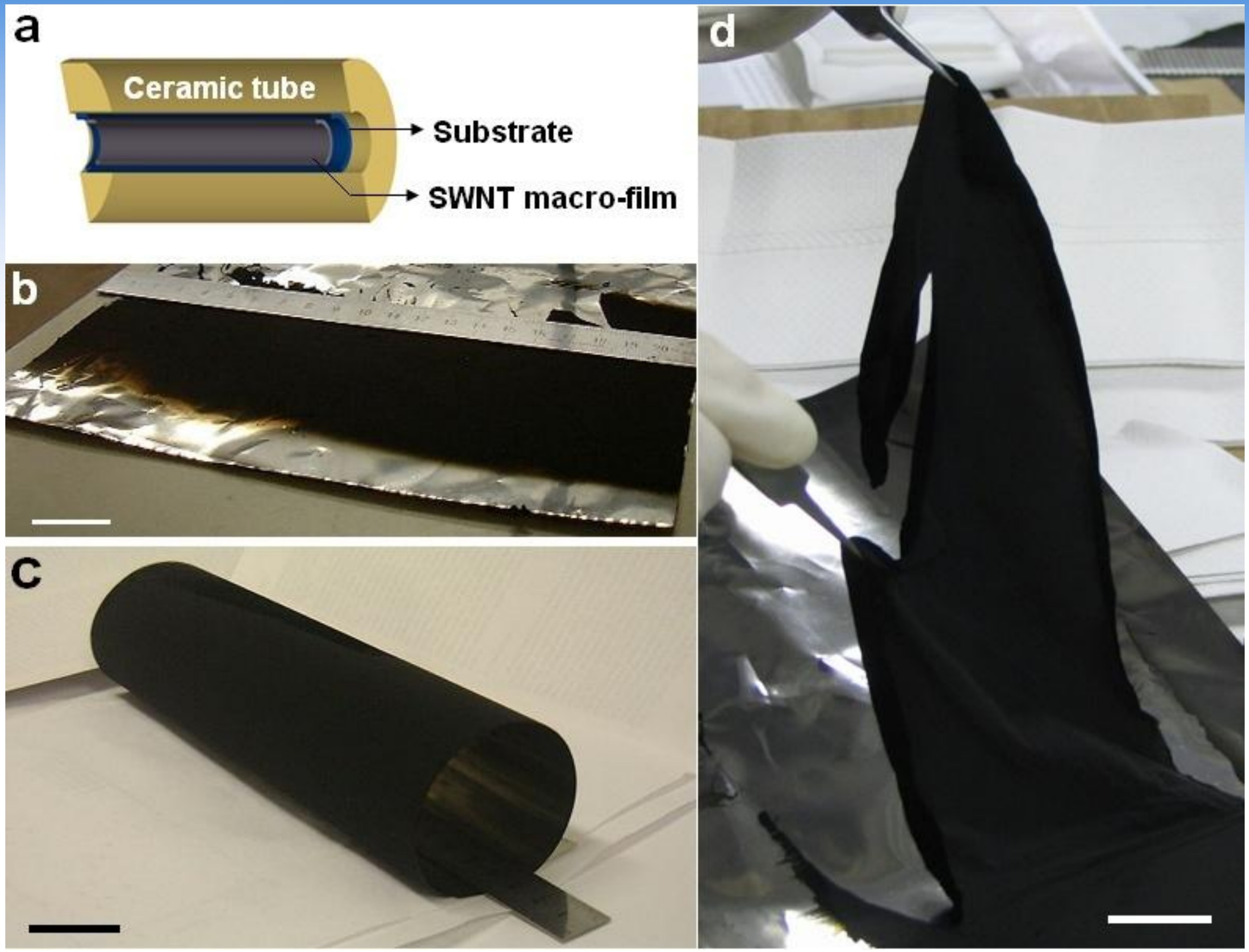
- **Low resistivity**
  Ballistic Electron Conduction
- **Small Dimensions**
- **Mechanical Robustness**
- **Chemical Stability**
- **Structural Stability**
- **High Thermal Conductivity**
  Low Dissipation
- **High Current Densities (~10^9 A/cm^2)**
- **High Surface Areas**

Synthesis of Flexible CNT Macro-Films

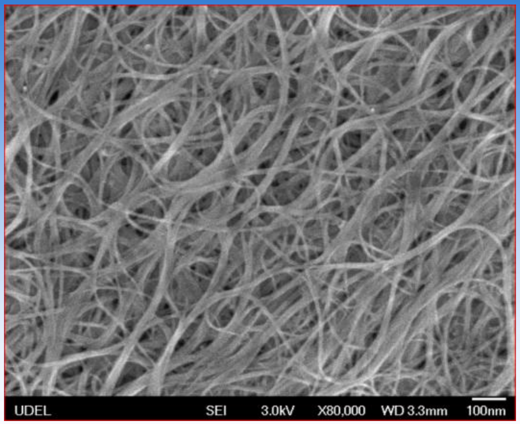
- Si
- Copper
- Stainless steel
- Aluminum
- Nickel mesh
- Polymer
- …

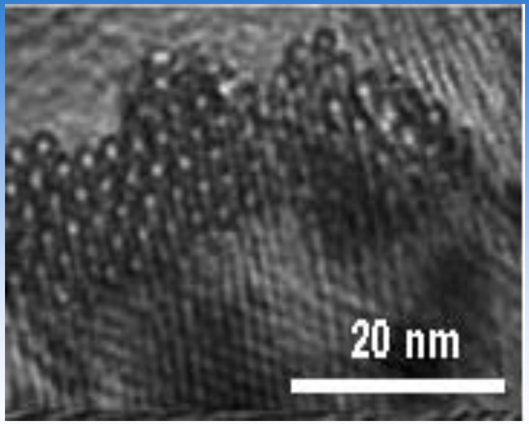


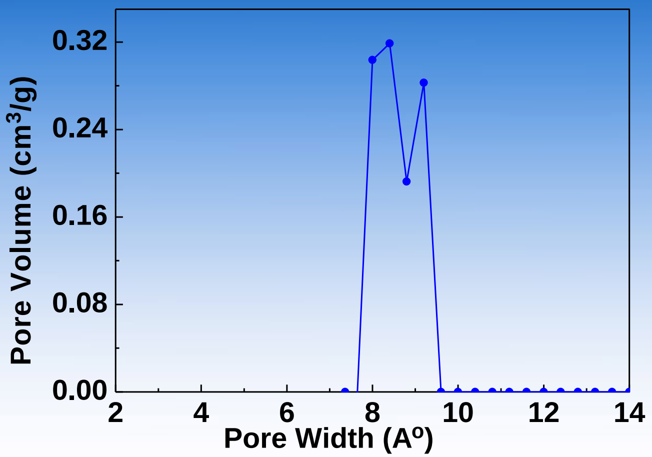
Zhu and Wei
Chem. Comm., 2007



Structural Features of SWNT Films



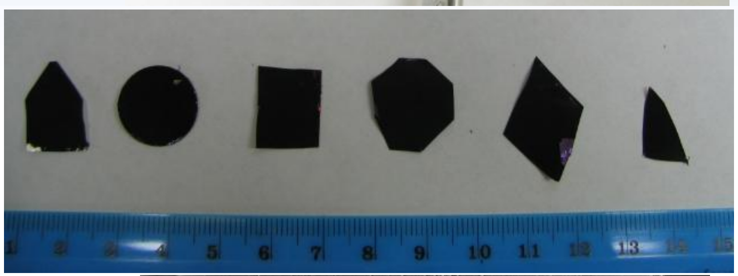


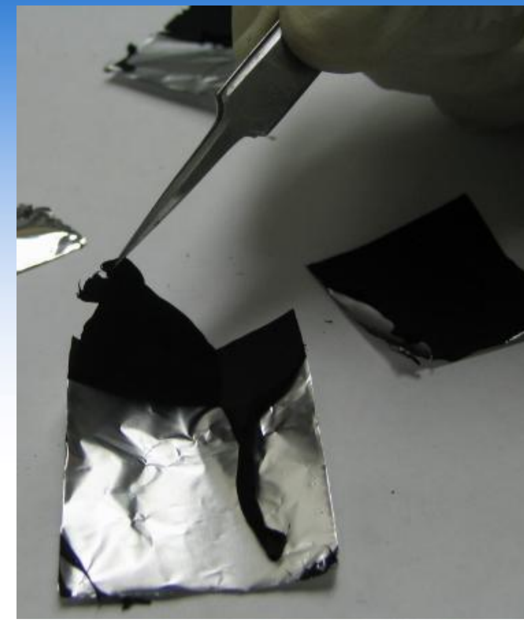


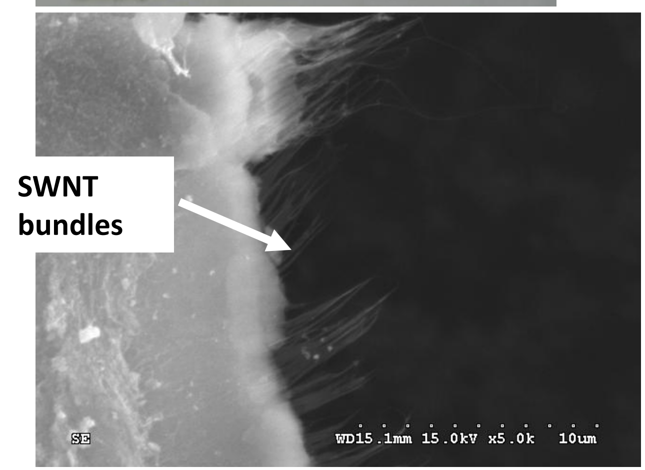
Surface area of SWNT film: 700 m^2/g

- Characteristic of SWNT film: demonstrates structural combination of mesoporous and macroporous materials.
- Compared with nanoporous carbon materials, counterions are expected to easily and quickly reside at the SWNT electrode/electrolyte interface without having to enter the pores, leading to an exohedral supercapacitor with a higher power density feature.

Flexible, Machinable, Freestanding SWNT films







Hydrophilicity

Hydrophilicity Tuning

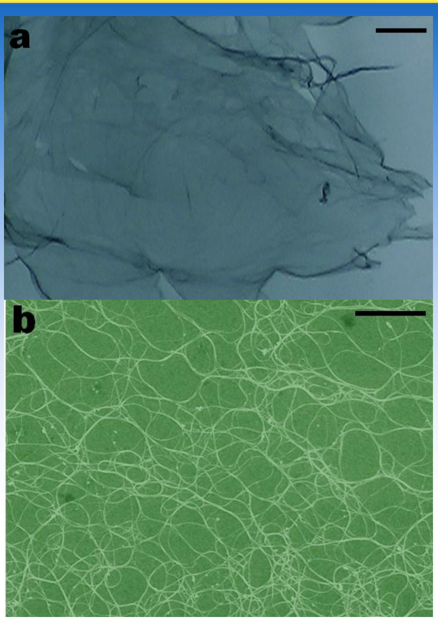
Hydrophobic

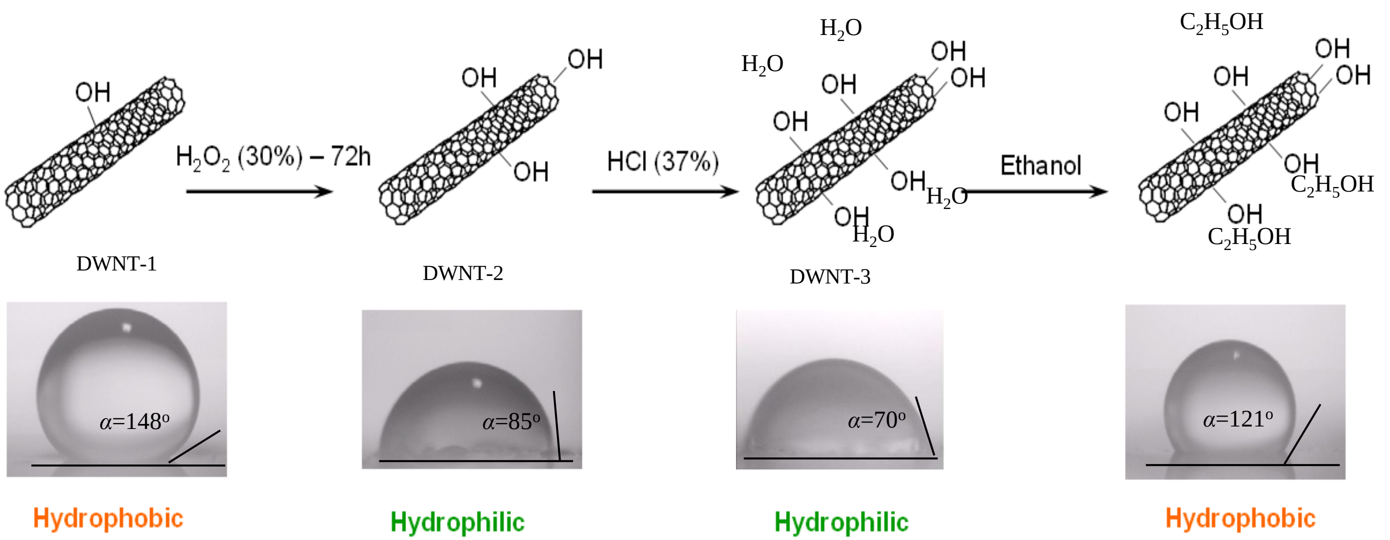
Hydrophilic

Wei, et al., Adv. Mater., 18, 1695 (2006).

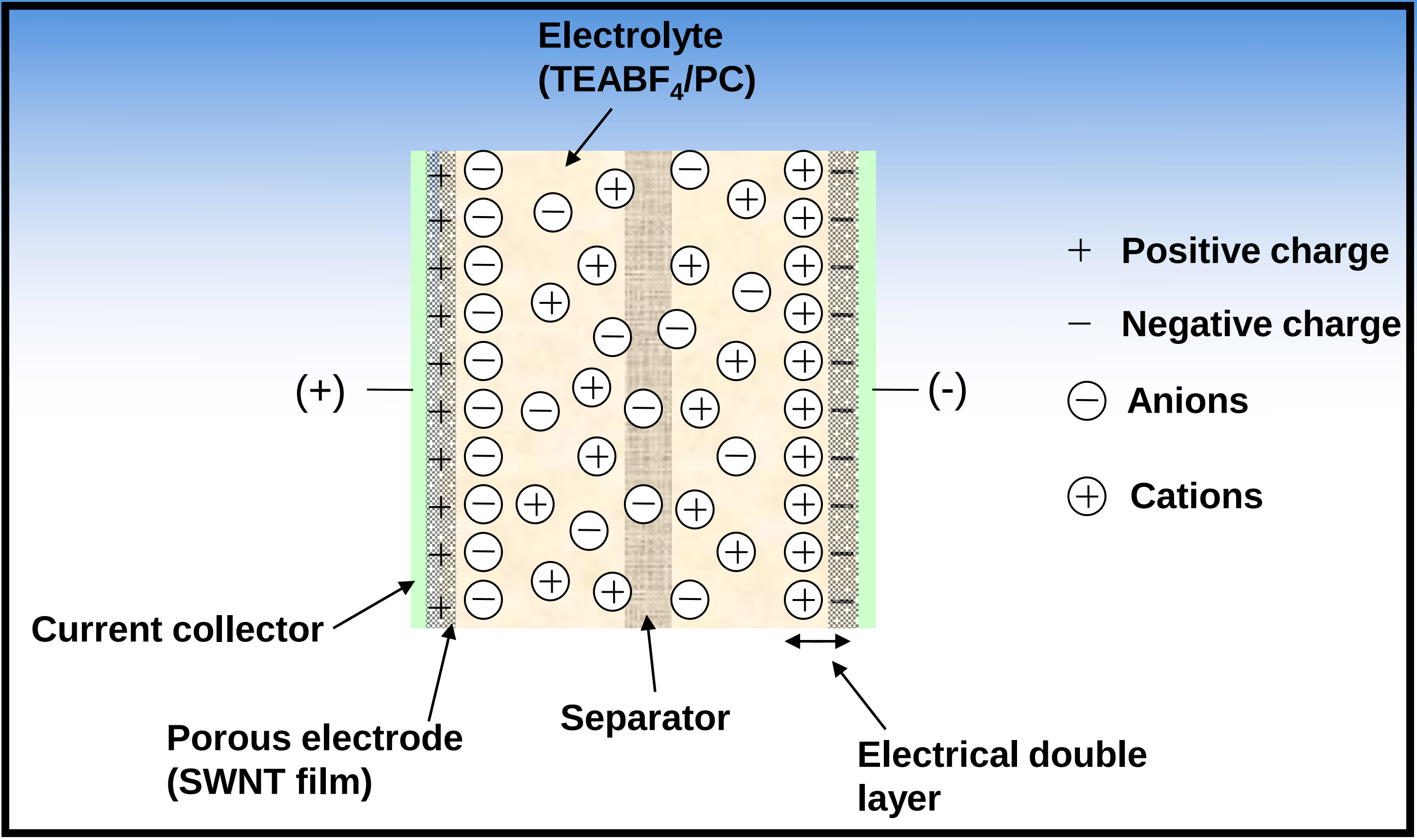
Purification

- **Heat treatment in air at 450 ^{0}C for half hour to remove amorphous carbon**
- **Treatment in 100% hydrochloric acid at room temperature for half hour to remove catalyst particles**





Schematic Representation of Electrical Double Layer Capacitor



- **Electrolyte: Tetraethylammonium tetrafluoroborate/Polypropylene carbonate**
- **Charge-Discharge cycles: Diffusion and charge accumulation near the electrodes**

Comparison of Li Ion Battery and Supercapacitor

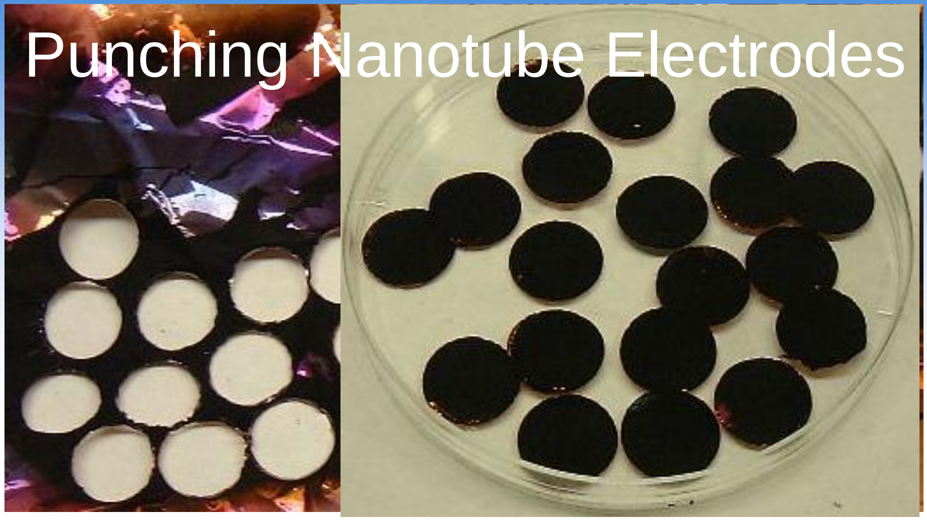
Rechargeable Li battery

- Involves chemical reactions
- Long duration charge discharge cycles (several hours)
- High energy density low power density device
- Low self discharge
- Life time: 1000 - 2000 cycles
- Typical energy density: 10 – 300 Wh/kg
- Typical power density: 100 – 1000 W/kg

Supercapacitor

- No major chemical reactions involved
- Short duration charge discharge cycles (few seconds to minutes)
- High power density-low energy density device
- High self discharge
- Life time: hundreds of thousands of cycles
- Typical energy density: 0.1 – 5 Wh/kg
- Typical power density: 1000 – 1000,000 W/kg

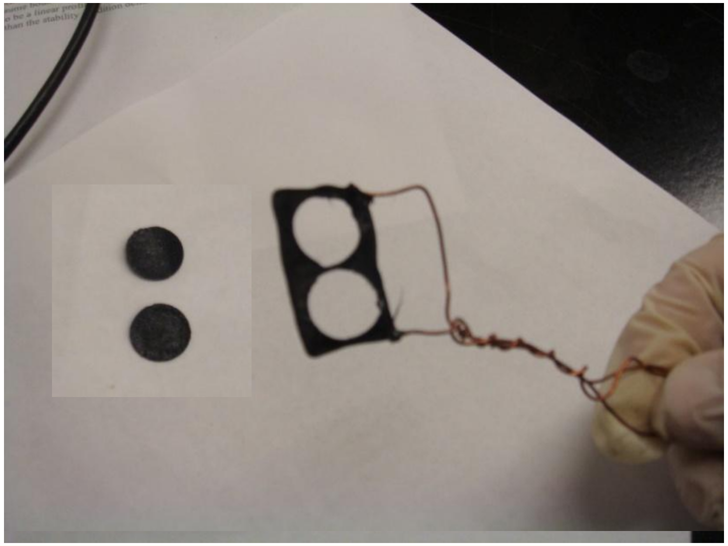
Flexible, Machinable, Freestanding SWNT films



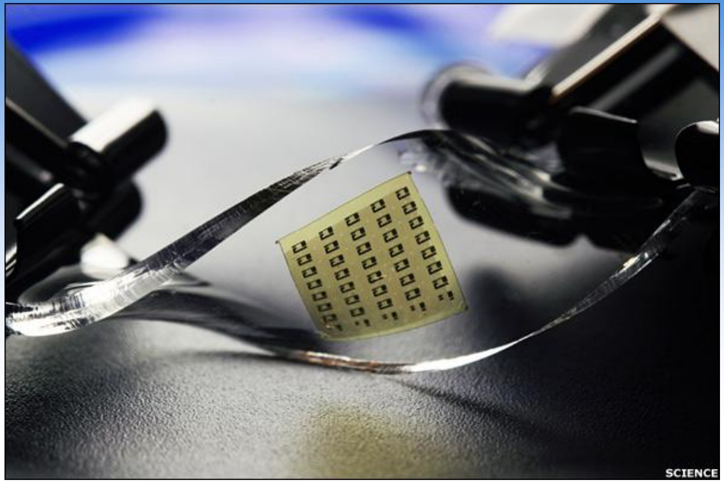
Purified SWNT films are dispersed in water and are deposited on a wire mesh to get a free standing film

↓

SWNT electrodes are directly obtained by punching using an arc punch with required diameter

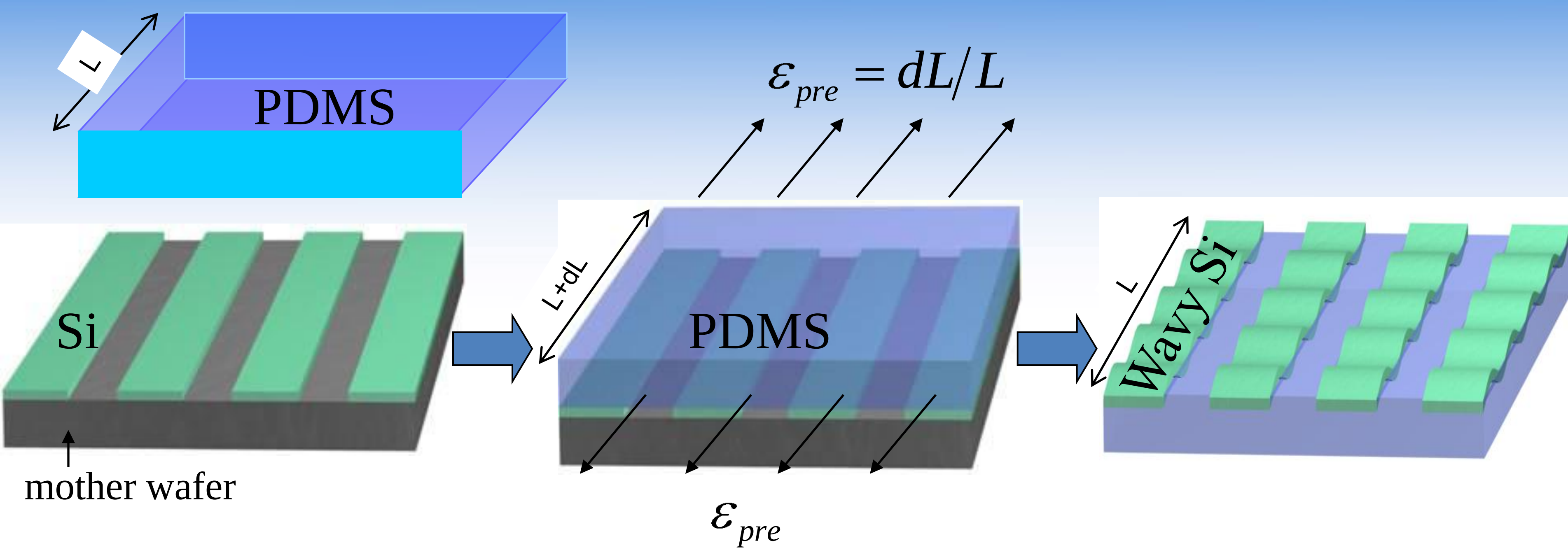


Motivation



Wavy Silicon Structures

Khang, Jiang, Huang, Rogers, *Science*, 2006



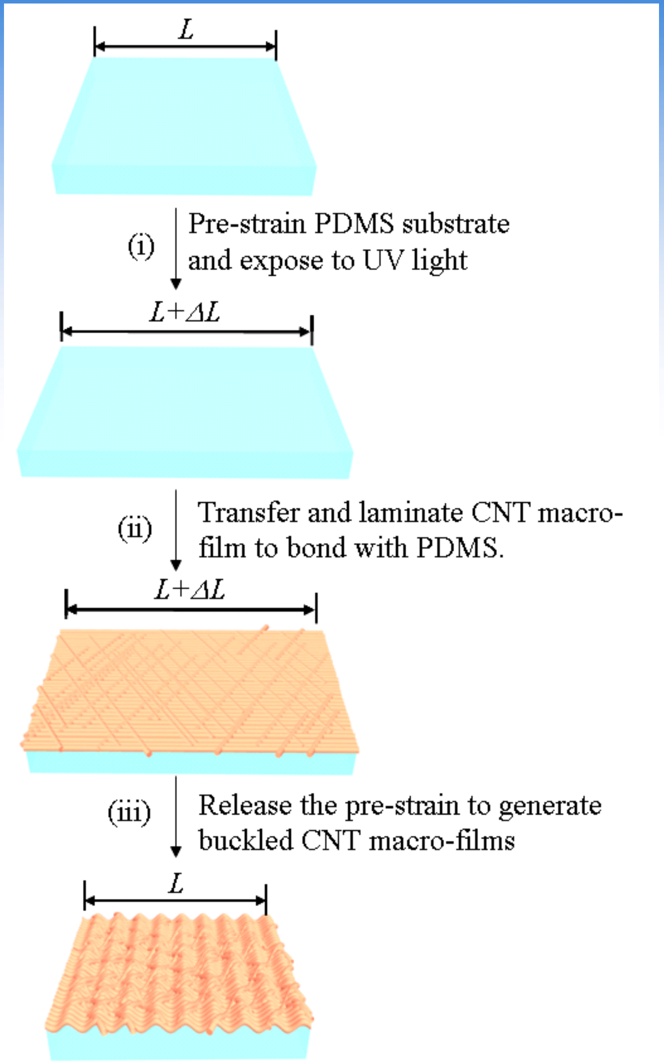
Fabricate thin ribbon Si device elements

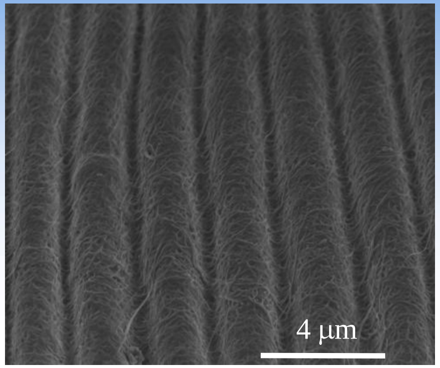
Bond elements to prestrained elastomeric substrate PDMS

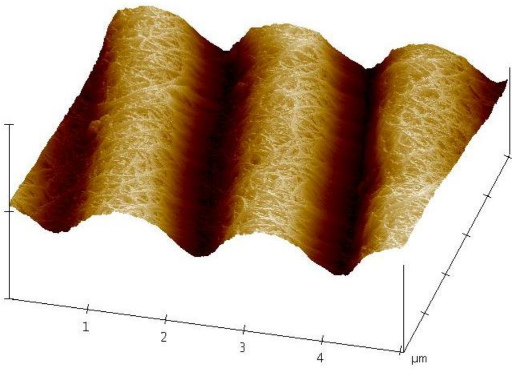
Peel back PDMS; flip over

- Flat Si ribbon becomes buckled due to pre-strained PDMS

Buckled CNT-Macro-films on PDMS







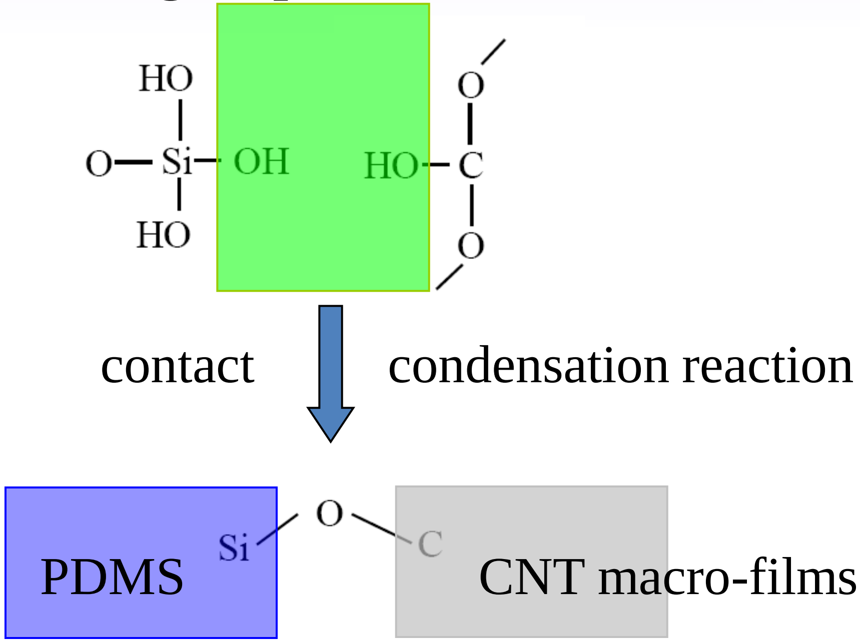
***Adv. Mater.*,** 2009.

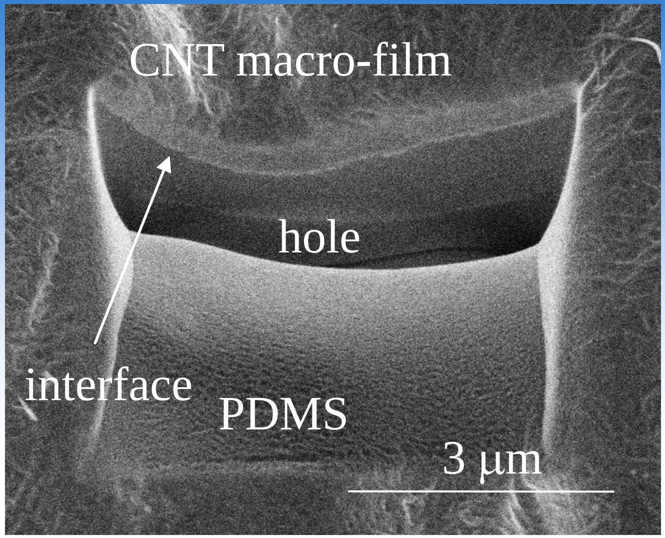
Interface Bonding

- Surface treatment on PDMS substrate

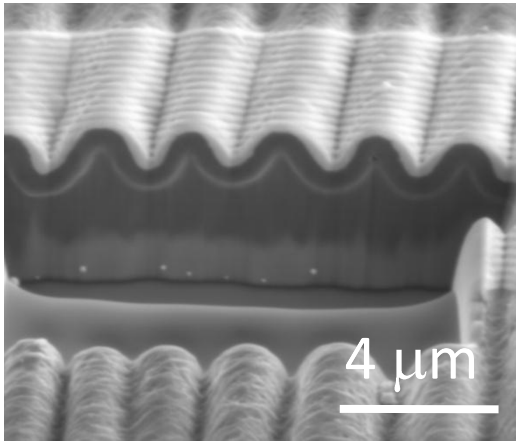
  Ultraviolet/ozone (UVO) treatment to oxide PDMS surface and generate active OH- group

- Functional group in CNT macro-films

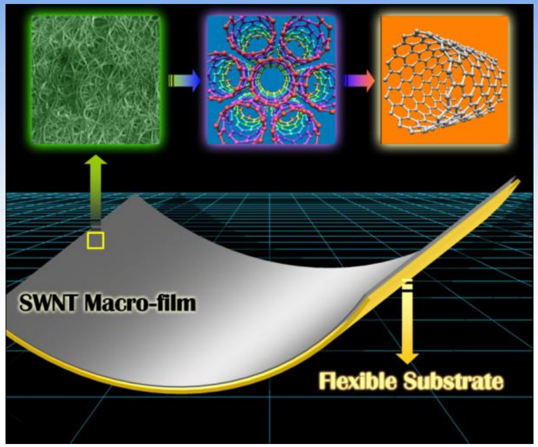


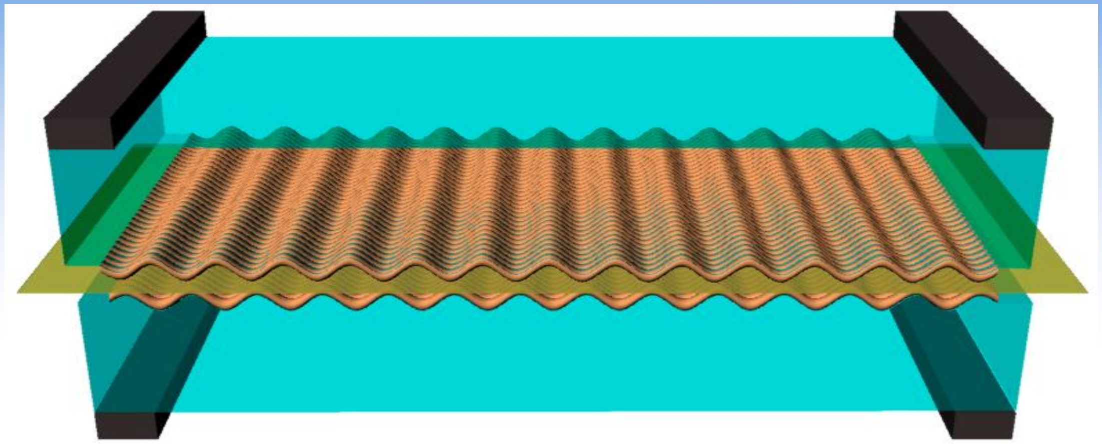


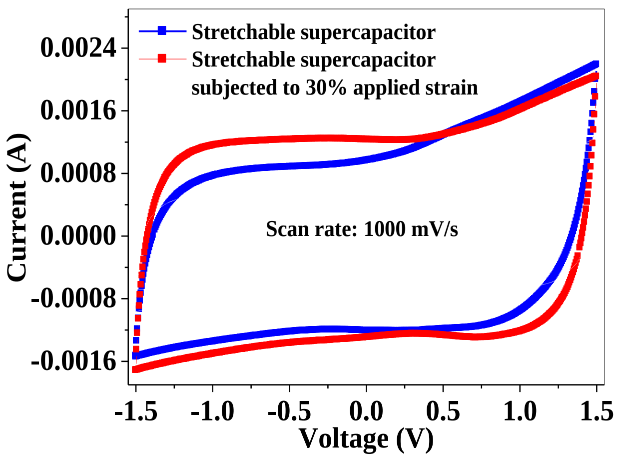
FIB/SEM image

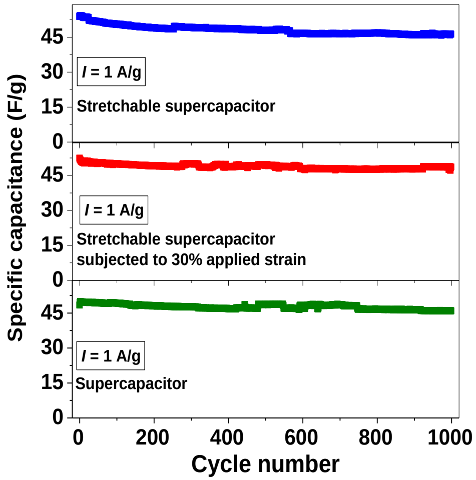


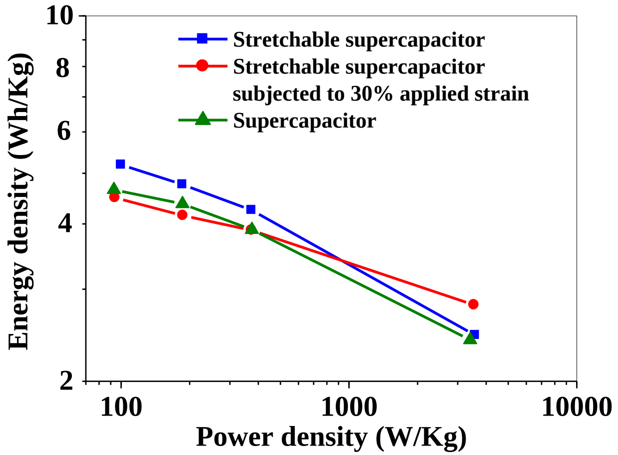
Reversibly Stretchable Supercapacitor



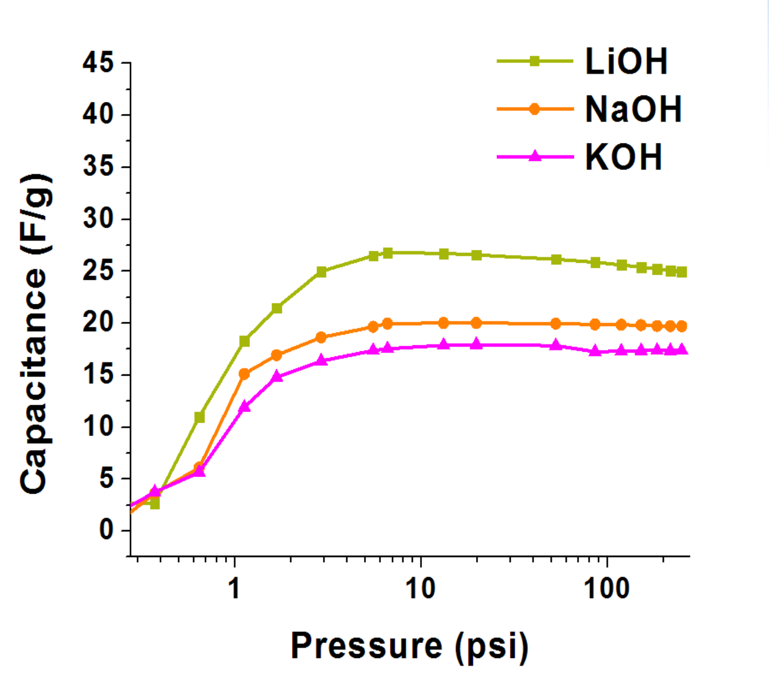


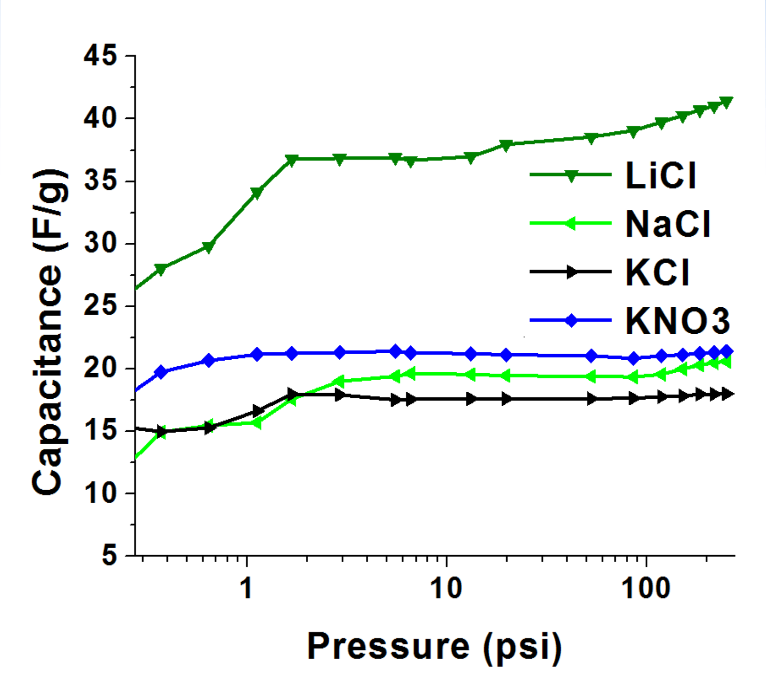






Wettability and Ion-size Effect of Different Aqueous Electrolytes



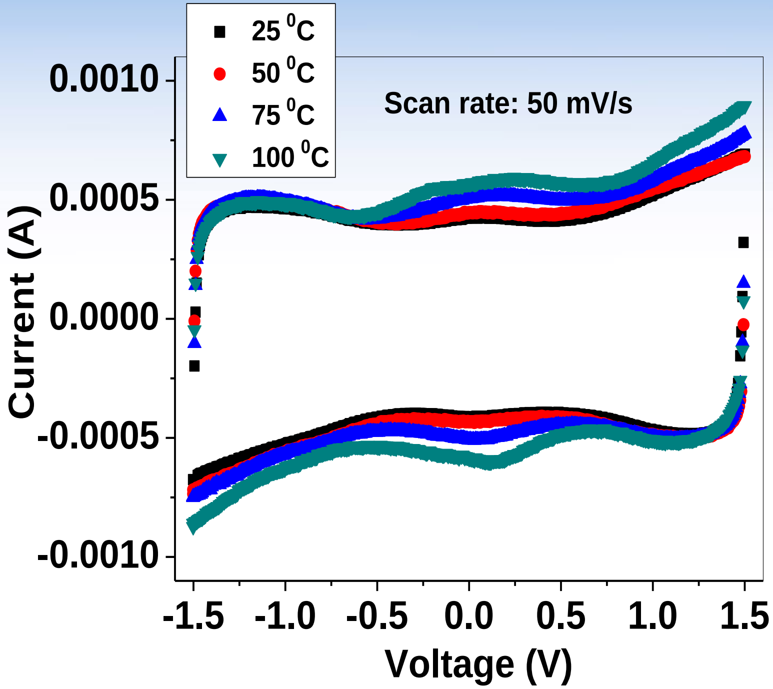


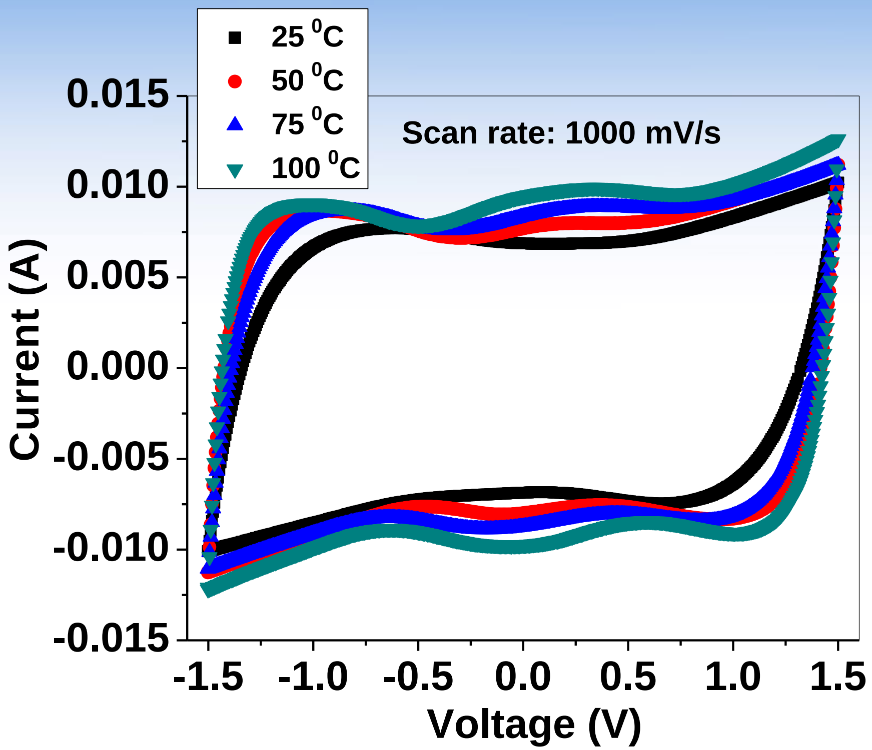
ACS Nano, 2010

Knee frequency (experiment data) vs. Pressure

Pressure (psi)	Knee frequency (Hz)						
	LiOH	NaOH	KOH	LiCl	NaCl	KCl	KNO_3
0.37	0.16	0.16	0.16	4	4	13	4
1.12	0.85	0.85	0.85	13	13	34	13
6.58	41	41	41	72	72	72	72
19.74	126	126	126	385	385	385	385
118.44	672	672	672	672	672	672	672
250.04	**1172**	**1172**	**1172**	**1172**	**1172**	**1172**	**1172**

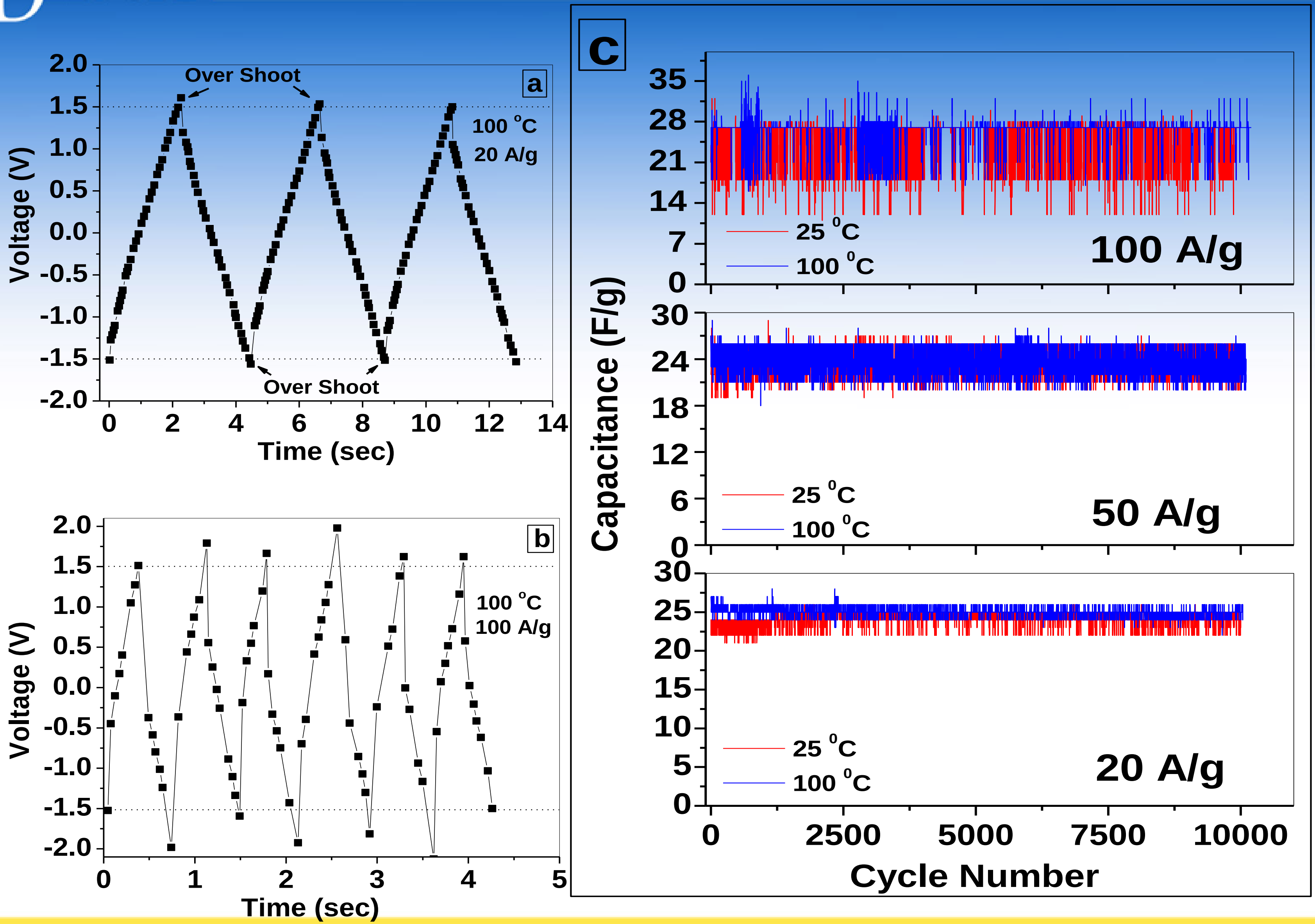
Capacitance obtained from CV at Different Temperatures with Different Scan Rates



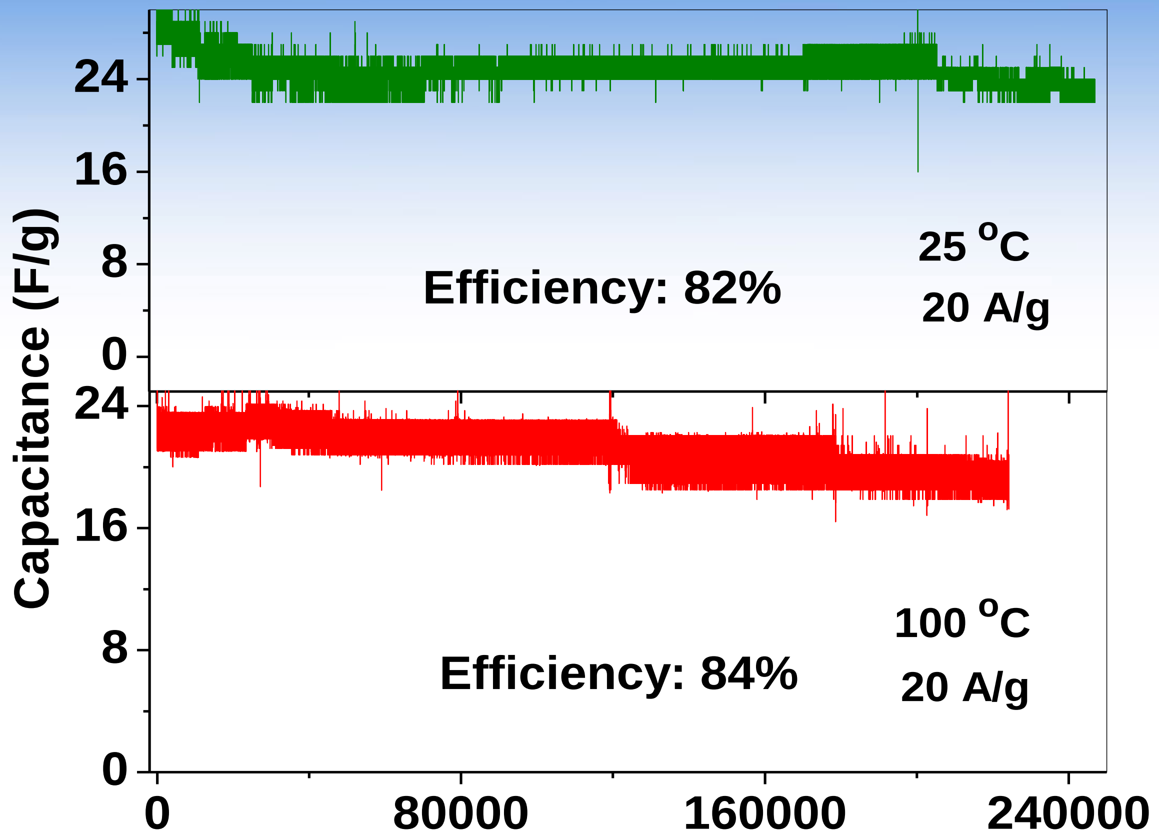


Masarapu, et al., ***ACS Nano***, 2009

Super-high Power Density



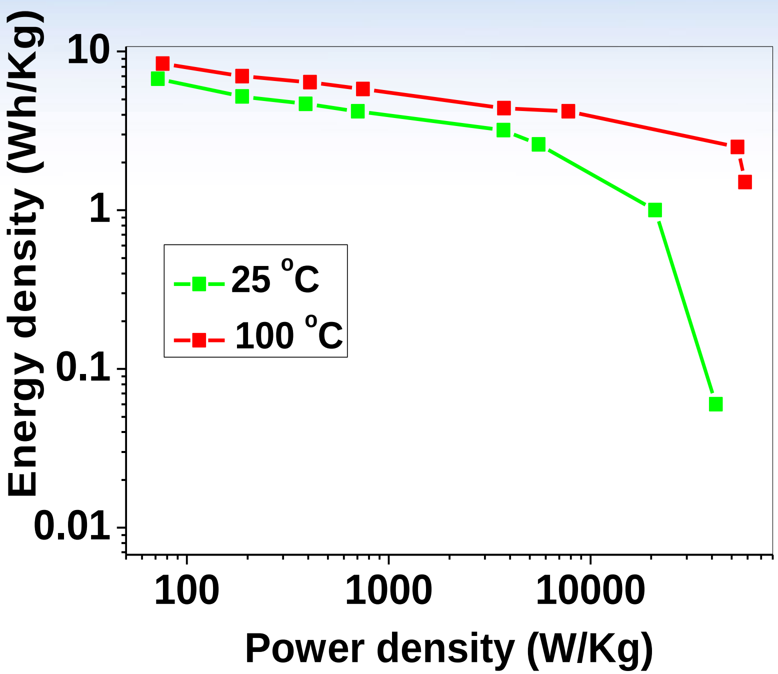
Long Lifetime Supercapacitors at a High Temperature



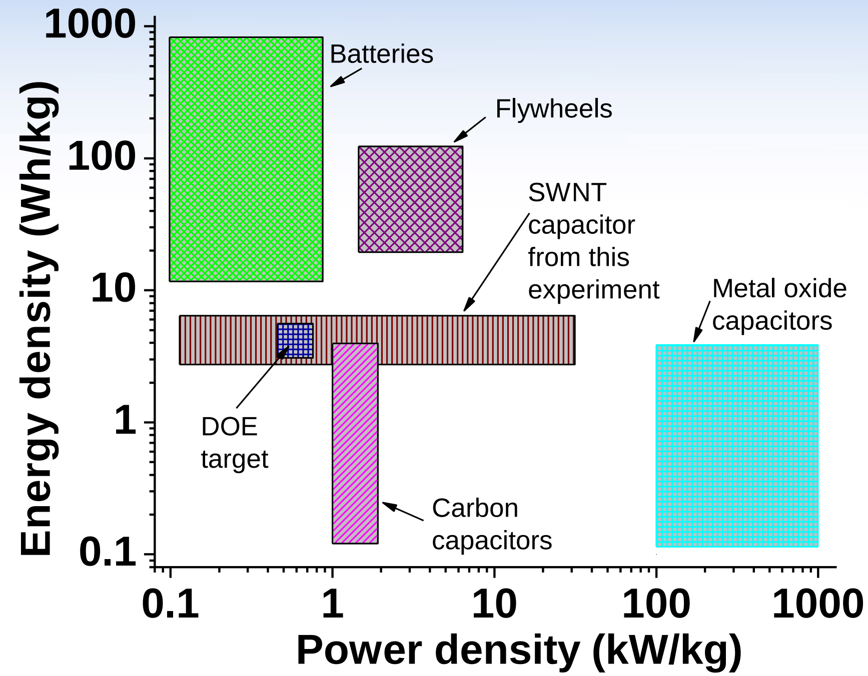
Masarapu, et al., ***ACS Nano***, 2009

Ragone Chart

SWNT Supercapacitor

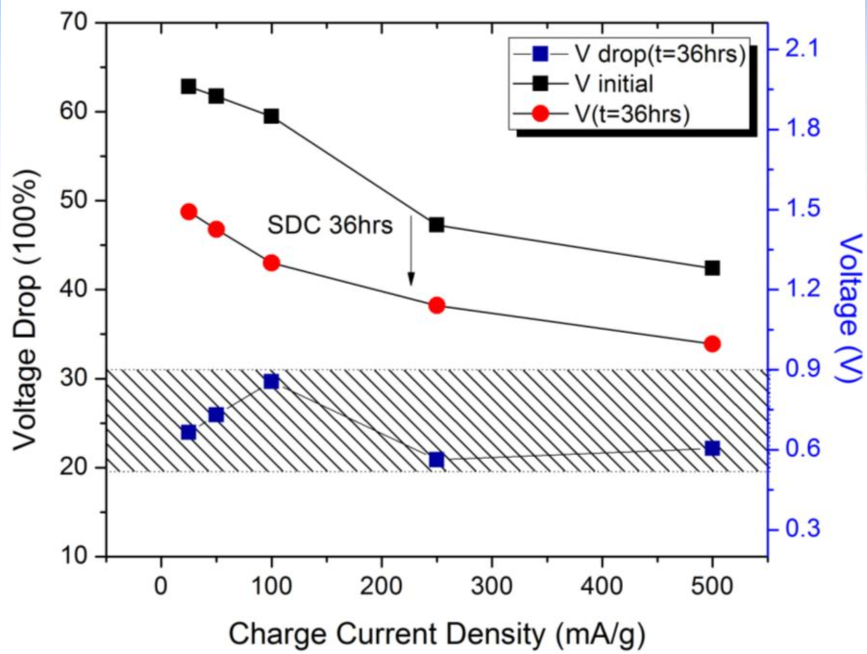


Department of Energy (DOE) Target

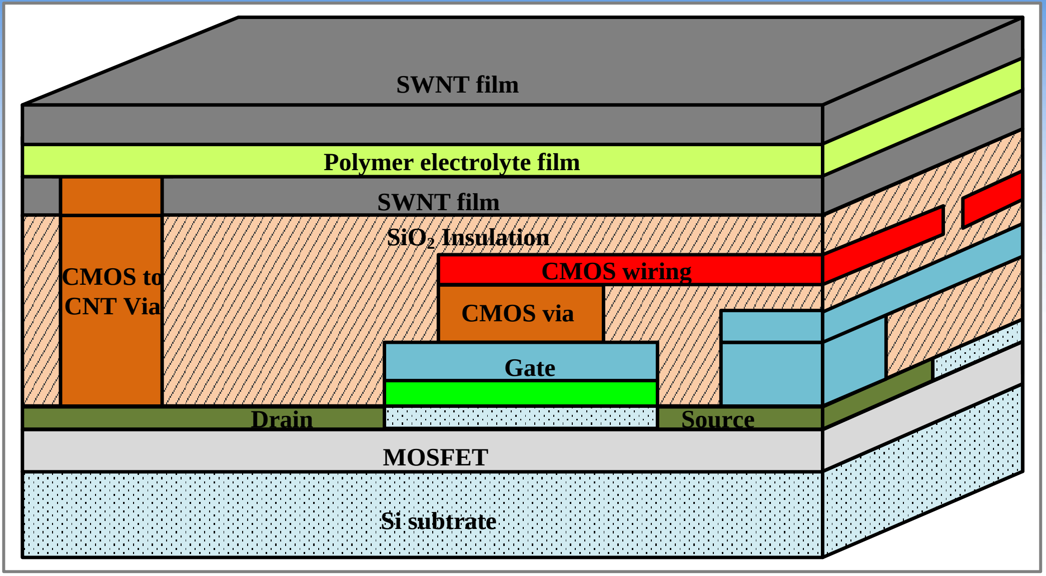


The best energy retention capability of SCs

We have studied and understood that there are different mechanisms over self-discharge of capacitors, indicating combination of electrode/electrolyte governs the self-discharge mechanism. By selecting the right combination of electrode/electrolyte, more than **70%** charged energy retained after self-discharge for **36 hrs**



Heterogeneous Integration of CNT supercapacitors on CMOS process

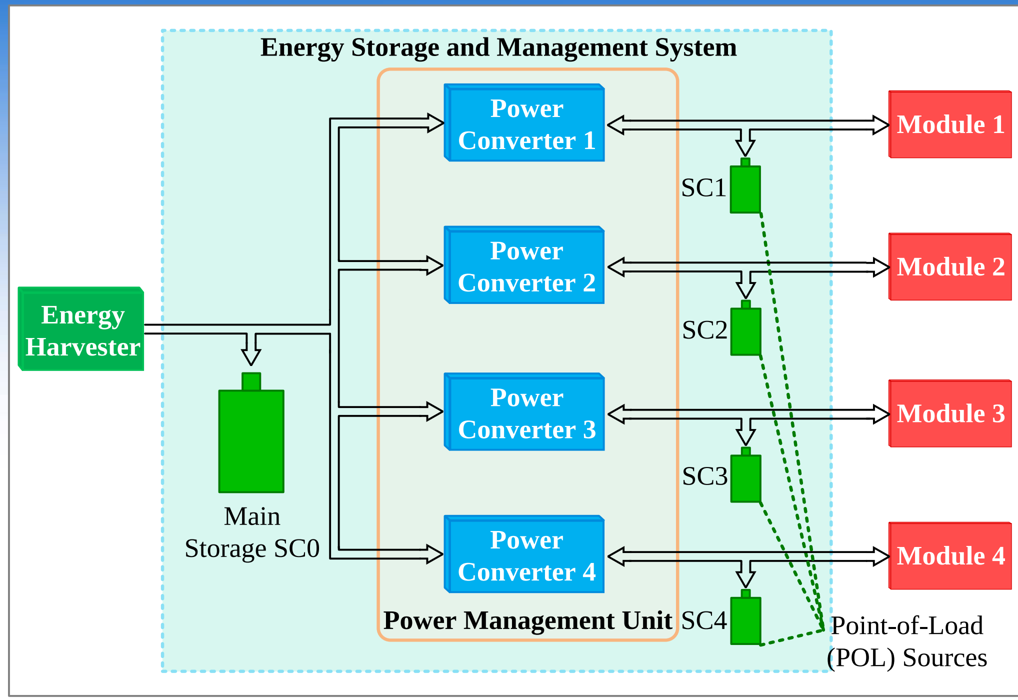


The CNT SCs will be attached to the top of CMOS chip with interconnection between them, using one extra post-CMOS process. Therefore, it will provide a new low-cost manufacturing method for highly functional and compact systems.

Fully on-chip capacitive devices for SoC design

Besides acting as the energy sources, CNT SCs can also be used to meet the requirements on large capacitor design for signal processing, sample and hold, frequency compensation, noise decoupling, tuned resonator, memory design and so on, enabling fully on-chip capacitive devices.

New Energy Storage and Management Structure



Energy Storage and Sources: a main storage SC0 and four point-of-load (**POL**) sources, SC1~SC4.

PMU: hardware-based executing platform for power management, mainly composed of power converters, i.e., DC-DC converters. **(four modules are shown as an example)**

Features:

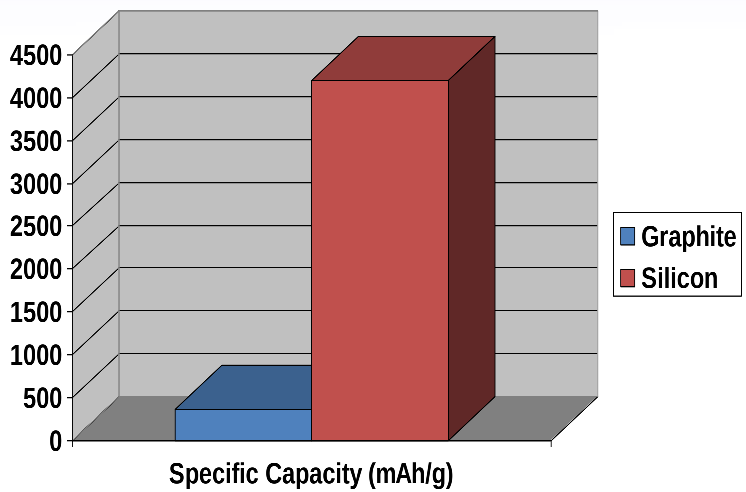
Multi-energy-source structure: SC0~SC4 are all energy sources for the MSN, which provides the system with flexibility to assign appropriate voltages to different functional modules. .

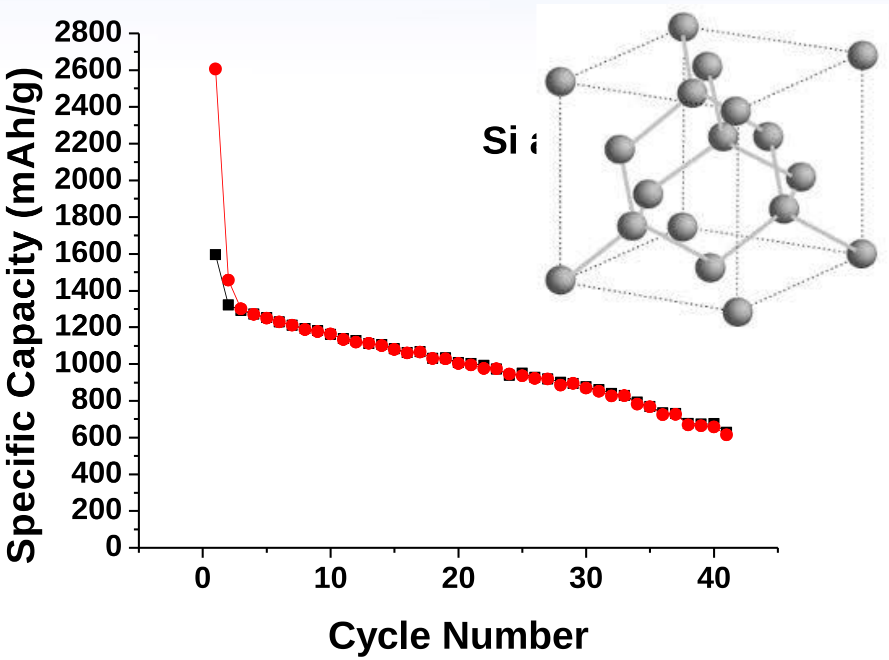
Global power management capability: a global energy management strategy can be introduced to deliver energy among energy storage and sources.

IEEE TRANSACTIONS ON POWER ELECTRONICS, 2010.

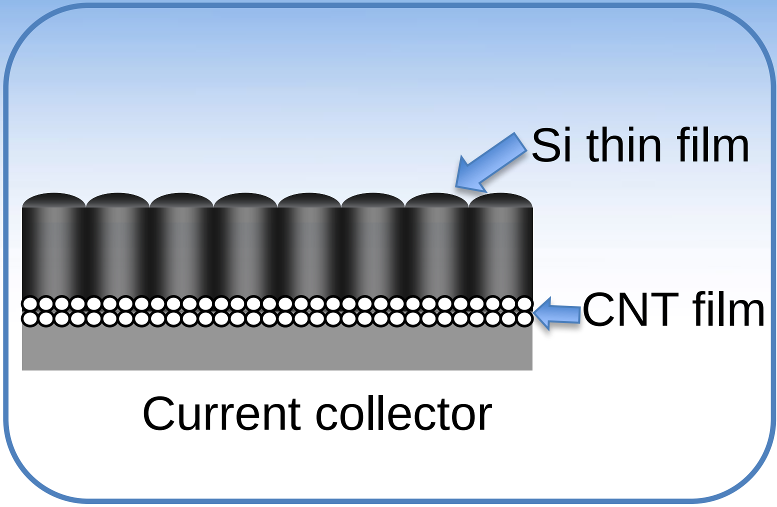
Si: An Excellent Material for Li-ion Batteries

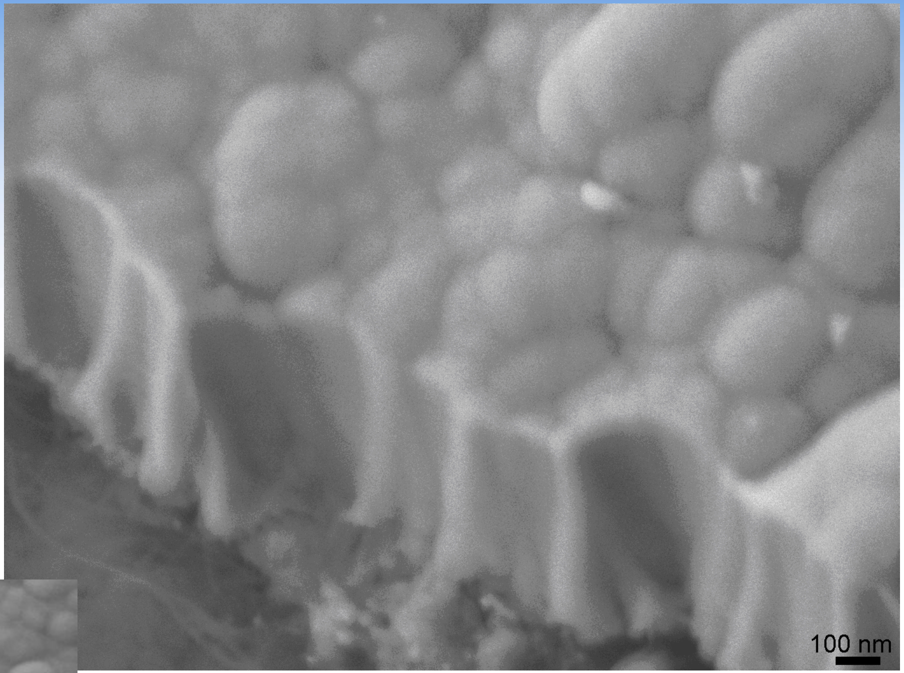
- Si makes it an excellent candidate for electrode materials in Li-ion batteries. However, volumetric change (400%) upon insertion and extraction of Li ($Li_{22}Si_5$ alloy), resulting in pulverization and early capacity fading.

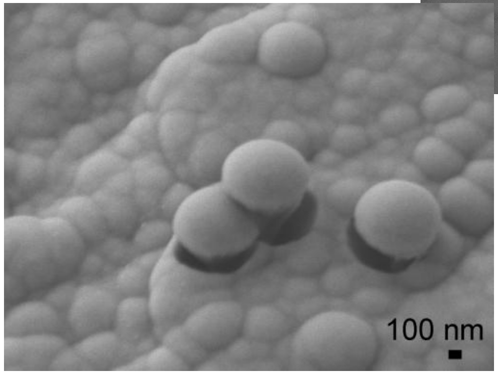




Tandem Structure Formation

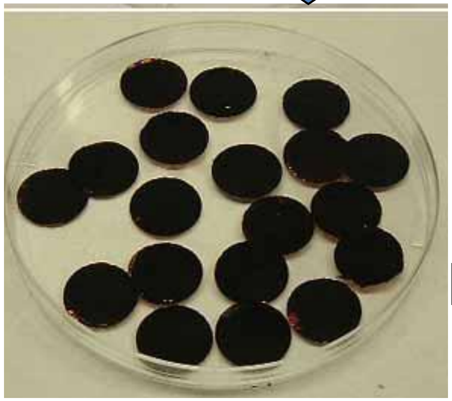




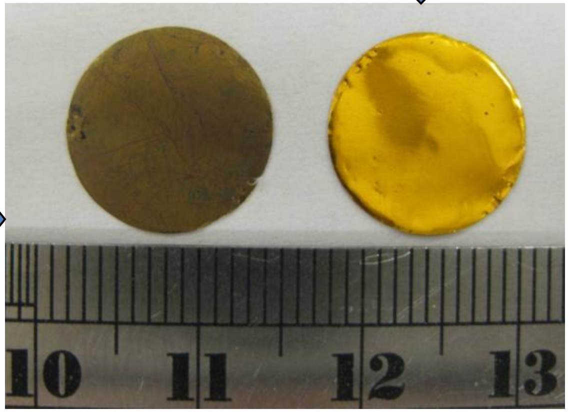


University of Delaware

Electrode Preparation



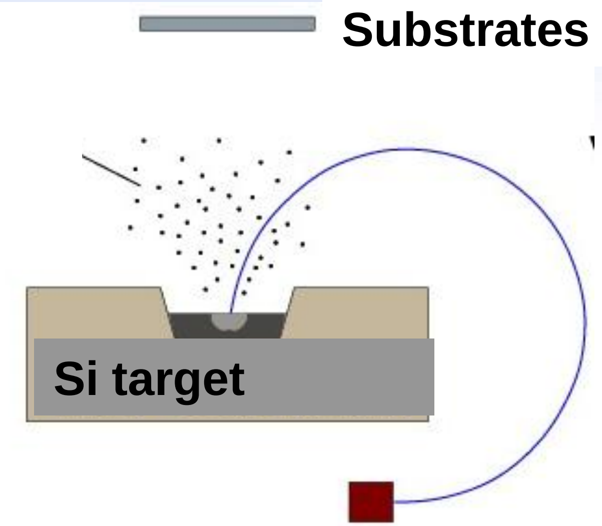
Vapor



Tandem Structure Si-Cu

Si-SWNT-Cu

High-Vacuum Electron-Beam Evaporation

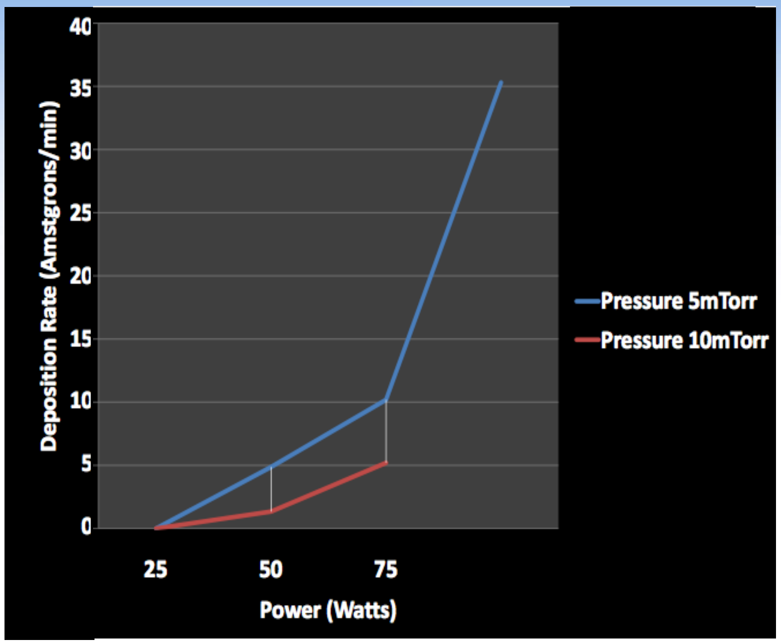


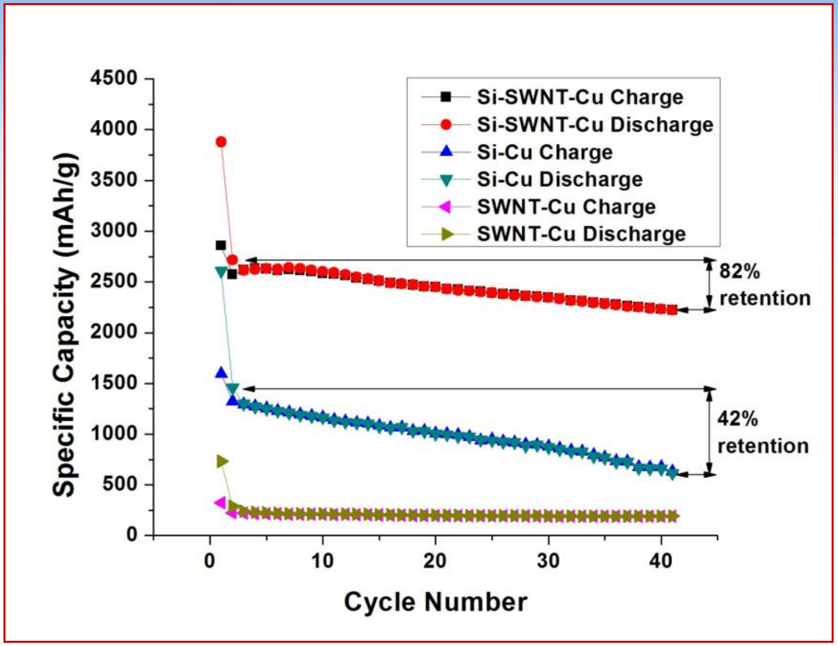
Electron Source

ACS Nano, 2010

Preliminary Results

Increased Energy Density by 3.6 times

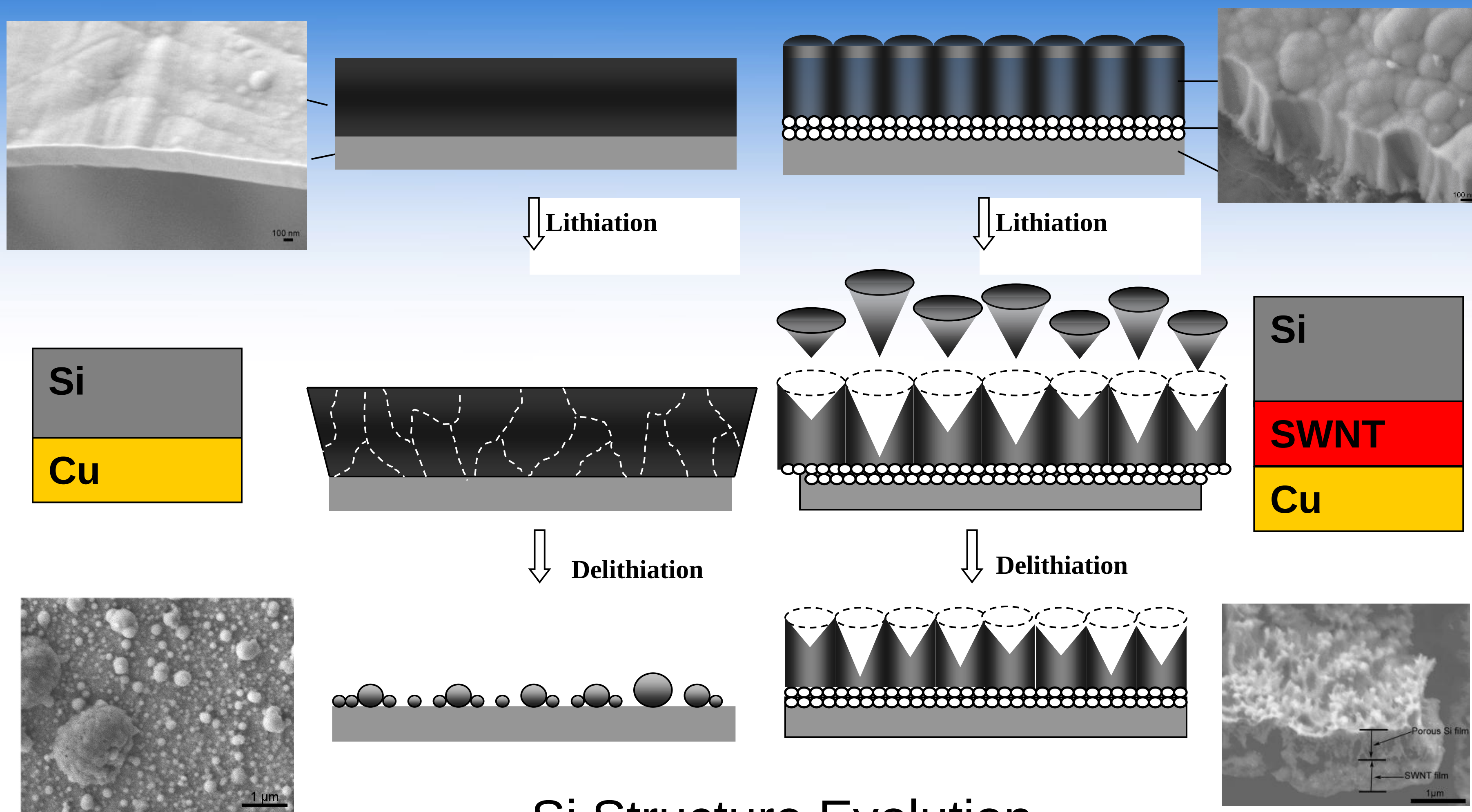




Si film thickness easily controlled within 1 nm, with ultimate thickness up to 1-2 µm achievable

Improved Cycle Life

Preliminary Results



Si Structure Evolution

Conclusions

- Different supercapacitors can be assembled that demonstrated different functions for promising applications in electronics:

High Flexibility/stretchability

High operation temperature

Long lifetime

Super-high power density

Mechanical robust under compression

High energy retention with small leakage

CNT Power Sources for: