# Plasma-functionalization of MWCNTs

*for energy storage, conversion and transport*

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Director, Centre for Innovation in Energy Storage and Conversion

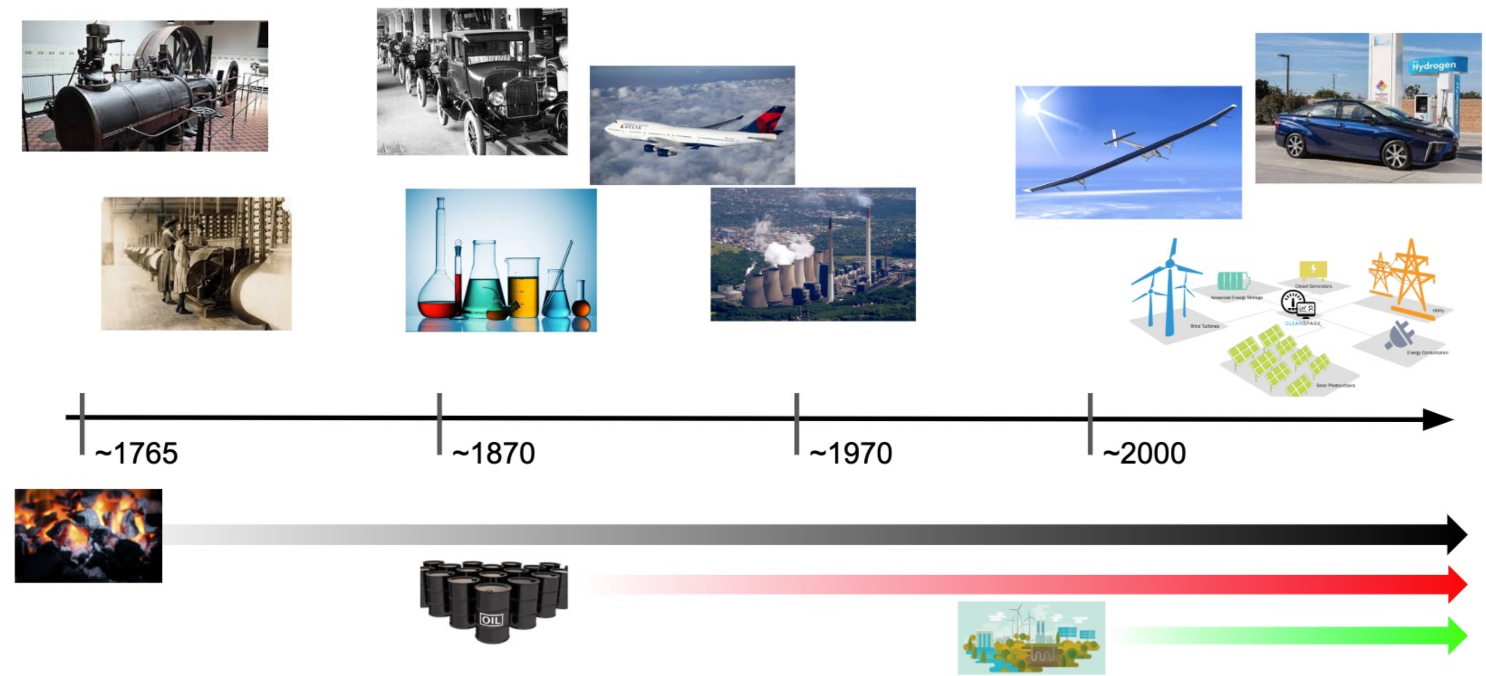
# Outline

- Context of Research
- MWCNT synthesis / CVD
- MWCNT functionalization / PLA-PECVD
- Applications: Solar thermal nanofluids, Electrocatalysts & Supercapacitors
- What’s next?

# CPPE

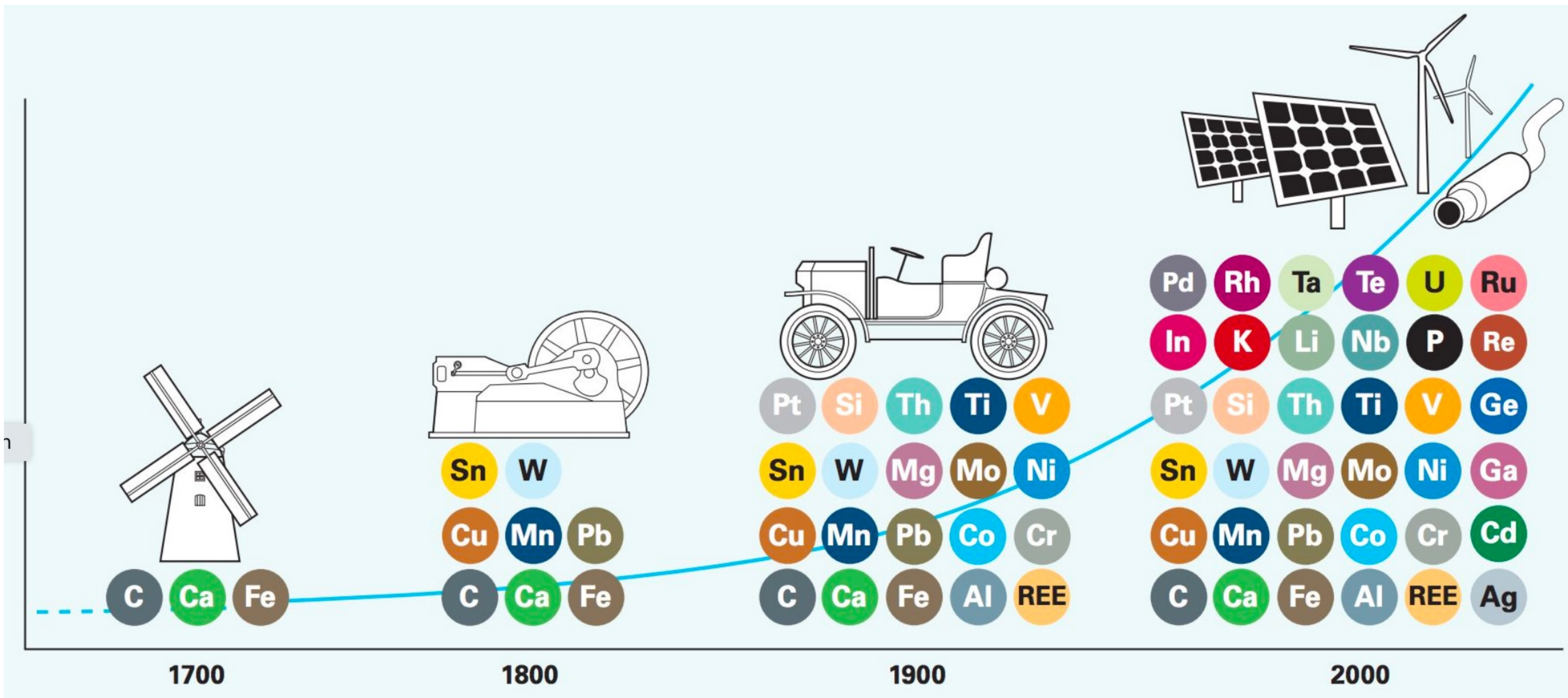
- Plasma processing research began in 1971 at McGill
- CPPE created in 2021 from the merge of the Plasma Processing Laboratory and the Catalytic Process Engineering laboratory
- Two professors, more than 15 graduate students and interns
- Active collaborations with national laboratories, private sector and international research laboratories
- Engaged in the development and understanding of catalytic and plasma processes, reactor engineering and material synthesis.

# Context of Research




Fossil fuels have driven our economy for more than 250 years / Transition with stranded assets
Massive electrification is underway / Process electrification and electrical energy storage are bottlenecks

# Context of Research

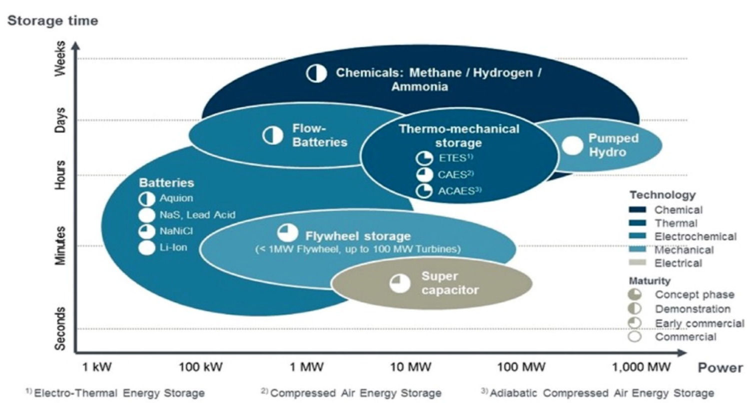



Energy transition ⇔ Material Transition

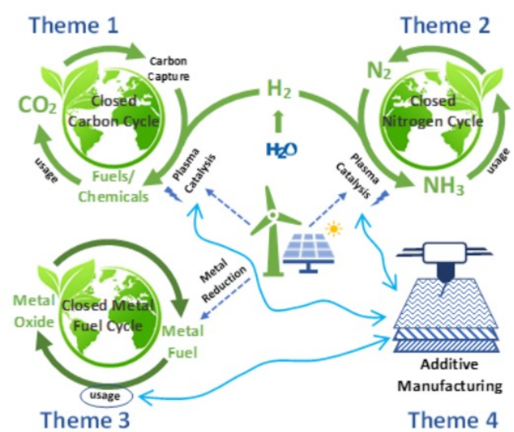
# Context of Research

Bases: Process electrification through plasma processing

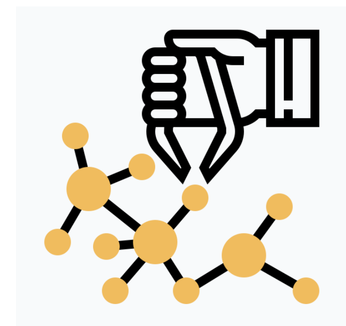
Materials and processes for sustainable engineering




Renewable energy storage




Circular Fuels



Nanomaterials at work

# Why plasma?

Science

- Access to energy levels not otherwise reachable
- Unique rxn environment for gas conversion and nanomaterial synthesis
- Moving away from thermochemical (equilibrium) processes (fossil fuel legacy)

Engineering

- Direct utilization of renewable electricity
- No solvent / Dry processes
- Reactor miniaturization and scale-up through parallelization
- Fast light-up/turn-down, decentralized on-demand production

# Electrical power deposition <=> Plasma chemistry

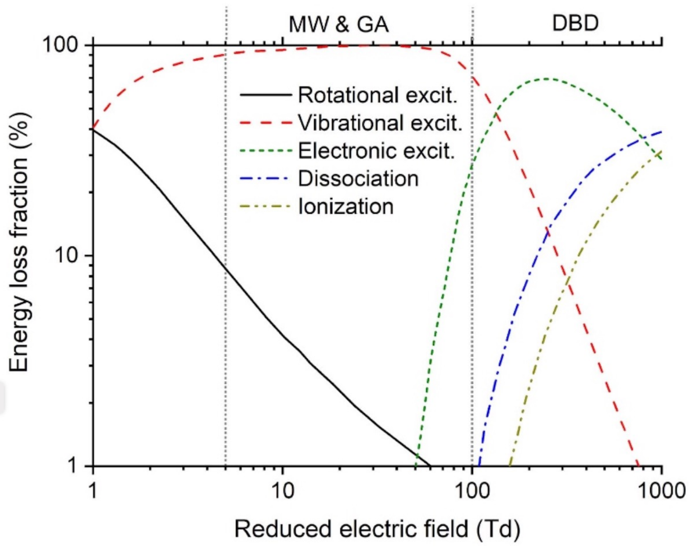
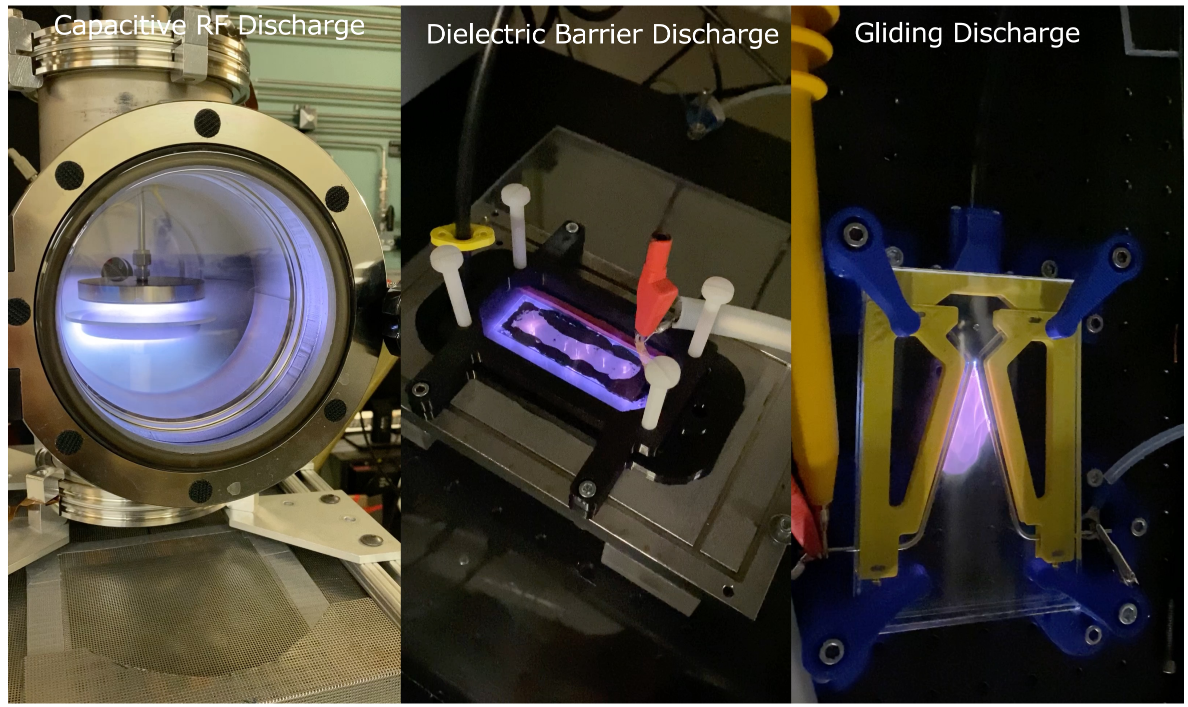


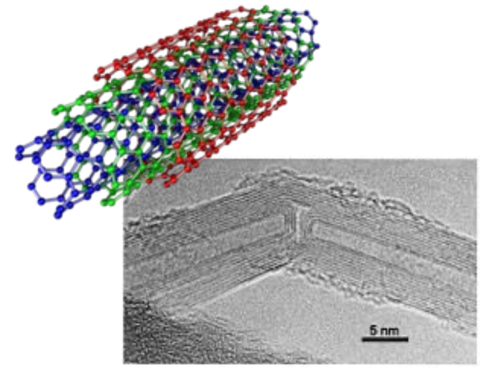

**Figure 17.** Fraction of electron energy transferred to different channels of excitation, and ionization and dissociation, of $N_2$, as a function of the reduced electric field. The region between the two vertical dashed lines, i.e. between 5 and 100 Td, corresponds to gliding arc (GA) and microwave (MW) plasmas, while the region above 100 Td corresponds to a DBD. Adapted with permission from [19]. Copyright (2018) American Chemical Society.

Bogaerts *et al.*, "The 2020 plasma catalysis roadmap," J.Phys. D: Appl. Phys. 53 p. 443001



# Why MWCNTs?

- Elongated nanostructures, high surface area
  (5-50 nm in diameter, $\mu$m in length)
- Relatively inert, and easy to functionalize
- Can be grown directly on some metals
- Broad UV-vis absorption spectrum
- Excellent mechanical/electrical properties
- Robust scaffold material
- Effective support for imaging other nanomaterials




Source: wiki MWCNT

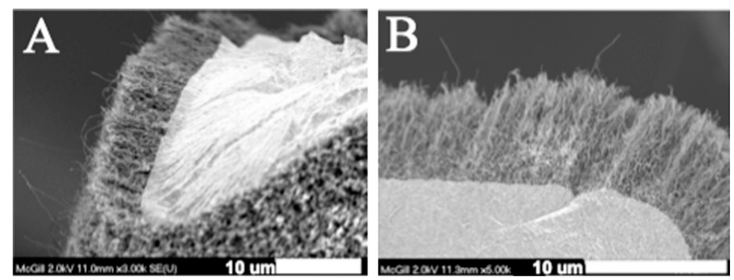
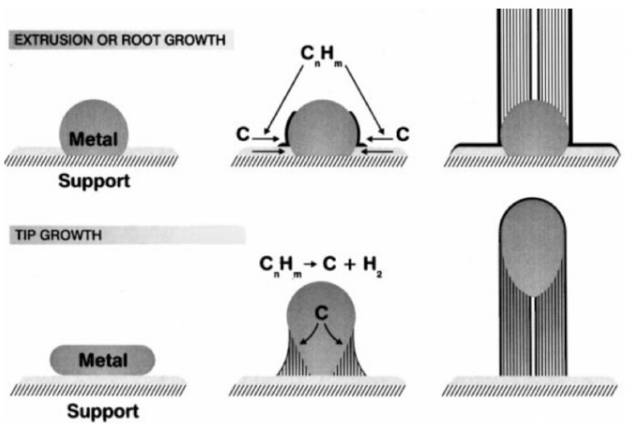



**Fig. 10 – Profile image of the CNT forest covering a fractured SS wire of larger diameter.**

CARBON 63 (2013) 348–357

# MWCNT Synthesis / CVD

- Direct growth on commercial SS mesh
- Pre-heating at 700 ºC in air to expose Fe islands (catalysts)
- Chemical vapor deposition in $Ar/C_2H_2$, 2 min gas injection




Sinnott, S.; Andrews, R.; Qian, D.; Rao, A.; Mao, Z.; Dickey, E.; Derbyshire, F. Model of Carbon Nanotube Growth Through Chemical Vapor Deposition. *Chem. Phys. Lett.* 1999, *315*, 25–30.



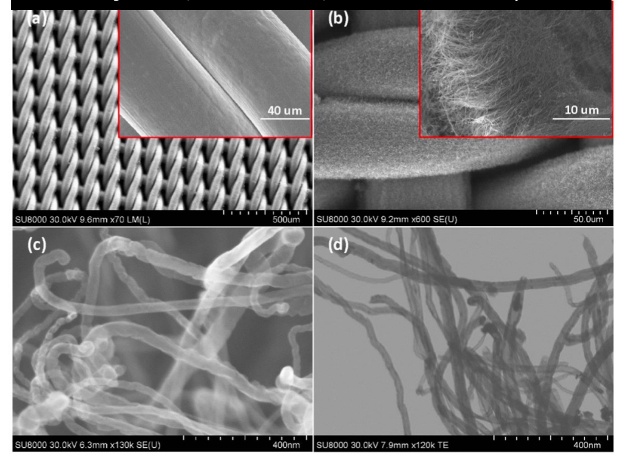



**Figure S5-5.** SEM images of (a) SS mesh, (b and c) MWCNTs directly grown on SS mesh, and (d) STEM image of MWCNTs.



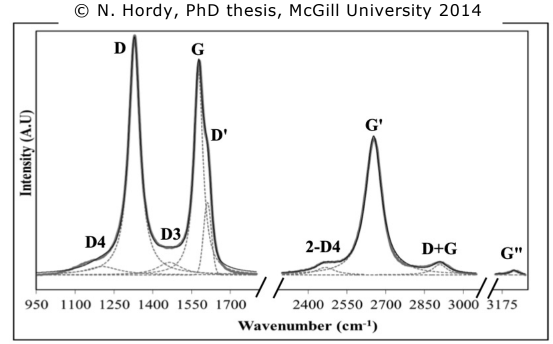



Figure 7-4: Raman spectrum of the CNTs with peak deconvolution measured using 1.96 eV excitation source.

# MWCNT Functionalization using PLA-PECVD

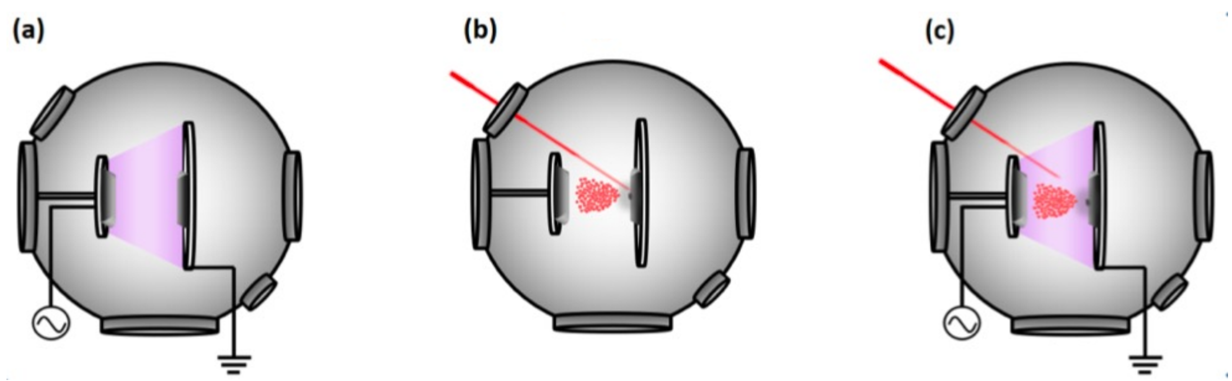
PECVD: Plasma-enhanced chemical vapor deposition

- Film deposition (nm), grafting of functional groups from gaseous precursors
- Plasma assists precursor decomposition, surface activation & cleaning

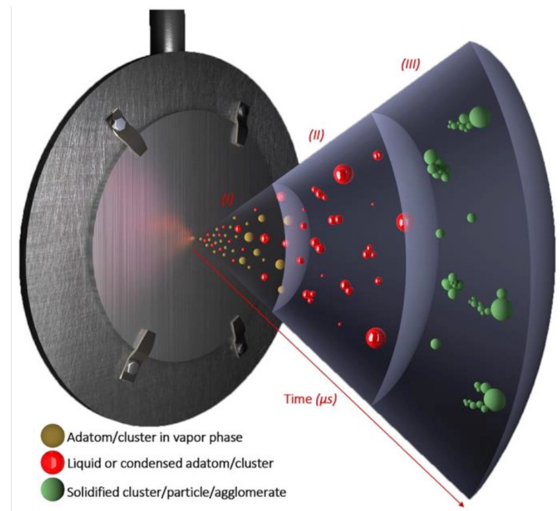
PLA: Pulsed laser ablation/deposition

- Films and coatings from solid targets
- Low pressure: continuous films
- High pressure: nanoparticles, granular coatings with high specific areas
- Ultralow nanoparticle loadings

# MWCNT Functionalization / PLA-PECVD

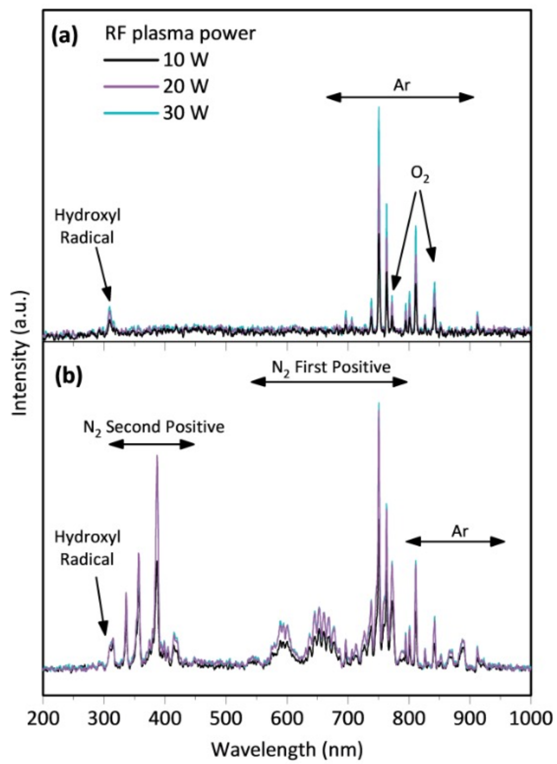


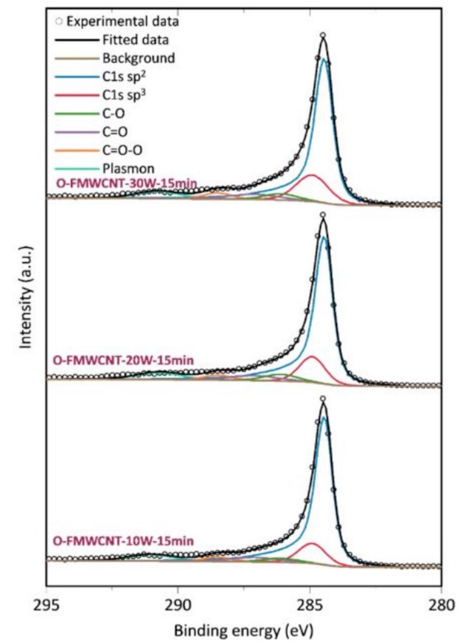

PECVD PLA PLA-PECVD

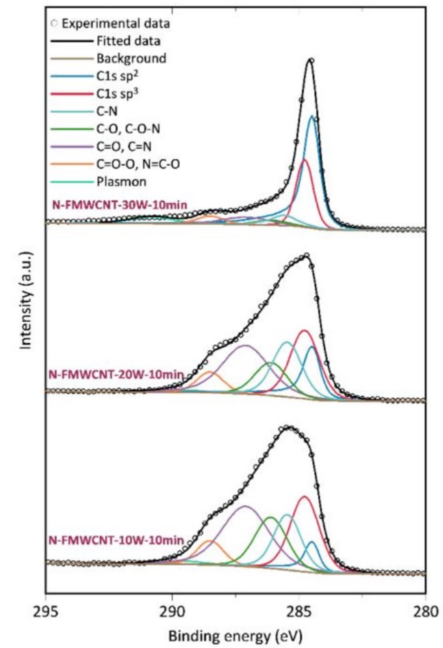


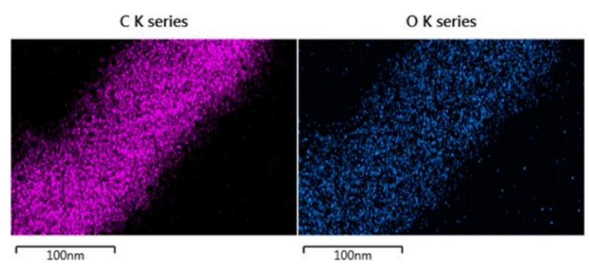

NP synthesis by PLA

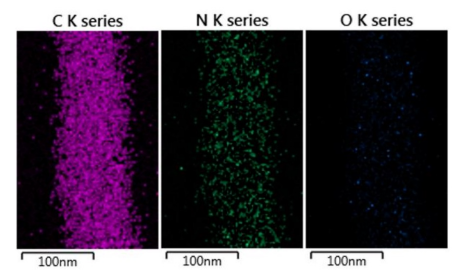
# MWCNT Functionalization

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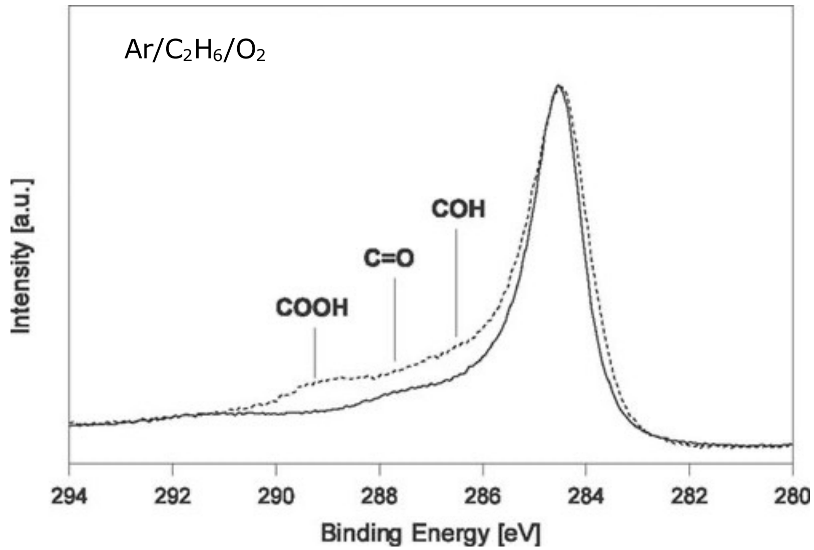
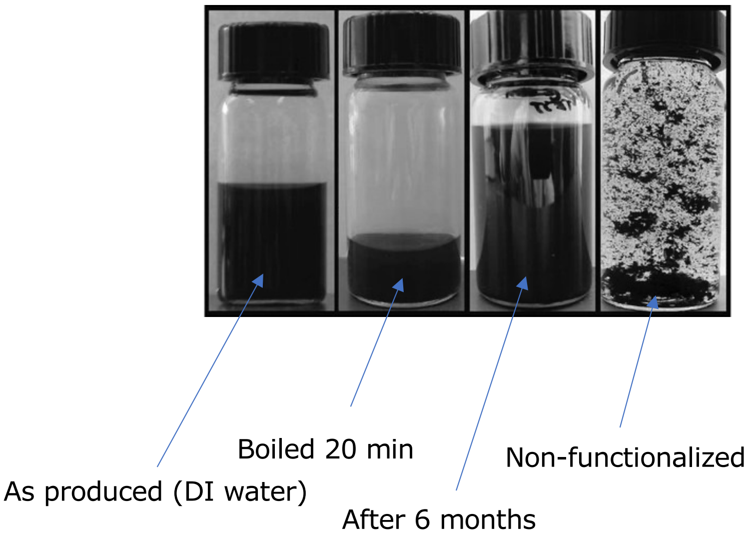
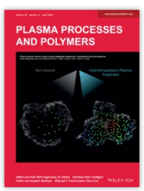
J. Phys. D: Appl. Phys. **55** (2022) 194001 (12pp)

# MWCNT Functionalization – Oxygen functionalities





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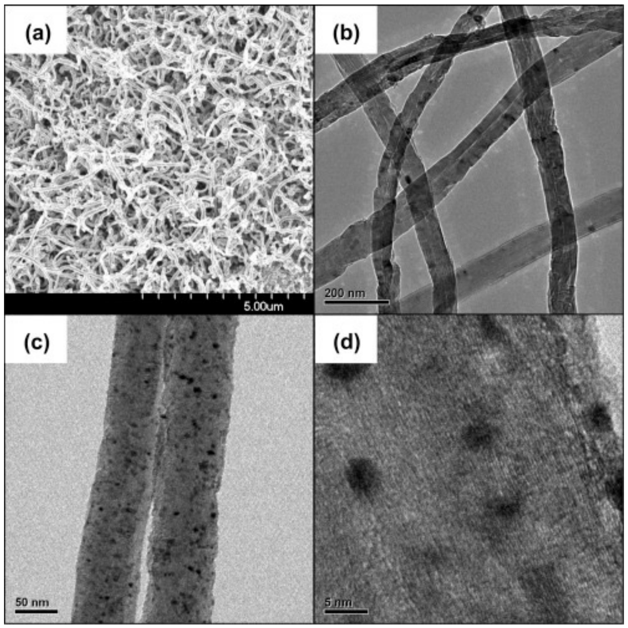
# MWCNT Functionalization / PLA

Journal of Power Sources
Volume 266, 15 November 2014, Pages 365-373




Ni NPs on MWCNTs

*ACS Appl. Energy Mater.* 2021, 4, 11514–11527

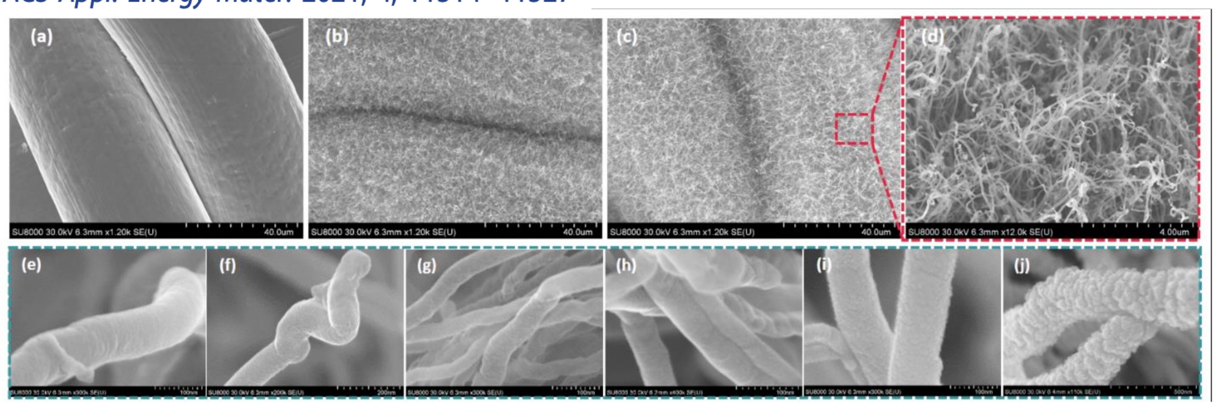
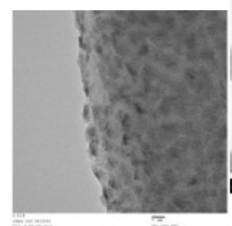
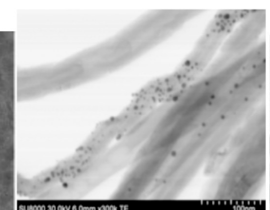


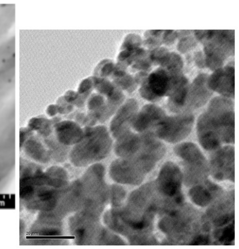

**Figure 6-1.** SEM images of (a) SS, (b) MWCNT/SS and (c and d) Pt/MWCNT/SS nanostructures. High magnification images of Pt/MWCNT/SS nanostructures obtained by PLA for 10 min and chamber pressures of (e) $10^{-5}$, (f) $10^{-4}$, (g) $10^{-3}$, (h) $10^{-2}$, (i) $10^{-1}$, and (j) 1 Torr.



CdSe on MWCNT

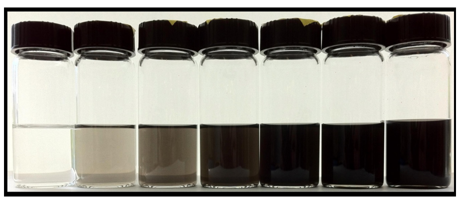


Au on MWCNT



Ni and Ag on MWCNT

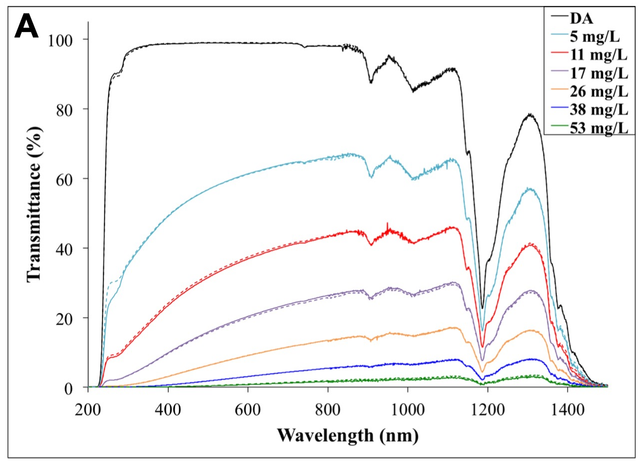
# Solar Thermal Nanofluids / Testing the high-T stability

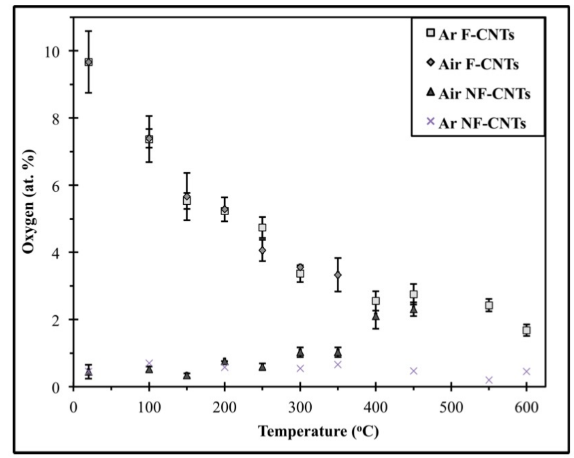


Solar trough

What if we used a volumetric (fluid) absorber?



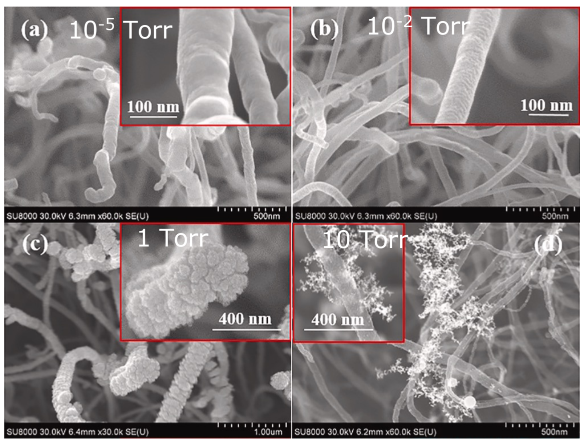


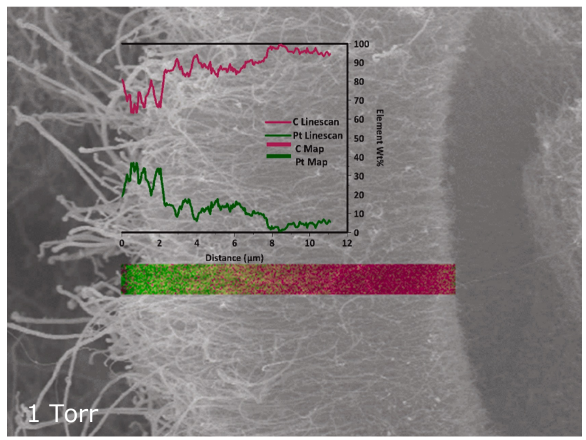



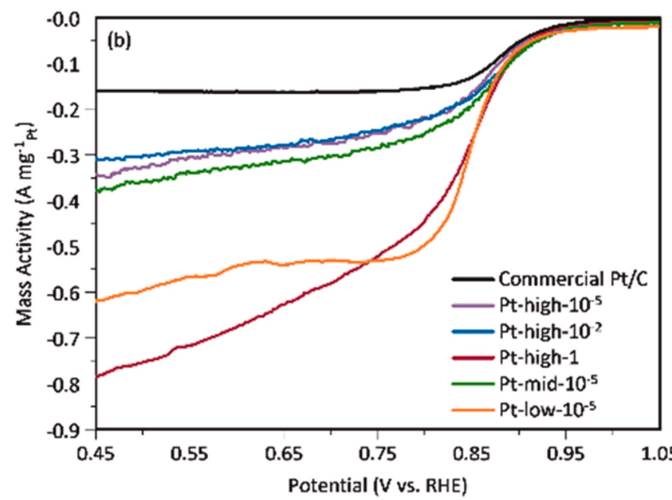

=> Solar distillation?

# Electrocatalysts

Achieving the lowest loading of active material, with highest performance / Working with the extrinsic properties




Binder-free nanostructured Pt/MWCNT/SS electrocatalyst outperforms commercial Pt/C for ORR

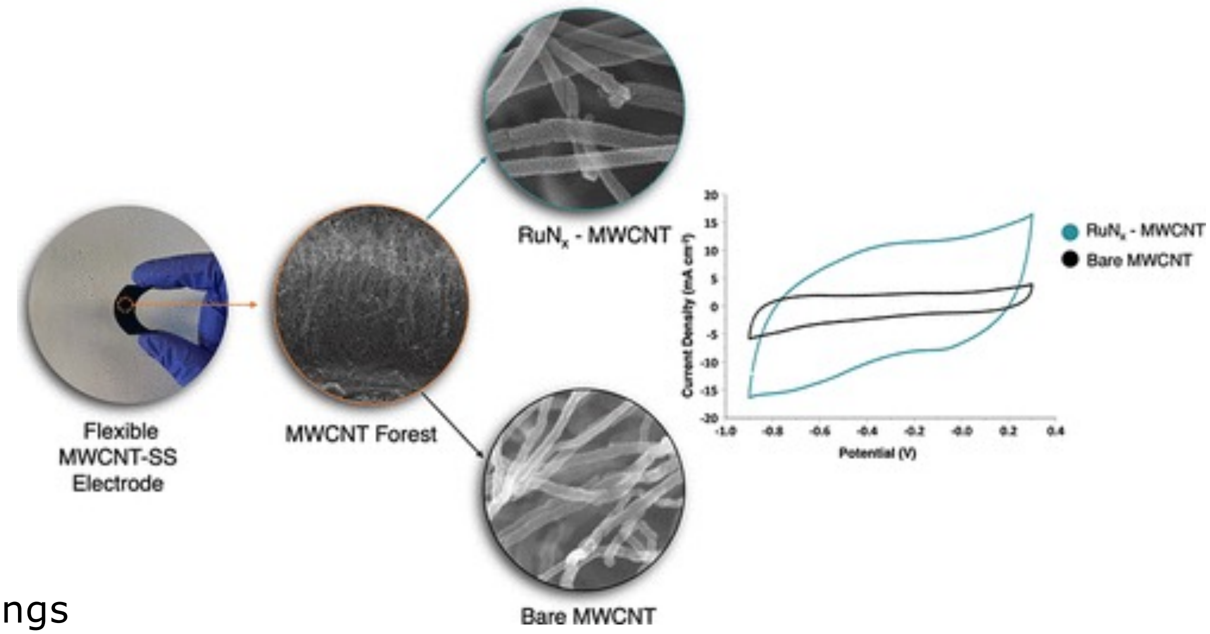
# Flexible SS/MWCNT/RuNx Supercapacitor Electrodes

Charge storage in an electric double layer and/or near-surface faradaic reactions

- Low-cost, flexible scaffold
- Ultralow metal loadings

Our approach enabled:

- Binder-less structure
- Deposition of challenging nitride
- Higher specific capacitance
with granular/nanoparticulate coatings
- 113.4 $F.g^{-1}$ with MWCNTs / 818.2 $F.g^{-1}$ with $RuN_x$

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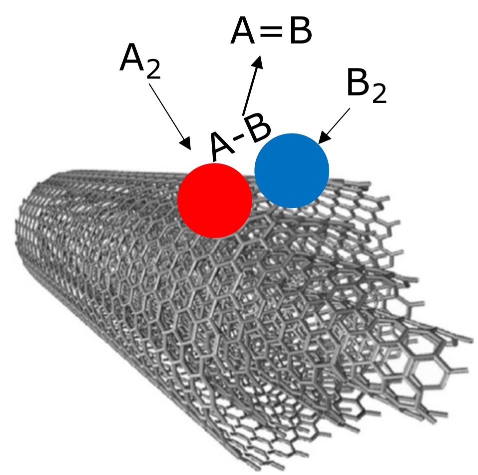
## Well, we’re not done after 15 years of MWCNT work…

- In-liquid processes which use MWCNT as shuttle and absorber
- Active scaffold for molecular immobilization/release
- NP adhesion force to MWCNTs (and others)
- Modeling effort for accelerated material discovery
- Design for circular material use



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