Plasma-functionalization of MWCNTs

for energy storage, conversion and transport

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Outline

• Context of Research
• MWCNT synthesis / CVD
• MWCNT functionalization / PLA-PECVD
• Applications: Solar thermal nanofluids, Electro catalysts & 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 $\iff$ Plasma chemistry

**Figure 17.** Fraction of electron energy transferred to different channels of excitation, and ionization and dissociation, of $\text{N}_2$, 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.

Why MWCNTs?

- Elongated nanostructures, high surface area (5-50 nm in diameter, µm 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
MWCNT Synthesis / CVD

- Direct growth on commercial SS mesh
- Pre-heating at 700 °C in air to expose Fe islands (catalysts)
- Chemical vapor deposition in Ar/C$_2$H$_2$, 2 min gas injection

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

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

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MWCNT Functionalization
MWCNT Functionalization – Oxygen functionalities

- As produced (DI water)
- Boiled 20 min
- Non-functionalized
- After 6 months
MWCNT Functionalization / PLA

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.
Solar Thermal Nanofluids / Testing the high-T stability

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 RuNₓ

ACS Appl. Mater. Interfaces 2022, 14, 15112–15121
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
Acknowledgements / Thank you!

• Former MEng and PhD students: Dr. Elmira Pajootan, Dr. Nathan Hordy

• Current PhD students: Hanie Kazari, Lynn Hein

• Funding: Natural Sciences and Engineering Research Council of Canada
  National Research Council of Canada
  Gerald Hatch Faculty Fellowship
  Canada Foundation for Innovation
  McGill University