Synthesis of MWCNTs-Based Nanostructures and Nanofluids

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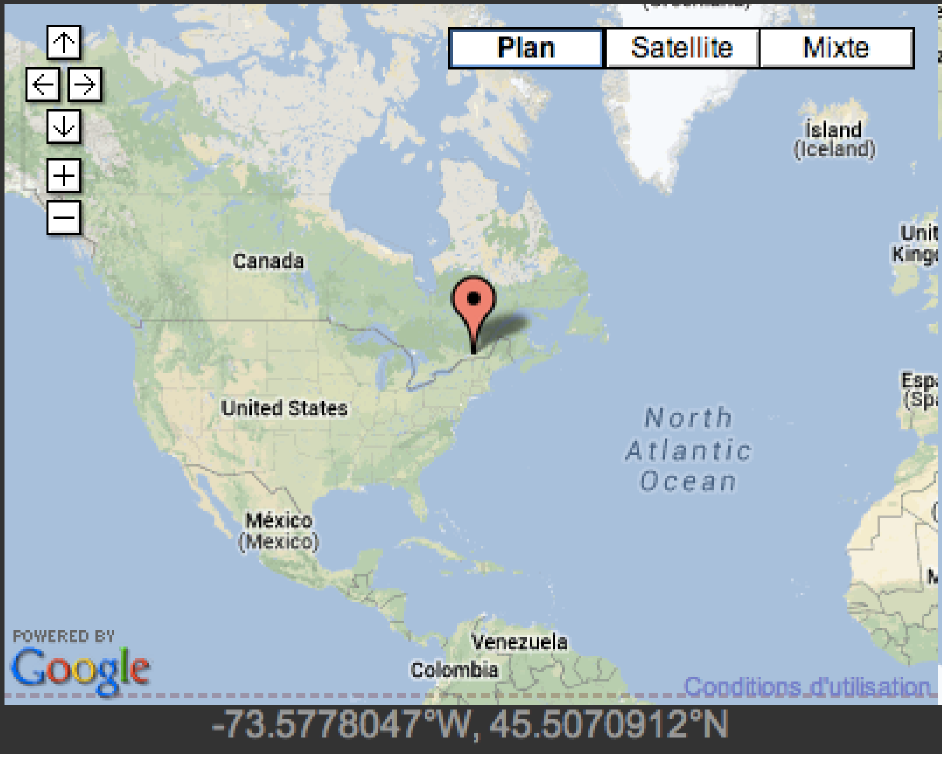
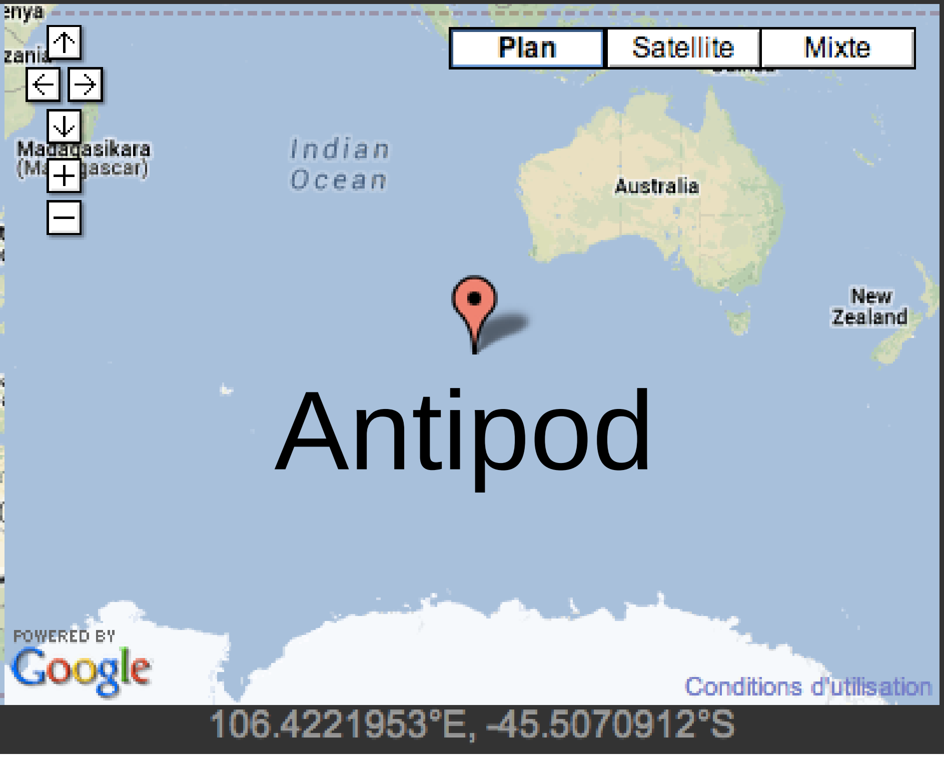
Plasma Processing Laboratory

McGill

McGill University – Where?





McGill University – Where?

McGill University and Chemical Engineering

McGill University
•Founded in 1821
•Land donated by James McGill
•Consistently rates 1st or 2nd in Canada
•Located in Downtown Montreal
•Language of instruction is English
•>35,000 students

Chemical Engineering
•Began as a part of Chemistry in 1908
•Became a standalone department in the 1940's
•16 Professors
•Offers BEng, MEng, PhD
•>350 undergraduates
•>120 graduates (~50% national)
•Housed in the MH Wong bldg since 1997

Plasma Processing Laboratory

- Plasma activities @ McGill began in the early 70's
- 5 professors, more than 30 graduate students
- Main research/development themes:
  - Novel plasma source design and characterization
  - Synthesis of nanomaterials, heterogenous nanostructures and nanofluids
    - MWCNTs, nanoflakes, metal and semiconducting nanoparticles
  - Plasma-assisted combustion and plasma medicine
  - Functional coating and functionalization
  - Femtosecond laser machining and multiscale surface engineering
  - CFD of plasma reactors

Anne KIETZIG

Dimitrios BERK

Pierre-Luc GIRARD-LAURIAULT

Jean-Luc MEUNIER

Sylvain COULOMBE

Coulombe's Group Activities (Current)

Stream 1 – Plasma-Assisted Synthesis of Nanofluids and Heterogenous Nanostructures

-Ni NPs-decorated MWCNT electrocatalysis for H_2 production (Mark McArthur, PhD)
-MWCNT nanofluid for solar thermal energy harvesting (Nathan Hordy, PhD)
-MWCNT nanofluid for CO_2 sequestration (Larissa Jorge, PhD)
-Au NP-MWCNT nanofluid for optical/chemical therapeutics (Dr. Philip Roche)

Stream 2 – Small-Scale Plasma Sources for Plasma Medicine and Plasma-Assisted Combustion
-Diagnostic/imaging of plasma-assisted combustor (Mathew Evans, MEng)
-Plasma/nanostructured catalylist for fuel reforming (Pablo Diaz, PhD)
-Miniature/high-speed plasma jet for plasma medicine and material deposition

- Wound healing (Isabelle Lacaille, MEng, just completed)
- OH radical injector (Florent Sainct, Jan. 2014)

Stream 3 – Twin Electrode Arc Furnace

-TiO2 ore treatment (Rio-Tinto, Marie-Ève Gosselin, MEng)
-Restarting issues in waste processing system (PyroGenesis Canada, to start soon)

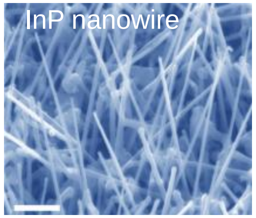
Nano…

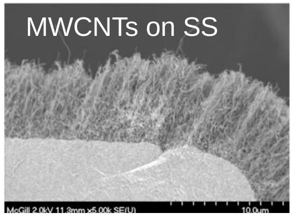
Nanomaterial: Material which size is <100 nm in at least one dimension. Forms may be a single crystal, nanoparticle, wire, tube/pillar, sheet, flake… Unique, nanosize-dependent properties. Enhanced properties w/r to bulk material due to extremely high specific surface area (>>100 m^2/g)

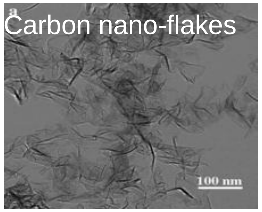
Heterogenous Nanostructure: Assembly of nanomaterials

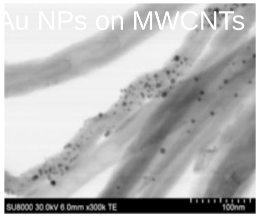
Nanofluid: Engineered colloidal suspension

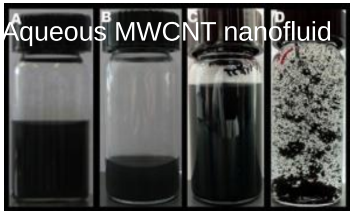
Enhanced/novel properties and multiple functionalities associated with assembly of various nanomaterials











Why MWCNT-Based Heterogenous Nanostructures and Nanofluids?

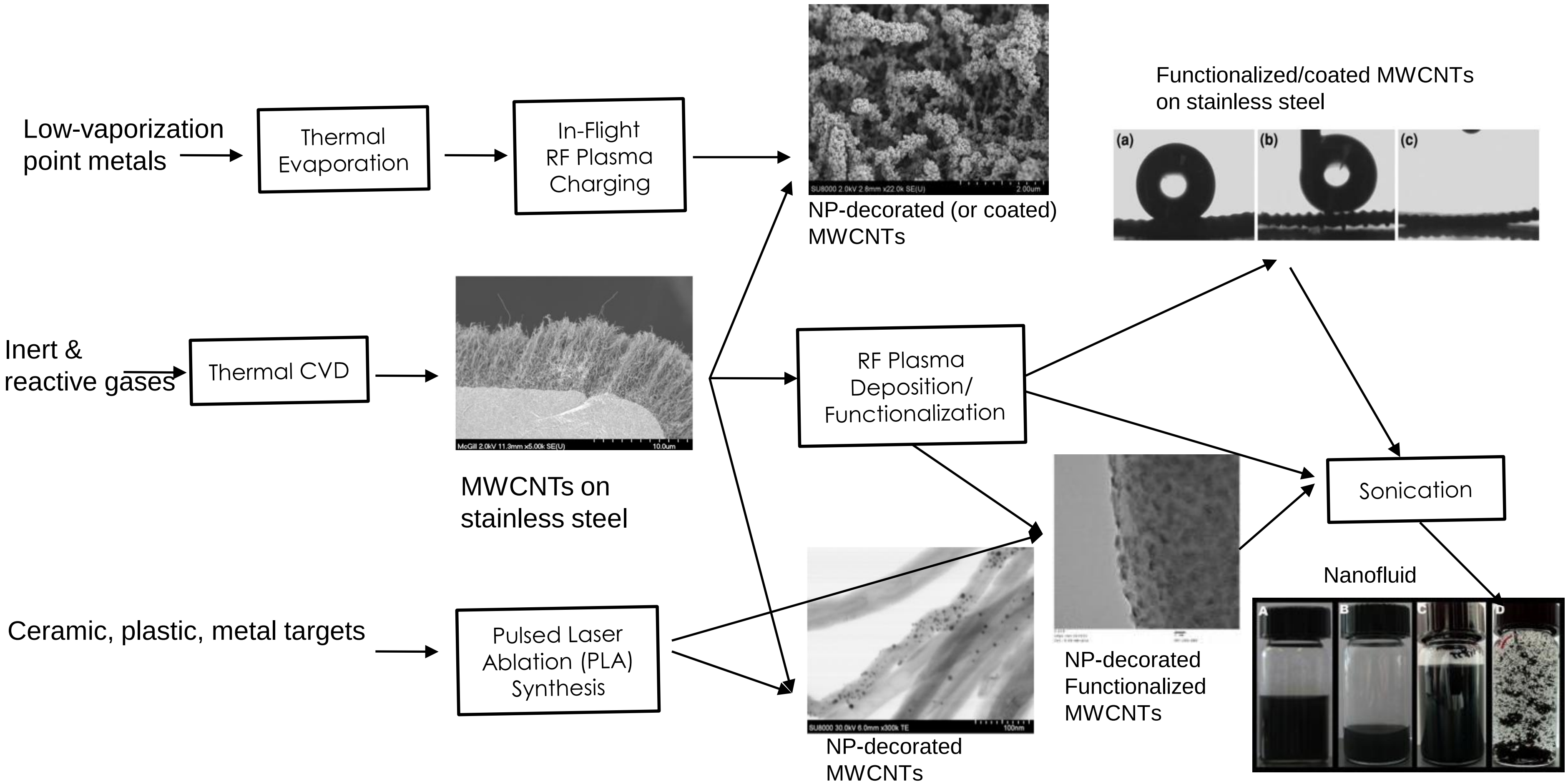
The obvious:

- High thermal and electrical conductivity
- High aspect ratio structure (~20-50 nm in diameter to ~1-20 μm in length)

The not-so-obvious:

- Easy to produce and functionalize (=cheap)
- Broadband absorber in the UV/VIS/NIR range
- Metallic conductor
- Ideal support structure for small nanoscale entities (decoration)

Current Capabilities

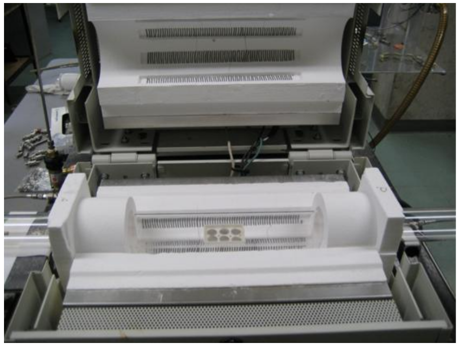


MWCNT Growth

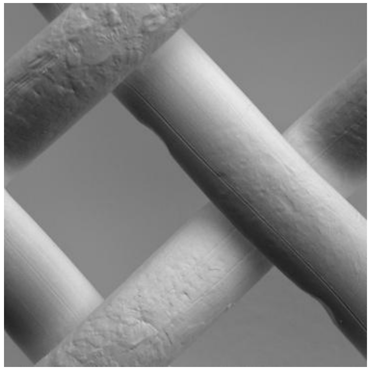
MWCNTs precipitate out of Fe islands produced by surface break-up caused by Cr migration to the surface upon heating

degrease SS mesh in acetone 30 min → heat in tube furnace (under Ar) at 700°C 30 min → inject C_2H_2 into tube furnace 4 min → maintain tube furnace at 700°C 30 min → allow tube furnace to cool ~2-3 hrs

process gas IN →



→ process gas OUT



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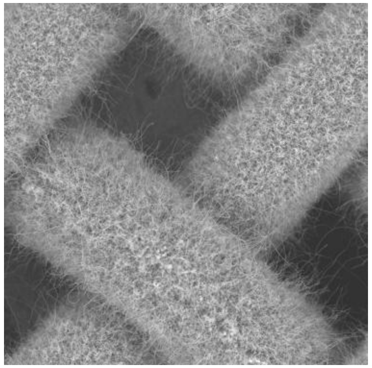
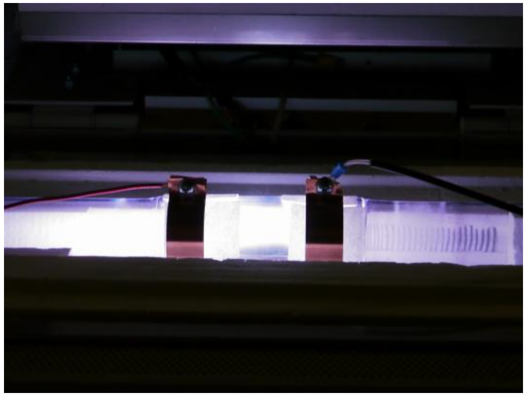


- MWCNTs are solidly anchored to Fe through covalent bounds which also provide an excellent thermal/electrical contact with SS
- MWCNTs cannot be uprooted, but they can be broken off by sonication

MWCNT Functionalization



Ar/C_2H_6/O_2 RF plasma functionalization

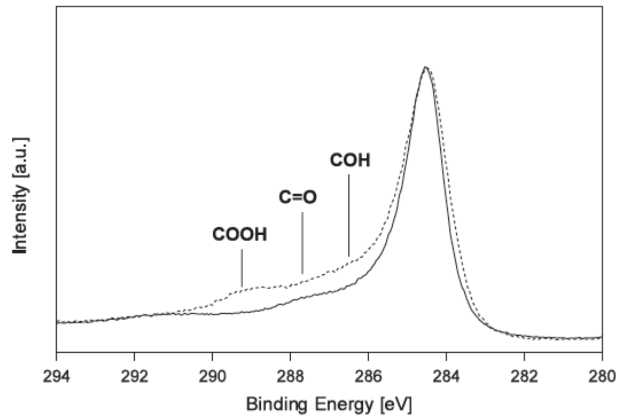
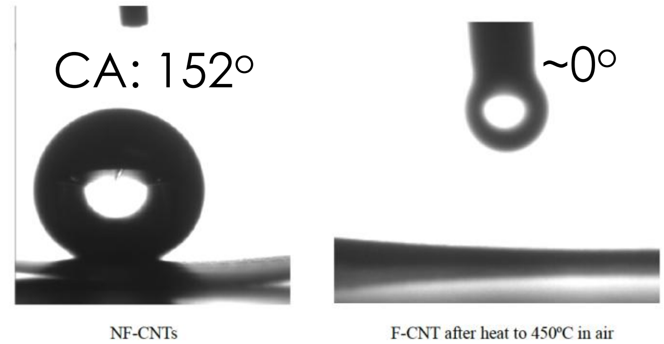


Figure 5. XPS C1s spectra comparing the NF-CNTs and the F-CNTs. The peak positions of the oxygen functional groups are also shown.

Wetting of MWCNT forest



Non-functionalized

Plasma functionalized

Plasma functionalization adds covalently-bound oxygen-containing functionalities (COOH, C=O, COH) to the MWCNTs

Functional groups are stable at very high temperatures (450 °C in air)

MWCNTs become highly dispersible in polar solvents and can withstand temperatures much above organic surfactant limits (~60 °C)

N. Hordy et al, Plasma functionalization of carbon nanotubes for the synthesis of stable aqueous nanofluids and poly (vinyl alcohol) nanocomposites, Plasma Process. Polym. 10 (2013), p. 110

MWCNT Functionalization & Nanofluid

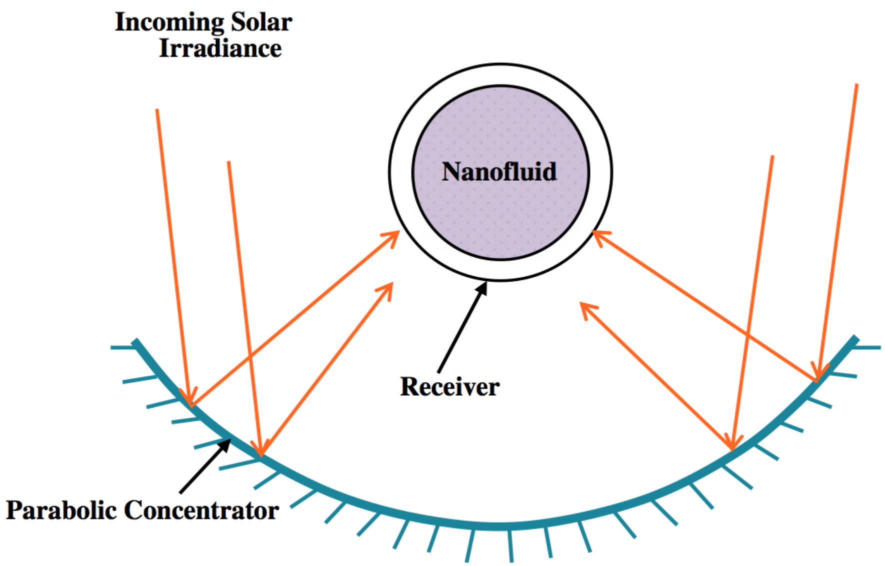
Hydrophobic (CA ~153^o)

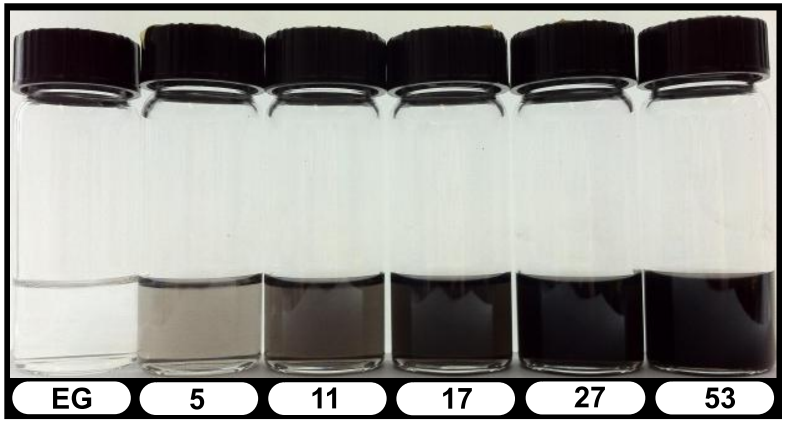
Non-functionalized CNTs

Hydrophilic (CA ~0^o)

Functionalized CNTs

MWCNT Nanofluid for Solar Thermal Energy

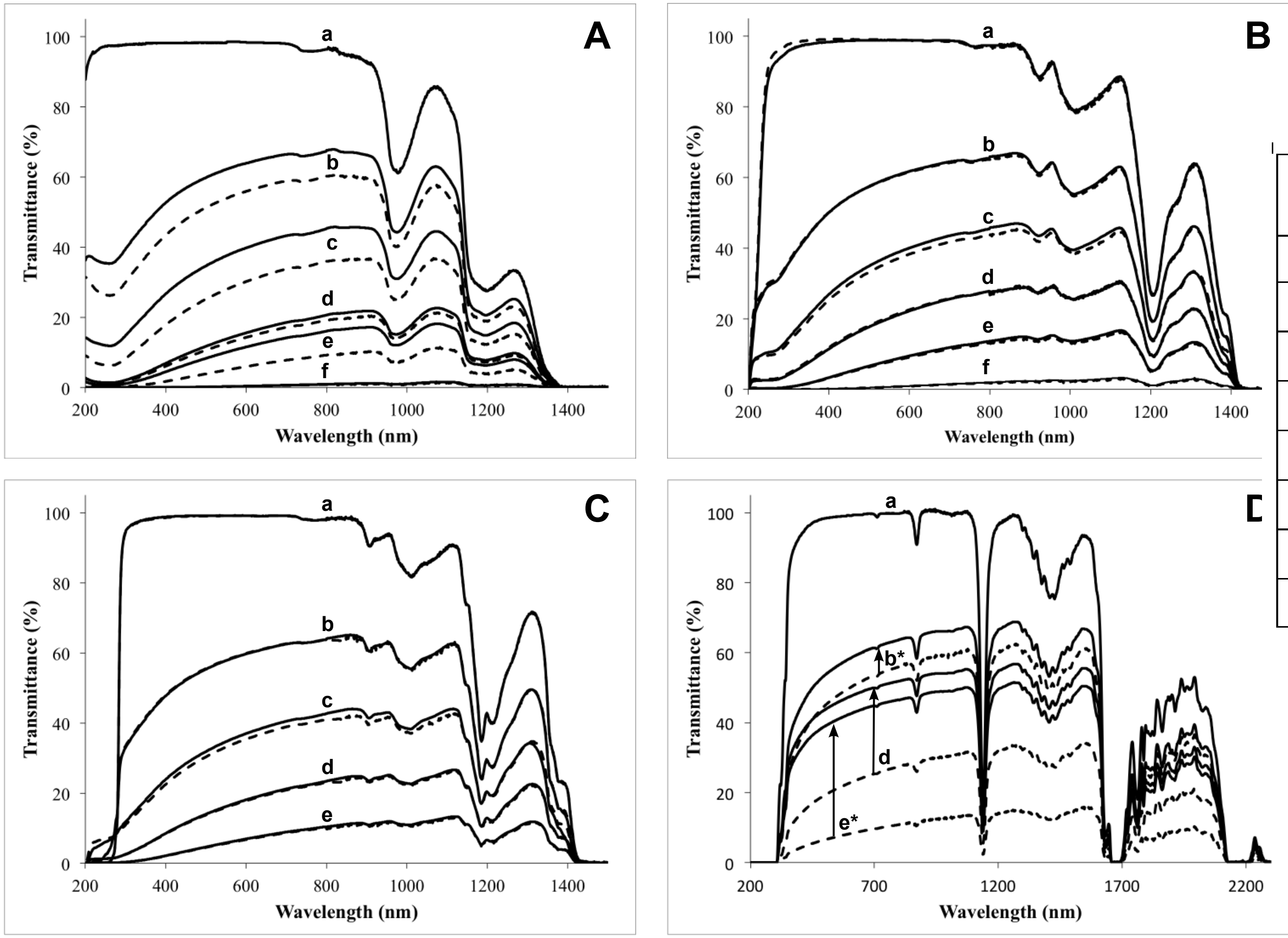




concentrations in mg/L

- Water
- Ethanol
- Methanol
- Isopropanol
- Denatured Alcohol
- Ethylene Glycol
- Propylene Glycol
- Therminol VP-1

MWCNT Nanofluids – Aging (3 months)



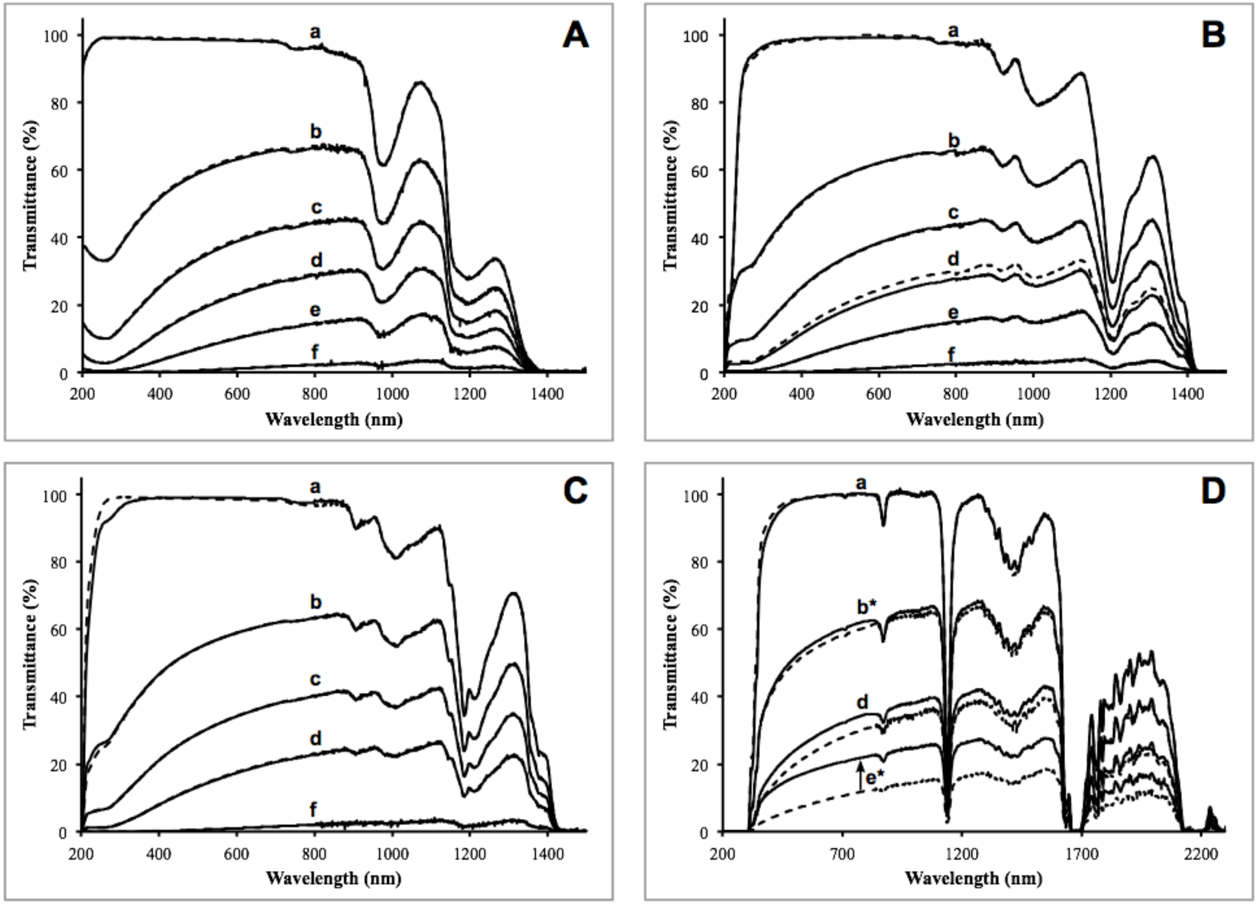
Label	MWCNT concentration (mg/L)
a	0
b	5.6 ± 0.4
b*	6.5 ± 0.5
c	11.0 ± 1.0
d	17.0 ± 1.4
e	27.0 ± 2.3
e*	33.0 ± 2.4
f	53.0 ± 5.6

Transmission spectra for various concentrations of nanofluids, immediately after synthesis (dash) and after 3 months (solid). A) water, B) ethylene glycol, C) propylene glycol, D) Therminol VP-1. Absorption pathlength was 1 cm.

MWCNT Nanofluids – High Temperature Stability

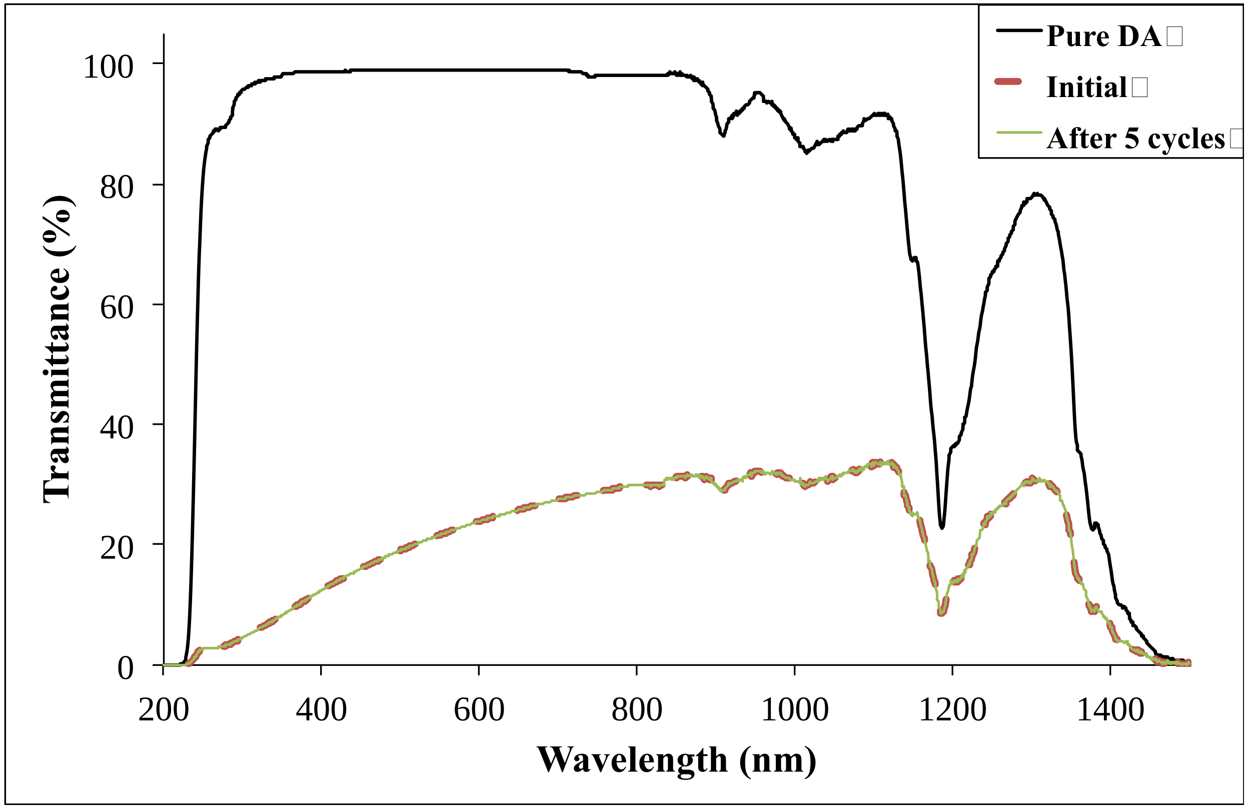
Non-Functionalized MWCNTs

MWCNT Nanofluids – High Temperature Stability



Transmittance spectra for various concentrations of nanofluids, after synthesis (dash) and after heating for 1 hour at approximately 85 % of the base fluids' boiling temperatures (solid). A) water (80 °C), B) ethylene glycol (170 °C), C) propylene glycol (170 °C), D) Therminol VP-1 (220 °C). Absorption pathlength was 1 cm.

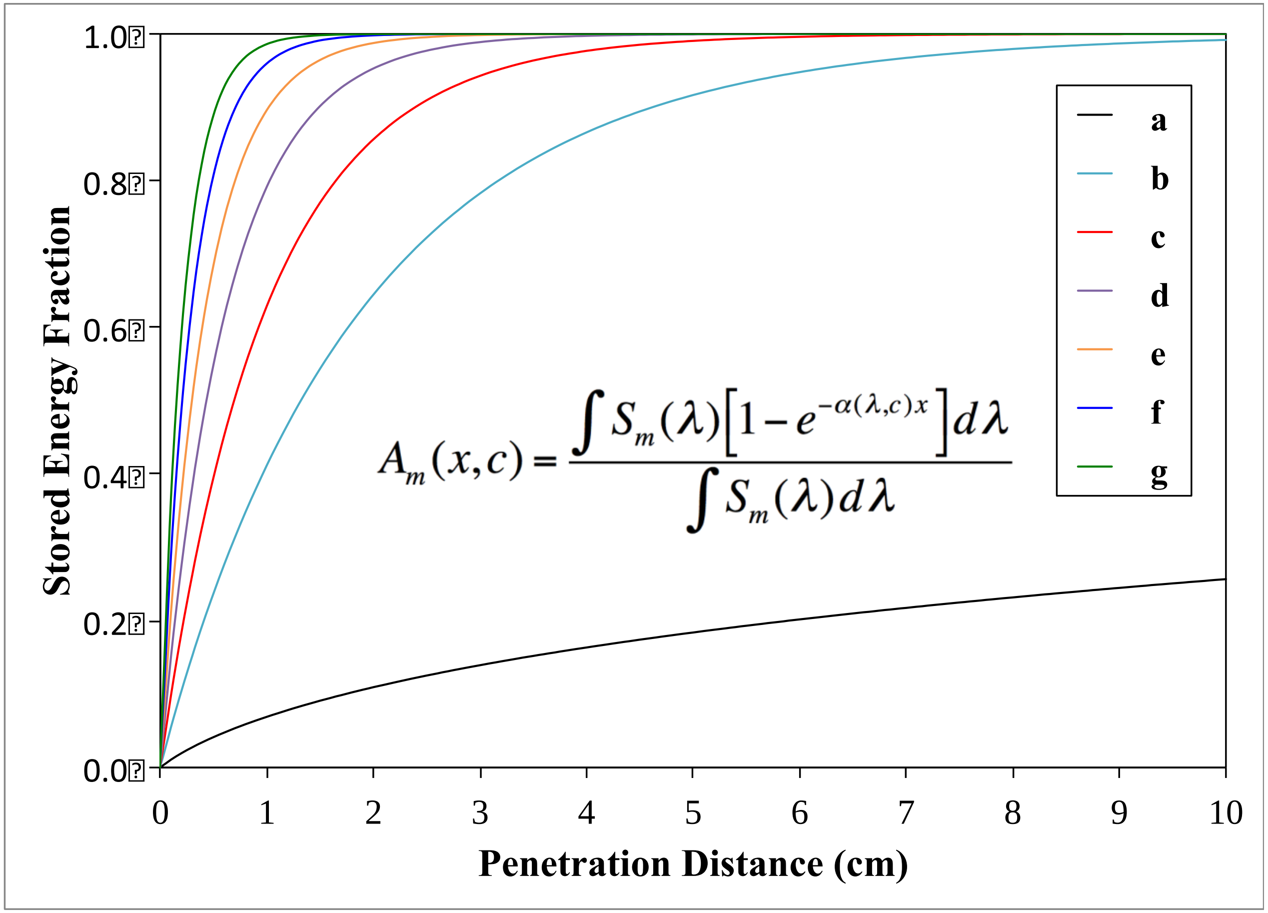
MWCNT Nanofluids – High Temperature Stability



MWCNT/denatured alcohol nanofluid (17 mg/L) after 5 evaporation/condensation cycles at 80 ^{o}C for 1 hour (heat pipe)

Continuous (localized) laser heating at ~10^6 W/m^2 (peak) for 6 hours showed no sign of destabilization

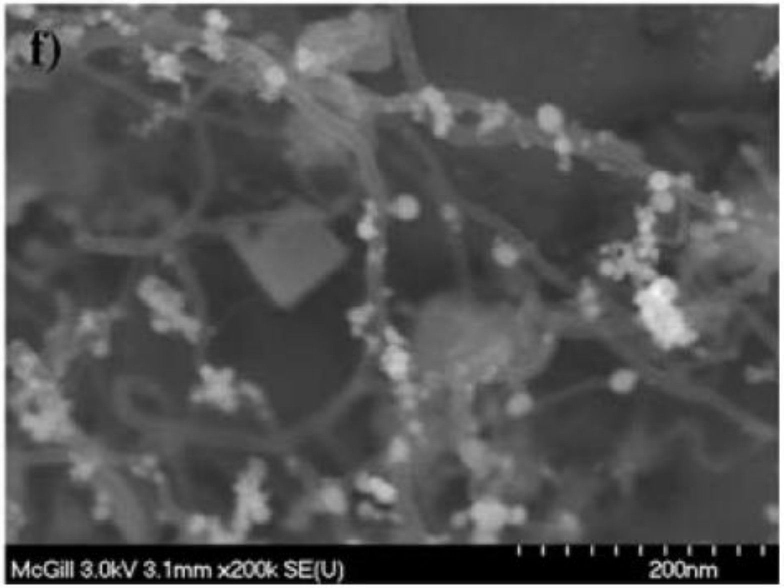
MWCNT Nanofluids – Design



a = Denatured alcohol
b = 5 mg/L
c = 11 mg/L
d = 17 mg/L
e = 27 mg/L
f = 36 mg/L
g = 53 mg/L

MWCNTs are excellent NP collectors…

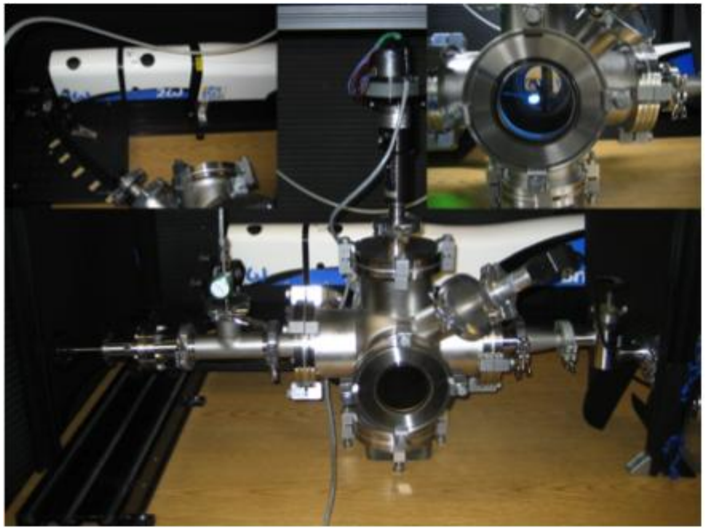
- MWCNTs can be used to collect NPs…
- MWCNTs become 3D support structure
- MWCNT *decoration* adds localized, NP chemistry-dependent properties
- Strong van der Waals interactions: NPs stay on MWCNTs even during intense sonication (MWCNTs are broken off while NPs stay on their surface)
- Challenge (nanofluid): Decorate MWCNTs without hiding all functional groups which stabilize the suspension



L. Rao et al, Carbon nanotubes as nanoparticles collector," J. Nanoparticle Res. 9 (2007), p. 689

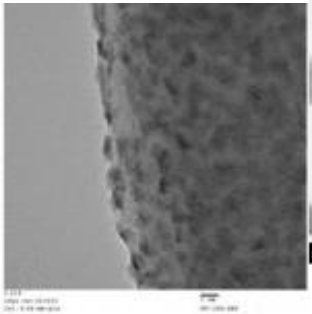
Synthesis of NPs by Pulsed Laser Ablation

Pulsed ns laser beam is focused (~1J/cm^2) on a target(metal, semiconductor, polymer) causing immediate vaporization of the material and formation of a high-density vapor plasma plume in rapid expansion (km/s). Supersaturation of the material vapor plume leads to nucleation => cluster formation => nanoparticle formation

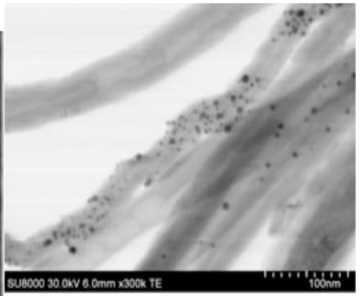


Buffer gas pressure control nanoparticle size, which can be adjusted between ~3 and ~60 nm.

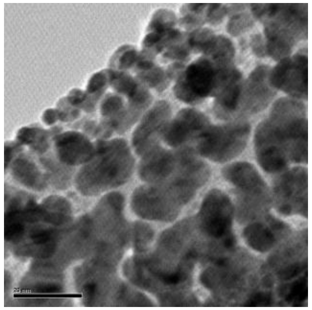
… and if MWCNTs happen to be on the way… MWCNTs can be *decorated*.



CdSe on MWCNT



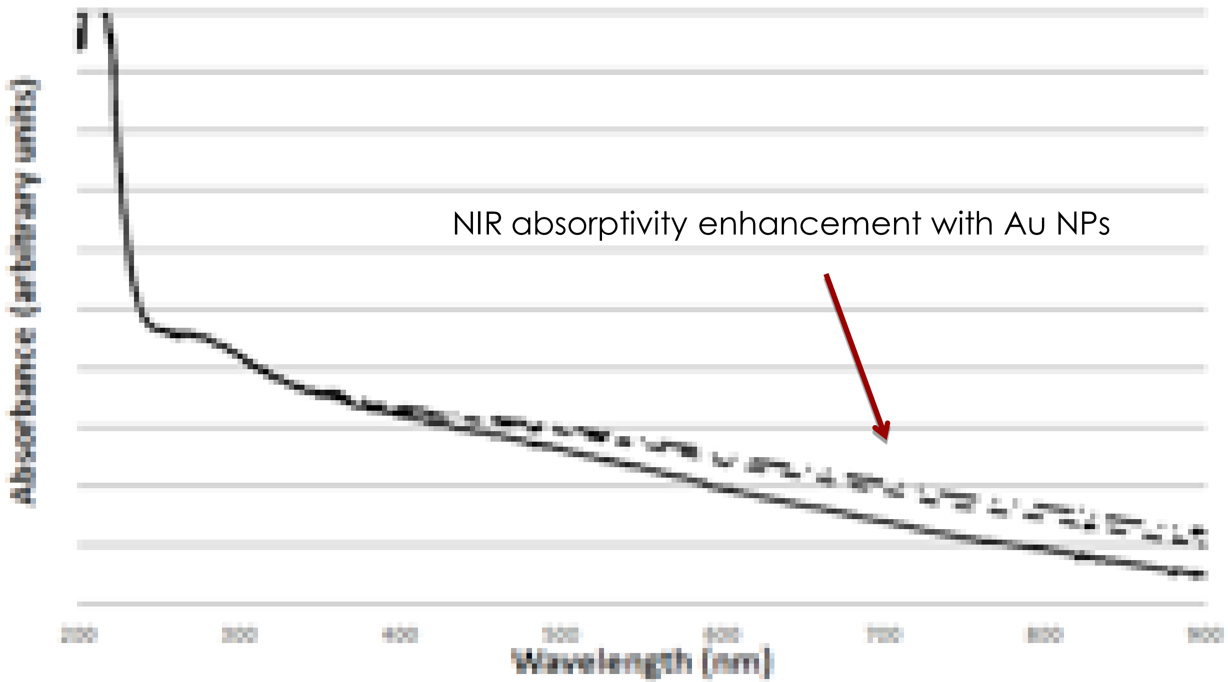
Au on MWCNT



Ni and Ag on MWCNT

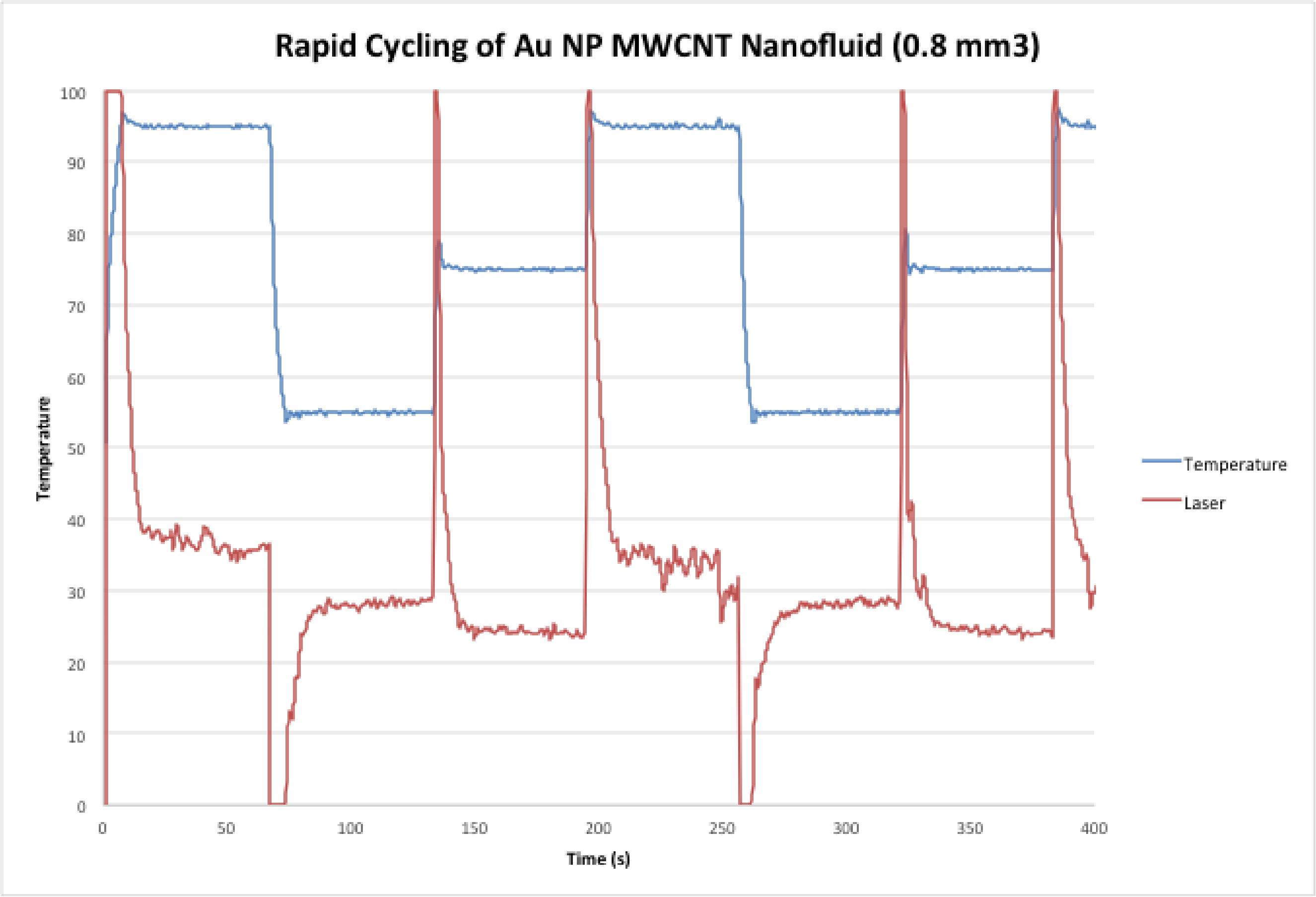
MWCNT-Supported Au NP Nanofluid for Optical/Chemical Therapeutics Applications*

MWCNTs: Volumetric absorber
Au NPs: Localized chemically-active sites
=> Highly localized heating in aqueous solutions (laser)
=> Imaging or localized chemical reaction with Au-attached molecules



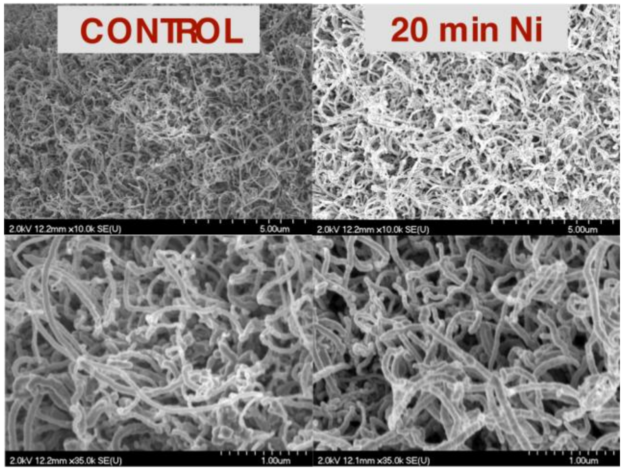
UV-vis-NIR absorption spectrum of aqueous Au NP-decorated MWCNT nanofluids. Lower to upper curves: PLA time =0, 240 and 300 sec.

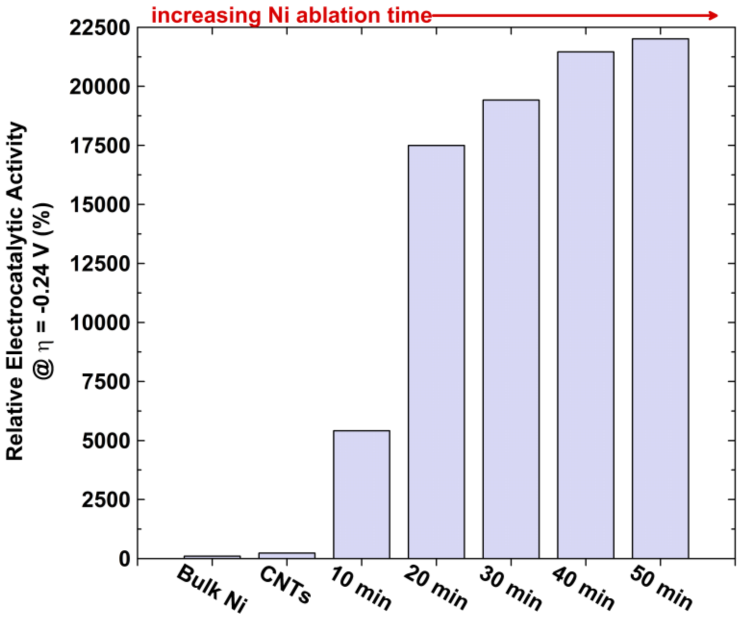
MWCNT-Supported Au NP Nanofluid for Optical/Chemical Therapeutics Applications

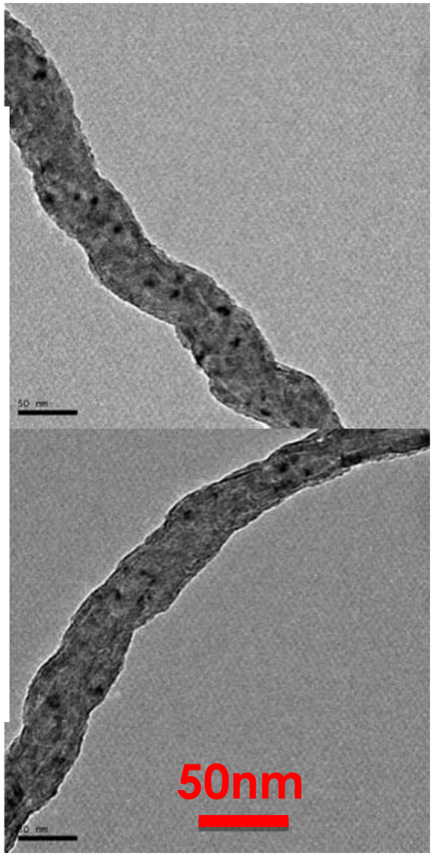


Heating cycles and accompanying laser power modulation (808 nm, 100% corresponds to 2 W).

MWCNT-Supported Ni NP Electrocatalyst for H_2 Production by Alkaline Electrolysis of Water







~5 nm nanoparticles
~615 m^2/g specific surface area

10^2 increase in electrocatalytic activity over bulk Ni

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