Quantification and Cytotoxicity of released carbon nanotubes from an epoxy-based nanocomposite

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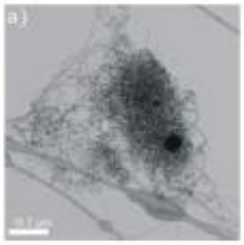
EMPA
Materials Science & Technology

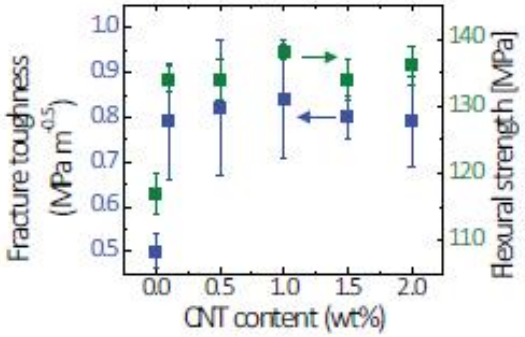
Motivation

Carbon nanotube (CNT) reinforced epoxy

epoxy +



Enhanced properties



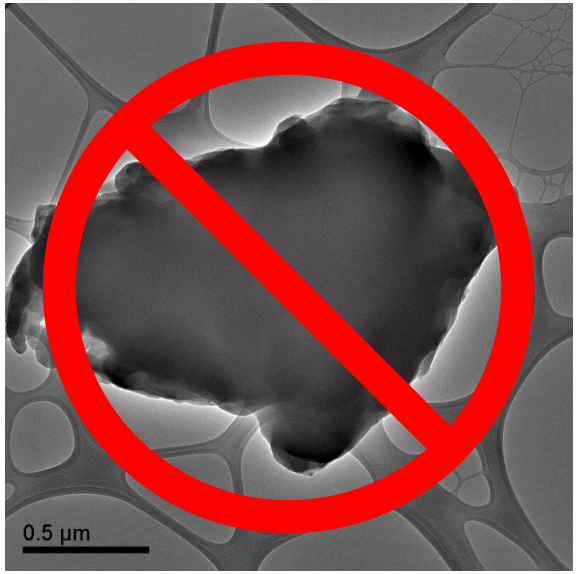
Applications

Safety?

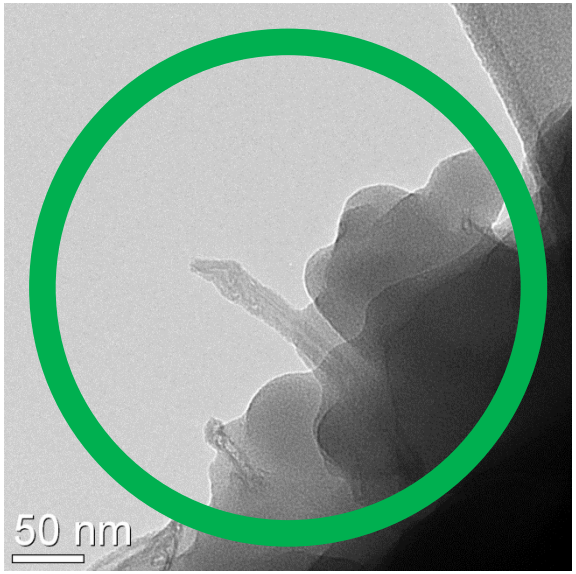
Schlagenhauf, Chu, Buha, Nüesch, and Wang, (2012), *ES&T,* 46, 7366 – 7372, DOI: 10.1021/es300320y.

Introduction

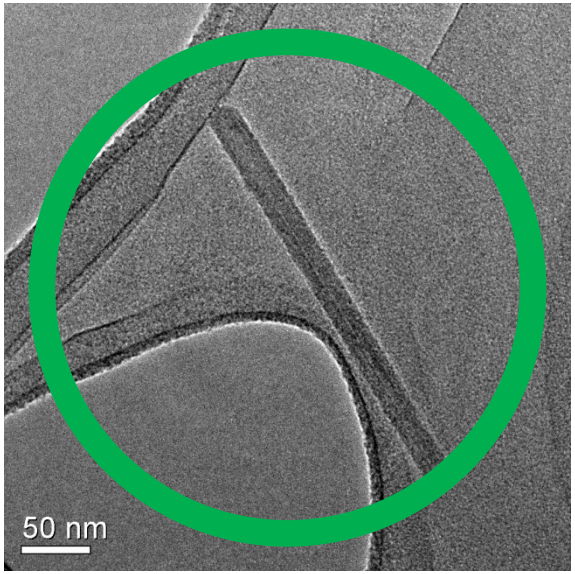
Different states for CNTs after an abrasion process



Embedded



Protruding

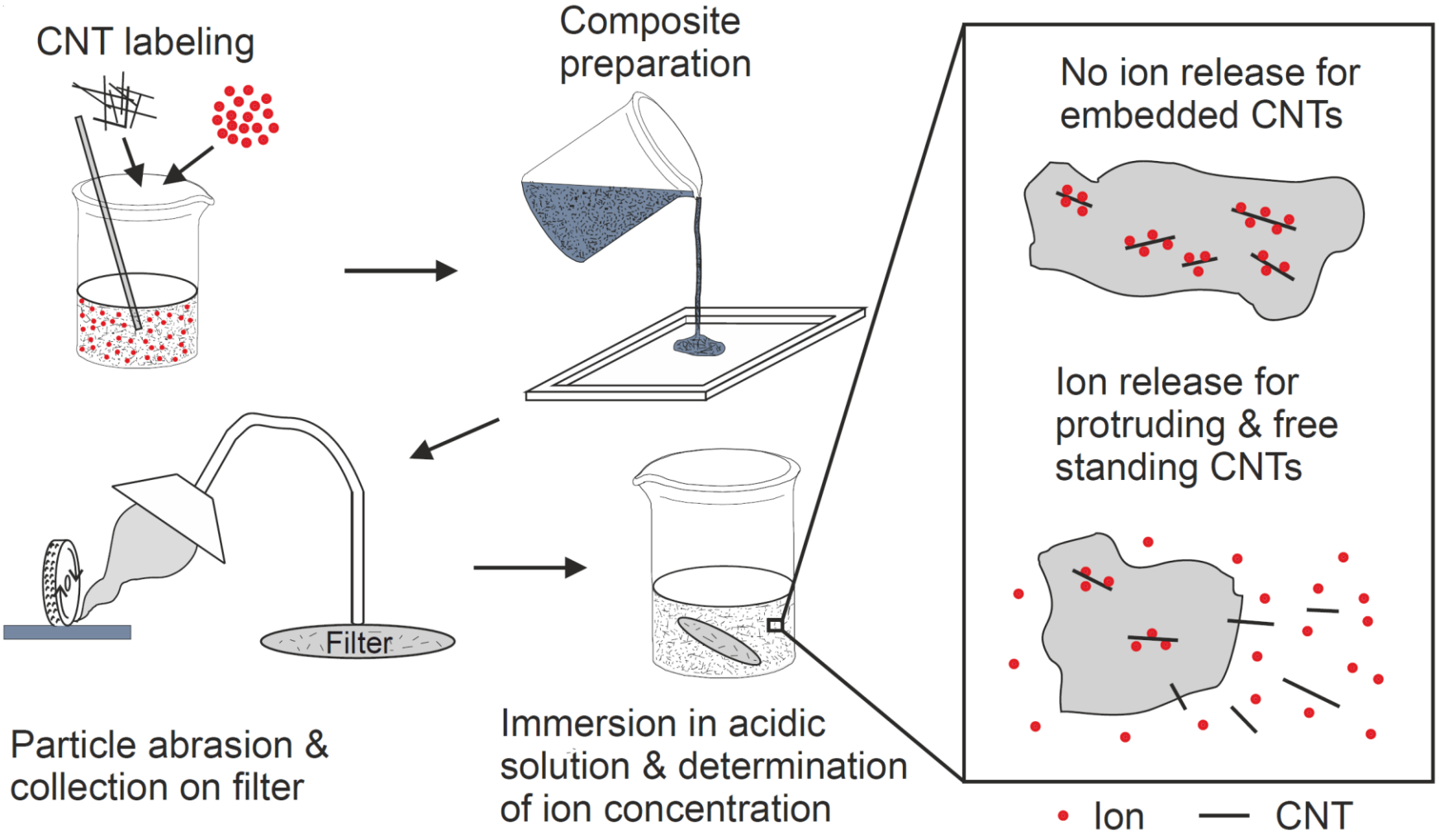


Free standing

There is a need to differentiate between the embedded CNTs and the potentially dangerous protruding and free standing CNTs.

→ Approach: Label the CNTs with ions that are released when immersed in an acidic solution. The ion concentration can be measured by ICP-MS.

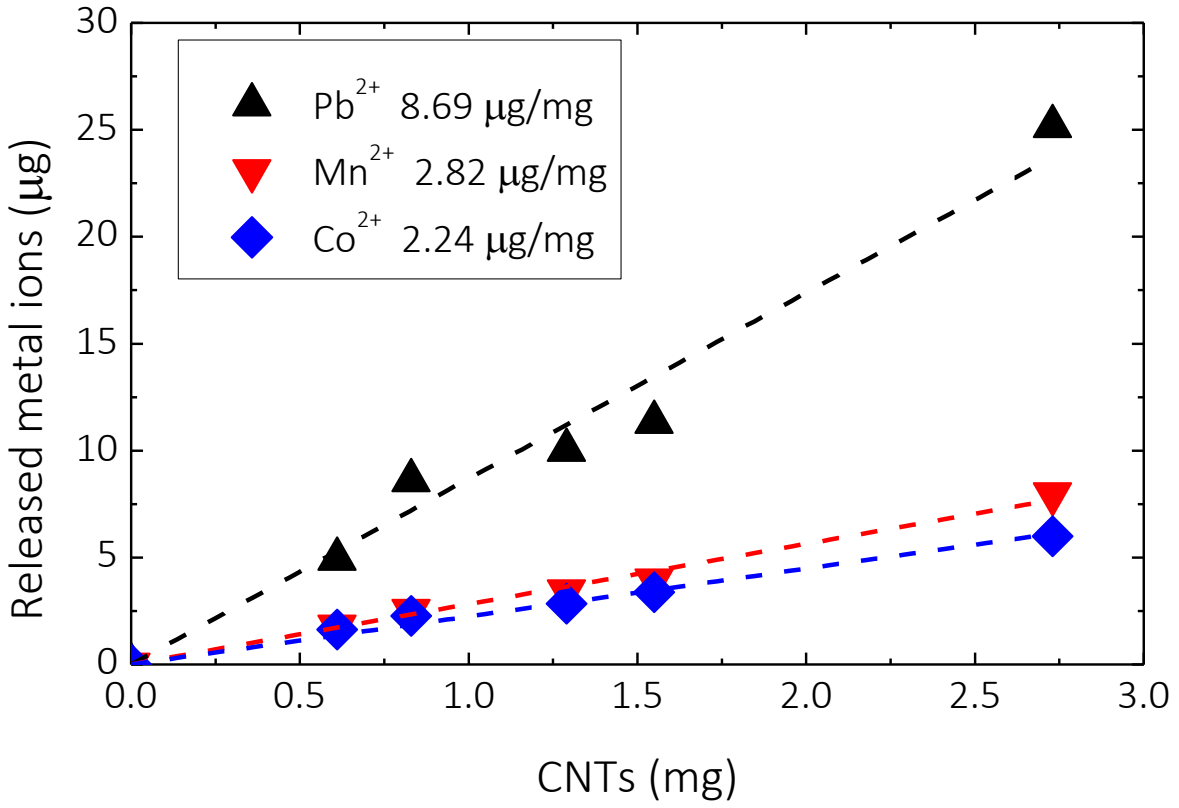
Quantification method



Schlagenhauf, Buerki-Thurnherr, Kuo, Wichser, Nüesch, Wick, and Wang (2015), *ES&T,* 49, 10616–10623, DOI:10.1021/acs.est.5b02750.

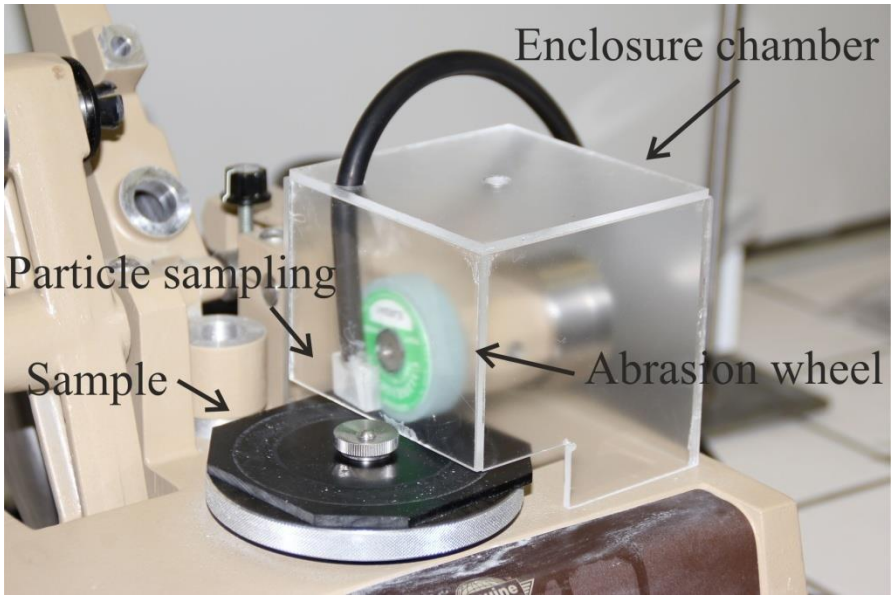
Ion loading capacities

Ion uptake and release capacity of Baytubes for Pb^{2+} ions and the release of catalyst ions (Mn^{2+} and Co^{2+})

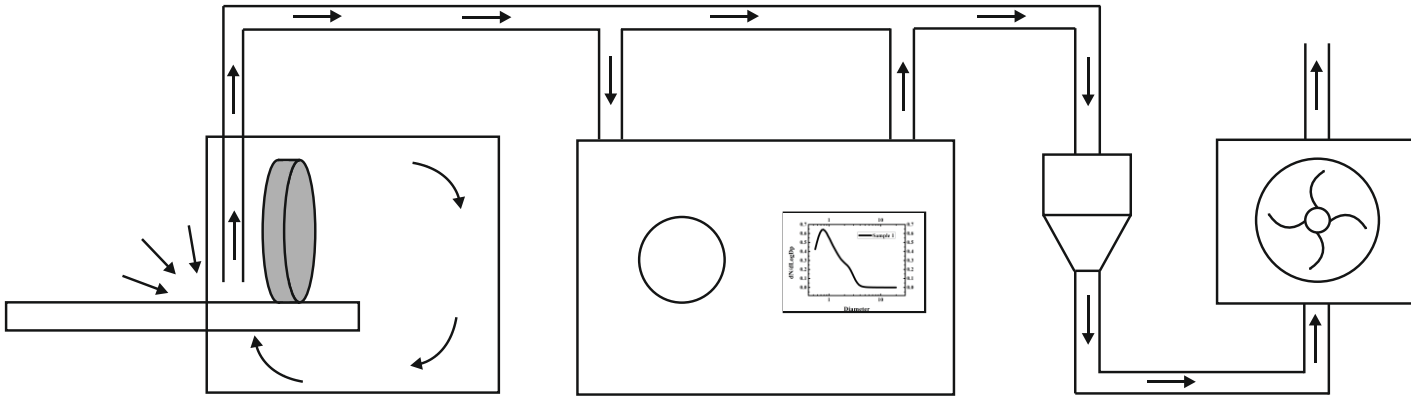


Theoretical detection limit ICP-MS: 6 ng CNT (Pb), 3 ng CNT (Mn & Co)

Abrasion experiments



a) Abrasion area, particle collection
b) Particle analysis: particle size distribution, surface area, particle concentration
c) Particle sampling: image analysis, particle composition
d) Pump



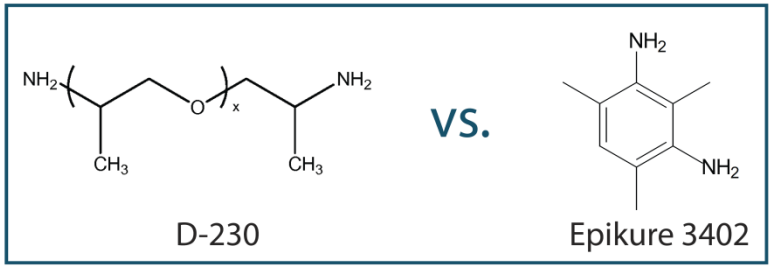
Nanocomposite samples

Control samples

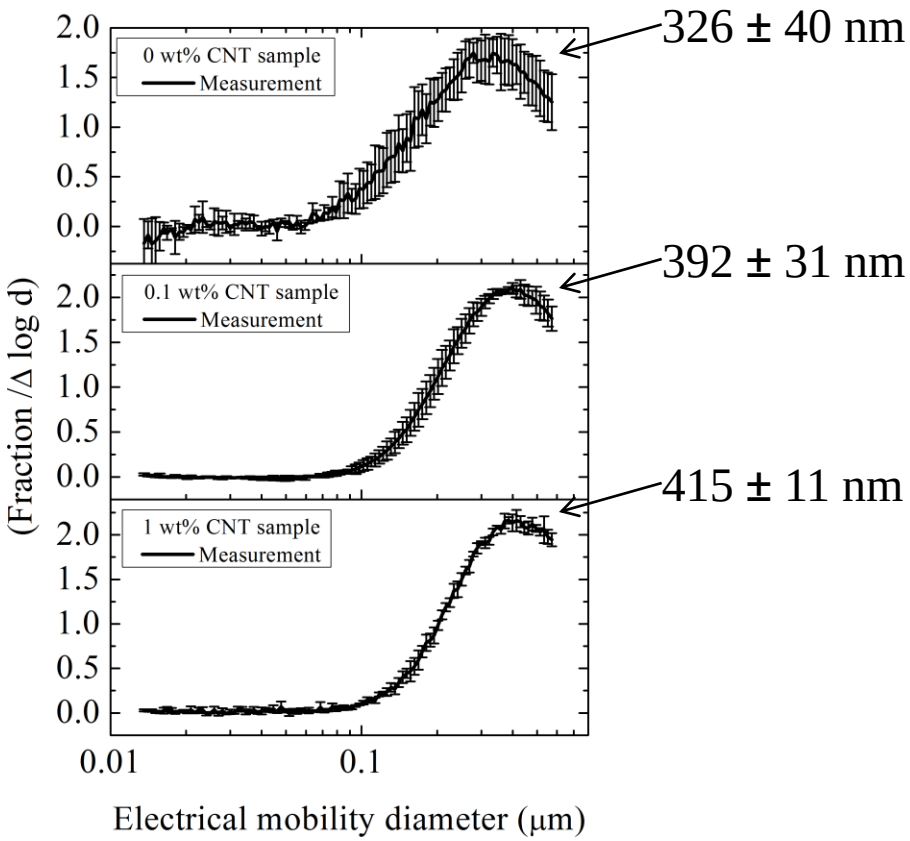
- Release of ions when CNTs are immersed in the resin?
  - Disperse CNTs in resin
  - Dissolve resin only
  - Ion concentration in resin?
- Diffusion of ions through epoxy particles?
  - One epoxy sample with dissolved ions
  - Measure ion relase from the abraded particles

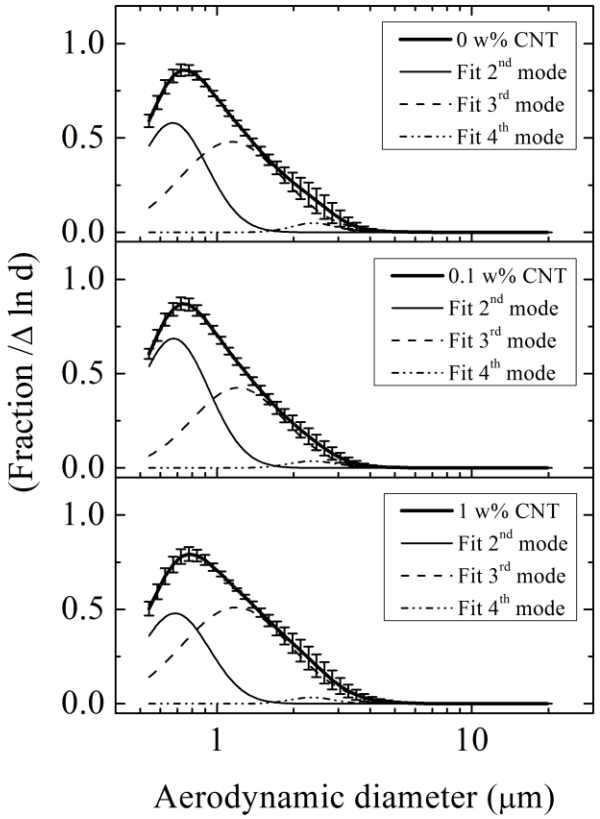
Release comparison

- Two samples with 1 wt% CNTs
- Two different curing agents
  - Curing agent D-230, no release of free standing CNTs detected by microscopy
  - Curing agent Epikure 3402, release of free standing CNTs detected by microscopy



Abraded particle size distribution

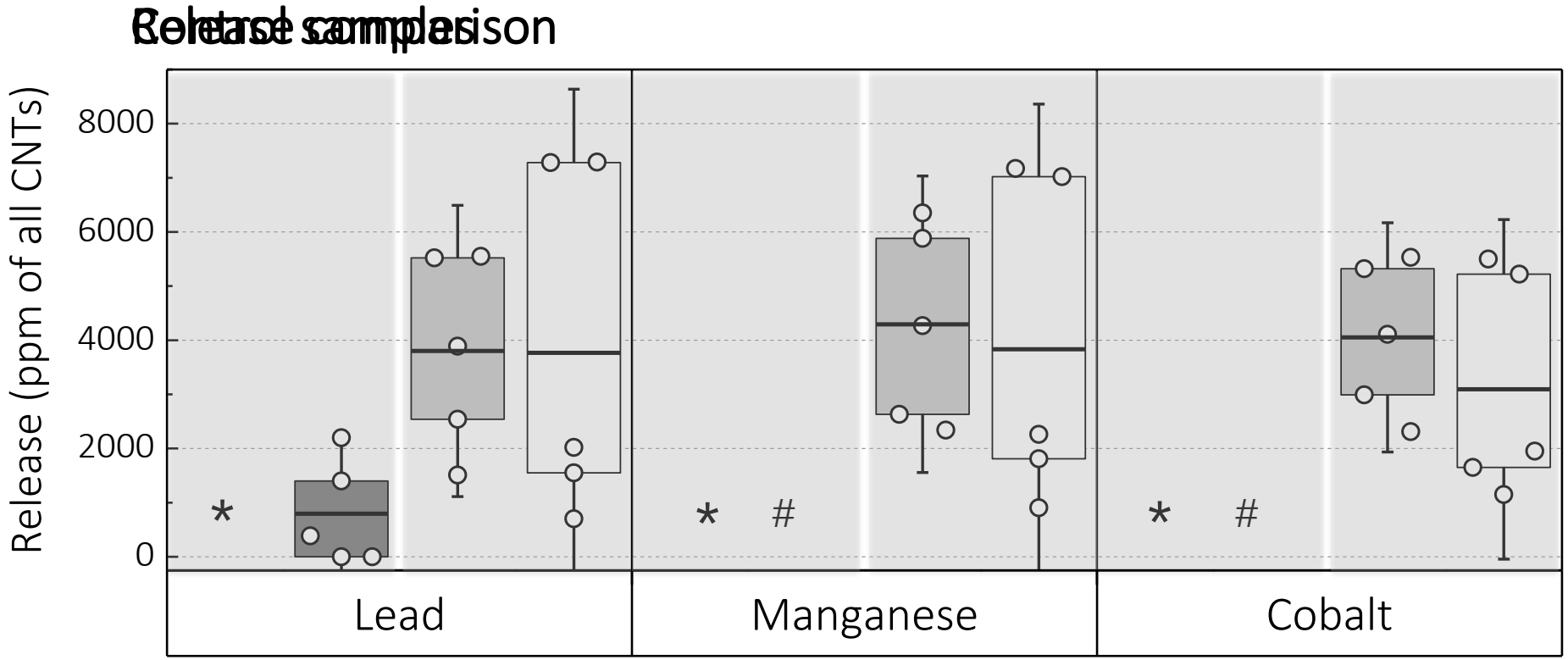




Particle size distributions of the three samples measured by SMPS (13 - 573 nm)

Particle size distributions of the three samples measured by APS (0.54 - 19.81 μm)

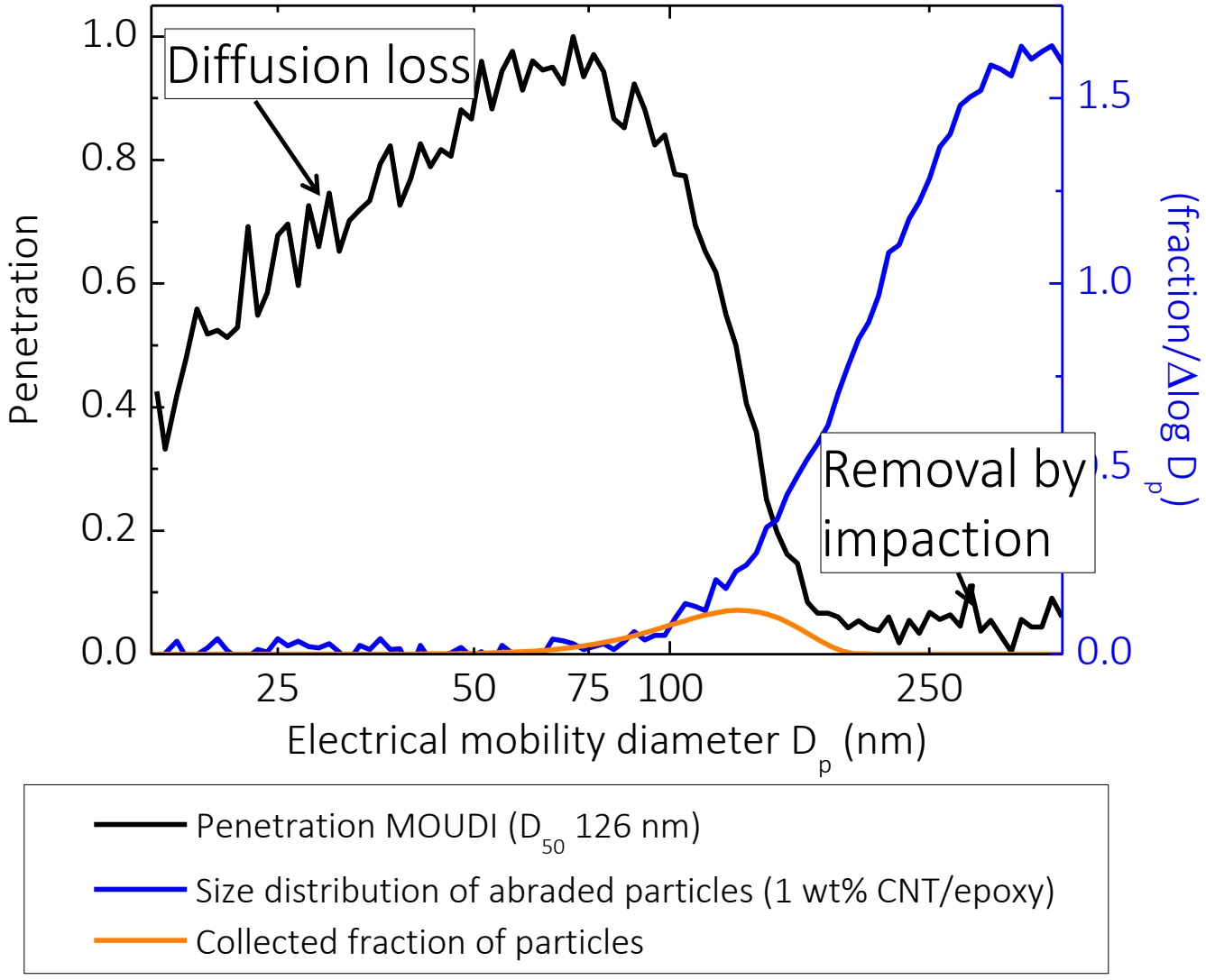
Quantification of exposed CNTs



Conversion for a 1 wt% CNT composite and the abrasion of 1 g of particles: 4000 ppm = 40 µg of CNTs are present in the respirable fraction and are either protruding or free standing.

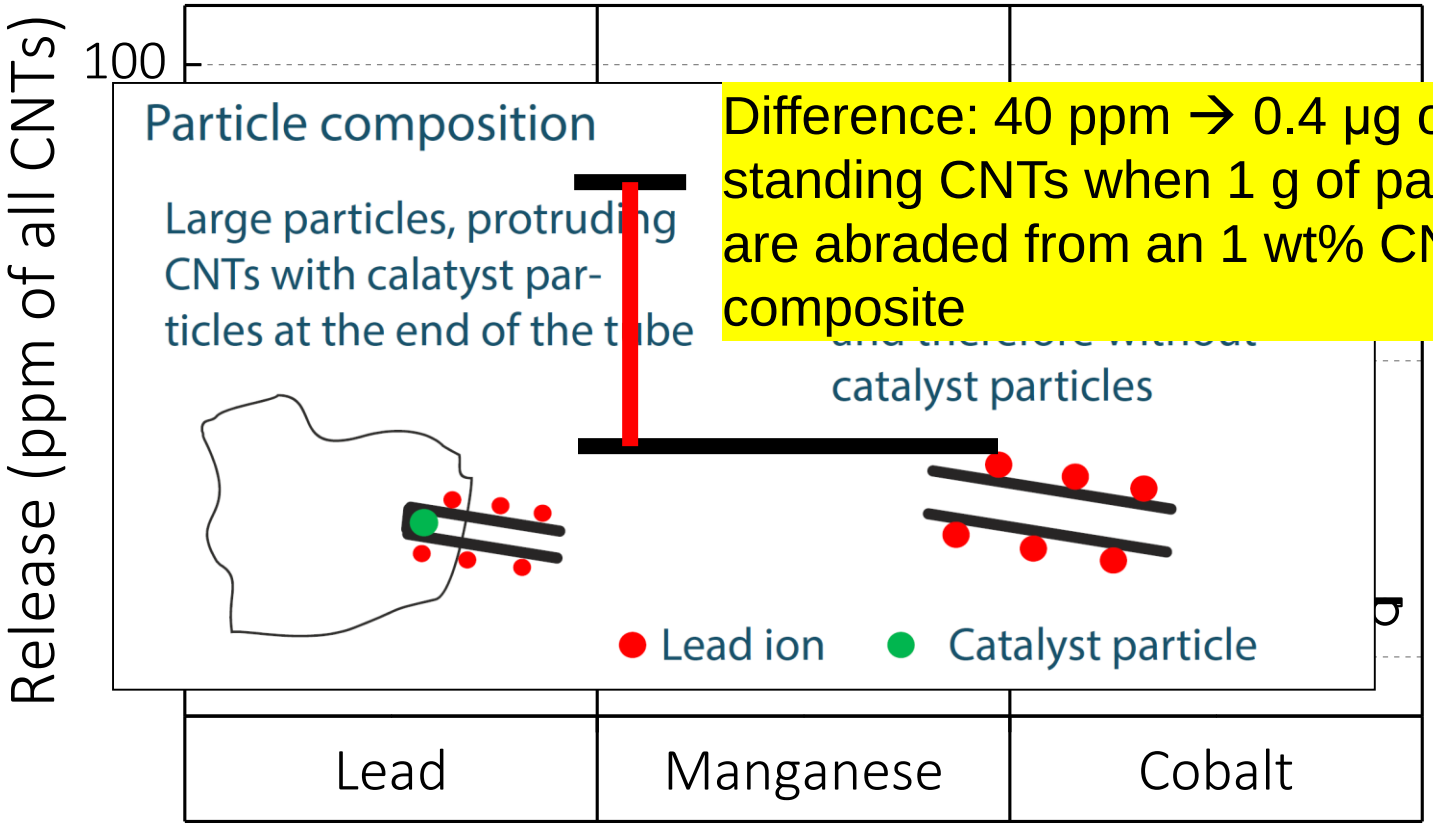
Collection of ultrafine particles

Collection of particles < 100 nm by MOUDI



Quantification of free-standing CNTs

Release comparison



Difference: 40 ppm → 0.4 µg of free standing CNTs when 1 g of particles are abraded from an 1 wt% CNT composite

1 wt% CNT D-230 epoxy
1 wt% CNT Epikure 3402 epoxy
Average values
Standard deviation

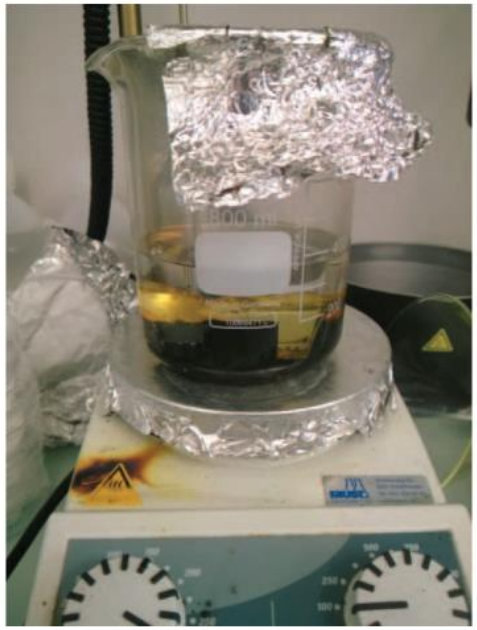
Weathering study

Exposure to UV light :

An accelerated weathering tester equipped with a UVA-340 lamp, corresponding to the light intensive in Florida at noon.

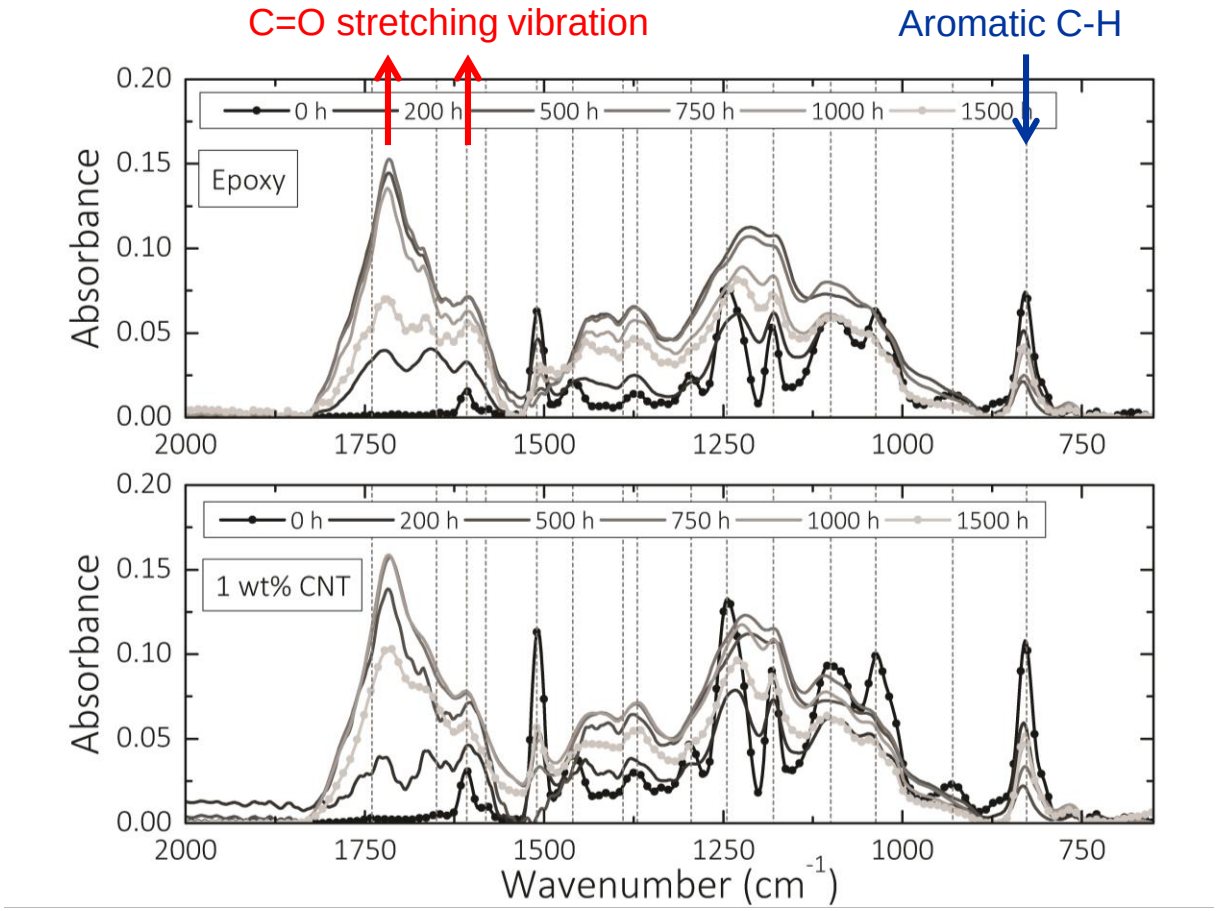
Immersion in water bath :

The diffusion of water can cause reversible or permanent change in the material properties.



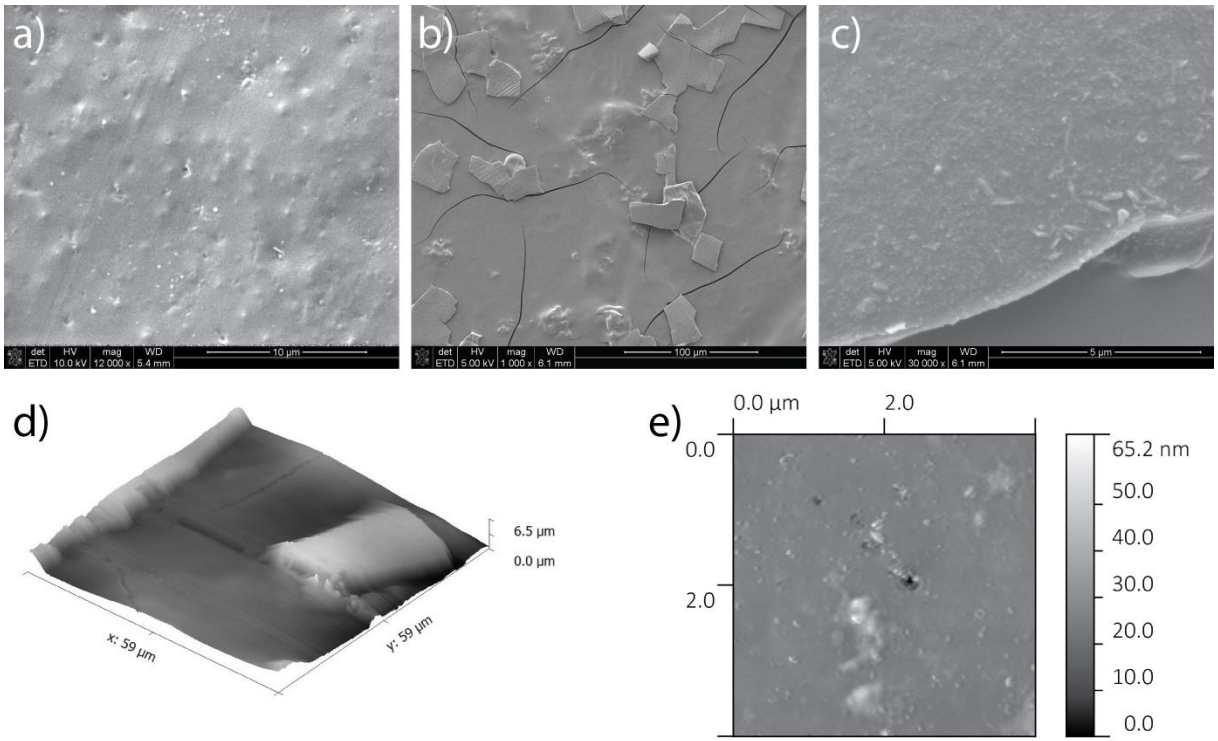
Schlagenhauf, Kianfar, Buerki-Thurnherr, Kuo, Wichser, Nüesch, Wick and Wang, *Nanoscale,* 2015.

ATR-FTIR measurement: surface chemistry



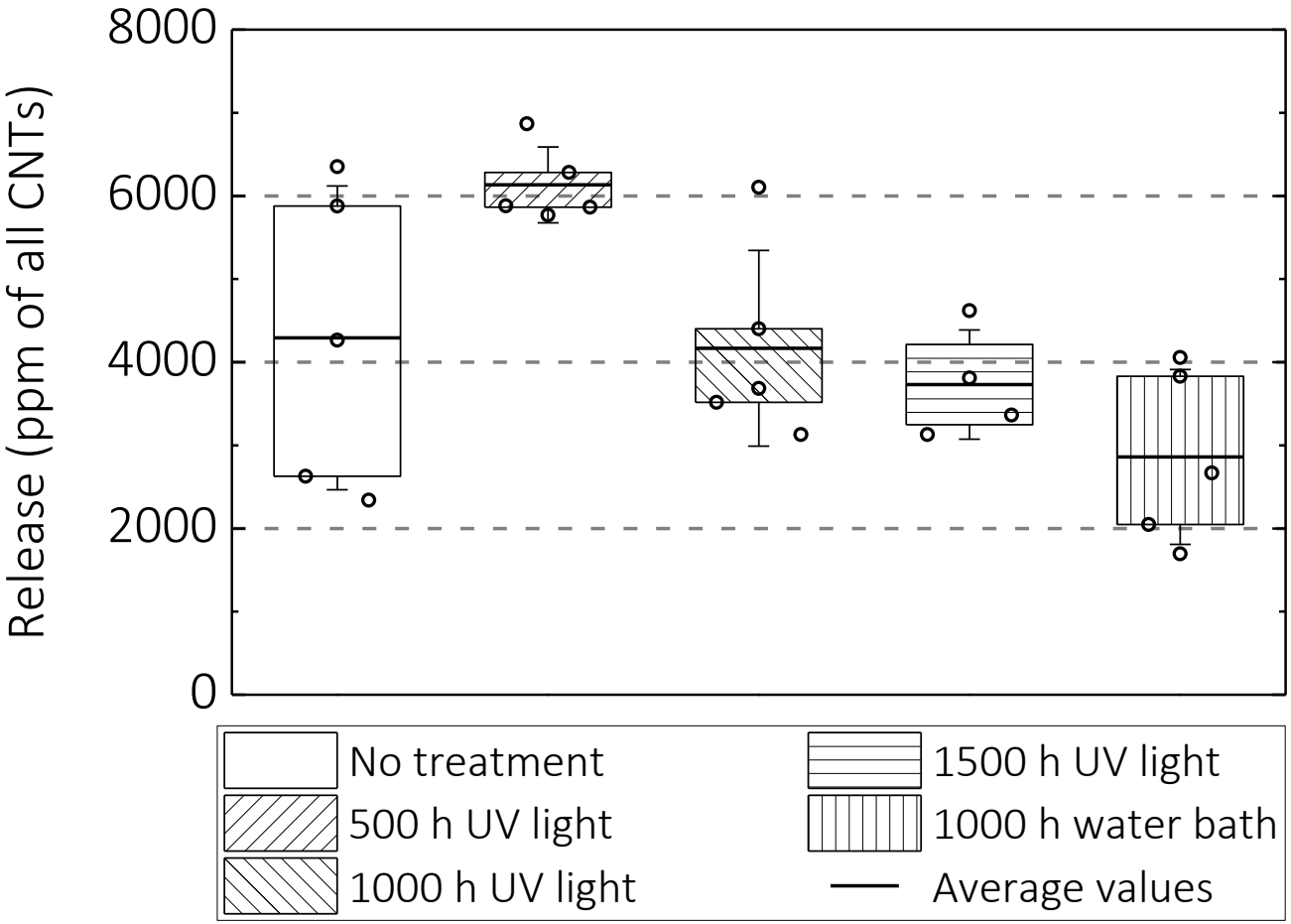
- A quasi-stable state was reached between 500h and 1000h
- Sample surface fall-off after an UV exposure between 1000h and 1500h

Impact on topography



- No change of the surface topography after 1000h of water bath
- Delamination of top surface layer after 1000 h of UV exposure
- UV light exposure damaged the surface in both micro and nano range

Quantification of exposed CNTs

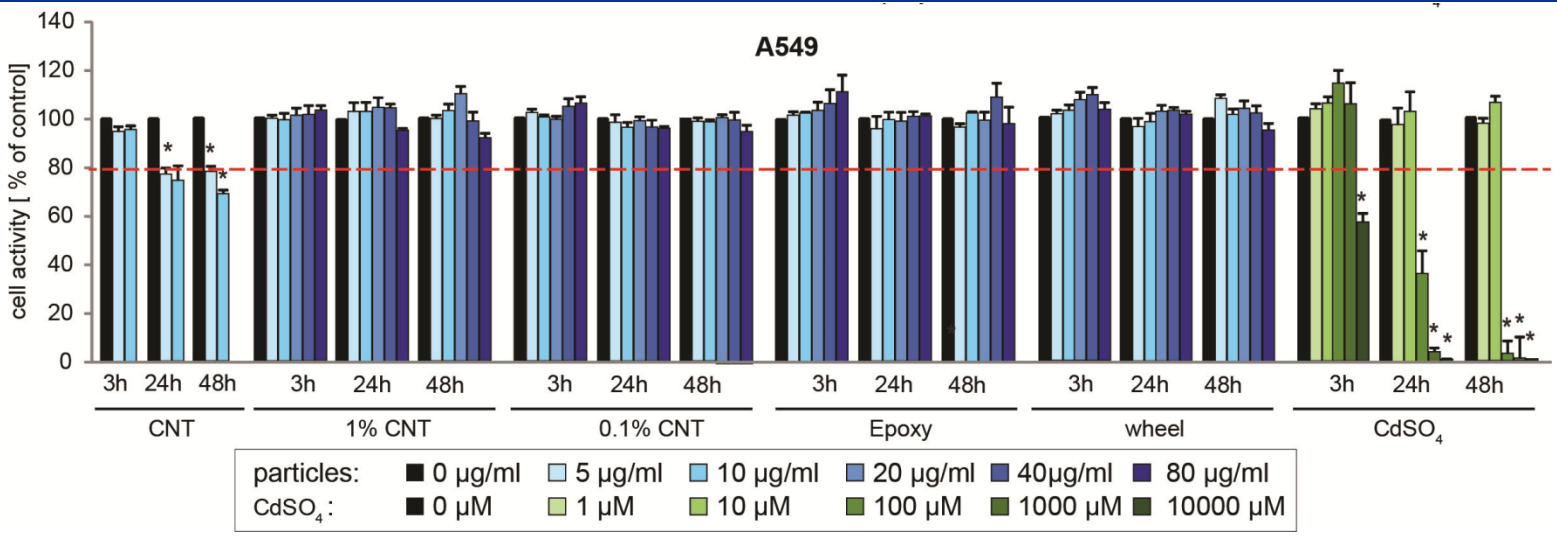


No increased release of exposed CNTs after the exposure to UV light up to 1500 h or immersion in water.

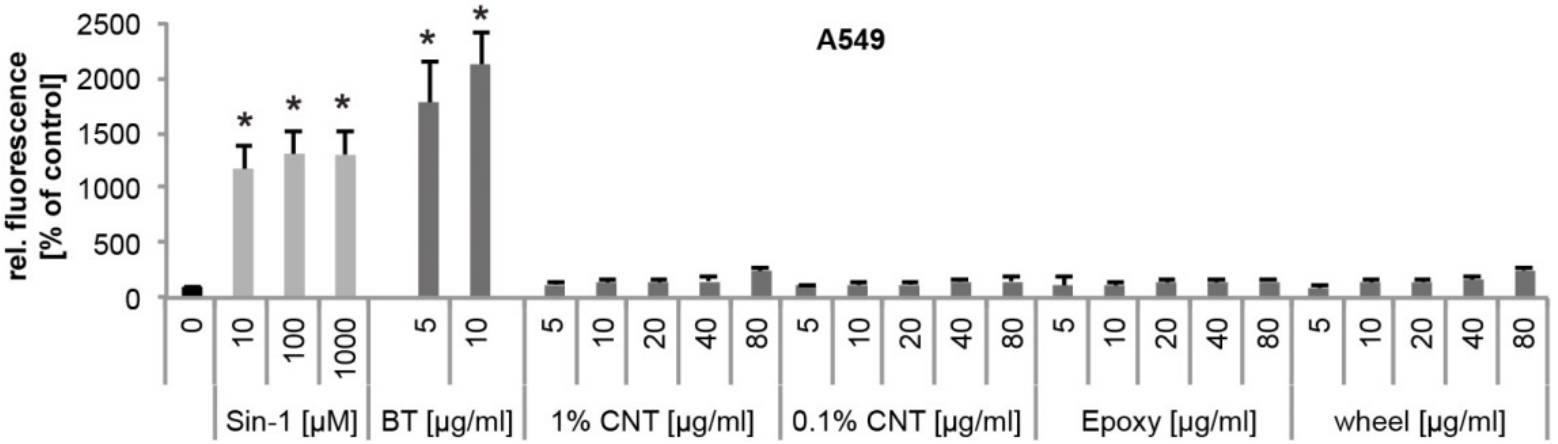
Schlagenhauf, Kianfar, Buerki-Thurnherr, Kuo, Wichser, Nüesch, Wick, and Wang (2015), *Nanoscale,* 7, 18524 – 18536, DOI: 10.1039/C5NR05387K .

Toxicity tests

Viability



Oxidative stress



CNTs but not abraded particles have effects on the viability of THP-1 macrophpages and A549 epithelial cells and oxidative stress.

Conclusions

- Release of extruded and free-standing CNTs from nanocomposites during abrasion is observed and quantified by a newly developed ion-labeling method.
- No increased release of exposed CNTs after the exposure to UV light up to 1500 h or immersion in water.
- Even though the CNTs have toxic effects, the abraded particles do not show significant toxicity.
- Material properties affect CNT release and general conclusions cannot be made for different nanocomposites.

Thanks for your attention

Opportunities and Risks of Nanomaterials
National Research Programme NRP 64

EMPA
Materials Science & Technology

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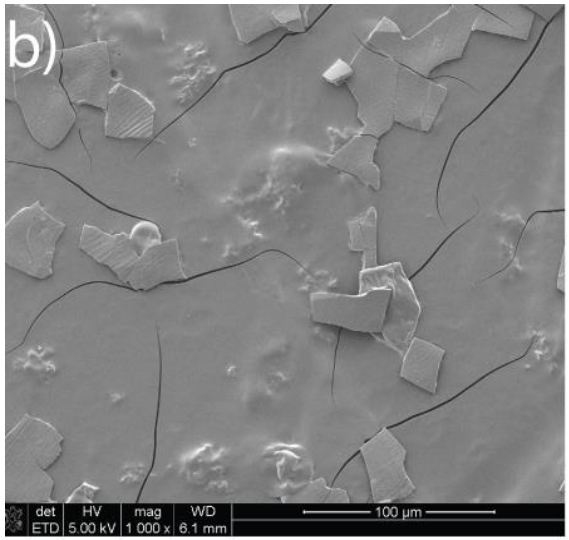
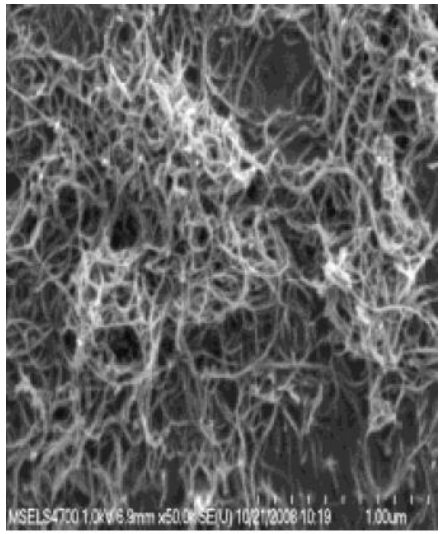
No release by weathering alone

Our study



Surface delamination and no CNTs were exposed.

Nguyen et al. (2011)



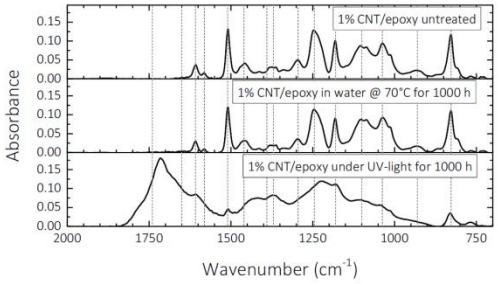
CNT network exposed on the surface.

Possible factors for the difference

- Our samples were thicker, thus stronger resistance;
- The humididy in our experiments was lower, thus more brittle.

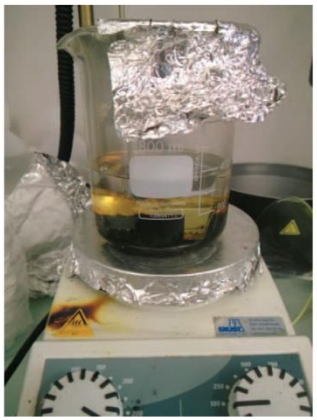
Weathering study

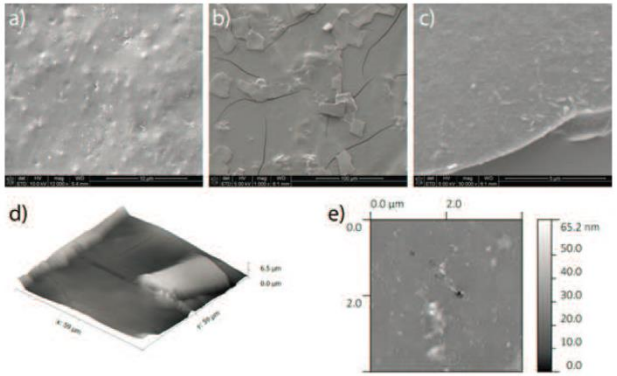
Exposure to UV light



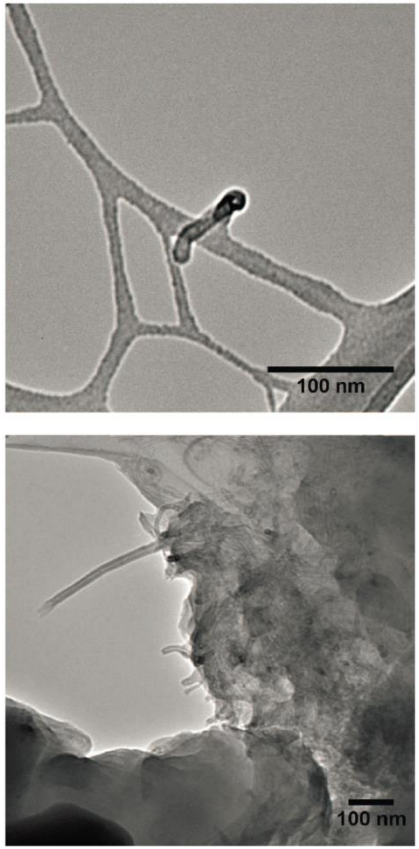
ATR-FTIR measuremet:
No changes for water bath
Strong degradation for UV

Immersion in water bath

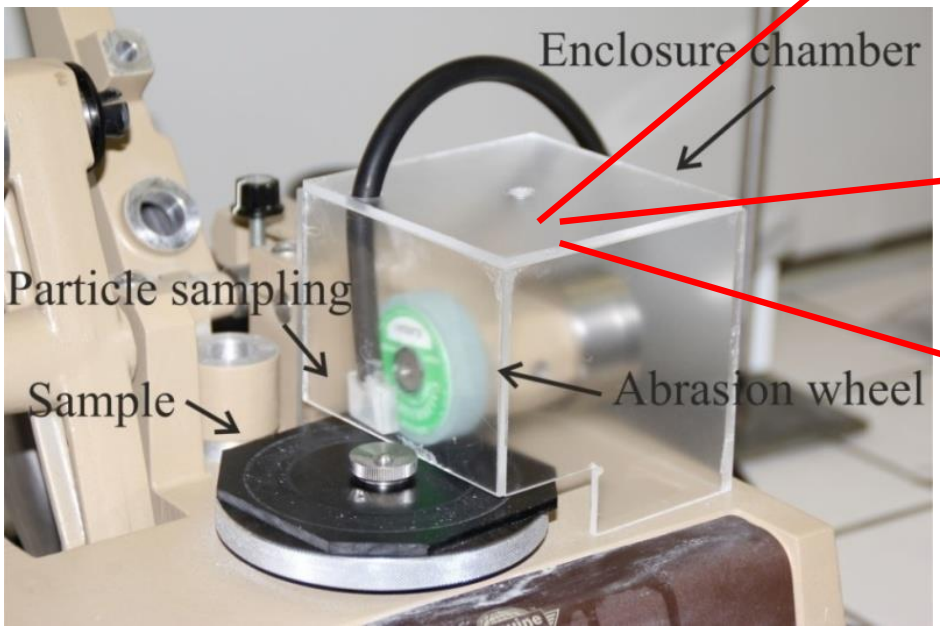


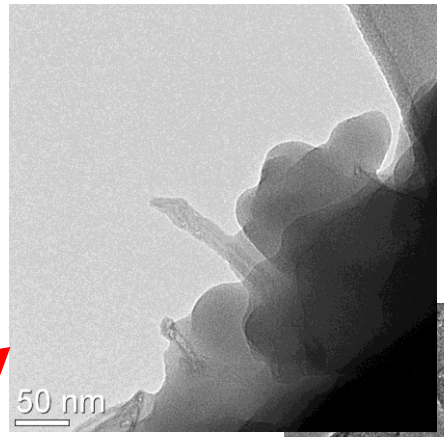


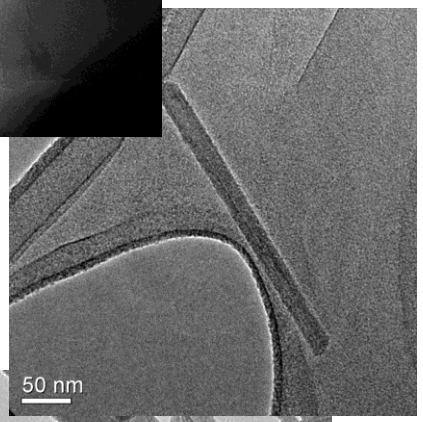
Impact on topography:
No changes for water bath
Delamination of top surface layer after 1000 h of UV exposure

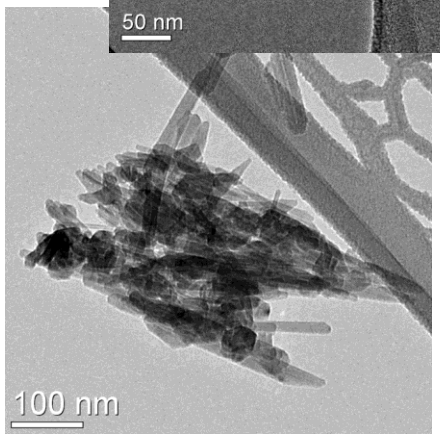


Released particles:
Only protruding, but no free standing CNTs detected


Enclosure chamber
Particle sampling
Sample
Abrasion wheel


50 nm


50 nm


100 nm

Peaks on the ATR-FTIR graphs

Peak (cm^{-1})	**Excitation**
3700 – 3100	OH and NH stretching vibration
1740	C=O stretching vibration
1650	C=O stretching vibration
1608	C=C stretching vibration
1581	C=C stretching vibration
1510	C=C stretching vibration
1460	CH_3- and CH_2- deformation, CH_2-O deformation
1370 – 1390	CH_3 symmetric deformation
1295	C-N stretch aromatic amine, C-C stretching, vibration aromatic ring
1245	C-O-C aromatic ether stretching deformation, bridge between benzene rings
1180	C-C symmetrical stretching vibration
1100	C-O-C out of plane deformation in aromatic rings, C-N symmetrical stretching vibration
1037	C-O symmetrical stretching
930	Antisymmetric deformation of epoxy ring
827	Aromatic C-H out of plane deformation