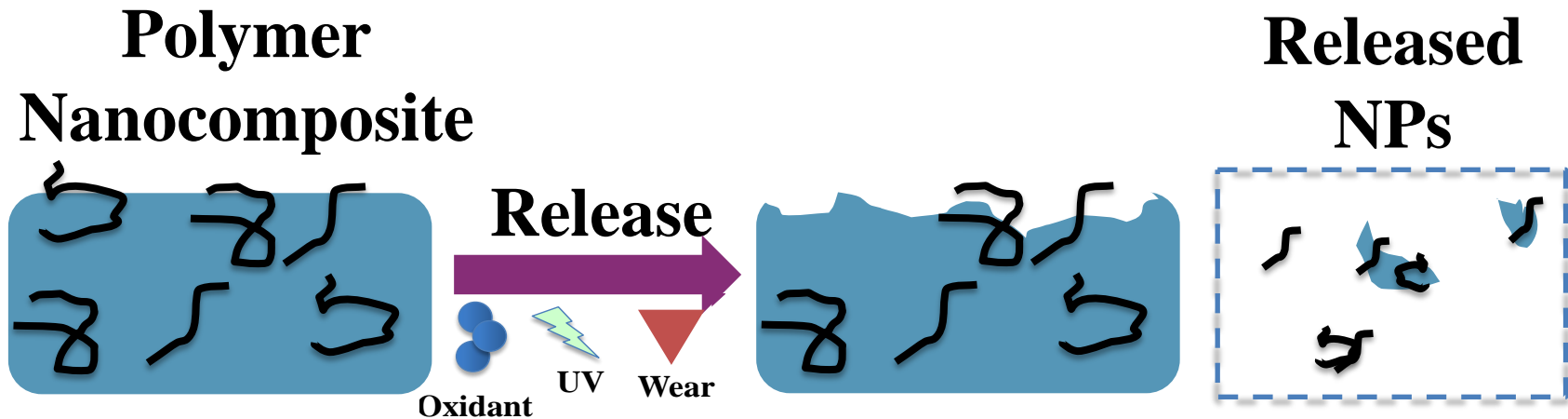


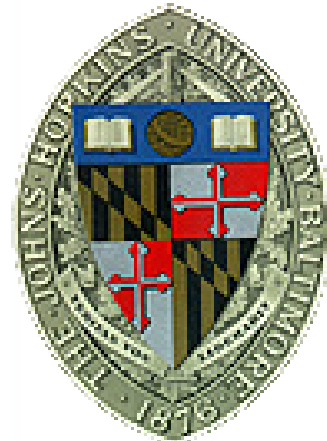
# Nanoparticle release from polymer nanocomposites



*Howard Fairbrother*<sup>1</sup>, James Ranville<sup>2</sup>,  
David Goodwin<sup>1</sup>, Ronald Iankone<sup>1</sup>, JJ Wang<sup>2</sup>, Angie  
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1) The Johns Hopkins University

2) Colorado School of Mines



# Overview

Introduction

Silver Release from Fabrics

Long-term Outdoor Weathering Studies

Accelerated Photolysis of SWCNT-Polymer  
Nanocomposites

- SWCNT Release and Detection

The Need for Model Systems

# Why Study NP Release?

$$\text{RISK} = \text{TOXICITY} \times \text{EXPOSURE}$$

NP toxicity is being studied by many...

NP Exposure is not

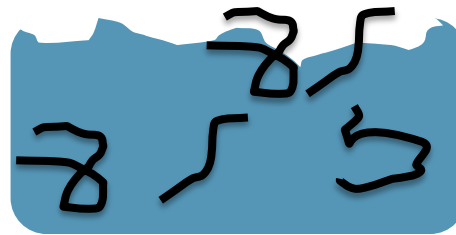
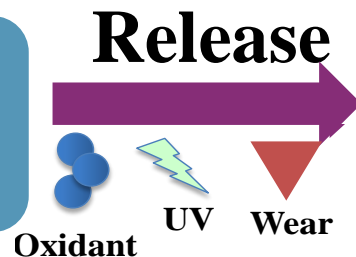
# Three Important Release Characteristics

Release Kinetics (time dependence)

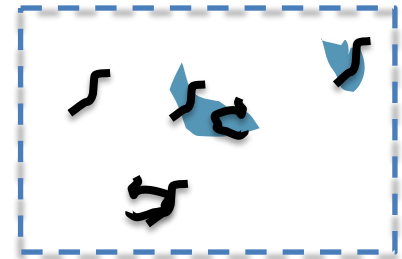
Released Quantity

Released Form

**Polymer  
Nanocomposite**



**Released  
NPs**



**Introduction**

**Silver Release**

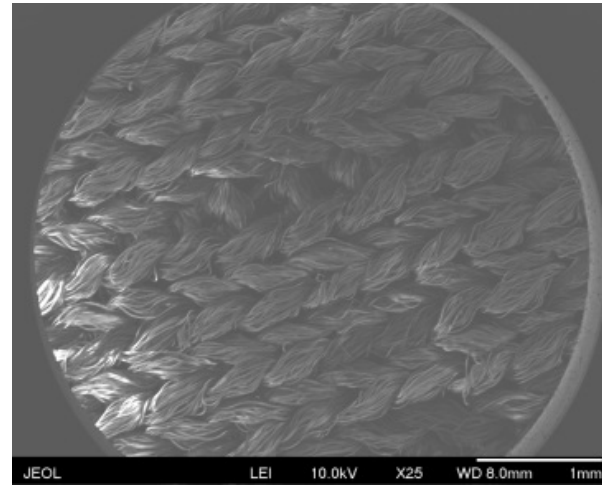
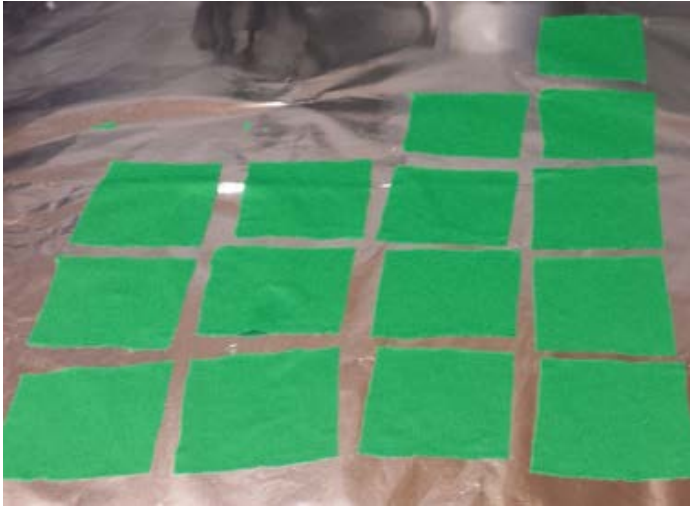
**Out Door Weathering**

**Accelerated Photolysis of SWCNT-Polymer  
Nanocomposites**

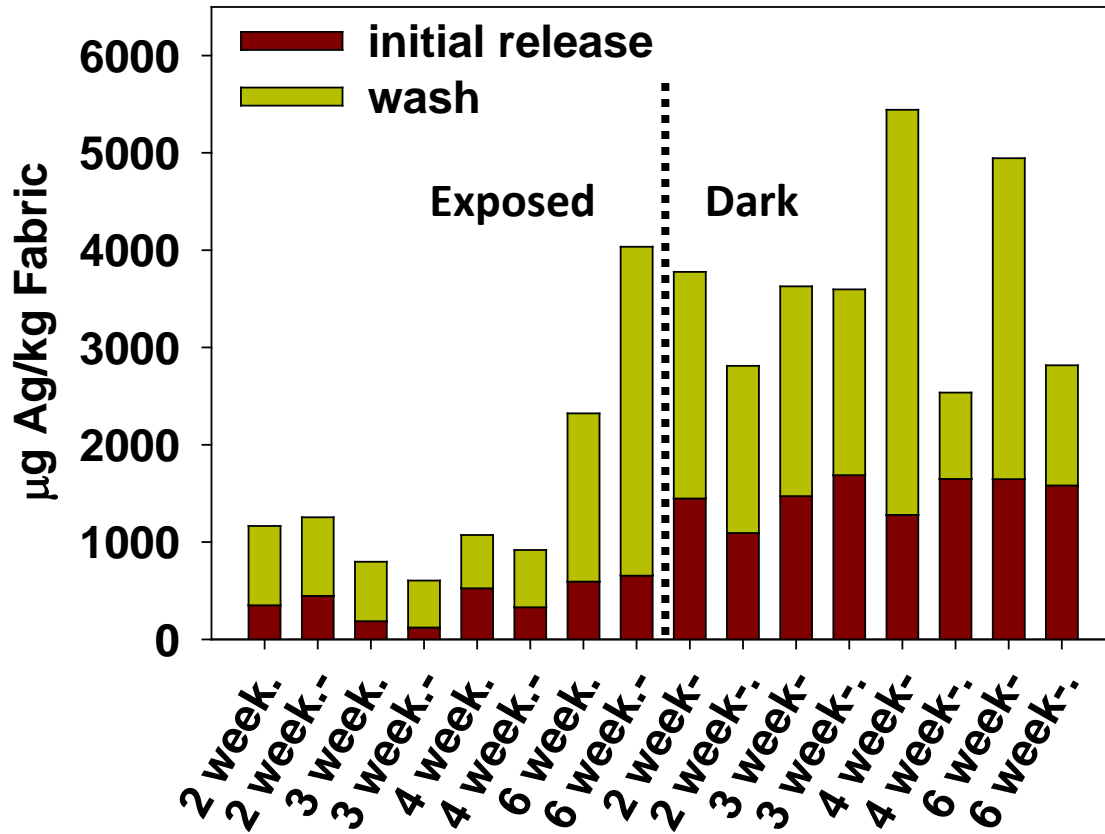
**SWCNT Release**

Silver Release

# *Effect of Photolysis on Silver Release from Fabrics*



## ICP-MS analysis shows that photolysis of nanotextile inhibits the initial release of silver



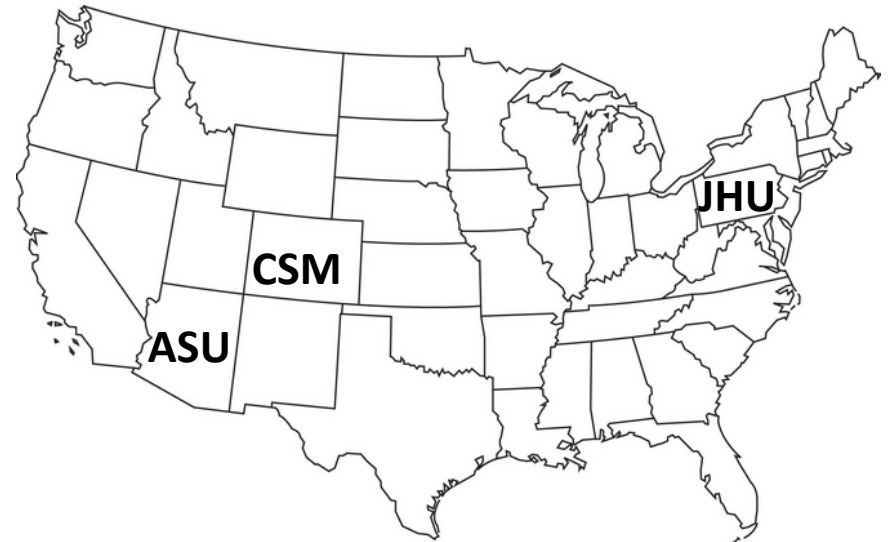
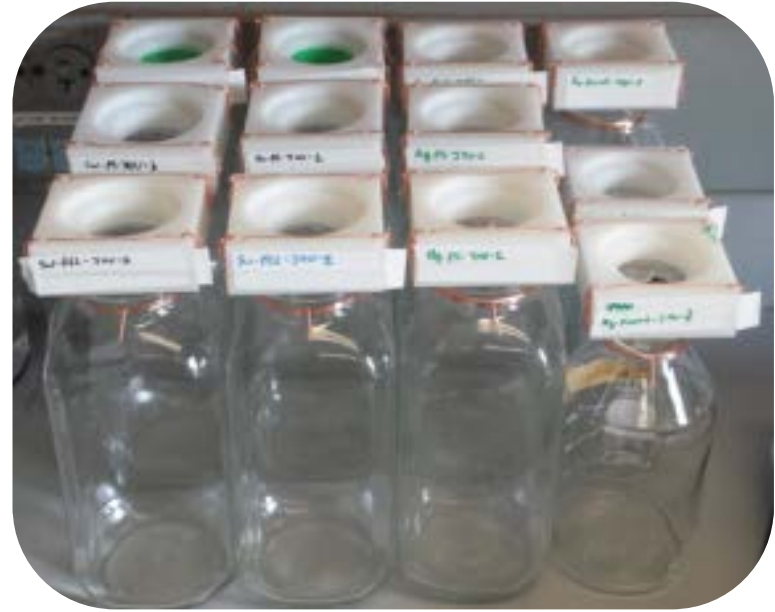


# Out Door Weathering

# Long Term Weathering Studies of Nanocomposites



**Nanocomposite**

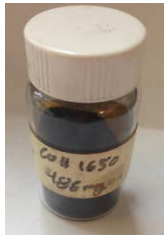


# **Accelerated Photolysis of SWNT Polymer Nanocomposites**

**- SWNT Release Characteristics and Detection**

**A Model System**

# Construction of Model CNT-Polymer Nanocomposites



CNT loading



Organic solvent



Polymer



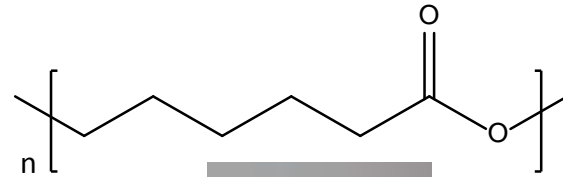
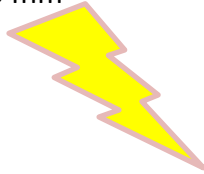
# ***Construction of Model CNT-Polymer Nanocomposites***



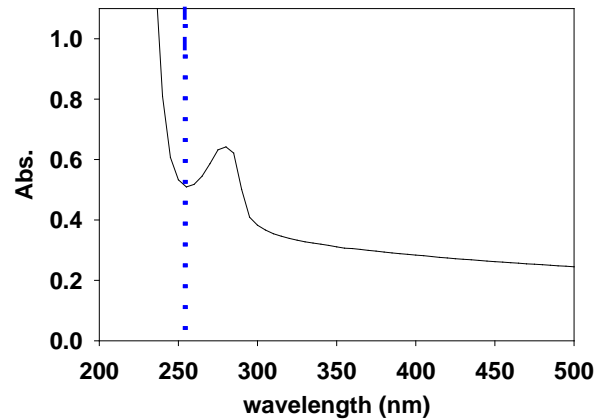
# Accelerated Photodegradation Study:

pristine Single Wall Carbon Nanotube – polycaprolactone  
(pSWCNT-PCL) composites

254nm

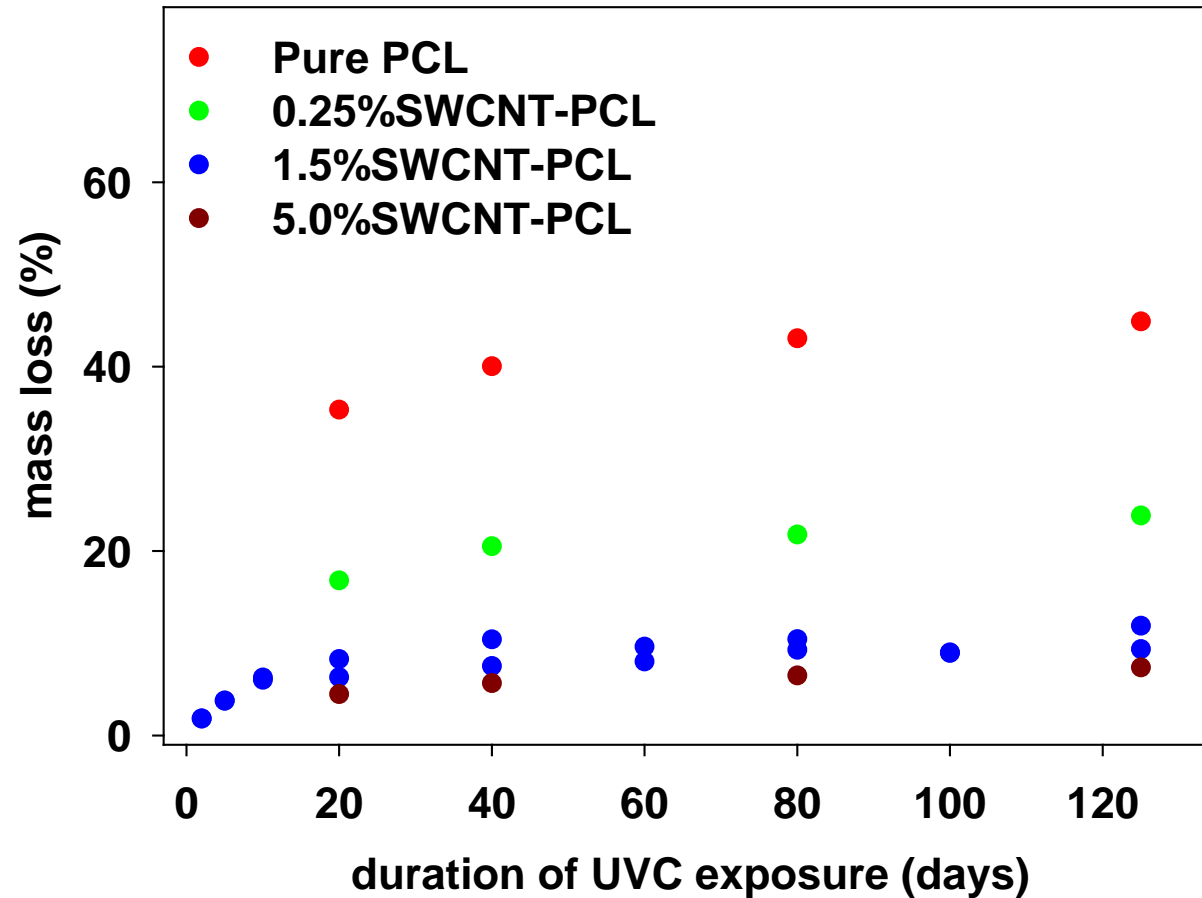


254nm light used in this study is  
absorbed strongly by poly-ε-caprolactone

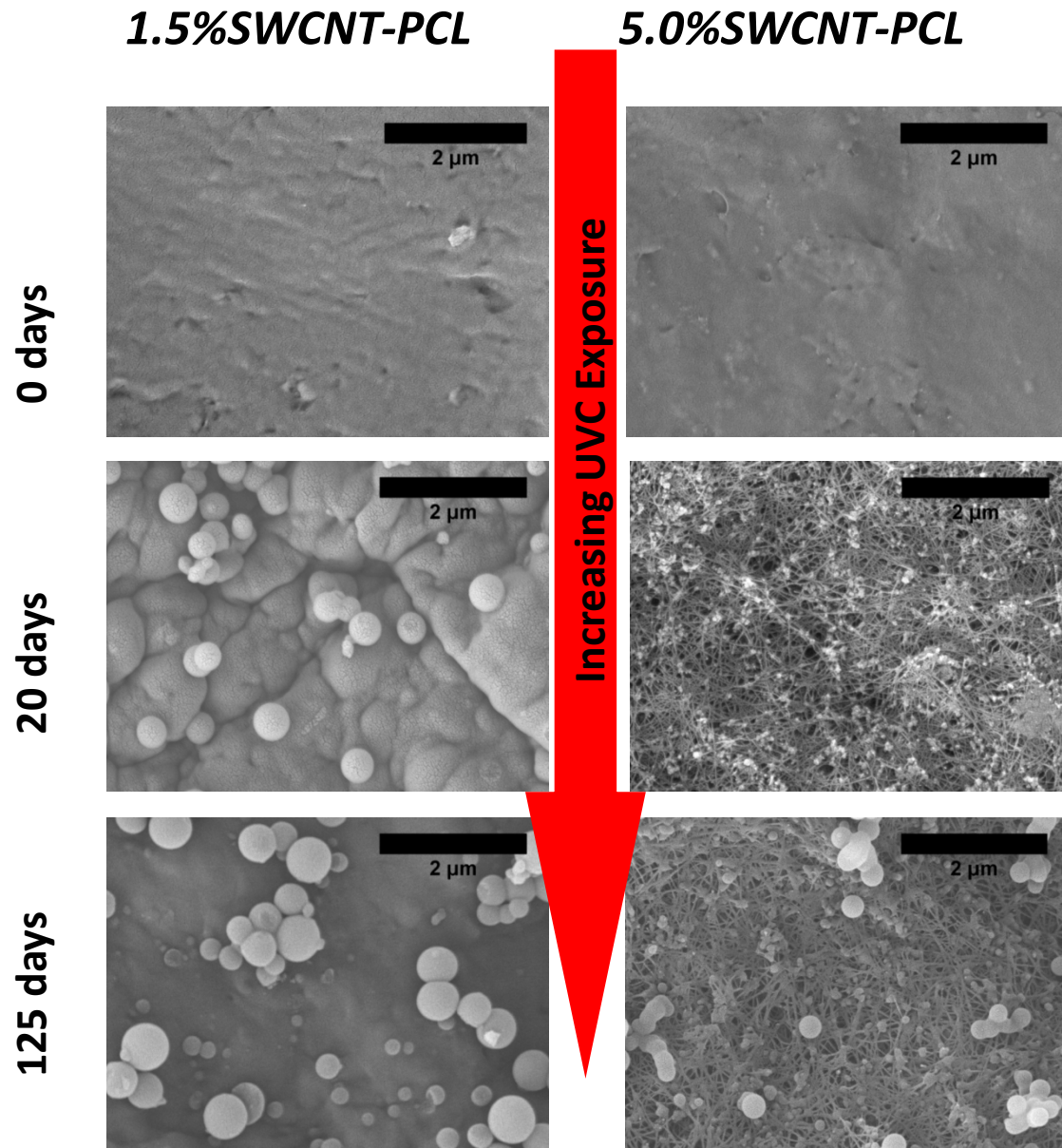


# *Photolysis of SWCNT-polycaprolactone nanocomposites*

**Nanocomposite photodegradation in 254nm light  
is strongly inhibited with the addition of CNTs**



***SEM imaging shows high concentration (5% w/w) of CNTs are required to for accumulation at the surface to occur***

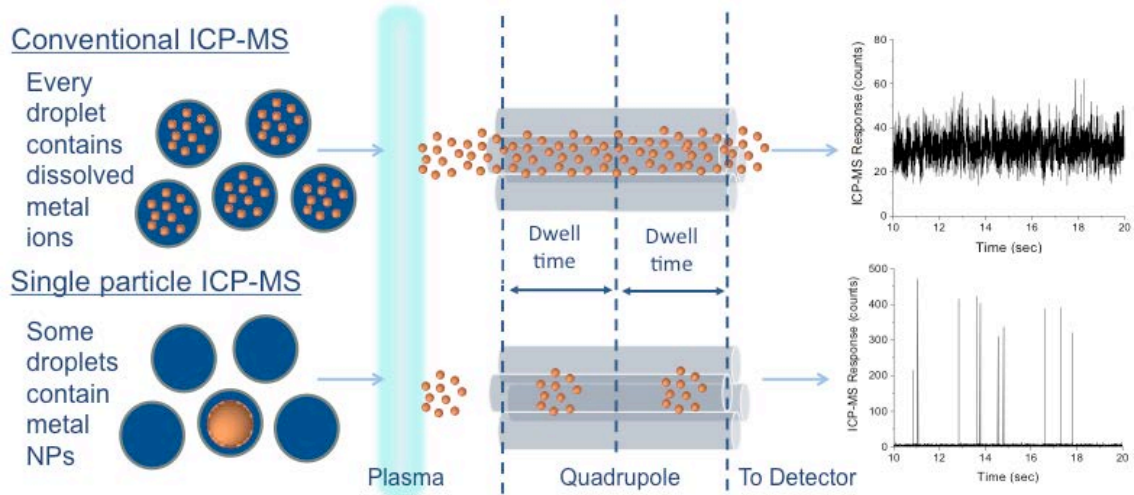




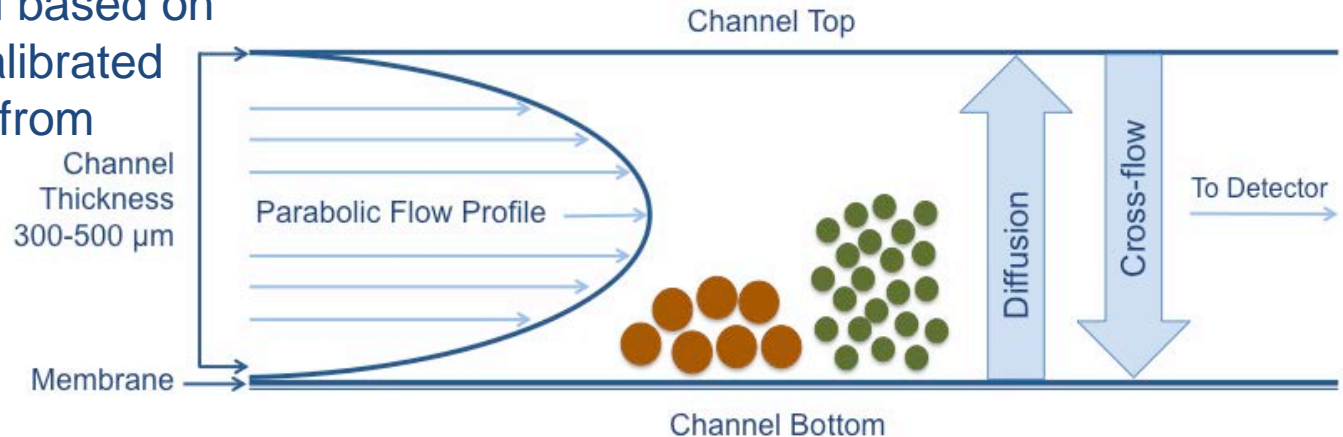
# Detection of CNTs

Single particle ICP-MS (spICP-MS) detects NPs particle-by-particle. The number of pulses is related to the particle **number concentration**.

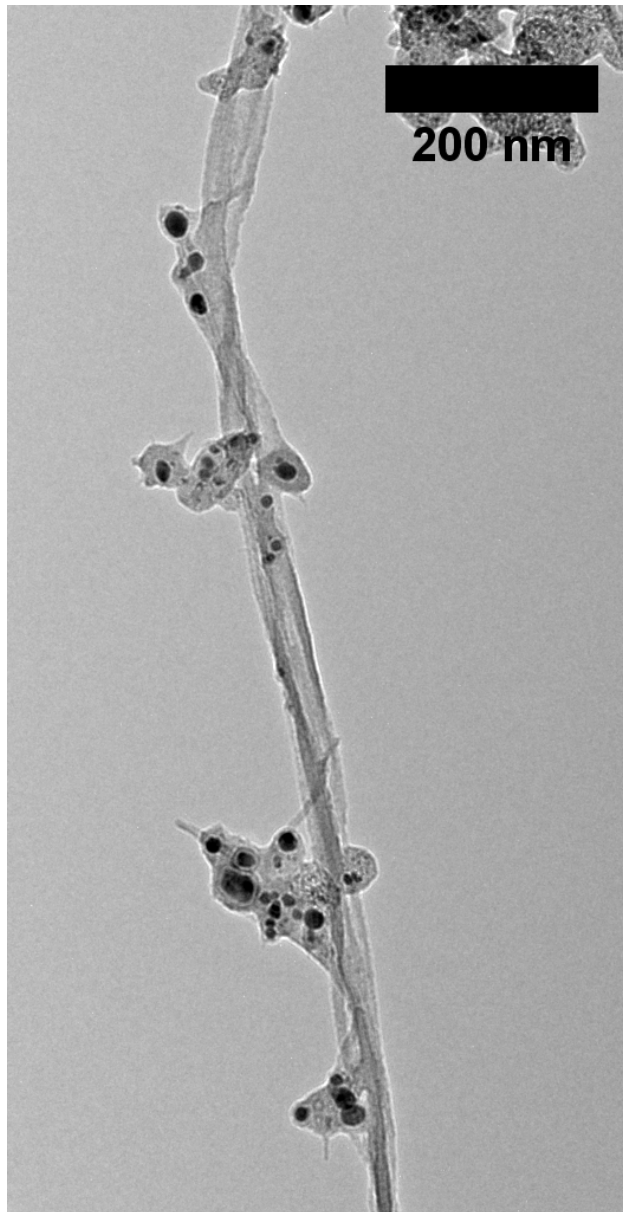
Intensity of the pulse is related to the **particle mass** (and size with assumed shape and density).



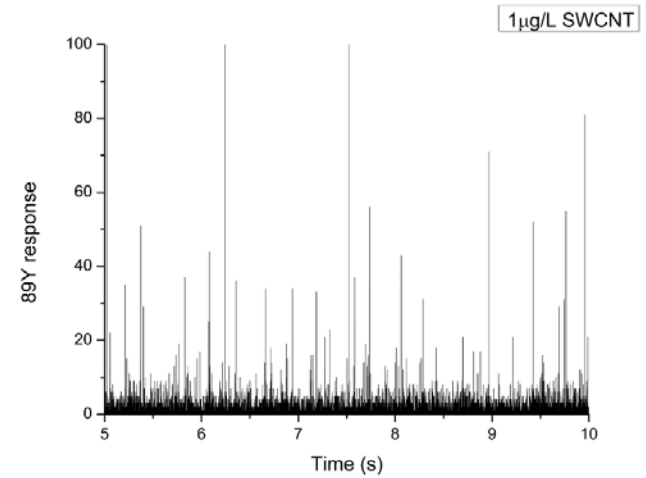
AF4 separates NPs based on their **hydrodynamic diameter**. Size can be determined based on retention times when calibrated (can also be computed from theory)



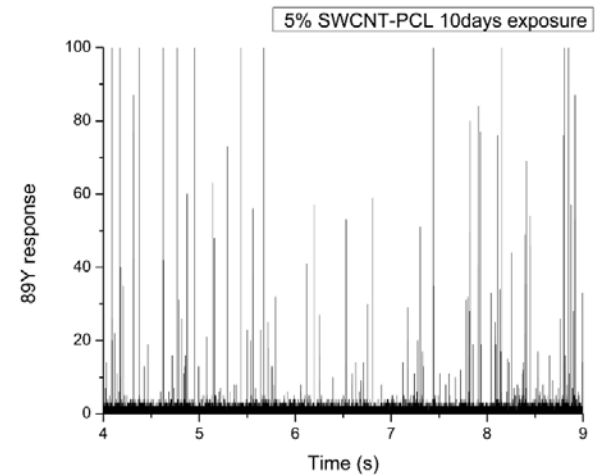
# *sp-ICP-MS Analysis of SWNCTs*



## Analysis of SWCNT suspension

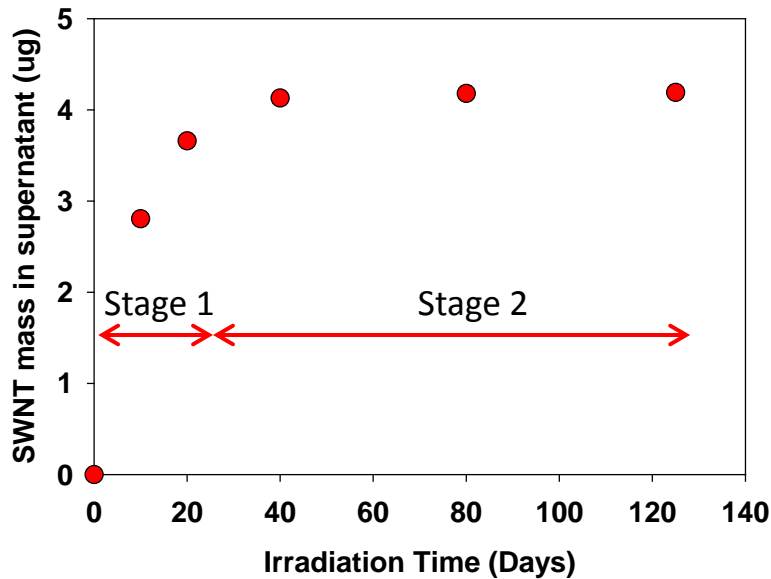


## Analysis of SWCNT-PCL release supernatant

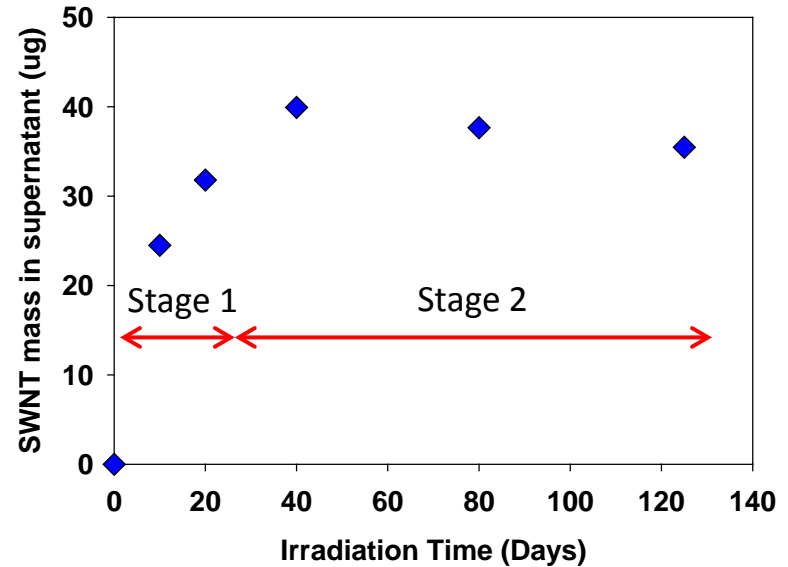


# Release Kinetics of CNTs from Polymer Nanocomposites

0.25 % CNT /PCL



5% CNT/PCL

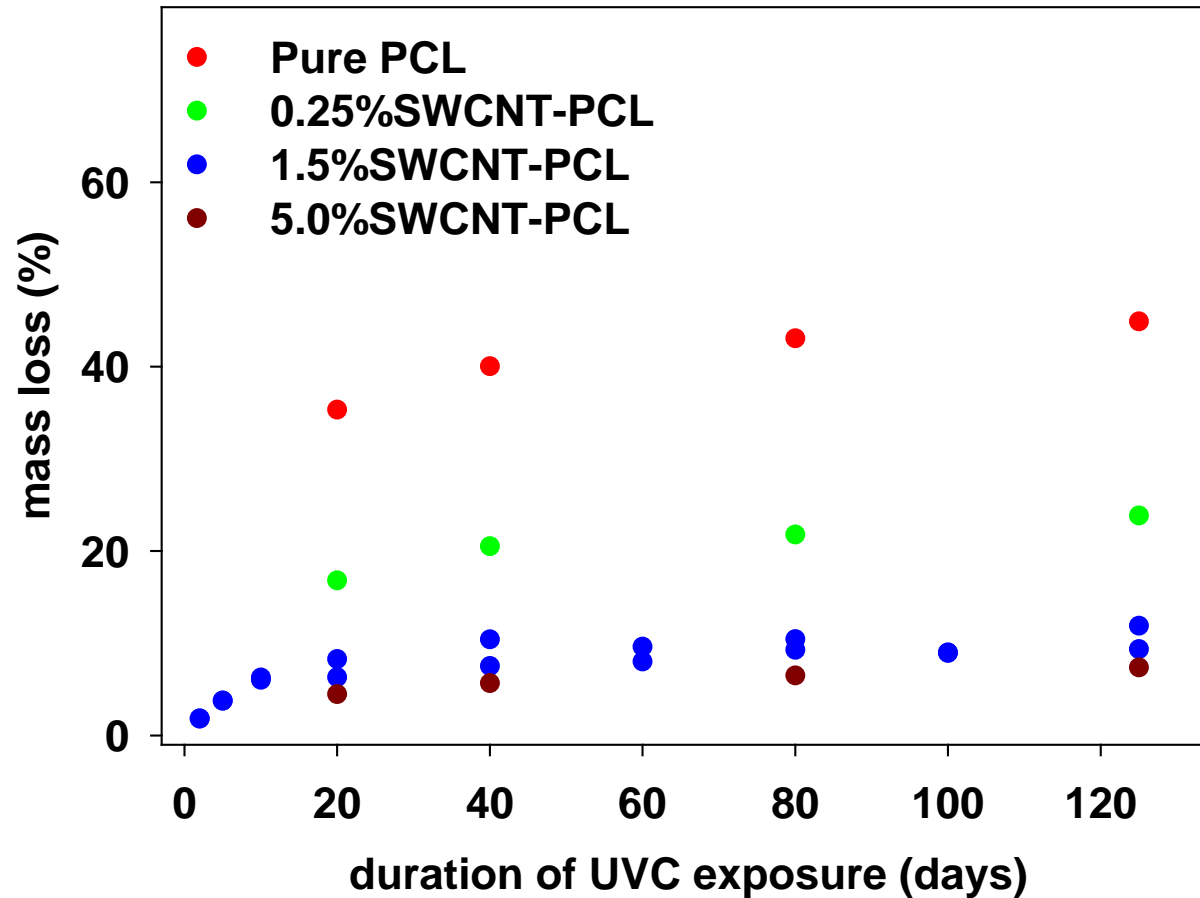


Stage 1: Initial CNT Release

Stage 2: No further CNT Release

# *Photolysis of SWCNT-polycaprolactone nanocomposites*

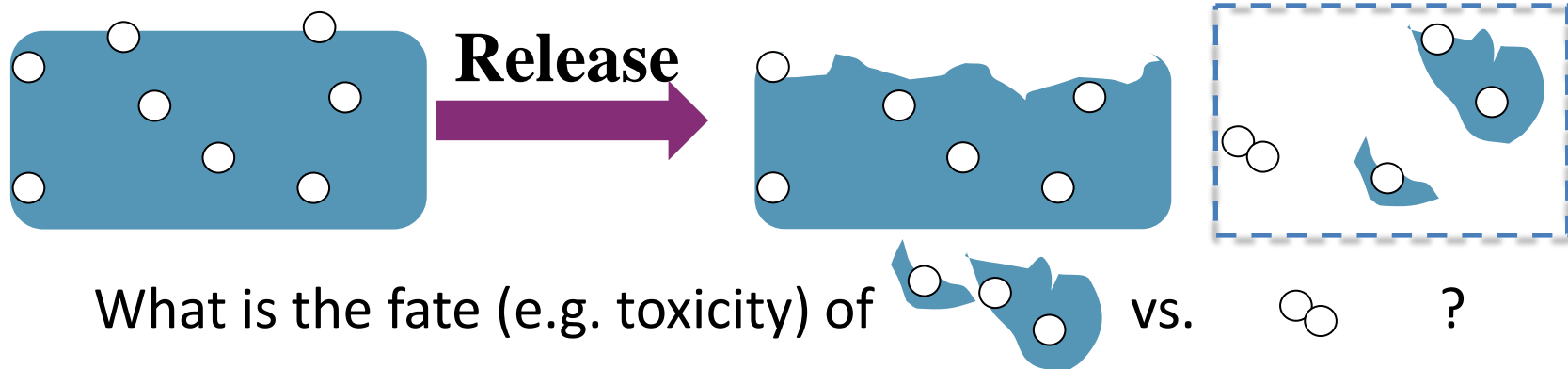
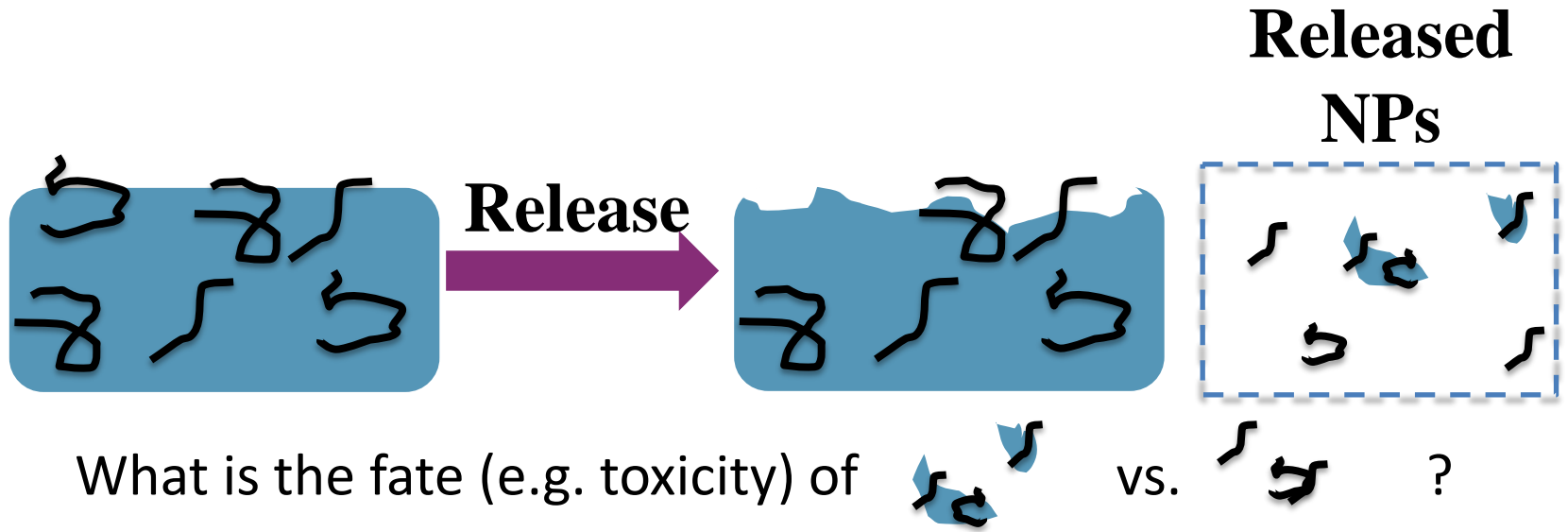
**Nanocomposite photodegradation in 254nm light  
is strongly inhibited with the addition of CNTs**



# The Need for Model Systems

# NP Release from Polymer

## Nanocomposites: Unresolved Questions

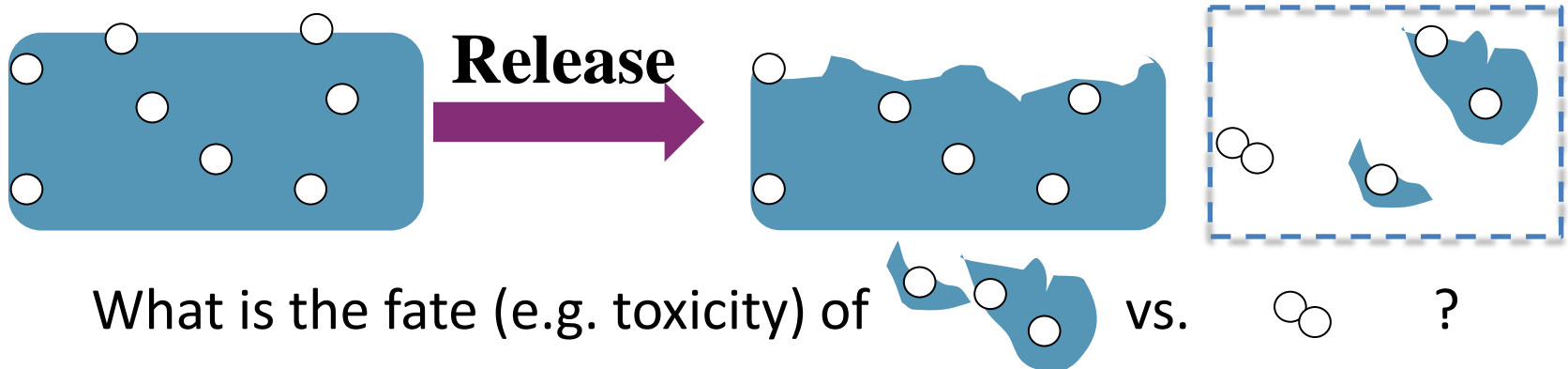


# NP Release from Polymer

## Nanocomposites: Unresolved Questions

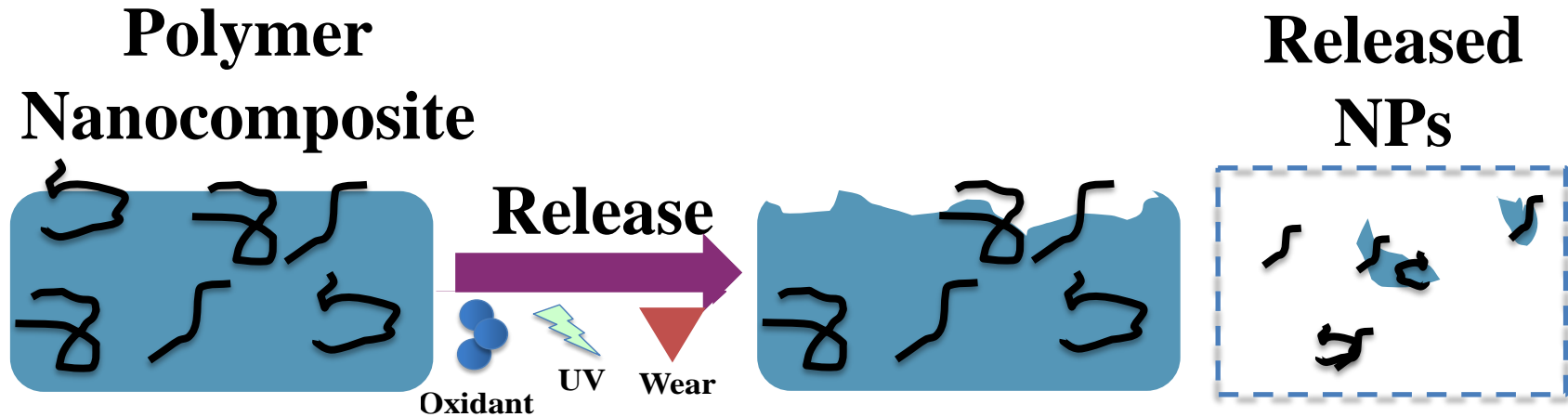


The Biggest Issue is Characterization of Released Materials and the Difficulties in Generating Enough (Release Quantities are Small)



# NP Release from Polymer

## Nanocomposites: Unresolved Questions



What is the yield of  vs.  and how will it depend on (i) polymer characteristics and (ii) potential release scenario?

To develop a fundamental understanding we need model composites and well-defined potential release scenarios. To date almost all studies have been performed on commercial products.



# Why Do We Need Model Systems?

- The number of potential polymer nanocomposites and release scenarios are almost limitless. In a model approach:
- Polymer nanocomposites can be prepared with well-defined and systematically varied characteristics (e.g. NP loading and type)
- Consequently studies on model systems have the potential to allow us to develop *predictive capabilities*

# Why Do We Need Predictive Capabilities?

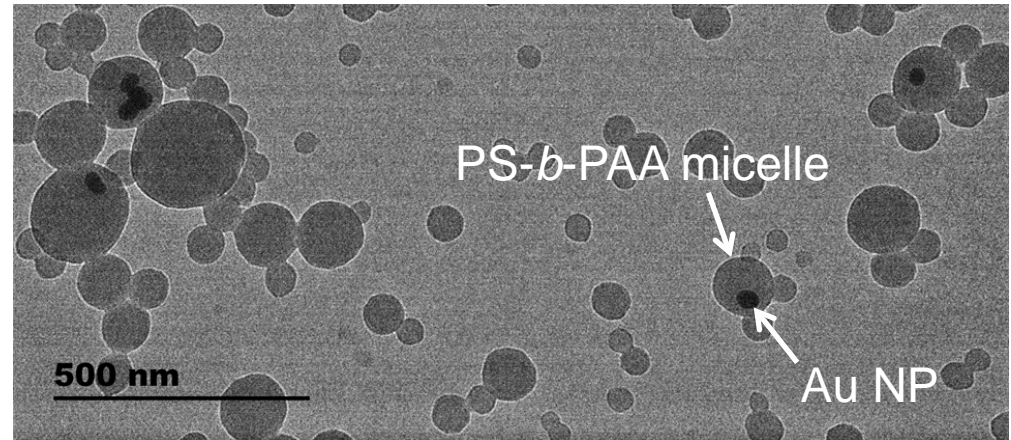
- Predictive Capabilities could allow us to:
  - Estimate release characteristics (released quantity, rate, and type) based on knowledge of the polymer and the NP under a given release scenario.
  - Or in other words... if we know the behavior of the polymer in a given release scenario and we know the details of the NP and nanocomposite, such as NP loading, can we predict release characteristics?
  - Predict release properties for nanocomposites *a priori*

# Acknowledgements:

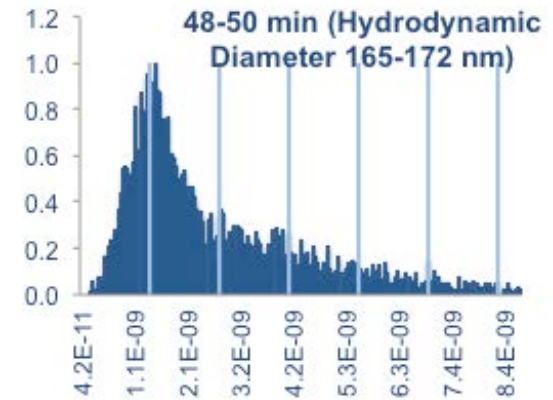
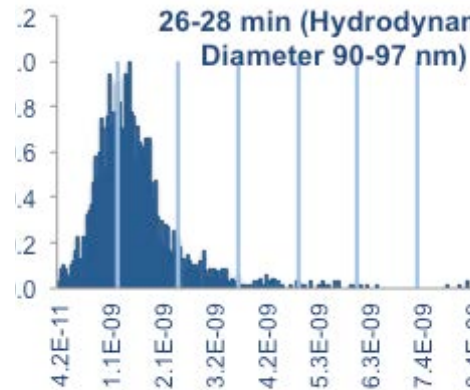
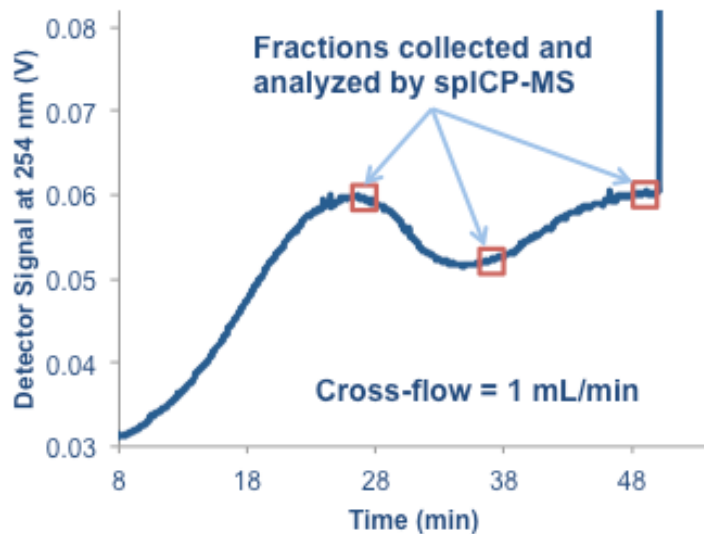


# Model Systems: Polymer –Au composites as model particles for released polymer fragment/ENP

Synthesis: 50 nm Au NPs were incorporated into amphiphilic block copolymer PS-*b*-PAA micelles by self assembly in a microfluidic reactor.



The Au-PS-*b*-PAA NP was analyzed by spICP-MS and AF4-UV-vis. Fractions collected during AF4 analysis were analyzed by spICP-MS.



Larger polymer particles contain more Au NPs