Sensors and Emerging Technologies for Tracking Nanomaterials in Complex Matrices

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NSF

United States Environmental Protection Agency

VE RI TAS
HARVARD

T.C. Millî Eğitim Bakanliği

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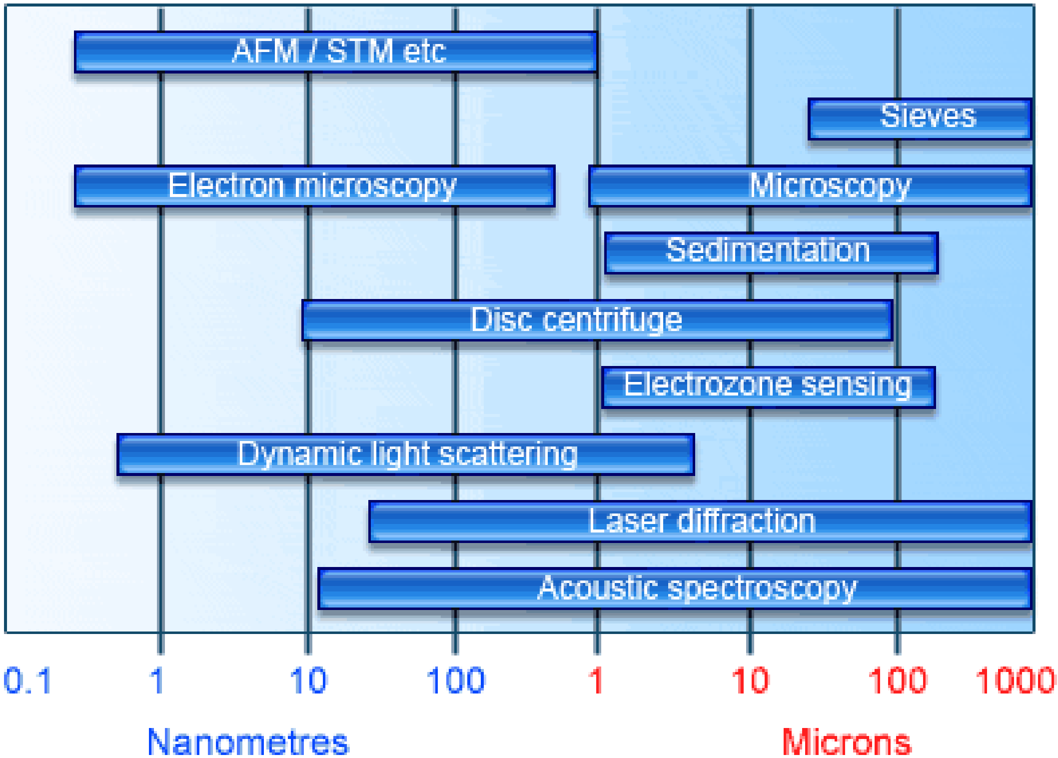
Instrumentation & Characterization

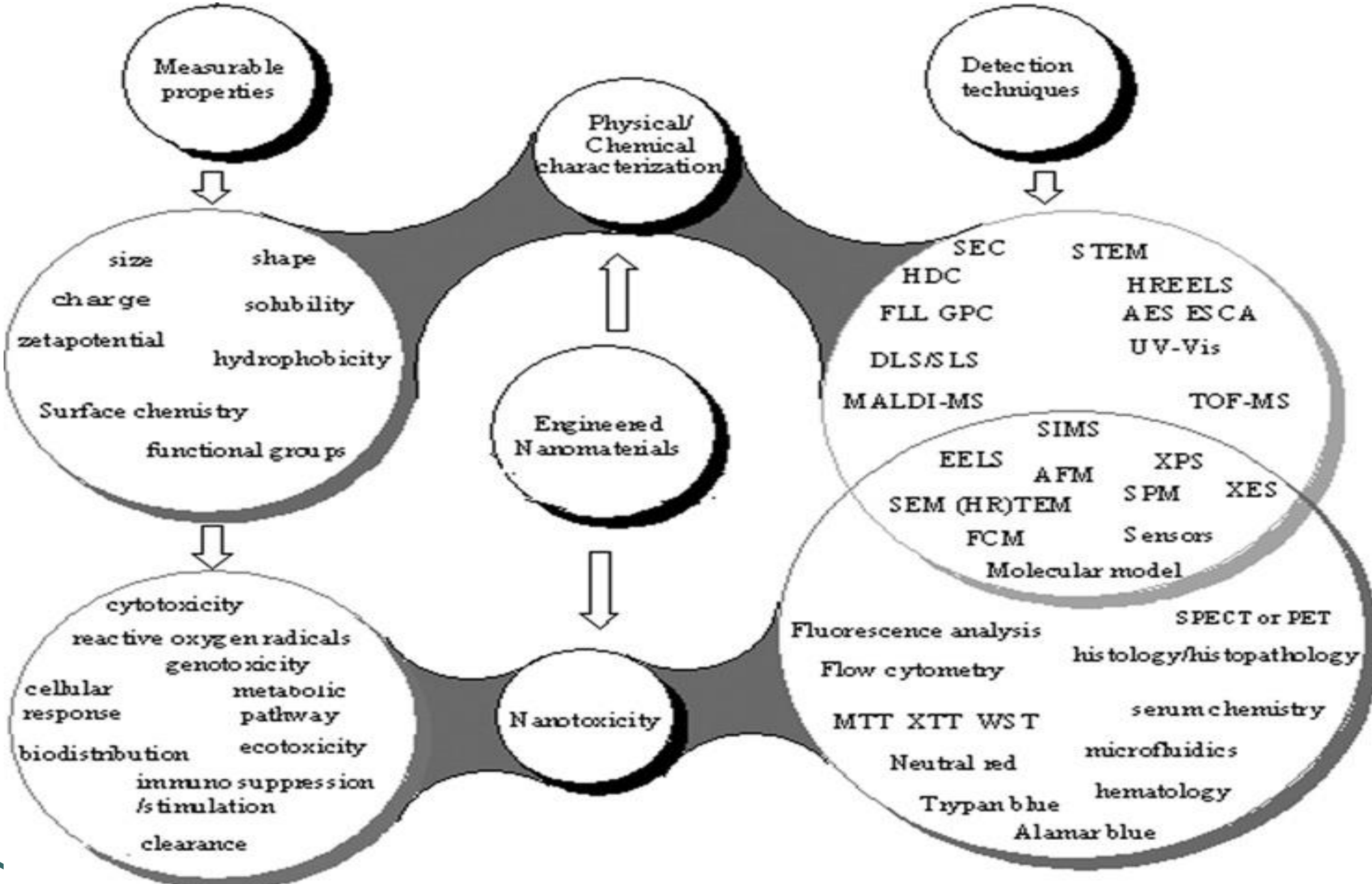


Dynamic Light Scattering (DLS): is the only technique able to measure particles in a solution or dispersion in a fast, routine manner with little or no sample preparation.

AFM and STM: only suitable for 'hard' materials or conductors, i.e. those not affected by the preparation technique and is poor from a statistical point of view as only tens or hundreds of particles are measured.

Electron microscopy: Provides information about the shape and surface structure of the particle than an ensemble technique like DLS.

Toxicity & Characterization Tools



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J. Environ. Monit., 2009, 11, 1782–1800 | 1785

Characterization Challenges

- Workplace exposure to nanoparticle is a potential health hazard and could pose a major threat to humans.
- Most studies employed a “proof of principle” approach using relatively high doses to ensure a clear demonstration of toxic effects
- “No effect” level studies available, especially in complex matrices.
- Characterization tools unavailable for on-site and real time measurements in complex matrices.
- Sample preparation is key to a successful characterization in complex matrices. No standard data reporting; no analytics(mass or dose metrics reporting?)

Paper-based sensors to capture, isolate and detect aerosol nanoparticles

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•ACS Sustainable Chemistry & Engineering, 2, 1707-1716, **2014**

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Poly(amic) Acid Membranes & Hybrid Nanostructure

- **Unique Properties**:
  - Electro-active, a semi-conductor, stable in many solvents, biodegradable, biocompatible and has free carboxyl and amide groups that acts as molecular anchors
- **Broad applications**:
  - Reductant, Chelator, electrode material, catalyst, membrane filtration, biosensor platform, capture, isolation and detection(CID) of airborne nanoparticles
- **Novel Chemical Forms**:
  - Pellets, membranes, solution, hybrid structures
- **Research Needs**:
  - Mechanical strength, electroactivity and hydrophobicity

Langmuir 26, 17 (**2010**): 14194-14202; *Langmuir* 21,15 (**2005**): 6891-6899
ACS Catalysis 1, 2 (**2011**): 139-146.

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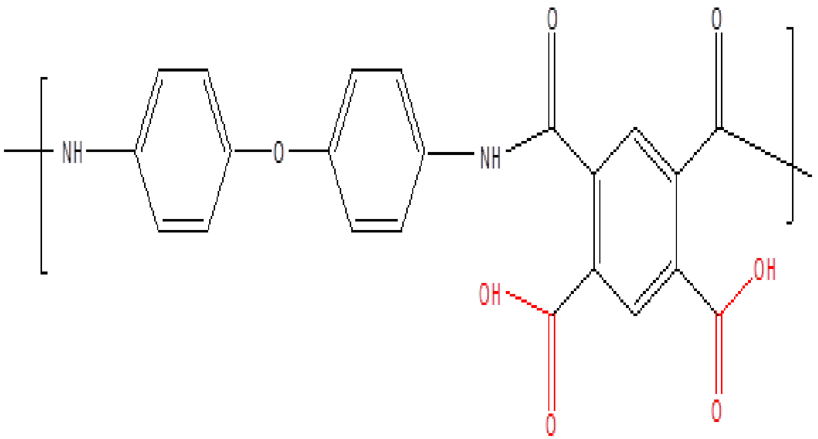
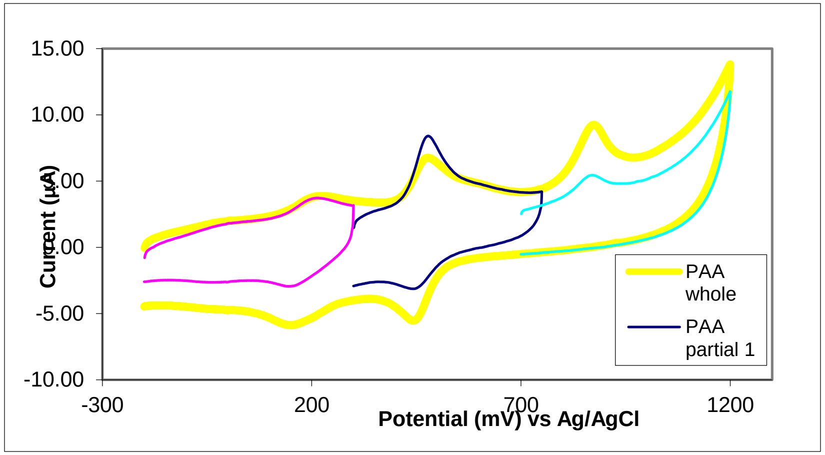
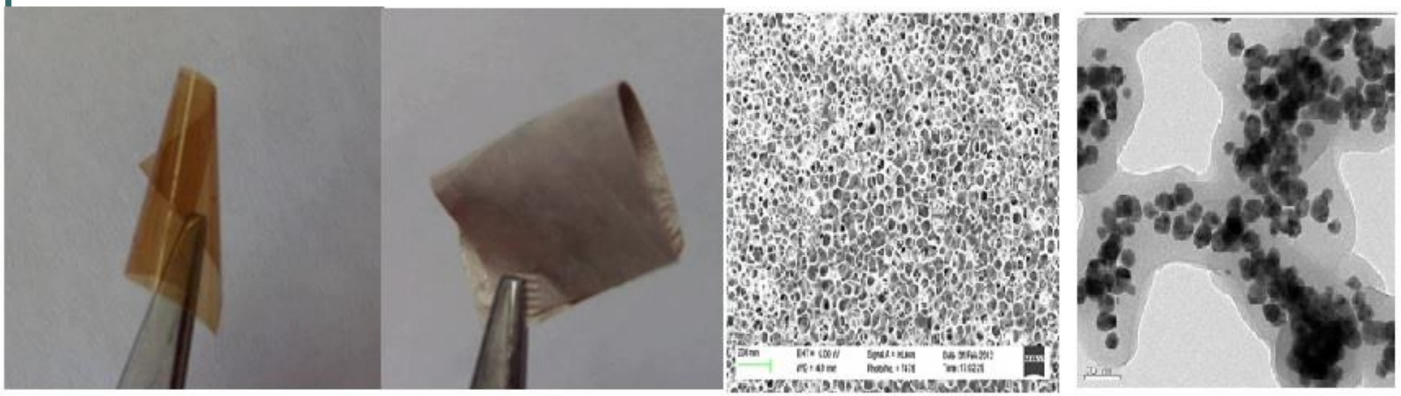
Why PAA?

- Conductive
- Ease to prepare
- Enables flow of electronic charges
- Redox stable
- Possesses surface functional groups
- Permeable
- Porous structures

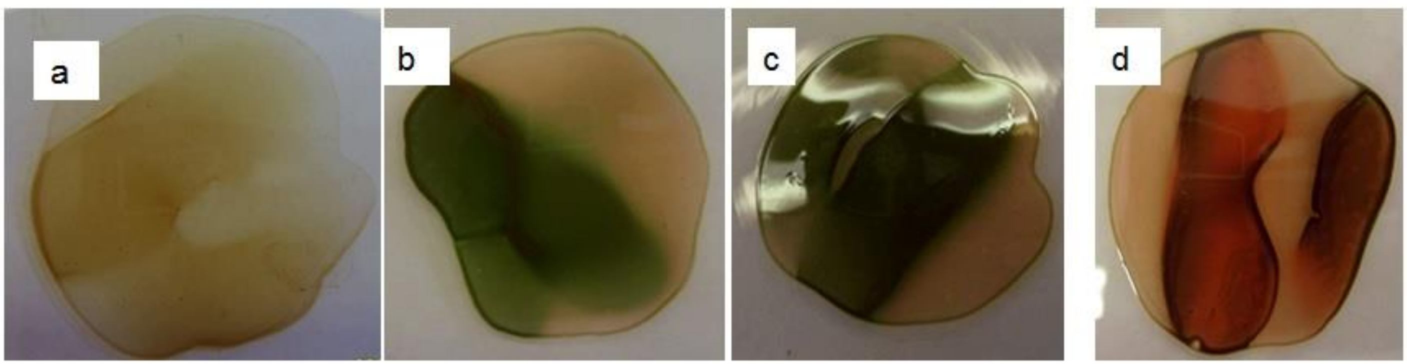




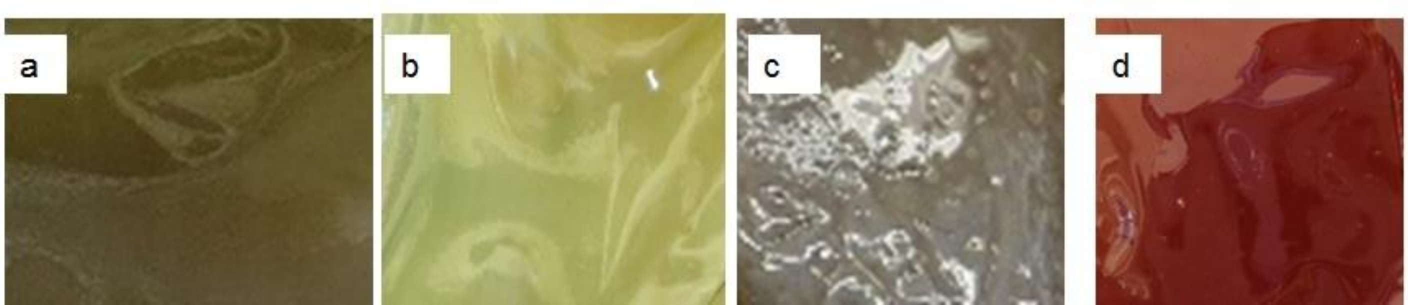
Classic PAAs



- Stable :300℃
- Flexible
- Mechanically strong
- Porous

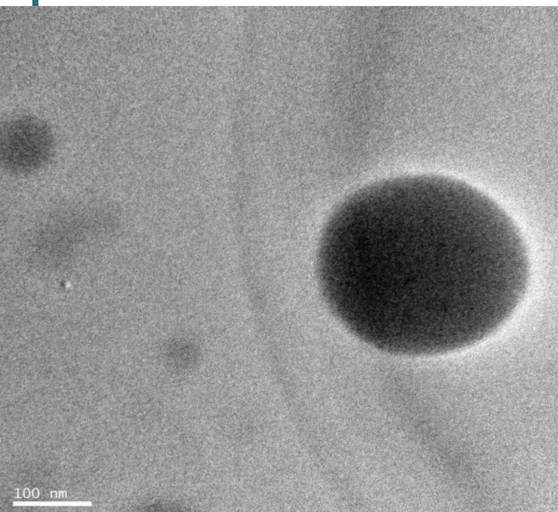


Temperature dependence of PAA a-75 ˚C,b-150˚C,c-250˚C,d-300˚C

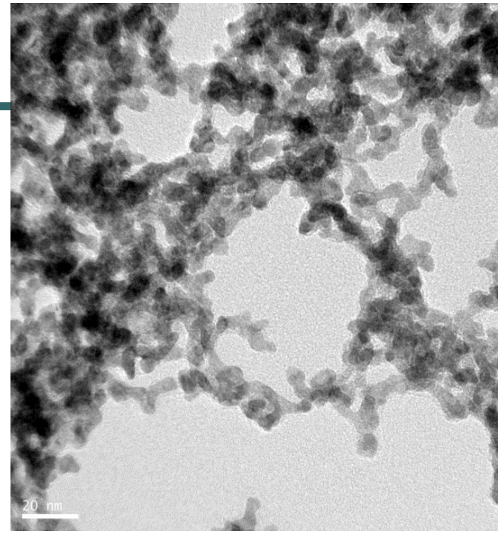


Fluorescent PAA biomembranes: A-PAA-CS with %0.3 GA, B-PAA-DA, C- l-PAA 15 h incubation D- m-PAA-DA with for 15 h

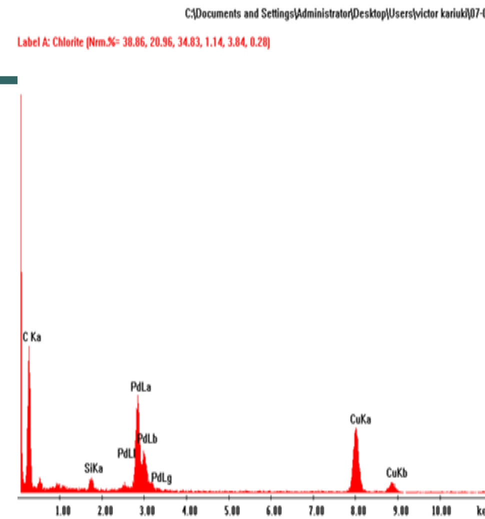
PAA stabilized nanoparticles while maintaining wettability

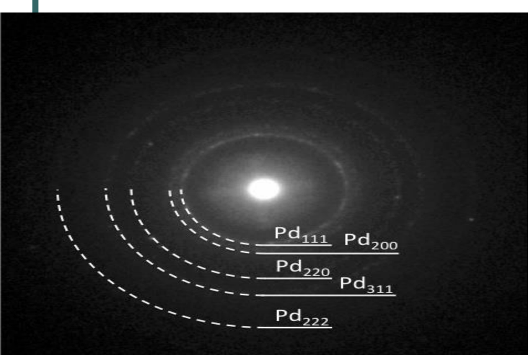


PdNPs stabilized with PAA

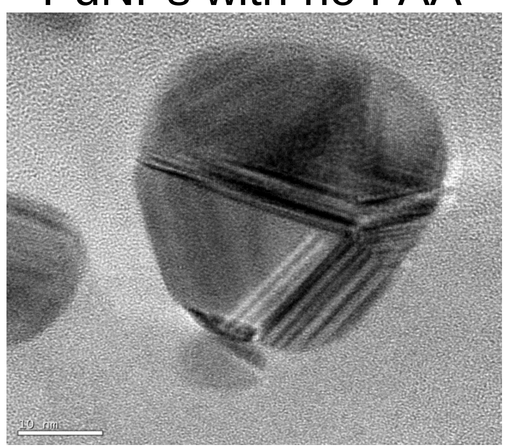


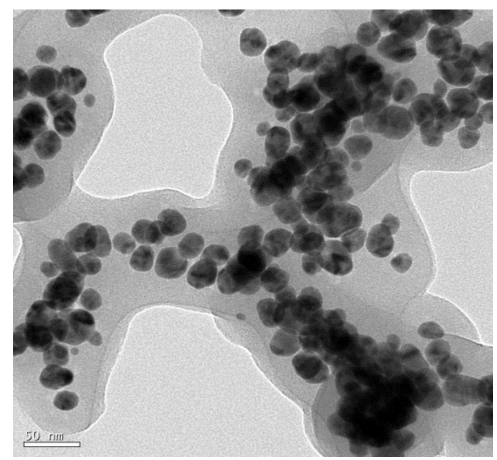
PdNPs with no PAA





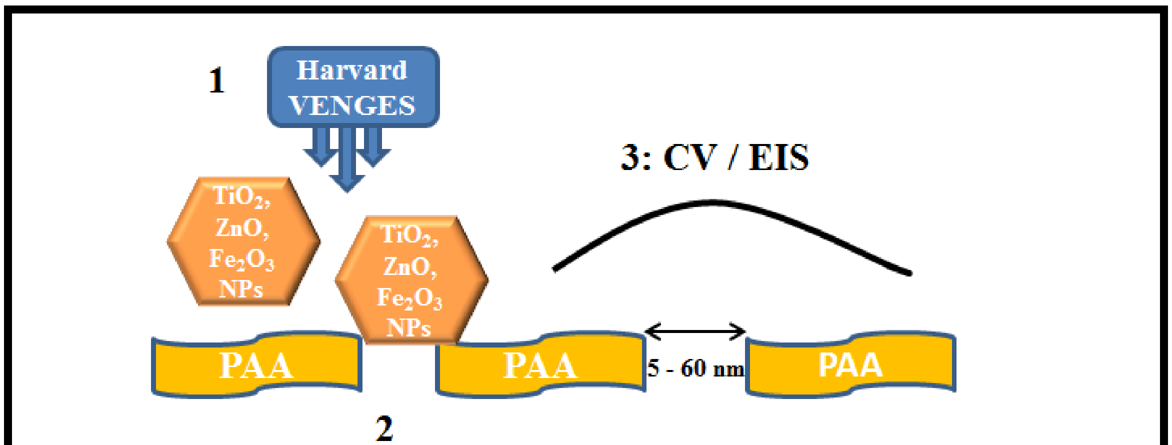
X-ray diffraction pattern shows crystalline particles were formed with uniform size & random size distribution.





HRTEM of nanosilver with PAA: Particles are twinned with 5 fold symmetry

Capture and Detection of Aerosol Nanoparticles using Poly (amic) acid, Phase-inverted Membranes



1. Aerosol synthesis **2**. Capture/separation **3**. Detection/electrochemistry

[1]SUNY-BINGHAMTON, NY
[2] HARVARD SCHOOL OF PUBLIC HEALTH, MA, Sadik, Demokritc

Journal of Hazardous Materials 279, **2014**, 365-374.

Project Objectives

- The overall objective is to isolate and detect industrially-relevant CeO_2 and Fe_2O_3 nanoparticles from air.
- Specific Aims:
  - Synthesize PAA-paper and PAA-stand alone filters
  - Synthesize the nanoparticles using VENGES
  - Characterize the nanoparticles using SEM-EDS, XRD and BET
  - Demonstrate ex-situ electrochemical detection

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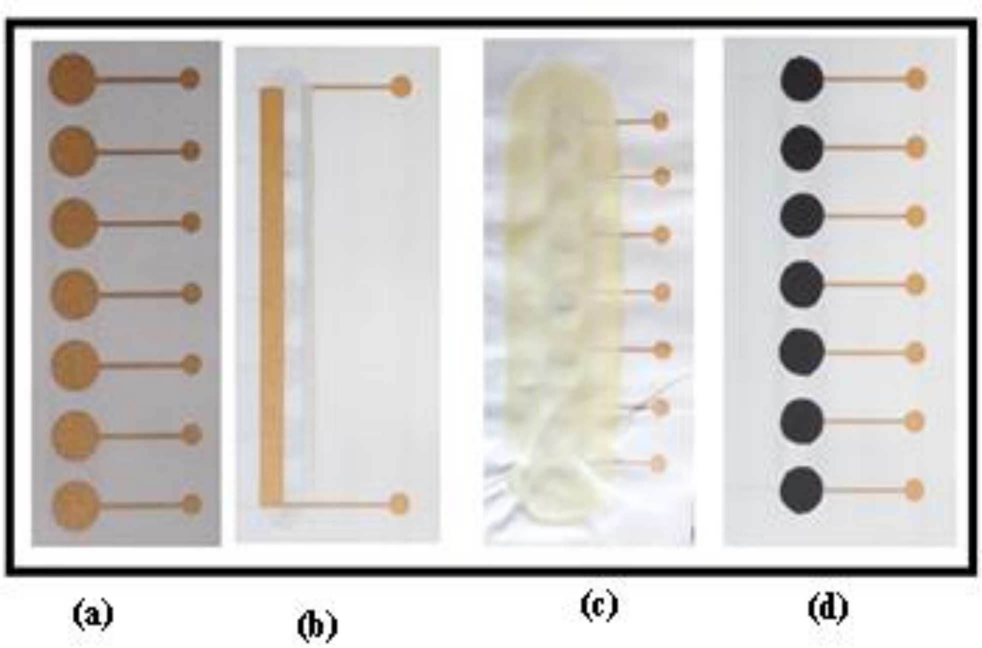
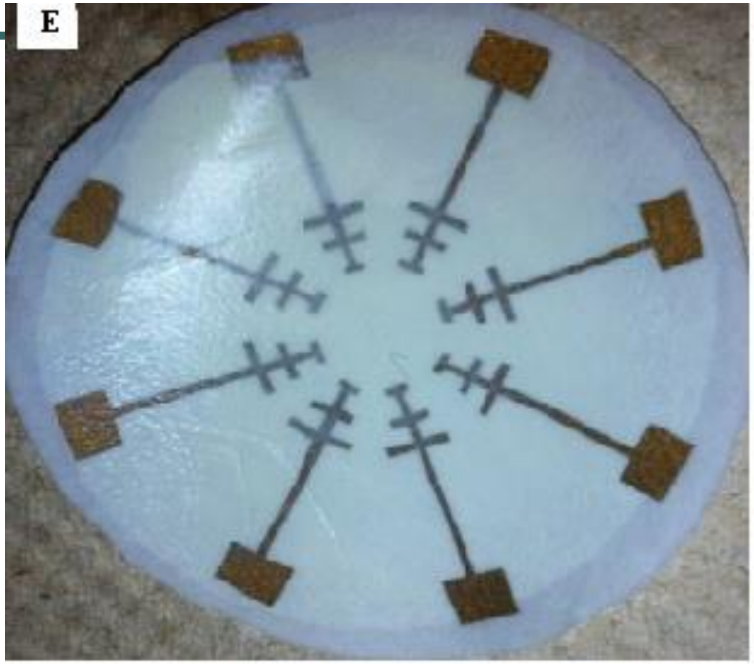
Journal of Hazardous Materials 279, **2014**, 365-374.

Paper-based PAA sensors





Sample PAA-on membrane electrodes (a) gold working electrodes on paper substrates, (b) gold counter and silver/silver chloride electrodes, (c) Working electrodes coated with PAA membranes, and (d) carbon working electrodes. Right: Gold array electrodes fabricated onto paper substrates; with subsequent coating of PAA membranes (notice the shiny PAA).

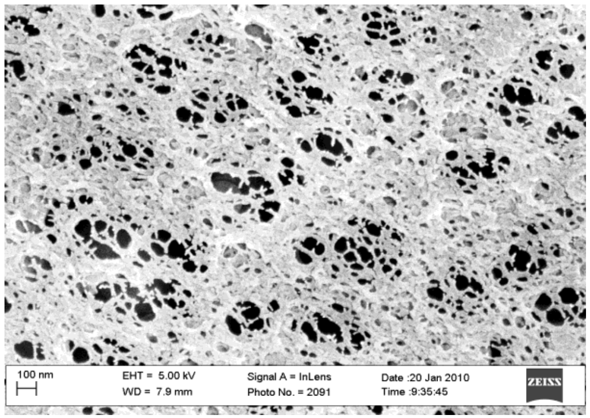
Journal of Membrane Science, 472(**2014**)261–271.

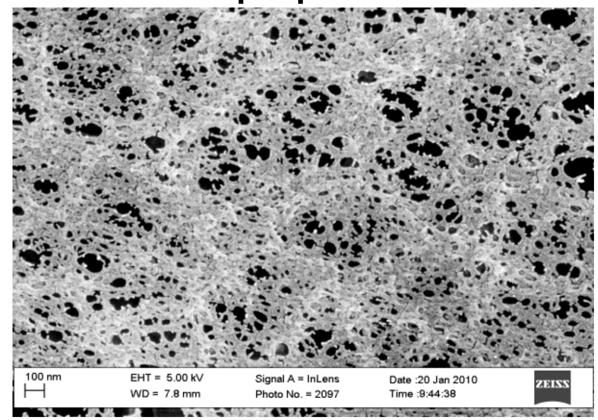
Surface morphology

PAA stand-alone membrane

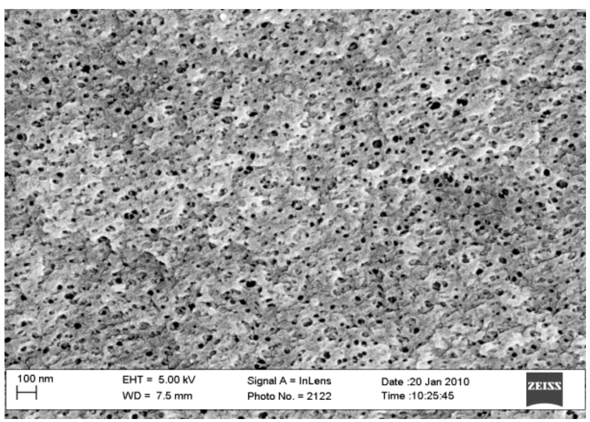
PAA coating layer on filter paper

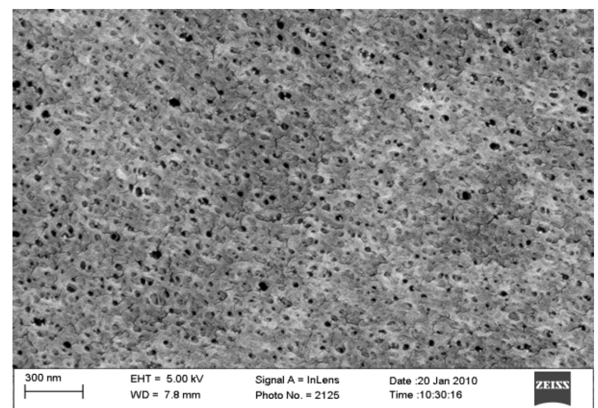
0.20 M



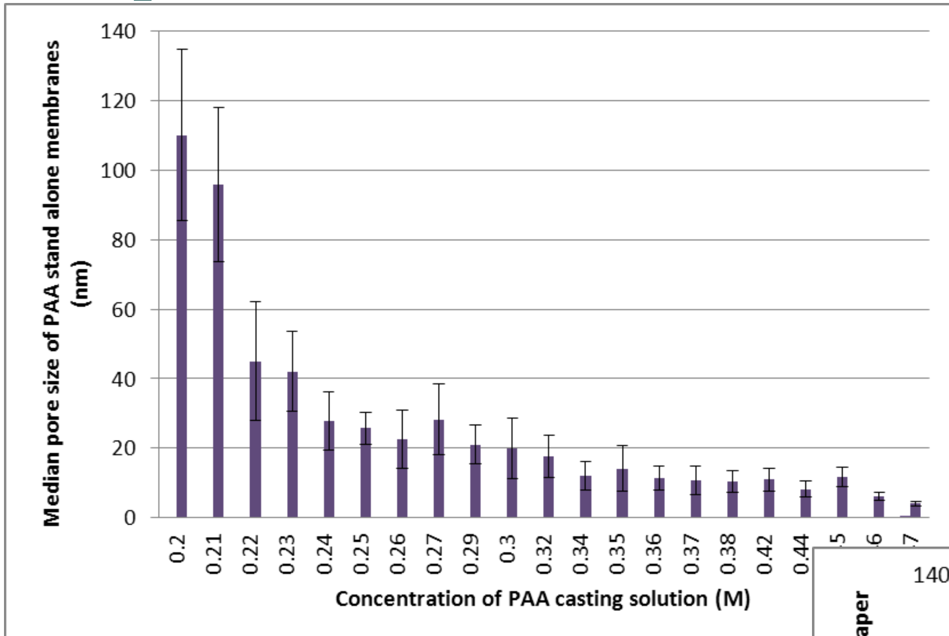


0.23 M

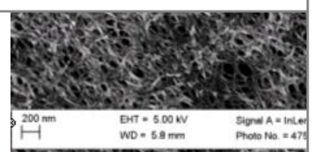




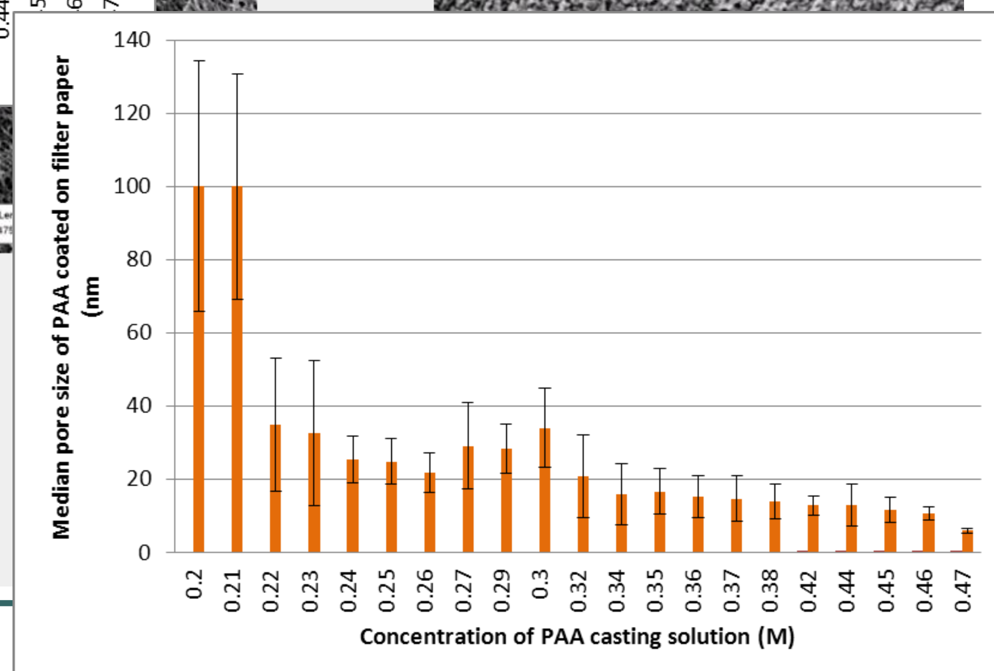
Optimization & Porosity



ents and aqueous solutions

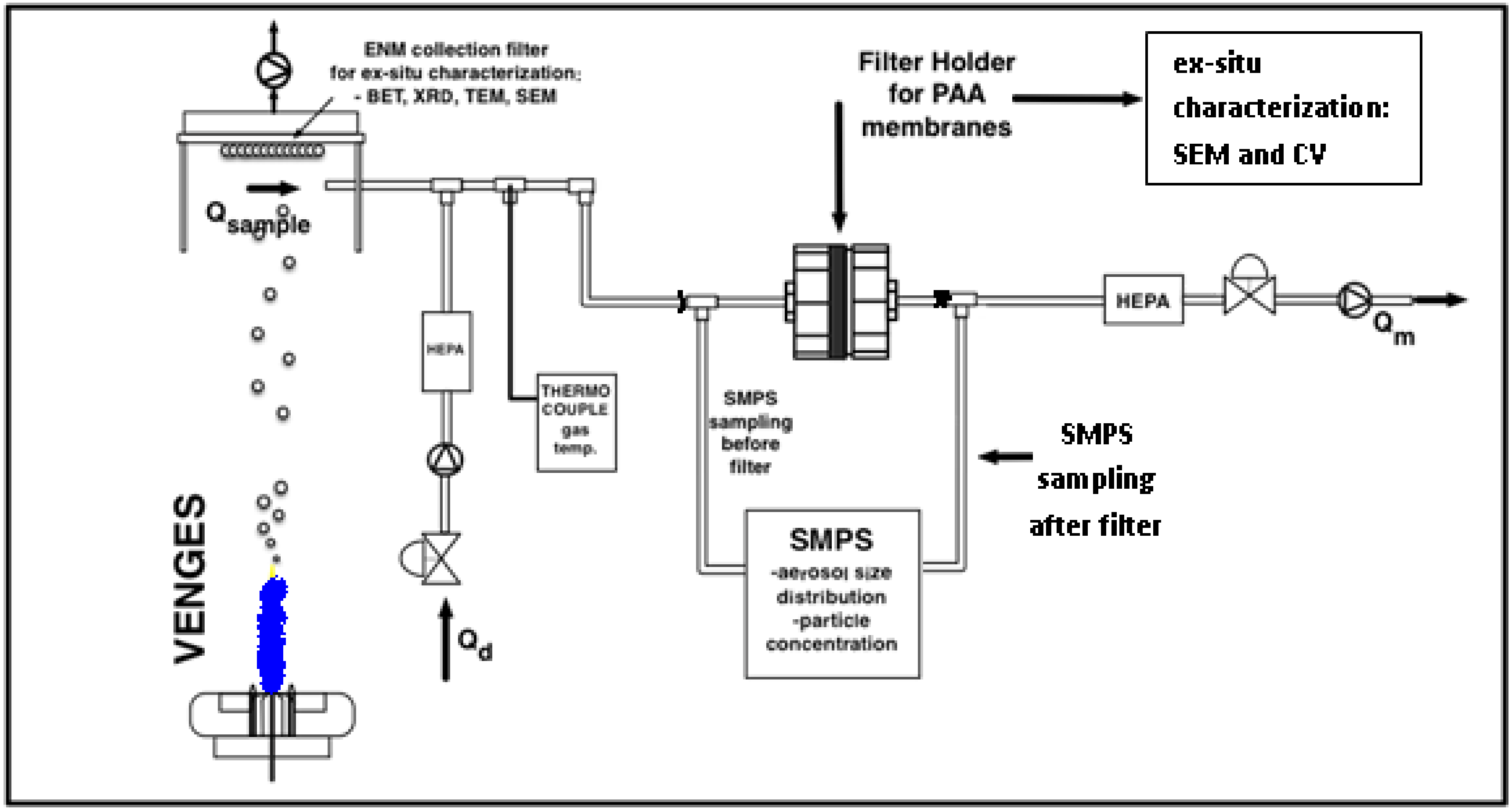


100nm – 200nm



Harvard's VENGES

New Platform for pulmonary and cardiovascular toxicological characterization of inhaled ENMs



Nanotoxicology, 2011; Early Online, 1–11

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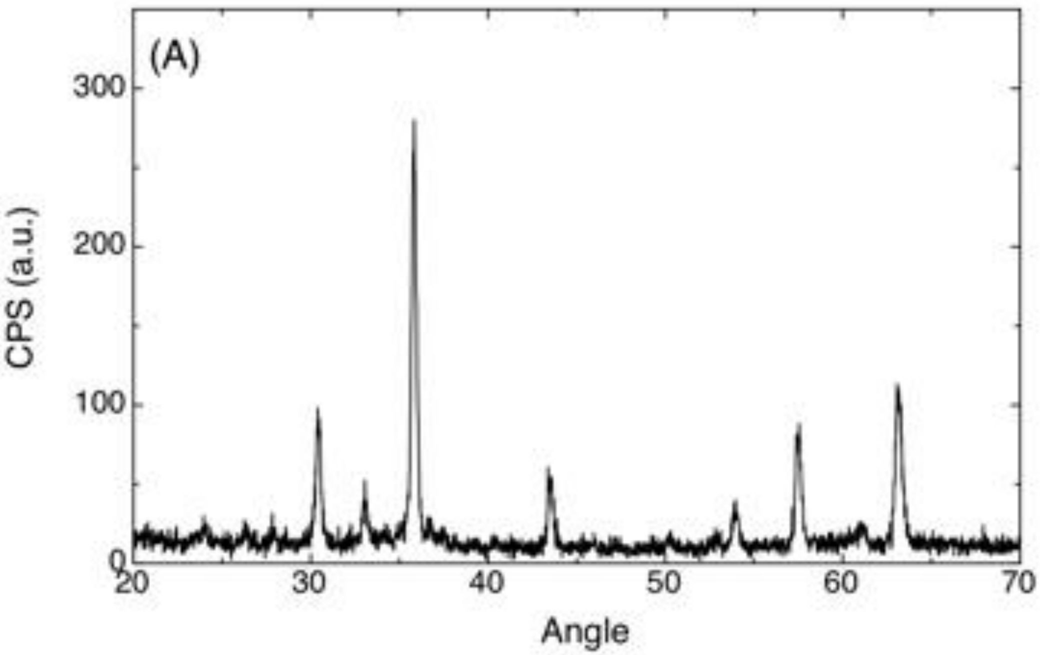
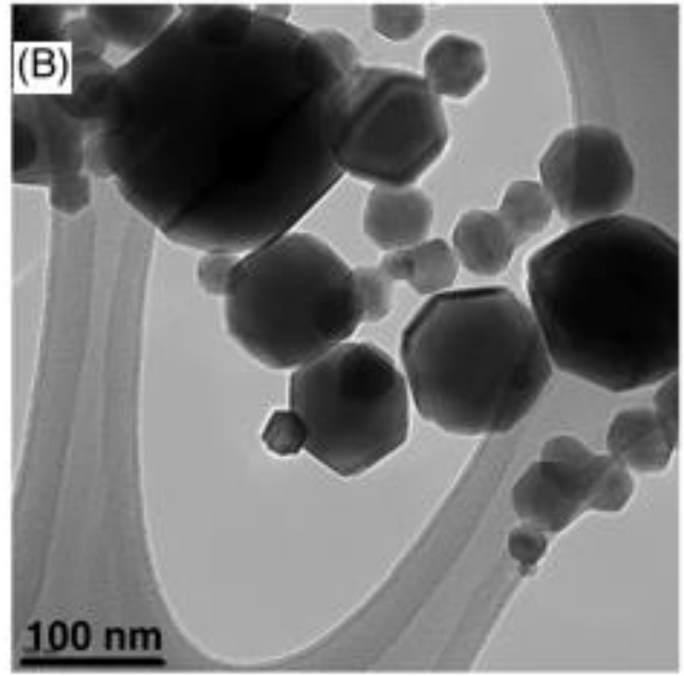
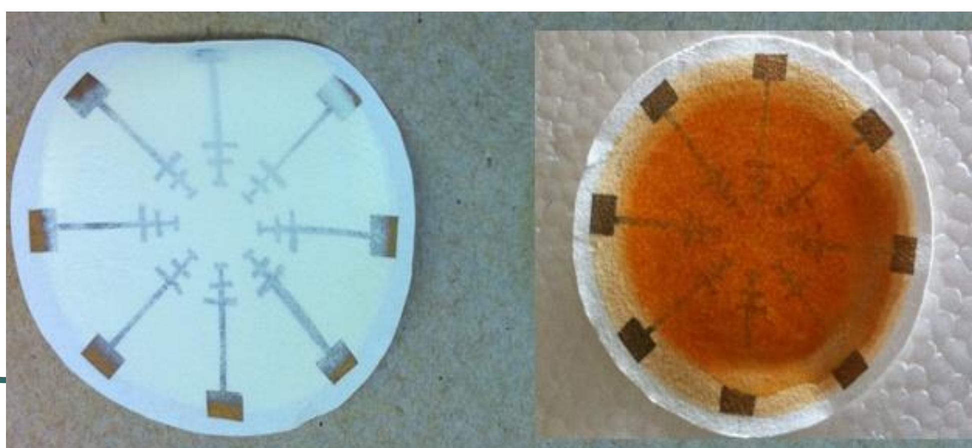
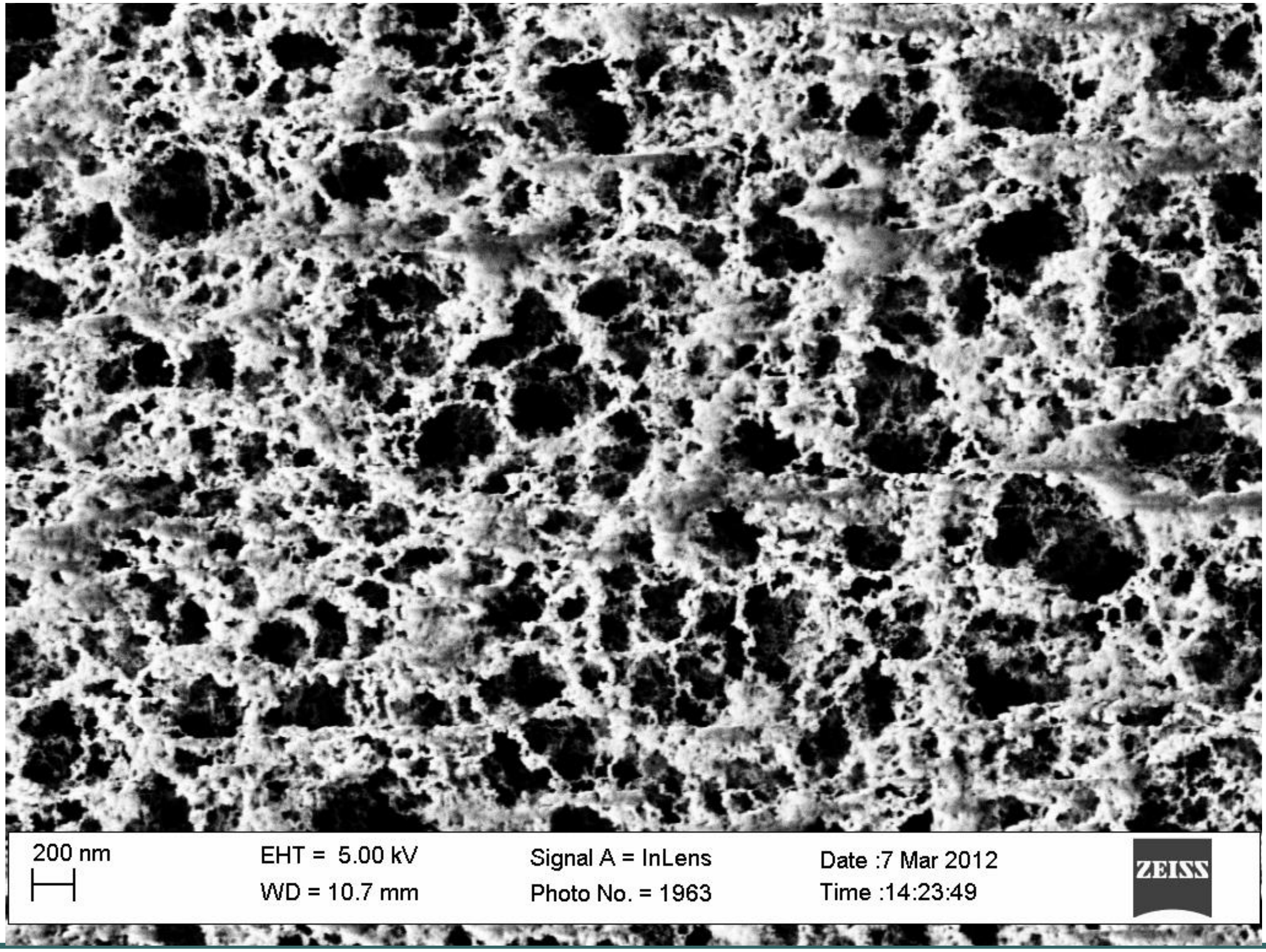
Surface Characterization





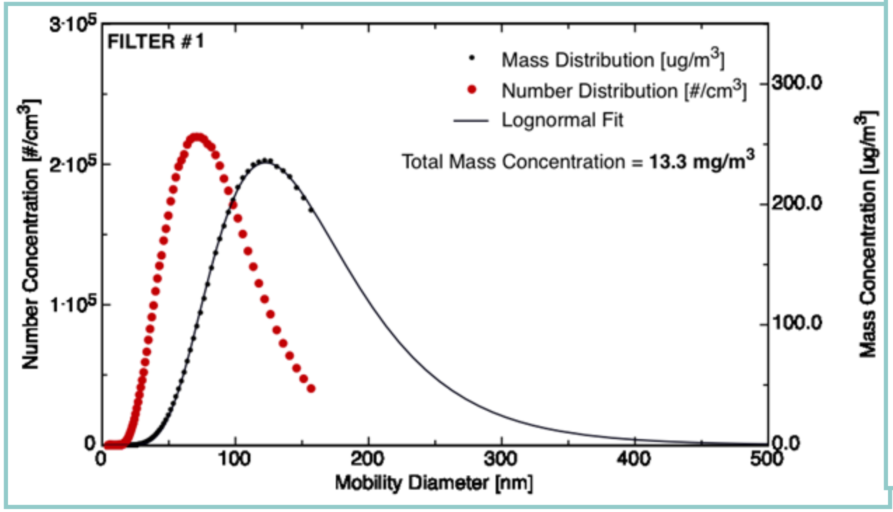


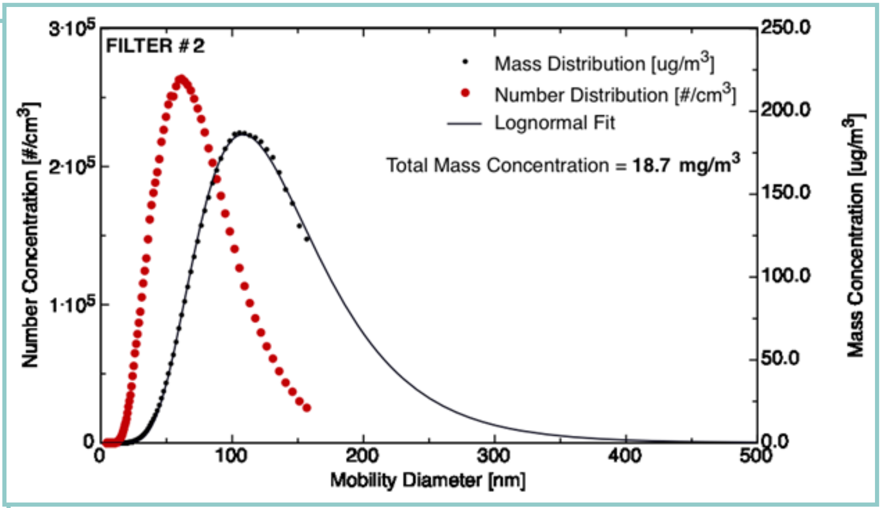
SEM after Capture



•Journal of Membrane Science, 472(**2014**)261–271.

Mass Deposition and Concentration

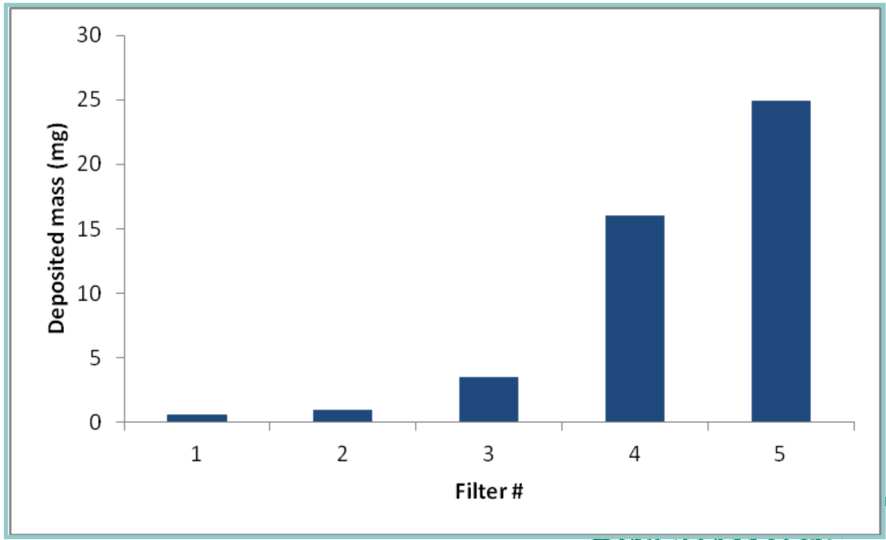




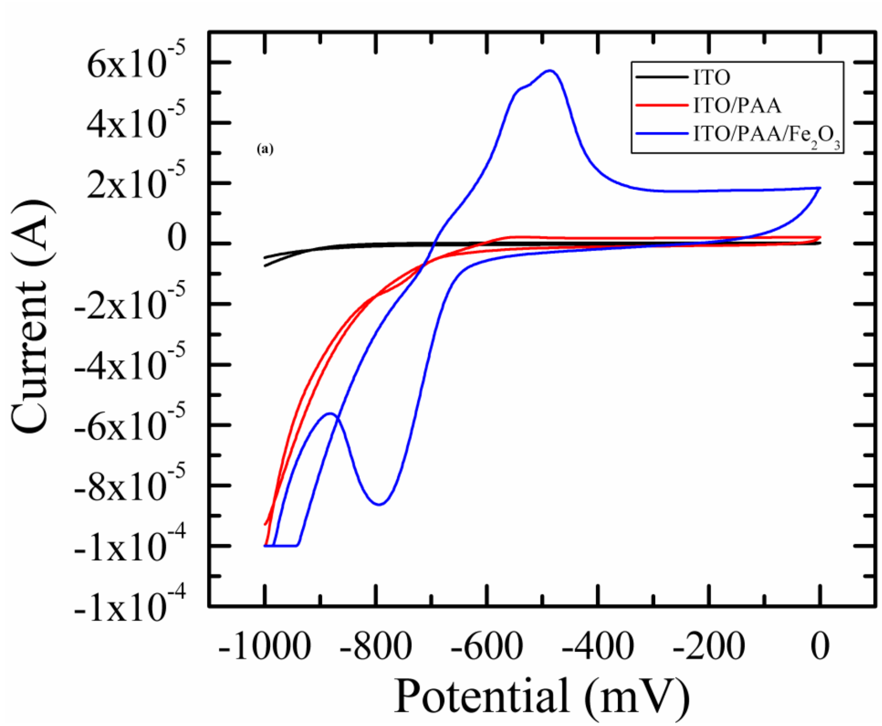
- Aerosol size distributions on PAA-filter paper membranes

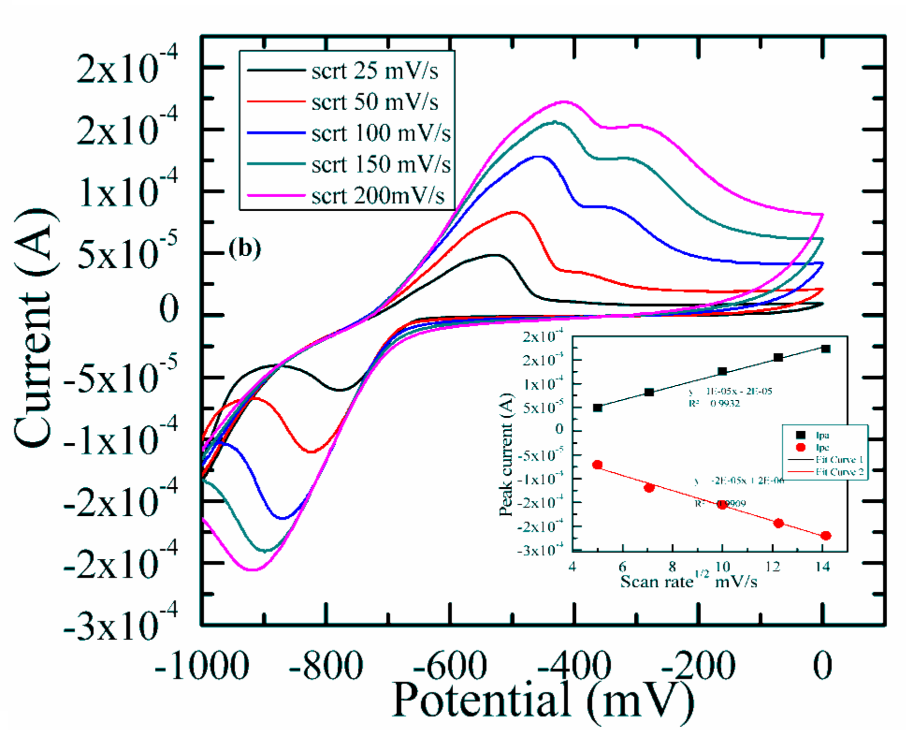
- There was a correlation between the deposition mass (mg) & the concentration (μg/m³)

- Filter # 5 had the highest concentration (8.30E+04 μg/m³)



Electrochemical studies





$Fe_2O_{3(s)} + 2e^- + 6\ H^+_{(aq)} \longleftrightarrow 2Fe^{2+}_{(aq)} + 3\ H_2O_{(l)}$……………………………………………eq.1

$3Fe^{2+}_{(aq)} + 2PO_4^{3-} + 8H_2O_{(aq)} \longrightarrow Fe_3(PO_4)_2 .\ 8H_2O_{(s)}$……………………………………eq.2

White precipitate: $Fe_3(PO_4)_2$

Quasi reversible reaction: ipc/ipa = 0.71; the position of the Ep altered with scan rate

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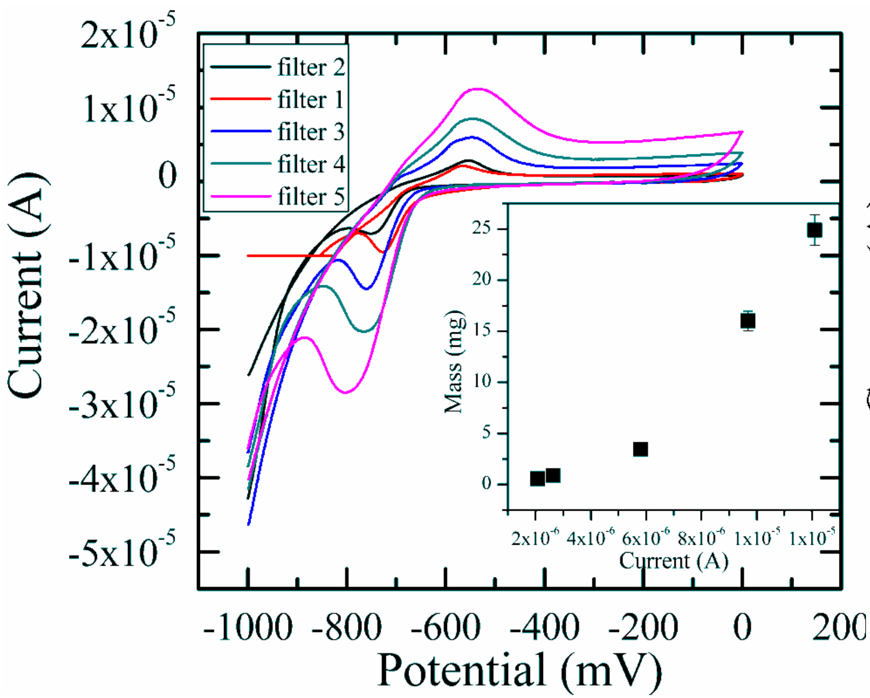
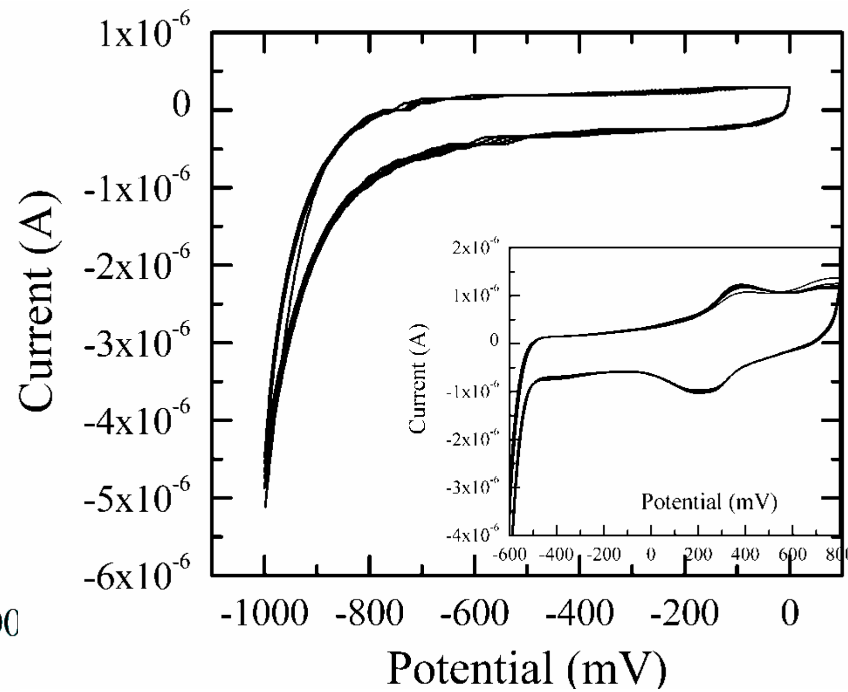
Dose dependent and electrode stability studies





- Correlation exists between the deposition mass (mg) & the current (A)
- The limit of detection (LOD): (3 *s_{blank}) /slope was found to be $4.998 \times 10^{1} \mu g/m^{3}$
- PAA is electroactive; redox peaks were observed at ~ 224 mV and 395 mV
- Electrode was stable.

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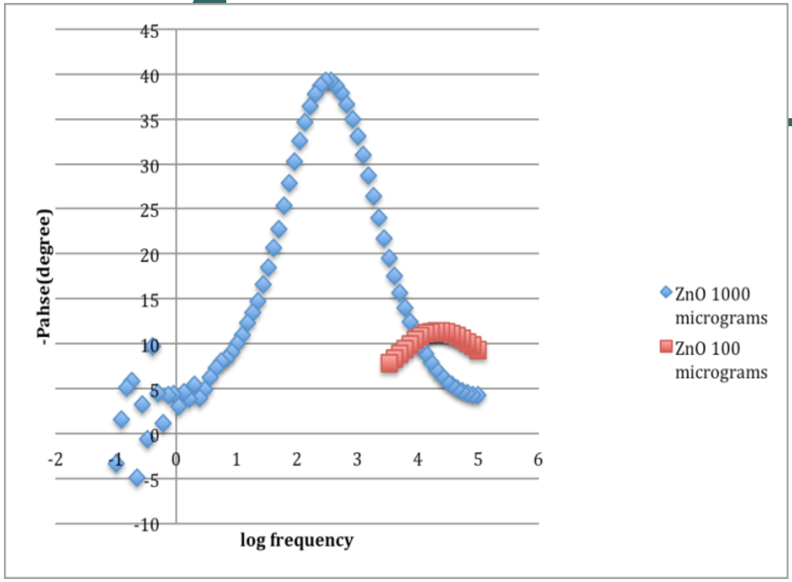
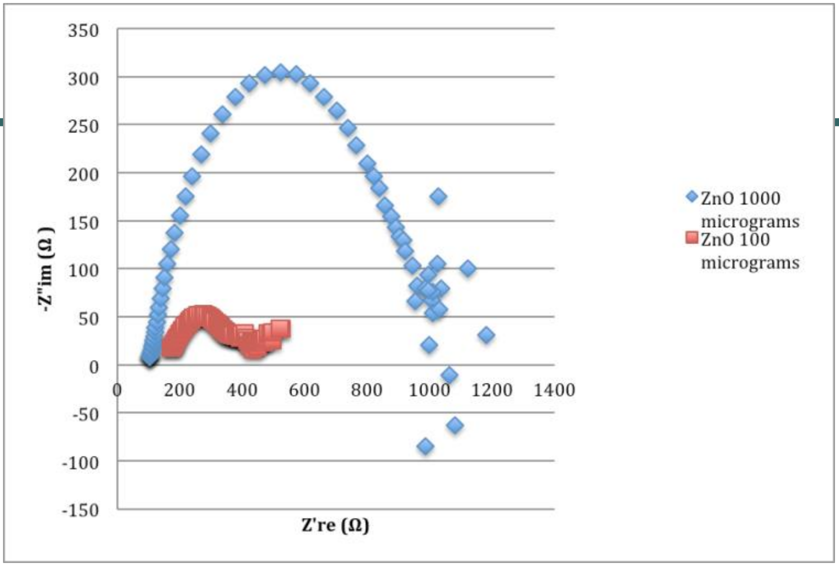
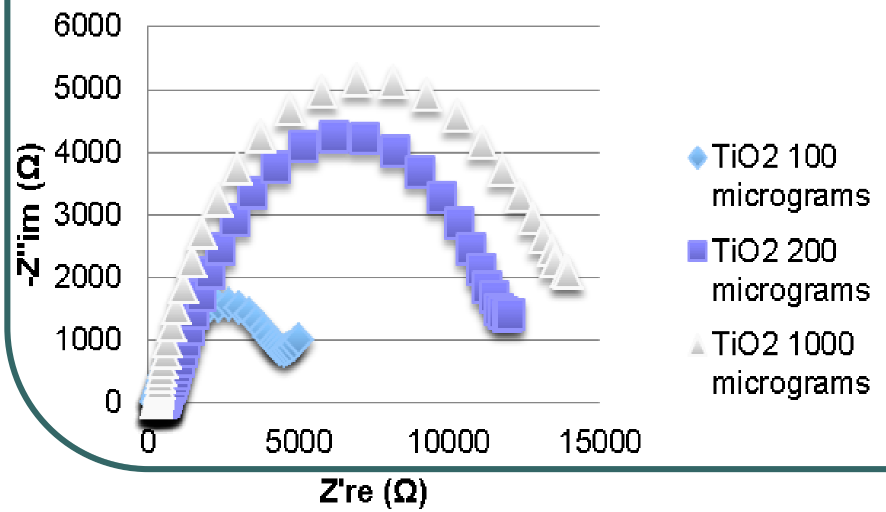
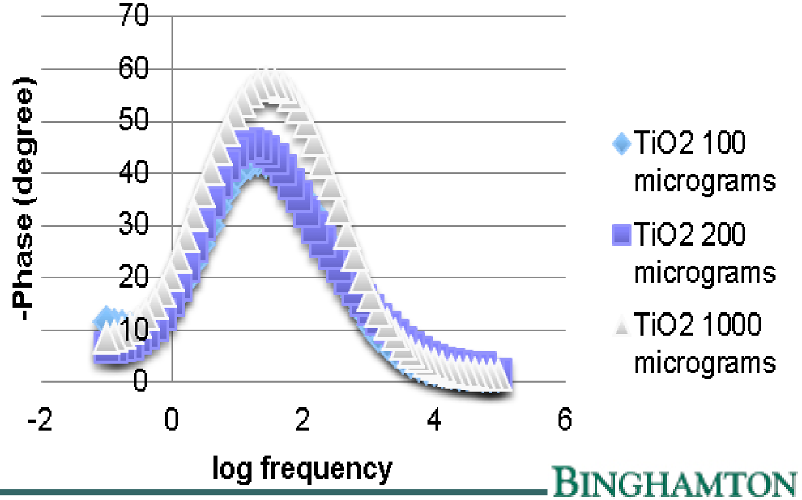
Electrochemical Spectroscopy for TiO_2 and ZnO Aerosols









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Highlights of PAA-based Sensors

- Exposure level assessment of aerosol nanoparticles reported using Harvard's VENGES
- Device equipped with pie-conjugated conducting PAA membrane filters/sensor arrays
- PAA membrane motifs used to capture, isolate and detect the nanoparticles
- Manipulating the PAA delocalized π electron enabled electrocatalytic detection
- Fe_2O_3, ZnO and TiO_2 quantified using impedance spectroscopy and cyclic voltammetry

Performance Evaluation with CANTOR*

Sampling	CANTOR (1)	PAA/VENGES
Weight	0.25Kg	Portable
Dimension	Small	Small
ENP Type	Carbon	Carbon-based, metal oxide, metal NPs
ENP Size	Bimodal 22/107nm	1-100 nm
ENP Concentration	6000 NP/cm^3	10^5-10^7 NP/cm^3
Sampling Time	15 min	3-25 min
Sampling Efficiency	1.32 %	> 99 %
Aerosol flow rate	0.68l/min	0.5 L/min.

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- **H.S. Wasisto, S. Merzsch, A. Waag, E. Uhde, Portable cantilever based**
- **airborne nanoparticle detector, Sensors and Actuators B, 187 (2013) 118-127.**

Summary & Conclusions

- *No real analytic science exists for measurement of engineered nanomaterials*
  - not high-throughput and are not mass quantitative; no best technique available, a single method is not sufficient; most techniques have advantages & drawbacks
  - Sample preparation is key; routine methods unavailable
- Developed paper-based sensors with PAA filter electrodes for aerosol nanoparticles
  - Paper-based sensors combined with Harvard VENGES platform and TFF for aerosol and water based NP measurements
  - Filtration efficiency of PAA membranes was over 99.9%
  - Fe_2O_3 nanoparticles were detected using electrochemical detection technique. LOD: 4.998×10^1 g/m^3

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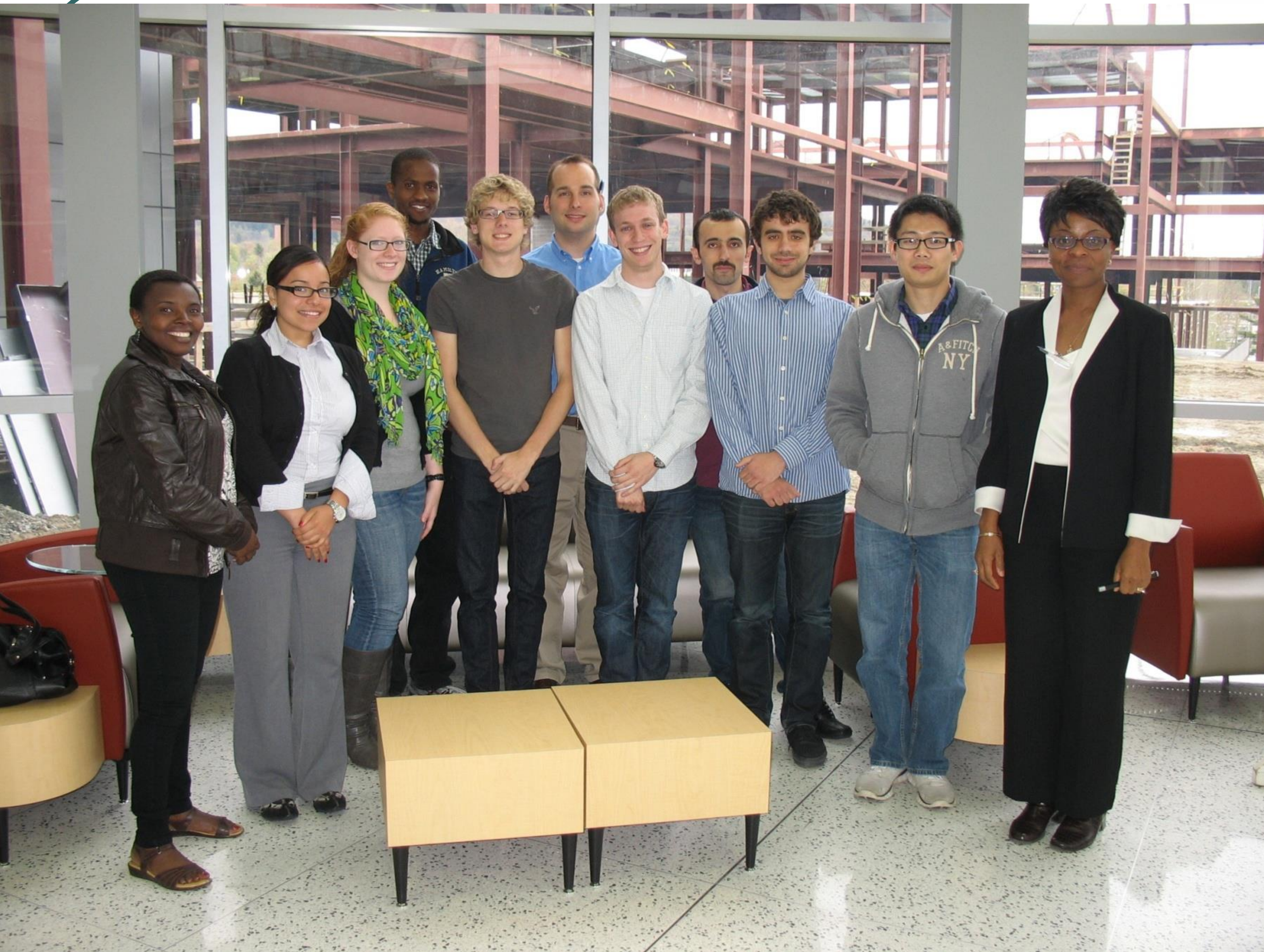
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Paper-based electrodes coupled with tangential flow filtration(EC-TFF)

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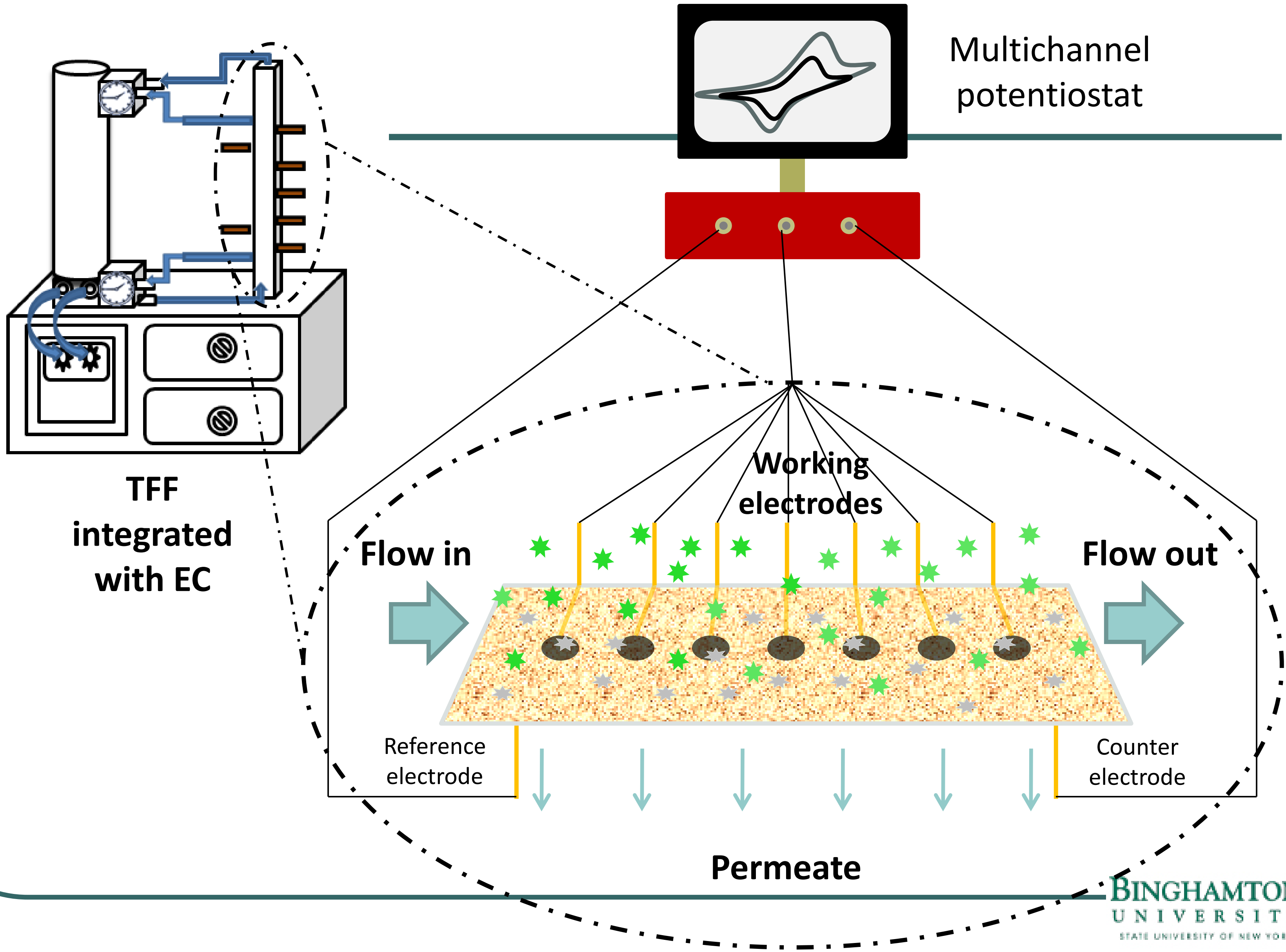
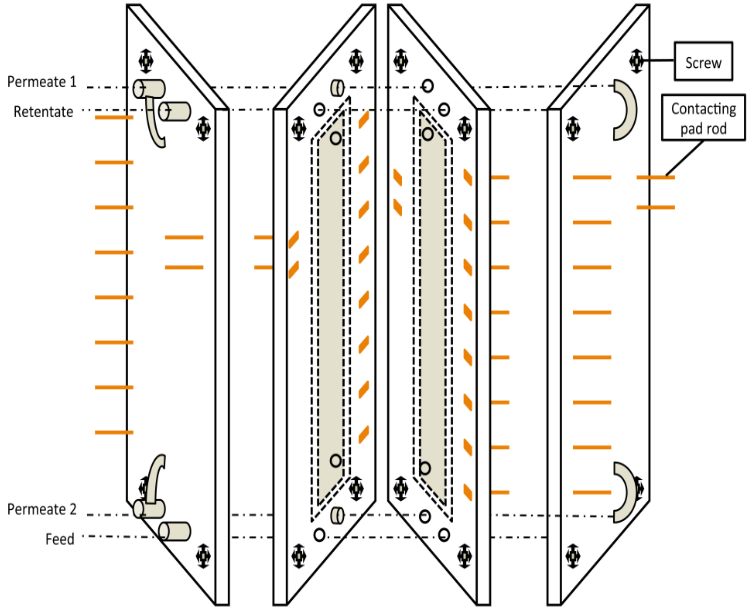
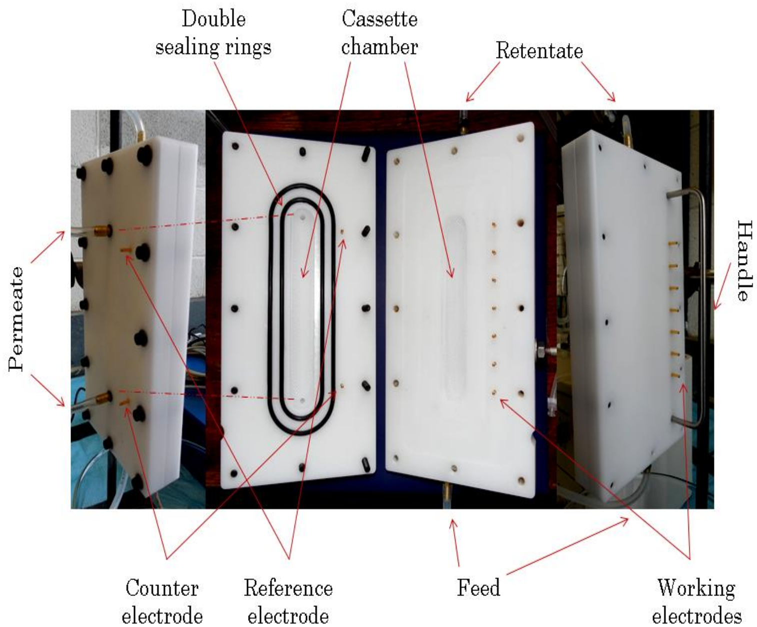
Portable EC-TFF



EC-TFF Design





Design of integrated PMFE and prototype cassette for EC-TFF (a) The cassette design and (b) the production version of the cassette

$$\eta = \frac{N(captured)}{N(total)} \times 100\% = \frac{C(captured)}{C(total)} \times 100\%$$
$$= \frac{C(total) - C(filtrate)}{C(total)} \times 100\%$$

Where η is filtration efficiency, N is number of NPs, C is concentration.

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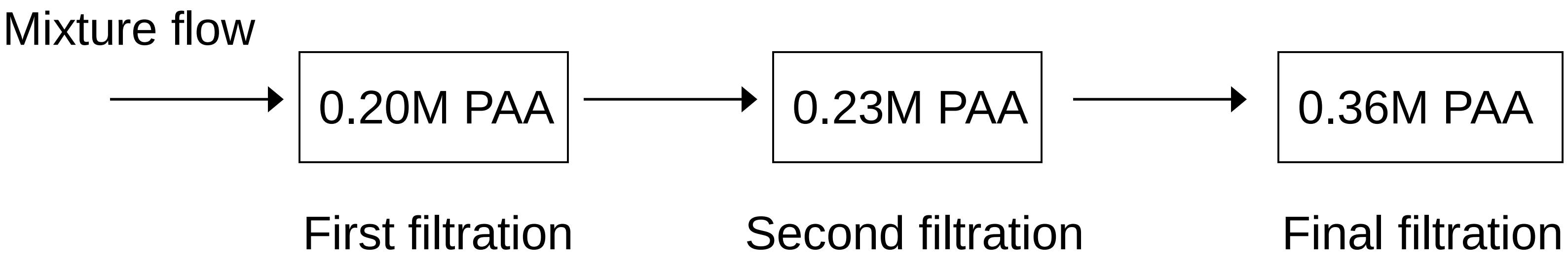
- CANTOR sensor uses a miniaturized electrostatic ENP sampler (NAS TSI 3089) for sample collection and a 2'' silicon wafer cantilever substrate that monitors the resonant frequency shift induced by the mass of the particles trapped on the cantilever. Other sensor types use surface acoustic waves and quartz crystal microbalance [10,11] .

Acknowledgement

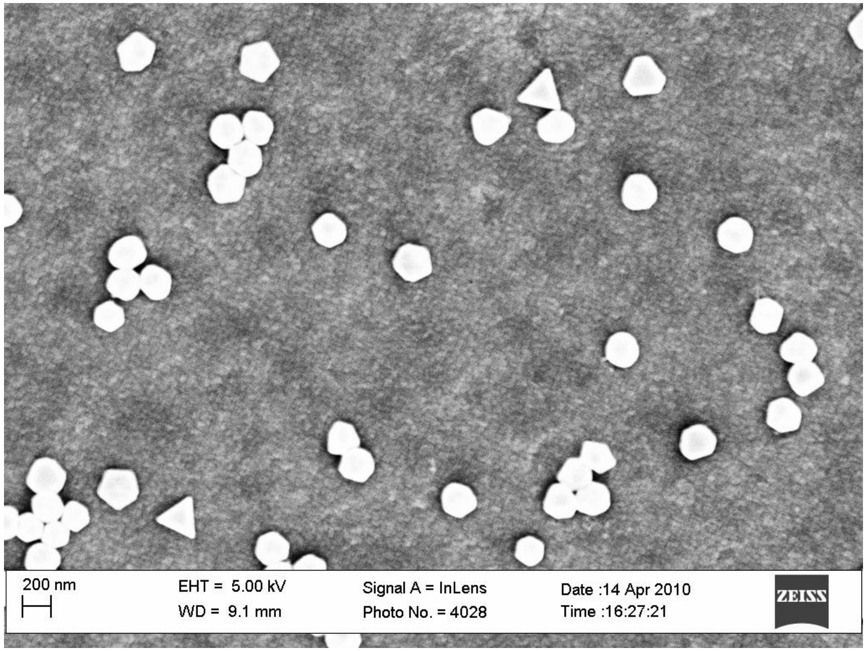
Multi-layered Separation

- Mixture: aqueous AuNPs solution(200nm, 50nm, 20nm)
- PAA membranes from different concentrations' casting solutions.

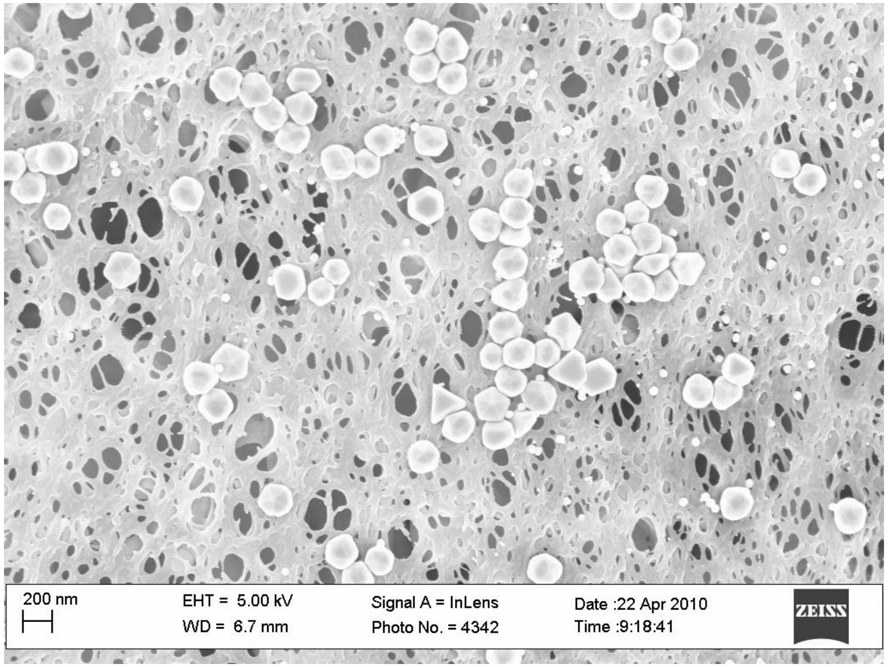


1st PAA membrane Layer

Standard

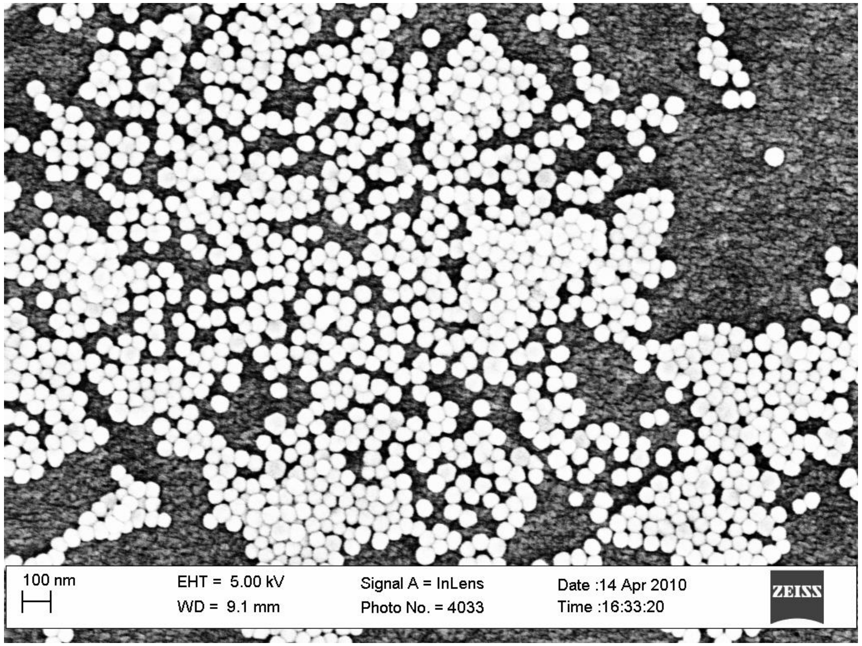


Continuous separation

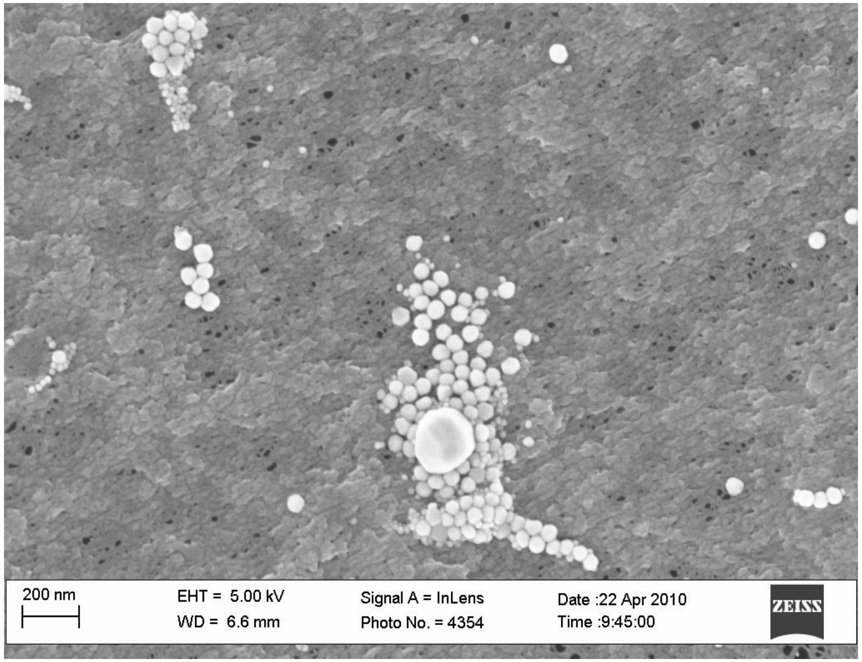


2nd PAA membrane Layer

Standard

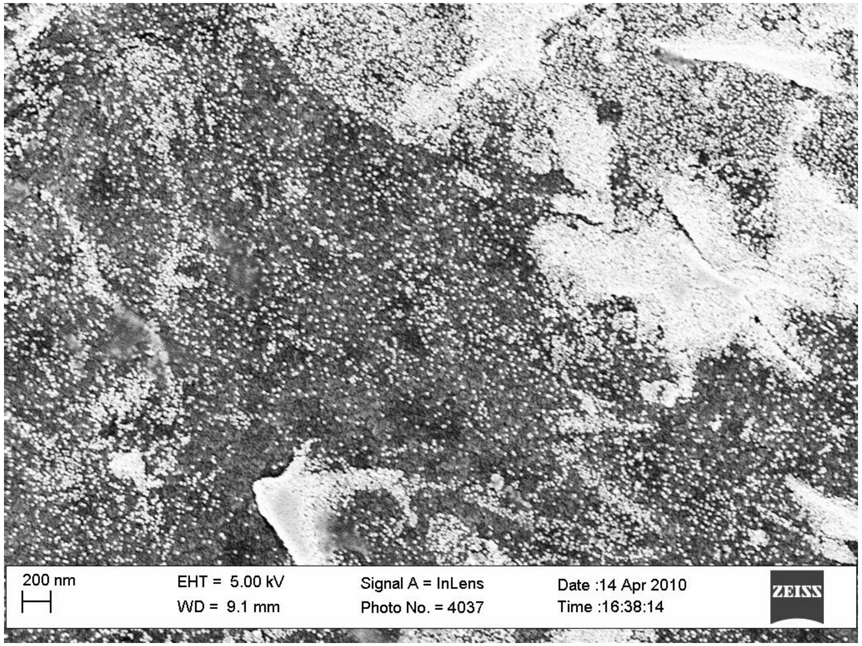


Continuous separation

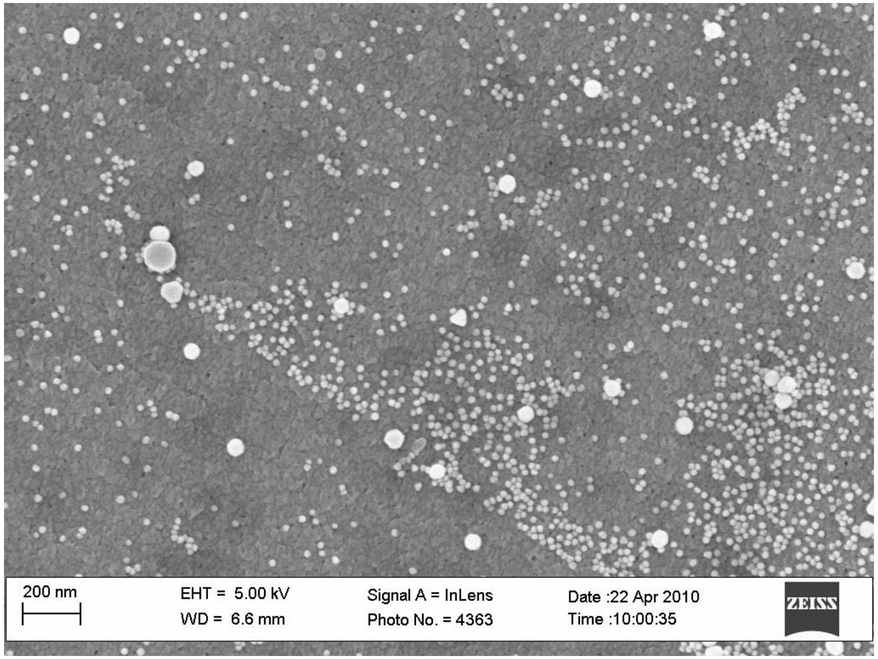


3rd PAA membrane Layer

Standard



Continuous separation



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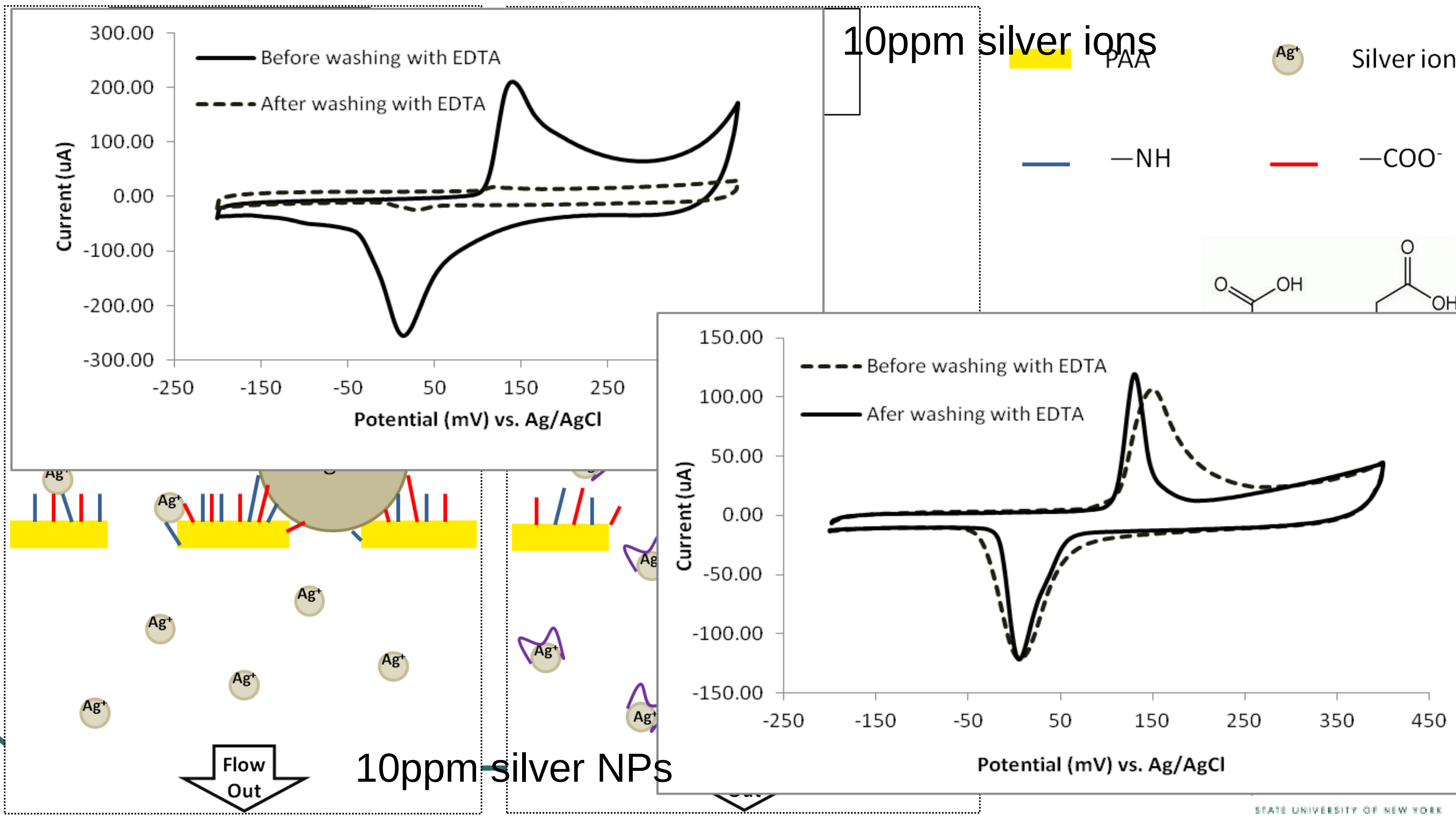
Inhibition of Silver Ions



10ppm silver ions

10ppm silver NPs

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State University of New York

NSF

Defense Threat Reduction Agency
DTRALink

New York State Department of
Environmental Conservation

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Grant #

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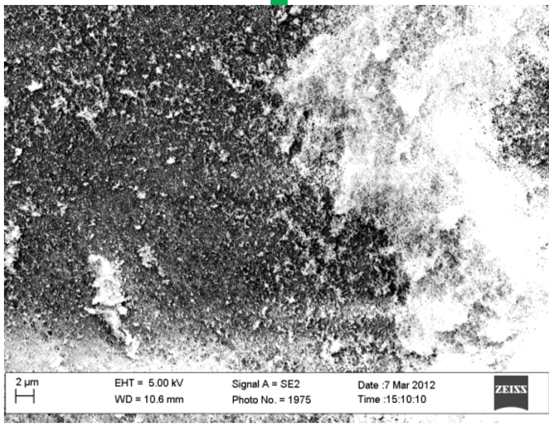
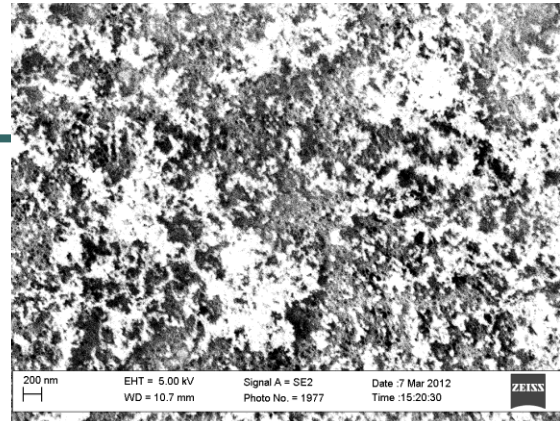
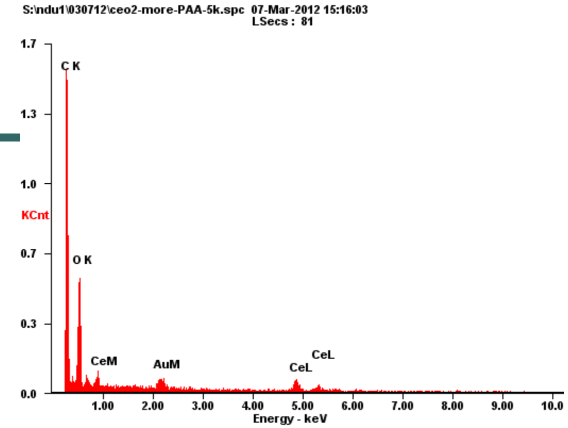
NIST

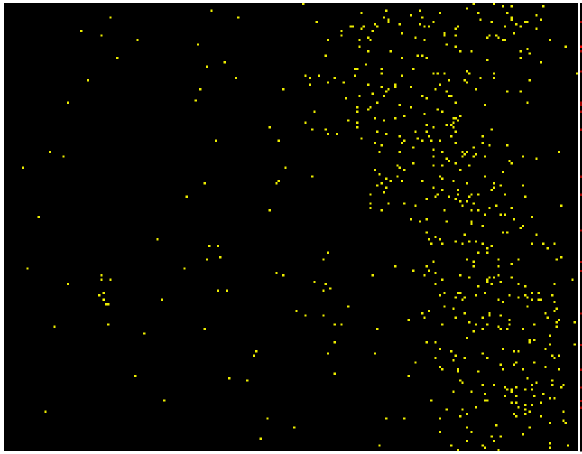
IEEC
Integrated Electronics Engineering Center
STATE UNIVERSITY OF NEW YORK

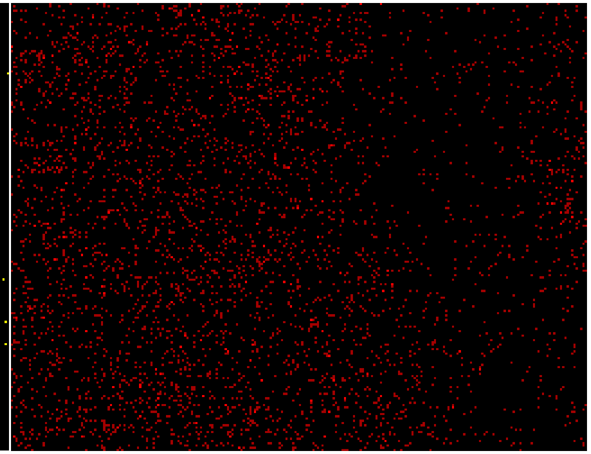
SEM-EDS images of CeO_2 Nanoparticles

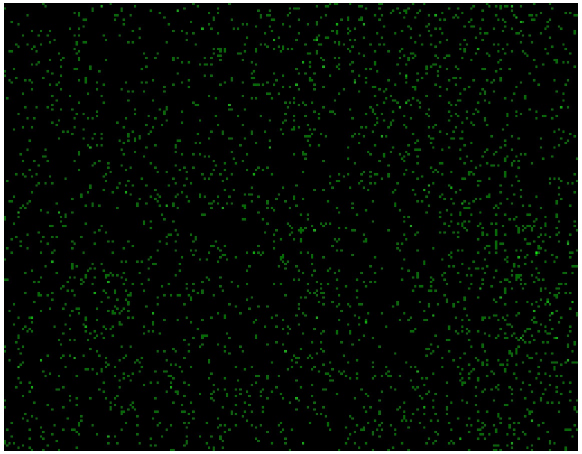












- ❑*SEM images of CeO_2 nanoparticle aggregates on PAA membrane at a magnification of 5000x; 50000x*
- ❑*EDS spectrum of the PAA surface with CeO_2 nanoparticles (KLM emission lines represents different electronic transition associated with x-ray emissions)*
- ❑*EDS elemental mappings for Ce, C and O, respectively, corresponding to elemental abundance.*

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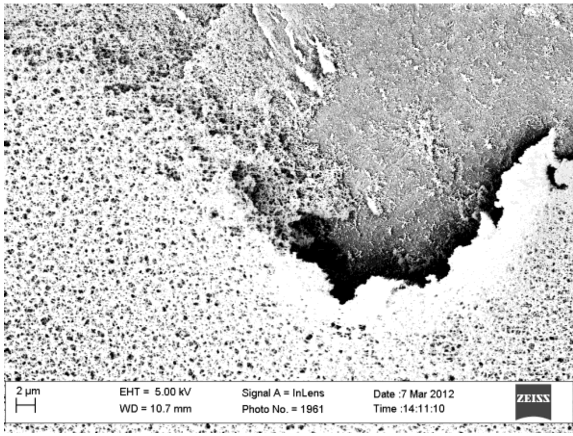
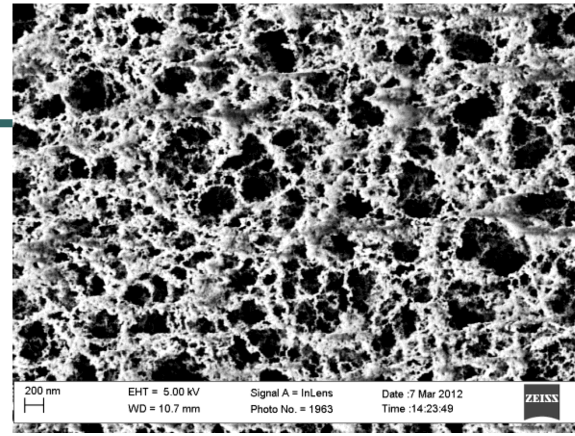
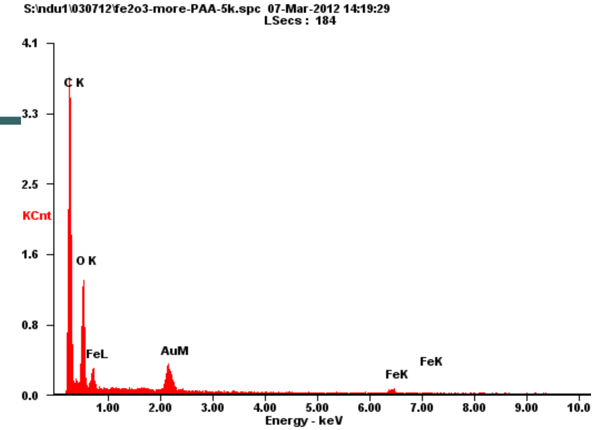
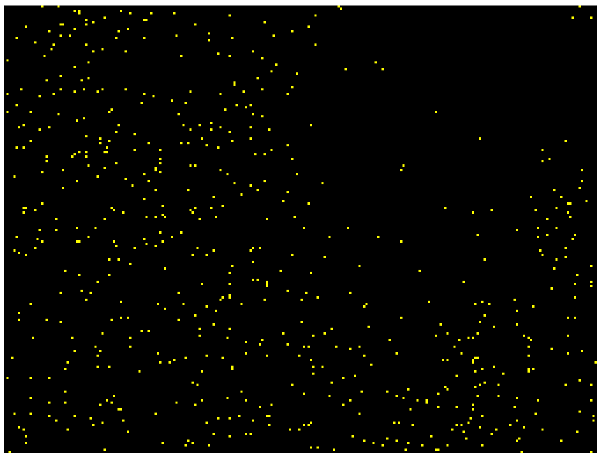
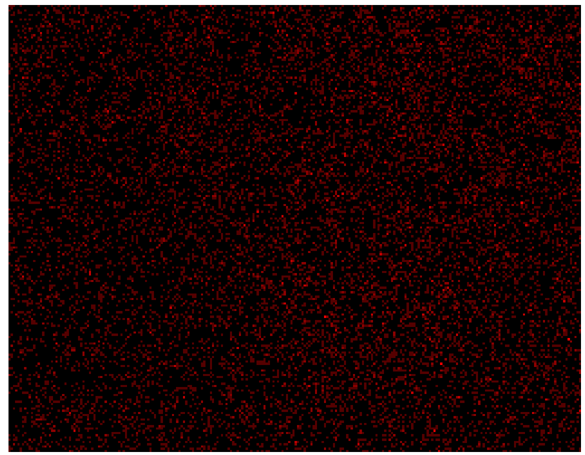
SEM-EDS images of Fe_2O_3 nanoparticles

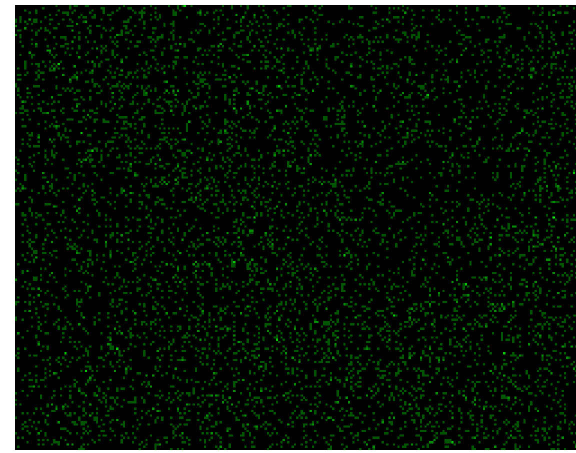












- *SEM images of Fe_2O_3 nanoparticle aggregates on PAA membrane at a magnification of 5000x; 50000x;*
- *EDS spectrum of the PAA surface with Fe_2O_3 nanoparticles; (KLM emission lines represents different electronic transition associated with x-ray emissions)*
- *EDS elemental mappings for Fe, C and O, respectively, corresponding to the respective abundance*

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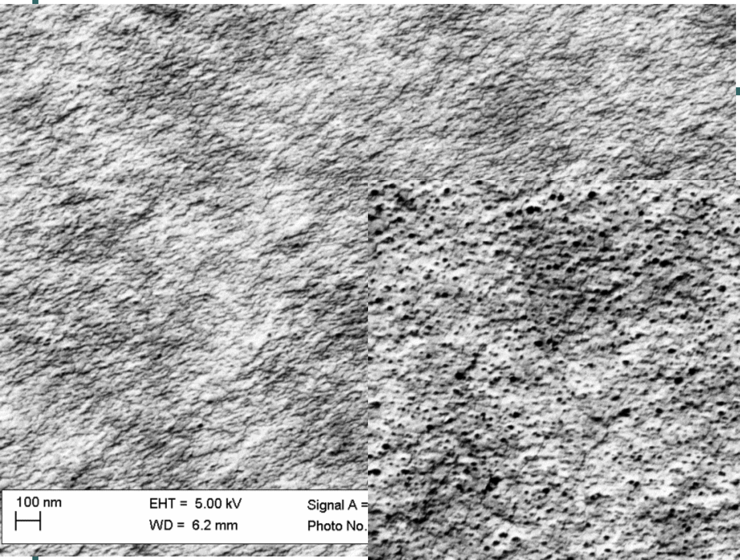
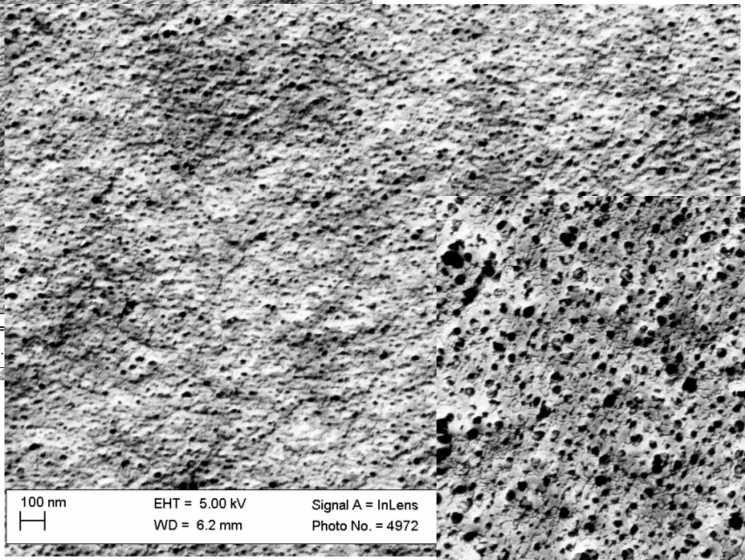
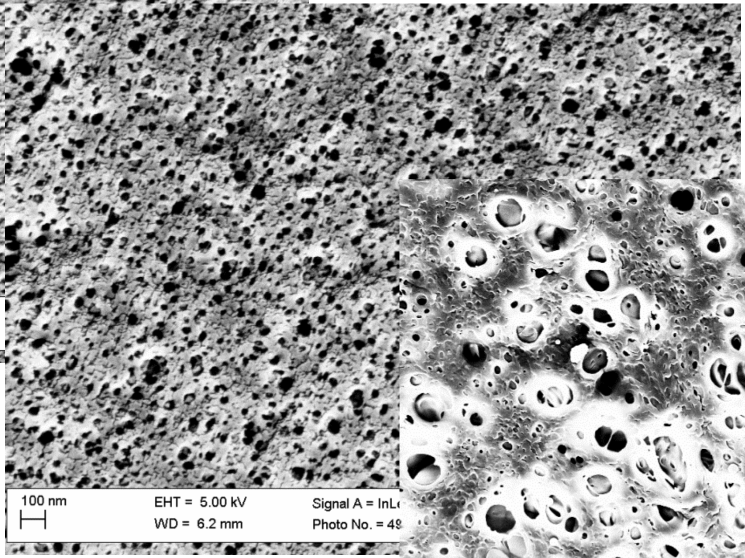
Phase inversion temperature



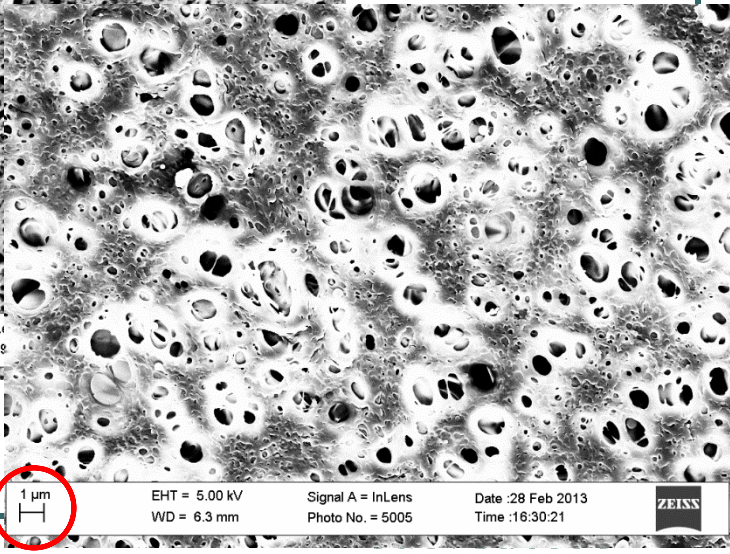
0°C



20°C



40°C

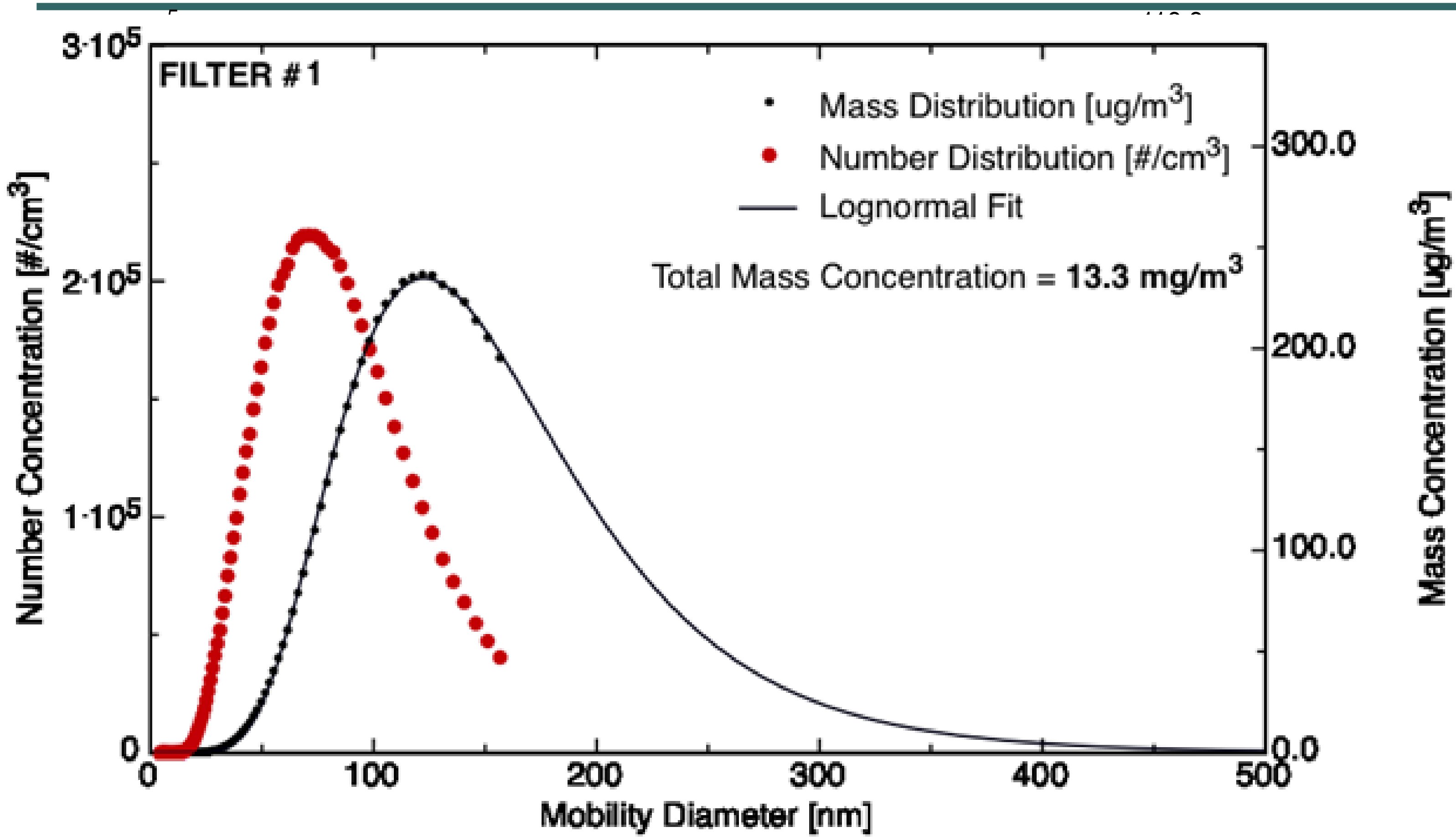


60°C

0.32M PAA

Aerosol size distributions on PAA- filter paper membranes

Filter with MEMBRANE (1)



Collection efficiency

Mode: 58.6 nm
Mean: 65.7 nm

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Demokritus, Sadik, et al 2013