Synthesis and Characterization of Conducting Composite Nanoparticles for Flow Battery Applications

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Motivation – Demand for energy storage technology

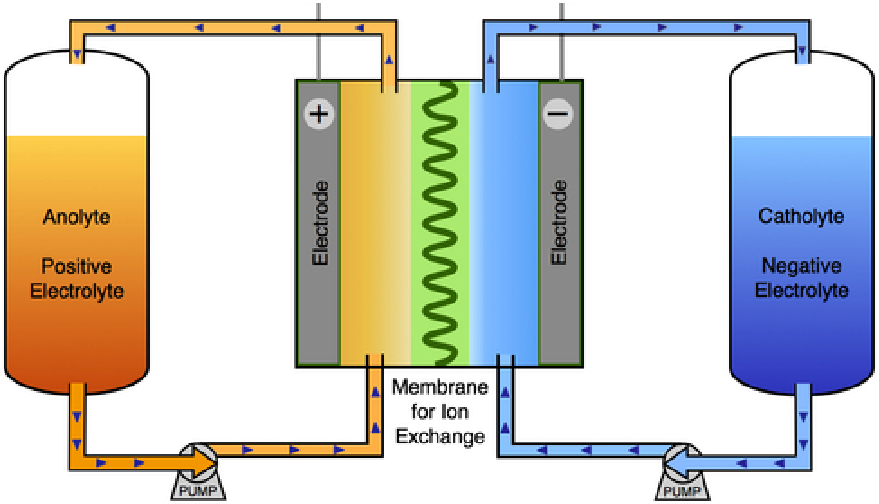
Challenge: Electrical power derived from renewable electrical sources requires storage for wide-scale adoption and implementation

Storage technologies that exist today are insufficient to meet capacity demands and cost requirements associated with the grid:

Flow batteries are currently being developed to address this need for low-cost and efficient energy storage

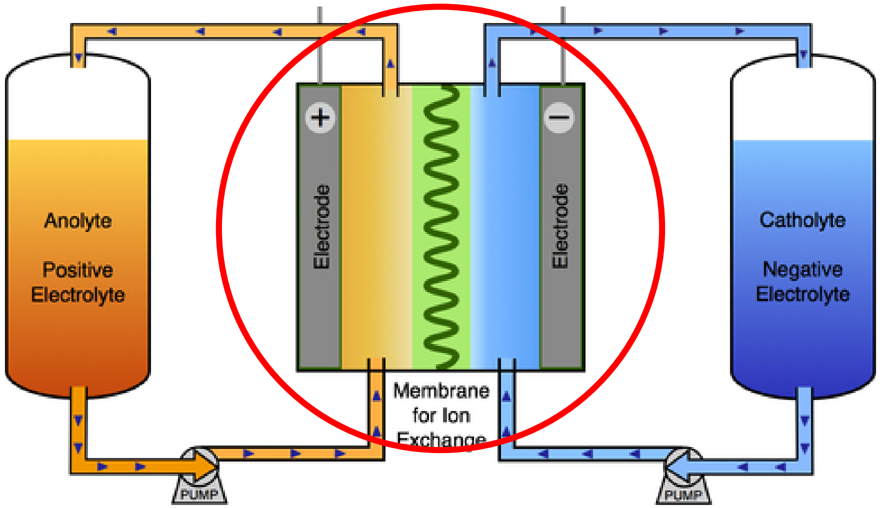
100% Renewable Energy – The Only Way Forward, theenergycollective.com 01/08/13;

Flow Batteries



- Redox active fluids are pumped into a flow cell from external storage tanks where they undergo reversible redox reactions

Flow Batteries



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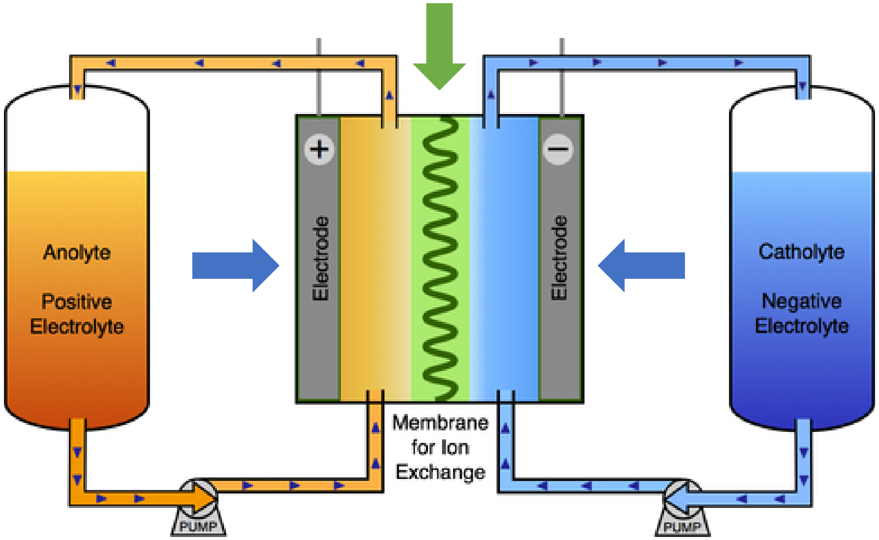
Flow Batteries



- Redox active fluids are pumped into a flow cell from external storage tanks where they undergo reversible redox reactions
  - Flow cell consists of two electrodes separated by a ion exchange membrane
  - Typical electrolytes consist of zinc/bromide or vanadium

Advantages:

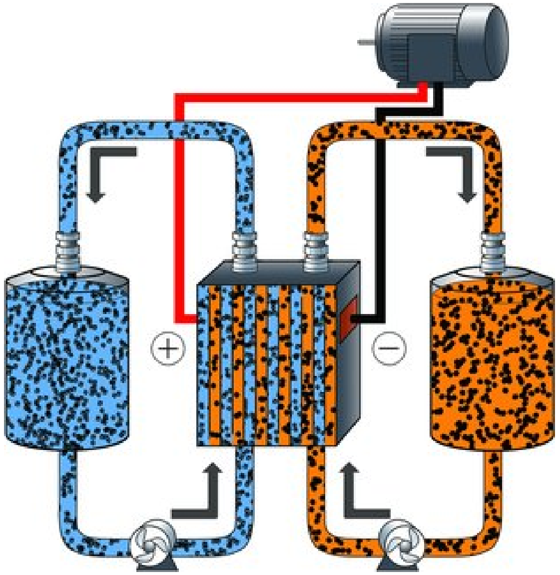
- Capacity of the battery is decoupled from the volume of its packaging
- Scaling up the battery requires only the installation of larger catholyte/anolyte tanks

Disadvantages:

- Energy density limited by solubility of active substances in electrolyte
- These redox materials are often dissolved in highly acidic solvents – makes the equipment more expensive

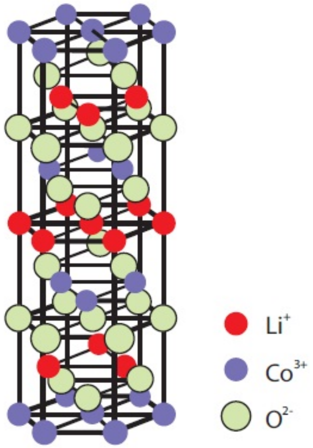
W. Antweiler, *Can flow batteries solve the electricity storage problem?*, University of British Columbia, 09/28/14

Semi-Solid Flow Batteries (SSFBs)



- Combine high energy density of lithium (Li) with benefits of flow batteries
- Suspensions of active solid metal oxides intercalated with lithium (e.g., $LiCoO_2$) instead of redox species dissolved in electrolyte
- Electrical energy is produced when Li is deintercalated from the metal oxide, Li-ion passes through the ion exchange membrane and the electron travels through an outside circuit to do work

$$Li_{1-x}CoO_2 + xLi^{+1} + xe^{-1} \longrightarrow LiCoO_2$$



- Carbon black (CB) is used to provide electrical conductivity and allows for charge transfer from material to current collector
- Unfortunately, the electrical percolation of the CB particles results in a high viscosity suspension and undesirable flow properties

Duduta et al., “Semi-Solid Lithium Rechargeable Flow Battery”, (2011) Advanced Energy Materials, 1, 511-516

Our Idea:

Carbon Black (CB)

CB requires hard sphere contact for electrical conductivity

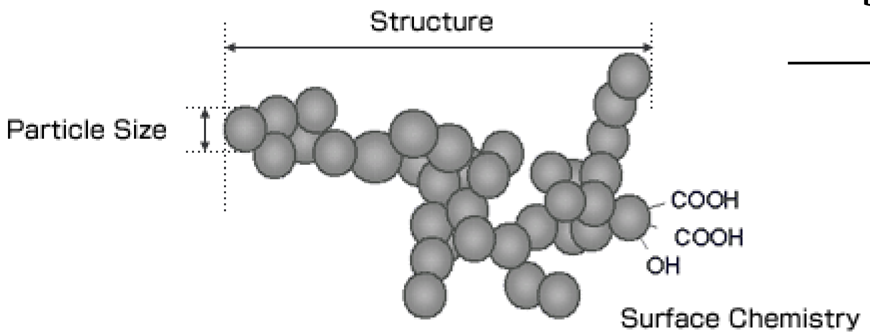
More energy required to break up CB to make it flow

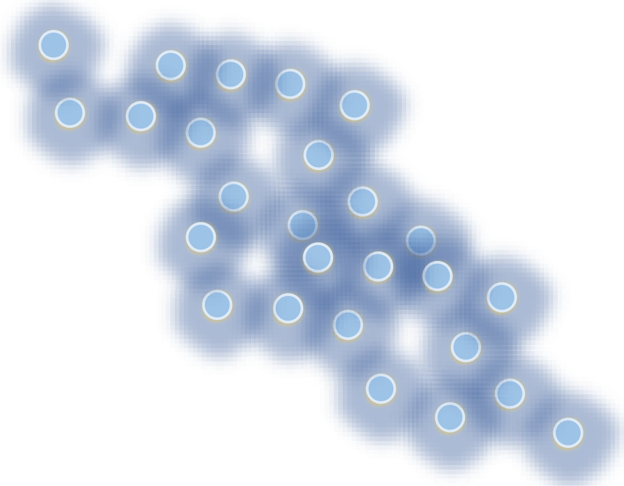
Hydrated Polymer Brush

Polymer brush only requires close proximity for charge transfer

Electrical percolation without mechanical percolation of composite particles makes flow much easier

Replace CB with a conductive polymer brush

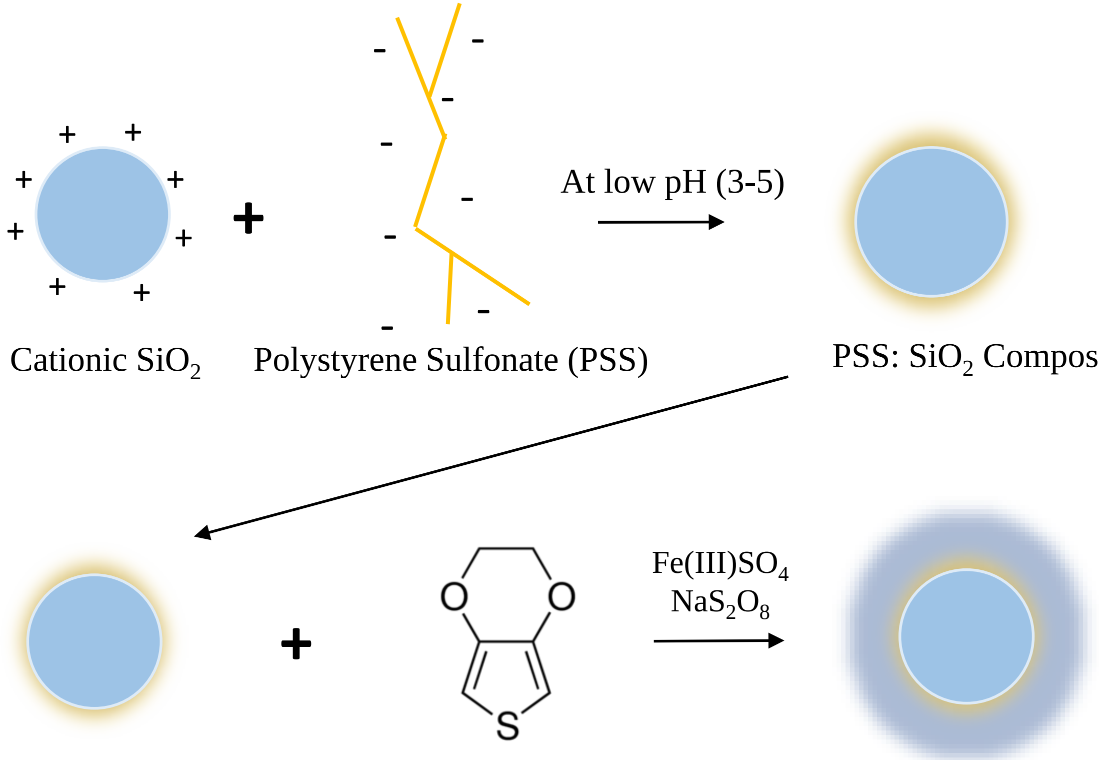




Mitsubishi Chemical Corporation, *Three Main Properties of Carbon Black*, (2006)

Our Approach

Metal oxide (MO) particles are positively charged at low pH, and we used cationic silica (SiO_2) as a model for metal oxides



Cationic SiO_2

Polystyrene Sulfonate (PSS)

At low pH (3-5)

PSS: SiO_2 Composite

Polystyrene sulfonate (PSS) provides colloidal stability and ionic conductivity

PSS: SiO_2 Composite

3,4-ethylenedioxythiophene (EDOT)

$Fe(III)SO_4$
NaS_2O_8

PEDOT:PSS:SiO_2 Composite

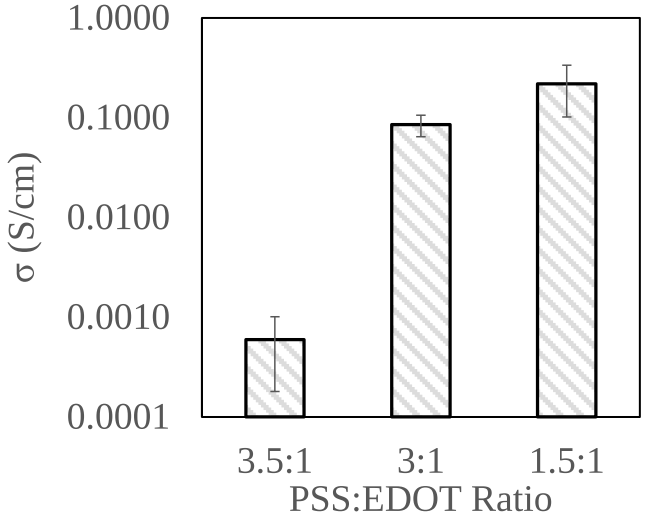
PEDOT provides electrical conductivity

Proof of Principle:

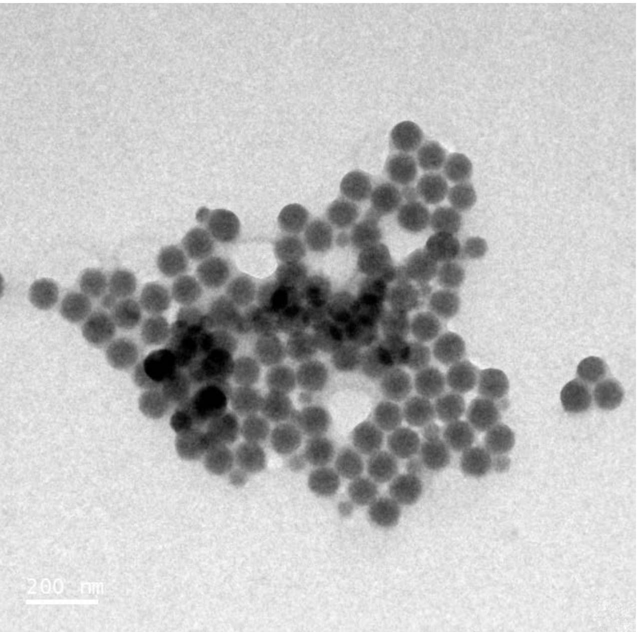
Demonstrated proposed synthesis method is capable of coating PEDOT:PSS brush layer on SiO_2

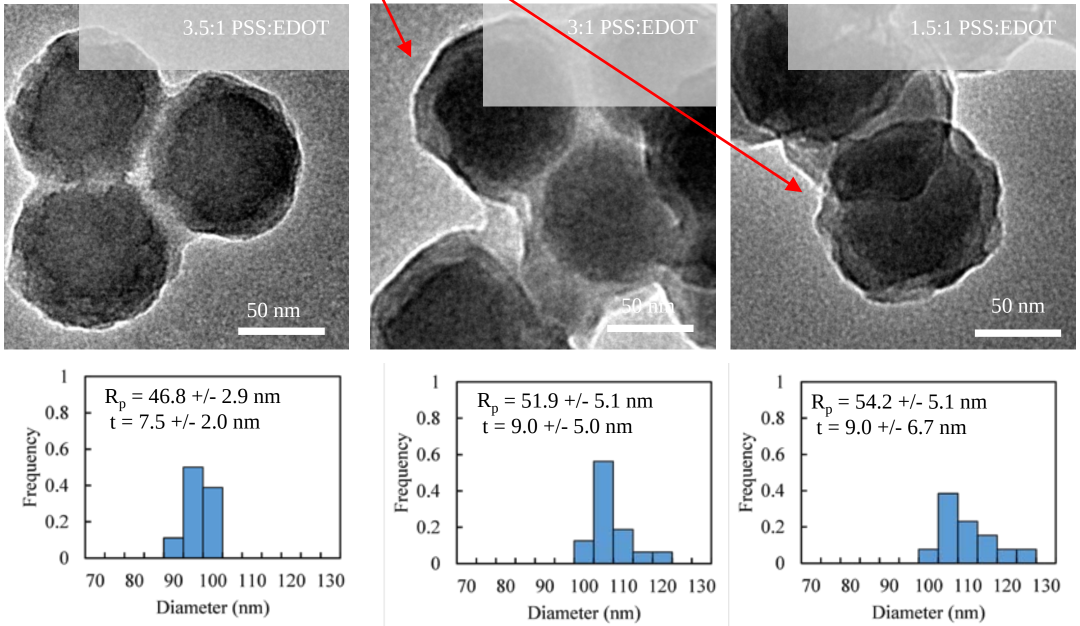
Thin films of coated particles were shown to be conductive

Core/shell structure with polymer brush surrounding SiO_2 particles



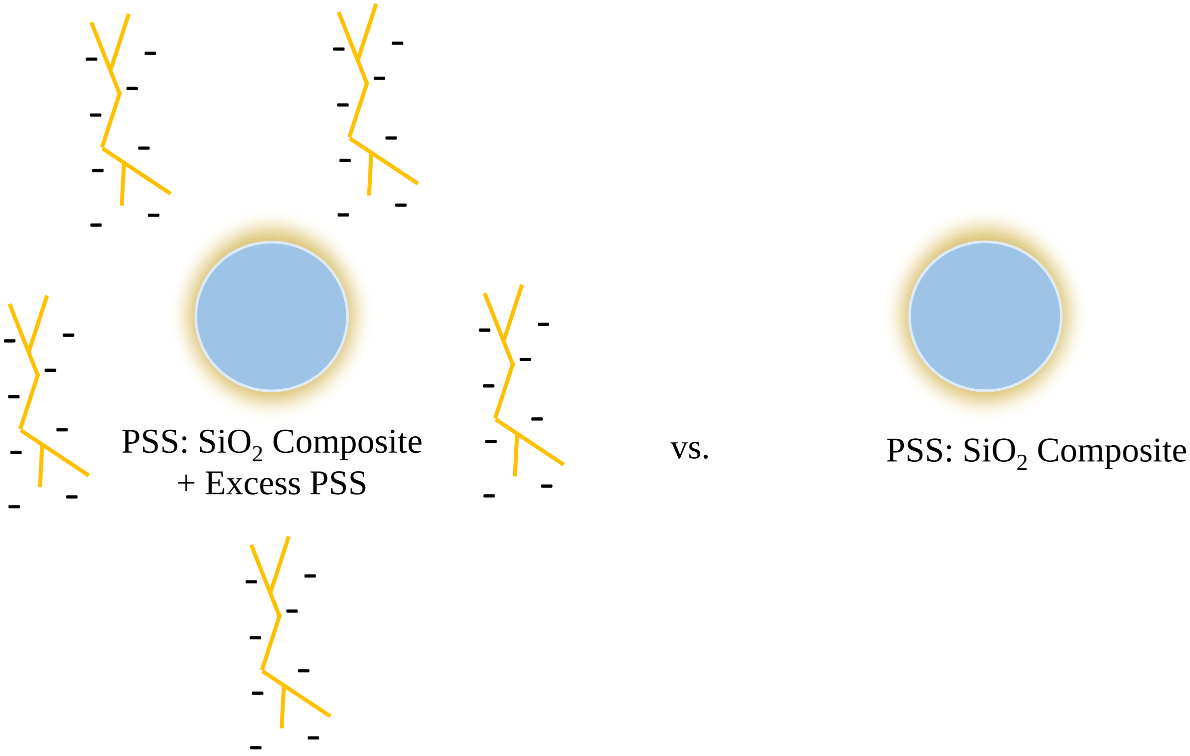
SiO_2





My Goal

- Understand the effect of removing unadsorbed PSS from the sample solution on the properties of the composite particles
- What role does the excess (unadsorbed) PSS play in the EDOT reaction?

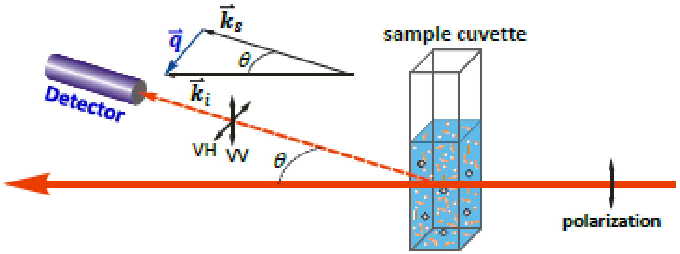


PSS: SiO_2 Composite + Excess PSS

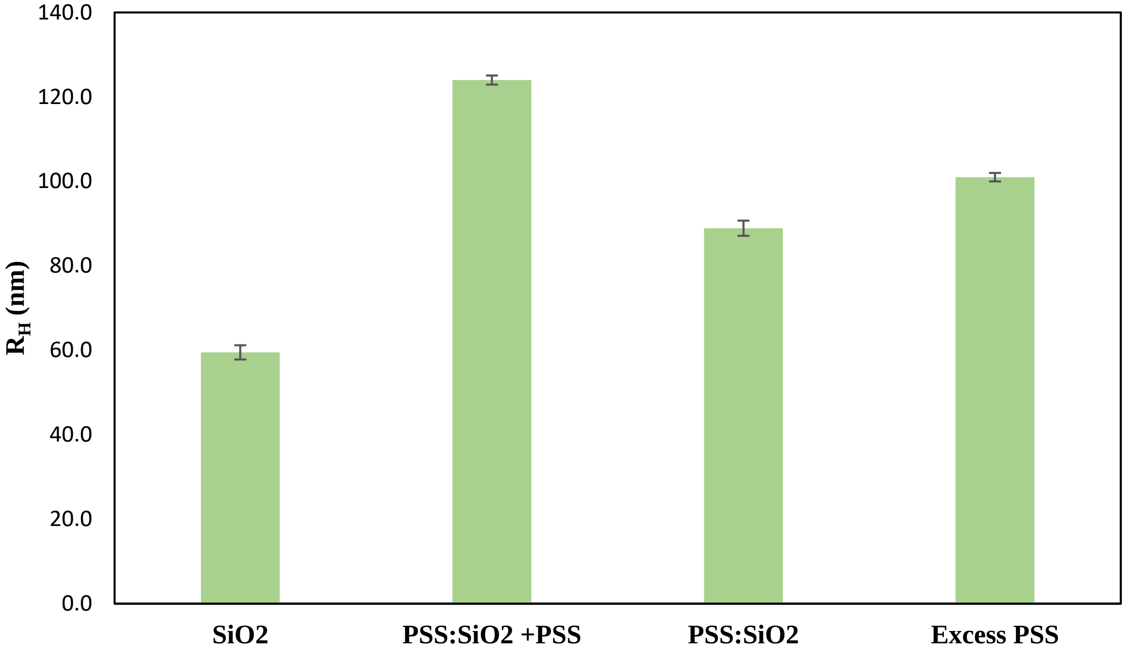
vs.

PSS: SiO_2 Composite

Initial Characterization



Dynamic Light Scattering (DLS) provides information about the size distribution of small particles in solution by measuring relaxation time



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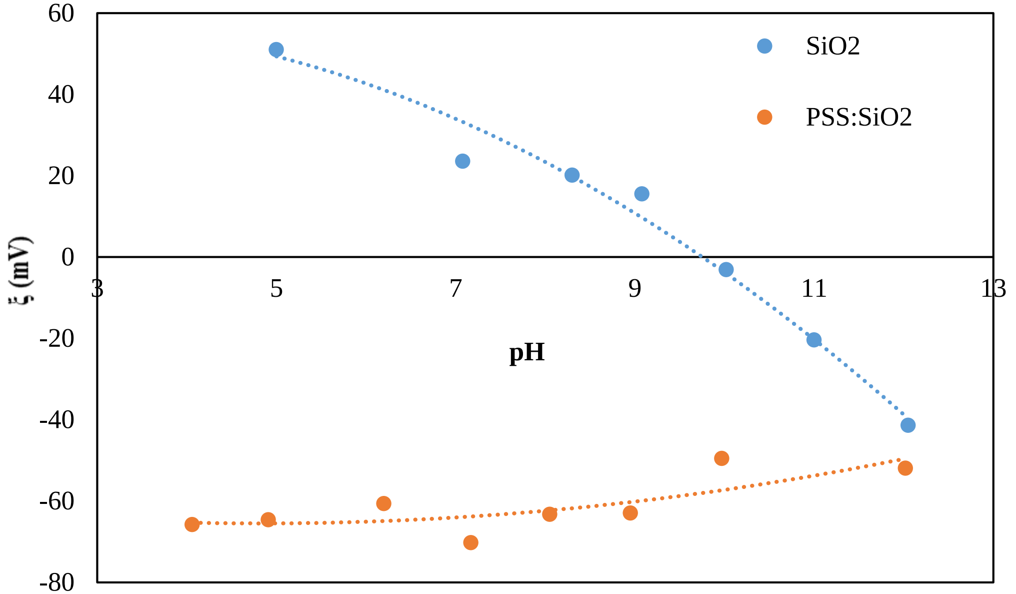
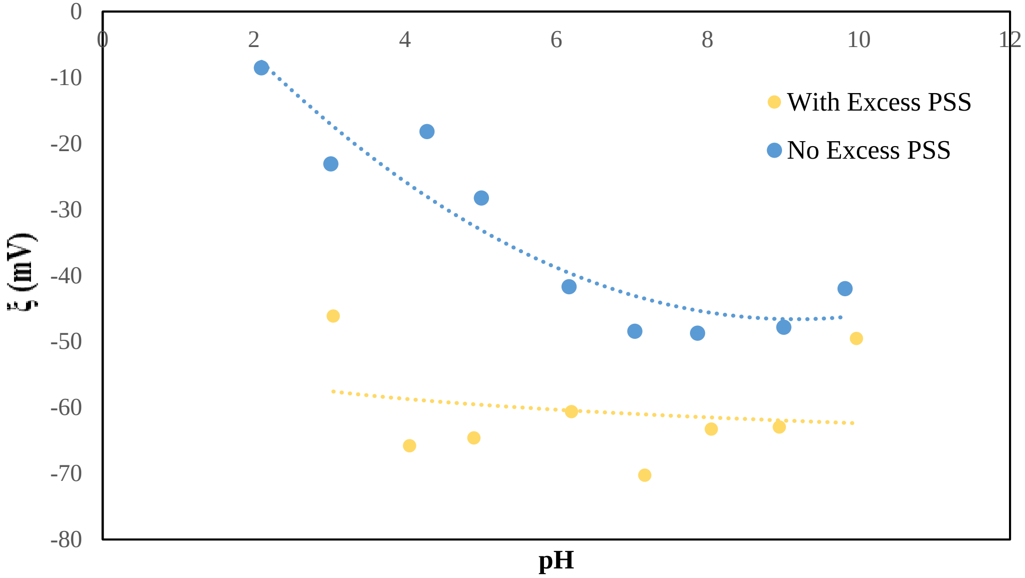


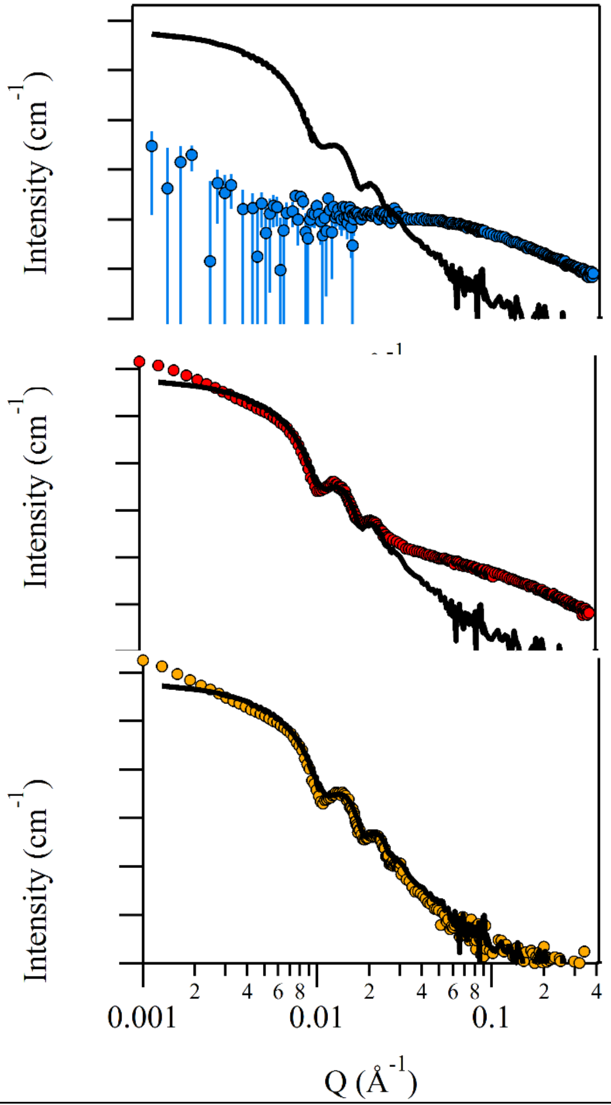


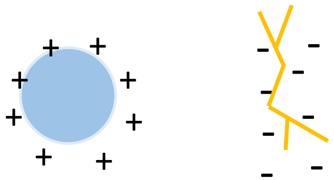
Zeta potential (ZP) can be thought of as simply the surface charge of particles in solution.

The ZP of particles can be determined from the electrophoretic mobility that is measured when an electric field is applied across the sample

Samples with excess PSS present show more negative surface charge at low pH indicating the contribution of the unadsorbed PSS to particle and solution properties

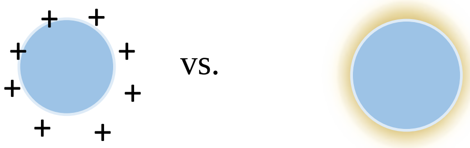
SANS measurements





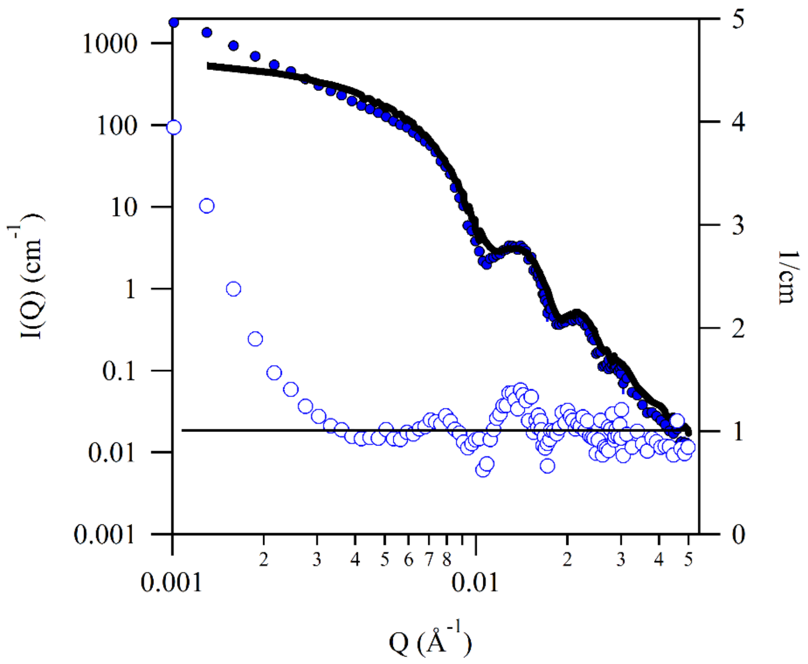
Cationic SiO_2 vs. PSS

Cationic SiO_2 vs. PSS: SiO_2 Composite + PSS

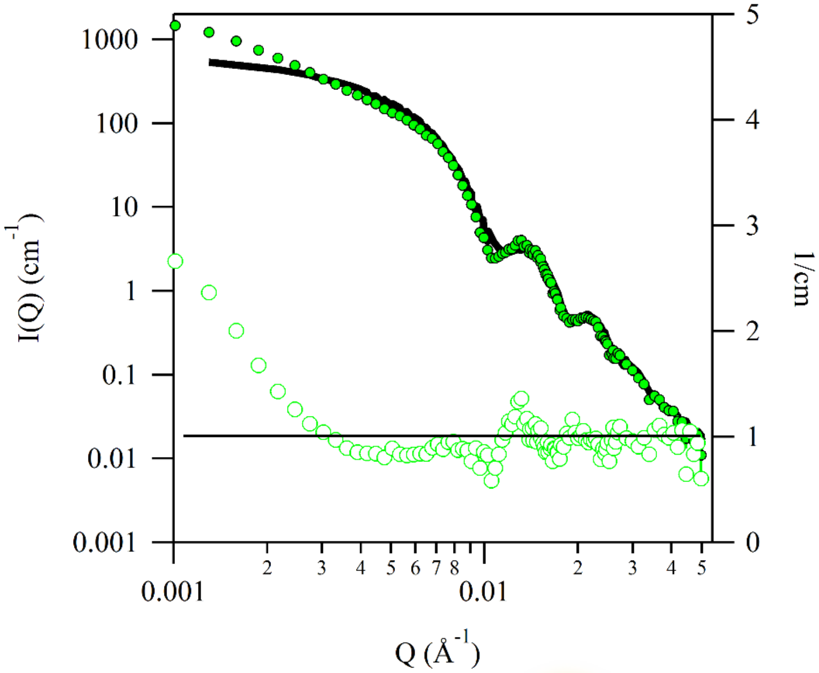


Cationic SiO_2 vs. PSS: SiO_2 Composite

SANS measurements



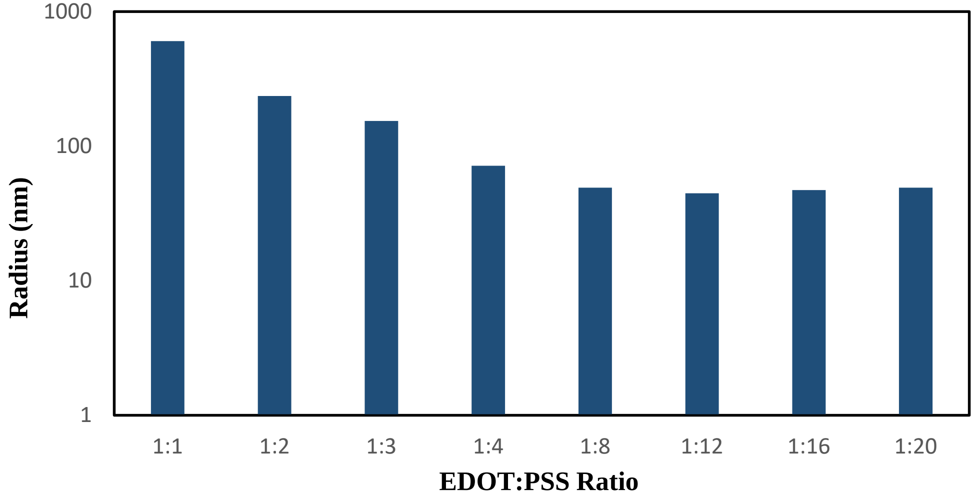
Cationic SiO_2 vs. PSS: SiO_2 Composite

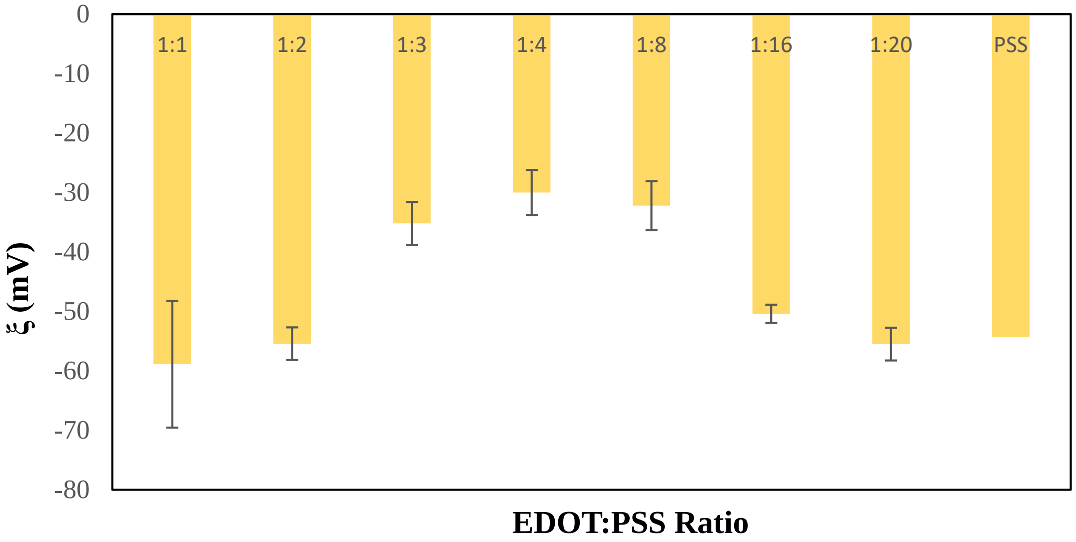


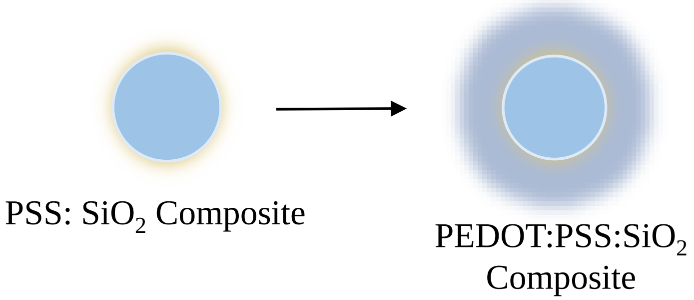
Cationic SiO_2 vs. PSS: SiO_2 Composite + PSS

Particles with and without excess PSS compared with their corresponding shape factors

Particle Size and Surface Charge






PSS: SiO_2 Composite

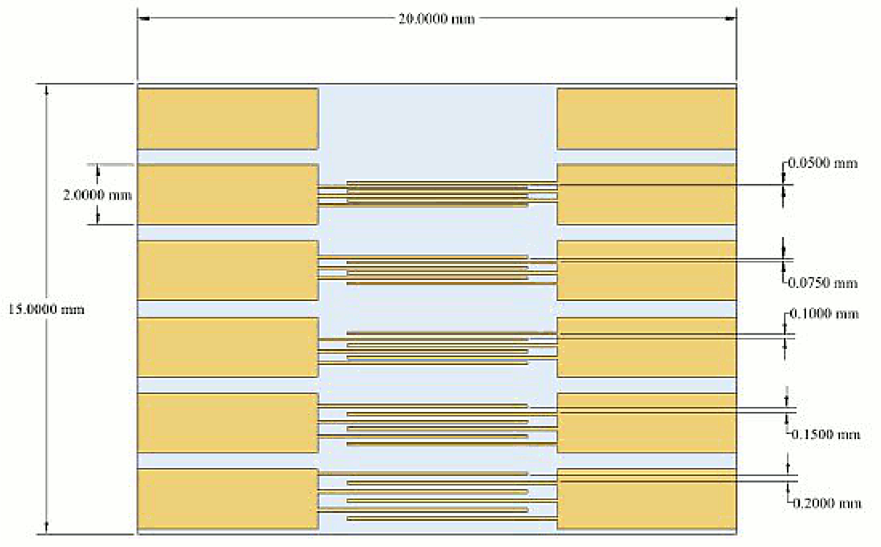
PEDOT:PSS:SiO_2 Composite

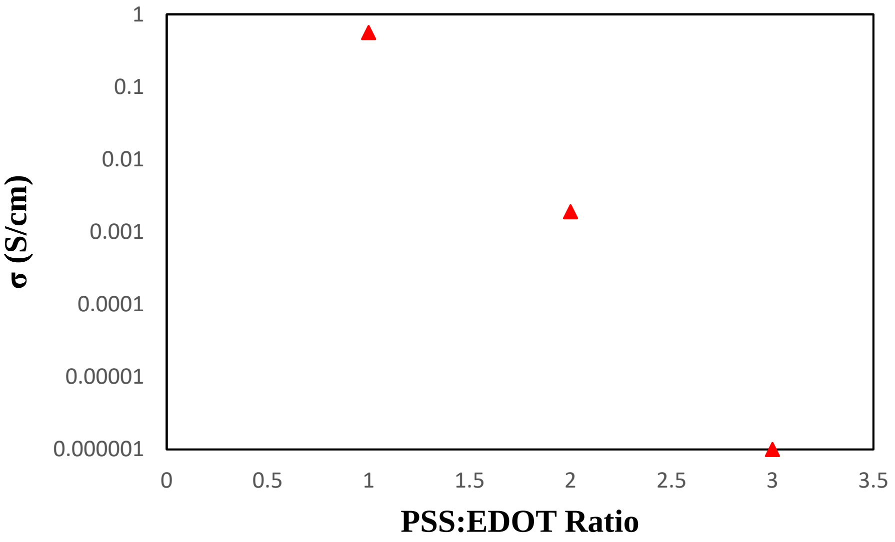
With PSS: SiO_2 content fixed, the amount of EDOT reacted was varied to gain an understanding of how the properties of the particles were affected

DLS measurements revealed a significant increase in hydrodynamic radius as EDOT:PSS ratio went from 1:4 to 1:1, as would be expected

It was determined that particle agglomeration was responsible for this increase, and for the decrease in surface charge above a ratio of 1:4

Conductivity Measurements





The conductivities of thin films of PEDOT:PSS:Silica composites were obtained by measuring the resistance of the films with varied EDOT content using Ossilla Variable Channel Length substrates

Conclusions and Future Work

- PEDOT:PSS: SiO_2 composite particles were successfully synthesized and characterized using various techniques
- Bulk PSS that is not adsorbed to the SiO2 particles likely plays a role in the incorporation of PEDOT onto the composite and adsorbs at high EDOT:PSS ratios
- SANS measurements revealed clear differences between pure SiO_2 and adsorbed PSS on SiO_2
- These particles showed conductivity when made into thin films
- At high EDOT:PSS ratios (1:1-1:2), large amounts of agglomeration was observed, resulting in a decrease in surface charge in this regime, but further studies and analysis must be done at these ratios to truly understand the behavior
- TEM micrographs supported DLS data that suggested the formation of a polymer surface layer on the metal oxide particles

Acknowledgements

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Questions?