Controlling the Hydrophobicity of Silica Nanoparticles by Altering Surface Chemistry

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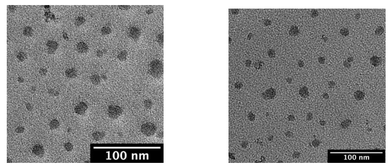
Introduction

Soft material membrane research is at the front of much sustainability research because of their abilities in separating green house gases, desalination of water, and other purposes. Membranes of this nature require special polymer grafted nanoparticles for casting. Polymerization initiated from the surface of nanoparticles requires compatibility between nanoparticles and common organic solvents like methyl ethyl ketone (MEK). The resulting "hairy" nanoparticles can be used to create gas-separation membranes with enhanced gas permeabilities and tunable gas selectivities. However, high polydispersity hiders selectivity.

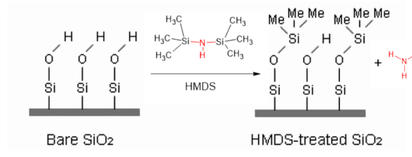


Motivation: Particle shape and size distribution can be improved using commercial silica colloids

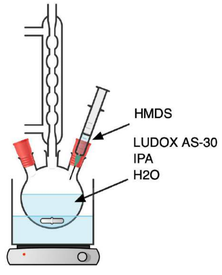
Problem: Monodisperse silica is too hydrophilic to be used in organic solvents

Methods

Reaction Mechanism



- LUDOX AS-30 (Commercial silica, SiO_2) reacts with HMDS to attach trimethylsilyl (TMS) groups to surface
- Reaction occurs at 70 °C for 3 hours
- Surface chemical change alters solubility properties



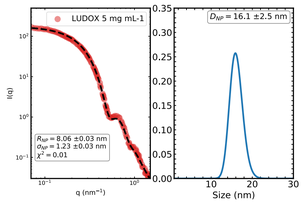
Scattering, Microscopy, Spectroscopy, and Gravimetric Analysis Used to Characterize Particles

- Dynamic Light Scattering (DLS)
- Small Angle X-Ray Scattering (SAXS) (Photo by Isabella Huang)
- Transmission Electron Microscopy (TEM)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Thermogravimetric Analysis (TGA)

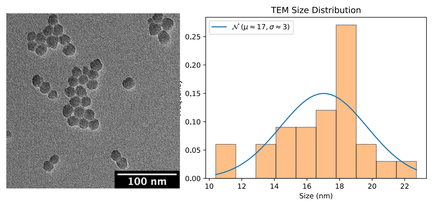
Results

LUDOX AS-30 Particle Size Distribution Comparison

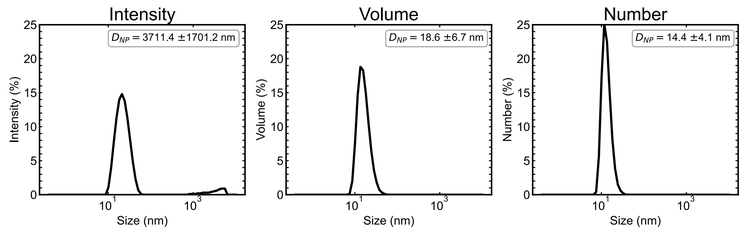
SAXS form factor image



TEM image analysis of LUDOX AS-30

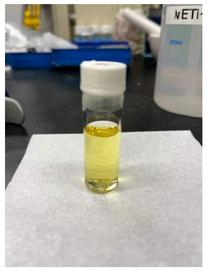


DLS: Intensity, volume, and number distribution



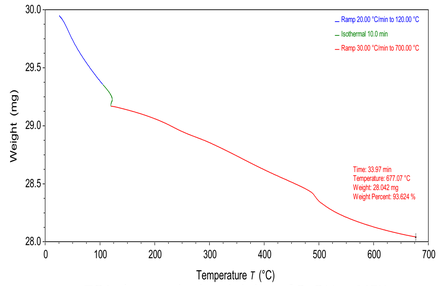
Characterization of Surface Chemistry Using ATR-FTIR

Solubility in Methyl Ethyl Ketone



Nissan MEK-ST solution

Modified LUDOX AS-30 in MEK

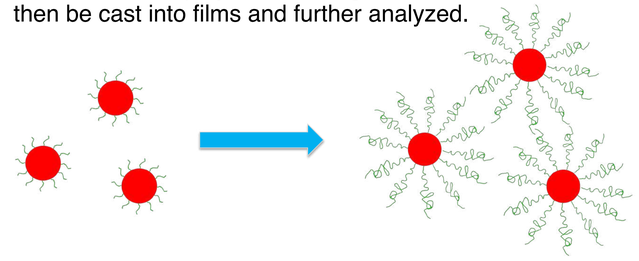


TGA showing high solubility of Si-OH in MEK

Above: The two images above left and middle show a comparison between MEK-ST and reacted LUDOX solution in MEK. TGA analysis done on 300 µL of reacted LUDOX shows a final weight of nanoparticle present of 28.04 mg, corresponding to a solution concentration of 93.5 mg/mL.

Conclusion and Next Steps

- A monodisperse particle size is observed (14-18 nm diameter), and the polydispersity in particle size relative to MEK-ST is significantly reduced.
- LUDOX AS-30 is capable of undergoing changes is surface chemistry, altering its hydrophobicity. This allows it to be a suitable starting material for creating hydrophobic monodisperse silica nanoparticles.
- Further improvement of the dispersion of the modified silica is the next challenge of this problem. Additional milling and drying techniques for the product will be tried to disrupt any particle aggregation that may be happening.
- Once dispersion is optimized and controllable, the next step is to attempt a matrix-free polymerization via a solution of monomers. The polymer chains grafted to the surface would then be cast into films and further analyzed.



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References

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