

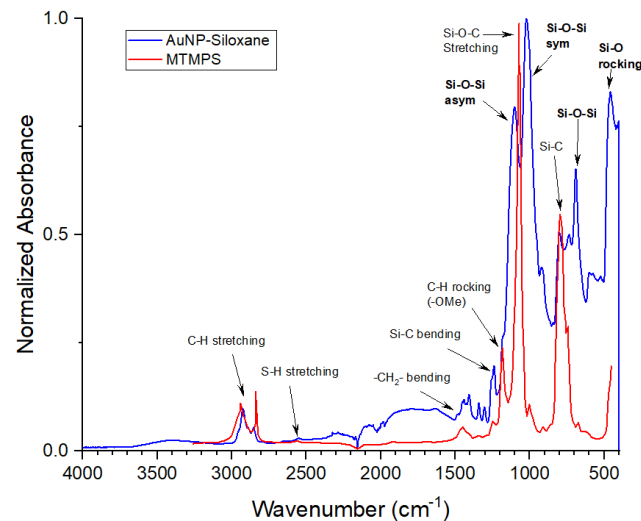
AuNP-SILOXANE NANOCOMPOSITE

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Under Prof. Karthik Shankar

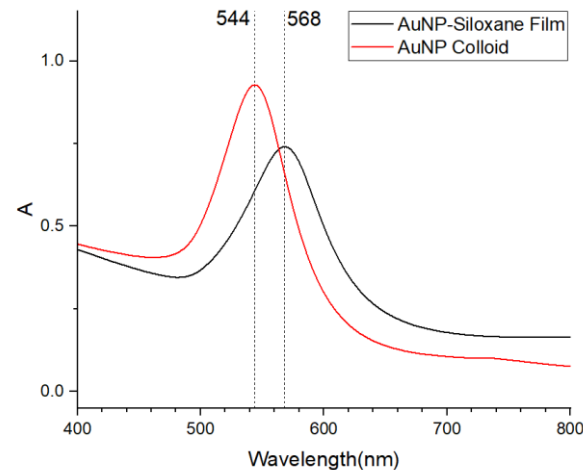
Abstract

- Faceted gold nanoparticles (AuNPs) were successfully incorporated into a siloxane polymer matrix using 3-mercaptoptrimethoxypropylsilane (MTMPS).
- The nanoparticles were first synthesized using the seed mediated approach. Their original stabilizer was then replaced with MTMPS and terminal silane groups were polymerized via condensation. The formation of Si-O-Si bonds was confirmed through Fourier-transform infrared spectroscopy (FTIR).
- As compared to typical one pot synthesis methods, synthesizing the nanoparticles first allows for superior control of the particles' morphology and optical response.



Abstract

- The resulting colloids were drop-cast onto fluorine-doped tin oxide (FTO) substrates, exhibiting excellent dispersion and retained their vibrant purple coloration. Optical characterization using UV-visible spectroscopy demonstrated the presence of a strong plasmonic peak, indicating the successful integration of AuNPs without significant loss in the Q-factor.
- The films exhibited a unique mechanical behavior, wherein they displayed their own intrinsic mechanical integrity. This was particularly evident in their ability to delaminate in ribbon-like structures without disintegration. To the best of our knowledge, this phenomenon has not been previously reported for MTMPS-capped AuNP.
- This report is divided into two parts:
 1. *Gold nanoparticles: synthesis and characterization*
 2. *AuNP-Siloxane nanocomposite: synthesis and characterization*



Literature on AuNP nanocomposites

- Buining et al (1997) reduced HAuCl_4 in the presence of MTMPS (one-pot synthesis) to obtain a monolayer of silane groups around polydisperse AuNPs which was further layered with APTES via Si-O-Si condensation.
- Lai et al (2017) capped seed mediated AuNRs with MTMPS for functionalizing with PEG. Other works have also used MTMPS to create a stable interface between AuNPs and a variety of polymers
- Bifunctional silanes have also been used to create a stable interface between AuNPs and SiO_2 .
- However, there are no known instances of a polymer matrix created solely from MTMPS
- **Other relevant literature mentioned throughout this report are listed in complementary material**

GOLD NANOPARTICLES

Synthesis

Overview

- The experimental procedure designed by Wu et al was used to synthesize faceted AuNPs.
- The process involves the stepwise syntheses of three aqueous solutions: Seed Solution (SS), Growth Solution A (GA) and Growth Solution B (GB). All three are stabilized by Cetyltrimethylammonium Chloride (CTAC). Nanoparticles in GB are the final product of this synthesis.
- Seed solution is prepared by rapid reduction of HAuCl_4 using NaBH_4 . This leads to the formation of small monodisperse growth sites (seeds) for the further steps.
- Both growth solutions (GA and GB) are prepared by slow reduction of HAuCl_4 using Ascorbic Acid (AA), which results in Au^+ ions. The concentration of Au^+ ions generated determines the kinetics of the subsequent reactions.
- A small quantity of SS is added to GA, initiating nanoparticle growth during which Au^+ ions are catalytically reduced on the surface of the seed particles. A portion of this modified GA is subsequently transferred to GB for further growth.
- Separating the nucleation and growth steps leads to more monodisperse nanoparticles
- The surface energies of various crystallographic planes in FCC gold differ, with $\{100\} > \{110\} > \{111\}$. Faster reaction kinetics result in nanoparticles predominant with higher-energy facets, while slower kinetics yield more thermodynamically stable products. Consequently, by precisely adjusting the concentrations of reagents, one can dynamically regulate the shape and morphology of the nanoparticles.

Experimental Procedure (for 30mL sol)

Preparation Seed Solution

1. Prepare 10mL of 0.1mL CTAC in a glass vial
2. Add 125 μ L of 20mM HAuCl_4 (aqueous)
3. Add 360 μ L of 25mM freshly prepared, cold NaBH_4 (aqueous) while stirring
4. Solution expected to turn brown immediately
5. Continue stirring at 40°C for 1h

Experimental Procedure (for 30mL sol)

Preparation of growth Solution A (B)

1. Prepare 10mL (30mL) of 0.1mL CTAC in a glass vial
2. Add 250 μ L (750 μ L) of 20mM HAuCl₄ which results in a faint yellow solution
3. Add (R x 200) μ L of 25mM AA while stirring (**R = AA/HAuCl₄ molar ratio**)
4. Solutions expected to turn colourless

Note: Carrying out the synthesis in smaller volumes leads to more uniform conditions leading to more monodisperse particles.

Experimental Procedure (for 30mL sol)

Volume Transfers

1. Keep both vials A & B on a hot plate and initiate stirring
2. Transfer 100 μ L of SS into vial A
3. Transfer 300 μ L of A into B within 10s of previous step
4. GA turns red quickly while GB turns wine red in some time
5. Continue stirring for 30 mins
6. **Vial GB** (having a superior quality factor and larger size compared to GA) is used for further experimentation and characterization



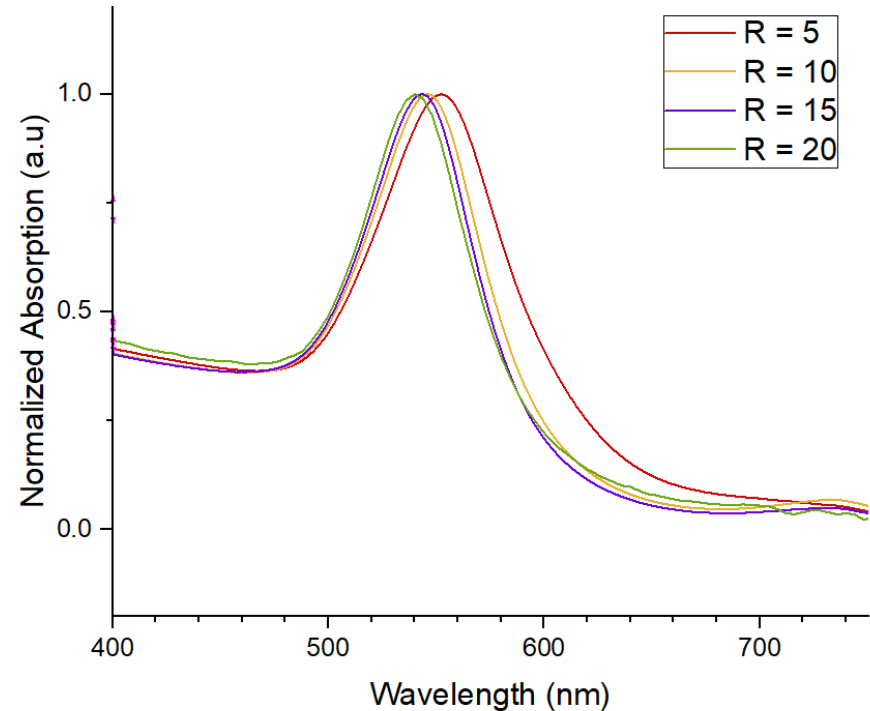
GA (left) and GB (right) after reaction completion

GOLD NANOPARTICLES

Characterization

UV-Vis Spectra

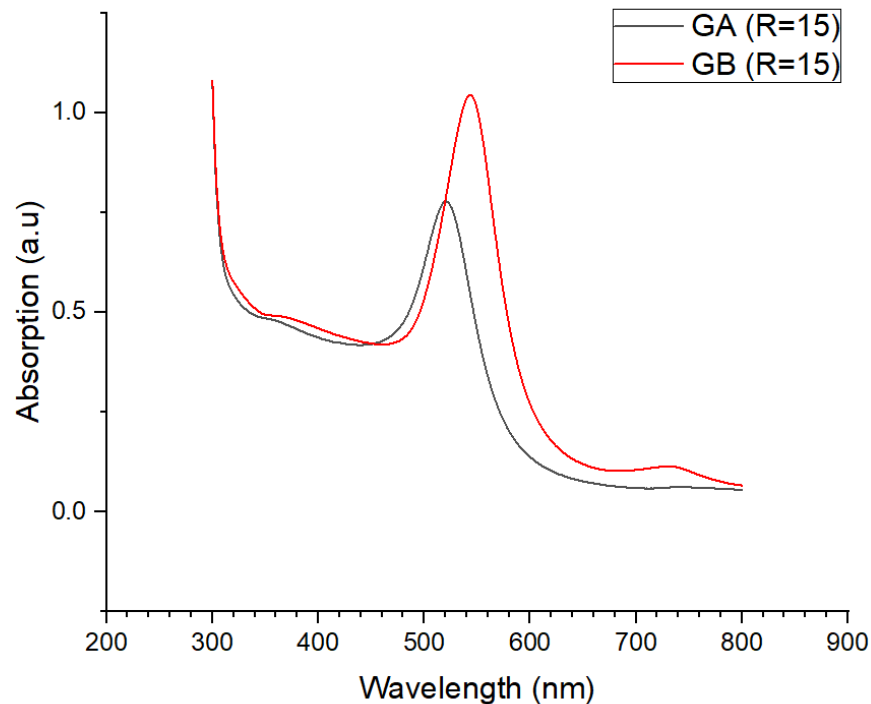
- Absorption spectra was measured on Perkin Elmer UV-Vis Spectrometer. Colloidal samples from GB are loaded into cuvettes without further processing or changes in concentration. Q-factors were obtained by applying Voigt fits to the absorption curves in Origin and adjusting the vertical offset (y_0) to **~0.1**
- A general blueshift is observed on increasing R , which partially contributes to an increase in the Q-factor
- Q-factor, in general is very sensitive to experimental conditions. A maximum Q-factor of **~9.3** was obtained for $R = 15$



Variation of absorption spectra of GB solution with varying R

UV-Vis Spectra

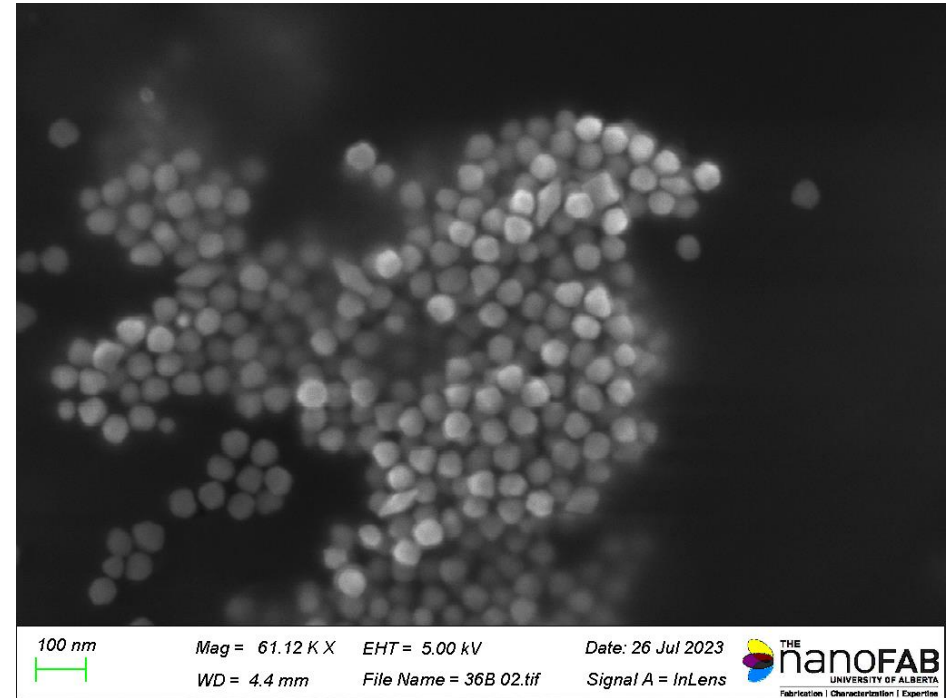
- A significant redshift and increase in Q-factor is observed when growth B is carried out
- This is attributed to the increasing size and faceted nature
- For example, the $R = 15$ sample peak evolves from 522 nm and $QF = 8.12$ to 544 nm and $QF = 9.29$
- A smaller second peak is also observed in the GB solution, corresponding to oblong growth of a small population of NPs



Variation of UV-Vis spectra of GA and GB solutions for $R = 15$

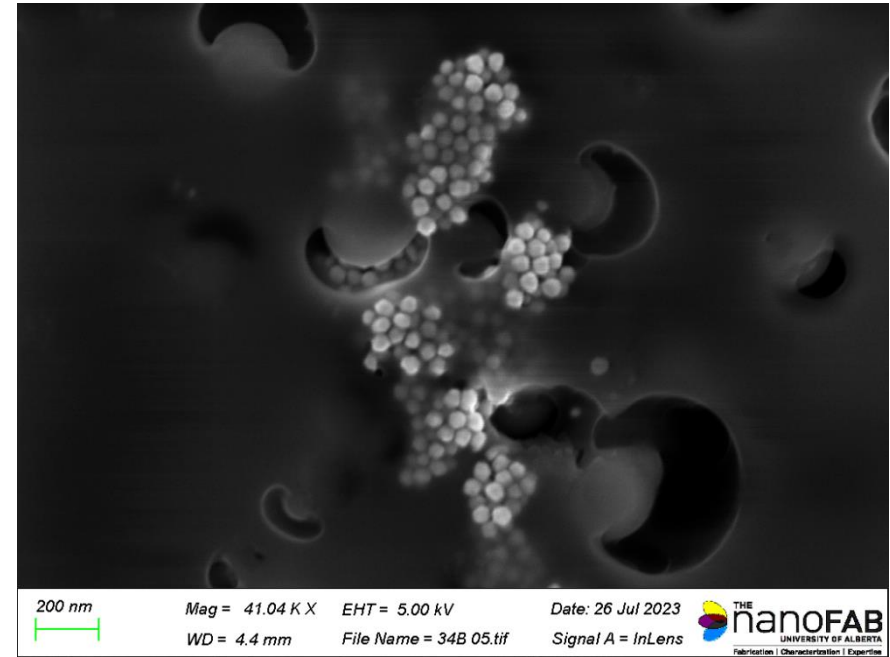
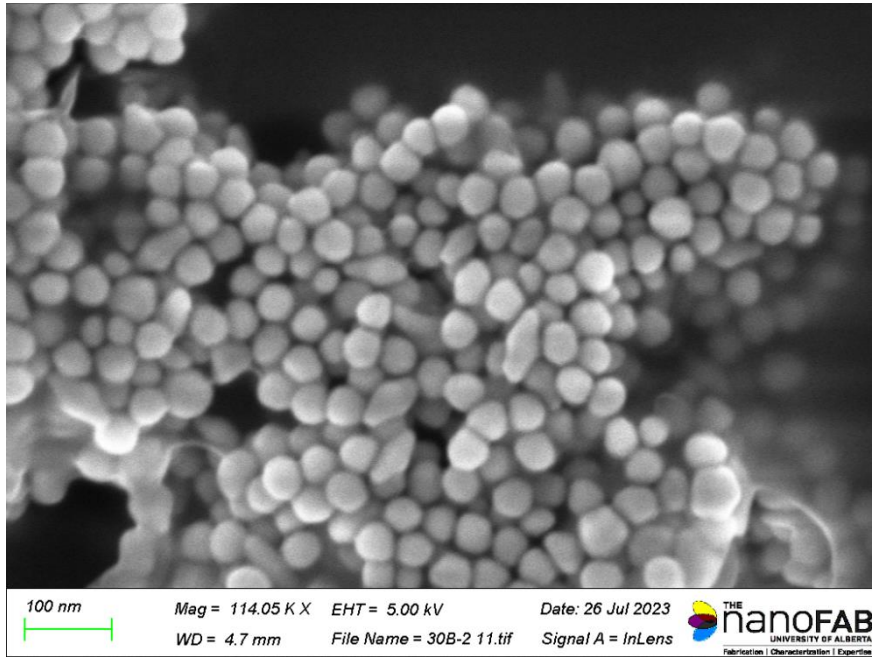
SEM Images

- For SEM characterization, nanoparticles were centrifuged and dropcast onto an Aluminum foil covered stub for improved conductivity. However, there is significant agglomeration which occurred after removal of solvent
- Secondary electron images were collected on Zeiss FESEM
- ImageJ was used for size analysis of the nanoparticles.
- Size of nanoparticles produced averages at **~55nm** with a standard deviation of **~6nm**
- Increasing R is observed to increase faceted nature of the nanoparticles while not significantly affecting the size
- A small population of oblong nanoparticles are also observed, which contributes to a small second peak observed in UV-Vis spectrographs



FESEM images for $R = 10$ ($QF=8.67$)

SEM Images



FESEM images for $R = 15$, $QF=9.29$ (left) and $R = 20$, $QF=8.76$ (right)

AuNP-SILOXANE

Synthesis

Overview

- Gold nanoparticles are centrifuged and then stirred with NaBH_4 to eliminate excess CTAC as demonstrated by He et al. CTAC on nanoparticles is then substituted with MTMPS. The stabilization mechanism for the colloid shifts from electrosteric to purely steric. This, along with the strong affinity of sulphur to gold allows the individual nanoparticles to be stable even in the absence of polar solvents
- The resulting AuNP-MTMPS complexes are then drop-cast onto cleaned FTO substrates and subjected to an analysis employing UV-Vis spectroscopy, FESEM, EDX, FTIR. Films formed are uniform and strongly adhered to the substrate. Moreover, they also produce a high Q-Factor plasmonic resonance
- The presence of Si-O-Si bonds, as evidenced by FTIR analysis, confirms the successful hydrolysis and condensation of Si-OMe groups, resulting in polymerization

Experimental Procedure






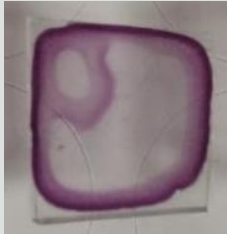

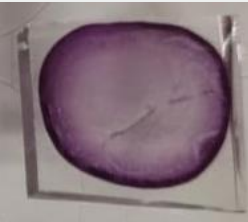
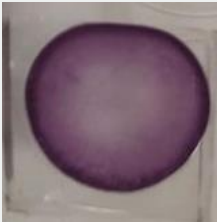
1. Centrifuge 2mL AuNP (from GB vial) at 2000 rpm for 20 mins and remove supernatant. Dilute to 1mL with DI water
2. Add 100 μ L of 100mM fresh, aqueous NaBH_4 . Stir for 1h at 60°C.
3. Centrifuge at 2000rpm for 20mins and remove supernatant. Dilute to 1mL with DI water.
4. Add V_1 μ L of MTMPS and V_2 μ L of MeOH. Stir for 1h at 60°C. Solution turns purple and opaque.
5. Centrifuge 2mL AuNP at 2000rpm for 20mins and remove supernatant, reducing the volume to 200 μ L.
6. Drop cast 100 μ L on 1x1 inch cleaned FTO substrate.



AuNP sol after MTMPS functionalization

Effect of reagent amounts

- Presence of small amounts of MeOH leads to better spread and uniform films. MeOH is also expected to have catalysed the Si-O-Si linking. However excess MeOH causes films to be more concentrated towards the edges
- Increasing MTMPS increases agglomeration and hinders spread, possibly due to larger extent of cross linking
- Samples prepared without NaBH_4 treatment result in colourless films, which is likely caused by inefficient ligand exchange
- **Ideal spread seems to occur when MTMPS:MeOH ratio is near 1:1**

	5 μL MTMPS	10 μL MTMPS	20 μL MTMPS
0 μL MeOH			
10 μL MeOH			
25 μL MeOH			
50 μL MeOH			

Delaminated Samples

- On drop-casting 100 μL AuNP-Siloxane on a larger (2x2 inch) area of FTO, delamination of the film was observed during drying, resulting in a ribbon like morphology.
- This indicated that the siloxane cross linking was effective enough to prevent disintegration when mechanical support from the substrate is lacking.
- Subsequently, these delaminated structures were carefully detached and ground into a powdered form, which was then utilized for FTIR characterization.



Powdered film



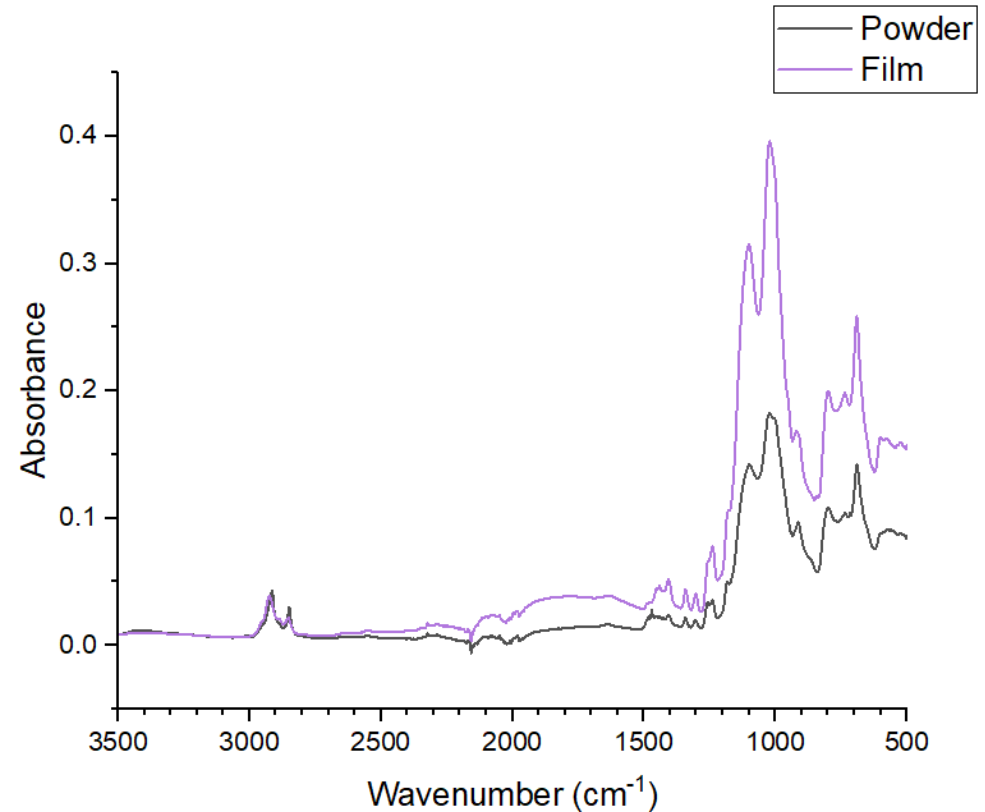
Delaminated Au-Siloxane Film

AuNP-SILOXANE

Characterization

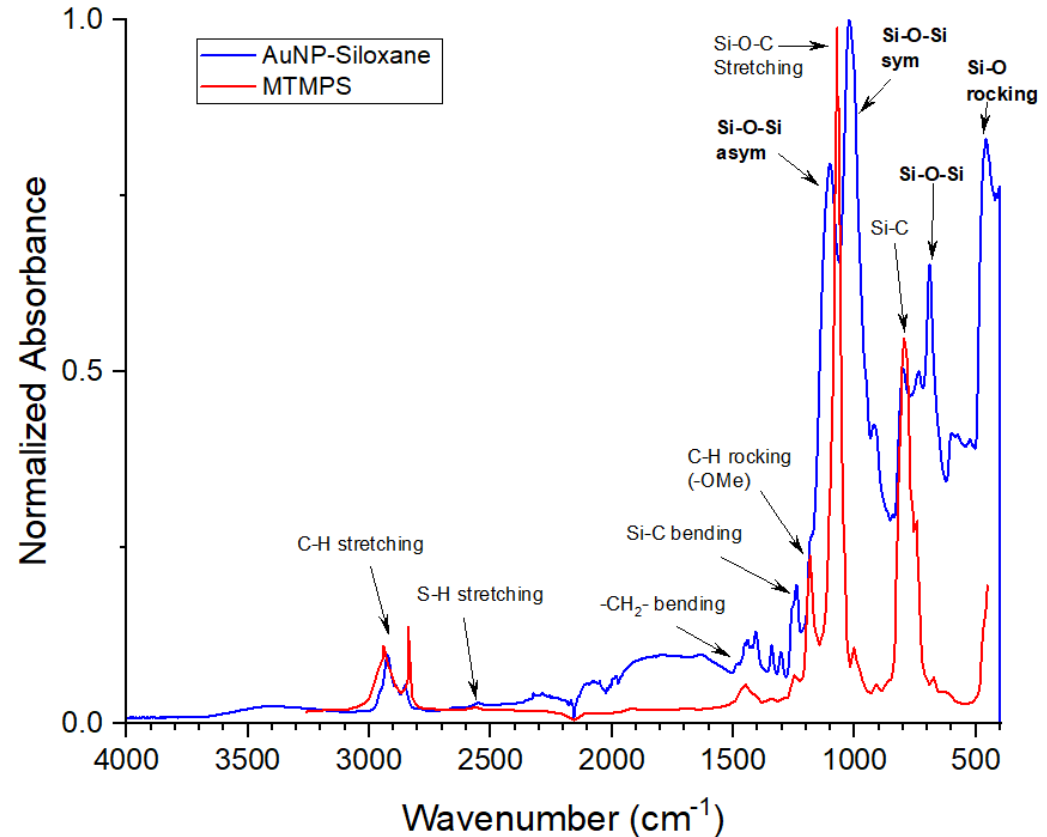
FTIR Spectrum of GSP

- Both powder and film samples analysed using ATR-FTIR
- Powder sample (from delaminated film) and uniform film exhibit identical peaks, implying that polymerization has taken place in both
- ATR spectra of pure MTMPS was obtained from FTIR spectra library ([Wiley and Sons](#))



FTIR Spectrum

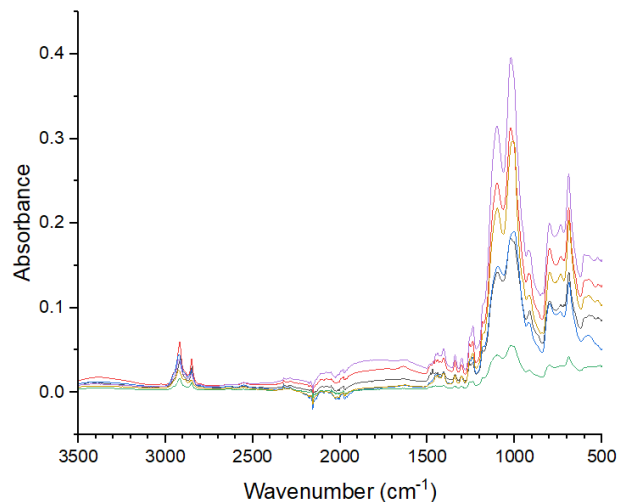
- Si-O-Si peaks have been assigned at 1105 cm^{-1} and 690 cm^{-1} based on Rubio et al's work on siloxane condensation of a similar molecule (APTMS) with $\text{Si}(\text{OMe})_3$ group
- Si-O-Si peaks have been assigned at 1105 cm^{-1} at 1024 cm^{-1} based on Buining et al's work on siloxane condensation of MTMPS and APTES
- Si-O rocking band is also present at 455 cm^{-1} which further proves the presence of siloxane (Launer et al)
- The absence of a peak at 3650 cm^{-1} suggests that silanol ($-\text{SiOH}$) group is absent



FTIR Spectrum of GSP

Presence of peaks at 1105, 1024, 690 and 455 imply the presence of Si-O-Si bonds, from which it can be concluded that condensation polymerization has taken place

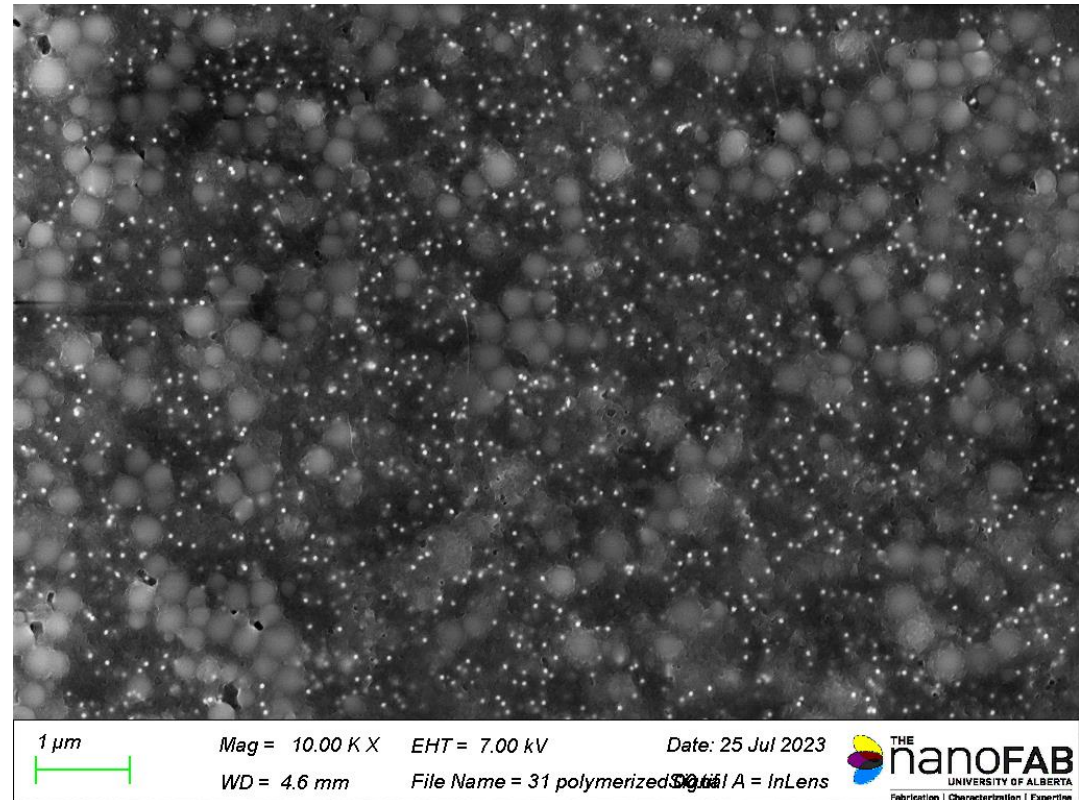
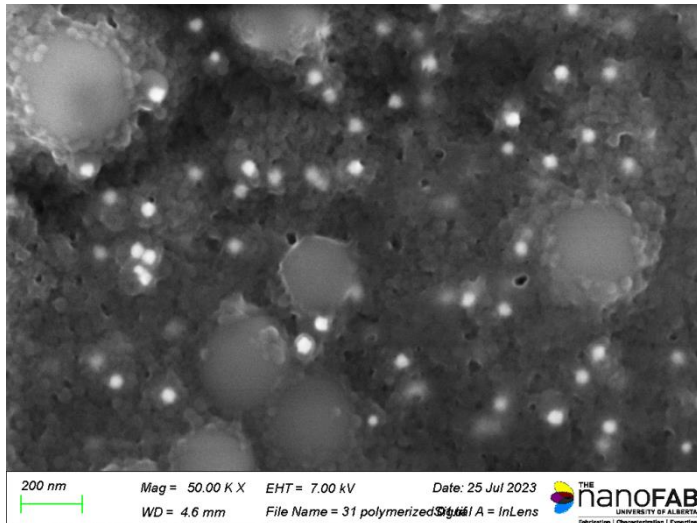
Moreover, identical peaks are observed across multiple samples (below)



Wavenumber (cm ⁻¹)	Assigned Mode
2800-2900	C-H Stretching
2560 (weak)	S-H Stretching
1450	-CH ₂ - Bending
1240	Si-C Bending
1182	C-H Rocking (in -OMe group)
1105	Si-O-Si asymmetric stretching
1070	Si-O-C Stretching
1024	Si-O-Si symmetric stretching
796	Si-C
690	Si-O-Si
455	Si-O rocking

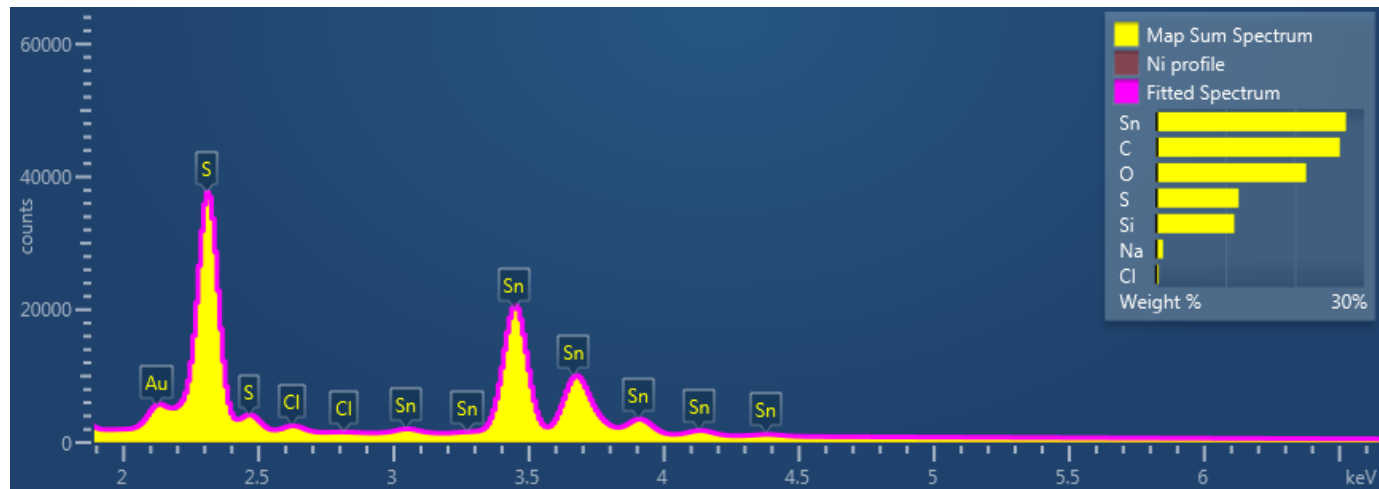
FESEM Images

- FESEM and EDX scans of the drop cast films on FTO were made on Zeiss.
- FESEM images show well dispersed Gold nanoparticles embedded in an organic matrix.
- There is a very significant improvement in the dispersion of the NPs compared to SEM images before MTMPS functionalization.



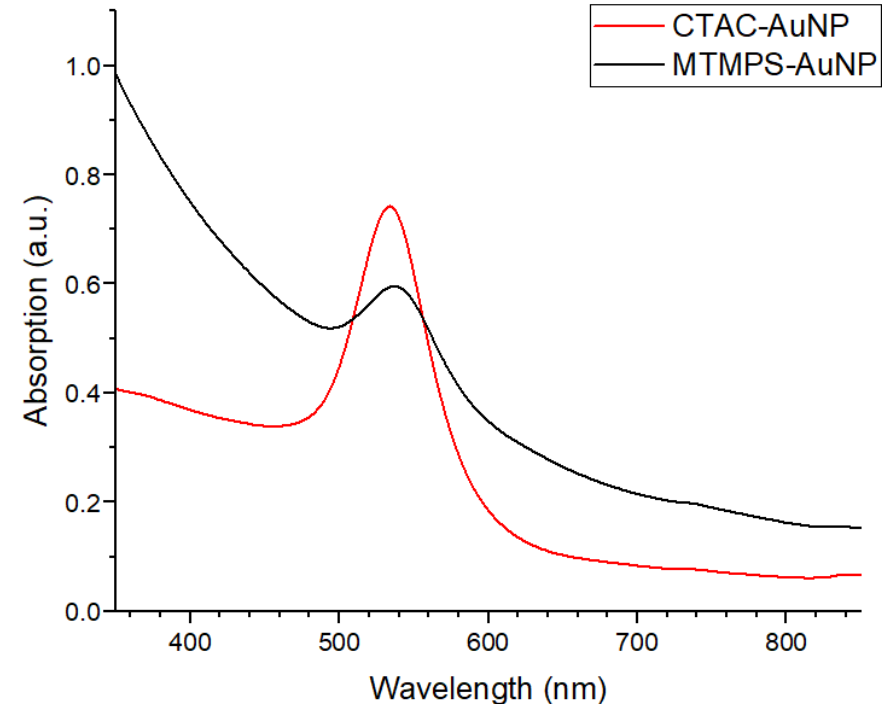
EDX Analysis

- Sn Peaks are from FTO substrate
- Presence of S and Si points to the fact that MTMPS is present
- Absence of N implies that removal of CTAC has taken place successfully
- However, Na and Cl peaks show that ions produced in earlier steps have not been removed perfectly during centrifugation



UV-Vis Spectroscopy

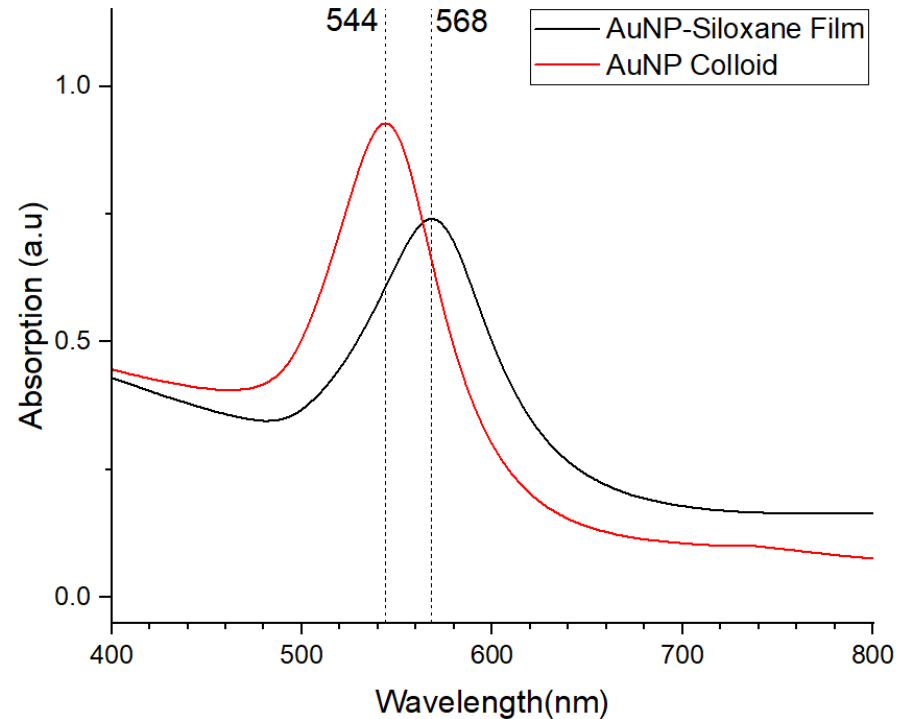
- Sample of CTAC-capped AuNP colloid shows a plasmonic resonance at 532 nm with a Q-factor of 8.54 (FWHM = 0.2855)
- Plasmonic peak in colloidal state of this NP sample after MTMPS ligand exchange is at 538 nm with a Q-factor of 8.06 (FWHM = 0.2864)
- The observed redshift is due to the higher refractive index of the MTMPS ligand shell as compared to the CTAC one



Comparison of absorption spectra of AuNP-Siloxane colloid and AuNP colloid (pre MTMPS)

UV-Vis Spectroscopy

- The shift of the plasmonic peak from original CTAC capped AuNP colloid to AuNP-siloxane film was observed for a different sample
- Drop-cast film on FTO shows a plasmonic resonance at 568 nm with a Q-factor of 7.66 (FWHM = 0.2853)
- The same NP sample, when in CTAC stabilized colloid (before MTMPS functionalization) has a peak at 544 nm with a Q-factor of 8.05 (FWHM = 0.2840)
- Thus, this method results in minimal deterioration of plasmonic resonance from the colloidal state



Comparison of absorption spectra of AuNP-Siloxane film and AuNP colloid (pre MTMPS)

Conclusion

- MTMPS was used to functionalize faceted AuNPs and made to undergo siloxane condensation which resulted in a nanocomposite having novel mechanical properties and excellent optical response
- Results were verified using UV-Vis spectroscopy, FTIR spectroscopy, FESEM and EDEX analysis
- The same methodology can be applied to a large variety of nanoparticle colloid system, allowing for a large flexibility in optical response