Gold Nanorod Based NOHMs that Exhibit Tunable Plasmonic and Viscoelastic Properties

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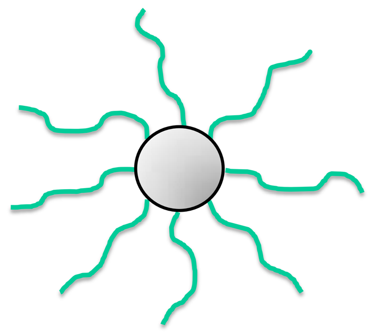
Introduction

Nanoparticle Organic Hybrid Materials, or NOHMs, are a class of nanocomposite materials recently discovered at Cornell University. NOHMs are made by attached an organic corona around a nanoparticle core. These materials can overcome traditional obstacles in polymer-nanoparticle composites such as mixing and dispersion.



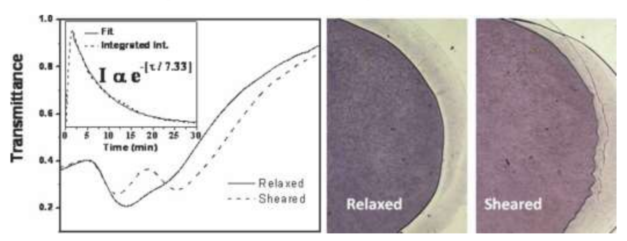
"Hairy particle" depiction of NOHMs showing the corona (green) and core (silver)

The advantage of NOHMs lie in the wide range of tunable properties (optical, rheological, thermal, etc.) that can be achieved by controlling the chemical and geometric characteristics of the components (core and canopy). This allows for the potential to design new novel materials for technological applications (battery electrolytes, carbon capture, desalination and water purification).

Aim

A thorough understanding of these systems is needed to explain the wide range of observed behaviours and predict the possible behaviour of future materials. As such, material characterization is critical to attaining this fundamental knowledge.

Recent work by Rama et al. (J. Mater. Chem., 2009, 19, 8728–8731) has shown that under special circumstances, gold nanorod (GNR) based NOHMs can display spectral changes when sheared due to changes in the surface plasmon resonance (see below).

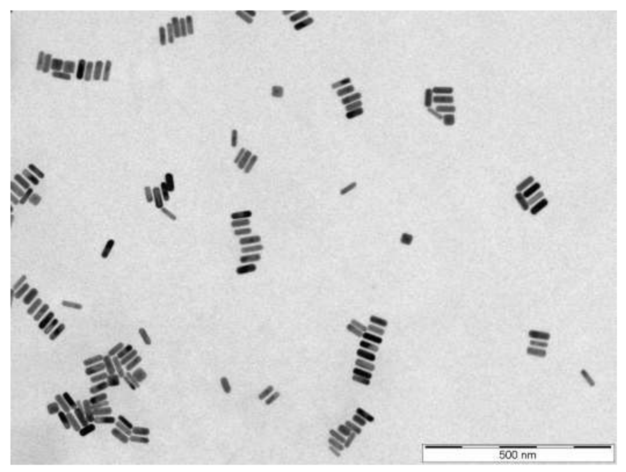


The goal of this research is to probe a similar system in an attempt to develop a fundamental understanding of the plasmonic (optical) phenomenon and rheological properties of these NOHMs.

Synthesis

Gold Nanorod Synthesis

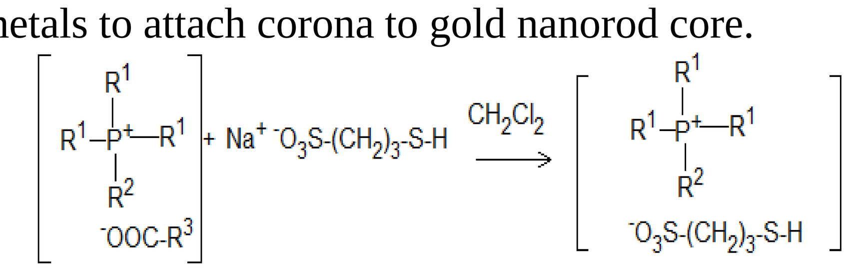
- Gold nanospheres made by reduction of gold salt
- The gold nanosphere "seeds" are further reduced in the presence of a surfactant (CTAB)
- The surfactant preferentially adsorbs to certain faces, pushing the growth of gold in one direction



TEM image of the synthesized gold nanorods. The rods had an aspect ratio of ~3 (45 nm long/15 nm diameter)

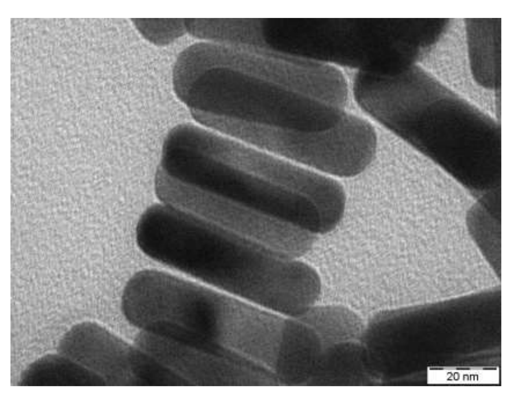
Corona Preparation

- Simple ion exchange
- Exploit chemical reactivity of thiol (SH) with noble metals to attach corona to gold nanorod core.

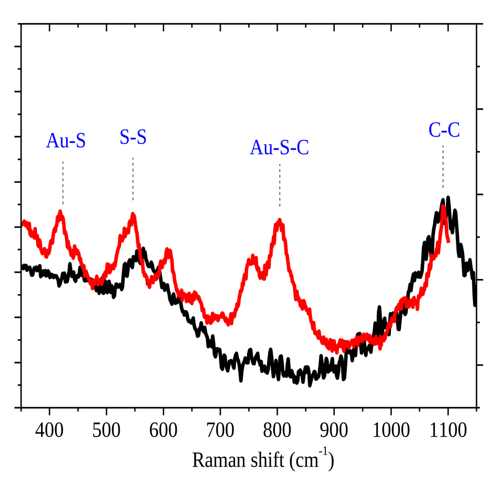


The corona (right) is prepared by simple ion exchange of a phosphonium salt with sodium mercapto-propanesulfonate and then filtration in dichloromethane.

NOHM Product



TEM of the GNR after the corona has been attached

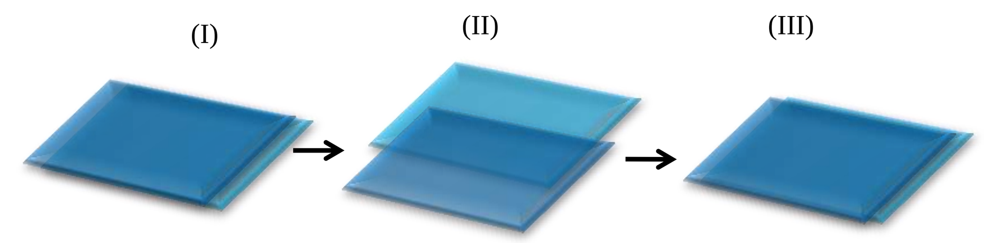


Raman Spectroscopy is an effective tool for detecting the presence of chemical bonds. Shown to the left is the normalized intensity Raman spectra of the bare corona (black) and the NOHM product (red). The characteristic Au-S, S-S and Au-S-C vibrations are indicated. This confirms that our corona has attached to the core.

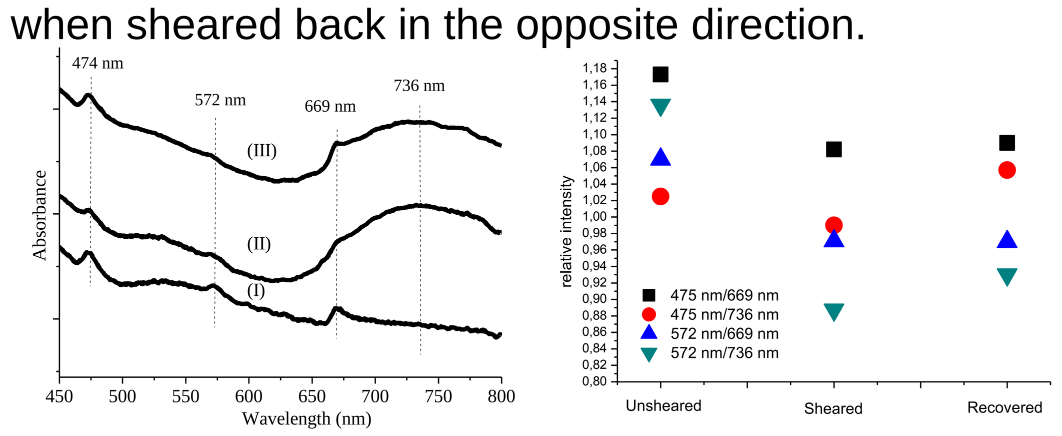
Results

Optical Properties

Samples were spin coated on to a glass slides before being covered by another slide. The spectrum of the samples were then measured before in this initial state (i), after shearing (ii) and then after sheared again in the opposite direction for "recovery" (iii).



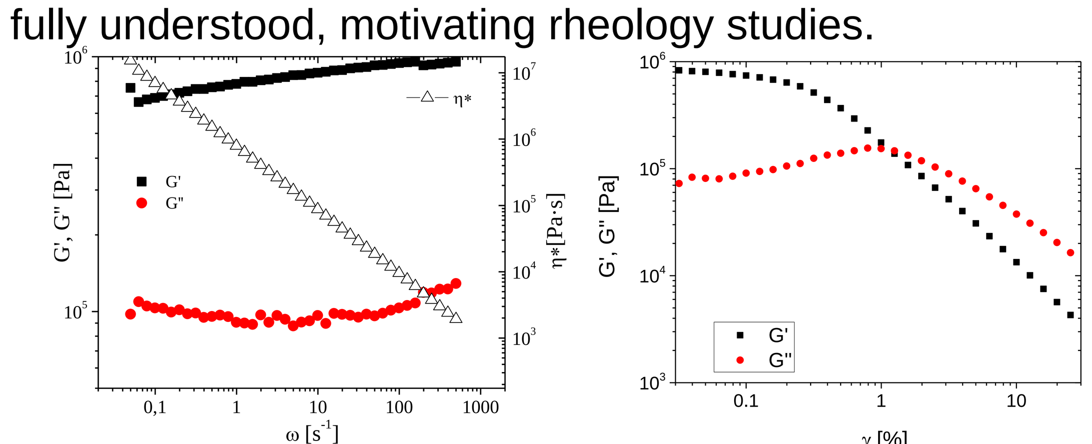
It was found that the ratio of the longitudinal (669nm , 736 nm) to transverse (475nm , 572 nm) plasmonic peaks decreased during shearing and recovered somewhat when sheared back in the opposite direction.



Left: The solid-state spectra of the gels in the initial state (I), after shearing in one direction (II) and sheared back in the opposite direction (III)
Right: Ratio of the absorbance intensity of the transverse and longitudinal bands in the initial spin coated film, after shearing and after being recovered to the initial position

Rheological Properties

NOHMs can exhibit a wide range of flow properties depending on their corona/core geometry and content. The viscoelastic behavior of self suspended rods is not fully understood, motivating rheology studies.



Left: Oscillatory amplitude sweep at ω = 50 s-1 showing the characteristic soft glass peak in G'' at crossover.

Right: Frequency sweep at γ = 0.1%, showing weak frequency dependence of the moduli and strong shear thinning in the complex viscosity.

Conclusion

We were able to successfully synthesis and covalently attach a thiol based corona to gold nanorods to form a NOHM system.

When spin coated to form films, this material displayed spectral shifts upon shearing and recovery.

These spectral shifts point to a responsive and partially reversible plasmonic interaction among the particles in the system.

This system also showed soft glass behavior in its rheology with strong shear thinning.

By correlating the spectral shifts with shear, this material has potential to be a nanoscale shear sensor.

Future Work

Conduct Small Angle X-ray Scattering (SAXS) on the sample before, during, and after shear to attempt to correlate the plasmonic shifts to the particle alignment and separation

Vary the core (aspect ratio of gold nanorods) and corona (grafting density, length of ologomers, nature of graft, etc.) to probe how these design parameters affect overall material performance.

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