

**Synthesis of Conformable 3-D Plasmonic Metamaterials Based on Composites of Covalently Crosslinked Soft Networks of Nanomaterials and Oxide Thin Films: 2019 Update**

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*Aim 1: Interparticle Spacing as a function of both ligand shell thickness and crosslinking molecule dimensions*

A series of thiol-capped gold nanoparticles, with gold core diameters in the range of 6-8 nm, were synthesized and purified. Additionally, a series of dithiol crosslinking ligands were synthesized, with calculated lengths of 0.93, 1.59, 2.44, and 4.83 nm. From a nanoparticle perspective, ligand shells expected to be in a liquid-like state at room temperature experienced facile crosslinking upon exposure to dithiol ligands. Here, both the minimum and maximum interparticle spacings closely matched the dimension of the crosslinking ligand. Conversely, nanoparticles having more rigid ligand shells proved to be more difficult to crosslink. Minimum interparticle spacings tracked with twice the thickness of the ligand shell, while maximum interparticle spacing corresponded to the length of the crosslinking ligand. The intermediate length ligands were most effective at crosslinking, while both the shortest and longest ligands were least effective- the shortest ligand is likely too small to penetrate all capping ligand shells, while the longest crosslinker might suffer from excessive conformational flexibility that hinders binding to gold cores.

Seeking further explanation for the failed crosslinking experiments with our shortest and longest ligands, we modeled the geometry of the ligands in solution with our casting solvent, chloroform. We recognized that as the length of the ligand increases, so too will the conformational flexibility. Moreover, the presence of heteroatoms might create a drive for significant intramolecular interactions that might block access to the terminal thiols, rendering the crosslinking ineffective. The results of our computational studies support this hypothesis. While our first three ligands maintain a relatively linear conformation in solution, our longest ligand is curled upon itself in its lowest energy conformation, with the thiols oriented toward the embedded heteroatoms. Though these computational studies were not included in the original research proposal, I believe we have strengthened our understanding of crosslinking mechanics. This data set is now complete and we are actively drafting a manuscript based on this aim of the work.

*Supercluster formation from triphenylphosphine-capped nanoparticles and crosslinking ligands with embedded heteroatoms*

Triphenylphosphine (TPP) capped nanoparticles, having an average core diameter of 1.5 nm, were crosslinked with a series of dithiol ligands, differing by the nature of embedded functional groups. Because supercluster formation was first noted for crosslinker molecules containing embedded amides, it was hypothesized that cluster formation could be due to either 1) coordination with proximal nanoparticles, or 2) lateral hydrogen bonding interactions between embedded amides. To differentiate these scenarios, analogous ligands containing embedded esters, ethers, and simple methylene units were synthesized and incorporated into TPP nanoparticle arrays assembled at the air-water interface of a Langmuir trough. Supercluster formation was observed only for ligands containing embedded amides, pointing to hydrogen bonding interactions between crosslinking ligands, rather than direct coordination to gold cores.

While our results initially drew my attention, further work on this particular concept with a new group of students has made me skeptical of our earlier conclusions. Unfortunately, some of the data generated by previous students appears to be faulty. It appears that mishandling of our 1.4 nm particle samples is the likely culprit. These particles are rather reactive and readily engage in ligand exchange reactions, but conversely, these particles are relatively unstable and prone to unwanted side reactions and size evolution. As such, the particles can easily grow to larger diameters if they are heated excessively during purification and processing, or stored improperly for extended time periods. We are in the process of repeating a number of key experiments using freshly prepared nanoparticles of known size.

*Outlook for Year 3: Demonstration of Structural Integrity of Nanoparticle Films Cast upon Textured Substrates*

Moving into the final year of this grant period, I seek to explicitly demonstrate that these covalently crosslinked nanoparticle films are highly flexible and can easily conform to the curvature of a textured substrate without disrupting interparticle spacing. This feature is critical in the development of metamaterials that can be applied to a wide range of surfaces. There are three particular scenarios that I hope to support with direct evidence from electron microscopy:

1. The crosslinked nanoparticle films are freestanding when draped over a surface with voids.

2. The films maintain structural integrity on substrates when applied to “rough” substrates having nanoscale features and irregularities.
3. The films maintain structural integrity when applied to substrates having micron-scale features and irregularities.

The completion of this portion of the work will involve applying crosslinked nanoparticle films to various substrates. The two primary factors will include the inherent flexibility of the film (dictated by ligand shell rigidity and length of the crosslinking ligand) and the scale of textured features on the substrate. We will first explore substrates with smaller features. Rigid, windowless TEM grids should allow us to demonstrate property (1), that the films are freestanding when draped over a void. Textured substrates for properties (2 and 3) will include commercially available rigid TEM grids and AFM calibration grids having variable features afforded by isotropic or anisotropic etching processes. This aim of the work will not only demonstrate that our films maintain their structural integrity (and thus will critically inform metamaterial behavior), but will also yield a description of a reliable processing method for these materials.

*Request for Budget Modification*

As this grant moves into year three, the PI requests a budget modification to strategically utilize the remaining funds. Notably, I request that I am allowed to draw a fourth summer stipend (stipend was previously drawn in summer of 2017, 2018, and 2019. The 2017 and 2018 were technically from the first year of the funding cycle, because of the early start date). A modified budget is attached for your consideration. If approved, my institution will require a memo authorizing the proposed allocation of the remaining funds.

PRF#	Inst. Acct. #	Funding Period	
57391-UR-10	AAB8961	from 9/1/2019	to 8/31/20
Balance forward		2392.09	
payment for 2019-2020		23330.00	
Total budget remaining		25722.09	
Proposed Amended Budget			
Stipends			
	PI fringe 2019***	581.43	*** Due to an unexpected increase in our institution's fringe rate, we drew \$8581.43 in PI compensation for summer 2019. We would like to compensate this oversight by drawing in funds from the final budget year for this grant.
	PI	8000.00	
	Grad Students	0.00	
	Undergraduates	10500.00	
	Postdocs	0.00	
Tuition		0.00	
Expendable Services and Supplies		6640.66	
Capital Equipment			
Travel (Conference)		2000.00	
Proposed total expenditures		25722.09	