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

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Progress

Our progress to date has been centered around isolating the factors that dictate interparticle spacing of nanoparticles in two-dimensional arrays. This is a key consideration for the fabrication of plasmonic metamaterials, as optimal plasmonic coupling is strongly dependent on core-to-core distances in periodic arrays. The prevailing scientific consensus suggests that interparticle spacing is primarily a function of the diameter of the particle, and the relative thickness of a surrounding ligand shell, if present.

Based on our previous observations of covalently crosslinked nanoparticle arrays formed at soft interfaces (i.e. the air-water interface of a Langmuir trough), we suspected that additional factors might play a significant role in governing interparticle spacing; because we are interested in creating plasmonic metamaterials, we made this the focal point of our investigations at the beginning of the funding period. We hypothesized that two other factors, beyond the size of the metal core of the nanoparticles, will influence interparticle spacing: both the *state of the ligand shell* (rigid and semicrystalline, or low-density and liquidlike) and the *length of the crosslinking molecules* will dictate the minimum and maximum interparticle spacings in an assembled arrays.

To explore this hypothesis, a series of gold nanoparticles capped by alkanethiols of various lengths (C6-C18, gold diameter ~5-6 nm) was synthesized and crosslinked by dithiol molecules of variable lengths (C6-C18). Our earliest findings suggested that the shortest interparticle spacings were observed in when nanoparticles with liquidlike ligand shells (C6, C8, C12) were crosslinked by dodecanedithiol, and these spacings were similar despite the difference in the dimensions of the capping ligand. Also, we note that dodecanedithiol should be too short to span the distance between two gold cores surrounded by two layers of octanethiol and dodecanethiol ligand shells. We propose that effective crosslinking occurs, despite this dimensional mismatch, because these ligand shells are in a compressible, liquidlike state at room temperature. In all of these cases, the interparticle spacing seemed to track with the length of the crosslinking ligand.

Conversely, native ligand shells capped by longer alkanethiols (C14, C16, C18) often failed to crosslink effectively, especially if the shortest crosslinkers were utilized. We believe this is due to the likelihood that these thicker native ligand shells are in a more rigid, semicrystalline state at room temperature. Not only does this make it more difficult for an incoming dithiol to penetrate the shell and bond to the gold core; it also presents a limitation on the minimum distance observed between gold cores.

The early results of our findings were shared in an oral presentation by the PI at the Great Lakes Regional Meeting of the American Chemical Society in Fargo, North Dakota. Aside from presenting the results described above, I also shared a surprising result observed in a system that extends from the present alkanethiol-capped gold nanoparticle/alkanedithiol crosslinker studies: in light of some of the difficulties observed when crosslinking alkanethiol-capped nanoparticles with thicker ligand shells, we opted to shift to a system of smaller (d~1.5 nm), phosphine-capped gold nanoparticles, and longer crosslinking ligands that included embedded amide linkages (which provided synthetic access to longer dithiol molecules). Our initial explorations of this nanoparticle/crosslinker system yielded two surprising results: when the longer crosslinker with embedded amides was used in conjunction with alkanethiol-capped nanoparticles, we observed much greater maximum distances between nanoparticles, seeming to correspond to the length of the crosslinker. When this same crosslinking molecule was utilized with more labile phosphine-capped nanoparticles, it appeared that these smaller particles coalesced into "supercluster" islands of about 4 nm. These two observations launched a series of investigations that were recently presented by undergraduate researchers at the spring 2018 meeting of the American Chemical Society on New Orleans, Louisiana. Our findings are summarized below.

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 may suffer from a nonlinear geometry in solutions that hinders binding to gold cores.

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.

Impact on PI's career

The three-year funding cycle from this grant has allowed the PI to dedicate time for this project with undergraduates, which has proven to be much more challenging than previous endeavors, but also far more intellectually engaging. The PI has become an active participant in regional and national ACS conferences, and the first research aim described above is nearing completion, as the PI is actively drafting a manuscript with undergraduate co-authors. This work has also spurred renewed grant-seeking efforts to sustain a long-term scholarship program. The scholarly activity supported by this grant is highly valued by the PI's home institution, and is paving the way toward a final promotion to full professor in 2020, making the PI only the second woman to earn that rank in her chemistry department.

Impact on Undergraduate Students

The undergraduate students that have contributed to this work are gaining a high-impact research experience at UWEC, honing their skills in synthesis, spectroscopy, and electron microscopy. The vast majority of the experimental work is carried out by undergraduate researchers under the direction of the PI, fostering a sense of independence and intellectual investment in the project. The students engaged in these studies have maintained excellent GPAs, and have attracted high-profile scholarships, with one student recently earning an honorable mention for the Goldwater Scholarship. Very few undergraduate researchers gain such a diverse skill set, but those who do stand to maximize opportunities for gainful employment and post-baccalaureate degrees. Four of the five students associated with this project have presented their work at national ACS meetings, and three of them are planning to seek a doctorate after graduation. Overall, the students are provided with an authentic, independent research experience, and it has motivated the students to seek higher professional goals than they had envisioned prior to engaging in undergraduate research.