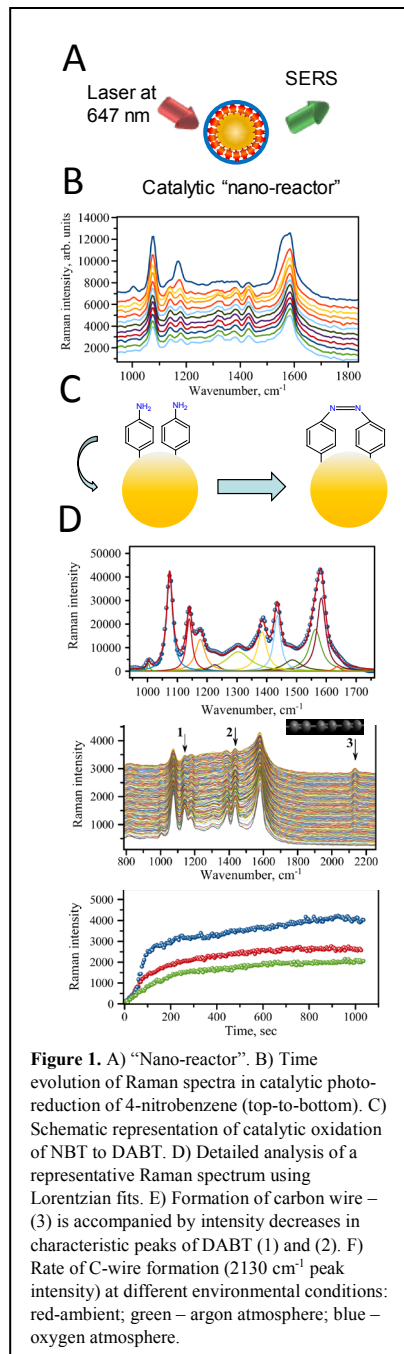


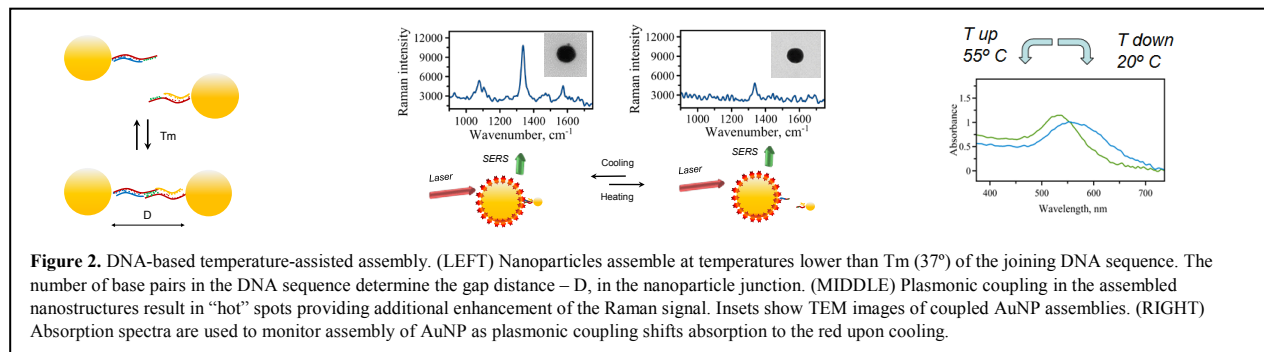
Project Title: “Exploring Synthetic Routes of Molecular Wire Formation via Photocatalytic Action of AuNP and AuNP-TiO₂ Assemblies.”

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In this project we seek to further our understanding of catalytic conversion of aromatic compounds, using a novel class of heterogeneous catalysts based on golden nanoparticles and their assemblies in a “nano-reactor” format. Figure 1, A demonstrates our experimental strategy. The SERS-based catalytic “nano-reactors” are constructed using golden nanoparticles (AuNP) and specific aromatic molecules attached to the surface of the particles via thiol-gold specific bond. One of the most dependable class of molecules are thiophenols, which are small, symmetric and capable of forming self-assembled monolayers (SAMs) on the surface of gold nanoparticles. These molecules are easily identifiable with only a few characteristic Raman bands. Golden nanoparticles have recently attracted a significant amount of attention as effective agents with great catalytic potential. Specifically, we utilize the power of *in-situ* SERS to observe Raman signals from self-assembled monolayers of aromatic thiols. A large Raman signal when Localized Surface Plasmon Resonance (LSPR) is achieved upon laser excitation. Our excitation line is 647 nm matching LSPR of gold nanoparticles. The high sensitivity of SERS contributes to our ability to observe conversion of aromatic molecules and SERS intensity reports on the amount of reactants/products in the “nano-reactor”. We have previously demonstrated that the Raman signal significantly decreases upon prolonged laser irradiation. (Krasnoslobodtsev *et al.* 2015) These changes are accompanied by the appearance of new Raman peaks, decline in intensity and shift in position of the original peaks. We assign these changes to plasmon-driven catalytic conversion of aromatic molecules by golden nanoparticles upon LSPR conditions. Additionally, thermal nature of molecular degradation can be the reason due to plasmonic heating. We have confirmed non-thermal nature of catalytic reactions by monitoring the ratio of Stokes vs anti-Stokes (Specific Aim 1), with more detailed analysis yet to come and we are also currently assessing the contribution of thermal effect in the AuNP assemblies (Specific Aim 2). Our results suggest that golden nanoparticles can act as both photo-oxidizing and photo-reducing agents. We are employing an electron accepting ability of golden nanoparticles to drive catalytic conversion of amino-substituted benzenes (anilines) – Figure 1, C. The catalytic reaction can happen very quickly and we have been detecting time evolution of peaks associated with conversion of anilines. Figure 1, B shows time evolution of Raman spectra for 4-amino-benzene. The shape of aromatic ring vibrations (1530-1580 cm⁻¹) change their shape and the peak at 1185 cm⁻¹ slowly disappears. At the same time, the spectrum features weak peaks at the following positions: 1136, 1384, and 1428 cm⁻¹. These peaks are assigned to -N=N- vibrations in diazobenzenethiol (DABT) which is formed by photocatalytic oxidation of ABT by AuNP and dimerization into DABT (Figure 1, C). The intensity of the DABT peaks grows with time indicating that prolonged exposure to laser light increases the yield of DABT. We compared the rate of ABT disappearance (by monitoring the peak at 1185 cm⁻¹) and the rate of DABT appearance (by monitoring the peak at 1428 cm⁻¹). Fitting these changes with exponential functions suggested that two exponents are required to fit DABT intensity variation and only one exponent is required to describe time dependence of ABT. With the help of DFT calculations, we now understand quite well the subtle structure of ABT/DABT Raman spectra and can easily distinguish peaks of reactants/products and monitor their evolution with time (Figure 1, D shows representative analysis of Raman spectrum obtained in one of the time series). We also observe that the formation of “carbon wire” product (polyene - linear carbon chain with alternating single and triple bonds) which is manifested by the appearance of the peak at 2130 cm⁻¹ (Figure 1, E (3)) does not happen until much later in the time dependencies and is accompanied by intensity decreases in characteristic peaks of DABT (Figure 1, E (1) and (2)). This observation and the discrepancy in the exponential fits for



ABT and DABT time evolution indicate a complex mechanism of catalytic conversion of ABT to DABT to polyene which most likely proceeds via quick accumulation of intermediate products in the reaction. Additionally, oxygen may play an important role in routing the catalytic reaction towards preferential formation of polyenes. We have monitored the rate of polyene formation at different environmental conditions (shown in Figure 1, F): ambient (red); inert atmosphere of argon (green); oxygen atmosphere (blue). It is quite obvious that the presence of oxygen stimulates formation of polyenes to a greater extent. It also suggests that the mechanism is complex and involves an interplay of ABT, DABT, AuNP, and oxygen. We are currently investigating these effects in detail.



Another goal of this project is to verify the efficiency of the AuNP assemblies in catalytic conversion of aromatic molecules (Specific Aim 2). Figure 2 schematically illustrates our strategy to couple golden nanoparticles into an assembly. We utilize a robust DNA coupling ability to create an “on demand” temperature-assisted assembly of AuNPs. Each particle-particle contact, so-called “hot junction”, is predicted to contribute to a larger enhancement of the Raman signal from molecules located within the junction. This additional plasmonic coupling seems to be a promising strategy to enhance the rate of aromatic molecule conversion. Our design involves a modification of AuNP with DNA fragments that are complementary to each other. By varying both the length and the sequence of the complementary strands we can control the temperature at which AuNP assemble. In our first design 6 bp sticky ends within 18 bp duplex provided $T_m = 37^\circ\text{C}$. Both Raman signal increase (Figure 2, middle) and red shift in absorption (Figure 2, right) at temperatures lower than T_m suggest that the temperature-assisted assembly of the particles does take place. As Figure 2 shows, the length of DNA couplers determine the distance, D , separating nanoparticles and thus, the gap of “hot” junction. We are currently investigating the effect of DNA length by varying the number of base pairs in the coupling duplex (12 bp, 18 bp, 24 bp). Next, we will vary the sizes of nanoparticles and correlate conversion efficiencies with sizes and assemblies of AuNPs. Once these studies are completed, we will use similar strategy for assembling AuNP and TiO_2 particles to evaluate the effect of TiO_2 on catalytic conversion of aromatic molecules (Specific Aim 3).

The primary utilization of this grant is to involve undergraduate students in research and to help them establish solid research skills through participating in the proposed studies. PI has involved 5 students so far in the studies with the help of this grant. Two students were involved during summer and during academic year and two more will be joining the lab next month. Two students were directly supported with salary; one student has used materials purchased using ACS PRF funds. Students have received training in a broad spectrum of research skills including review of relevant literature, experimental design, data collection, analysis and interpretation, as well as keeping lab journal entries. All students practiced oral research presentations and reported their results at the Department Seminar series in front of their peers and faculty members. Support from this grant is helping undergraduate students under my supervision to commit more time to research, which translates into more solid research skills, more conference presentations, and even publications. Two students had several poster presentations at regional, national, and international conferences. These include: 8th Structural Biophysics Workshop (Omaha, NE); 5th Midwest Single Molecule Workshop (Ames, IA); Gold2018 (Paris, France). One student has recently published a paper in “Nanomaterials” as the first author, which was selected as a “Feature Paper” in that issue of the journal. He is also currently preparing another manuscript, which we plan to publish in “Molecules”. One of the students was able to compete for internal funds at UNO using results he obtained during summer months. He is now funded through academic months to continue working on creating assemblies of AuNPs. The third student, who was doing summer studies, is now continuing research in the field of medical physics with the mentor she met during her scientific presentation. Not only students but also the PI benefited from the support of ACS PRF funding. PI was able to increase the number of students working in his lab. This resulted in more ideas, more discussions, and more results. The results we obtained allowed us to present a poster at “Gold2018”– international conference that gathers scientists from around the world working on various applications of gold nanostructures including catalysis. Our presentation received very good attendance and we were able to establish collaborative interactions. This, in turn, amounted to collaborative grant applications currently pending at NSF and EPSCoR NE.