PRF # 56686-ND1

Title of Project: **Heterogeneous Colloid Catalysts for Visible Light Photochemistry**

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The aim of this proposal is the development of efficient, low-cost colloidal catalysts for visible-light photocatalysis. The central hypothesis is that because these catalysts have: 1) facile tunability with particle size in the energy of the photoexcited state, 2) excellent photochemical stability and robustness, and 3) a high photoluminescence quantum yield, they will be highly versatile catalysts for visible-light photocatalysis. Indeed, just prior to the beginning of this funding period, we accomplished one of the goals of our proposal, the validation of colloidal catalysts for visible light photoredox catalysis (Figure 1).

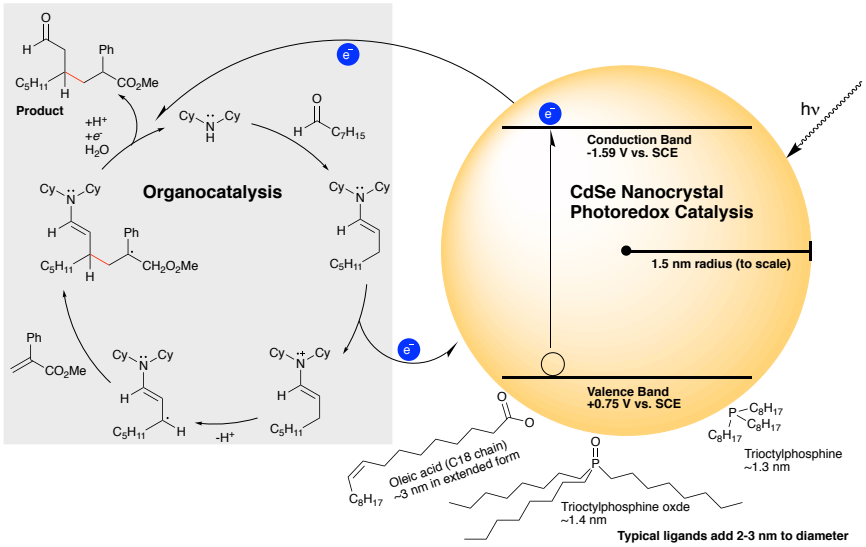

Figure 1. Basic scheme showing use of colloidal semiconductor nanocrystals as photoredox catalysts.

We considered our initial results a starting point for further improvements because the photocatalysts we used were standard, as synthesized colloidal nanoparticles that had never been optimized for catalysis. In that vein, in the last year of the project we explored how commercially available nanoparticle colloidal catalysts would perform relative to the catalysts synthesized in the laboratory of the PI. We found somewhat unexpectedly that for a variety of different photoredox catalytic reactions (Figure 2) the commercial colloidal nanoparticle catalysts did not perform on par with the photoredox catalysts synthesized by the PI. The likely reason is that the commercial catalysts were passivated on their surface by molecules that were not compatible with the specific chemistries as outlined in Figure 2. By contrast, the acid/alkane functionalized photoredox catalysts synthesized by the PI were quite versatile and robust. The important conclusion is that the specifics of the ligands used to suspend the colloidal catalyst are critical and must be tested for reaction compatibility.

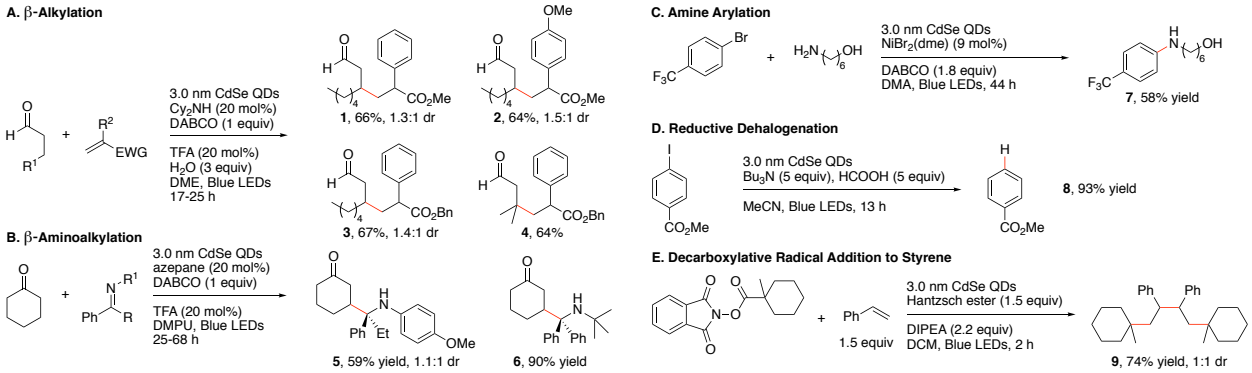

Figure 2. Reactions that were used for a comparison between commercial colloidal nanoparticle catalysts and those from the PI.

In the last year we also focused our work on the development of improved, tailored colloidal catalysts. This work involved exploring how catalyst core chemical composition and size can be optimized with respect to catalytic performance. Overall, we found that changing the reduction potential was important and led to improved photocatalytic performance. In particular, we tuned the photoexcited state reduction potential by changing the catalyst core composition to a compound with a larger energy gap, which allowed for the use of catalysts that had a larger surface area.

Traditionally, colloidal catalyst ligands can also play a critical role, by allowing or preventing access to the particle for electron transfer, by stabilizing the catalyst in solution. In a particularly exciting avenue of research, we explored the idea of using the ligands on the catalyst surface as a way to self-assemble a co-catalyst to be attached to the surface of the nanoparticle. Work in this area is ongoing.

In terms of workforce development, the ACS PRF grant has been instrumental in the development of a new, cross-disciplinary direction for the research programs of both investigators. The results obtained under this grant will lay the foundation of a new field of research in organic synthesis and materials chemistry. In the laboratories of the PI, several new directions in this space have arisen due to the collaborative work on this project, which are projected to lead to at least two applications for major federal funding in the next 12 months. Because this work involves disparate fields, the several students trained as a result of the support from this grant gain valuable experience working across disciplines and learning important concepts from several fields. Thus, these students are more marketable as they pursue careers beyond their doctoral studies.