1. PRF# 58097-ND10
2. Project Title: Homogeneously catalyzed biphasic reactions enabled by BIJELs
3. P.I. Name, Affiliation: Daeyeon Lee, University of Pennsylvania

Homogeneous catalysts offer several advantages over their heterogeneous counterparts such as high selectivity and easy access to the catalytic sites. However, difficulties associated with the separation of products from the catalyst remains a major roadblock to its industrial-scale implementation. Although biphasic water-oil systems have been used to enable facile separation between the catalyst and the product, such an approach nevertheless cannot be implemented at the industrial scale because conventional biphasic homogeneous catalysis cannot be performed in a continuous mode. The objective of this study is to study fundamental aspects of biphasic homogeneous catalytic reactions in bicontinuous interfacially jammed emulsion gels (BIJELs).

BIJELs are a new class of soft matter consisting of bicontinuous network of oil and water phases with densely packed layers of nanoparticles at the interface between the two liquid phases. One of the key applications that have been envisioned for these BIJELs is their use in continuous reactive separations. In the first year of this grant, we fabricated robust BIJELs that can withstand chemical, thermal and mechanical stresses that may be present under reaction conditions. Moreover we also successfully implemented BIJELs to run reactive separations using an enzyme.

In Year 2 of this grant, we have developed a method to produce BIJELs without using any surfactants. Our previous method of producing BIJELs involved using a surfactant to modify the wetting property of nanoparticles to facilitate their adsorption and jamming at the interface between the oil and water phases. Although this is a very effective method, the use of surfactants can significantly limit the application of BIJELs in certain applications. For example, surfactants may interfere with reactions. Surfactants can poison catalysts or render them ineffective by interacting with them. In this past year, we have used a mixture of hydrophilic and hydrophobic nanoparticles to stabilize BIJELs. Here, we hypothesized that hydrophilic and hydrophobic nanoparticles would cluster at the interface and induce jamming. We found that it is critical to optimize the ratio of the two nanoparticles to enable fabrication of stable BIJELs with bicontinuous morphology. Moreover, the optimal ratio of the two nanoparticles depends strongly on the polarity of the oil phase. A higher ratio of hydrophilic-to-hydrophobic nanoparticles was necessary to stabilize BIJELs prepared with a polar oil phase. The use of two nanoparticles also opens the possibility to create bifunctional interface that can run two tandem reactions by using two different catalytic nanoparticles. We will further test the use of these surfactant-free BIJELs in performing reactive separations that involve surfactant-sensitive catalyst such as enzymes and metal nanoparticles.

This ACS PRF award has enabled me to explore a completely new area of research, namely reactive separation involving homogeneous catalysts. Moreover, it has allowed us to establish a new international collaboration. The student who worked on this ACS PRF has benefitted greatly from this project by developing a completely new reinforcement method for BIJELs, which has led to a provisional patent filing. The award also has led to a new method of fabricating bijels without using surfactants as described in this report, which we believe will further expand the potential application of BIJELs. Overall the award has had a significant impact on the careers of the PI and the student.