1. PRF# 58097-ND10
2. Project Title: Homogeneously catalyzed biphasic reactions enabled by BIJELs
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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). In Year 1 of this grant, we have accomplished two major aschievements: 1. We have imparted mechanical, thermal and chemical stability to BIJELs to enable homogeneous reaction, in particular base-catalyzed saponification reaction; 2. We have enhanced the reaction rate of enzymatic reaction – another important class of homogeneous catalyst. In this report, I summarize these two developments.

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. Although bijels of different compositions have been developed, their use in reactive separation has not been reported, in part due to the chemical, mechanical and thermal instability of the BIJEL structures. BIJELs lose their morphology when they are subjected to environmental changes (e.g., temperature, pH, mechanical stress etc) that accompany typical chemical reactions. In this work, we overcame this critical bottleneck by reinforcing the interfacial nanoparticle layer in BIJELs via room temperature *in situ* silica deposition (**Figure 1**). Silica nanoparticles that reside at the interface between oil and water phases of bijels prepared using solvent transfer-induced phase separation (STRIPS) are partially fused via a treatment with tetraethyl orthosilicate (TEOS). Reinforced bijels maintain their bicontinuous structure and interphase permeability under mechanical, chemical and thermal stresses. We demonstrated that reactive separation involving based-catalyzed hydrolysis reaction at elevated solution pH and temperature can be achieved using these robust bijels. We believe our work represents a major development that will enable the application of bijels in continuous reactive separations in biofuel upgrade reactions and phase-selective catalysis. This work has been submitted for review and is currently undergoing revision.

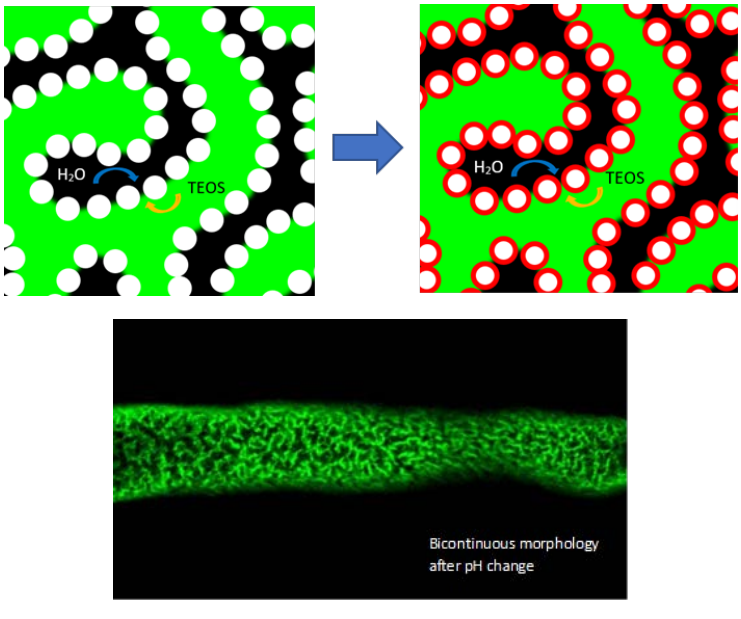

Figure 1. (Top) Schematic illustration showing the room temperature reinforcement of BIJELs using TEOS treatment and (bottom) confocal image of BIJEL retaining its bicontinuous morphology after a chance in the solution pH.

In collaboration with Dr. Gyoo Yeol Jung at POSTECH, we have used BIJEL to enable simultaneous enzymatic conversion and separation of highly water insoluble substrates. Enzymes have long been recognized as ideal catalysts to induce conversion of various petrochemicals due to their specificity and efficiency. Despite their versatility, their efficacy in converting highly hydrophobic (i.e., water-insoluble) substrates is very low because enzymes are typically only water-soluble. Various ways to enhance the conversion efficiency of hydrophobic substrates using enzymes have been explored; however, these methods typically require high-energy processes such as continuous agitation of a biphasic mixture and the separation of the product presents another challenge. In this work, we overcame these challenges by using BIJELs with high interfacial area and interphase mass transfer capability. By dissolving an enzyme and a hydrophobic substrate in the water and oil domains of BIJELs, respectively, we demonstrated that reactive separation with high conversion rate can be achieved. We showed that using a recently developed STRIPS it is possible to load a model hydrophobic substrate (tributyrin) of a bicontinuous BIJELs and induce enzymatic reaction by placing a hydrophilic enzyme (lipase) in the water phase. The products partition into the aqueous phase spontaneously through the pores in the nanoparticle layer at the oil-water interface, enabling one-pot reactive separation. Our work addresses one of the key challenges in enabling enzymatic reactions in non-aqueous media working on petroleum substrates, one of the core areas of research support of ACS PRF.

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 student has also had an opportunity to present his work at the ACS Colloid and Surface Science Symposium held in June, 2018 at Penn State University. Overall the award has had a significant impact on the careers of the PI and the student.