Special Issue on "Nanocatalysis"

David K. Leahy[§]* and Sachin Handa[†]*

[§]Biohaven Ltd, 215 Church Street, New Haven, Connecticut, 06510, United States

[†]Department of Chemistry, University of Louisville, 2320 S. Brook Street, Louisville, Kentucky 40292, United States

*Email: david.leahy@biohavenpharma.com; sachin.handa@louisville.edu

Nanotechnology has revolutionized many areas of science, including sustainable catalysis. It has uniquely contributed to sustainable and greener organic synthesis, enabling powerful catalysis in greener media, including water and other sustainable solvents.[1-4] To highlight the recent advancements in the field, we organized a special issue on nanocatalysis. In this thematic issue, we covered efficient nanocatalysis using earth-abundant metals and low loading of precious metals, hybrid metal nanocatalysis in sustainable media, biocatalysis, and electronanocatalysis. We invited contributions that clearly demonstrate the discovery, development, and application of the above technologies, where their merit related to sustainably is clearly articulated. All manuscripts passed through rigorous peer review, following the policies of *Curr. Opin. Green Sustain. Chem*.

Many organic molecules in high demand require better synthetic methods, and biocatalysis and nanocatalysis have contributed significantly to meeting sustainable demand-supply challenges. Likewise, the continued growth in the application of noncanonical amino acids (ncAAs) in drug discovery necessitates their efficient, sustainable, and scalable production, granting access to new chemical entities. Related to this topic, Arnold, Alfonzo, and Das describe the biocatalytic synthesis of ncAAs. These amino acids merge the conformational behavior and native interactions of proteinogenic amino acids with nonnative chemical motifs and have proven valuable in developing modern therapeutics. In this mini review, the authors extended the biocatalyst arsenal for synthesizing ncAAs with natural enzymes. For more details, see: https://doi.org/10.1016/j.cogsc.2022.100701.

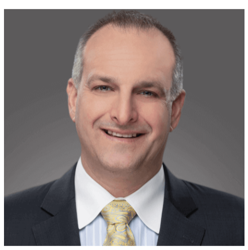
The same special issue covers nanoparticles in sustainable reaction media, such as water and deep eutectic solvents. Water has a lot to offer in terms of better and cleaner chemistry. However, its usage as a reaction medium has not reached its full potential. Harnessing the compartmentalization effect, micellar catalysis enabled chemistry in water. Lipshutz and co-workers showcased the synthesis and applications of nanoparticles of iron-containing ppm levels of palladium. In this article, the authors only covered the work from their lab, although several other researchers have contributed significantly to the same field. The authors have described the sustainable Suzuki–Miyaura, Sonogashira, Mizoroki–Heck, and Negishi couplings catalyzed by ligated iron ppm palladium nanoparticles. In addition, nitro group reductions and click reactions in water are also discussed. More details can be found in the arti-cle: https://doi.org/10.1016/j.cogsc.2022.100686. Along the same lines, Gallou and co-workers have showcased nanocatal-ysis in the pharmaceutical industry. While describing nanoca-talysis, the authors have critically showcased the use of nanomicelles in water. The authors highlighted the recent development of nanocatalyst-enabled chemical transformations in water, leveraging the aqueous nanomicelle chemistry. In this article, a variety of the most frequently used transformations in the pharmaceutical industry are discussed, which includes work from multiple labs. For more details, see https://doi.org/10.1016/j.cogsc.2022.100691. Handa's group has also significantly contributed to the field of micellar nanocatalysis. In this thematic issue, the group has discussed the design of proline-based amphiphile PS-750-M and its applications in aqueous nanocatalysis. The authors have demonstrated the multiple roles of surfactants in aqueous micellar catalysis. The micelles of PS-750-M act as a solvent, ligand, and shield to protect water-sensitive intermediates, enabling challenging chemistry in water. In the contribution, the authors demonstrated the applications of PS-750-M in highly useful transformations, including completely organic solvent-free amide couplings, C–H fluorination of (hetero)arenes, selective hydrogenolysis, and cross-couplings of water-sensitive acid chlorides in water, catalyzed by phosphine ligand-free palladium (0) nanoparticles. In addition, metal-micelle interaction is also discussed: https://doi.org/10.1016/j.cogsc.2022.100690.

Other than aqueous solvents, Deep Eutectic Solvents (DESs) obtained from bio-renewable, cheap, and non-toxic precursors have significantly contributed to green and sustainable chemistry. DESs have been vastly explored in nanocatalysis. Capriati and co-workers have elegantly described the applications of DESs in transition-metal-based nanoparticles-catalyzed C–C and C–X (X = N, O, S) couplings, oxidation/reduction processes, cycloisomerizations, and polymerization reactions. For more details, see: https://doi.org/10.1016/j.cogsc.2022.100723.

In much of Lipzhutz, Gallou, and Handa groups' contributions, the organometallic nanocatalysis makes use of palladium catalysis in aqueous micelles. The authors have depicted that the ligand often costs more than the palladium and have its own environmental consequence. Often in micellar catalysis, either ligands are not required, or the palladium is needed only in ppm amounts minimizing this cost and environmental burden. This special issue also covers nanocatalysis that doesn't rely on palladium. Huang and co-workers have showcased copper nanocatalysis for sustainable transformations. It includes C–C, C–N, and C–O bond-forming reactions, such as Mizoroki–Heck, Suzuki–Miyaura, Glaser-Hay, Chan-Lam, Buchwald–Hartwig, Ullmann, and Goldberg couplings. For details, see: https://doi.org/10.1016/j.cogsc.2022.100698. Although the authors of above-mentioned contributions have covered the majority of cross-couplings, state-of-the-art selective reductions were invited as a separate collection. Kusi and Grela compiled the recent advances in the application of metal nanoparticles for the selective hydrogenation of C–C double bonds, focusing on alkenes, arenes, and aromatic heterocycles; see: https://doi.org/10.1016/j.cogsc.2022.100678. Besides organic transformations valuable to the pharmaceutical and agrochemical industry, the greener synthetic methods of metal nanoparticles, especially nanoparticles synthesized from bacteria, fungi, and algae, are elaborated by Jonnalagadda and coworkers. The authors also demonstrated nanoparticles' unique physical and chemical properties arise due to their size and structure. The applications of nanoparticles to reduce environmental issues, including wastewater treatment, production of biofuel, and environmental protection, are discussed. The toxicological issues in nanoparticle's applications are also revealed in this article: https://doi.org/10.1016/j.cogsc.2023.100788.

Another unique contribution included in this special issue is a summary of the fundamental aspects of nano-electrocatalysis by Wilson and Joshi. The short review highlighted the advancements in fundamental understanding of electrocatalysis at nanoscale and single atom electrocatalysts obtained using operando vibrational spectroscopies: https://doi.org/10.1016/j.cogsc.2022.100682.

In summary, this special issue has focused on nanocatalysis significant to the synthetic, material, and analytical chemistry community. In all articles, subtopics critically presented the pros and cons of each technology. Collecting these pieces from the broader community will potentially help attract the wider chemistry community to solve challenges associated with sustainable chemistry while advancing fundamental science. Hopefully, researchers worldwide will continue developing greener and more sustainable nanocatalysis for industry and academia.



Dr. David K. Leahy has 19 years of pharmaceutical process chemistry experience, with expertise in drug substance manufacturing, catalysis and green chemistry. Prior to joining Biohaven in 2020, he had roles of increasing scope from Takeda Pharmaceuticals and Bristol-Myers Squibb. At Takeda, he built capabilities in process chemistry automation, biocatalysis, and green micellar chemistry leading to one of the industry's first manufacturing processes of a complex API almost exclusively in water instead of organic solvents. He also led multiple academic collaborations to solve complex chemistry challenges leading to advances in catalytic asymmetric nucleotide couplings, as well as nanocatalysis in aqueous micelles. At Bristol-Myers Squibb, he led process chemistry efforts to develop the manufacturing route and process for the drug substance of Nurtec® ODT. Dr. Leahy also has extensive experience in green chemistry and sustainability, having served as a co-chair of the ACS Green Chemistry Institute Pharmaceutical Roundtable and program chair and advisory board member of the ACS Green Chemistry and Engineering Conference. He completed his Ph.D. in organic chemistry from Indiana University.

Sachin Handa was raised in Patti, a small town of Punjab (India), where he completed his undergraduate studies. He received a Ph.D. degree under the guidance of Prof. LeGrande Slaughter in the USA, where his research focus was the development of nonracemic acyclicdiaminocarbenes. Subsequently upon completing postdoctoral training under Prof. Bruce H. Lipshutz at UC Santa Barbara, he started his independent career as an assistant professor at the University of Louisville in August 2016. In July 2021, he was promoted to associate professor with tenure. His research laboratory focuses on the development of sustainable catalysts and reaction pathways. He is a recipient of the 2018 Ralph E. Powe Junior Faculty Enhancement Award by ORAU, the 2018 Peter J. Dunn Award for Green Chemistry and Engineering Impact in Industry by the American Chemical Society, and the NSF CAREER Award in 2021.

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