Metal-Catalyzed Electrochemical Diazidation of Alkenes

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Electrochemistry offers an efficient and sustainable alternative to conventional chemical approaches for organic synthesis. The group of Professor Song Lin at Cornell University (USA) has been developing novel efficient and sustainable synthetic processes in recent years. Professor Lin said: “Our research was built on tremendous pioneering work in the area of electroorganic synthesis, but also gained inspiration from creative research on small-molecule activation using electrocatalysis.”

Professor Lin continued: “Our main contribution to the area through this work we published in *Science* is the integration of electrochemistry and catalysis, which synergistically controls the direct generation of highly reactive radical intermediates and the selective downstream reactivity of these open-shell species.”

The group’s strategy culminated in a reaction involving radical intermediates under very mild conditions, which...
resulted in a broad substrate scope and exceptionally high functional group compatibility compared to existing protocols for alkene diamination. “This reaction protocol thus serves as a general approach to accessing vicinal diamines, structural motifs highly prevalent in bioactive compounds and privileged molecular catalysts,” said Professor Lin.

He explained: “Our new mode of redox catalysis, where different anodic catalytic events are joined to complete the full transformation, is reminiscent of but complimentary to photoredox catalysis where an oxidative and a reductive event are combined.”

Concerning the future directions of this work, the group intends to continue exploring the tremendous potential of electrocatalysis in innovating chemical synthesis. “In the near future, we are looking to understand the reaction mechanism of the electrocatalytic diazidation of alkenes and use these mechanistic insights to guide future design of a variety of new alkene functionalization reactions,” said Professor Lin. He continued: “In collaboration with industrial partners, we also hope to apply our new methods to streamline the synthesis of key intermediates en route to medicinally relevant products. We hope that, in the long term, our efforts can contribute to improving the cost efficiency and sustainability of pharmaceutical production.”

The Lin lab is very young as it was established in the summer of 2016. The authors of this paper include a postdoctoral associate (Niankai Fu), who obtained his PhD in organic chemistry, a then-first-year graduate student (Greg Sauer), and two undergraduate researchers. Although Professor Lin conducted postdoctoral research in electrocatalytic CO₂ reduction, none of the group members had extensive experience in synthetic electrochemistry. “With the help of colleagues and friends, we learned the theory and experimental techniques as a group,” said Professor Lin. He concluded: “After a year of learning and exploration, now I can proudly say that we have become experts in synthetic electrochemistry.”

Scheme 2 Proposed mechanism for the electrocatalytic diazidation of alkenes
About the authors

Niankai Fu was born in Hubei Province (P. R. of China). He obtained his B.S. at Hubei University in 2009 and Ph.D. in organic chemistry under the guidance of Professor Sanzhong Luo at the Institute of Chemistry, Chinese Academy of Sciences (P. R. of China) in 2014. In July 2016, he began his postdoctoral appointment with Professor Song Lin at Cornell University (USA) where his research is focused on the development of electrocatalytic methods for organic synthesis.

Greg Sauer was born and raised in Pittsburgh, PA (USA). He completed his B.S. at Binghamton University (USA) where he conducted his undergraduate research under Dr. Zhitao Li in carbohydrate synthesis and post-baccalaureate research under Dr. Mathew Vetticatt studying organocatalytic mechanisms.

Ambarneil Saha was born in Starkville, MI, and grew up in Cupertino, CA (USA). He joined Professor Song Lin’s lab in 2016 as a junior and will graduate with an A.B. in the spring of 2018. His current research is focused on electrochemical synthesis.

Aaron Loo grew up in New York City (USA) and moved to Ithaca for college in 2015. He joined Professor Song Lin’s lab in 2017 as a sophomore. His research interest lies in the application of electrochemistry to sustainable organic synthesis.

Song Lin was born and raised in Tianjin (P. R. of China). After earning his B.S. from Peking University (P. R. of China) in 2008, he pursued graduate studies at Harvard University (USA) working under the direction of Professor Eric Jacobsen. His doctoral research was focused on the development and mechanistic understanding of enantioselective organocatalysis. He then carried out postdoctoral studies with Professor Chris Chang at UC Berkeley (USA) on electrocatalytic reduction of CO₂ using covalent organic frameworks. In the summer of 2016, Professor Song Lin joined the faculty at Cornell University (USA). His research focuses on the discovery of new catalytic strategies for organic synthesis.

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