

University of Louisville
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Research Seminar

When: March 28, 2024

Time: 12:00 PM

Location: CBLL-16

Understanding the origin and effect of local heating in plasmon-assisted electrochemistry

ABSTRACT:

Utilizing the strong light-matter interaction of plasmon resonances to boost activity or modulate selectivity in electrochemistry has garnered increasing interest.^{1–3} When plasmonic electrodes interact with light, they generate energetic (hot) charge carriers and are heated, both of which can contribute to enhancing electrochemical reactions. The processes of hot charge carrier and local heat generation in plasmonic electrodes occur sequentially at fast time scales, which makes differentiating their relative contributions to enhanced electrochemistry an outstanding challenge. Despite numerous studies designed to understand the origin and magnitude of plasmon-assisted chemical reactions, additional control experiments are required to accurately simulate local heating and to differentiate photothermal and nonthermal effects. To address this knowledge gap, we use cyclic voltammetry to examine the electrochemical response of a model redox probe at plasmonic Au electrodes in dark conditions and under light irradiation.⁴ To measure and simulate local heating, we designed and employed a Au electrode that is coupled with a temperature control system and thermocouple that is isolated from the bulk electrolyte. Our results show that, under plasmon excitation, a temperature gradient is created at the electrode-electrolyte interface which induces natural convection and increases mass transport-limiting current density. At slow scan rates, an electrode surface temperature rise of 1 K can increase current density greater than 100%. Direct interband excitation of Au exclusively enhances current density by local heating, while plasmon excitation leads to photothermal and nonthermal enhancements. Further, because plasmonically-excited electrodes can accumulate charge and disperse heat into the surrounding electrolytic solution, we hypothesize that the solvent's static dielectric constant and thermal conductivity can, in part, dictate the mechanism by which plasmon excitation enhances electrochemical reactions.⁵ Future work will focus on developing a fundamental understanding on how electrochemical solvent properties affect plasmon-assisted electrochemistry.

REFERENCES:

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- (2) Zhao, J.; Xue, S.; Ji, R.; Li, B.; Li, J. Localized Surface Plasmon Resonance for Enhanced Electrocatalysis. *Chem. Soc. Rev.* **2021**, *50* (21), 12070–12097
- (3) Li, S.; Miao, P.; Zhang, Y.; Wu, J.; Zhang, B.; Du, Y.; Han, X.; Sun, J.; Xu, P. Recent Advances in Plasmonic Nanostructures for Enhanced Photocatalysis and Electrocatalysis. *Adv. Mater.* **2021**, *33* (6), 2000086
- (4) Al-Amin, Md.; Hemmer, J. V.; Joshi, P. B.; Fogelman, K.; Wilson, A. J. Quantification and Description of Photothermal Heating Effects in Plasmon-Assisted Electrochemistry. *Commun. Chem.* **2024**, *accepted*
- (5) Joshi, P. B.; Wilson, A. J. Plasmonically Enhanced Electrochemistry Boosted by Nonaqueous Solvent. *J. Chem. Phys.* **2022**, *156* (24), 241101