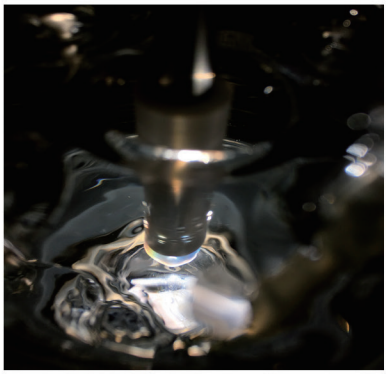
Localized surface plasmon-induced change in a reaction pathway

In situ monitoring of the light-induced suppression of hydrogen peroxide formation



The oxygen reduction reaction in alkaline electrolytes is critical for developing electrochemical systems for energy conversion. This reaction is especially critical for metal-air battery and fuel cells, which represent alternative opportunities to utilize cleaner and greener energy sources while reducing exhaust. In addition to the activity of electrocatalysts, the formation of a hydrogen peroxide intermediate is a crucial factor that must be considered when selecting the catalyst for oxygen reduction. This hydrogen peroxide (H_2O_2) intermediate produces undesirable side reactions and may lead to a loss in overall efficiency. Improvements in the performance of electrocatalysts, along with continuing advances in selective pathways for target reactions, have great potential in the design of competitive reactions; those using photophysical processes are particularly promising because of their tunable properties.

Recently, a team led by Professor Chen in the Department of Chemistry of National Taiwan University (NTU) provided the first empirical evidence of the suppression of the formation of an undesirable peroxide intermediate. They achieved this result via plasmonic effects by designing a custom-made rotating ring-disk electrode working station, which enabled them to induce *in situ* plasmon effects during the target reaction. They concluded that plasmon-induced hot electron transfer governed the suppression of peroxide formation; by contrast, plasmon-induced heating would have had the opposite effect (i.e., an increase in peroxide yield). Hot electron transfer within the Ag nanostructure generated sufficient energy to populate the antibonding orbital of oxygen, as illustrated by *in situ* X-ray absorption. The rapid light-dependent nature of the reaction, which corresponded to localized surface plasmon resonance in the system, could offer synergetic strategies for altering chemical reactions or reaction pathways in numerous fields.

These results enhance the understanding of localized surface plasmon-induced effects at the interface between electrocatalysts and reactants during a reaction, as well as advancing the reaction pathway by eliminating the peroxide intermediate.

X-ray absorption techniquesare powerful tools for investigating the electronic structure of electrocatalysts and could be used to study other catalytic systems. These techniques also have practical applications, such as in solar water splitting or artificial photosynthesis devices. These applications require integrating a reliable catalytic system with a photovoltaic solar cell, which captures light energy to generate sufficient force for chemical fuel generation. Professor Chen remarked, “This study can serve as a new strategy to realize the behaviors of localized surface plasmon resonance and to integrate the plasmonic electrocatalysts for various chemical reactions.”

Professor Chen’s group is currently working on developing novel *in situ* techniques to understand and the mechanisms that drive these reactions. In the future, such strategies could be used to achieve artificial photosynthesis.

Reference

Sheng-Chih Lin, Chia-Shuo Hsu, Shih-Yun Chiu, Tzu-Yu Liao, Hao Ming Chen*, (2017). Edgeless Ag-Pt Bimetallic Nanocages: *In-situ* Monitor Plasmon-induced Suppression of Hydrogen Peroxide Formation. *Journal of the American Chemical Society*, 139 (6), 2224–2233. DOI: 10.1021/jacs.6b09080.

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