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Selective Glycerol Oxidation on ITO-functionalized Hybrid Electrocatalytic System

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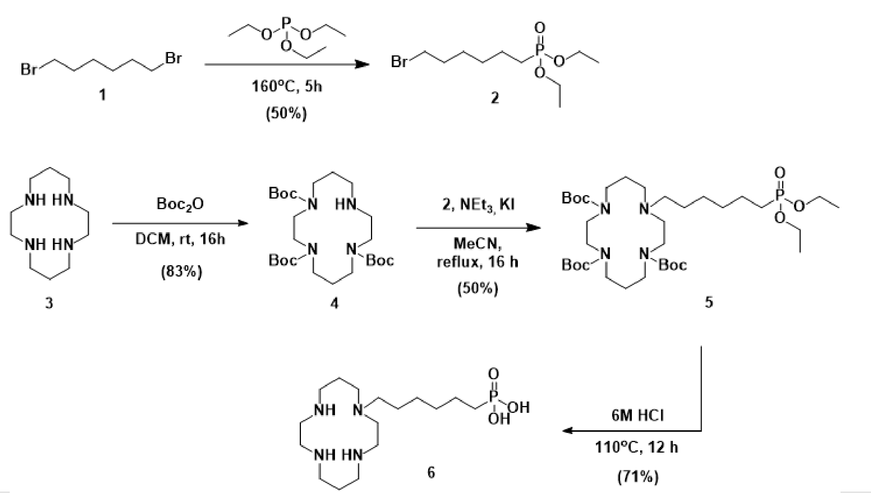
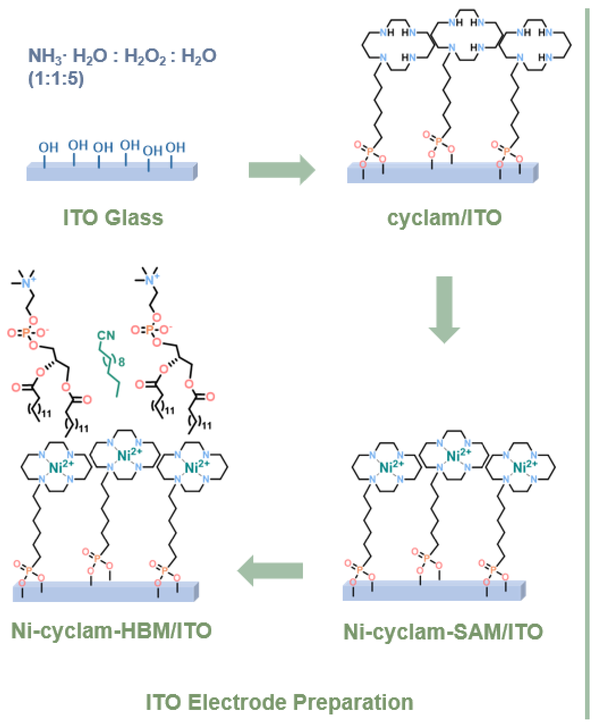
Introduction

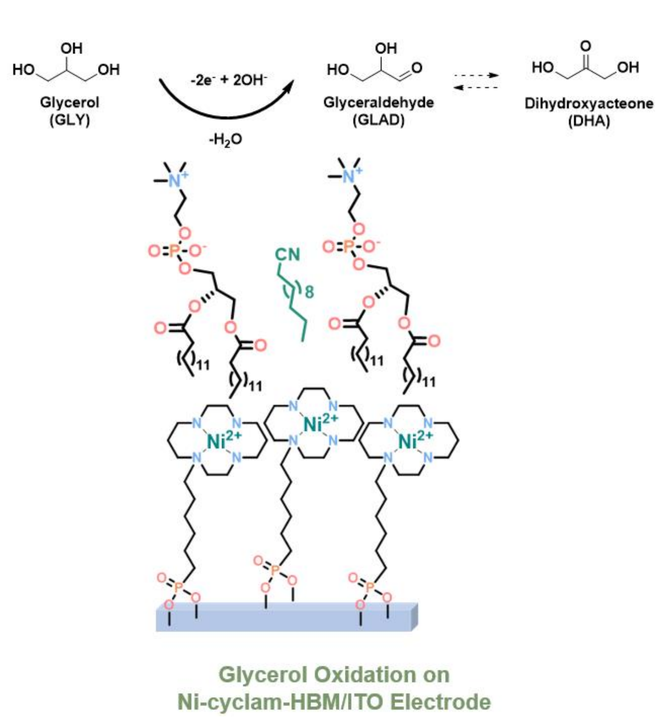
Hybrid bilayer membrane (HBM) system consists of a monolayer of lipid molecules coated on self-assembled monolayer (SAM) that is attached onto an electrode surface.[1] Many studies have indicated that the HBM system could influence the product selectivity of oxygen reduction reaction (ORR) by controlling the rate of electron and proton transfer.[2-6] Similar to ORR, selective glycerol oxidation is challenging because multiple proton and electron transfer steps and parallel reaction pathways are involved. In this work, we demonstrate that selective electrocatalytic glycerol oxidation can be performed on Ni(II)-cyclam functionalized ITO electrode surface in a HBM system. Our results show that the system could regulate the thermodynamics of glycerol oxidation reaction to undergo a two-proton two-electron pathway for selective oxidization of glycerol into glyceraldehyde as the major value-added product.

SAM Molecular Synthesis

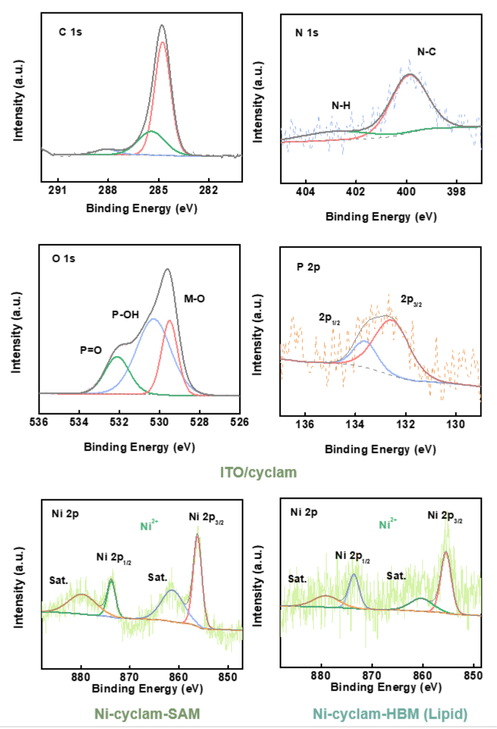


HBM System Preparation for Electrocatalytic Glycerol Oxidation





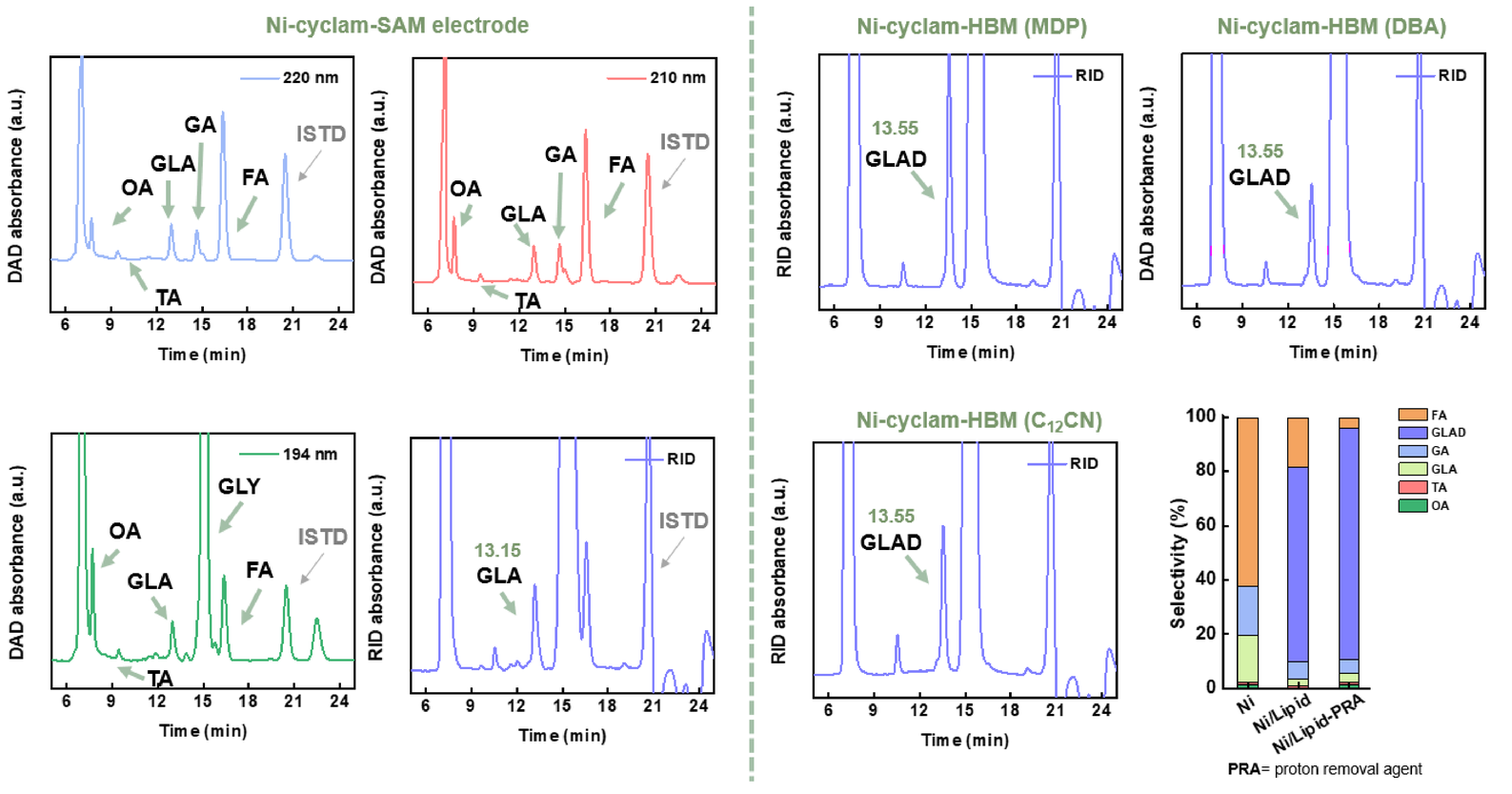
On-Surface Composition Characterization



XPS results demonstrate that organic molecules are anchored on the ITO surface. This molecular attachment results in SAM formation after the condensation reaction between cyclam-phosphonic acid and the hydroxyl group on ITO electrode surface.

Upon addition of nickel (II) ion onto SAM and HBM system, XPS data shows that nickel (II) ion is attached on the ITO surface. This attachment is attributed to the nickel (II) coordination towards cyclam molecules on ITO surface. This Ni(II)-cyclam motif would act as the active center for selective electrocatalytic glycerol oxidation reaction.

Product Analysis



Nickel-catalyzed electrochemical glycerol oxidation was carried out at 1.55 V versus RHE in pH 13 solution. The product selectivity and reaction yield of glycerol oxidation were determined by HPLC. The results show that the glyceraldehyde (GLAD) selectivity in glycerol oxidation reaction could increase up to 80 % in HBM system. It implies that the reaction could selectively proceed through primary alcohol oxidation pathway by regulating the rate of protons and electrons transfer in HBM system.

Conclusions & Future Work

The current HBM system could regulate the thermodynamics of glycerol oxidation reaction that selectively oxidizes glycerol into glyceraldehyde as the major value-added product.

In the future, we aim to apply such HBM system for different types of metal-catalyzed electrochemical reactions that involve proton-coupled electron transfer (PCET) steps.

Acknowledgements

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