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Dissertation Defense

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ELECTRODEPOSITION STUDIES OF GOLD NANOPARTICLES AND ALGINATE HYDROGELS

ABSTRACT:

This dissertation delves into the processes of electrochemical deposition (ECD) and electrodeposition (EPD) involving calcium alginate (Ca-Alg) hydrogels and Au nanoparticles (NPs). ECD involves the reduction of metal ions or complexes to metallic form on a conductive surface, usually via a nucleation and growth mechanism.¹ It is commonly used in depositing metal nanowires, nanoparticles, or other structures on electrode surfaces.² Numerous studies have explored the nucleation and growth phenomenon of metal ECD on different electrode materials.³ The first part of this dissertation scrutinizes the impact of NP size, ligands, and scan rates on the electrochemical growth of Au on Au NPs, revealing factors affecting reversibility and kinetics.⁴ A comprehensive study investigates the electrochemical growth of Au on Au NPs with alkanethiol layers, highlighting their impact on kinetics. Insights from this study lead to a two-step electrodeposition amplification detection technique, demonstrating the detection of 10 fM Au NP with simplicity, speed, and low cost.

Ca-Alg is a pH-shift polysaccharide that occurs naturally and is used as a matrix (hydrogel) to entrap and immobilize enzymes, other proteins, live cells, and NPs at the microscale.⁵ One common approach to forming Alg hydrogel on a conductive electrode surface is the anodic EPD of Alg solution via the electrochemical oxidation of water at relatively high potentials.^{6,7} The dissertation further explores the EPD of Ca-Alg and Ca-Alg-Au NP hydrogel films using Au NP-catalyzed electrooxidation of hydroquinone.⁸ This method improves EPD potential and holds promise for sensors, biological studies, electrocatalysis, and energy research applications. Another goal is to investigate the electrochemical behavior of $\text{Fe}(\text{CN})_6^{3-/4-}$ on various electrodes coated with Ca-Alg hydrogels. The study also explores the impact of hydrogel modifications on mass transport within the hydrogel.

This dissertation also expands Alg hydrogel applications on conductive electrode surfaces for electrochemical processes in a spatially confined environment. It explores the consequences of Ca-Alg hydrogels on the anodic stripping voltammetry (ASV) of Au NPs, achieving size-dependent stripping behavior. The spatially confined ASV of Au NPs is demonstrated using Alg hydrogels deposited at various electrodes, with the pipette electrode identified as the most effective for future spatially confined detection applications. Additionally, the ECD of Au on glass/ITO electrodes is explored using Alg hydrogels, revealing successful electrodeposition with decreased radius through controlled spatial confinement. The Pt/Ir/Alg-AuCl₄⁻-KClO₄ electrode setup is identified as the optimal configuration for achieving ECD of Au on glass/ITO electrodes with spatial confinement.

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