Electrochemical Feedback for Closed-Loop Facet Control in Pd Nanoparticles

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1. Introduction

Electrocatalysis has advanced rapidly through the development of electrode-supported nanomaterial electrocatalysts. Accordingly, significant research has been devoted to engineering catalyst surface properties to enhance interactions at the catalyst–reactant interface. In particular, nanoparticle facet distribution has been shown to play a critical role, where exposure of specific crystal facets can significantly enhance activity and selectivity.[1–3] However, despite extensive experimental exploration, many developments in electrocatalyst design remain largely empirical, with catalytic performance often optimized through trial-and-error. This has resulted in a limited mechanistic understanding of how nanoscale surface structures and crystallographic facets, govern electrocatalytic activity and selectivity.

Self-driving laboratory platforms aim to address this by enabling systematic, autonomous experimentation, where robotic workflows guided by data-driven experimental design improve efficiency, reduce redundant trials, and enable more optimal exploration of electrocatalyst structure–performance relationships. However, progress in this area is increasingly constrained by a critical bottleneck: nanomaterial characterization. Conventional methods for evaluating nanoparticle facets—such as electron microscopy, X-ray diffraction,[4] and atomic force microscopy[5]—are often resource-intensive, low-throughput, and poorly suited for integration into closed-loop optimization workflows. While automated electron microscopy protocols have been reported,[6] they require expensive equipment and remain impractical. Alternatively, spectroscopic characterization techniques such as UV–vis absorption and photoluminescence spectroscopy have also been employed.[7–9] However, their applicability is fundamentally constrained by instrumental wavelength limitations and the absence of strong or accessible plasmonic features in many catalytically relevant metals. Consequently, a broadly applicable, electrochemically compatible, and automation-ready method for nanoparticle surface characterization remains lacking.

Underpotential deposition (UPD) offers a promising alternative. UPD involves the deposition of a foreign metal monolayer at potentials more positive than those required for bulk deposition.[10] Since UPD energetics depend strongly on surface atomic arrangement, the resulting electrochemical signatures encode information about nanoparticle facet distribution and surface structure.[10–12] In addition, UPD measurements are rapid, require minimal experimental complexity, and are inherently compatible with electrochemical automation, making them well suited for integration into self-driving electrochemical workflows.

In this work, we establish UPD as a practical and effective nanomaterial characterization strategy for autonomous electrocatalyst optimization. We aim to develop a closed-loop optimization framework in which UPD electroanalysis serves as the feedback mechanism for controlling facet distributions in electrodeposited nanoparticles (Fig. 1). As a proof-of-concept, palladium nanoparticles (Pd NPs) are selected due to their widespread use in electrocatalysis, e.g. in fuel cells.[13] More broadly, this work demonstrates how electrochemical surface characterization can alleviate a key bottleneck in self-driving laboratories, enabling more rational and efficient discovery of structure–function relationships in nanomaterial electrocatalysts.

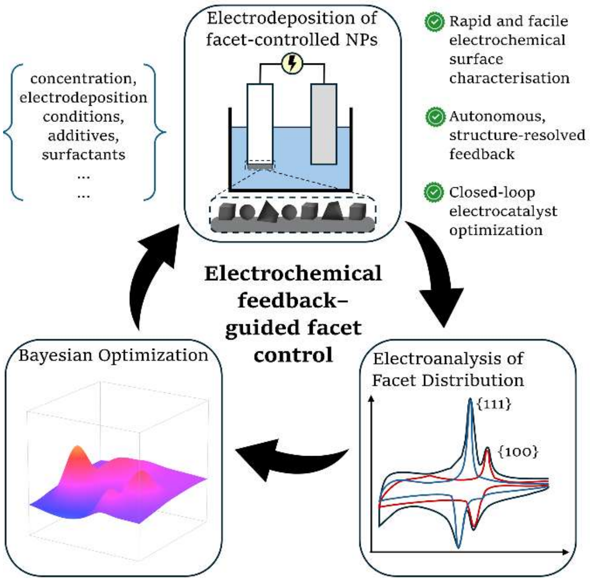

Fig. 1: Overview of the closed-loop optimization framework. 3D plot made with Desmos

2. Methodology

Fig. 2 illustrates the self-driving experimental setup, which integrates automated Pd nanoparticle synthesis and UPD-based electrochemical characterization. The system supplies stock solutions for nanoparticle electrodeposition and UPD analysis to an electrochemical cell, where all reactions and measurements occur. A syringe pump, valve switcher, and fluidic tubing actively direct solutions between the stock reservoirs, the electrochemical cell, and waste. A microcontroller interfaces with the various devices and a personal computer to coordinate fluid handling, electrochemical measurements, and subsequent experimental direction.

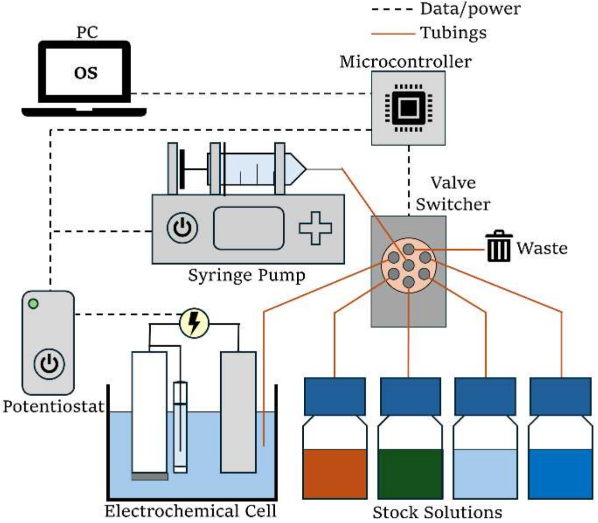

Fig. 2: Schematic of the self-driving electrochemical set-up

We synthesized Pd nanoparticles using an adapted electrodeposition protocol,[14] in which the system delivers separate stock solutions of H_2PdCl_4 and surfactant into the electrochemical cell, followed by an initial electrochemical equilibration step. The workflow then applies a nucleation pulse at a negative potential and initiates nanoparticle growth under more positive potentials. After electrodeposition, the system drains the electrolyte and rinses the electrode. We also adapted the UPD protocol from literature,[12] introducing an electrolyte containing $CuSO_4$, H_2SO_4, and NaCl into the cell. The system then performs cyclic voltammetry and transmits the data to the computer for analysis. It then autonomously polishes and rinses the electrode for subsequent experiments.

An automated algorithm then deconvolutes cyclic voltammetry data to extract nanoparticle facet distributions which are periodically validated by electron microscopy. A Bayesian optimization algorithm then quantifies the influence of individual synthesis parameters on facet evolution and optimizes the target facet fraction by adaptively tuning precursor concentrations, nucleation potential and duration, and nanoparticle growth potential and duration. Based on the optimization outcome, the computer autonomously updates subsequent experimental conditions, thereby establishing a closed-loop, data-driven optimization workflow.

3. Related Work

Recent studies have demonstrated the potential of autonomous platforms for materials-based electrode design. Notably, Sayama and co-workers reported a closed-loop system for the autonomous optimization of composite metal oxide electrocatalysts for O_2 and HClO generation.[15] Robotic workflows enabled high-throughput synthesis and systematic evaluation of catalysts. This approach enabled the identification of clear relationships between catalyst composition and selectivity. Similarly, Cherevko and co-workers applied automation to electrocatalyst discovery, but employed a multi-objective Bayesian optimization to simultaneously select for oxygen evolution activity and catalyst stability.[16] The multi-objective optimization achieved a 17-fold acceleration in discovery, requiring exploration of only ~6% of the total compositional space to identify optimal compositions.

Unlike prior autonomous electrocatalyst studies that focus on optimizing performance metrics like activity and stability, this work emphasizes the autonomous investigation of material characteristics, specifically crystal facet distributions. Central to this approach is the use of UPD as a rapid, automation-compatible method for probing nanoparticle surface structure and providing feedback for data-driven optimization. Together, these elements enable deeper mechanistic insight into how material characteristics govern electrocatalytic performance.

4. Conclusion

In summary, this work presents a closed-loop and autonomous investigation of crystal facet distributions in electrode-supported Pd NPs, enabled by UPD as a rapid and automation-compatible characterization method. This approach moves beyond outcome-only optimization toward structure-resolved understanding of catalyst behaviour. More broadly, this study demonstrates how self-driving laboratory platforms can leverage electrochemical characterization to transform nanomaterial electrocatalysis from empirical trial-and-error experimentation into a rational, data-driven discovery process.

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