Optical Fluorescence Microscopy for Spatially Characterizing Electron Transfer across a Solid-Liquid Interface on Heterogeneous Electrodes

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ABSTRACT

Heterogeneous catalytic materials and electrodes are used for (electro)chemical transformations, including those important for energy storage and utilization [1-2]. Due to the heterogeneous nature of these materials, activity measurements with sufficient spatial resolution are needed to obtain structure/activity correlations across the different surface features (facets, edges, defects, etc.). Because catalytic surfaces restructure with changing environments [1], it is important to perform measurements *in operando*.

In addition to scanning electrochemical methods [2-3], sub-diffraction fluorescence microscopy is well suited to this problem because it can operate in solution with resolution down to a few nm. By utilizing a redox reactive dye that activates fluorescence upon oxidation on an electrode surface, we aim to spatially quantify reactivity differences. These structure/activity correlations will reveal underlying reaction mechanisms and enable engineering of more active materials.

Keywords: fluorescence microscopy, heterogeneous electrocatalysis

1 INTRODUCTION

1.1 Background and Motivation

Catalysts are critical to supporting modern society and are used in petroleum refining, air and water pollution removal, and chemical reactions for energy applications [4]. An important class of catalysts for all these sectors is heterogeneous (solid) catalysts, which include nanoparticles. Due to the intrinsic heterogeneity of these materials, there are many different surface features available as binding sites for chemical species. It has long been understood that only a minority of the available surface sites are responsible for catalytic activity [5]. Further, different exposed surface facets or features can have preferential catalytic activity towards one chemical transformation over another [6-7]. In order to develop new catalysts with higher activity, it is first necessary to quantify the desired activity at the different surface features of a catalyst. In the past, this information was collected by studying single crystals with known surface facets exposed [2, 8]. However, single-crytals are not very accurate model systems for the dispersions of nanoparticles or heterogeneous electrodes used in practice. Ensemble scale characterization and testing of catalysts has led to structure/activity relationships [6,7,9,10], although these measurements suffer from an inherent averaging of activity over all surface features/particles. Measurements have been made at the single nano-particle level and within domains of single catalyst particles to reduce the degree of ensemble averaging to smaller and smaller domains [11]. The challenge still remains to structually characterize and quantify catalytic activity at the single active site level on heterogeneous materials. A complicating feature of such measurements is the dynamic nature of active sites that structually rearrange during the catalytic cycle, which necessitates methods that are compatible with catalytic conditions (usually atmospheric pressure or solution phase).

Optical fluorescence microscopy is readily compatible with imaging through solution. Moreover, sub-diffraction techniques such as photoactivated localization microscopy (PALM) and stochastic optical reconstruction microscopy (STORM) improve the spatial resolution of fluorescence microscopy beyond the diffraction limit to under 10 nm [12]. Instead of using an external stimulus to activate fluorescence as in PALM, we have incorporated a redox sensitive dye that is activated upon electron transfer occurring at the electrode surface. By imaging the locations of thousands of activated dyes, a spatial histogram can be built that resolves the active features and can be compared to structural characterization data from the same area. Again, because of surface reconstruction, the structural characterization has to take place under catalytic conditions. This requirement makes vacuum techniques with high spatial resolution, such as scanning tunneling microscopy (STM) and scanning and transmission electron microscopy (SEM and TEM) unsuitable, although advancements are underway to integrate liquid cells into SEM and TEM instruments [13-14].

1.2 Platinum as Electrocatalyst

Pt is a widely used heterogeneous electrocatalyst for reactions such as the hydrogen oxidation and oxygen reduction reactions used in fuel cells. Fuel cells typically use electrodes impregnated with Pt nanoparticles where the active sites are very close together. This constraint makes using fluorescent microscopy to find active sites on

nanoparticles unpractical as this would result in an ensemble average of the activity of part of or the whole particle. To circumvent this limitation, we use annealed polycrystalline Pt electodes with grains larger than 100 nm to look for activity differences between various exposed facets, grain boundaries, defect sites, and other surface features. The activity for oxidation reactions is probed with p-aminophenyl fluorescein as the redox sensitive fluorophore. Before oxidation, the probe is non-fluorescent due to internal quenching from the aminophenyl group. Oxidation cleaves the quenching group to produce highly emissive fluorescein.

1.3 Fluorescence Microscopy Applied to Catalysis

Sub-diffraction fluorescence microscopy relies on fitting the recorded point spread function of single emitters to a model. The localization uncertainty in this measurement is inversely proportional to the square root of the number of detected photons [15]. To achieve a localization precision less than 5 nm, thousands of photons need to be detected. Although a single fluorophore can theoretically emit close to one billion photons per s at saturation, this rate of photon flux requires excitation powers far above the damage threshold of most samples. Commonly used experimental excitation power for single molecule microscopy is on the order of $kWcm^{-2}$ which corresponds to a fluorescent flux of approximately 10,000 photons s^{-1}. Under these conditions, the fluorophore must remain stationary for tens to hundreds of milliseconds in order to collect enough photons for accurate localization. If the fluorophore is to be imaged while bound to the active site without overlapping fluorescence from other fluorophores bound to nearby sites, this situation corresponds to a turnover frequency on the order of 10 $Hz\mu m^{-2}$, a full 10 orders of magnitude slower than that of a diffusion limited catalytic system. Due to this fundamental mismatch between the timescales of fast catalytic systems and single-molecule fluorescent imaging systems, previous work has focused on catalysts with low inherent activity [16].

A catalyst's turnover rate is related to the binding energy of the different chemical species involved in the catalytic cycle. Inhibition of the reaction occurs when products bind too strongly; whereas weak binding results in insufficient surface coverage or insufficient reactant residence time. This behavior leads to the familiar volcano plot with the highest catalytic activity corresponding to binding energies such that the chemical species stay on the catalytic surface just long enough to react and then leave [17]. Thus, in trying to study optimized (fast) catalysts with fluorescence micrscopy, the fluorophore probe must be engineered to spend an appreciable amount of time bound to or near the active site so that it can be detected.

1.4 Trapping Layer for Fluorescence Detection

To use fluorescence microscopy to characterize the active sites on a catalyst that does not bind the fluorophore strongly enough to keep its position fixed during the requisite measurment time, an additional modification can be made to the experimental setup to trap the activated fluorescent probe in the vicinity of the active site long enough to acquire an image. Such an approach has been pursued previously by covering the catalyst with a high surface area, porous silica layer that non-specifically adsorbs the fluorescent probe [16]. By using a porous detection layer, the spatial resolution of the measurement is compromised because the probe can diffuse isotropically away from the active site before binding and being imaged. Thus, in order to maintain the highest spatial resolution, the porous detection layer should be as thin as possible. To address this issue, we use a detection layer based on the principles of ion-exchange chromatography in order to introduce specific, coulombic interactions between the anionic fluorescein probe and a polymer hydrogel containing cationic groups. In this system, the interaction strength can be modulated by changing the ionic strength of the electrolyte solution such that the probe has enough affinity to the stationary phase to be bound long enough to image but not so strong that charged species are excluding from reaching the electrode surface.

2 EXPERIMENTAL

Our microfluidic measurement platform and reactor shown in Figure 1a is made by depositing thin metal films on a fused silica wafer using standard photolithography equipment. The working and counter electrodes are Pt. The reference electrode is Ag that has been anodized in hydrochloric acid to produce a Ag/AgCl reference electrode. A cationically-modified polyvinyl alcohol polymer and a low degree of cross-linking agent is coated on the working electrode to create the detection layer. The microfluidic channel is enclosed with a cover glass spaced off the wafer surface, and a syringe pump is used to flow the fluorophore/ electrolyte solution. An inverted microscope fitted with a water immersion objective and the appropriate filters for fluorescein are used. The fluorophore excitation source is a 488 nm laser with optics to provide widefield illumination. Fluorescent photons are recorded on a scientific grade camera. A potentiostat is used to drive the three-electrode cell in the microfluidic reactor, which controls the electrocatalytic activity of the Pt working electrode. The working electrode is Pt that has been annealed in a tube furnace under H_2/Ar to increase the grain size (Figure 1c).

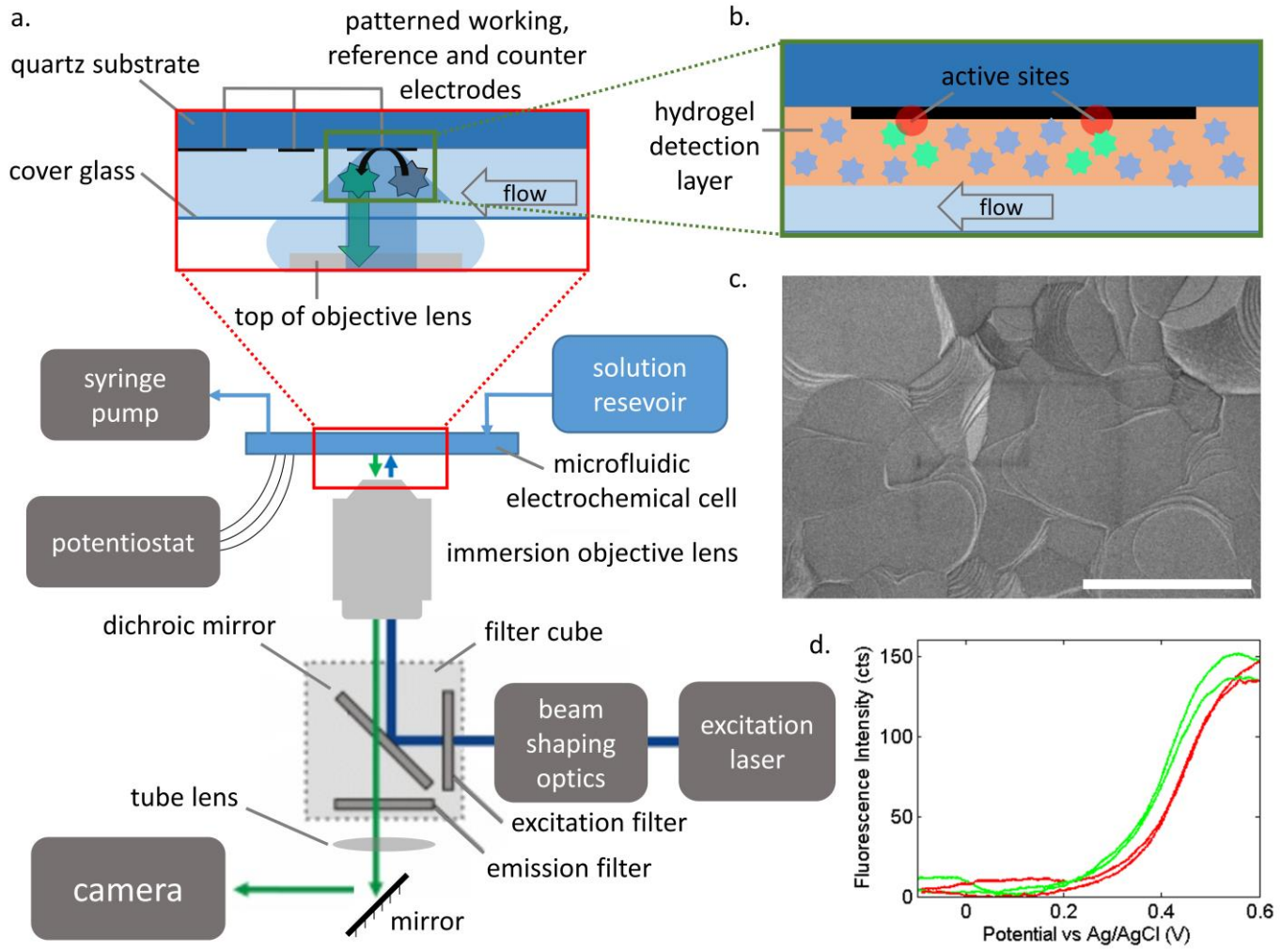

Figure 1: a) Diagram showing the optical layout of an inversion microscope focused on a thin, microfluidic, electrochemical cell with a heterogeneous electrocatalyst as the working electrode. A solution containing a redox active dye is pumped through the cell. Initially the dye is internally quenched (blue star) until it *undergoes* a 1-e^- oxidation at the surface of the working electrode (green star). A laser is focused on the back focal plane of the objective lens to provide wide-field excitation illumination for the activated dye. The red-shifted fluorescence signal is collected by the objective lens and focused onto a camera. By collecting many fluorescent events over a period of time, a 2-D histogram can be made representing the surface activity with a spatial resolution of several nanometers. b) Close up schematic of the surface of the electrocatalyst covered with a hydrogel polymer as the detection layer. Fluorophores can penetrate this layer and reach the electrode surface to undergo oxidation. Activated fluorophores will be trapped near the active site due to interaction with the detection layer and allow for them to be imaged. c) A scanning electron micrograph of an annealed Pt film showing different grains, facets, and terraces. The scale bar is 1 µm. d) A plot of the fluorescence signal recorded from a solution containing p-aminophenyl fluorecein cyclic potential sweeps of the Pt working electrode. The anodic scans are plotted as the green lines and cathodic scans in red.

3 FUTURE APPLICATIONS

Fluorescence microscopy can be a powerful measurement tool for studying catalytic systems becaust it is compatible with operation under catalytic solution conditions, has nanometer scale spatial resolution, and captures catalytic events with single-turnover sensitivity. Once fully optimized, our measurement platform will allow fluorescence microscopy to be applied to a much greater number of high-activity catalytic systems where the probe fluorophore would otherwise be adsorbed to the active site for too short of a time to be imaged. In addition to Pt, other heterogeneous electrocatalysts are well suited to this measurement method because an applied potential can be used to control the catalytic turnover rate such that probe molecules are activated at a low enough density to allow for individual point spread function fitting. Further, this principle can be applied to numerous additional ionic

fluorescent probes for targeting other catalytic chemical transformations. More work remains to correlate catalytic activity maps with structural characterization of the underlying active sites. This knowledge will help elucidate the mechanisms through which catalysis occurs and eventually lead to the engineering and development the next generation of more active catalysts for a variety of commercial sectors.

REFERENCES

[1] N. M. Markovic and P. N. Ross Jr, "Surface Science Studies of Model Fuel Cell Electrocatalysts," Surface Science Reports, 45, 117-229, 2002.

[2] A. J. Bard, "Inner-Sphere Heterogeneous Electrode Reactions. Electrocatalysis and Photocatalysis: The Challenge," Journal of the American Chemical Society, 132, 7559-7567, 2010.

[3] B. D. Aaronson, C. H. Chen, H. Li, M. T. Koper, S. C. Lai, P. R. Unwin, "Pseudo-Single-Crystal Electrochemistry on Polycrystalline Electrodes: Visualizing Activity at Grains and Grain Boundaries on Platinum for the Fe^{2+}/Fe^{3+} Redox Reaction," Journal of the American Chemical Society, 135, 3873-3880, 2013.

[4] J. B. Ronge, T. Bosserez, D. Martel, C. Nervi, L. Boarino, F. Taulelle, G. Decher, S. Bordiga, J. A. Martens, "Monolithic Cells for Solar Fuels," Chemical Society Reviews, 43, 7963-7981, 2014.

[5] H. S. Taylor, "A Theory of the Catalytic Surface," Proceeding of the Royal Society of London, 108, 745, 105-111, 1925.

[6] S. W. Lee, S. Chen, J. Suntivich, K. Sasaki, R. R. Adzic, Y. Shao-Horn, "Role of Surface Steps of Pt Nanoparticles on the Electrochemical Activity for Oxygen Reduction," Journal of Physical Chemistry Letters, 1, 9, 1316-1320, 2010.

[7] I. Lee, R. Morales, M. A. Albiter, F. Zaera, "Synthesis of Heterogeneous Catalysts with well Shaped Platinum Particles to Control Reaction Selectivity," Proceedings of the National Academy of Sciences, 105, 40, 15241-15246, 2008.

[8] R. W. Joyner, "Catalysis by Single-Crystal Surfaces," Catalysis, 5, 1-47, 1982.

[9] S. Mostafa, F. Behafarid, J. R. Croy, L. K. Ono, L. Li, J. C. Yang, A. I. Frenkel, B. R. Cuenya, "Shape-Dependent Catalaytic Properties of Pt Nanoparticles," Journal of the American Chemical Society, 132, 15714-15719, 2010.

[10]. M. Varrkamp, J. T. Miller, F. S. Modica, D. C. Koningsberger, "On the Relation between Particle Morphology, Structure of the Metal-Support Interface, and Catalytic Properties of Pt/γ-Al2O3," Journal of Catalysis, 163, 2, 294-305, 1996.

[11] J. B. Sambur and P. Chen, "Approaches to Single-Nanoparticle Catalysis," Annual Review of Physical Chemistry, 65, 395-422, 2014.

[12] E. Pastrana, "Fast 3D Super-Resolution Fluorescence Microscopy," Nature Methods, 8, 46, 2011.

[13] E. A. Sutter, P. W. Sutter, "Determination of Redox Reaction Rates and Orders by In Situ Liquid Cell Electron Microscopy of Pd and Au Solution Growth," Journal of the American Chemical Society, 136, 48, 16865-16870, 2014.

[14] N. de Jonge, F. M. Ross, "Electron Microscopy of Specimens in Liquid," Nature Nanotechnology, 6, 11, 695-704, 2011.

[15] R. E. Thompson, D. R. Lason, W. W. Webb, "Precise Nanometer Localization Analysis for Individual Fluorescent Probes," Biophysical Journal, 82, 5, 2775-2783, 2002.

[16] P. Chen, X. Zhou, N. M. Andoy, K.-S. Han, E. Choudhary, N. Zou, G. Chen, H. Shen, "Spatiotemporal Catalytic Dynamics within Single Nanocatalysts Revealed by Single-Molecule Microscopy," Chemical Society Reviews, 43, 1107-1117, 2014.

[17] J. K. Norskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jonsson, "Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode," Journal of Physical Chemistry B, 108, 46, 17886, 2004.