

Optimization of Proteomics-based Substrate Trapping with Histone Deacetylase 1

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Histone writers and erasures – the proteins that add or remove histone post translational modifications – are key drivers of epigenetic transcriptional events inside the cell. Many enzymes that control epigenetic modifications are dysregulated in human diseases. For example, overexpression of the erasure histone deacetylase (HDAC) enzymes can lead to epigenetic changes in transcription and ultimately disease, such as cancer. We recently pioneered a simple method called substrate trapping to isolate HDAC1 substrates using an inactive HDAC1 mutant. Our recent publication documented that different HDAC1 mutants preferentially bound different substrates, suggesting that three mutants (H141A, F150A, C151A) should be used for efficient trapping. Based on this observation, we performed a

proteomics-based trapping study of HDAC1 using all three optimal mutants simultaneously. In this study, using trapping with three mutants, 12 potential HDAC1 substrates were identified that were not observed when only a single mutant was used. Although trapping with three mutants identified novel substrates of HDAC1, the throughput of the experiment was low compared to trapping with a single mutant. Therefore, this study confirms that trapping with a single mutant is simple and effective, although three mutants may be desirable when high efficiency or a large number of substrates is necessary.

Keywords: Epigenetic, HDAC1, Trapping

Highly Efficient Hydrogen Evolution and Hydrazine Oxidation of Platinum via Tuning the Interfacial Dissolved-Gas Concentration

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Regulating the dissolved-gas concentration at the electrode solution interface represents a promising universal strategy to achieve high efficiency towards gas evolution reactions. Here, we present a facile fluorsurfactant modulation strategy to control the dissolved-gas concentration at the electrode/gas/electrolyte interface for enhanced hydrogen evolution reaction (HER) and hydrazine oxidation reaction (HzOR). With the fluorsurfactant modulation, lowered dissolved gas concentrations at the catalytic interface and sufficient surface-active area exposure can be achieved. For HER, we used perfluorooctanesulfonate (PFOS), and for HzOR we used cationic fluorinated pyridinium sulfonate (CFPS). The low concentration of dissolved hydrogen near the electrode/electrolyte interface can

significantly decrease overpotential at the interface and thus elevated hydrogen evolution current. Therefore, it is meaningful and fundamentally essential to control the dissolved-gas concentration at electrode/gas/electrolyte interface for HER. Herein, by using platinum as the platform, we present a facile and straightforward strategy to tune the dissolved-gas concentration at electrode/gas/electrolyte catalytic interface via potassium perfluorooctanesulfonate (PFOS) modulation for dramatically enhanced HER. The addition of PFOS was demonstrated to lower the dissolved-H₂ concentration at the reaction interface. When surfactant concentration increases, the solution surface tension decreases resulting in a lower nucleation energy barrier. Consequently, a lower supersaturation concentration is required for gas

nanobubble. Moreover, the desorption of PFOS from the electrode during HER facilitate sufficient exposure of the surface-active area. Benefiting from the lowered dissolved-gas concentration and sufficient exposure of surface area at the interface, the PFOS-modulated Pt exhibited a excellent electrocatalytic performance towards HER. Relative to pure Pt, the PFOS-modulated Pt yielded a much lower overpotential of 27 mV at a cathodic current density of 10 mA cm⁻². Moreover, the PFOS-modulated Pt showed a current density of 27 mA cm⁻² at the overpotential of 40 mV, which was 2.4-fold higher than that of pure Pt. All the measurements are obtained by running the three independent experiments and getting the average value. Guided by the previous work, we developed a new facile cationic fluorosurfactant-modulation strategy to achieve enhanced HzOR activity. We synthesized a fluorinated pyridinium sulfonate surfactant (CFPS). Owing to the high surface activity of CFPS, the activation energy for N₂ bubble nucleation is reduced, leading to a decreased dissolved-

gas concentration at the HzOR interface. The positive charge of CFPS also ensures the effective exposure of active sites during hydrazine oxidation. Benefited from both effects, the CFPS-modulated Pt showed a boosted catalytic activity towards HzOR. The CFPS modulated Pt exhibited a current density of 10 mA cm⁻² at 562 mV vs. RHE, which was 2.1 times higher than that of pure Pt under the same potential. In summary, we develop PFOS and CFPS modulation strategy with precisely managed dissolved-gas concentration at electrode/gas/electrolyte interface for highly efficient hydrogen evolution and hydrazine oxidation, respectively. This work provides a systematic understanding of the gas-involved catalytic process and a convenient approach to realize high-performance electrocatalysis based on precisely controlling the dissolved-gas concentration at the catalytic interface.

Keywords: Electro catalyst, surfactant modulation, efficient hydrogen evolution and hydrazine oxidation

Abstract No: SB 1

Synthesis of Precursors of Cycloparaphenylenes Using Ullmann Coupling

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[n]Cycloparaphenylenes ([n]CPPs) are carbon and hydrogen containing macrocycles which constitute of 'n' number of para-phenylene groups connected via 1,4-biphenyl -C-C- linkages. The chemical, photochemical and electrochemical properties of [n] CPPs make them potential candidates for a broad range of applications. Although [n]CPPs have aesthetically appealing chemical structures, their high energy geometries make them a synthetically challenging class of molecules. Synthesis of [n]CPPs reported thus far associated with expensive catalysts, starting materials and sophisticated reaction conditions. Therefore, this research project was focused on the synthesis of a series of precursors of [n]CPPs; dimer, trimer, tetramer and other oligomeric precursors of 1,4-chlorobenzene using Ullmann coupling with the eventual intention of cyclizing those precursors to obtain a series of [n]CPPs which is feasible in the Sri Lankan context. A number of synthetic

attempts followed by the reaction condition optimization attempts were made using 1,4-chlorobenzene as the starting material and activated copper as the catalyst in various solvents at various temperatures to synthesize the [n]CPP precursors. Dimerization of 1,4-chlorobenzene was carried out using activated copper as the catalyst in N-methyl-2-pyrrolidone (NMP) solvent at 140 °C. The crude mixture was subjected to column chromatography to obtain clear light yellow color liquid which was characterized using UV-visible, fluorescence and NMR spectroscopy. UV-visible spectra of the obtained product in chloroform exhibited a characteristic absorption peak for the $\pi \rightarrow \pi^*$ transition of the conjugated biphenyl rings which shows λ_{\max} at 272 nm. The fluorescence spectra of the obtained product demonstrated a significant enhancement of the fluorescence activity compared to the starting material. The two doublets appeared in between chemical shift values of 7.00 - 8.00 ppm in the ¹H NMR