Project 6: Nanostructured Catalytic Membranes as Optical Sensors

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Project Summary

Background: Continuous monitoring of volatile organic compounds (VOCs) in the ambient as well as in human breath can provide significant advances to human health but is a longstanding analytical challenge. For example, trimellitic anhydride (TMA) is used as a plasticizer in polymer fabrication. This material is highly toxic occupational hazard even at ppb levels and very expensive health monitoring protocols must be instituted by industry due to the time delays associated with batch air sampling and off-site instrumental analysis.[1] In the area of medical diagnostics, correlations between acetone content in the human breath and blood glucose have been identified yet invasive blood-based procedures are still being used by diabetes patients due to identical analytical limitations.[2]

Our lab has recently demonstrated that perflurosulfonic acid (PSA) polymer membranes may be used to catalyze reactions between immobilized dye molecules (resorcinol) and various toxic reagents for optical sensing at sub-ppb exposures.[1,2] The optical response arises from the synthesis of unique products immobilized within the membrane and is more highly selective than common organic dye optodes that rely on generic protonation/ deprotonation or metal-ion complexation phenomena. By way of example, the optical response that arises from reaction of immobilized resorcinol with various concentrations of toxic trimellitic anhydride (TMA) in the ambient is shown in Figure 1.

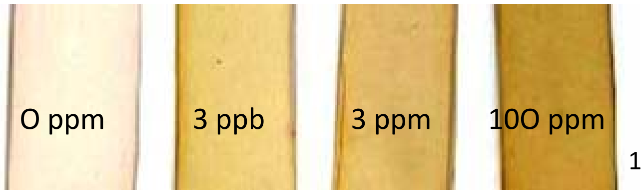


Figure 1. Catalytic Optodes After Exposure to Indicated TMA Concentrations

The color response shown in Figure 1 has been shown to arise from the Friedel-Craft acylation between the immobilized resorcinol and rapidly diffusing TMA (catalyzed by PSA) to produce a quinone. The schematic in Figure 2 depicts the mechanistic process involved in this transformation. The dashed lines represent the rapidly diffusing TMA molecules. The resorcinol molecules are depicted as being immobilized within hydrophilic clusters (circles in the schematic) of the PSA polymer membrane. The catalyzed reaction upon interaction of the two reagents is shown to produce a quinone. We note in Figure 2 that the nanostructure of the membrane will play a critical role as to catalytic properties and the associated optical response. This is due to the impact of the local environment on the solubility of both reactants and products and therefore the activation energy associated with a particular reaction.

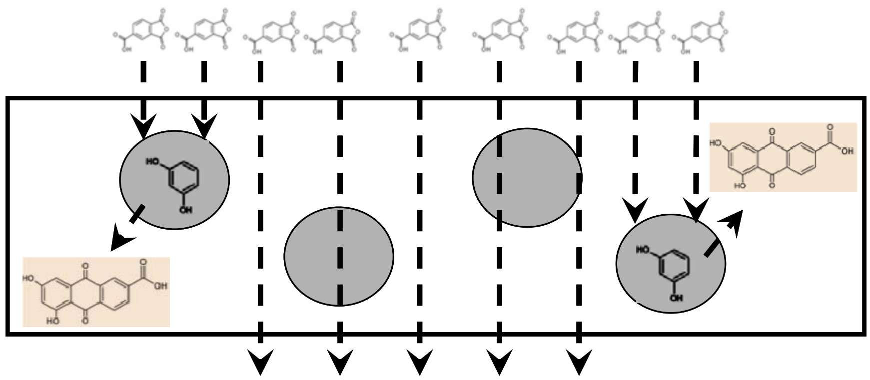


Figure 2. Schematic of Optical Sensing Mechanism

In Figure 3, the selectivity of such a catalytic optode approach to TMA is demonstrated by the UV/VIS spectral response of immobilized resorcinol relative to the chemically similar maleic anhydride (MA) and phthalic anhydride (PA). Such selectivity arises from the synthesis of the three unique quinone products shown by **Schemes 1 through 3**.

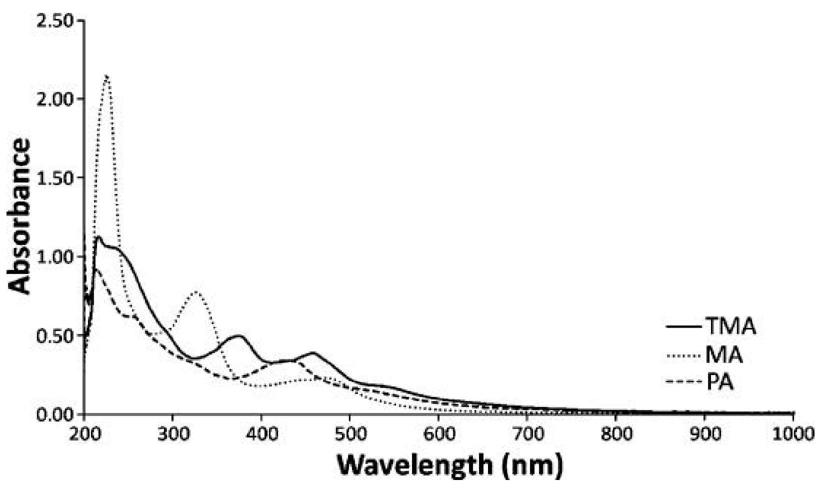
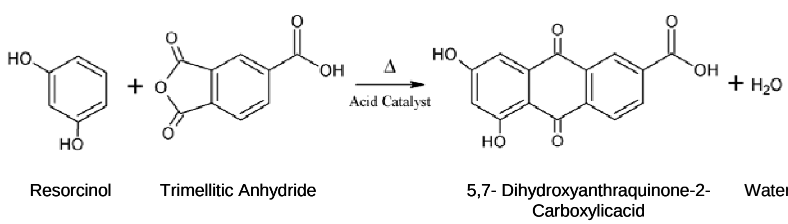
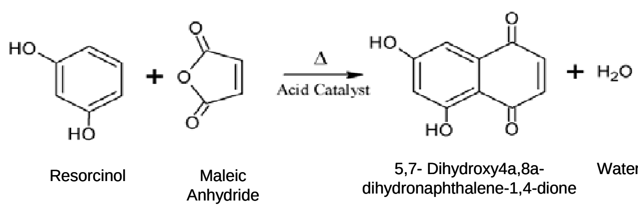


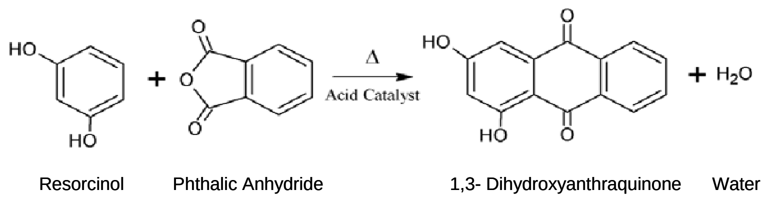
Figure 3. UV-VIS Spectrum After Exposure of Catalytic Optode (PSA Membrane with Immobilized Resorcinol) to Various Anhydrides



Scheme 1. Friedel-Craft Acylation with Trimellitic Anhydride



Scheme 2. Friedel-Craft Acylation with Maleic Anhydride



Scheme 3. Friedel-Craft Acylation with Phthalic Anhydride

Objective and Tasks: The objective of this six week NSF RET research program is to determine whether the UV-vis colorimetric response of these membranes may be calibrated so as to achieve clear correlations to exposure levels for various chemicals. Individuals chosen to work on this study will carry out careful exposures of catalytic membranes previously prepared by the graduate student mentor to various concentrations of chemical and monitor the response. The membranes are prepared so as to systematically vary their morphology and thereby both the catalytic and optical response to various challenges. Exposure procedures and chemicals will vary from the use of VOC's in flowing gas to proteins present in liquid solution.

Participants on this project will first be taught, through hands on experience, the basic principles of how light interacts with matter and, more specifically, how the Beer-Lambert Law may be used to characterize such interactions and calibrate optical responses to chemical composition. These principles will then be applied to understand how the solid-phase polymer morphology can influence the catalytic activity, and thereby the optical response.

It has only relatively recently been recognized that the solid catalyst environment can itself act as a solvent to impact reactivity during heterogeneous synthesis. For example, the influence of local "solvation" effects (intermolecular interaction on or within the solid catalyst) on the apparent activation energy of a reaction can thus be described in terms of Figure 4.

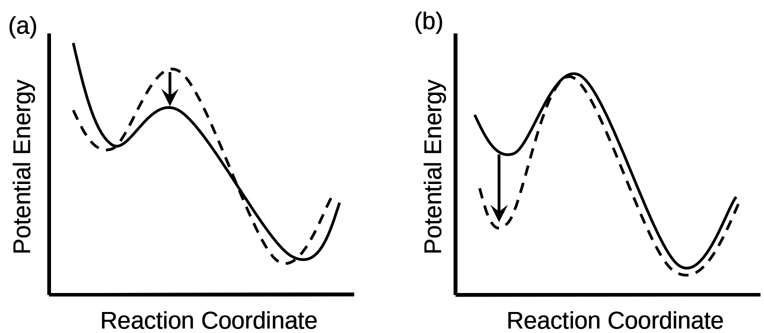


Figure 4. Effect of Solvation on Activation Energy (Dashed Curves Represent the Energy Profile in the Absence of Solvation): (a) Solvation of the Activated State - (Reduced Activation Energy), (b) Solvation of the Reactant (Increased Activation Energy) (Adapted from Ref. 3)

The role of thermodynamic phase behavior (the equilibrated structure formed between heterogeneous catalyst, reactants, products, intermediates, and any co-adsorbates) on catalytic activity has not been previously investigated. In-situ analysis of the polymer catalyst reactivity under various experimental conditions as will be performed as part of this investigation can provide detailed information on the role of phase behavior in heterogeneous catalysis.

Possible Ideas for Classroom Implementation

Classroom implementation of the learning obtained during this project will naturally grow out of the use of trapped product and reactant species within these membranes. Classroom demonstrations can be done with minimal materials on a bench top: a hot plate and membrane samples from this project. For example, we have discovered that the presence of water can have a significant impact on some reactions. Thus, one idea for a demonstration is to simply have students breathe on a sample to change its color (due to high humidity in exhaled breath). Then, the membrane sample can be placed on a hot plate to drive off the water that is imbibed and return the sample back to its original color in less than a minute. This process can be repeated as many times as desired by every student in the class without losing color intensity. Such hands-on participation is a simple way of initiating discussions on some very sophisticated concepts in physics and chemistry: (1) light-matter interactions and the source of color (wavelength) and intensity (amount), (2) the source of vision how we see the world around us, (3) the difference between reaction equilibrium and reaction kinetics, (4) the importance of water as both reactant and solvent in nature. Classroom implementation of this topic is dependent only the creativity and motivation of the participants and is not at all limited by the cost of materials.

References:

1. Ayyadurai, S. M., Worrall, A. D., Bernstein, j. A., and Angelopoulos, A. P**.** (2010). "Perfluorosulfonic Acid Membrane Catalysts for Optical Sensing of Anhydrides in the Gas Phase," *Analytical Chemistry, Vol. 82, Issue 16,* June 18, pgs. 6265-6272,

2. Worrall, A. D., Bernstein, j. A., and Angelopoulos, A. P**.** (2010). „Optical Sensing of Acetone in Exhaled Breath Utilizing Acid Catalyst Membranes," Paper presented at the *AIChE Annual Meeting*, November 7-12, Salt Lake City, Utah.

3. Buncel, E., Stairs, R., and Wilson, H. (2003). *The Role of the Solvent in Chemical Reactions*. Oxford University Press: Oxford, 2003.