Project #6: Nanostructured Catalytic Membranes as Optical Sensors

(2011 Summer RET Program)

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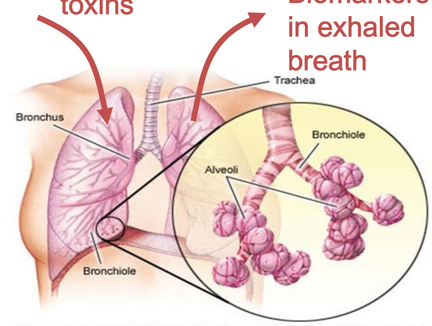
PROBLEM: Real-time analysis of environmental toxins and biomarkers of human health at ppb levels is essential for accurate diagnosis and treatment of exposure and disease.

Unfortunately, existing methods that are both sufficiently sensitive and selective involve off-line laboratory testing.

Ambient toxins

Biomarkers in exhaled breath



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Commercialization of proton-exchange membrane (PEM) fuel cells for automotive applications requires a significant reduction in the amount of Pt used as catalyst. Attempts to enhance the specific catalytic activity of Pt toward the oxygen reduction reaction (ORR) by reducing the size of supported catalyst nanoparticles to increase the available specific area have been unsuccessful. Only hypothetical explanations for such behavior exist due to the difficulties associated with structure determination of supported nanoparticles (Indy, confirm and provide reference). This gap in the knowledge base is a serious problem because it prevents the development of rational approaches to improve Pt utilization. In the present investigation, we employ a rarely investigated technique of $PtCl_2$ reduction in solution that results in the formation stable suspensions of anionic particles via a specifically adsorbed chloride ion shell. This shell permits electrostatic layer-by-layer (LBL) assembly of the nanoparticles into well-defined, unsupported electrocatalyst structures utilizing a strong cationic polyelectrolyte as binder.

1) Your synthesis technique allows us to make LBL assembled electrodes (i.e., without carbon support) by creating stable suspensions of Pt nanoparticles without the use of organic surfactants.

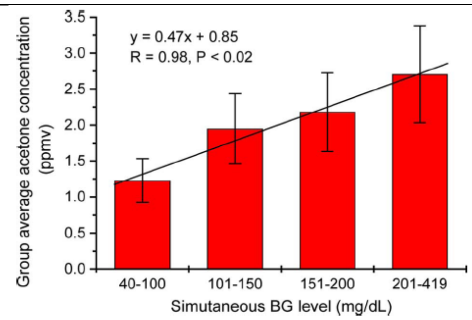
2) Your synthesis technique forms monodisperse particles very simply compared to other approaches.

3) You've shown that clusters are electrocatalytically active!

Loss of activity with increasing dispersion limits specific activity gains with pure Pt. However, no one has provided direct experimental evidence for why. Your synthesis/LBL approach can for the reasons given above. Such structural information will also provide learnings for new bimetallic and non-Pt catalyst systems. Such direct observation of structure variation with Pt particle size and activity would fill a significant gap in our knowledge base and also suggest boundaries for alternate electrocatalyst synthesis strategies.

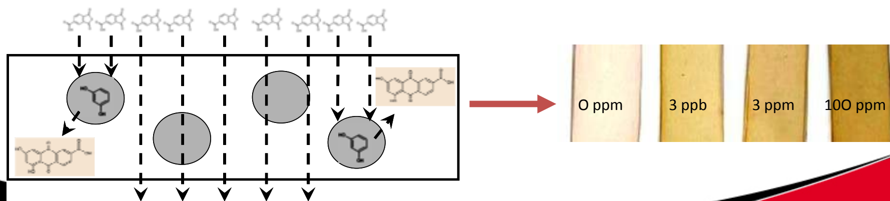
Research Objective:

Develop portable sensor capable of highly selective analyses of organics of at ppb levels. Specifically, we will focus on: (1) highly toxic anhydrides used as plasticizers in polymer industry and (2) organics in the exhaled breath of diabetes patients.



Approach:

Use well-defined morphology of catalytic perflurosulfonic acid membranes to control reactions of immobilized, optically active molecules and agents of interest. For example, the schematic below depicts the Fridel-Craft acylation of resorcinol with trimellitic anhydride to produce the desired optical response.



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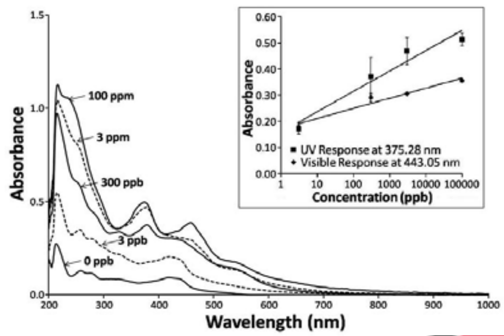
Be sure to contrast to other synthesis methods (dendrimer templating, precipitation, surfactant capping).

Primary Experimental Method to be used:

UV-vis Spectroscopy

Batch Exposure of Membrane to Agent (Organic Vapor)

Sample UV-vis spectrum of membranes with a given concentration of resorcinol after exposure to various levels of trimellitic anhydride.



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