Optochemical Sensing using Metal Oxide Nanoparticles: Adsorption and Detection

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While a large amount of literature exists related to the use of metal oxide nanoparticles for chemical sensing, most of those studies have involved measuring chemical resistance changes of heated metal oxide nanoparticle films upon exposure to gases or vapors. One disadvantage of this type of sensor is the relatively high electrical power needed for heating the film. However, many metal oxide nanoparticles are photoluminescent, with their emission spectrum related to the presence of defects and surface states. This offers a new opportunity for chemical sensing, since adsorption is expected to affect the emission spectrum. Zinc oxide is a particularly interesting photoluminescent metal oxide with a bimodal room temperature emission spectrum that consists of an excitonic recombination peak at 380 nm and a visible, defect-related peak in the 500-600 nm range. Examples of other photoluminescent metal oxide nanoparticles include zirconium oxide and cerium oxide. The goals of this work are to measure and understand the changes in the photoluminescence spectra of metal oxide nanoparticles upon exposure to various gases and vapors. In addition to atmospheric gases, reactive gases such as sulfur dioxide, methanethiol, hydrogen chloride and chlorine have been investigated. Experiments using nitrogen saturated with various organic vapors have also been performed, including methanol, benzene, toluene and pyridine. Photoluminescence measurements have been carried out in real-time using a custom-built UV LED-based fluorometer, and these have been accompanied by surface science studies on the powders to determine if irreversible chemisorption occurred. It has been found that molecules that chemisorb on ZnO nanoparticles, such as benzene and pyridine, cause an irreversible decrease in the intensity of visible emission peak and an increase in that of the UV peak. For physisorbates, such as methanol, the changes are completely reversible. Density functional theory (DFT) calculations have also been performed in an attempt to correlate the strength of adsorption to the photoluminescence changes.

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