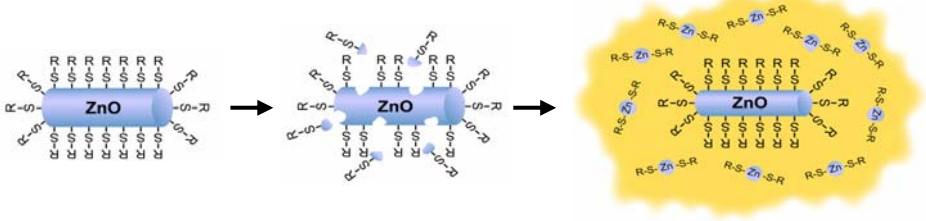
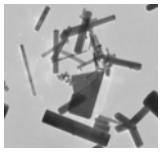
The Role of Surface Effects on the Electro-Optical Properties of Nanocrystalline ZnO

Metal oxide nanoparticles, nanotubes, nanorods, nanowires and whiskers are finding important applications ranging from catalysis to optoelectronics to photovoltaics. Nanocrystalline zinc oxide (nano-ZnO) is a semiconductor that has been the subject of much research due to its wide band gap, high exciton binding energy (60 meV), mechanical/thermal stability and ability to emit in the UV. Furthermore, nano-ZnO exhibits a unique inherent bimodal photoluminescence (PL) spectrum, consisting of both UV and visible emission bands. Our research efforts focus on understanding what is responsible for generating the unique optical properties of nanocrystalline-ZnO, so that they may be tailored for targeted electro-optical responses. The current investigation introduces unique surface passivation methods utilizing various surface modifiers covalently attached to the nano-ZnO. Our ability to tailor the PL properties of the nano-ZnO has been demonstrated through the use of a silane-modifier, which increased the UV emission with maintenance of the visible emission; a mixed-modifier (silane/thiol), which increased the UV emission while decreasing the visible emission; a thiol-modifier, which decreased both the UV and visible emissions.

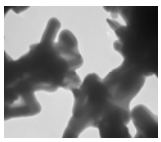
The manipulation of the inherent optical behavior of the nano-ZnO through surface modification creates an opportunity to use this modified material as a novel taggant for friend vs. foe applications or for authentication applications where a dual signal or targeted optical response is desirable. An additional result of this work was the discovery of a novel encapsulation process that results in the formation of a thick layer of thiol-functionalized molecules on the surface of the nano-ZnO. The encapsulation layer thickness, morphology and subsequent chemical reactivity are controllable by choice of thiol and preparation conditions. A theory explaining the encapsulation process, which involves the partial dissolution of the nano-ZnO, was hypothesized. While previous studies have demonstrated that alkanethiols adsorb on ZnO surfaces and nanoparticles, the present work is the first to demonstrate encapsulation of ZnO nanoparticles. This method may be useful in future photovoltaic applications in which one wishes to surround ZnO nanorods and whiskers with light-absorbing molecules, which could be achieved by using thiol-terminated dye molecules.



Schematic representation of the thiol encapsulation process of nano-ZnO



Unmodified ZnO



Thiol-modified ZnO

Singh, J., Im, J., Whitten, J. E., Soares, J. W., and Steeves, D. M., *Encapsulation of Zinc Oxide Nanorods and Nanoparticles*, (submitted to Langmuir, March 2009)

Patents or other steps toward commercialization: Invention disclosure in preparation.

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