

# Surface Chemistry of Metal Oxide Nanoparticles and Attachment of Metal Nanoclusters: Sensor, Optoelectronic and Photocatalytic Applications

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## ABSTRACT

Metal oxide nanoparticles are surprisingly reactive, and some undergo changes in color or in their photoluminescence (PL) spectra upon reaction. In the latter case, visible emission arises from electron decay from surface related states, and PL changes should be an indicator of chemisorption. A variety of surface science techniques, including X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), have been used to investigate adsorption of various molecules, including thiols, from the gas and solution phases, on metal oxide powders and films and to measure changes in the electronic structure of the surface due to adsorption. Examples of metal oxide nanopowders that have been studied include zinc oxide, zirconium oxide, gold oxide and tungsten oxide. In many cases it is shown that thiols reduce metal oxides to metals, with concomitant oxidation of the thiol to disulfide. Reactions with gases such as sulfur dioxide often lead to sulfite formation on the surface. Possibilities of using metal oxides for chemical sensing or optoelectronic device tuning are discussed.

Dithiols can be used as chemical linkers to attach gold nanoparticles (AuNPs) to metal oxides, including zinc oxide nanorods. Various methods of sintering the nanocomposites to remove the ligands and place the AuNPs in physical contact with ZnO have been explored, and the effect of the AuNPs on the chemistry and optical properties of the ZnO have been investigated. It is demonstrated that the AuNPs enhance the photocatalytic oxidative properties of the nanorods, and possible applications for their use in the photocatalytic destruction of hazardous materials have been explored.

**Keywords:** gold, metal oxide, photoluminescence, thiols

## 1 INTRODUCTION

Metal oxides are reactive to some gases and vapors. Zinc oxide and titanium dioxide are among the best-studied metal oxides, with applications that include heterogeneous catalysis, electronic devices, and chemical sensors. Examples of molecules that are known to react with metal oxide surfaces include water, alcohols, carboxylic acids, aldehydes, hydrogen sulfide, nitrogen dioxide and sulfur dioxide [1]. Metal oxide nanoparticles, with average sizes in the range of 10-100 nm, have the important property that

adsorption may affect their electronic and optical properties. In a recent study [2], we showed that reactions of nanoparticulate ZnO with NO<sub>2</sub> and SO<sub>2</sub> result in nitrate and sulfite adsorption, respectively. Chemisorption of these molecules alters the photoluminescence (PL) spectrum of the ZnO nanoparticles. Toward the ultimate goals of correlating PL changes with adsorption for possible sensor applications and modification of the optical, electronic properties (e.g., work function and surface states), and catalytic efficiencies of metal oxide nanoparticles and films, we are in the process of studying adsorption of other molecules, including thiols, on a variety of metal oxides. Some initial results are presented in this paper.

## 2 EXPERIMENTAL

Two types of experiments were performed. The first involved flowing gas through a Schwartz tube containing the metal oxide nanoparticle powder. This type of experiment was at atmospheric pressure. The second consisted of pressing the metal oxide powder onto a sample stub covered with vacuum-compatible, double-sided copper tape and installing it in a multi-chamber ultrahigh vacuum photoelectron spectrometer. The base pressure of the spectrometer was in the 10<sup>-10</sup> Torr range. After pump-down and transfer to the preparation chamber, the sample could be dosed with various gases, including methanethiol (MT), using variable leak valves. The dosing pressure was monitored with either an ionization gauge or Baratron transducer. After dosing, the sample could be transferred to the analysis chamber, and X-ray photoelectron spectroscopy (XPS) could be performed to determine whether adsorption had occurred. One complication of XPS of metal oxide powders is that surface charging may occur that shifts the apparent binding energies of the core level electrons to higher values. These were corrected by shifting all peaks the same amount such that one of them (e.g., the Zn2p peak) matched the known literature value.

## 3 RESULTS AND DISCUSSION

Zinc oxide is an interesting material in that it exhibits a bimodal PL spectrum, with the UV emission peak arising from excitonic recombination of an excited electron in the conduction band with a hole in the valence band. Visible emission originates from an excited electron that decays radiatively from a defect-related surface state to the valence

band. An example of how morphology affects the PL spectrum of nanoparticulate zinc oxide is shown in Figure 1. While the energy of the UV emission peak in both samples is essentially identical, the wavelength (and relative intensity) of the visible emission peak is different for nanospheres compared to nanorods. It is also noteworthy that the relative intensity of the visible peak for the higher surface area nanosphere sample is greater than that of the nanorod sample.

Photoluminescence Spectra of ZnO Nanorods and Nanospheres

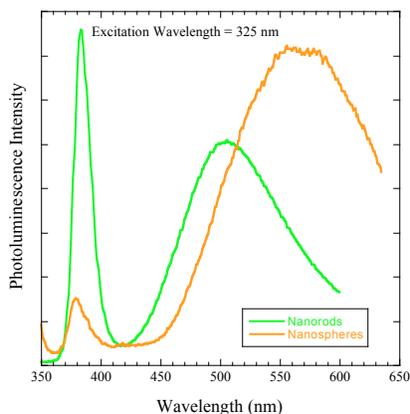


Figure 1: PL spectra of zinc oxide nanorods and 20-50 nm nanospheres. The excitation wavelength was 325 nm.

Previous research by our group has shown that thiols adsorb on zinc oxide surfaces via formation of Zn-S bonds [3]. Figure 2 shows how the PL spectrum of the nanosphere sample changes upon exposure to MT. This experiment was performed by packing ZnO nanorods (Nanocerox, Inc., 50-100 nm wide and 100-700 nm long) in a Suprasil tube that was installed in the sample compartment of a fluorometer operating in front-face reflection mode, with an excitation wavelength of 325 nm. The ZnO nanorods were held in place with a glass wool. Either dry nitrogen or MT could be flowed through the tube while fluorescence spectra were acquired. The gas flow rate was  $67 \text{ cm}^3/\text{min}$ . The following procedure was used: 1) dry nitrogen was flowed through the ZnO nanorod sample for 60 min. while monitoring photoluminescence; 2) the nitrogen gas flow was terminated, and MT was immediately flowed for 5 min.; 3) the MT flow was terminated, and nitrogen was flowed for 60 min. to purge the sample of physisorbed MT, during which time PL was monitored.

The key findings from this experiment are that drying the nanorods affects the PL spectrum by removing physisorbed water and increasing the UV peak intensity, but once dried, the intensity of the visible emission peak decreases relative to that of the UV one. This decrease in the relative intensity of the visible emission peak likely arises from adsorption of MT on defects (e.g., oxygen vacancies), which quenches defect-related emission. This is consistent with XPS measurements on the MT-exposed ZnO nanorod sample, which indicate S 2p signal at 163.3 eV.

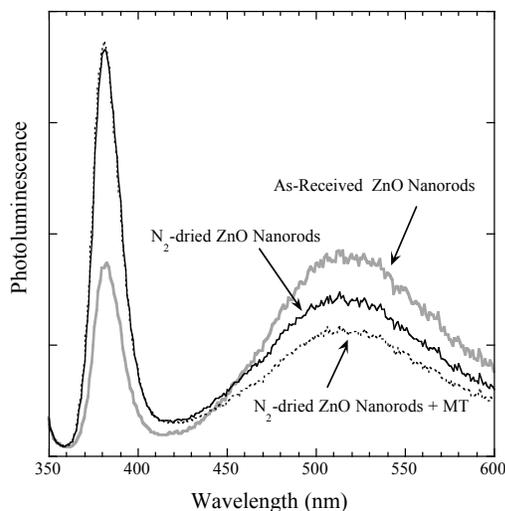


Figure 2: PL spectra of as-received ZnO nanorods, and the same sample after flowing dry nitrogen gas over it for 60 min, and a spectrum after flowing methanethiol (MT). The excitation wavelength was 325 nm. Modified from ref. [3].

Toward the goal of understanding whether thiol adsorption on ZnO is unique, screening experiments have been performed on a variety of as-received nanoparticulate metal oxides by exposing them to large doses of MT gas (0.1 Torr for several hours) or by flowing MT gas through a Schwartz tube containing the powder. XPS was used to assess adsorption. The overall conclusion from screening common metal oxide nanoparticles, including silicon oxide, zirconium oxide, aluminum oxide, and tungsten oxide is that non-negligible adsorption only occurs on titanium dioxide and zinc oxide.

Tungsten oxide presents an interesting situation. When MT gas is flowed through a Schwartz tube containing the powder, it changes from light green to dark green in color. XPS demonstrates that negligible adsorption occurs, however. It also shows that the powder is substoichiometric with respect to oxygen. The O:W ratio is equal to about 2.4 and changes negligibly following MT exposure. Research is ongoing to understand the details, but it appears that reduction of some of the  $\text{W}^{+6}$  to  $\text{W}^{+5}$  may be responsible for the color change, and this occurs with concomitant oxidation of methanethiol to dimethyldisulfide.

XPS experiments on CuO nanoparticles and on gold oxide nanoshells (made by exposing gold nanoshells to oxidizing agents such as ozone) show that methanethiol reduces the oxide, again with concomitant oxidation of the thiol. These results indicate that oxidation/reduction cycles may be carried out using ozone and methanethiol. Unlike tungsten oxide, however, these nanoparticles adsorb thiols following the (non-negligible) reduction. Gold nanoshell films, drop-cast onto quartz slides, undergo changes in their UV-vis absorbance spectra due to oxidation and then reduction by methanethiol. Possible sensor applications exist.

Because of the affinity of thiols for zinc oxide, it is possible to use dithiols to tether gold particles to ZnO nanorods, as we have previously demonstrated [4]. Figure 3 displays the process. The experiment was performed simply by stirring a colloidal suspension of the nanorods, the dithiol, and octanethiol-protected gold nanoparticles (3-4 nm). Attachment of one end of the dithiol to the nanorod occurs by Zn-S bond formation, and attachment to the gold nanoparticles takes place through a ligand place-exchange reaction. The surface concentration of gold nanoparticles can be varied by changing the molar ratios of the reagents.

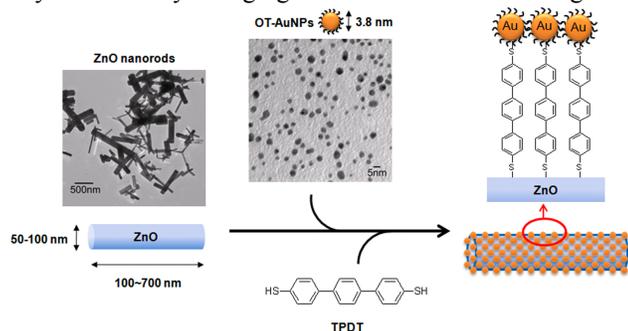


Figure 3: Dithiols, such as terphenyldithiol (TPDT), may be used to link gold nanoparticles to zinc oxide nanorods. The process is illustrated, along with transmission electron microscope images. From ref. [4].

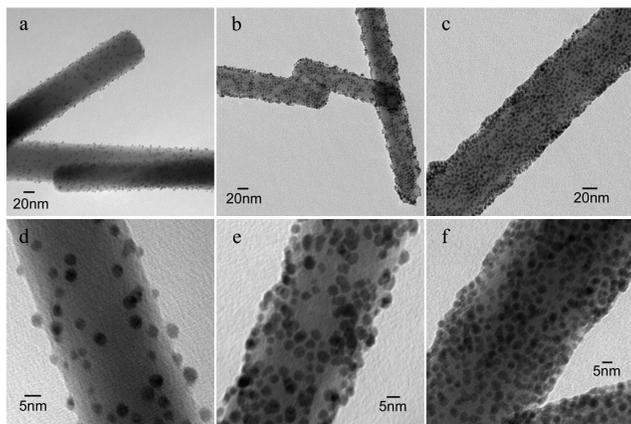


Figure 4: TEM images of gold nanoparticles tethered to zinc oxide nanorods using the methodology outlined in this manuscript. From ref. [4].

Figure 4 shows examples of the types of composites that can be made using this method, and Figure 5 demonstrates that these metal-decorated nanorods are photocatalytically active toward the decomposition of rhodamine B (RhB) dye. In this particular case, the nanocomposite materials were sintered at 400°C in air. This process decomposes/desorbs the ligands but causes minimal agglomeration, with the average particle size of the gold increasing to ca. 14 nm.

The photocatalysis experiment consisted of irradiating a cuvette filled with a 1.5 wt. % aqueous RhB solution and 0.8 mg of the nanocomposite powder with ca. 390 nm light while stirring. The optical power was 4.5 mW/cm<sup>2</sup>. The

absorbance of the solution was measured periodically. As shown in the figure, it decreased markedly as a function of irradiation time. A control experiment on a similar sample without the nanocomposite powder did not change its absorbance. Furthermore, control experiments on pure ZnO nanorods and unsintered nanocomposite material show that while they are photocatalytically efficient, they are not as efficient as the sintered sample. The likely reason for the enhancement is the reduced rate of electron-hole pair recombination due to the presence of gold particles on the ZnO surface.

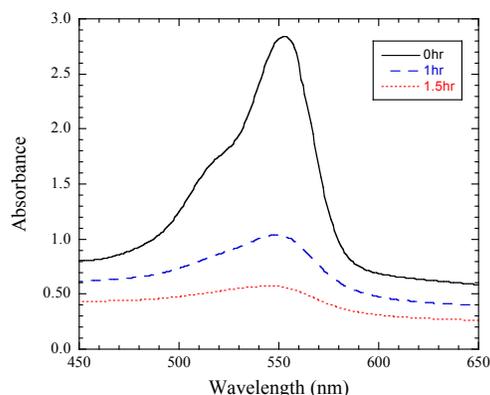


Figure 5: Absorbance spectra of a cuvette containing 1.5 wt. % aqueous rhodamine b before and after 1.0 and 1.5 hr irradiation with 380-400 nm light.

## 4 CONCLUSIONS

These studies demonstrate that the potential exists to monitor adsorption on photoluminescent metal oxide nanoparticles, such as ZnO, using fluorescence. It also shows that thiols bond to certain metal oxides, and in some cases reduce them, with concomitant formation of disulfide. Possibilities of forming advanced multifunctional materials exist, using dithiols as covalent linkers. Theoretical and experimental studies are underway to understand the details of thiol adsorption and reactions with metal oxide surfaces.

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