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14. ABSTRACT This final report describes fundamental surface chemistry studies of photoluminescent metal oxide nanoparticles, toward the goal of demonstrating that changes in photoluminescence (PL) may be correlated to adsorption. One application of this research is the use of PL as a residual life indicator for air filtration media. In addition to adsorption studies on metal oxide nanoparticles, experiments were also carried out on well-defined single crystal					
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Report Title

Surface Chemistry Studies Related to Residual Life Indicators

ABSTRACT

This final report describes fundamental surface chemistry studies of photoluminescent metal oxide nanoparticles, toward the goal of demonstrating that changes in photoluminescence (PL) may be correlated to adsorption. One application of this research is the use of PL as a residual life indicator for air filtration media. In addition to adsorption studies on metal oxide nanoparticles, experiments were also carried out on well-defined single crystal surfaces. Research focused on exposure of nanoparticulate zinc oxide, cerium oxide, tungsten oxide, and zirconium hydroxide to hydrogen chloride, sulfur dioxide, and nitrogen dioxide gases. Experiments were also performed with methanethiol. Correlation of PL measurements with surface science experiments demonstrated the feasibility of using fluorescence as an indicator of adsorption. It was demonstrated that sulfur dioxide at concentrations lower than 35 ppm may be detected by monitoring the PL of zinc oxide during gas exposure.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

At least one publication is in preparation.

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Anupama Mukherjee	0.25
FTE Equivalent:	0.25
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Jagdeep Singh	0.80
FTE Equivalent:	0.80
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
James Whitten	0.07	No
FTE Equivalent:	0.07	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PhDs

<u>NAME</u>

Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Sandip Sengupta	0.00	No
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FTE Equivalent:	0.00
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Total Number:	1
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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Surface Chemistry Studies Related to Residual Life Indicators

Final Report (Submitted March 20, 2011)

Submitted by: Prof. James E. Whitten (University of Massachusetts Lowell)

Introduction

This final report describes fundamental surface chemistry studies of photoluminescent metal oxide nanoparticles, toward the goal of demonstrating that changes in photoluminescence (PL) may be correlated to adsorption. One application of this research is the use of PL as a residual life indicator for air filtration media. In addition to adsorption studies on metal oxide nanoparticles, experiments were also carried out on well-defined single crystal surfaces. This nine-month STIR project officially began on April 1, 2010 and ended Dec. 31, 2010.

Research focused on exposure of nanoparticulate zinc oxide, cerium oxide, tungsten oxide, and zirconium hydroxide to HCl, NO₂, and SO₂ gases. Experiments were also performed with methanethiol, CH₃SH. Correlation of PL measurements with surface science experiments demonstrated the feasibility of using fluorescence as an indicator of adsorption. It was demonstrated that sulfur dioxide at concentrations lower than 35 ppm may be detected by monitoring the PL of zinc oxide during gas exposure.

Summary of Reactivity Based on XPS and TGA

Most of the experiments were carried out by diluting a reactive gas (e.g, SO₂, NO₂, HCl) with nitrogen, such that the reactive-to-inert carrier gas was ratio was 1:5 by volume. The gas mixture was flowed through a glass Schwartz tube (**Figure 1**) packed with the metal oxide to be tested. Fluorescence measurements, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA) were subsequently performed after removal of the powder from the tube. This procedure allowed a number of gases and metal oxides to be conveniently tested, with the entire apparatus contained in a fume hood.

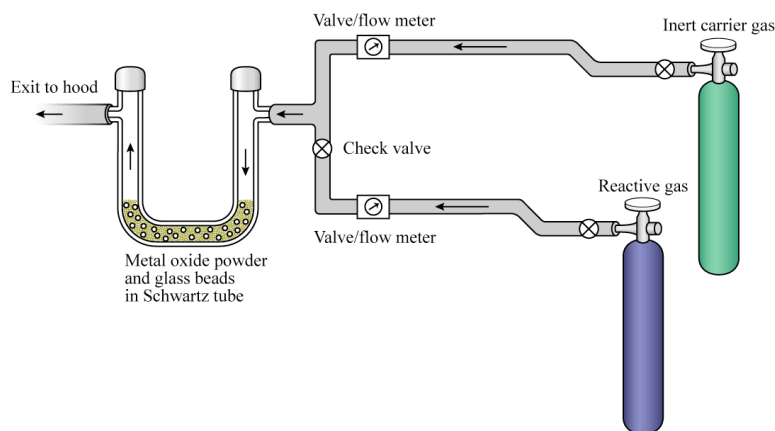


Figure 1: Apparatus used to flow reactive/inert gas mixtures over metal oxide powders.

Based on XPS and TGA, it is concluded that nanoparticulate zinc oxide (average diameter of 20 nm) reacts with HCl to form zinc chloride. The reaction is exothermic, and water is a by-product, as concluded from observations that the outside of the Schwartz tube gets hot during the reaction, and droplets of water appear on the inside of the tube. A zinc-terminated single crystal

Zn(0001) sample was also sputter-cleaned in ultrahigh vacuum and exposed to HCl gas. XPS of the surface revealed ZnCl on top of ZnO, consistent with the nanoparticle studies.

Exposure of as-received nano-ZnO to nitrogen dioxide and sulfur dioxide leads to adsorbed NO₃ and SO₃ (or possibly SO₄), as indicated by XPS measurements (**Figure 2**) that show high binding energy N1s and S2p peaks at ca. 407 and 169 eV, respectively. Strong bonding is suggested by XPS heating studies and TGA. In the case of the SO₂-exposed sample, XPS shows the S/Zn atomic ratio to be constant at 0.15±0.03 at room temperature and after heating to 100 and 200°C. Heating to 260°C decreases this value to 0.09. For the NO₂-exposed sample, the N/Zn atomic ratio is 0.92 ± 0.03 at room temperature and after heating to 100°C. This ratio decreases to 0.82 and 0.34 after heating to 200 and 260°C. In both cases, substantial desorption, with concomitant decreases in S- and N-containing molecular species, only occurs after heating to 260°C. The XPS atomic ratios indicate that approximately six times more NO₂ is adsorbed on nano-ZnO compared to SO₂. Thermal gravimetric analysis data, shown in **Figure 3**, are consistent with these conclusions. The weight loss associated with NO₂ desorption from ZnO is 5 to 6 times greater than that due to SO₂ desorption. Furthermore, in both cases, the greatest weight loss occurs above 200°C. Transmission electron microscopy shows that the morphology of the nano-ZnO changes upon NO₂ exposure, with decomposition and dissolution of the particles. This accounts, at least in part for the greater NO₂ adsorption, due to the larger resulting surface area.

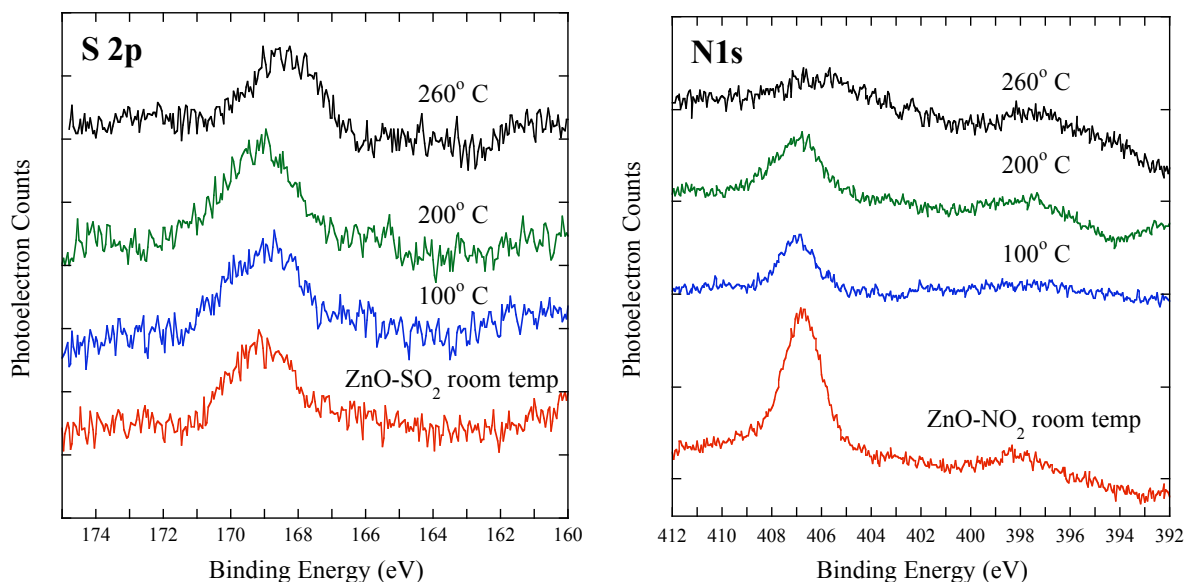


Figure 2: MgK α XPS of the S2p and N1s regions of SO₂ and NO₂ exposed ZnO. Spectra are also included after heating in a vacuum oven at the indicated temperatures for one hour.

In the case of exposure of nano-cerium oxide (30-50 nm diameter) to these gases, it is observed that NO₃ and SO₃ (and possibly SO₄) species are adsorbed, similar to ZnO reactivity. TGA indicates that SO₃ (ads) is more strongly bound than NO₃ (ads), as shown in **Figure 3**. For nanoparticulate tungsten oxide (WO₃) having an average diameter of 30 nm, XPS and TGA demonstrate essentially no reactivity. Therefore, it is concluded that the order of reactivity is nano-ZnO > nano-CeO₂ >> nano-WO₃.

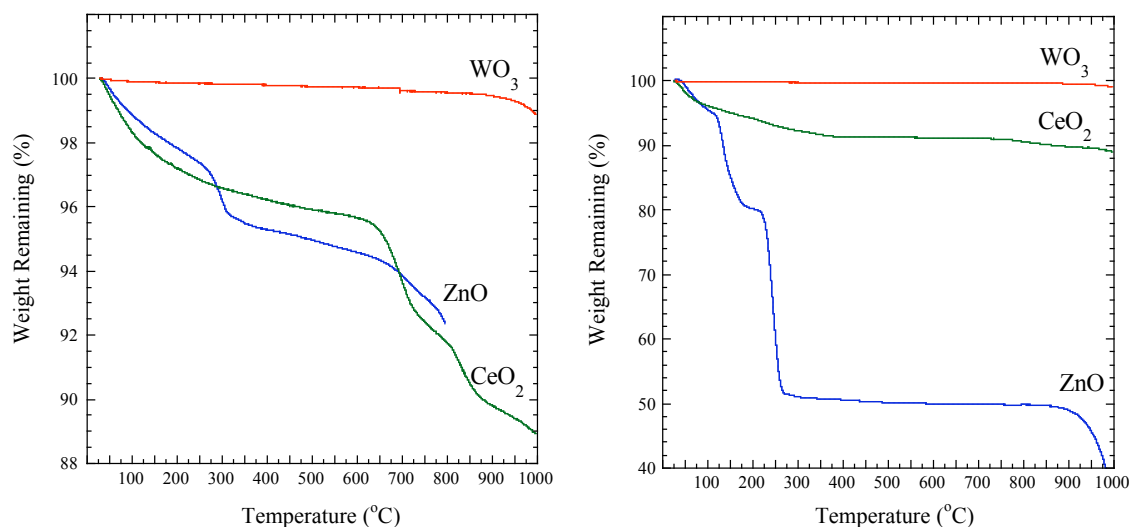


Figure 3: Thermal gravimetric analyses of SO₂ (left panel) and NO₂ (right panel) exposed nanoparticulate zinc oxide.

The role that adsorbed water plays in reactivity was investigated by drying nano-zinc oxide in a vacuum oven at 200°C to drive off physisorbed water. Comparison experiments were run on nano-ZnO that had been allowed to sit overnight in a container filled with air saturated with water vapor. This ZnO is referred to as "hydrated ZnO". For both SO₂ and NO₂ reactivity, it was found that drying decreased the reactivity, and hydration increased the reactivity, compared to as-received ZnO. In the case of sulfur dioxide, the S/Zn atomic ratios after exposure is 0.11 and 1.3 for the dried and hydrated samples, respectively. The corresponding N/Zn values for nitrogen dioxide exposure are 0.20 and 0.40. These data confirm that hydroxyl groups and/or physisorbed water lead to enhanced reactivity of nanoparticulate ZnO with respect to SO₂ and NO₂.

Some experiments have also been performed for reaction with methanethiol. Surprisingly, a dramatic color change of nano-WO₃ powder from yellow to bluish gray is observed upon exposure to this gas. XPS and TGA, however, indicate no adsorption. It is postulated that methanethiol reduces the WO₃ powder and that the color change is due to a reduction in stoichiometry from WO₃ to WO_x, with $x < 3$. So far, XPS has not succeeded in reproducibly confirming this. Further experiments should be performed to understand this interesting result, including mass spectrometric detection of possible oxidized methanethiol fragments.



Figure 4: Photograph of as-received nanoparticulate tungsten oxide before (left) and after (right) exposure to methanethiol gas. CH₃SH exposure causes the powder to appear darker.

Changes in Photoluminescence

A goal of this project is to correlate surface reactions with changes in photoluminescence of nanoparticulate metal oxides. For ZnO, which displays a bimodal PL spectrum having both visible and UV emission peaks, reaction with HCl causes both peaks to disappear. Reactions with SO₂ and NO₂ result in dramatic changes in the ratios of these emission peaks, as shown in **Figure 5, left panel**. In both cases, the UV emission peak (at ca. 380 nm) becomes less pronounced. Adsorption of SO₂ and NO₂ leads to a decrease and an increase, respectively, in the intensity of the visible emission peak. The reasons for these differences are not yet fully understood but may be related to the greater amount of NO₂ adsorbed, as discussed earlier. For CeO₂ (included in **Figure 5, right panel**) only a broad UV emission peak (at ca. 360 nm) due to 290 nm excitation is observed, and the shape and intensity of this peak change upon exposure to the three gases.

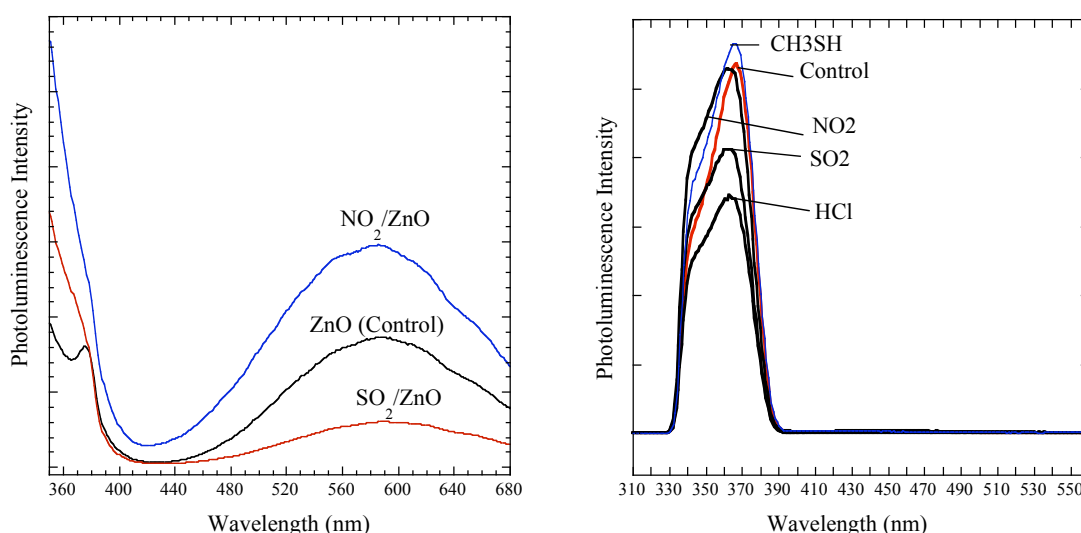


Figure 5: Left panel: Photoluminescence spectra of ZnO nanoparticles after exposure to SO₂ and NO₂. The excitation wavelength is 325 nm. Right panel: Photoluminescence spectra of CeO₂ nanoparticles after exposure to various gases. The excitation wavelength is 290 nm.

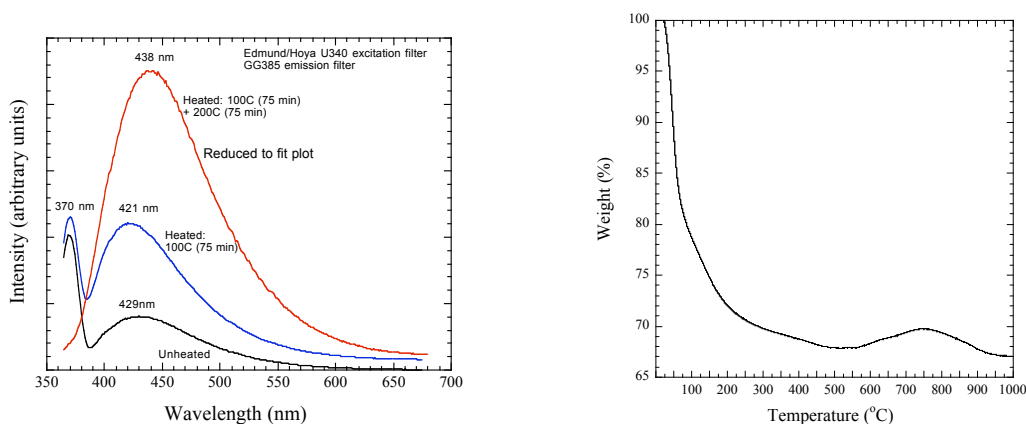


Figure 6: Photoluminescence spectra (left panel) of nano-zirconium hydroxide powder before and after heating at 100 and 200°C for 75 minutes (left panel); TGA spectrum (right panel) of nano-zirconium hydroxide, indicating continuous hydroxyl group desorption during heating from room temperature to 1000°C.

Photoluminescence results for zirconium hydroxide powder (provided by ECBC) indicate strong PL emission of ultraviolet and blue light. **Figure 6 (left panel)** depicts the spectra for the as-received (unheated) powder and those resulting from heating at 100 and 200°C in a vacuum oven. Heating at these temperatures causes desorption of hydroxyl groups, as confirmed by TGA (**Figure 6, right panel**). It is interesting that the UV peak disappears upon heating, while the blue peak increases dramatically. **Figure 7** displays spectra obtained after exposure of hydrated $\text{Zr}(\text{OH})_4$ to SO_2 and NO_2 . In both cases, the intensities of the UV and visible emission peaks decrease. Note that the ratio of the visible and UV emission peaks could be monitored as an indicator of adsorption.

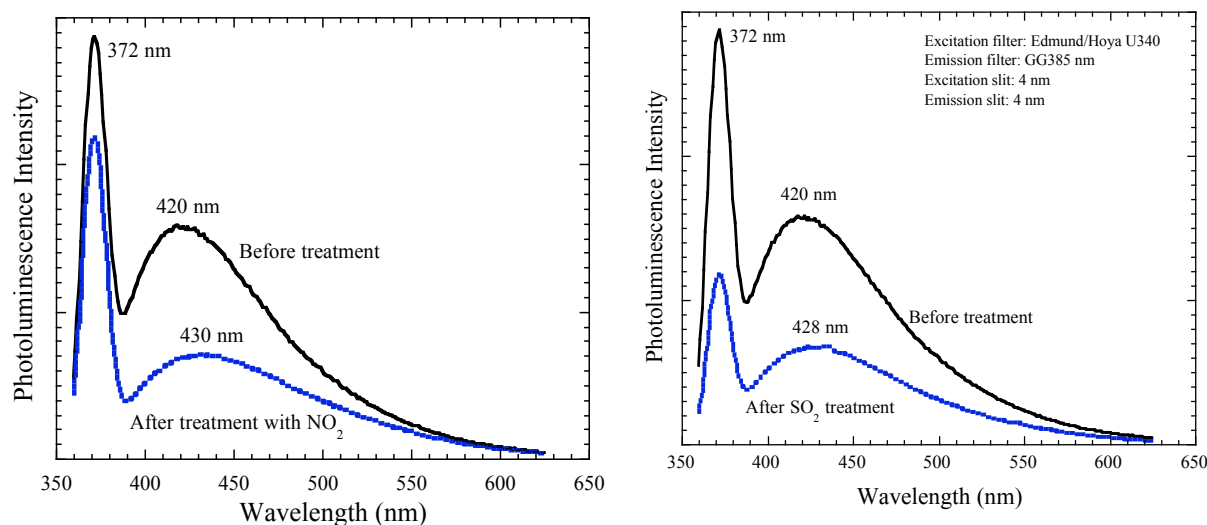


Figure 7: Photoluminescence spectra of hydrated nanoparticulate zirconium hydroxide exposed to nitrogen dioxide (left panel) and sulfur dioxide (right panel).

In order for changes in photoluminescence of metal oxides to be useful for residual life indicator applications, it is important that they be quantified for exposure to low concentrations of reactive gases. Most of the studies that we performed in the STIR project were at very high concentrations toward the goal of correlating adsorption with changes in the PL spectrum. These experiments were typically carried out by diluting a reactive gas (e.g., SO_2 , NO_2 , HCl) with nitrogen, such that the reactive-to-inert carrier gas was ratio was 1:5 by volume. They were performed by flowing the gas mixture through a Schwartz tube (**Figure 1**) packed with the metal oxide to be tested. Fluorescence measurements, XPS, and thermogravimetric analysis (TGA) were subsequently performed after removal of the powder from the tube. This procedure allowed a number of gases and metal oxides to be conveniently tested, with the entire apparatus contained in a fume hood. However, this methodology did not allow PL changes to be measured in real-time. A preliminary experiment using significantly lower concentrations was performed in which PL was measured, as a function of exposure time, by carrying out in-situ PL measurements using a flow tube installed in a fluorometer. The in-situ flow cell setup consisting of a Suprasil tube (4 mm inner diameter) installed in the sample chamber of a fluorometer. SO_2 at a concentration of 35 ppm was delivered to the flow cell, filled with nanoparticulate zinc oxide (ca. 10 nm dia.), using a commercially available gas permeation source (installed in a glass bottle) immersed in a 40°C constant temperature water bath. **Figure 8** shows data obtained from this study. Exposure

of the ZnO to this gas mixture for 90 minutes caused a decrease in intensity of the visible emission peak and an increase in intensity of the UV peak. Longer exposure (e.g., 260 min) caused almost complete disappearance of the visible peak.

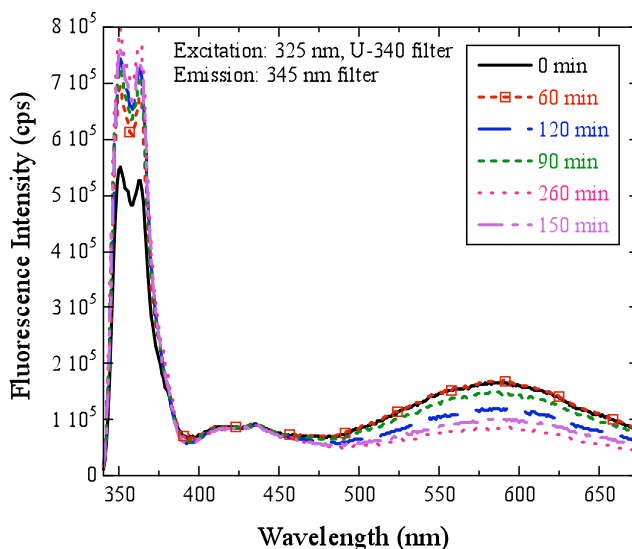


Figure 8: In-situ photoluminescence spectra (left panel) of zinc oxide nanopowder as a function of time obtained by flowing 35 ppm SO₂ gas over the powder.

These data demonstrate that the PL spectrum of nanoparticulate ZnO is sensitive to low concentrations of SO₂. It should further be noted that the experiment represented in **Figure 8** only interrogated the center portion of the volume of ZnO powder in the tube. Faster response times would be observed if the fluorescence measurements were to interrogate the entire volume of powder exposed to the gas. Future work will use an improved in-situ PL flow cell in which fluorescence of the entire volume of metal oxide powder will be monitored.

Summary

Funding from this STIR project has successfully demonstrated that photoluminescence changes occur in nanoparticulate ZnO, CeO₂, and Zr(OH)₄ upon exposure to hydrogen chloride, sulfur dioxide, and nitrogen dioxide gases. Some experiments were also performed with methanethiol. For ZnO, it was shown that exposure to moisture increased the uptake of the gases. Most of the gas exposure experiments were performed by flowing high concentrations (16% by volume) of reactive gases over metal oxide or metal hydroxide particles. However, it was also shown that ZnO undergoes distinct changes in photoluminescence upon exposure to just 35 ppm of sulfur dioxide. Surface science experiments, including X-ray photoelectron spectroscopy, demonstrated correlation of reactivity and adsorption with the PL changes.

These results indicate that in-situ monitoring of photoluminescence could be used for residual life indication for filtration monitoring. Future research, if funded, will study changes in PL with respect to particle size, sintering temperature, and coadsorbed water. Electron microscopy, X-ray photoelectron spectroscopy, and thermal gravimetric analysis will be performed to correlate adsorption to the PL changes, and fluorescence studies will be coupled with ultraviolet photoelectron spectroscopy measurements of the energies of occupied electronic states toward the goal of understanding adsorbate-induced PL changes. Photoluminescent

nanoparticles could also be incorporated into ASZM-TEDA filter beds, and PL at different locations could be measured and correlated with residual filtration capacity. A quartz cell could be constructed for single wavelength fluorescence measurements along its length using ultraviolet light-emitting diodes and photodiode detectors. This cell would permit simultaneous PL and breakthrough measurements. These studies would permit the full potential of the PL method of monitoring residual life of filters to be evaluated.

Funded Personnel

This work at UMass Lowell has been performed by Dr. Jagdeep Singh (part-time postdoctoral), Anupama Mukherjee (graduate student), Sandip Sengupta (senior scientist), and Prof. James Whitten.