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14. ABSTRACT
How surface chemistry can modify the electronic properties of metal oxide semiconductor nanomaterials relevant to improving sunlight driven military technologies was investigated. Photoluminescence was used to probe the surface band-bending of TiO2 nanoparticles to help identify properties that can control the flow of charge to the semiconductor surface. First, the effects of oxygen exposure on band-bending induced by both healing defects at the surface and molecular chemisorption were studied. Second, probing the band-bending of the TiO2 surface under

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Report Title

Final Report: Controlling the Efficiency of Semiconductor-TiO2 for Sunlight-driven Technologies for Military Needs

ABSTRACT

How surface chemistry can modify the electronic properties of metal oxide semiconductor nanomaterials relevant to improving sunlight driven military technologies was investigated. Photoluminescence was used to probe the surface band-bending of TiO2 nanoparticles to help identify properties that can control the flow of charge to the semiconductor surface. First, the effects of oxygen exposure on band-bending induced by both healing defects at the surface and molecular chemisorption were studied. Second, probing the band-bending of the TiO2 surface under the influence of gases with different electron accepting and donating strengths revealed that band-bending at the surface modulates electron trapping into gold nanoparticles at the surface, when present. Electron donation from the TiO2 surface to gold particles has been shown to be critical in the reactivity of Au/TiO2 nanoparticle catalysts and our ability to measure band-bending at the surface aids in understanding how catalysts might be more optimally doped with intrinsically enhanced upward or downward band-bending. Third, the electron mobility changes in TiO2 nanopowder decorated with conductive carbon nanotubes concluded fruitful studies on the effect of surface conductors on charge recombination. Finally, the role that free carriers and neutral donors play in producing visible emission from ZnO nanoparticles was more fully elucidated.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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

Received		Paper
08/18/2014	1.00	Ana Stevanovic, John T. Yates. Electron Hopping through TiO2 Powder: A Study by Photoluminescence Spectroscopy, The Journal of Physical Chemistry C, (11 2013): 0. doi: 10.1021/jp407765r
08/18/2014	2.00	Shiliang Ma, Ana Stevanovic, John T. Yates. Effect of Gold Nanoparticles on Photoexcited Charge Carriers in Powdered TiO2-Long Range Quenching of Photoluminescence, The Journal of Physical Chemistry C, (08 2014): 0. doi: 10.1021/jp507156p
08/18/2014	3.00	Zhen Zhang, John T. Yates. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces, Chemical Reviews, (10 2012): 0. doi: 10.1021/cr3000626
08/18/2014	4.00	John T. Yates. Electron stimulated desorption, DIET, and photochemistry at surfaces: A personal recollection, The Journal of Chemical Physics, (09 2012): 0. doi: 10.1063/1.4746798
08/18/2014	5.00	Petro Maksymovych, Dan C. Sorescu, Oleksandr Voznyy, John T. Yates. Hybridization of Phenylthiolate- and Methylthiolate-Adatom Species at Low Coverage on the Au(111) Surface, Journal of the American Chemical Society, (04 2013): 0. doi: 10.1021/ja4000905
08/26/2015	8.00	Ana Stevanovic, Shiliang Ma, John T. Yates. Photoexcited Electron Hopping between TiO2 Particles- Effect of Single-Walled Carbon Nanotubes, The Journal of Physical Chemistry C, (10 2014): 23614. doi: 10.1021/jp508061w
08/26/2015	9.00	Monica McEntee, Ana Stevanovic, Wenjie Tang, Matthew Neurock, John T. Yates. Electric Field Changes on Au Nanoparticles on Semiconductor Supports – The Molecular Voltmeter and Other Methods to Observe Adsorbate-Induced Charge-Transfer Effects in Au/TiO, Journal of the American Chemical Society, (02 2015): 1972. doi: 10.1021/ja511982n

TOTAL: **7**

Number of Papers published in peer-reviewed journals:

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

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

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

Received	Paper

TOTAL:

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

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

Received	Paper

TOTAL:

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

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Shiliang Ma	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Matthew Reish	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Ian Harrison	0.09	
FTE Equivalent:	**0.09**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
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

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report: Controlling the Efficiency of Semiconductor-TiO_2 for Sunlight-driven Technologies for Military Needs

July 2016

I. Foreword

During this support period we have further expanded on the theory and techniques developed previously. New instrumentation designed and built during this period further expanded the unique capabilities available in our lab. Also during this period ARO supported PhD student Ana Stevanovic graduated and found employment at the National Institute of Standards and Technology (NIST). ARO supported postdoc Matthew Reish will also move on to another Army supported position at AMRDEC, bringing surface science experience learned under this ARO project to a new project.

Sadly, during this period the project's PI, John T. Yates Jr., became ill and passed away. During an extraordinary research career Professor Yates accomplished more than can be listed here, placing him into the upper echelons of scientific accomplishment. He also inspired all those he mentored with his passion for understanding difficult scientific problems with careful experimentation and clear communication. His long and fruitful support from ARO led to many important results that will continue to further the ARO mission and make a lasting positive impact on this world.

II. Statement of Problems Studied

Band bending at a semiconductor surface is an important driver for making free charges available at the surface. Controlling the sign and magnitude of this band bending determines the type (hole or electron) and concentration of the charges at the surface.[1] These surface charges can then be used to perform oxidation or reduction reactions on surface adsorbates. These reactions have a wide range of practical applications including photoelectrochemical cells, photochemical decomposition of unwanted chemicals, and energy storage.

Under previous ARO support our group has developed the ability to use photoluminescence (PL) intensity from TiO_2 nanoparticles to detect the relative band bending at the TiO_2 surface and measure the interparticle hopping rate.[2,3] Over this support period we used this technique to study the effect of interparticle linkers which have been hypothesized to increase the hopping rate between particles. The two linkers studied were gold nanoparticles and single walled carbon nanotubes.

Additional applications of the ability to measure both PL intensity and IR absorbance in the study of metal oxide electronics under high vacuum and applications of the developed theories were also discovered. The use of simultaneous PL and IR spectroscopies in the study of visible emission in annealed zinc oxide have revealed a wealth of information about the mechanism of emission. Continuation of this work will focus on enhancement of the PL using the insights gained into the mechanism of the visible PL with the goal of generating low-cost and non-toxic visible phosphors of interest in lighting applications.

III. Summary of Important Results

a. Effect of Gold Nanoparticles on Photoexcited Charge Carriers in Powdered TiO2−Long Range Quenching of Photoluminescence

TiO_2 particles were decorated with a low coverage of gold nanoparticles with intent of enhancing the interparticle charge hopping rate which can be measured by the decrease in PL over time after gold/TiO_2 UV exposure is halted.[2,4] However we found that in gold/TiO2 there is a complete quenching of the TiO_2 defect luminescence. Figure 1 shows the development of PL over time in both neat (red) and covered with gold TiO_2 nanoparticles (black).

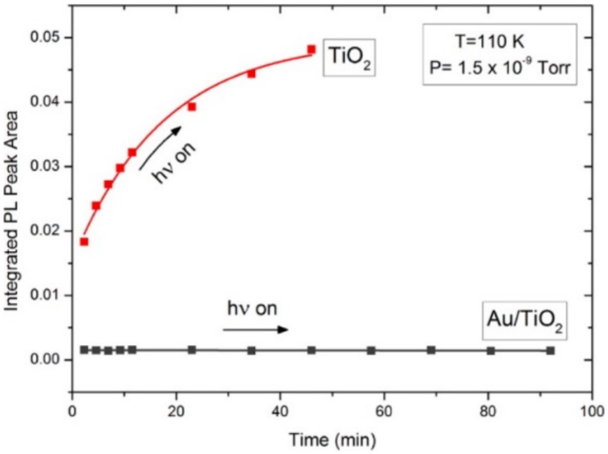

Figure 1. Integrated PL intensity during UV exposure of TiO_2 (red) and Gold/TiO_2 (black).

In this case resonance energy exchange between the gold plasmon and the TiO_2 emission can be ruled out because of the lack of plasmonic absorption in the gold/TiO_2 sample.[5] Photoluminescence quenching occurs as a result of photoexcited electron transfer from TiO_2 to gold nanoparticles. However, the continuous quenching of PL suggests that the electron transferred into Au must recombine with a hole in TiO_2 across the interface. The short-circuit with photoexcited electrons transfering to Au and electron hole recombination across the Au/TiO_2 interface causes the continuous quenching of PL, as shown in Figure 2.

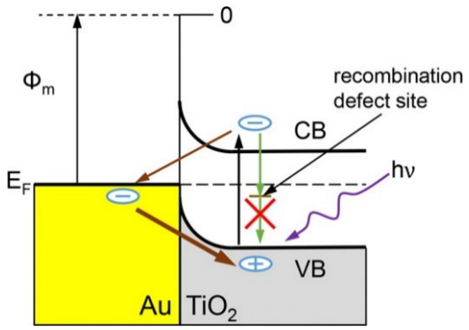

Figure 2. Schematic of the short-circuit which quenches TiO_2 photoluminescence when the gold nanoparticles are deposited on the surface.

By identifying the surface coverage of gold we can also determine the minimum trap distance of the gold particles to completely withdraw photoexcited electrons from TiO_2. Our calculation shows that Au nanoparticles can withdraw electrons from at least 4 nm beyond the Au nanoparticle boundary. This shows that gold particles on the TiO_2 surface have a relatively long range interaction with excited electrons and even at low coverages gold particles can effectively trap electrons and separate them from holes.

Peer Reviewed Report of these Results: Stevanovic, A., Ma, S. and Yates Jr, J.T., 2014. Effect of Gold Nanoparticles on Photoexcited Charge Carriers in Powdered TiO_2− Long Range Quenching of Photoluminescence. *The Journal of Physical Chemistry C*, *118*(36), pp.21275-21280.

b. Photoexcited Electron Hopping between TiO_2 Particles: Effect of Single-Walled Carbon Nanotubes

One design challenge in TiO_2 photovoltaics is the low mobility rate of charges though nanopowders which can hamper device performance.[6] We proposed to create interconnections between TiO_2 by the addition of conducting single walled carbon nanotubes (SWNTs) to the TiO_2 surface. The mobility of electrons in SWNT is $\sim 10^8$ m^2 V^{-1} s^{-1}, and this high conductivity makes SWNTs a likely candidate for increasing charge hopping rates.[7] In this study we mixed samples with 1, 3, and 5% carbon nanotubes by weight with P25 TiO_2 with an SEM micrograph of the 5% sample shown in figure 3.

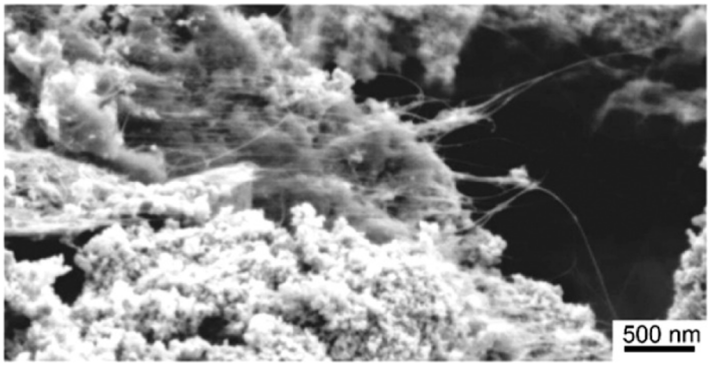

Figure 3. SEM micrograph of 5 wt % SWNT/TiO_2 composite

When measuring the charging and discharging of PL intensity under UV exposure we found two important factors which describe the charge hopping process in the SWNT/TiO_2 composites. First, SWNTs exhibit electron accepting behavior as the PL intensity of SWNT/TiO_2 composites systematically decreases with increase of the fraction of SWNTs mixed into the TiO_2 powder. The fractional decrease in PL intensity is proportional to the average number of SWNT/TiO_2 contact points in the first-layer of TiO_2. Second, the PL charging/discharging rate of all SWNT/TiO_2 mixtures is identical to that of pure TiO_2 (Figure 4), indicating that SWNTs only accept photoexcited electron from TiO_2 but do not transport electrons under conditions of the experiment. This is due to the effect of positively charged TiO_2 particles due to charge separation (i.e. electron injection into SWNTs) which immobilize the photoexcited electrons transferred to SWNTs at the interface between first-layer TiO_2 and SWNTs, inhibiting charge transport through SWNT channels.

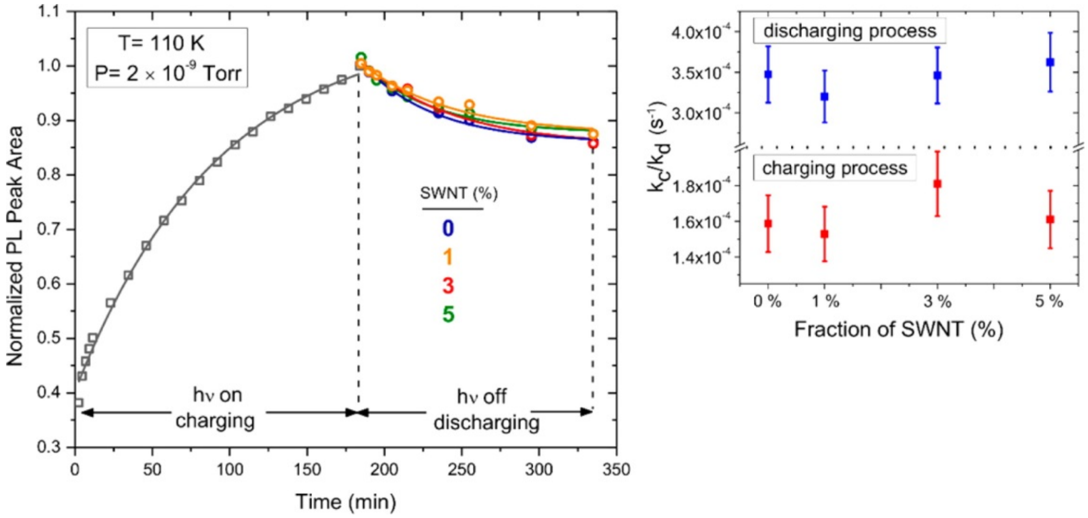

Figure 4. Charging and discharging curves neat of SWNT intercalated TiO$_2$ nanoparticles. While the final PL intensity of different coverages varies the charging and discharging rates are the same within error.

Peer Reviewed Report of these Results: Stevanovic, A., Ma, S. and Yates Jr, J.T., 2014. Photoexcited Electron Hopping between TiO$_2$ Particles: Effect of Single-Walled Carbon Nanotubes.*The Journal of Physical Chemistry C*, *118*(41), pp.23614-23620.

c. Band Bending at the Surface Affects the Potential and of Electrons in Gold Deposited on TiO_2

Gold/TiO_2 is also an important substrate material for several important catalytic reaction including water-gas shift and CO oxidation.[8] The activity of the catalyst has been shown to be highly dependent on the charge state of the gold particles which is in turn influenced by band bending of the TiO_2 supports as shown in Figure 5.[5]

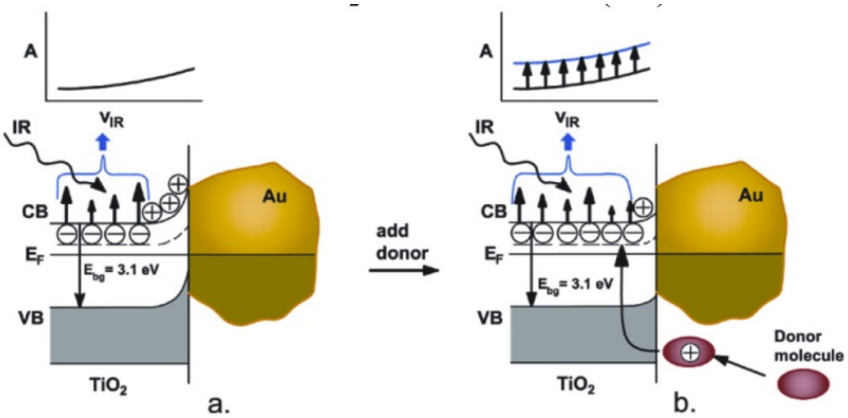

Figure 5. The band bending effect of adsorbed molecules on TiO_2 influence the charge state and electron potential of gold deposited on TiO_2.

Recent work in our group has used CO as a reporter for the charge state of gold and we have found that the reversible adsorption of donor or acceptor molecules shifts the vibrational frequency of the adsorbed CO molecules in opposite directions.[9] The determination of band bending by the PL method on nano gold TiO_2 with same donor (alkane) and acceptor (sulfur hexafluoride) molecules was also performed to show that band bending at the TiO_2 surface could be used to explain the change in gold charge. The results of this study for propane and sulfur hexafluoride are shown in Figure 6. The adsorption of the donor molecule, propane, decreases the band bending as indicated by the increase in PL while for the acceptor molecule, sulfur hexafluoride, the opposite effect is noted.

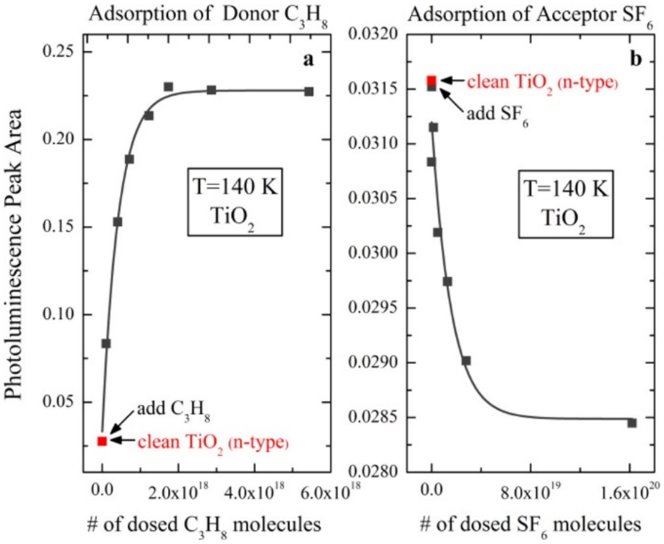

Figure 6. Opposite effects of van der Waals bound donor-C_3H_8 and acceptor-SF_6 molecules on the magnitude of PL intensity. (a) The results indicate that donor-C_3H_8 molecules reduce upward band bending in n-type TiO_2, causing an increase in PL intensity. (b) Conversely, acceptor-SF_6 molecules enhance upward band bending in n-type TiO_2, causing a decrease in PL intensity.

Peer Reviewed Report of these Results: McEntee, M., Stevanovic, A., Tang, W., Neurock, M. and Yates Jr, J.T., 2015. Electric Field Changes on Au Nanoparticles on Semiconductor Supports–the Molecular Voltmeter and Other Methods to Observe Adsorbate-Induced Charge-Transfer Effects in Au/Tio2 Nanocatalysts.*Journal of the American Chemical Society*, *137*(5), pp.1972-1982.

d. The Effect of Free Charges on PL Intensity in ZnO

The development of PL and IR spectroscopy for the application to polar metal oxide electronics also helped clarify the role of free charges in the defect emission of zinc oxide. It is well known that high temperature annealing of zinc oxide can create intrinsic defects which act as recombination centers and generate highly efficient visible emission. However details of the emission mechanism in annealed zinc oxide are not well understood.[10]

IR spectroscopy of polar metal oxides can be used to measure the concentration of high-mobility free or polaronic electrons generated by intrinsic defects by the drude metallization of the oxide with leads to low frequency IR absorption with a characteristic power-law band shape. Much of the pioneering work on TiO_2 defect electron detection by IR was completed in the Yates lab and this technique gives us a unique tool for understanding the relation between intrinsic defects and PL.[11] Simultaneous transmission IR absorption and PL during stepwise annealing revealed that free electron concentration rises in ZnO at annealing temperature below 1000 K indicating oxygen loss.[12] However this free electron increase is not accompanied by a rise in PL intensity. At annealing temperatures above 1000 K the free electron concentration begins to fall with an inverse rise in the PL as shown in Figure 7.

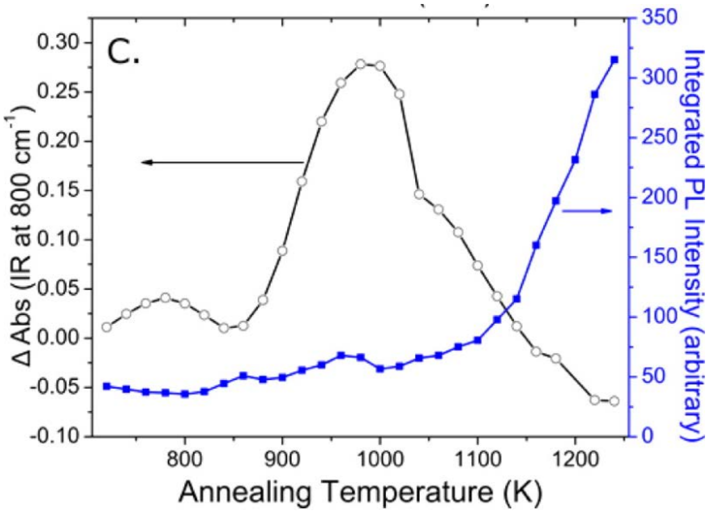

Figure 7. IR background absorption (black) and integrated PL intensity (blue) during stepwise annealing of ZnO nanoparticles. The IR background signal is proportional to the free electron concentration and has an inverse relationship with the PL intensity.

Exposure of the annealed samples to hole (methanol) and electron (O_2) scavengers shows that free charges have an influence on PL intensity and free electron concentration in high temperature annealed ZnO. The top section of Figure 8 shows the change in the normalized PL in vacuum and then under different pressures of methanol (black) and O_2 (red) and the bottom shows the change in IR absorbance during the same experiment, which is which is propotional to the free electron concentration. Initially in vacuum there is a decrease in PL intensity but when exposed to hole scavenging methanol there is strong increase in PL intensity accompanying an increase in free electron concentration. Electron scavenging O_2 significantly decreases the electron concentration but has only a minor effect on PL efficiency. These results suggest that free holes quench PL intensity in annealed ZnO and the removal of hole buildup likely generates more efficient PL.

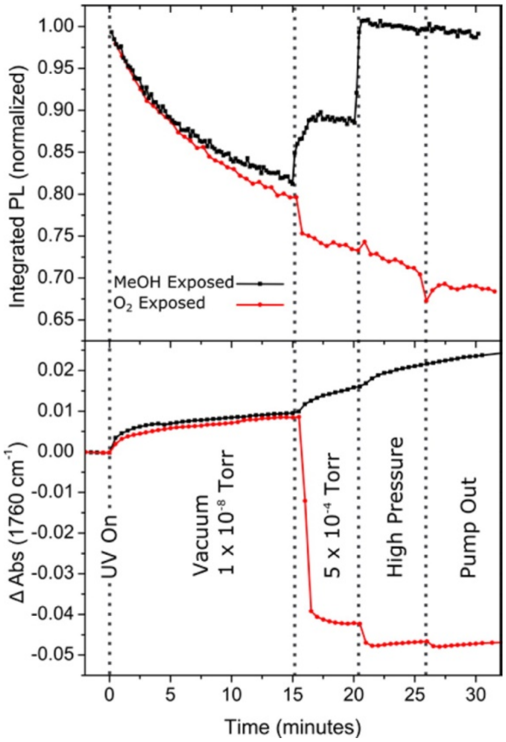

Figure 8. Top: Normalized integrated PL in vacuum and during exposure to labeled pressures of O_2 (red) and methanol (black). Bottom: Differential absorbance at 1760 cm^{-1} during exposure to UV light and charge scavengers (same conditions as top)

Rather than band bending, which plays a dominant role in PL intensity changes in TiO_2, we suggest that the buildup of holes in ZnO is effective at removing the excited intermediate that leads to PL, namely the donor bound exciton. Neutral donor bound excitons, with no available ionized states, have previously been shown to be important intermediates for visible emission in ZnO and we therefore suggest that free holes act to effectively ionize donor bound excitons and therefore remove an efficient path for the creation of visible emitting states. The insights garnered from this work suggest that passivating the surface with a hole extracting layer may serve to enhance PL efficiency. Work on ZnO particles coated in a hole-extracting ZnS layer is underway.

Peer Reviewed Report of these Results: Reish, M.E., Zhang, Z., Ma, S., Harrison, I. and Everitt, H.O., 2016. How Annealing and Charge Scavengers Affect Visible Emission from ZnO Nanocrystals. *The Journal of Physical Chemistry C*, *120*(9), pp.5108-5113.

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Changes on Au Nanoparticles on Semiconductor Supports – The Molecular Voltmeter and Other Methods to Observe Adsorbate-Induced Charge-Transfer Effects in Au/TiO2 Nanocatalysts. *J. Am. Chem. Soc.* **2015**, *137*, 1972–1982.

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(12) Reish, M. E.; Zhang, Z.; Ma, S.; Harrison, I.; Everitt, H. O. How Annealing and Charge Scavengers Affect Visible Emission from ZnO Nanocrystals. *J. Phys. Chem. C* **2016**, *120*, 5108–5113.