Effects of Exposure to Staphylococcus Aureus on Excitonic Luminescence of Nano- and Microcrystalline ZnO

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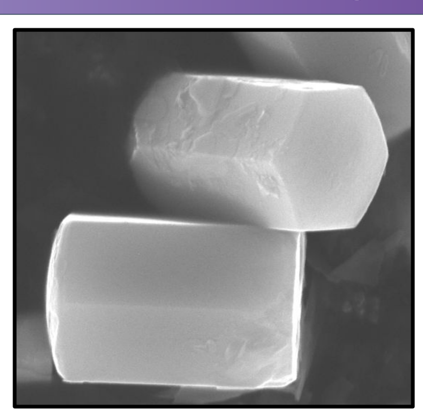
Abstract

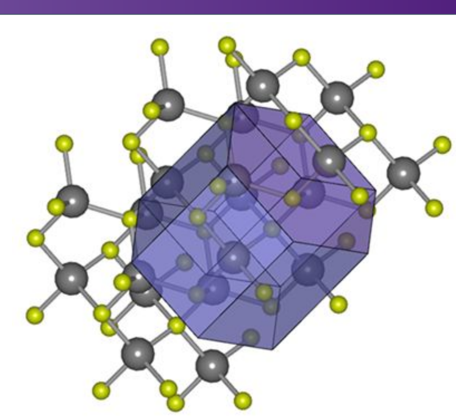
It has been well established that ZnO is a versatile material with multiple existing and potential applications owing to its numerous and unique properties. ZnO in the nano- and microscale forms has been a focus of attention in recent years due to demonstrated utilities in pharmaceutics, bioengineering and medical diagnostics. Of particular interest is the utilization of ZnO as an antibacterial agent. With growth inhibition observed for both gram-positive and gram-negative bacteria as well as antibiotic strains, the antibacterial action of ZnO is well documented. Yet, there exists much debate over the fundamental mechanisms underlying the antibacterial action of ZnO. Commonly proposed mechanisms include the generation of various reactive oxygen species, release of Zn ions, surface-to-surface interactions, etc. In this work, we investigate the surface and near-surface optoelectronic properties of ZnO microcrystals as they relate to the antibacterial figures of merit. As microscale ZnO particles exhibit comparable antibacterial action to those at the nanoscale, while minimizing effects related to internalization, they are well-suited to serve as a platform to investigate the role of the crystalline free surfaces in this behavior. A bottom-up hydrothermal growth method was employed to synthesize ZnO microcrystals with tunable morphology and a well-controlled relative abundance of polar and non-polar surfaces. The quality of the crystalline lattice and free surfaces as well as the predominant morphology of these samples were confirmed by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and surface photovoltage spectroscopy. The antibacterial efficacy of these particles was characterized via minimum inhibitory concentration assays, performed using Staphylococcus Aureus in a Mueller Hinton broth media. We performed a series of optoelectronic experiments including temperature dependent photoluminescence spectroscopy as well as spectroscopic and transient surface photovoltage as a means to observe changes occurring at the ZnO surface during these assays. Our results revealed that the antibacterial action of ZnO microparticles is primarily rooted in the interactions between the crystalline surfaces and the extracellular material of the bacteria. We detected significant spectral changes due to interactions with bacteria and growth media. In particular, we showed that interactions with s.aureus resulted in considerable modifications of the excitonic luminescence.

Introduction

- ZnO widely employed as antibacterial agent
- Fundamental mechanisms driving antibacterial action for ZnO are still unknown.
- Antimicrobial behavior of ZnO is most likely driven by surface-surface interactions
- These are, in turn, influenced by ZnO lattice properties and surface chemistry

Zinc Oxide Crystal Structure





- ZnO has hexagonal structure composed of alternating layers of zinc and oxygen atoms
- Hexagonal (polar) faces are defect rich due to surface stabilization mechanisms
- Rectangular (non-polar) sides surfaces are net neutral and contain little to no defects

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Traditional antibiotics are exhibiting reduced effectiveness due to the rise of antibiotic resistant bacteria. This poses a great threat to global health and food security. A potential solution is to use inorganic nano/microparticles such as ZnO. Despite their effectiveness, lack of understanding in how they kill bacteria limits application. By looking at how interactions with bacteria change the electronic properties of the particles we can better understand how these interactions take place and what drives them. Here we look at one such change that can give us great insight into potential electronic interactions that may contribute to killing bacteria.

Near Band Edge Activity

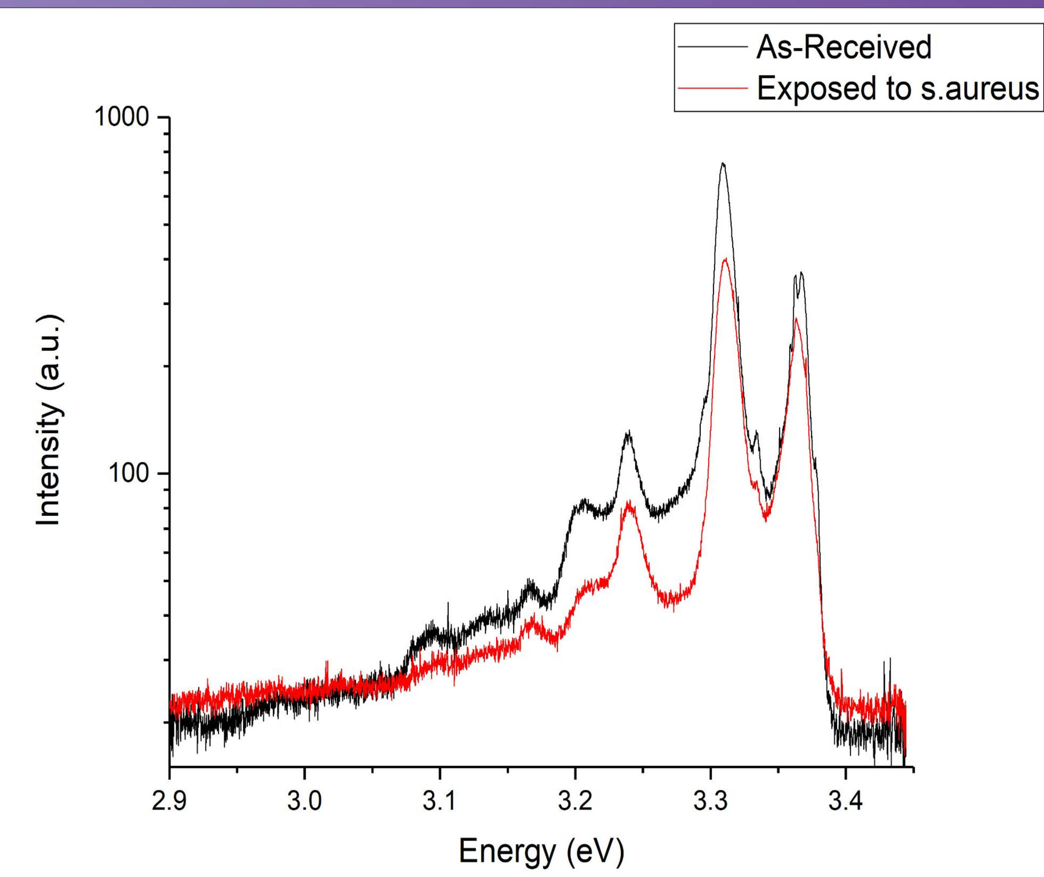


Figure 1: Photoluminescence spectrum of the near band edge emissions of nanocrystalline ZnO at 8K before and after exposure to *s.aureus*

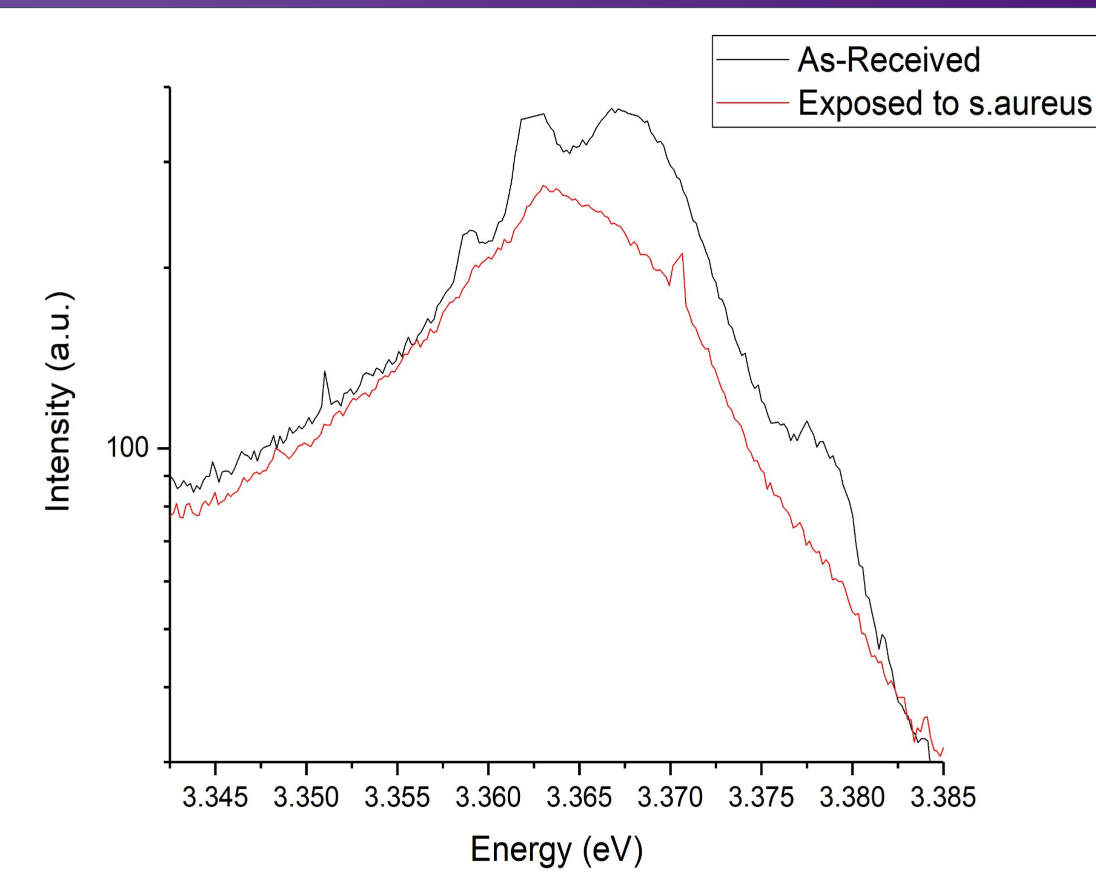


Figure 2: Photoluminescence spectrum from 3.34 eV to 3.385 eV for nanocrystalline ZnO at 8K before and after exposure to *s.aureus*

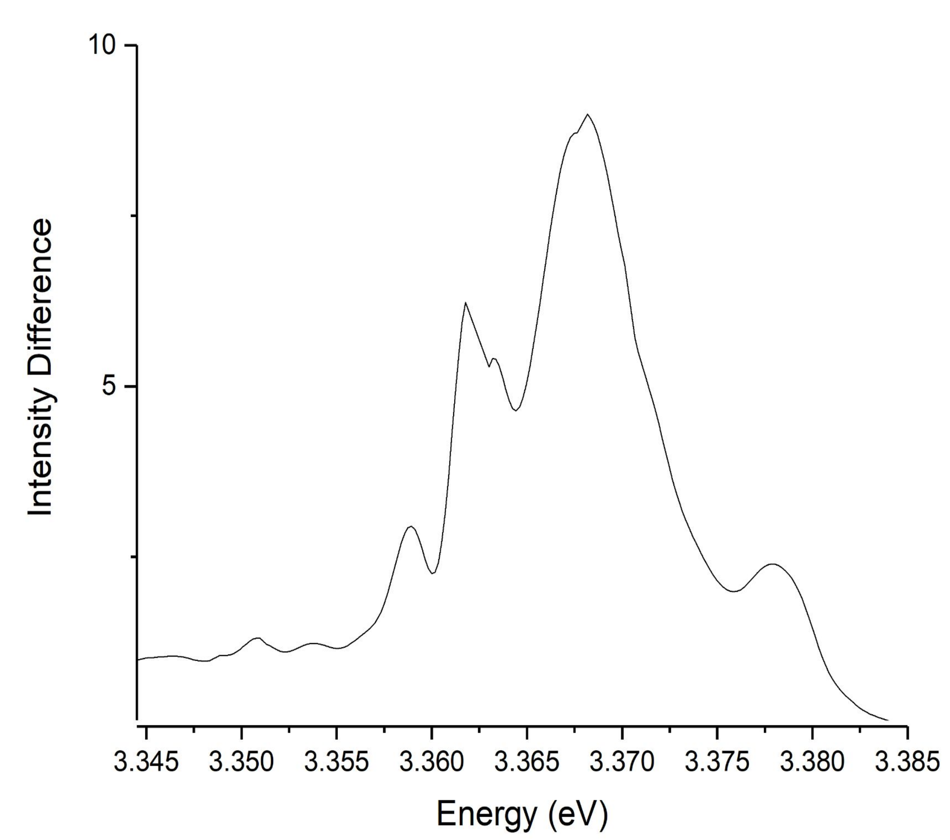


Figure 3: Difference of photoluminescence spectrum from 3.34 eV to 3.385 eV for nanocrystalline ZnO at 8K before and after exposure to *s.aureus*

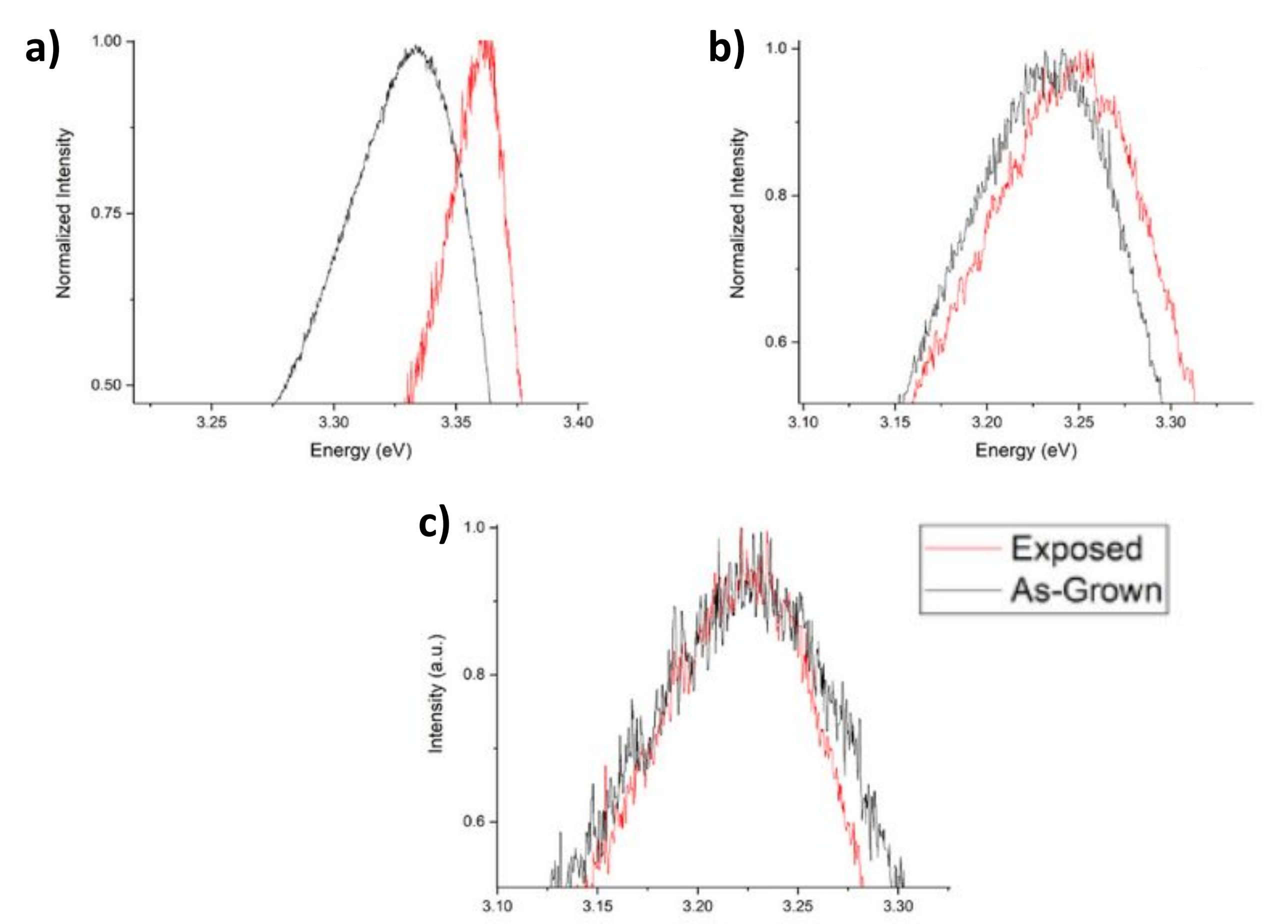
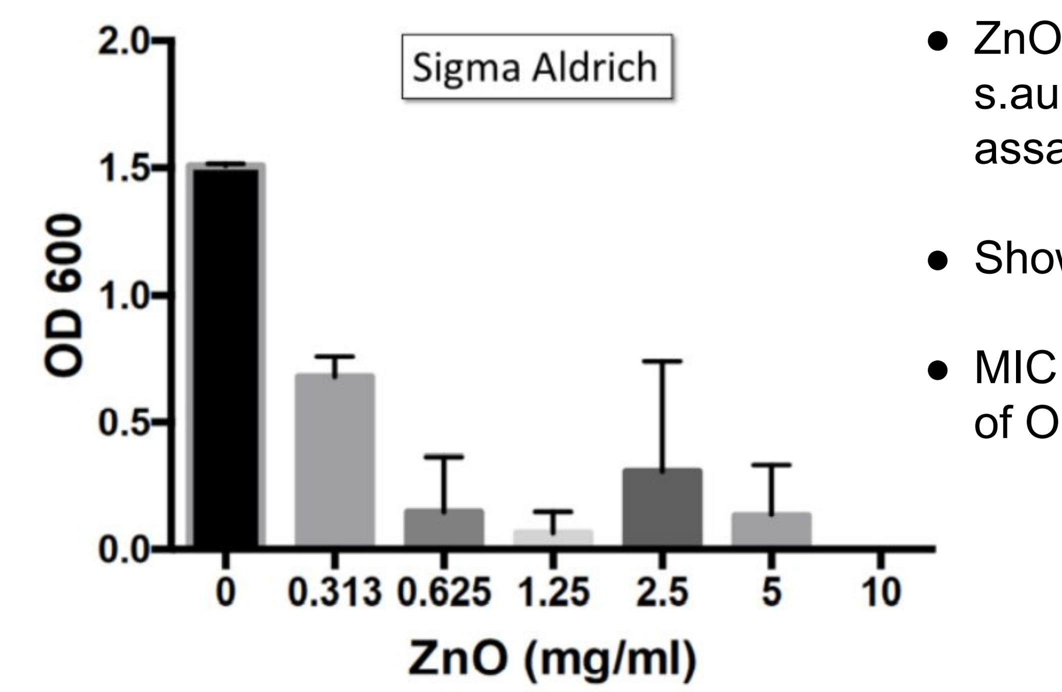


Figure 4: Room-temperature photoluminescence spectra of varying microcrystalline ZnO morphologies a) Polar rods, b) Balanced prisms, c) Non-Polar plates before and after exposure to *s.aureus*

Bacterial Growth Inhibition



- ZnO Particles exposed to s.aureus in MHB via MIC assays
- Showed MIC of 0.625mg/ml
- MIC determined by measure of Optical Density

Figure 5: Minimum Inhibitory Concentration Assay Results for nanocrystalline ZnO

Conclusions

- Exposure to *Staphylococcus Aureus* bacteria in Mueller-Hinton Broth growth media exhibited significant modification of the bound exitonic luminescence structure of nanocrystalline ZnO
- Recombination routes for specific binding sites was shown to be significantly suppressed
- Interactions associated with antibacterial behavior significantly influence electronic structure of our material

Future Directions

- Temperature dependence of excitonic features before and after exposure
- Investigate influence of media on excitonic behavior
- Effects of remote plasma treatment on these recombination routes
- Investigate near surface optoelectronic phenomena (SPV experiments)