Effects of Phosphate-Rich Aqueous Environments on Surface Charge Dynamics in Microcrystalline ZnO

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Introduction

- ZnO exhibits potential as antibacterial agent
- Applications are limited by fundamental uncertainty in the physical mechanisms underlying the antimicrobial properties of ZnO
- We focus on the ZnO particle response to interactions relevant to antibacterial action with *Staphylococcus Aureus* bacteria
- We expose ZnO to phosphate buffered saline (PBS) in isolation to investigate the nature of interactions with aqueous phosphates

Surface Photovoltage (SPV)

Kelvin Probe Method

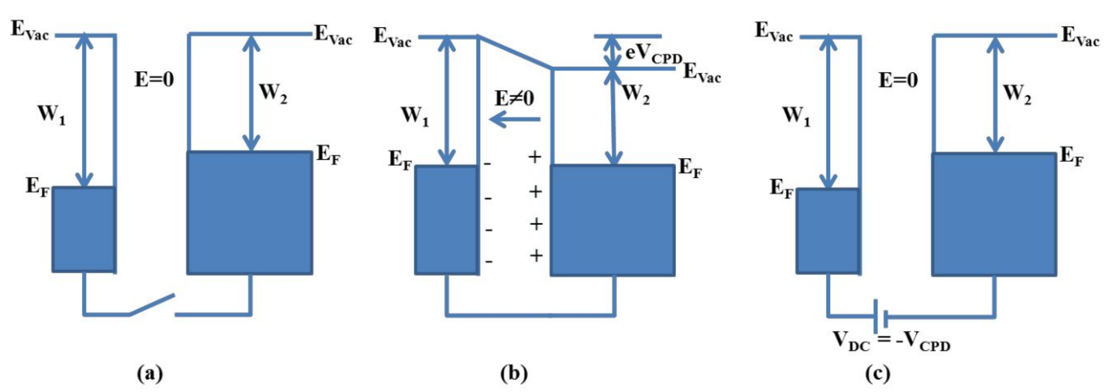

Fig.1. Energy band diagrams of two materials having different work functions (a) without contact, (b) with external electrical contact, where E is electrical field between plates and (c) with external bias (VDC). W1 and W2 represent Fermi levels of Kelvin probe and sample, respectively. [1]

- A metallic reference electrode is placed in a parallel arrangement with our sample surface
- Alignment of Fermi levels upon electrical contact generates a potential difference which we can measure
- Monitoring potential with time or incident wavelength gives insight into surface electronic structure and charge dynamics

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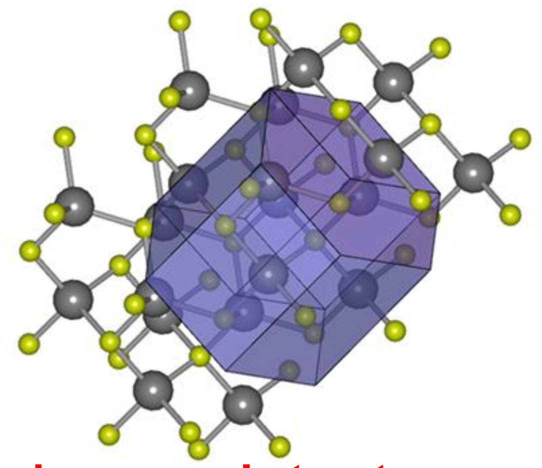
Traditional antibiotics are exhibiting reduced effectiveness due to the rise of antibiotic resistant bacteria. This poses a great threat to global health and food security. A potential solution is to use inorganic nano/microparticles such as ZnO. Despite their effectiveness, lack of understanding in how they kill bacteria limits their application. By looking at how interactions with bacteria and bacterial environments change fundamental properties of the particles we provide insight into fundamental mechanisms underlying these behaviors. Here we show how interactions with the bacterial environment are important to consider and describe how they may limit our ability to kill bacteria.

ZnO Microparticle Properties



- ZnO has hexagonal structure composed of alternating layers of zinc and oxygen atoms
- Liquid precursors are mixed to form zinc carbonate and 99.999% pure Zn foil is added
- Reaction is catalyzed in excess of 90°C to within stainless steel autoclave to form ZnO

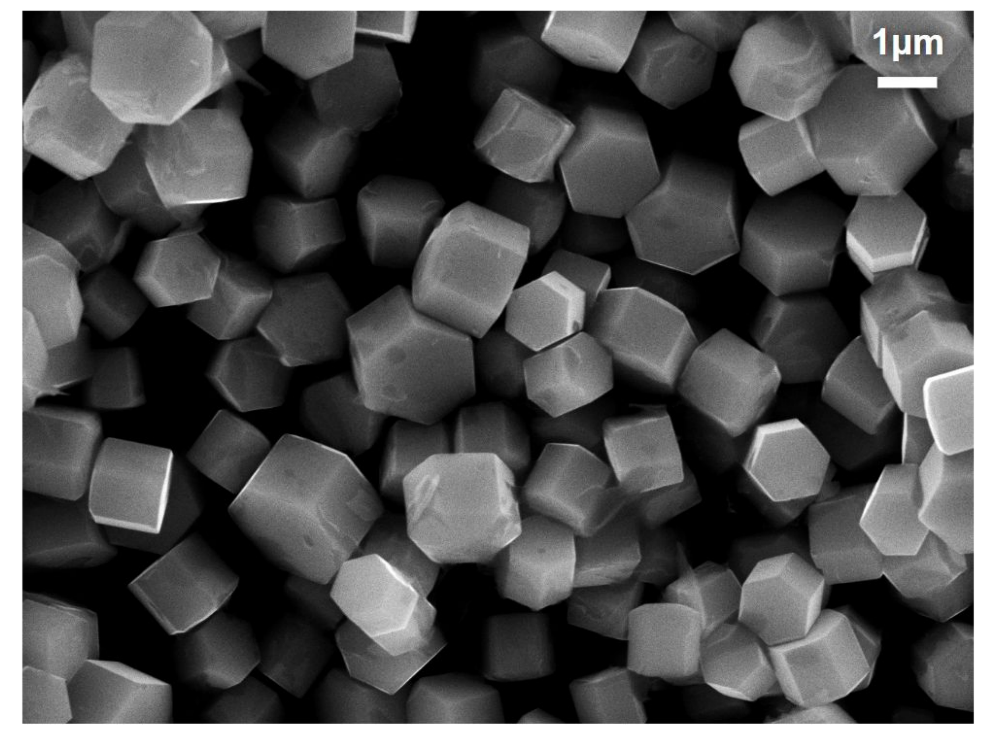


Fig.2. Field Emission Scanning Electron Microscope (FE-SEM) image depicting crystalline ZnO with characteristic hexagonal prism-like structures on the order of a few micrometers.

- Particles used in these studies had a relatively balanced morphology
- Exhibit notable sub-bandgap states due to irregularities in the crystalline lattice
- ~1.5 eV trap to CB transition associated with oxygen vacancies
- ~2.6 eV trap to CB transition associated with zinc vacancies
- ~2.4 eV VB to trap transition associated with oxygen interstitials

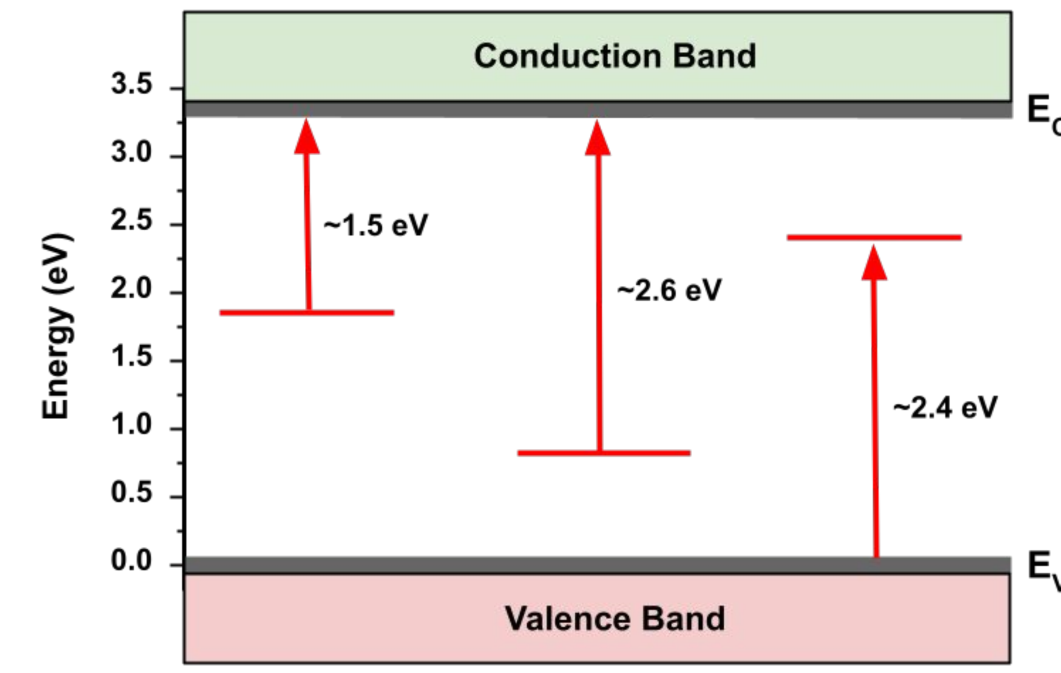


Fig.3. Energy diagram depicting sub-bandgap transitions observed in the Surface Photovoltage (SPV) spectra of as-grown ZnO MPs of balanced morphology.

Exposure to Bacteria

Fig.4. FE-SEM images of ZnO MPs after exposure to S. Aureus in MHB. Where the smaller spheroids are bacteria and the larger structures ZnO [2]

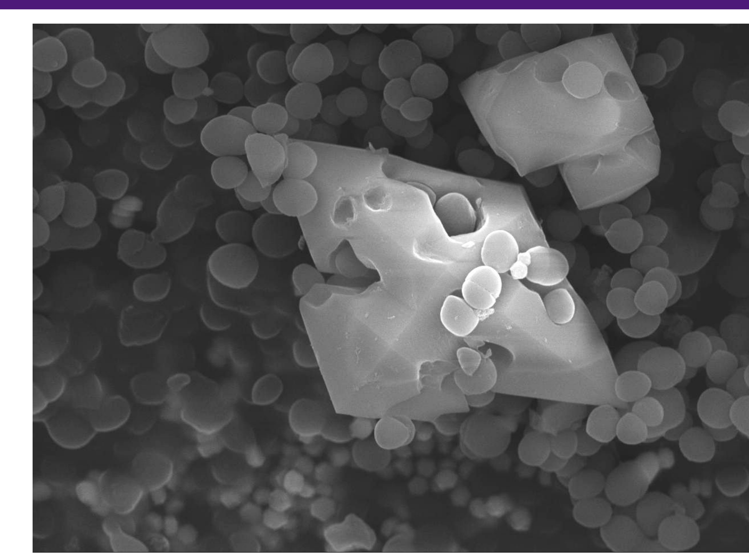


Fig.5. FE-SEM images of secondary crystalline phases in solution with hydrothermally grown ZnO MPs after exposure to MHB with *S. aureus.* [3]

- Our particles are exposed to solution with and without bacteria by incubating at sub-minimum inhibitory concentrations (MIC)
- In doing so it was observed that increased concentration of aqueous phosphates is accompanied by increased development of secondary crystalline phase
- This suggests significant interaction with ZnO particles or compounds released into solution by ZnO

Conclusions

- Changes in the surface charge dynamics after exposure to PBS media with and without the presence of S. aureus demonstrate that there exist significant interactions at the ZnO free crystalline surface.
- This surface is a highly dynamic and complex system with both oxygen-deficient and zinc-deficient defects despite the relatively high quality of crystals utilized.
- Domination of slow processes in the SPV transients after exposure to PBS indicates that much of the surface interaction involves phosphate adsorption.
- The SPV spectra shows the removal of oxygen-rich states after exposure to PBS, attributed to ligand exchange with hydroxyl groups at these oxygen-rich sites.
- We also provide evidence for the predicted cross interaction between bacteria and aqueous phosphates via the preservation of the oxygen-rich defect states and suppression of the effects of PBS on slow surface charge exchange processes.

Electrochemical Changes at the ZnO Surface

- Significant changes in surface charge dynamics after exposure to PBS with and without *S. aureus*

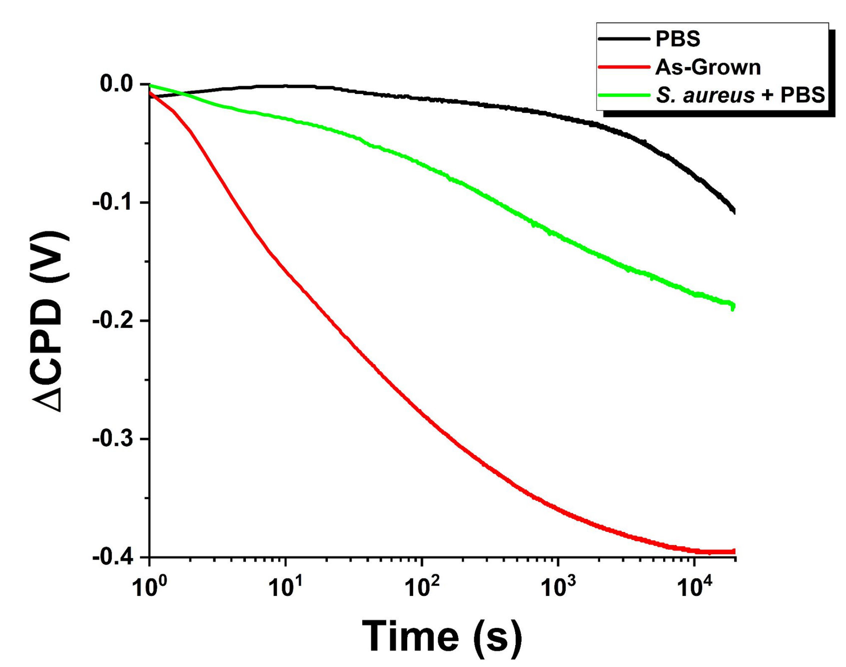


Fig.6. SPV "light-on" transients under exposure to panchromatic light for ZnO MPs of balanced morphology, as-grown and exposed to indicated environments.

- We model these processes as a series of charging/discharging capacitors in series

$$\Delta V_{CPD}(t) = V_0 + \sum_{i}^{n} V_i^n \left(1 - e^{-\frac{t}{\tau_i}}\right) + \sum_{j}^{m} V_j^m e^{-\frac{t}{\tau_j}}$$

- We see that PBS has a large effect on the characteristic time and reservoir size of the longest lived SPV process
- Indicative of phosphate adsorption

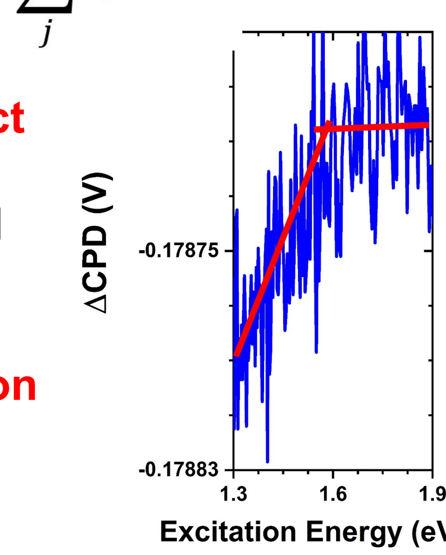


Fig.7.SPV spectral transition in hydrothermally grown ZnO MPs of balanced morphology after exposure to PBS without the presence of *S. aureus* bacteria depicting a trap-to-conduction band transition at ~1.5 eV.

- We see removal of Zinc deficient surface traps in PBS marking them as adsorption sites
- Presence of bacteria suppresses PBS effects and does not remove any existing states thus limiting adsorption

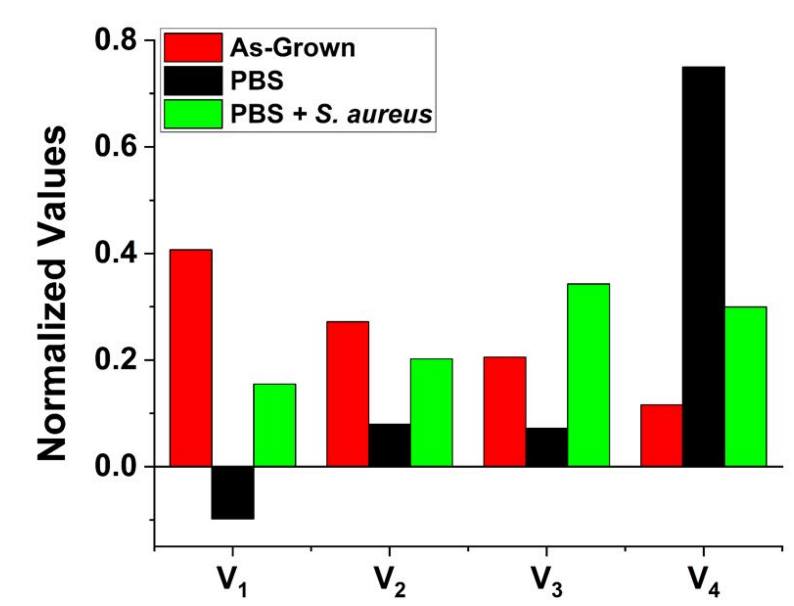


Fig.8. Normalized fitting parameters Vi for as-grown ZnO MPs as well as those exposed to PBS with and without the presence of *S. aureus* bacteria. They have been normalized to the sum of all Vi for each sample. V1 is plotted negative for the sample exposed to PBS alone to indicate that this component has a directionality opposite to the others.

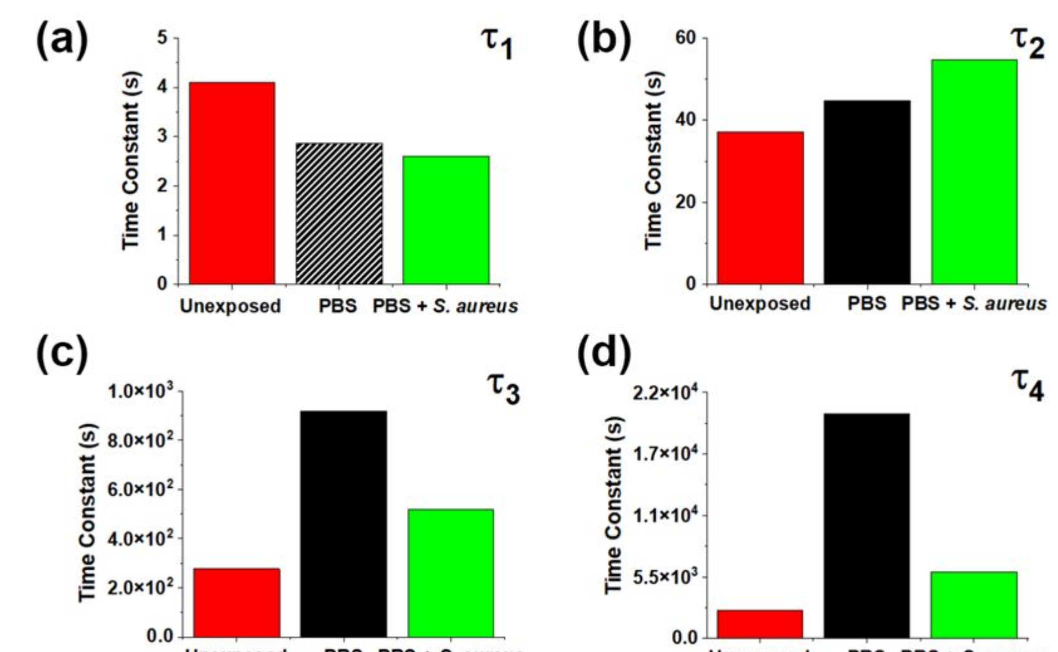


Fig.9.Fitting parameters τi for characteristic times for as-grown ZnO MPs and those exposed to PBS alone and with *S. aureus* bacteria. The hash pattern for τ1 indicates a "rising" process.

1. Chapagain, P.R., Surface photovoltage studies of environmental influence on charge dynamics in nanostructured silicon [electronic resource]. Texas Christian University dissertation., 2015.
2. Johnson, D.; Reeks, J.M.; Caron, A.; Tzoka, I.; Ali, I.; McGillivray, S.M.; Strzhemechny, Y.M. Influence of Surface Properties and Microbial Growth Media on Antibacterial Action of ZnO. Coatings 2022, 12, 1648.
3. Reeks, J.M.; Ali, I.; Moss, W.J.; Davis, E.; McGillivray, S.M.; Strzhemechny, Y.M. Microscale ZnO with controllable crystal morphology as a platform to study antibacterial action on Staphylococcus aureus. Biointerphases 2021, 16, 031003.