Enhanced Porosity and Exciton-Phonon Coupling in Zinc Oxide Nanopopcorn

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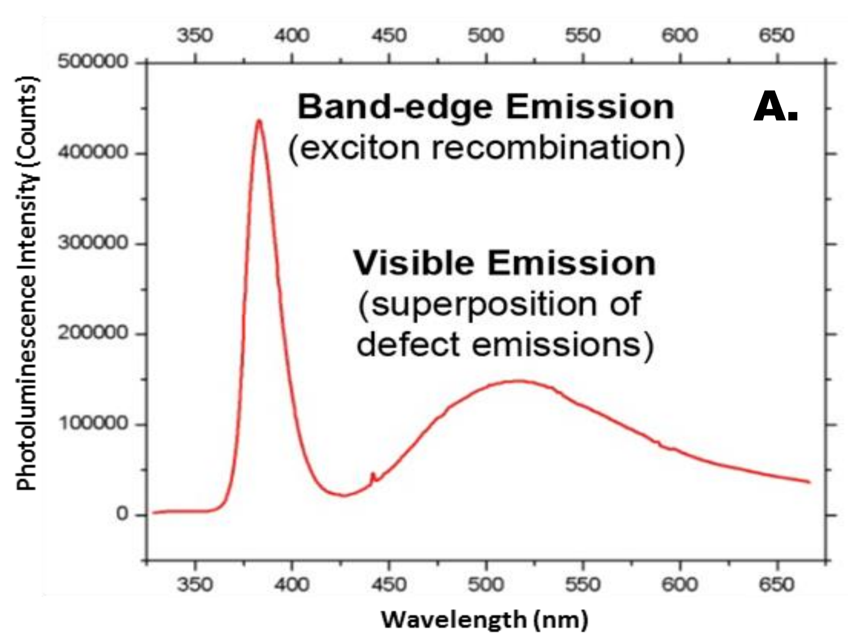
Motivation

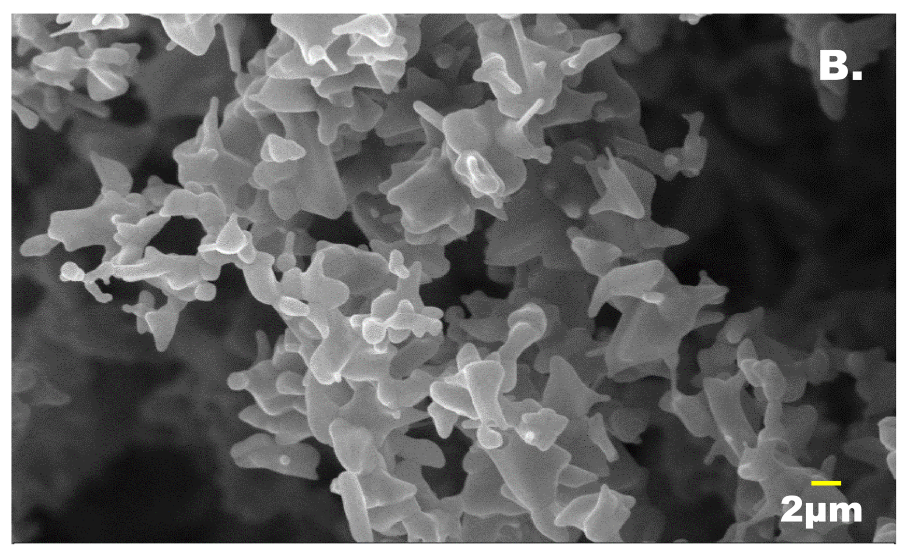
Objective:

- Use image analysis to examine surface area to volume ratio in nanowires and nanopopcorn
- Determine porosity of ZnO nanostructures
- Determine temperature dependence of exciton-phonon coupling and the resulting photoluminescence (PL)
- Compare nanostructure data to ascertain potential for biological and molecular sensing applications



ZnO Material Properties:

- Efficient optoelectronic material
- Direct bandgap of 3.37 eV (380 nm)
- Stable UV emitter at room temperature ($E_{binding}$= 60 meV)
- Typical PL spectrum (figure A)



ZnO Nanopopcorn Properties:

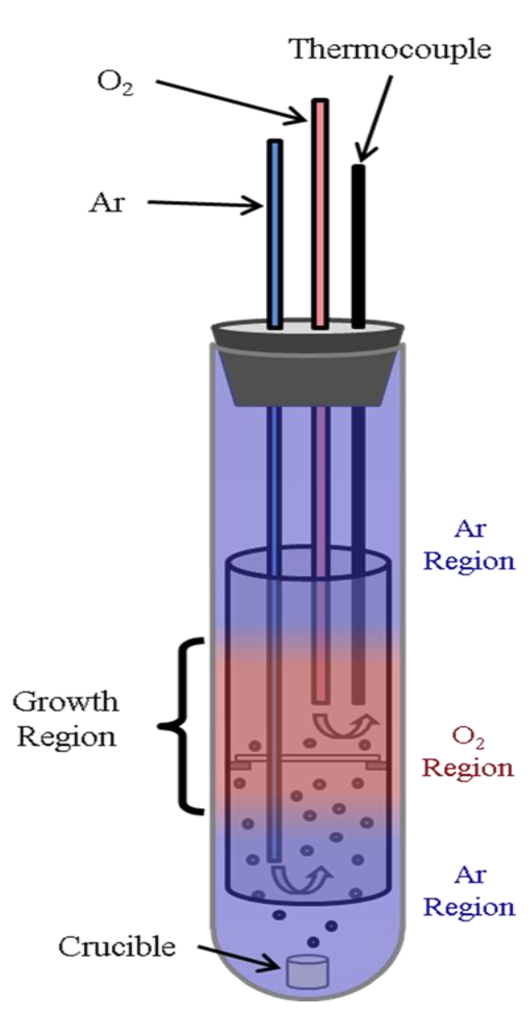
- Enhanced surface area-to-volume ratio compared to planar structures (figure B)
- Multiple distinct exciton transition peaks in near-ultraviolet
- Highly porous; good for sensing applications, possibly for catalysis

Experimental Setup

ZnO Nanopopcorn Growth

ZnO nanopopcorn synthesis by modified vapor-solid method:

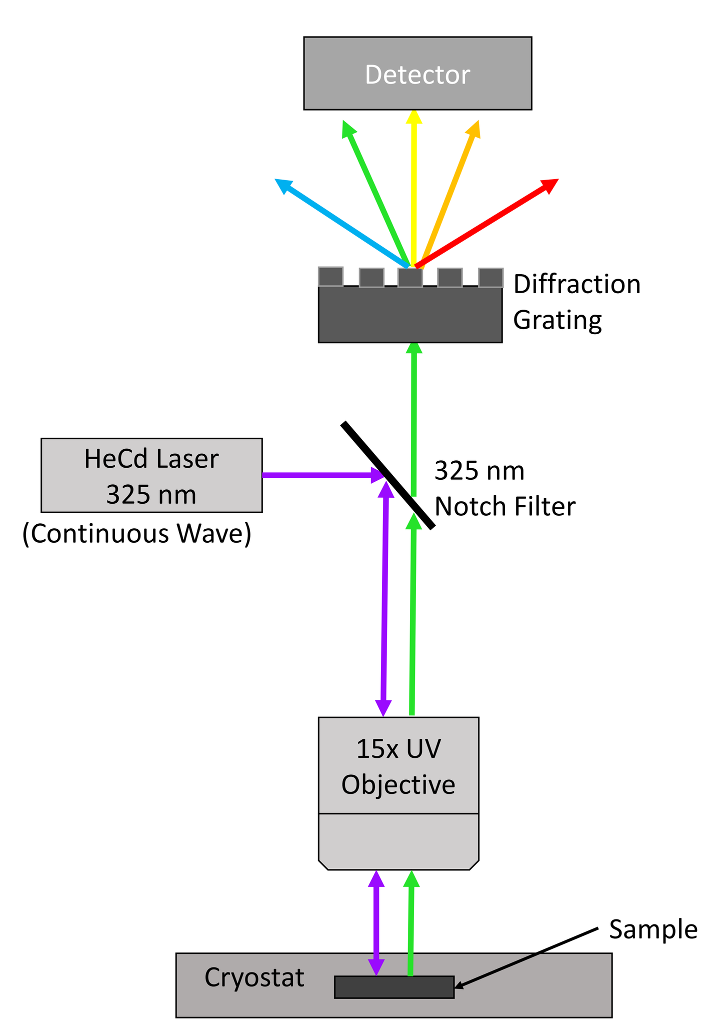
- 700°C, high Ar pressure lowered after Zn evaporation begins
- 7.5% O_2 throughout growth period



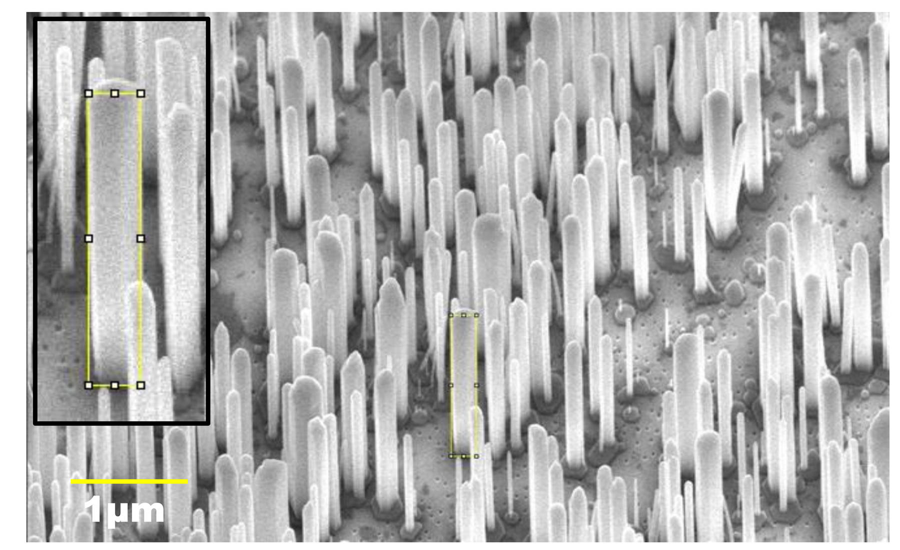
Temperature Dependent Photoluminescence Study

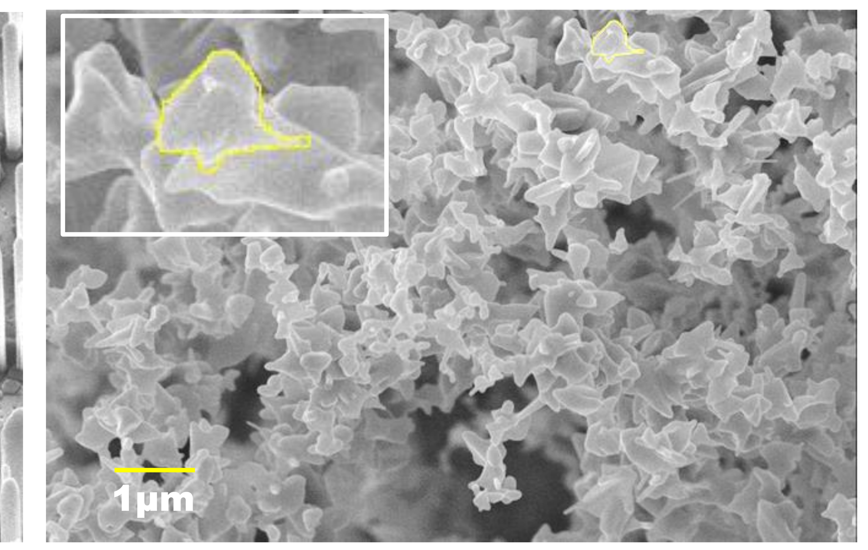
Photoluminescence temperature-dependent study:

- N_2 cooled: temperature range (70 K – 730 K)
- Wavelength Range (200 nm -1100 nm)



Surface Area to Volume Characterization



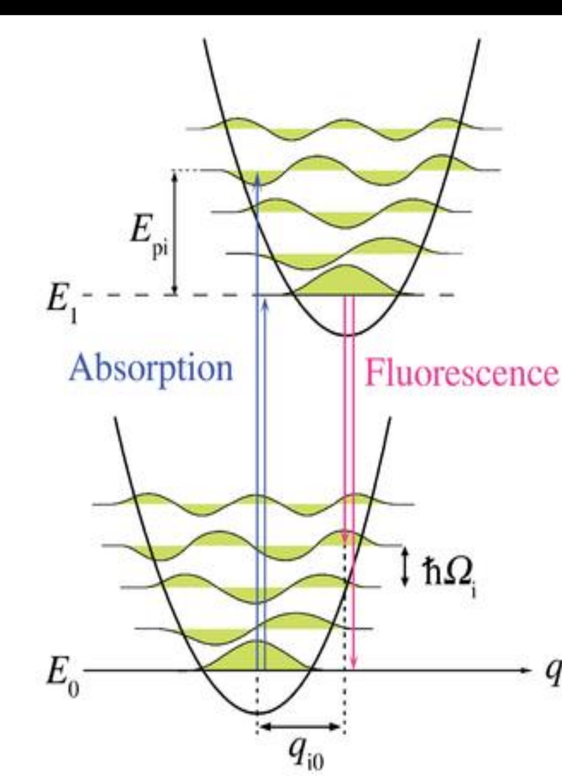


- Image J used for analysis
- Collected maximum and minimum diameter of drawn field

	Average Surface Area (SA)	Average Volume	Ratio SA:Volume
	(nm²)	(nm³)	
Nanowire	(1.28 ± 0.23)x10⁶	(8.76 ± 0.26)x10⁷	0.017:1
Nanopopcorn	(4.63 ± 0.17)x10⁵	(3.95 ± 0.24)x10⁷	0.020:1

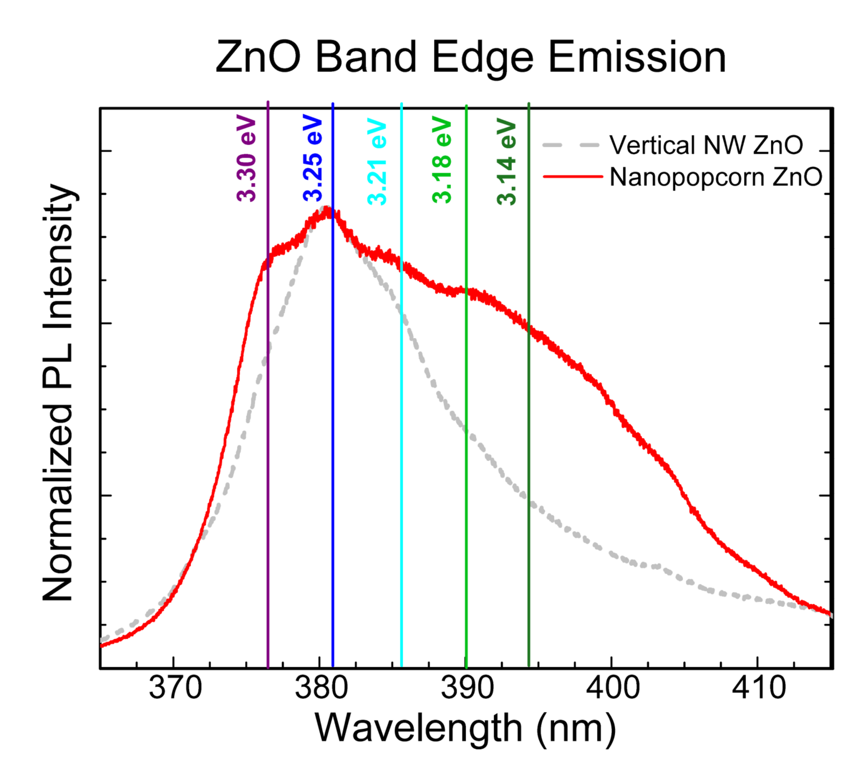
- Nanopopcorn measured as a spherical SA and volume
- Nanowire measured as a hexagonal cylinder for SA and volume
- SA of nanopopcorn is an underestimate, due to the non-uniform shape of the nanostructure
- This leads to a comparable, but slightly higher SA:V ratio in nanopopcorn than in nanowires

Room Temp. Photoluminescence: Exciton-Phonon Coupling



Exciton-phonon coupling:

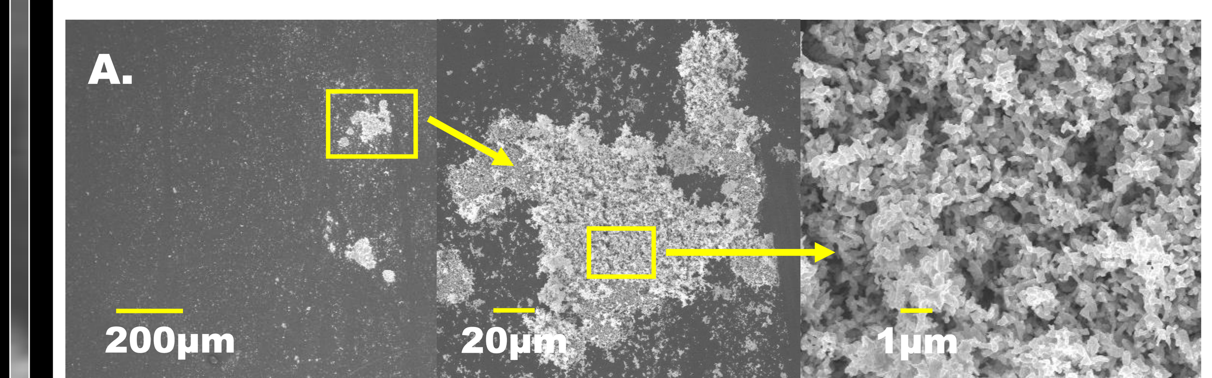
- Excitons can lose energy during transmission by coupling to phonons
- Energy phonon << energy exciton, each exciton can couple to multiple phonons
- After coupling to a phonon, the exciton emits at a lower energy (decreased by phonon energy)
- PL blue-shifts as temperature decreases

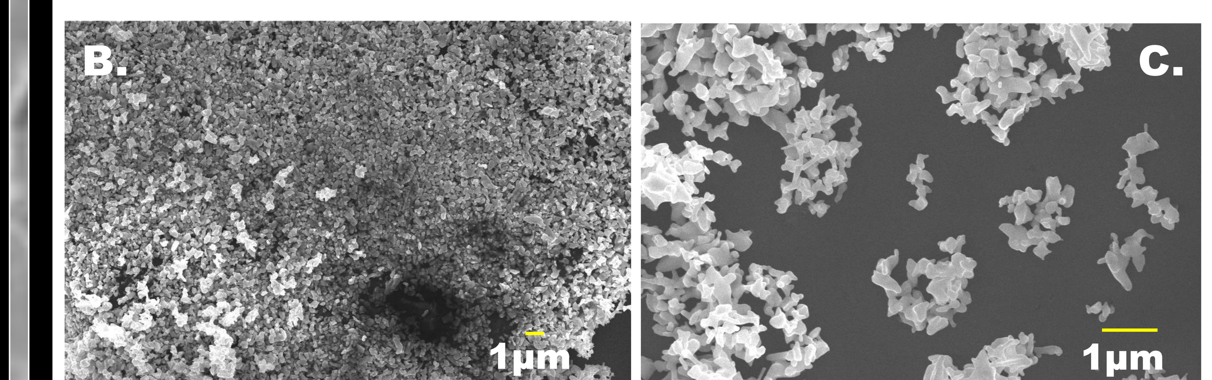


Five identified peaks within near-band edge emission of nanopocorn (not in nanowire):

- Peaks are caused by A and B excitons and their phonon replicas
- ZnO longitudinal optical phonon (72 meV) couples to ZnO excitons, causing excitons to lose energy and emit at lower frequencies (phonon replica)

Popcorn Break-Off Study





- Nanopopcorn growth found to detach from substrate easily, depositing on sample holder lids
- Does it keep its free-form structure while detaching from substrate?
  - Nanopopcorn collected from lids by pressing a silicon substrate against lid for 30 s (figure A)
  - When pressed for 30 s, free-form structure compacted, losing porous nature of the original structure (figure B)
  - Nanopopcorn that is transferred without being pressed keeps its free-form nanoporous shape (figure C)
  - In all cases, individual grains of ZnO keep their integrity, even when experiencing pressure

Conclusions & Future Work

- **ZnO nanopopcorn has a similar, yet slightly higher, surface area to volume ratio than ZnO nanowires**
- **ZnO nanopopcorn has increased exciton-phonon interaction at room temperature over that of ZnO nanowires**
- Nanoparticle structure easily breaks from substrate
- Broken-off popcorn grains retain individual integrity while pressure causes free-form structure to become compacted

Future:

- Temperature-dependent studies of the exciton-phonon coupling
- Expect to see blue-shift of exciton emission as temperature decreases, along with sharpening of the exciton transition peaks

Acknowledgements

Eion thanks VINSE NSF REU (DMR-1263182) for sponsoring him in this research opportunity at Vanderbilt University. Claire Marvinney and Richard Haglund thank the US Department of Energy: DE-FG02-01ER45916 for sponsoring their research. Richard Mu is acknowledged for use of his materials and optical labs at Fisk University.