Synthesis and Characterization of ZnO Particles in Solutions of Ethanol-Water and Oleic Acid

*Tamara A. Bright, K. Mikhail Anfinson and Maria C. Gelabert
Undergraduate Student, Winthrop University, Undergraduate Student, Winthrop University, and Professor, Winthrop University

Keywords: nanoparticles, ZnO, fluorescence, powder X-ray diffraction

This research explores aqueous synthesis of zinc oxide (ZnO) nanoparticles, with potential application to water purification applications. Fundamental synthetic study of broadly useful materials is aligned with advanced materials goals within *SC Vision 2025* and *NSF Big Ideas*. Zinc oxide is a compound commonly found in sunblock and antibacterial topical creams as well as bacterial remediation and a variety of optoelectronic applications over many length scales. For technologies requiring small crystals, the habit and size of crystals are intimately connected to its optical and surface properties (*1*), and thus reproducible preparations of samples with specific habits, sizes and surface characteristics are in demand. This project explores the relevant synthetic parameters for nanoparticles, but with additional supersaturation calculations for optimization of pH (OLI Systems software) *(2)*, as well as planning for future study of particle surface defects (*3*) with fluorescence spectroscopy. Working exclusively with zinc chloride and sodium hydroxide, this exploratory research examined aqueous synthesis parameters, with extension to capping agents polyethylene glycol and oleic acid. ZnO particles were synthesized at room temperature in varying water-ethanol solutions with the presence or absence of polyethylene glycol (PEG) or oleic acid capping agents to inhibit growth and limit particle size. For synthesis, 0.02 M $ZnCl_2$, either in ethanol or water, were added together to prepare varying quantities of ethanol/water solvent. To 25.00 mL of zinc solution, 5.00 mL of 0.50 M NaOH was added slowly over 30 minutes while stirring, then allowed to stir for another 30 minutes before separation and analysis. With capping agent oleic acid, the ternary phase behavior of water/base, ethanol and oleic acid was explored prior to synthesis. After centrifuging and washing with water and ethanol, samples were analyzed by X-ray powder diffraction, particle size analysis, UV-Vis spectroscopy and fluorimetry. X-ray powder diffraction revealed consistent synthesis of zinc oxide, but none of the trials resulted in nanoparticles by optical scattering size analysis. Powder data were refined by Rietveld methods, revealing minimum average particles of 15-27 nm. Particle size analysis showed the full distributions, with the smallest sizes of 0.100 microns and typical size ranges of 30-70 microns. Fluorescence data, collected with excitation wavelengths of 200 nm or 250 nm, revealed emission peaks around 397, 450, 470, 480, 500 and 600 nm, partly attributed to different point defects in zinc oxide that affect surface reactivity for catalytic applications (*4*). Broadly, fluorescence measurements for several samples indicated two emission spectra groups with identical peaks: one group with a larger peak around 500 nm and one below 400 nm, and this correlates with pH, where high-pH syntheses at (pH >10) result in lower wavelength (blue) spectral profiles. Ultraviolet-visible absorption data indicate broad absorption bands with onsets close to the band edge for ZnO (3.37 eV ≈ 370 nm).

1. McLaren, A.; T. Valdes-Solis, T.; Li, G.; Tsang, S.C. Shape and size effects of ZnO nanocrystals on photocatalytic activity. *J. Am. Chem. Soc.* **2009**, *131*, 12540-12541.

2. OLI Systems, Inc. OLI Studio Stream Analyzer. https://www.olisystems.com/oli-studio-stream-analyzer (accessed March 19, 2019).
3. Dutta, R.K.; Nenavathu, B.P.; Gangishetty, M.K. Correlation between defects in capped ZnO nanoparticles and their antibacterial activity. *J. Photochem. Photobiol. B* **2013**, *126*, 105-111.
4. Bardhan, R.; Wang, H.; Tam, F.; Halas, N.J. Facile chemical approach to ZnO submicrometer particles with controllable morphologies. *Langmuir* **2007**, *23*, 5847.