Synthesis and Characterization of ZnO and PbI_2 Colloidal Nanoparticles

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Abstract

Many applications have been found for various nanocrystals. Specifically, zinc oxide (ZnO) can be used for various biomedical applications such as tissue imaging and deoxyribonucleic acid (DNA) detection while lead iodide (PbI_2) can be used as an x-ray detecting nanoscintillator. This project focused on the synthesis of quantum dots which emit in narrow spectral band for subsequent biomedical applications. ZnO was first synthesized by a low temperature colloidal process utilizing a Schlenk line set up. In an attempt to increase the intensity of the photoluminescence (PL) that the ZnO nanoparticles emit, the quantum dots were annealed at various temperatures and time intervals. PbI_2 was also synthesized through a low temperature colloidal process.

In order to characterize the nanoparticles, a spectrofluorometer was used to measure the excitation spectra. Low-temperature photoluminescence was measured using a closed-circuit helium cryostat and a helium-cadmium laser. Tunneling electron microscopy (TEM) and scanning electron microscopy (SEM) were performed to measure the size of the nanoparticles.

Experimental Procedure

ZnO was synthesized through a one-pot low temperature method utilizing a Schlenk line apparatus. First, 25 mL of *m*-xylene (≥ 99.0%, Fluka) and 50 mL of 1-pentanol (≥ 99.0%, Fluka) were added to a three-neck flask. Subsequently, 0.68g of *p*-toluene sulfonic acid (*p*-TSA) (≥ 98.5%, Sigma-Aldrich) was added under the assumption of a decrease of spectral band width and increase of PL intensity [1]. The solution was stirred, and 2.5 g of zinc acetate dihydrate (≥ 99.0%, Fluka) was added to the solution.

Under argon and reflux, the solution was heated for 1 hour and 20 minutes at 130°C and 1 mL aliquots were taken every 20 minutes. The solution was then centrifuged at 4000 rpm in 5 minute cycles with the addition of a 50% ethanol and deionized water stock solution until a white precipitate formed. The precipitate was diluted with ethanol and the solution was placed under vacuum until ZnO powder was obtained.

Annealing measurements for ZnO were conducted with a tube furnace. The ZnO powder was annealed at 200, 300, 400, and 500°C. At each temperature the powder was annealed in three 10 minute cycles. Cryostat measurements were conducted using a cold finger at decreasing temperatures up to 10 K.

PbI_2 was similarly synthesized through a low-temperature one-pot synthesis with a Schlenk line [2]. 100 mg of lead iodide powder (≥ 99.999%, Aldrich) was dissolved in 15 mL of tetrahydrofuran (THF) (≥ 99%, Sigma). The solution was sonicated until the powder was completely dispersed in the THF. The solution was then centrifuged at 4000 rpms in 10 minute cycles until a deep yellow colored solution formed above a precipitate. The deep yellow colored solution was decanted into a three-neck flask.

10 mL of anhydrous methanol was injected into the solution under nitrogen and the solution was stirred at room temperature for 24 hours. 1 mL aliquots were taken at 10 minute, 1, 2, 4, and 8 hour intervals. 1 mg of dodecylamine (≥ 98.0%, Fluka) was added to each aliquot immediately after it was taken. After 24 hours, the amount of solution inside the three-neck flask was measured and dodecylamine was added according to a 1 mg/mL ratio.

Results and Conclusions

ZnO synthesis was highly successful, producing nanoparticles that ranged from 4 to 10 nm. Figure 1 shows a 4 nm sized nanoparticle with parallel lines indicating the presence of a crystalline structure. The PL of the ZnO in Figure 2 shows the band-to-band emission of ZnO located at 380 nm, but also reveals a shoulder mound at longer wavelengths peaking at ~500 nm. In the cryogenic measurements under vacuum, as the temperature decreases, it is possible to see that this shoulder mound decreases in intensity, suggesting the possibility that this mound is caused by solvent-related defects on the surface of the ZnO. The annealing measurements (Figure 2) also showed this shoulder, and the ratio of shoulder to ZnO band-to-band emission decreased until 300°C.

Subsequent increases in temperature resulted in an increasing ratio, until the ZnO band-to-band emission was barely visible at 500°C. The ZnO sample at high annealing temperatures turned a dark charcoal color, indicating the possibility of carbon decomposition, the carbon possibly present from the solvents in the synthesis.

PbI_2 synthesis also proved to be highly successful. Figure 3 indicates that there is a distinct, narrow spectral range emitted from the lead iodide suggesting the presence of nanoparticles. Furthermore, the TEM in Figure 4 shows nano-structures on the range of 4 nm. The three differing parallel line structure present on the PbI_2 particle suggests that the crystal might be pyramidal in structure.

Future Work

Although distinct spectra existed for both ZnO and PbI_2, in order to increase PL intensity and minimize surface defect related PL, the particles will need to be coated. For subsequent biomedical applications, ZnO will need to be made water-soluble and bioconjugated. Water solubility will be achieved through the process of cap exchange, while bioconjugation will be made possible through the attachment of a protein layer. Finally, various tests and characterization methods must be conducted in order to prove the validity of these successive results.

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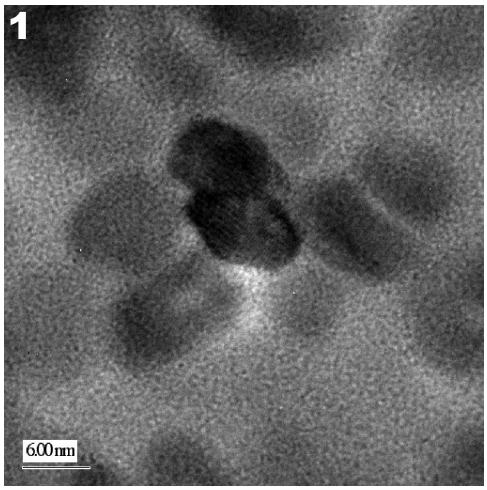

Figure 1, top: TEM image of ZnO nanoparticles.

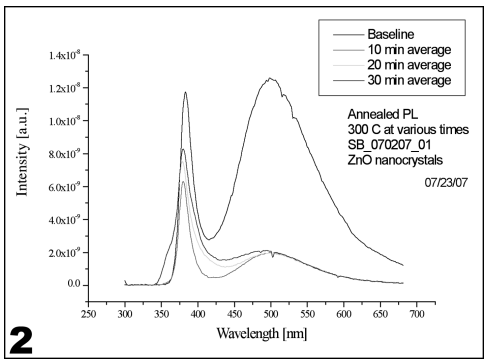

Figure 2, upper middle: PL of ZnO annealed at 300°C for varying time intervals.

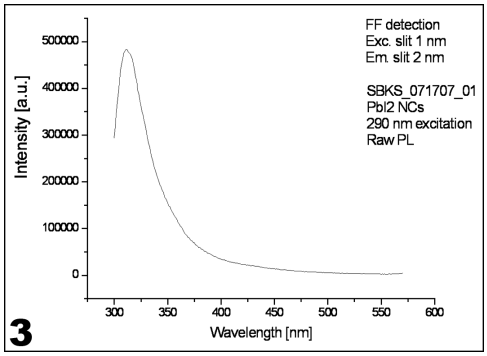

Figure 3, lower middle: PL of PbI_2 nanoparticles at 290 nm excitation.

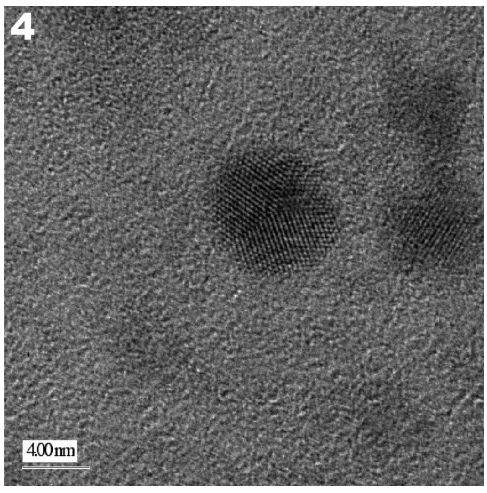

Figure 4, bottom: TEM of PbI_2 nanoparticles.