Synthesis of Semiconductor Nanoparticles

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Abstract:

Three secondary amines, N-methylaniline, diisopropylamine and diethylamine, were reacted with carbon disulfide in the presence of diethylzinc to yield the corresponding bis (dialkylamidodithiocarbamato) zinc complexes in yields ranging from 10 to 24%. Benzoic acid was reacted with diethylzinc to afford bis (benzoate) zinc in 62.7% yield. The metal complexes were characterized via FT-IR spectroscopy. The precursors were then combined with trioctylphosphineoxide and trioctylphosphine (TOPO/TOP) and thermally decomposed to afford ZnS and ZnO nanoparticles respectively. The nanoparticles were evaluated via UV-Vis spectroscopy and light scattering. The λ_{max} for ZnO was 279 nm, which was different from that of the bulk material (370 nm). The λ_{max} range for ZnS was 272-287 nm, which was different from that of the bulk material (340 nm).

Introduction:

Nanoparticles have recently attracted significant attention from the materials science community. Nanoparticles, particles of material with diameters in the range of 1 to 20 nm, promise to play a significant role in developing technologies [1]. They exhibit unique physical properties that give rise to many potential applications in areas such as nonlinear optics, luminescence, electronics, catalysis, solar energy conversion, and optoelectronics. Two fundamental factors, both related to the size of the individual nanocrystal, are responsible for these unique properties. The first is the large surface to volume ratio, and the second factor is the quantum confinement effect [2].

The synthesis of single source precursors for use in the preparation of semiconducting nanoparticles is of significant interest to the materials scientist in that it allows for excellent control of product stoichiometry. Nanoparticulate zinc sulfide has recently been targeted for use in electronics. Synthesis of this zinc based material has been previously achieved via a three step process where the salt of a dialkylamidodithiocarbamate is prepared and subsequently made to undergo a metathesis reaction with a zinc halide to give the single source ZnS precursor, zinc bis(dialkylamidodithiocarbamate). The third and final step is the decomposition of the prepared zinc bis(dialkylamidodithiocarbamate) in the presence of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO). Herein, we describe our results from a two step route where the zinc bis(dialkylamidodithiocarbamate) is prepared from the reaction of a secondary amine with carbon disulfide (CS_2) and diethylzinc (DEZ) (Figure 1). The isolated zinc bis(dialkylamidodithiocarbamate) is then thermally decomposed in TOP/TOPO affording the ZnS nanoparticle (Figure 2).

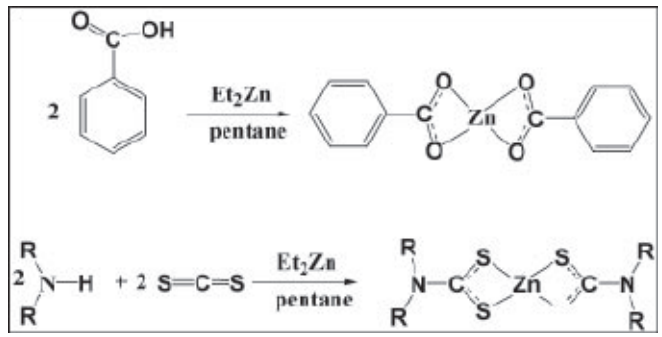

Figure 1: Synthetic scheme for the preparation of ZnO and ZnS precursors.

General Procedures:

Synthesis of bis(dialkylamidodithiocarbamato) zinc: Synthesis of the zinc complexes were carried out by combining 5 mmol of the appropriate secondary amine with an equimolar amount of carbon disulfide in pentane (20 ml) in a round bottom flask. Next, 2.5 mmol of diethylzinc (DEZ) was added via syringe and the reaction mixture was heated to reflux for 1 hr. The reaction mixture was then brought to room temperature and the solvent was removed *in vacuo* to afford the crude solid product. The solid was washed with cold pentane to remove any unreacted amine and carbon disulfide. The products were isolated in yields ranging from 24-65%.

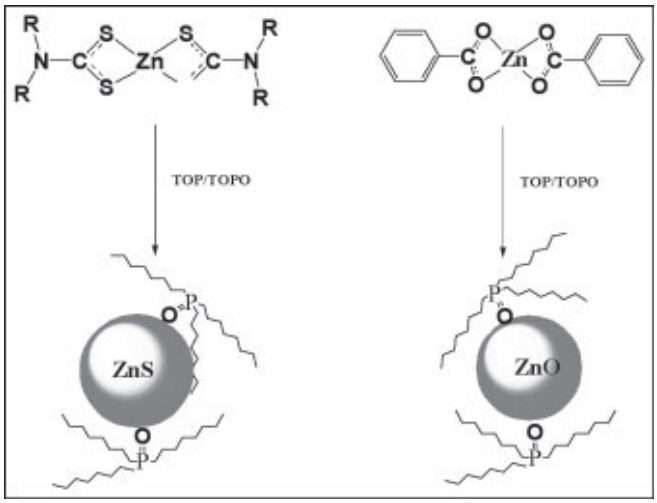

Figure 2: Precursor decomposition and nanoparticle formation.

	Name of Nanoparticle	Sample Name	Particle Size (nm)	PDI
1	Zinc Sulfide	Diisopropylamine Precursor	1287	0.46
			1762	0.59
2	Zinc Sulfide	N-methylaniline Precursor	1184	0.41
			1243	0.43
3	Zinc Sulfide	Diethylamine Precursor	1574	0.48
			1806	0.69
4	Zinc Oxide	Benzoic Acid Precursor	3279	0.66
			2924	0.69

Figure 3: Particle size determination via light scattering.

Synthesis of bis(benzoate) zinc: To a round bottom flask was added benzoic acid (5 mmol) and 50 ml toluene. Next was added 4 mmol of diethyl zinc via syringe. The mixture was refluxed for 30 minutes and the solvent was removed *in vacuo* to afford the product as a white solid in 62% yield.

Nanoparticle Synthesis: Synthesis of the nanoparticles was carried out by adding a trioctylphosphine solution of the appropriate zinc complex to a heated (175°C) solution of trioctylphosphineoxide. The mixture was heated for 2 hrs and then allowed to cool to room temperature. The particles were extracted from solution via the addition of methanol and dispersed in hexane for analysis.

Results and Discussion:

The dialkylamidodithiocarbamate and benzoate based precursors were isolated in yields ranging from 10-62%. The three secondary amines that were used to prepare the dithiocarbamate based metal complexes were N-methylaniline, diethyl amine and diisopropylamine. The lowest yield was obtained from the reaction that made use of N-methylaniline. This is believed to be due to the poor solubility of the amine in pentane. The bis (benzoate) zinc complex was prepared in toluene and isolated in good yield (62.7%). The isolated metal complexes were characterized via FT-IR spectroscopy to confirm the formation of the desired product. The isolated nanoparticles were characterized via UV-Vis spectroscopy and light scattering methods. The expected λ_{max} for bulk ZnS is 340 nm while that for the particles isolated in our experiments ranged from 272-287 nm. Light scattering data showed that the particles ranged in size from 1184-3279 nm with PDI's ranging from 0.41-0.69 indicating that the particles were not monodisperse (Figure 3).

The significantly larger than expected (1-20 nm) particle size was due to the fact that the isolated solution was not properly stored after synthesis and prior to analysis. We believe that the particles began to decompose/aggregate as evidenced by the precipitation of solid material prior to the light scattering experiment.

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References:

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[2] N.L. Pickett, P. O'Brien, Chemical Record, 2001, 1, 467-479.