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OAK RIDGE NATIONAL LABORATORY
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Small Business Voucher Pilot

Technical Assistance from Oak Ridge National Laboratory to Nano Elements Source, LLC

SCALABLE PROCESSING OF ZNS NANOPARTICLES FOR HIGH PHOTOLUMINESCENCE EFFICIENCY QUANTUM DOTS

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Contents

1. ABSTRACT

Nano Elements Source, LLC, a biotech startup has licensed the NanoFermentation technology from Oak Ridge National Laboratory to further commercialize low cost, cadmium free photoluminescent nanoparticles produced using affordable, environmentally-friendly. This project aimed to develop post chemical processing of biosynthesized ZnS quantum dots (QD) to improve their efficiency of luminescence to make them suitable for solid state lighting applications. Several post processing approached were proposed and tested using to biosynthesized of ZnS QD. Optical properties of ZnS nanoparticles including soft chemical etching, and photonic etching have been tested and quantified against standard materials. We applied the developed chemical modification approach to control quality of chemically synthetized ZnS QD's, and to calculate the maximum achievable efficiency of photoluminescence. We estimated the cost of the proposed post-processing treatment of nanoFermented nanoparticles and proposed several approaches to further the development of low cost nanoparticles for electro-optical and other applications relevant to DOE mission.

2. STATEMENT OF OBJECTIVES

The goal of this project is to develop a solution allowing the NanoFermentation technology to move to mass production of nanoparticles to TRL--4-5. The current quality (low fluorescence efficiency) of nanoparticles produced through this process is not competitive with the targets sets by current BTO and SSL programs at EERE. The goal of the SBV funded research and development effort is to develop advanced low-cost post processing of NanoFermentation nanoparticles and demonstrate high photoluminescence quantum efficiency (PL QE) of ZnS. We plan to further the development of this new technology by application to high PL QE of ternary, tertiary and core-shell nanoparticles through BTO and SSL programs. The results of R&D efforts funded through the SBV program will serve as an example, proof-of-principle for new proposals. It will also access economic structure and cost of post-treatment. The SBV provides access to expertise and instrumentation, which is unavailable in the private sector.

3. BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

The need for economical and quality materials is a growing concern as technology is becoming more complex and difficult to manufacture. Nanoparticle quantum dots (QD) offer possible alternative solutions for electronics, optoelectronics and medical imaging. Due to their high luminescent efficiency and tunable band gap, making scalable and cost effective QD's is optimal in today's marketplace, especially for lighting and display applications. Methods currently used to generate QDs utilize high temperature and multi-step processing schemes to yield high luminescent, but high-cost QD's.[(13)] Low temperature synthesis methods such as sonication, UV irradiation and surfactants have the potential to reduce energy and labor costs for labs and commercial manufactures. Such development may improve the growth and advancement of green chemistry methods, safer businesses practices and efficient material fabrication.

In addition to energy savings gained from implementing QDs, there has been expressed government interest in improving the QD and QD Solid State Lighting markets. This research will further two specific goals of EERE's BTO: Emerging Technologies Program (by 2020, reduce building energy use 30%), and Commercial Buildings Integration Plan (by 2025, cut energy use of market leaders by 35%). These energy savings, through commercialization of biosynthesized low-cost QDs, would address DOE's National Goal of doubling energy productivity, dollars of gross domestic product (GDP) per unit of energy, by 2030.

4. TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

The research and development efforts conducted at ORNL were focused on 1) the development of post-processing approach to suppress negative effects of surface defects in Nanofermented ZnS nanoparticles and 2) maximize photoluminescence efficiency of ZnS in aqueous solution. The second effort targeted application of post-processing treatment techniques (developed in first focus effort) to maximize photoluminescence efficiency of ZnS nanoparticles produced at low temperature. The shelf-life of nanoparticles produced through post-treatment of nanoferemented ZnS (nf-ZnS) and low temperature chemically-synthesized ZnS (lts-ZnS) nanoparticles was estimated.

Several postprocessing approaches to suppress negative effects of surface defects in nanofermented ZnS nanoparticles were tested, including:

<u>Approach 1:</u> *Ligand passivation of nanoparticles,* which is based on idea that the surface defects are commonly associated with uncompensated charge/vacancy on the surface of the nanoparticle, which could be used to attract ligands of opposite charge, and thus, reduce non-radiative relaxation and increase the efficiency of band gap emission.

<u>Approach 2:</u> *Soft etching of the surface of nanoparticles.* This approach is based on a photo-corrosion process, initiated by exposure of a nf-ZnS solution to high-flux ultra violet (UV) light. Upon excitation the non-radiative pathway for relaxation of the excited state would lead to increase in surface temperature of nanoparticle. This would lead to locally increased solubility of ZnS (at the solid-liquid interface), which would be the most active at the defect site. Higher concentration of Zn^{2+} and S^{-2} ions removed from the surface of ZnS nanoparticle create favorable condition for surface restructuring, where both ions could return to the surface, restoring the crystallinity of ZnS.

4.1 CHEMICAL PASSIVATION OF SURFACE DEFECTS

Surface modification of nf-ZnS was carried using Na_2S, urea and thiourea. The nf-ZnS nanoparticles were exposed to Na_2S, urea or thiourea for 12 h following centrifugation and washing cycles. The photoluminescence spectra were corrected to the values of corresponding absorbance at 320 and 350 nm.

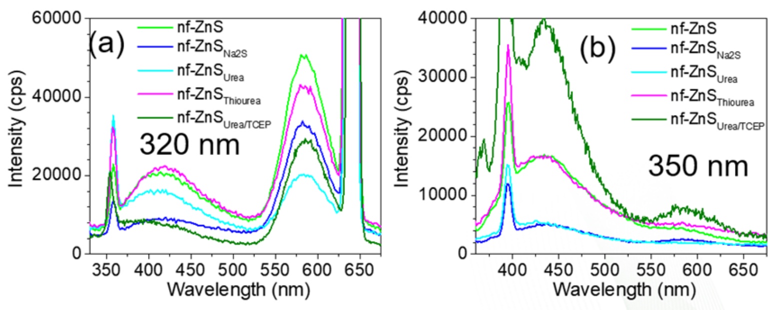


Figure 1 Effect of chemical treatment (Na_2S, urea and thiourea) on photoluminescence of ZnS. The excitations was at (a) 320 nm and (b) 350 nm.

The highest efficiency enhancement (4.5 times higher compared to untreated nf-Zn) was demonstrated (for 350 nm excitation) and urea/TCEP treated sample (nf-ZnS Urea/TCEP) at pH=7, 12h). The results suggest that urea/TCEP passivate slow energy defect states, whereas higher energy states are almost unchanged as indicated by photoluminescence with 320 nm excitation. Chemical treatment at higher temperature (60^{o}C) or higher pH (pH=10) led to a decrease in photoluminescence efficiency (for 320 and 350 nm excitation) and an increase in particle size.

4.2 PHOTOETCHING.

The effect of extended UV irradiation on optical properties of ZnS (during the surface modification process) was investigated starting with as-synthesized ZnS nanoparticles in reactive media and exposed to fiber optic coupled UV light (404 nm, 75 mW for 3h) under continuous stirring. The reactive media was an aqueous solution, purged with nitrogen and adjusted to pH=10 (by 0.1M NaOH) . The nf-ZnS were rinsed/centrifuged 4x in DI H_2O and 1x in MeOH, and subsequently dispersed in 1% H_2O in MeOH. Figure 2 below shows the effect of irradiation on optical properties of nf-ZnS. The samples were irradiated for 3.5, 14 and 24 h at pH 7, 10 and 12.

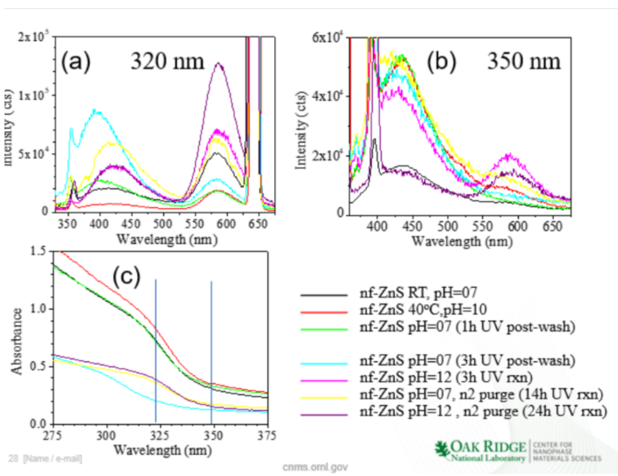


Figure 2 Effect of photoetching time and acidity on photoluminescence properties of nf ZnS excited with 320 nm (a) and 350 nm (b). The spectra are normalized to the absorbance of nanoparticles at 320 nm and 350 nm. High intensity line around 640 nm (c) is due to unfiltered second order Raleigh scattering. Vertical lines on panel c indicate excitation wavelength.

PL spectrum of nf-ZnS exhibits two strong broad emission bands at 420 and 590 nm with FWHM of about 50 nm. The black-color lines of absorbance and photoluminescence spectra show properties of as received nf-ZnS. Prolonged photoetching results in partial solubilization of nanoparticles, reducing the size of nf-ZnS as evidenced by a shift in the edge of absorbance spectrum. The highest photoetching effect was observed at neutral pH=7 and exposure of solution for 3h to UV light. Normalization of PL spectra to the absorbance at excitation wavelength allows direct comparison of the PL spectra, the largest area under the spectrum indicates the material with the highest PL efficiency. We conclude that the 3h and 12 h irradiate leads to the formation of the best material. The emission color characteristics of these materials are very different, the 3.5h UV irradiated sample at neutral pH shows PL dominated by “blue” emission (320 nm excitation) while the 12h sample with higher pH exhibits a mixed “blue- yellow” emission. The same pair of samples shows predominantly “blue” emission (maximum around 425 nm) when excited at 350 nm. These results suggest that the photo-etching reduced the density of shallow energy defects, increasing the photoluminescence efficiency almost by a factor of 2.5- 3 compared to as-received nf-ZnS, for either 320 or 350 nm excitation.

4.3 REACTIVE PHOTOETCHING.

Modification of pH environment between neutral and pH=12 lead to significant improvement in the photoluminescence intensity of nf-ZnS nanoparticles. We further investigated possibility of photoetching combined with surface repair, which was provided by high concentration of repairing ions present in the etching environment. For surface repair during photoetching we used urea (CH_4N_2O), thiourea(CH_4N_2S) and urea/TCEP binary system. The role of thiourea is to provide sulfide ions to Zn terminated nanoparticles, thus repairing the ion vacancy. Tris(2-carboxyethyl) phosphine hydrochloride (TCEP) is a strong reducing agent which is also used to break disulfide bonds (possible defects or residual of protein bound to the surface of nf-ZnS). Urea is used as protein denaturant (for surface cleaning of nf-ZnS). The figures below demonstrate the results of reactive photoetching. The results of reactive photoetching are shown in figure 3, below.

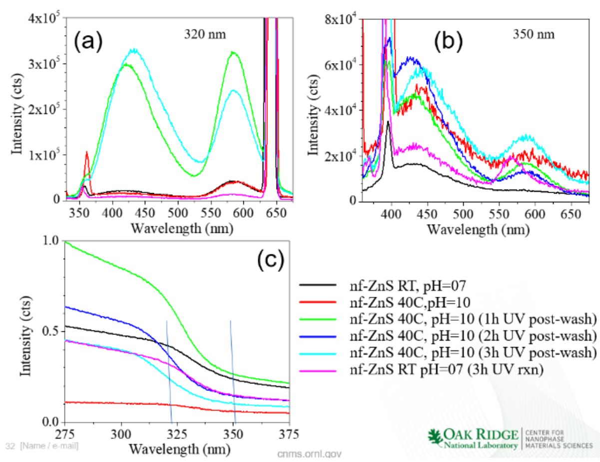


Figure 3. Changes in optical properties of reactively photoetched nf-ZnS with thiourea. (a) absorption corrected photoluminescence generated using 320 nm excitation, (b) absorption corrected photoluminescence obtained with 350 nm excitation.

It is apparent, that for 320 nm excitation the best improvement in photoluminescence efficiency was the factor of 20 increase, compared to as-received ZnS, observed for nf-ZnS treated by thiourea and exposed to UV for 1-3h at pH=10 and T=40^{o}C. It is interesting to note that improvement of PL efficiency for excitation with 350 nm was only a factor of 3, suggesting that excess of S^{-2} ions under photoetching conditions does not allow complete removal of defects. The presence of the 580 nm emission band in treated samples further supports that additional defects associated with excess of S^{-2} may be produced. When nf-ZnS was exposed to UV light photoetching in the presence of Na_2S, pH=10 and T= 40°C, an improvement by a factor or 15 was demonstrated for samples treated for 1 and 3 hours (considering 320 nm excitation as a reference point), Figure 4.

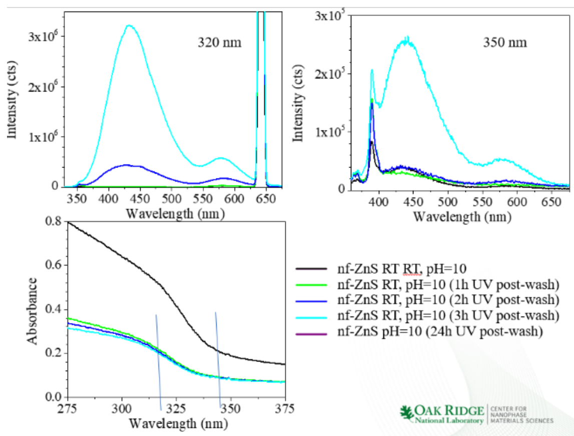


Figure 4. Effect of reactive photoetching in the presence of Na_2S on optical properties of nf-ZnS. The photoluminescence of nf-ZnS was normalized to the absorbance at the excitation wavelength.

For both samples the intensity of emission at 420 nm and 570 nm is about the same. For samples excited at 350 nm the improvement in the photoluminescence efficiency is smaller, but the band gap fluorescence shows double the efficiency than that with only the defect originated emission at 570 nm. While photo-etching at basic pH in the presence of Na_2S indeed improved the photoluminescence properties of as-received nf-ZnS, without photoetching the bandgap photoluminescence is completely quenched and only defect related PL is observed. This observation allows us to make a conclusion that excess of S^{-2} ions completely covers the surface of the ZnS nanoparticle, however, and this excess also creates a pathway for non-radiative relaxation of the excited states. The absorbance spectra show slight increase at high energy part of the spectrum.

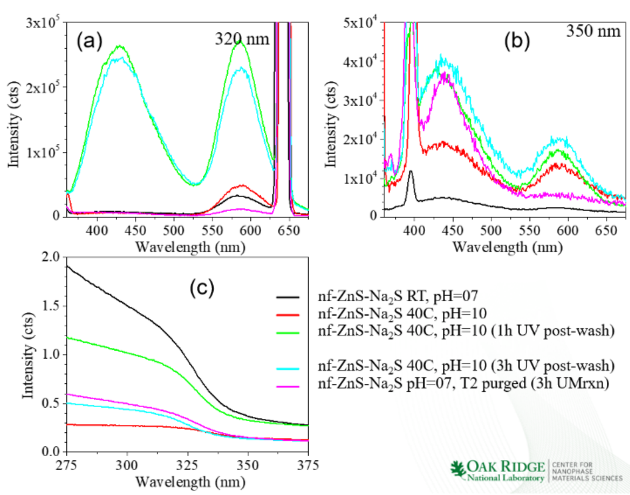


Figure 5. The effect of photoetching in basic media (pH=10), urea/TCEP at room temperature.

Low temperature photoetching of nf-ZnS in urea-TCEP media requires 2-3 hours to reach highest enhancement of photoluminescence properties (by a factor of 4), predominantly improving band gap emission, (Fig. 5). The photoetching also reduces the absorption at wavelengths longer than the band gap, the observation is concomitant with reduction in defect-originated luminescence.

The effect of irradiation time (1, 2, 3, 4, and 24 h) on the efficiency of photoluminescence was studied for urea and thiourea modified in the presence of TCEP. Photoluminescence observed with 320 nm excitation indicates that irradiation of urea/TCEP for longer than 3 h does not result in additional improvement beyond those observed for 3h irradiation. However, with thiourea, the best photoluminescence was observed after 24h irradiation.

In previous experiments we observed changes on the band gap of ZnS, indicating that the diameter of nanoparticles reduced. We therefore tested the higher energy excitation (300 nm) to probe photoluminescence of smaller particles, which are expecting to absorb at much higher energy.

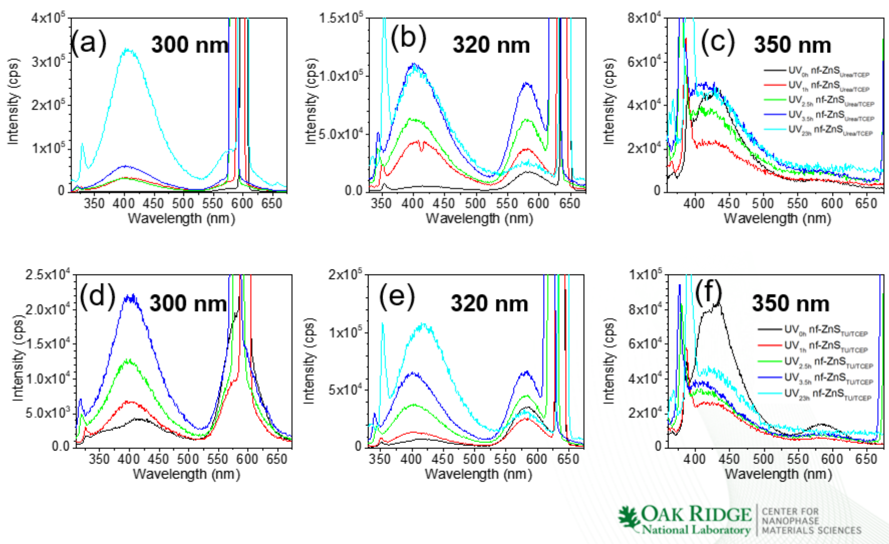


Figure 6. Normalized photoluminescence of photoetched of urea/TCEP modified nf-ZnS (chemically modified in N_2 purged H_2O, RT for 16h, rinsed/centrifuged 3x in H2O and 1x in methanol, then re-dispersed in 1% H_2O in methanol. UV-a under air at 404 nm, 75 mW in 1% H_2O in methanol) and excited with (a) 300nm, (b) 320nm and (c) 350 nm. Normalized photoluminescence of photoetched treatment of thiourea/TCEP modified nf-ZnS (chemically modified in N_2 purged H_2O, room temperature for 16h, rinsed/centrifuged 3x in H_2O and 1x in methanol, then re-dispersed in 1% H_2O in methanol. UV-irradiation under air at 404 nm, 75 mW in 1% H_2O in methanol.)

Figure 6, panels (a) and (d) show the effect of 16h photoetching with urea/TCEP and 3h irradiation in the presence of thiourea/TCEP on photoluminescence properties of nf-ZnS. We observed that the nanoparticles excited at 350 nm show predominantly bandgap emission, with minimum defect photoluminescence. Interestingly, the best photoluminescence at 350 nm excitation was observed for thiourea/TCEP without irradiation. It suggests a possible low-cost pathway to modify nanoparticles without expense associated with implementation of UV etching system. The summary of the optical properties of nf-ZnS nanoparticles exposed to a different photoetching time are shown in Table . They demonstrate that a factor of 5 improvement can be achieved after 1h of treatment.

Table 1. A summary of optical properties of nf-ZnS nanoparticles which underwent photoetching postprocessing treatment.

	UV Time	ε_{320nm}	A_{320nm}	F_x ($\int_{Corr}$)	f_x	F_x/f_x	Φ_x(%)
nf-ZnS	0	341.8	0.731	1.239	0.814	1.521	0. 50
	1h	226	0.484	5.073	0.672	7.549	2.50
	2h	140	0.301	0.525	0.500	1.051	0.34
	2h + 3d	92	0.197	0.451	0.364	1.237	0.41
	2h+4d	86	0.180	0.466	0.340	1.372	0.45

4.4 CONTROL OF THE SURFACE DEFECT DENSITY IN LOW TEMPERATURE SYNTHESIS OF ZNS NANOPARTICLES.

We demonstrated that the surface defects of nf-ZnS nanoparticles can be partially removed through a carefully controlled photoetching in the presence of reducing or surface passivation agents. However, the applicability of the approach is limited to the surface defects of nanoparticle which are exposed to the liquid media and modification agents, and it does not affect defects embedded within the nanoparticle structure. The excess of surface material needs to be etched off to access buried defects (which may be within a monolayer from the surface). Such etching may reduce the size of the nanoparticles and therefore shift the emission of nanoparticles to the higher energy, making them less suitable for solid state light applications. Implementation of the surface passivation during the low temperature synthesis of nanoparticle could potentially allow mitigation of defects during synthesis of nanoparticles. The nanoparticle growth may be slowed because surface passivation may render some area of particle inactive. However, slow growth of nanoparticle of higher quality may be economically more advantageous compared to the cost of post-treatment processing of nf-ZnS.

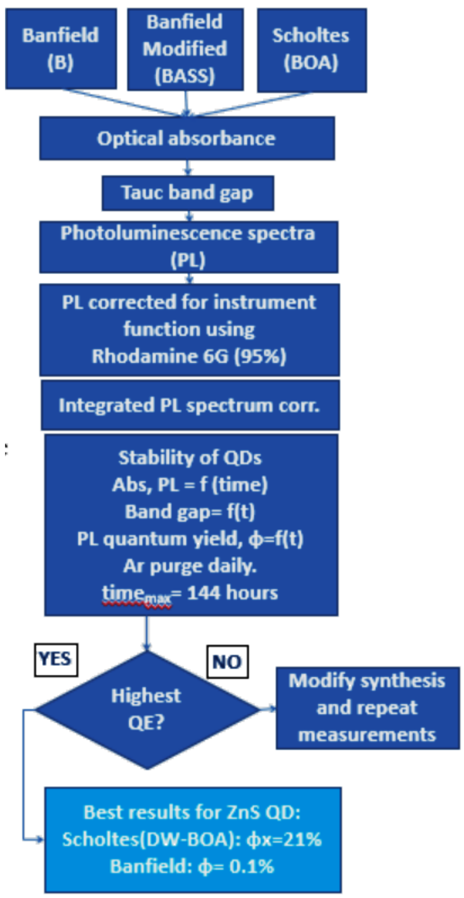


Figure 7 Experimental workflow used for chemical synthesis of ZnS targeted the development nanoparticles with the highest photoluminescence efficiency

ZnS QD nanoparticles were prepared in the media of anhydrous methanol (MeOH) by combining 1mM sodium sulfide (Na_2S) and 1mM zinc chloride ($ZnCl_2$) under inert Ar atmosphere, while under continuous sonication [5]. Oleic acid (OA) was selected as the primary capping agent to reduce oxidation of nanoparticle surface [1,2]. Samples identified as *BASS* and *BOA* were synthesized with and without oleic acid surfactant respectively. The samples marked as Zn3x contained an excess of Zn in respect to sulfur. Samples were centrifuged at 10,000 rpm before sonication or vortex spinning. Shelf life of samples was measured daily, keeping samples under argon atmosphere. The PLQE quantum yield (ϕ_F) of re-dispersed OA-nf ZnS colloid was determined by comparative methods using a solution of Rhodamine B with matching optical density at excitation wavelength as a standard. The (ϕ_F) of OA-nf ZnS was found to be 5.8%. Band gap of ZnS/bio ZnS was estimated to be 4.1 eV. Optical propertied of the metal sulfide nanoparticles (absorbance and photoluminescence) were measured.

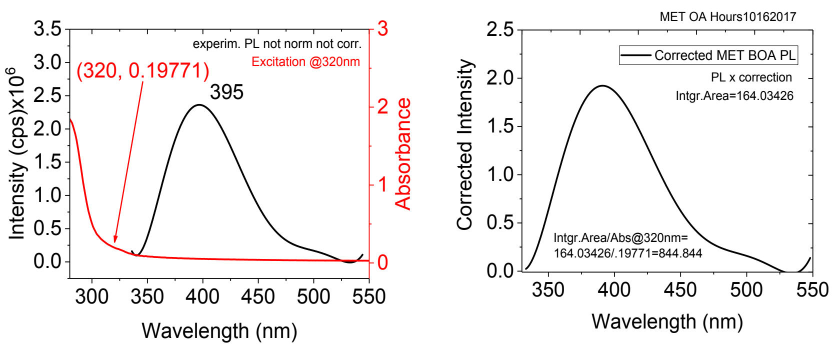


Figure 9. Optical properties of ZnS QD's prepared with DW- OA synthesis. Absorbance (red) and photoluminescence spectrum for 320nm excitation showing the emission peak at 395nm. Photoluminescence normalized to absorption at excitation wavelength is shown on the right panel.

Banfield synthesis of ZnS quantum dots with oleic acid (BASS & BOA): The zinc chloride ($ZnCl_2$) and the sodium sulfide stock solutions were prepared first. Then, 50ml stock solutions of 1mM of $ZnCl_2$ in methanol (MeOH) and the 1mM of Na_2S in methanol (MeOH) were prepared. The stoichiometric mixture of Na_2S was added into the $ZnCl_2$ under inert atmosphere (Ar bubbled through a septum in a round bottom flask for 15 minutes). The 1% vol. OA was added to the solution as Na_2S. Zn3x sample (ratio of 3:1 Zn:S) was synthesized using method mentioned above.

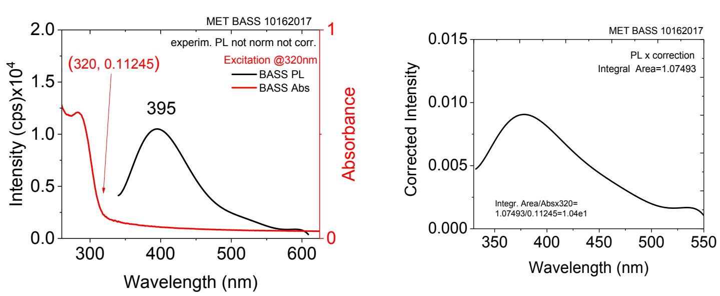


Figure 8.DW ZnS BASS. Absorbance excited at 320nm and Photoluminescence emission at 395nm and corrected photoluminescence to the right.

Synthesis of Zn3x-C/S centrifugation & sonication : we used 1mM stock solutions of $ZnCl_2$ degassed with Ar for 5 minutes before synthesis. Samples were centrifuged at 10,000 rpm for 15 minutes after nanoparticle synthesis. An excess of MeOH extracted with equivalent volume of MeOH then quickly purged with Ar before sonication at

100% power (Ingenieurbüro CAT, M. Zipperer GmbH) (Type: X120 130W 50/60Hz) at a distance of 5cm for 3 minutes. This sonication cycle was repeated three times.

Sy*nthesis using drop-wise (DW) ZnS:* OA (1% vol.) 1mM $ZnCl_2$ stock solution was degassed with Ar for 5 minutes. Then a 1mM Na_2S solution under Ar was slowly added at 1ml/min dropwise to the $ZnCl_2$/OA mixture under a smooth stir (maintained while dropwise addition) and bubbled Ar for 15 minutes.

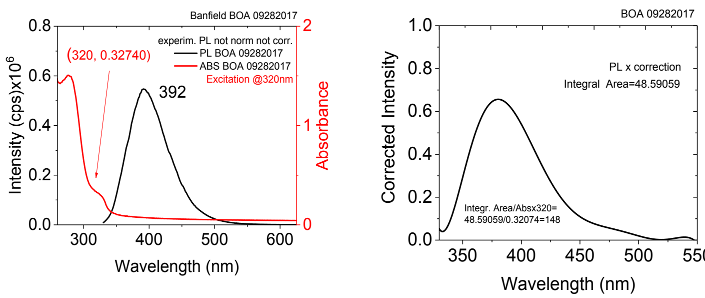


Figure 10. Optical properties of ZnS nanoparticles synthesized using BOA. Absorbance and photoluminescence produced by 320 nm excitation with a maximum at 395 nm. The absorbance- photoluminescence is shown on the right panel.

The DW ZnS BOA recipe produced the highest normalized PL with stability like BOA Zn3x with centrifugation. The PL intensity of ZnS BOA was over an order magnitude higher than that of Zn3x C/S sample and the stability after 144 hours was also higher compared to the normalized PL intensity of Zn3x C/S. The photoluminescence of DW ZnS BOA sample stabilized after 24 hours.

The DW ZnS BASS sample had better stability over the Zn3x C/S sample, yet the value of absorbance-normalized PL intensity was lower. The DW method produced significant results in the BOA sample, yielding the highest normalized PL and QY for all the BOA samples. We modified the original Banfield synthesis to run it under argon, and showed that while the absorbance of DW ZnS N_2 BASS and BOA samples was the same, the photoluminescence of samples produced under N_2 atmosphere was much lower than that produced under argon. Synthesis in an excess of Zn^{2+} ions led to a decrease in the normalized PL, most likely due to formation of amorphous ZnS clusters in the BASS and BOA samples. Increasing the concentration of OA from 1% to 5% led to an increase in the stability of the sample. The DW ZnS BOA 10mM at 5% OA displayed an order of magnitude higher efficiency after 48 hours compared to the same sample with 1% OA. The absorbance of DW ZnS 10mM BASS sample was about 1.159 compared to 0.113

in the DW ZnS BASS sample. The absorbance of the DW ZnS 10mM BOA sample was 0.875 compared to 0.196 in the DW ZnS BOA sample. Table 2 summarizes optical properties of chemically synthetized ZnS nanoparticles by all methods mentioned above, including band gap information and efficiency of photoluminescence. The highest efficiency of ZnS fluorescence (21%) was obtained in DW- BOA synthesis, this is a factor of 5 higher than the DW-BASS approach.

Table 2 Optical properties of chemically synthetized ZnS nanoparticles

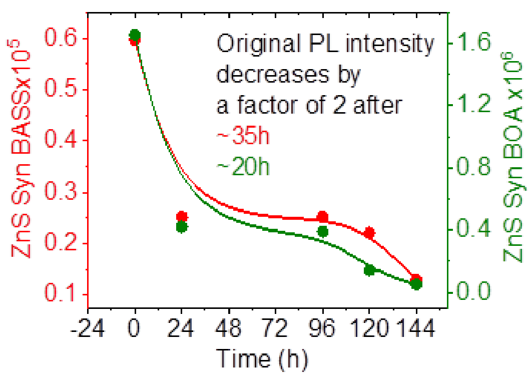
	BASS		BOA	
Synthesis	ϕx	Bandgap (eV)	ϕx	Bandgap (eV)
ZnS	0.04	4.06	3.74	4.10
Zn3x	1.06	4.17	2.33	4.10
Zn3x-C/S	2.11	4.20	1.69	4.09
DW ZnS N_2	0.1	4.03	5.33	4.08
DW ZnS	0.26	4.01	20.91	4.04
DW ZnS Sonic	0.15	4.21	6.41	4.18
DW ZnS UV	0.23	4.24	0.61	4.12

*ϕx values compared to photoluminescence efficiency of Rhodamine 6G (95%)

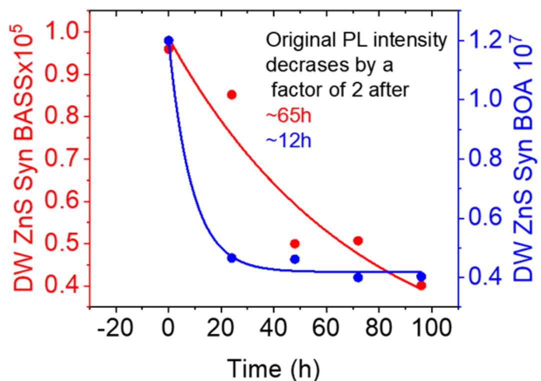
It is interesting to note that the bandgap (and the size of nanoparticles) of ZnS prepared by DW-BOA and DW-BASS methods are about the same, and their band gap is about 4.0 eV. The second to the best DW-ZnS efficiency of about 20.91% was the efficiency of DW-ZnS-sonic (6.4%).

4.5 INVESTIGATION OF THE STABILITY OF CHEMICALLY SYNTHESIZED ZNS NANOPARTICLES

The stability of chemically synthesized ZnS nanoparticles was studied by following changes in absorbance and photoluminescence over 144 hours while keeping solutions under inert atmosphere. All nanoparticles produced by BOA, BASS, Zn3x-BASS and Zn3x-BOA approaches showed rapid decline of photoluminescence over the first 24 hours, followed by stabilization of photoluminescence. After the first decline, the efficiency of luminescence of Zn3x nanoparticles did not change over the 144 h period, whereas nanoparticles obtained through the BASS and BOA approach showed a second decline in efficiency after 120 h.



(a)



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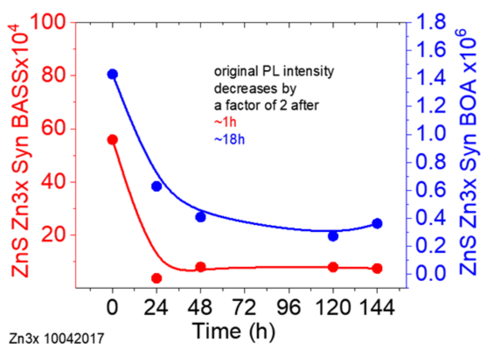

Figure 11. Stability of chemically synthesized ZnS prepared using different methods. (a) Changes in the intensity of normalized photoluminescence (392 nm peak) to absorbance (at 320nm) of chemically synthesized ZnS in MeOH purged with argon under excited. (b) Changes in the intensity of normalized photoluminescence to absorbance (395nm peak) of synthesized DW ZnS in MeOH purged with argon excited 320 nm over 144 hours. (c) Changes in the intensity of normalized photoluminescence (392nm peak) of synthesized ZnS (Zn:S 3:1 ratio) in MeOH purged with argon excited 320nm over a 144 hours.

The PL intensity of DW-ZnS BASS decreased by a factor of 2 over ~65 h while the PL intensity of DW-BOA ZnS decreased by a factor of 2 over first 12 hours, and then stabilized at about 40% of original value. Samples of ZnS obtained in 3x excess of Zn^{2+} showed relatively similar stability with the PL intensity decreasing over first 24 h by a factor of 2. Thus, depending on application, the tradeoff high efficiency and long shelf life of ZnS nanoparticles should be considered. UV photo etching was used during synthesis and for post processing of chemically synthesized ZnS, resulting in a higher rate of PL intensity reduction for the BOA samples, compared to the BASS samples, as seen in table below 3. The post processing photoetching of chemically synthetized ZnS BASS lead to increase in sample absorption after 45 minutes, while absorbance of ZnS BOA samples did not increase of the same time. The absorbance Zn3x BOA samples was higher compared with the ZnS BOA samples, while the absorbance of the Zn3x BASS and ZnS BASS samples decreased in a comparable manner.

Sonication- assisted synthesis of ZnS. DW-ZnS-sonic-BASS samples displayed absorbance comparable to DW ZnS samples, however, the absorption-normalized photoluminescence values were lower than those of the DW ZnS Sonic BASS and BOA samples.

Table 3. Normalized photoluminescence to absorption at 320nm. (Photoluminescence intensities are divided by 1000).

Synthesis	BASS			BOA		
Processing	No UV	15 min.	45 min.	No UV	15 min.	45 min.
ZnS UV	18	14	6	3190	2130	180
Zn3x UV	220	64	11	4700	3920	290

4.6 COST ANALYSIS

NanoFermentation of ZnS quantum dots costs \$0.067 per gram. This is in sharp contrast to commercial quantum dots which cost ~\$200 per gram. The majority of this cost, 83%, is the media required to grow the bacteria while nanoparticle precursors are 8% and equipment is 5%. The post processing improvements described here only add 1.5% to the cost of ZnS quantum dots while greatly improving their value to the market. With these improvements nanofermented ZnS quantum dots remain an economically viable option.

4.7 MARKET FIT.

The most lucrative market for quantum dot is next generation of phosphor for display technology. The technical requirements of quantum dots for this market are defined by purity and quality of color and the efficiency of electroluminescence along with the stability of their optical properties under application conditions. Some specific properties include red emitter emission maximum at ~620 nm (20 nm FWHM), and green emitter with maximum at~520 nm (20nm) FWHM). The efficiency of luminescence should exceed 75% and preferably approaching 90%. The quantum dots are expected to perform without degradation of the properties over 10,000 hours under elevated temperature of 100^{o}C in the film.

4.8 COMMERCIALIZATION POSSIBILITIES

Production of high photoluminescent efficiency ZnS nanoparticles with low cost techniques demonstrated in this project opens several commercialization opportunities.

1) The technology verified in this project allows for the improvement of nf-ZnS photoluminescence efficiency by a factor of 20, using the post-processing approach. This technology can potentially be extended to other composition of nanoparticles produced through NanoFermentation.
2) Commercialization of ZnS QDs as a phosphor screen in electronic devices. We have demonstrated that ZnS nanoparticles (modified nf-ZnS and chemically synthetized ZnS) can be deposited on the surface of quartz/glass forming stable coatings.
3) Commercialization of ZnS QD as antibacterial and antifungal components. The technology was recently disclosed (ORNL IDEA) and demonstrated in collaboration with Texas AM medical center. (manuscript accepted for publication).
4) Chemical synthesis of ZnS nanoparticles with efficiency above 20% can be implemented using H_2S outgas from the NanoFermentation process (ORNL disclosure, patent application)

4.9 PLANS FOR FUTURE COLLABORATION

The results of R&D efforts in this project clearly indicate the possibility to design low-cost technology of high efficiency luminescent nanoparticles, which can be applied to other nanoparticle compositions. Several opportunities have been identified to further the nanoparticle technology through future collaboration.

The *first opportunity* is to use the procedures demonstrated here to lower the cost and increase the photoluminescence efficiency of the quantum dots/nanoparticles which are currently used as LED phosphors. There include core-shell nanoparticles with different composition of core (i.e. CdS) and shell made of ZnS. The chemical synthesis procedures developed and verified in this project allow production of low defects of ZnS shell, thus creating a potential to further improve efficiency of photoluminescence of core-shell nanoparticles.

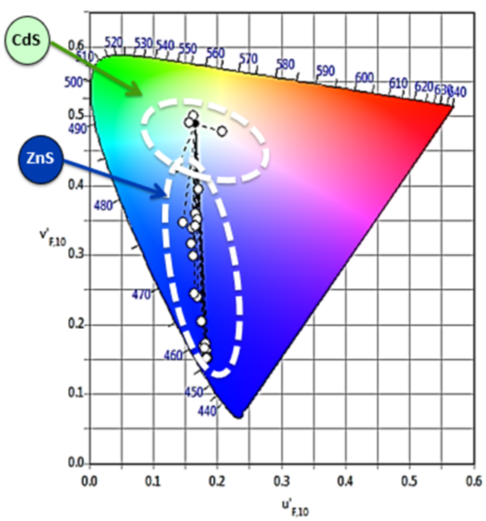

Figure 12. Chromaticity diagram showing broad range of photoluminescence colors (from blue to white) which can be produced in CdS:ZnS co-colloids.

The second opportunity includes incorporation of the technology developed in this project for production of green, red and white-color QD suitable for application in solid state lighting devices. Our preliminary investigation (conducted as part of CNMS fundamental research program) demonstrated one possible strategy to produce CdS:ZnS co-colloids, the emission color of which can be controlled by changing the ratio of CdS and ZnS components. Figure 12 demonstrates the *color quality* of broad range of CdS:ZnS co-colloids generated in our laboratory (open circles) on the human color perception map (in terms of two CIE parameters x and y). The *chromaticity* diagram is designed to display objective specification of the quality of a color independent of it luminance (intensity). Further development may include demonstration of green and red- luminescent particles.

The third opportunity involved implementation of optimized chemical synthesis using outgas from the fermentation chamber. The concept of this technology was recently disclosed and patented by ORNL (Ji Won Moon et. all). There, the H_2S outgassed from the fermentation can be used to synthesized quantum dots or nanoparticles, including those which present commercial interest, as mentioned above. We believe that this opportunity presents the shortest commercialization route out of three opportunities mentioned above.

Based on our contacts with other companies, future research could target application of quantum dots for new markets (including lighting). With focused R&D efforts on the development & enhancement of core shell structures, and integration with the improved ZnS quantum dots described here, NanoFermented quantum dots could be optimized for horticultural lighting applications (with peak emission at 470 nm and 660 nm). Additionally, quantum dots that demonstrate fast switching speeds between their on and off states would be ideal for enhanced data transfer. Of particular interest is the development of stable UV emitting QDs for UV sterilization.

5. CONCLUSIONS

We investigated a broad range of techniques to improve efficiency of nf ZnS nanoparticles and provided several routes to improve their photoluminescence efficiency through postprocessing. We also concluded that even higher efficiencies can be achieved for nanoparticles synthetized under strict environment of chemical synthesis. We also showed that postprocessing does not increase the cost of nf-Zn, keeping them a low- cost material comparing with current commercial cost of ZnS.

7. ACKNOWLEDGMENTS

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