Physical and Optical Characterization of Mn-doped ZnS Nanoparticles Prepared via Reverse Micelle Method Assisted by Compressed CO2

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Abstract. This paper presents the study on the Mn-doped ZnS (ZnS:Mn) nanoparticles synthesized using reverse micelle method assisted by compressed CO2 at 60 bar and 40°C. Effects of retention time (30-120 min) on the particle formation were studied. The optical properties, size, morphology, and structure of the resulting particles were investigated. The results showed that ZnS:Mn nanoparticles were successfully formed with particle size ranging from 2 to 3 nm, which showed quantum size effects. The highest photoluminescence (PL) intensity ratio was found at 60 min retention time. The increase in photoluminescence (PL) intensity ratio indicated an increased homogeneity of nanoparticle growth with decreased surface defects.

1. Introduction
Zinc sulfate (ZnS) is a nontoxic II–VI semiconductor material with direct and large bandgap that is widely studied because of its numerous potential applications, including solar cells, bio-imaging, wavelength-tunable lasers, and electronic and optoelectronic nanodevices [1–3]. The presence of optical impurities affects the physical and chemical characterization of ZnS. Incorporating suitable dopants is an approach to enhancing the potential of ZnS semiconductor as a phosphor. Issues commonly encountered in the synthesis of nano-particles are size control and agglomeration of the particles. In the case of doped ZnS nanoparticles, a suitable synthesis method is not only required to prevent agglomeration but also to improve the optical properties. Among various techniques for producing nanoparticles, reverse micelle method is considered a promising technique to prepare less agglomerated and more monodispersed nanoparticles [4-6]. The advantage of this method is the ability...
to control excess particle growth when particle size approaches that of a H2O nanodroplet. However, difficulty is usually encountered in post process recovery step that affect particle size and dispersion [7-8].

In recent years, some researchers have carried out combination of antisolvent CO2 and reverse micelle method for the formation of nanoparticles [9-11]. It is expected that the properties of the water-in-oil in reverse micelle system can be easily tuned by the pressure and temperature of CO2. Nanoparticle synthesis using reverse micelle assisted by CO2 as antisolvent is an interesting phenomena and needs further study. Therefore, the aim of this work is to produce ZnS:Mn nanoparticles with better particle characteristics and optical properties.

2. Materials and Methods

2.1. ZnS:Mn Particle Synthesis
The ZnS:Mn solution was prepared using reverse micelle method reported previously [12]. In this study, the desired amount of ZnS:Mn2+ (4%) sample solutions were then loaded into a 1 L standard steel cylinder with a sight glass. The cell was then sealed and pressurized with CO2 antisolvent with four different retention times (30–120 min). The conditions in the vessel was kept at relatively low pressure of 60 bar and temperature of 40oC. The precipitated ZnS:Mn particles were collected and then washed by aqueous ethanol solution, centrifuged and dried in an oven.

2.2. Particle Characterization
The X-ray diffraction (XRD) patterns of the powdered samples were investigated using a D8 Advance AXS X-ray diffractometer at diffraction patterns ranging from 20° to 80°. The crystal size was estimated at full width half maximum (FWHM) of the XRD peaks. The fluorescence measurements were performed on a photoluminescence (PL) SP920 spectrophotometer. Physical characterizations of the particles were then performed using transmission electron microscopy (TEM).

3. Results and Discussion

3.1. Physical Characterization of ZnS:Mn
The XRD patterns (Figure 1) of ZnS:Mn nanoparticles at different retention times exhibit three diffraction peaks at 2θ = 28.50°, 48.30o, and 56.50°, which corresponded to the (111), (220), and (311) planes, respectively. These peaks were indexed as a zinc blende structure corresponding to JCPDS file no. 05-0566 with no impurity peak observed. The average of crystal size as calculated according to the Debye-Scherrer formula [13] ranging between 2.0 to 3.0 nm (Table 1), which fell within the quantum confinement region. However, additional peak appeared at 32° when retention time was set at 120 min. It shows that the dissolution of CO2 at long retention time in the micelle core leads to micellar instability and gives excess energy to segregate the Mn2+ atom out of the ZnS lattice. Generally, the shape of the particles for the samples are spherical and they are homogeneously dispersed as characterized by TEM (Figure 2). These results provide indirect evidence of the role of CO2 to effectively improve surfactant capping on the surface of ZnS:Mn nanoparticles.

| Retention Time (min) | Particle Size (nm) | Emission (nm) | PL Intensity Ratio |
|----------------------|-------------------|---------------|------------------|
| 30                   | 2.53              | 602           | 12.02            |
| 60                   | 2.21              | 608           | 32.42            |
| 90                   | 2.39              | 608           | 23.31            |
| 120                  | 2.48              | 608           | 19.28            |

Table 1. Characterization of ZnS:Mn Particles
Figure 1. XRD patterns of ZnS:Mn at different retention times

Figure 2. Transmission electron microscope (TEM) image of ZnS:Mn at 60 minutes

3.2. Characterization of ZnS:Mn
Figure 3 shows that even though the ZnS:Mn particles showed small size differences at different retention times, the relative intensities of PL varied significantly. This might be due to the control of the droplet size by surfactant concentration in the water–heptane matrix. The orange emission intensity increased linearly with the quenching of the blue emission and started to decrease when using the samples with 90 min retention time. Table 1 and Figure 3 show high value of PL intensity ratio at 60 min exposure to compressed CO2, thus indicating the formation of monodisperse nanoparticles. This phenomenon could be discussed based on the nanoparticles-surfactant-solvent interaction. Upon pressurization with CO2, the gas continues to dissolve into the micelle core and decreases the
solvation of the AOTcap nanoparticles, thus causing the removal of water in the reverse micelle droplet. Therefore, trap sites on the nanoparticle surface were decreased and crystallinity was promoted, which dramatically improved the PL intensity.

Previously, several researchers studied the modification of ZnS:Mn nanocrystal by using different surfactants\cite{14-15}, W ([H2O]/[CTAB]) values \cite{16} and types of mixing method in a reverse micelle of H2O/AOT/n-heptane \cite{17}. However, tuning the properties of surfactant solution using CO2 is a new progress in modification of nanoparticles. The mechanism for CO2 to stabilize reverse micelle and improve the surface defect of nanoparticles has never been discussed before. Therefore, this research will greatly contribute to the understanding of nanoparticles formation using compressed CO2 as the antisolvent.

![Figure 3. Photoluminescence spectrum of ZnS:Mn at different retention times](image)

4. Conclusion
A quaternary AOT/CO2/n-heptane/H2O reverse micelle system was found to be effective in producing uniform, monodisperse and nanosize Mn-doped ZnS particles. The ZnS:Mn nanoparticles exhibited strong quantum-size effect due to dopant incorporation into the ZnS host structure, which reduced surface defects and enhanced optical properties.

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