

## Rapid Synthesis of AgInS<sub>2</sub>/ZnS Core/Shell Nanoparticles and Their Luminescence Property

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**ABSTRACT:** We have successfully synthesized AgInS<sub>2</sub> core and AgInS<sub>2</sub>/ZnS core/shell nanoparticles by the sonochemical method. The ultrasonic based AgInS<sub>2</sub> and AgInS<sub>2</sub>/ZnS nanoparticle synthesis can be utilized as a simple and rapid method. The AgInS<sub>2</sub>/ZnS nanoparticles show the higher fluorescence intensity and quantum yield than AgInS<sub>2</sub> nanoparticles. Fluorescence wavelength of AgInS<sub>2</sub>/ZnS shows blue shift from 635 nm to 610 nm against AgInS<sub>2</sub> because of reducing the defect sites and increasing spatial confinements. For the fluorescence lifetime, AgInS<sub>2</sub>/ZnS (124.8 ns) has longer lifetime than AgInS<sub>2</sub> (54.8 ns).

There is considerable interest in the development of quantum dots (QDs) for solar cells, optical devices, sensors, and bio imaging because of their unique properties such as high stability, high absorption coefficients, tunable fluorescence wavelength by size or composition, and high bright fluorescence. However, most quantum dots have limitation for real application in industry because they include heavy metals with toxicity such as cadmium, selenium, and tellurium.<sup>1,2</sup>

For the problem of toxicity, one research group has focused encapsulated cadmium based quantum dots with organic or inorganic materials such as SiO<sub>2</sub>, protein. The other groups have focused cadmium free quantum dots such as InP, CuInS<sub>2</sub>, AgInS<sub>2</sub>, and ZnS-AgInS<sub>2</sub>.<sup>3-10</sup>

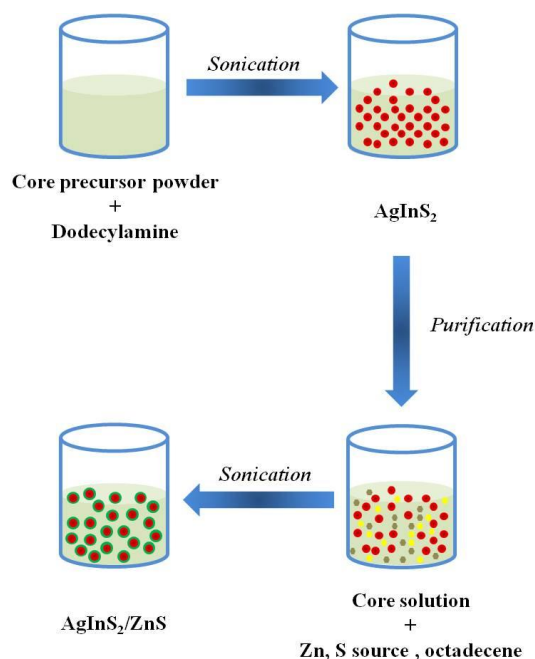
Nevertheless, these Cd-free quantum dots have less toxicity, they have still limitation for application because of lower quantum yields against Cd based quantum dots. The core/shell structure is one candidate for low quantum yields. Most quantum dots with core/shell structure were synthesized by thermal reaction, hydrothermal reaction, microwave, and sonochemistry.

The sonochemistry method uses ultrasound to obtain a rapid reaction time, milder operating conditions (e.g., lower temperature and pressure), and a reduced synthesis steps. The effect of ultrasonic radiation on a reaction is attributed to the acoustic cavitations within collapsing bubbles, which generates localized hot spots with extreme conditions (temperature = 5000 K, pressure = 1800 atm, and cooling rate = 10<sup>10</sup>K/s).<sup>11</sup>

Herein we synthesized AgInS<sub>2</sub>/ZnS with core/shell structure through an ultrasonic irradiation (Scheme 1). The detail process for

synthesis of precursor powder was reported previous work.<sup>12</sup> 0.1g core precursor powder and 10 mL of dodecylamine were added into a 20 mL reaction vial and ultrasonically treated (Sonic dismembrator 500, Fisher Scientific) for 10 min at 20 kHz power in air. The solution

**Scheme 1.** Synthetic routes for AgInS<sub>2</sub>/ZnS nanoparticles with core/shell structure

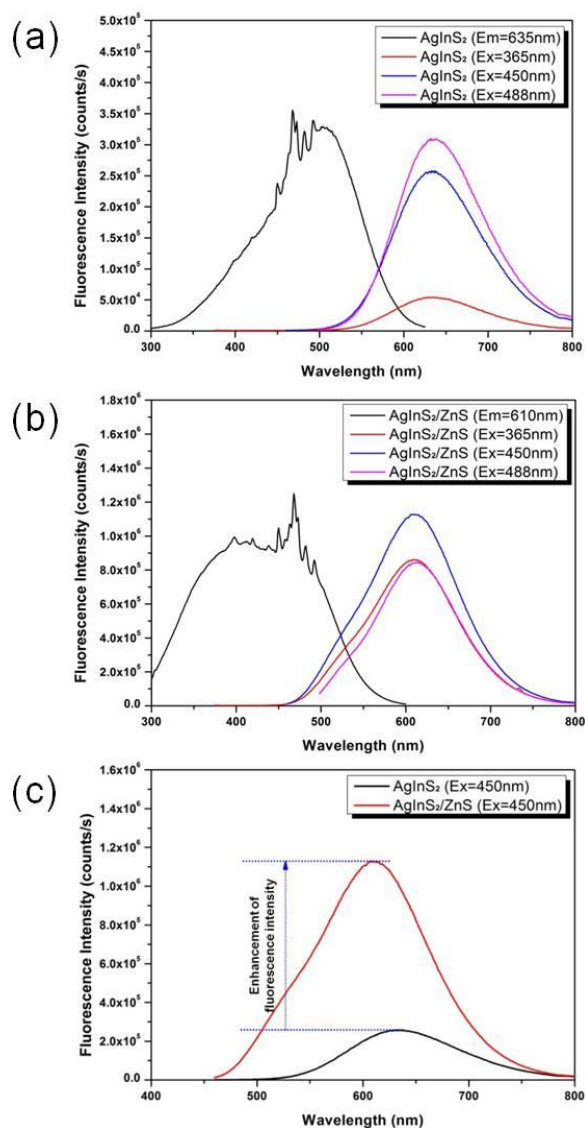


was centrifuged to remove the by-products and washed with chloroform and methanol several times. The purified core quantum dots were re-dispersed 5 mL octadecene. Zinc undecylanate and S powder were dissolved in 5mL octadecene by vigorous stirring. The core solution is added into the solution with Zn and S. The mixture solution was ultrasonically treated for several times at 20 kHz power in air. The final solution was centrifuged with chloroform, 1-butanol, and methanol several times.

The excitation and emission spectra of AgInS<sub>2</sub> and AgInS<sub>2</sub>/ZnS nanoparticles were showed in Fig. 1. As can be seen Fig. 1, AgInS<sub>2</sub> shows the red emission with maximum wavelength at 635 nm. Unusually, AgInS<sub>2</sub> shows highest emission intensity at 488 nm

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excitation (Fig. (a)). AgInS<sub>2</sub>/ZnS shows the different excitation and emission spectra. AgInS<sub>2</sub>/ZnS shows highest emission intensity at 450 nm excitation because of changing the excitation region by ZnS shell (Fig. (b)). The AgInS<sub>2</sub> core may have been weakly crystalline with multiple defects on the quantum dot surface.

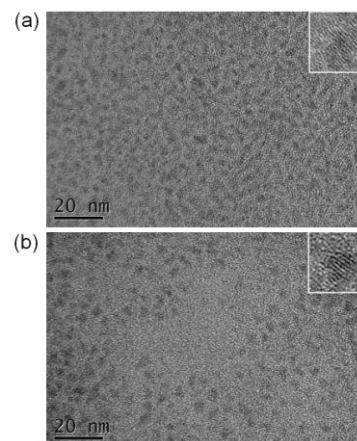


**Figure 1.** Excitation and emission spectra of (a) AgInS<sub>2</sub> and (b) AgInS<sub>2</sub>/ZnS. Emission spectra of AgInS<sub>2</sub> and AgInS<sub>2</sub>/ZnS at 450 nm excitation (c). All emission wavelength scans were obtained at 365 nm, 450 nm, and 488 nm excitation. Excitation wavelengths were scanned at a fixed emission wavelength either at 635 nm (a) or at 610 nm (b).

The ZnS shell typically leads to a blue shift of the emission spectrum because etching of core surface was performed under shell growth conditions and the degree of spatial confinement was increased (Fig. 1(c)).<sup>13</sup> The use of ZnS results in a dramatic improvement of the fluorescence emission intensity and fluorescence quantum yield. AgInS<sub>2</sub> nanoparticles show the fluorescence quantum yield of 18%. While AgInS<sub>2</sub>/ZnS nanoparticles show higher fluorescence quantum about 65% (Table 1).

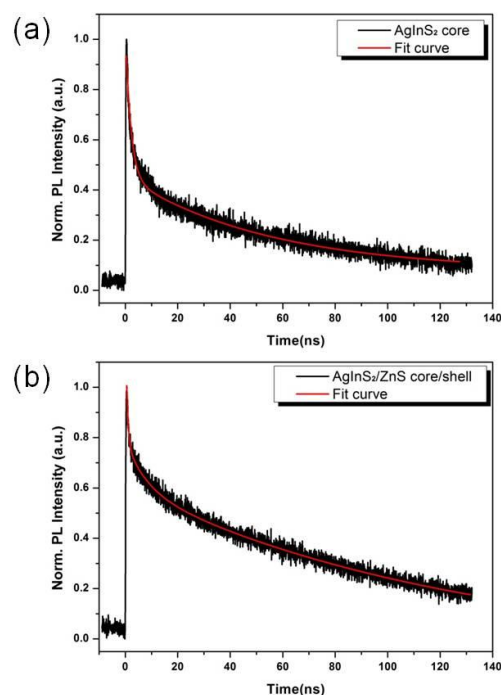
**Table 1.** Absolute quantum yields of AgInS<sub>2</sub> and AgInS<sub>2</sub>/ZnS

Sample	Emission Max. (nm)	Absolute Quantum Yield
AgInS <sub>2</sub>	635	0.18
AgInS <sub>2</sub> /ZnS	610	0.65



**Figure 2.** TEM images of AgInS<sub>2</sub> core (a) and AgInS<sub>2</sub>/ZnS core/shell (b) nanoparticles. Diameters of core and core/shell structures are 4 nm and 5 nm, respectively.

The shell growth increased the mean particle size. TEM image of the particles are shown in Figure 2. As can be seen Fig 2, AgInS<sub>2</sub> core nanoparticle was about 4 nm in diameter. The AgInS<sub>2</sub>/ZnS core/shell structures are approximately 5 nm in diameter. The high resolution inset in the TEM images show a clear lattice fringes.



**Figure 3.** Fluorescence lifetime of AgInS<sub>2</sub> core (a) and AgInS<sub>2</sub>/ZnS core/shell (b) nanoparticles. Lifetimes of AgInS<sub>2</sub> nanoparticles are 2.1 ns and 54.8 ns. Lifetimes of AgInS<sub>2</sub>/ZnS nanoparticles are 0.7 ns, 7.8 ns and 124.8 ns.

**Table 2.** Fluorescence lifetime of AgInS<sub>2</sub> and AgInS<sub>2</sub>/ZnS

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)
AgInS <sub>2</sub>	2.1	54.8	-
AgInS <sub>2</sub> /ZnS	0.7	7.8	124.8

To understand the improvement in fluorescence emission intensity and quantum yield, we measured the fluorescence lifetime of AgInS<sub>2</sub> core and AgInS<sub>2</sub>/ZnS core/shell nanoparticles. Figure 3 show fluorescence lifetime curves of the AgInS<sub>2</sub> core and AgInS<sub>2</sub>/ZnS core/shell nanoparticles. The fluorescence lifetime curves were obtained using time-correlated single photon counting system (TCSPC).<sup>14,15</sup> A 40 MHz pulsed diode laser (405nm, LDH-P-C-405 with PDL 800-B driver, PICOQUANT) was used as light source. The detection of fluorescence were performed using an avalanche photodiode (APD, SPCM-AQD, Perkin Elmer) and a Becker-Hickl PMS module (Becker & Hickel GmbH). As can be seen in Fig. 3, fluorescence from AgInS<sub>2</sub> and AgInS<sub>2</sub>/ZnS decay bi-exponentially and tri-exponentially. Decay curves were fit with two-exponential function for AgInS<sub>2</sub> and triple-exponential function for AgInS<sub>2</sub>/ZnS. Compared to lifetimes for AgInS<sub>2</sub> nanoparticles ( $\tau_1=2.1$  ns,  $\tau_2=54.8$  ns), AgInS<sub>2</sub>/ZnS nanoparticles show much longer decay times ( $\tau_1=0.7$  ns,  $\tau_2=7.8$  ns,  $\tau_3=124.8$  ns) in table 2.

In conclusion, we have successfully synthesized AgInS<sub>2</sub> core and AgInS<sub>2</sub>/ZnS core/shell nanoparticles by the sonochemical method. The ultrasonic based AgInS<sub>2</sub>/ZnS nanoparticle synthesis can be utilized as a simple and rapid method. The AgInS<sub>2</sub>/ZnS nanoparticles show the higher fluorescence intensity and quantum yield than AgInS<sub>2</sub> nanoparticles under long wavelength excitation. Fluorescence wavelength of AgInS<sub>2</sub>/ZnS shows blue shift from 635 nm to 610 nm because of reducing the defect sites and increasing spatial confinement. For the fluorescence lifetime, AgInS<sub>2</sub>/ZnS (124.8 ns) has longer lifetime than AgInS<sub>2</sub> (54.8 ns). AgInS<sub>2</sub>/ZnS with high quantum yield, long lifetime, and good fluorescence intensity at long wavelength excitation could assist in bio imaging, photocatalysts and solar cell applications.

**KEYWORDS:** AgInS<sub>2</sub>/ZnS, Sonochemistry, Fluorescence lifetime

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