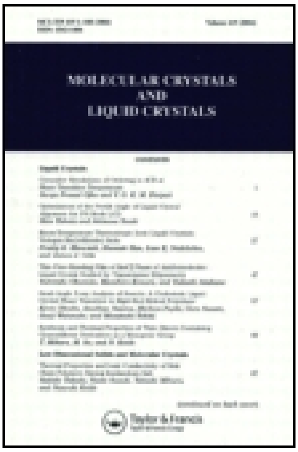

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ZnS Nanoparticle Treatment to Enhance its Luminescence, Shape, and Stability

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ZnS Nanoparticle Treatment to Enhance its Luminescence, Shape, and Stability

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The luminescence, shape, and stability of ZnS nanoparticles in ethanol are enhanced by capping the surface with (3-mercaptopropyl)trimethoxy silane (MPS) or by treating the surface with SiO_2. While MPS forms an exterior network to encapsulate the ZnS surface, SiO_2 surrounds ZnS nanoparticles to smoothen the surface. Both MPS and SiO_2 reform ZnS nanoparticles into more stable shapes and increase their luminescence, especially in the visible region. Thus both treatments are suggested to improve various properties of optoelectronically valuable ZnS nanoparticles.

Keywords (3-mercaptopropyl)trimethoxy silane; surface modification; SiO_2; ZnS nanoparticle; photoluminescence; picosecond kinetics

INTRODUCTION

Nanoparticles (NPs) have a variety of unique spectroscopic, electronic, and chemical properties that germinate from their quantum-confinement effects and high surface/volume ratios and thus exhibit new optical properties which are observed neither in molecules nor in bulk materials.[1-3] In particular, the optical properties of semiconductor NPs are of great interest in basic and applied researches.[2] There has been extensive research to modify the surface of luminescent semiconductor NPs such as ZnS NPs with organic materials because the modification often enhances their optical properties and applicability.[1,4] Organosilanes have been reported to modify the valuable properties of semiconductor NPs.[4]

Here we will show with picosecond emission kinetics and absorption and luminescence spectra that the luminescence, shape, and stability of ZnS NPs are greatly enhanced by treating the NPs with (3-mercaptopropyl)trimethoxy silane (MPS) or SiO_2.

METHODS, RESULTS, AND DISCUSSION

For the synthesis of ZnS NPs, 1 mL of 50 mM $Zn(NH_3)_2 \cdot 6H_2O$ and 1 mL of 50 mM $Na_2S \cdot 9H_2O$ solution were added to the solution of 40 mL ethanol and 10 mL acetic acid. Then untreated ZnS colloids were prepared by diluting the resulting solution to its 1/10 concentration with ethanol. ZnS NPs were treated with MPS by adding 1 mL of MPS, 1 mL of ammonia solution, 13 μL of 3-aminopropyl triehoxy silane, and 5 mL of ZnS colloids to 43 mL of ethanol. SiO_2 NPs was synthesized following the method of Willner et al.[5] and 1 mL of the SiO_2 colloids and 5 mL of ZnS colloids to 44 mL of ethanol to prepare SiO_2-treated ZnS colloids. All the optical measurements, the detailes of which are described elsewhere,[2,6,7] were carried out at room temperature. A 10 ps streak camera (Hamamatsu, C2830) was exployed to detect emission kinetic profiles after exciting samples with 266 nm pulse from a 25 ps Nd:YAG laser (Quantel, YG701)

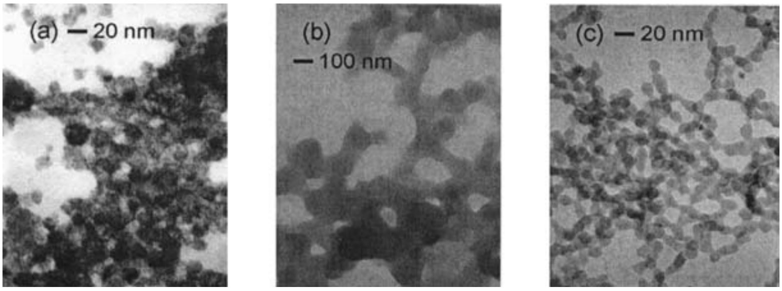

FIGURE 1 TEM images of untreated (a), MPS-treated (b), and SiO_2-treated (c) ZnS NPs.

While untreated ZnS NPs are obscure and indiscernible in morphology, MPS-treated ones are smoothened, annealed, and clearly improved in shapes (Figure 1). SiO_2-treated ZnS NPs are even more uniform in shapes and sizes although they have the characteristics of SiO_2 NPs. Whereas surface-adsorbed MPS forms an exterior networks and interconnect the ZnS NPs into large agglomerate, SiO_2 surrounds ZnS NPs to smoothen the surface.

Although the absorption spectra of both MPS-treated and SiO_2-treated ZnS NPs in ethanol are similar to the spectrum of untreated ones, the luminescence spectra of treated ones are significantly different from that of untreated ones (Figure 2). Considered that the luminescence intensity becomes stronger, especially in visible region, both surface-adsorbed MPS and SiO_2 passivate the defects of ZnS NPs to enhance the luminescence quantum efficiency strongly.

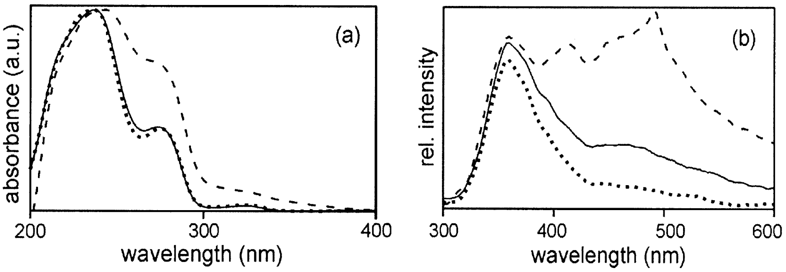

FIGURE 2 Absorption (a) and luminescence (b), excited at 266 nm, spectra of MPS-treated (solid), SiO_2-treated (dashed), and untreated (dotted) ZnS NPs in ethanol.

Untreated ZnS NPs in ethanol show two decay times of 110 and 1000 ps (Figure 3 and Table 1). While the fast one is the transfer time of the excitation energy from the conduction band to surface defects, the slow one is the relaxation time of the excited defects. MPS treatment slows down both decay components significantly, indicating that MPS passivates the defects of ZnS NPs effectively. SiO_2 treatment also slows down both components. However, the increase of the fast component's contribution suggests that SiO_2 treatment is not effective in defect passivation although it improves the shapes.

We have shown that both MPS and SiO_2 reform ZnS NPs into more stable shapes and increase their luminescence, especially in the visible region. In particular, MPS forms an exterior network to passivate the defects of ZnS NPs effectively. This enhances the luminescence and stability of ZnS NPs.

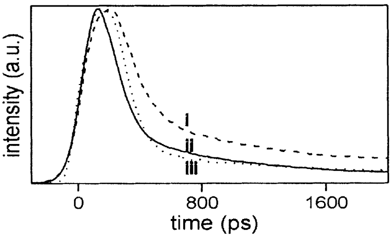

FIGURE 3 Luminescence decay profiles at 360 nm of MPS-treated (**i**), untreated (**ii**), and SiO_2-treated (**iii**) ZnS NPs in ethanol.

TABLE 1 Decay kinetic constants extracted from Figure 3.

profile	decay time (ps)
i	160 (89%) +1500 (11%)
ii	110 (92%) +1000 (8%)
iii	130 (98%) +2000 (2%)

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