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ARTICLE TYPE

Design and Synthesis of Photostable Multi-shell Cd-free Nanocrystal Quantum Dots for LED Applications

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Electrical Supplementary Information

Materials and Methods

1-Octadecene (Aldrich, 90%), trioctylamine (Aldrich, 98%), oleic acid (Alfa, 99%), indium acetate (Aldrich, 99.99%), Se powder (Alfa Aesar, 99.999%), zinc acetate (Aldrich, 99.99%), and 1-octanethiol (Aldrich, 98.5+%) were used without further purification. The absorption and photoluminescence were characterized with a UV-vis spectrophotometer (SD-1000, Scinco, Korea) and a fluorometer (Fluorolog, Horiba JOBIN YVON, France). TEM micrographs were obtained with an FE-TEM (Tecnai G^2 F30 S-TWIN, FEI, The Netherlands). The LED lamp was evaluated by an LMS LED 1060 spectral light measuring system (Labsphere, USA) with a Keithley 2400 power supply.

Synthesis of InP/ZnS/ZnSe

515-nm InP multi-shell: To make the InP core, 0.0230 g of indium acetate and 0.0703 g of myristic acid were dissolved in 6 mL of 1-octadecene (ODE) at 188°C in a N_2 atmosphere. This solution was maintained at reduced pressure until reaching 110°C. A solution of 0.029 mL tris(trimethylsilyl)phosphine and 0.3 mL 1-octylamine in 1 mL ODE was rapidly injected into the indium solution.

The ZnS shell was fabricated by injecting 2.8 mL of zinc oleate solution (0.2201 g zinc acetate and 0.68 g oleic acid in 12 mL trioctylamine dissolved at 200°C in a N_2 atmosphere) and 0.14 mL 1-octanethiol solution into the InP solution described above. This process immediately facilitated InP growth. The solution was heated to 300°C, held for 40 min, and then cooled to 200°C.

The ZnSe shell was fabricated by injecting 2.8 mL of zinc oleate solution (0.2201 g zinc acetate and 0.68 g oleic acid in 12 mL trioctylamine dissolved at 200°C in a N_2 atmosphere) and 0.14 mL TOPSe (2 mol Se and 1 L trioctylphosphine) into the InP/ZnS core/shell solution. The solution was then heated to 300°C and cooled to room temperature after 40 min. The resulting nanoparticles were washed with acetone, chloroform, butanol, and methanol, centrifuging and decanting between wash steps. The final decantated powder was redispersed in hexane.

541-nm InP multi-shell: The InP core was synthesized as described above except the mixing of indium acetate and myristic acid solutions was performed at at 230°C.

For the ZnS shell coating, 2.8 mL of the zinc oleate solution (0.2201 g zinc acetate and 0.68 g of oleic acid in 12 mL of trioctylamine was dissolved at 200^{o}C in an N_2 atmosphere) and 0.14 mL of the 1-octanethiol mixed solution was injected into the InP solution immediately after InP core formation. After incubating at 300^{o}C for 40 min, the reaction mixture was cooled to 200^{o}C. ZnSe shells were prepared as described above.

556-nm InP multi-shell: The InP core was synthesized as described above except that after injecting the tris(trimethylsilyl)phosphine and 1-octylamine solutions into the indium solution, the mixture was heated to 270°C and cooled to 170°C after 30 min.

The ZnS shell was fabricated as described above except 5.6 mL of zinc oleate solution were injected into the InP core solution, and the mixture was heated to 230°C for 20 min. A solution of 1-octanethiol (0.28 mL) was then injected into the solution, and the mixture was heated to 300°C for 20 min and cooled to 170°C.

The ZnSe shell was fabricated by injecting 5.6 mL of zinc oleate solution into the InP/ZnS core/shell solution and heating to 230°C for 20 min. TOPSe solution (0.28 mL) was then injected into the mixture. After 20 min, the mixture was cooled to 170°C. After an additional 40 min, the mixture was cooled to room temperature. The resulting nanoparticles were washed as described above.

583-nm InP multi-shell: The InP core was fabricated as described for the 515-nm particles except that the indium acetate and myristic acid solution was injected into the ODE at 188°C, and the final solution was heated to 300°C for 15 min.

For the ZnS shell coating, 2.8 mL of zinc oleate solution were injected into the InP core solution and heated to 300°C for 20 min. A soluton of 1-octanethiol (0.14 mL) was then injected into the solution, and the temperature was maintained for an additional 20 min.

The ZnSe shell coating was fabricated by injecting 2.8 mL of zinc oleate solution into the InP/ZnS core/shell solution and heating for 20 min. TOPSe solution (0.28 mL) was then injected into the mixture and cooled to room temperature after 20 min. The resulting nanoparticles were washed as described above.

608-nm InP multi-shell: InP core particles were created by dissolving 0.0230 g of indium acetate and 0.0703 g of myristic acid in 6 mL of 1-octadecene (ODE) at 200°C in a N_2 atmosphere. This solution was held at reduced pressure until reaching 110°C. A solution of 0.029 mL tris(trimethylsilyl)phosphine and 0.3 mL 1-octylamine in 1 mL ODE was then rapidly injected into the indium solution and heated to 300°C. After 20 min, the solution was cooled to room temperature. Solutions of indium (0.0115 g of indium acetate and 0.0352 g of myristic acid dissolved in 3 mL of 1-octadecene) and phosphorus (0.015 mL tris(trimethylsilyl)phosphine and 0.3 mL 1-octylamine in 1 mL ODE) were then injected into the InP core solution, and the temperature was increased to 300°C. After 20 min, the mixture was cooled to room temperature. These additional precursors increased the diameter of the InP core.

The ZnS shell coating was fabricated by injecting a mixed solution of 4.2 mL of zinc oleate solution and 0.1 mL of 1-octanethiol into the InP core solution at 300°C. After 20 min, the mixture was cooled to room temperature.

The ZnSe shell coating was fabricated by injecting a mixed solution of 4.2 mL zinc oleate solution and 0.1 mL TOPSe solution into the InP/ZnS solution at 300°C. After 20 min, the mixture was cooled to room temperature. The nanoparticles were washed and redispersed as described above.

629-nm InP multi-shell: InP cores were synthesized as described for the 608-nm particles except that after mixing, the initial InP solution was cooled to 200°C instead of room temperature. Additional indium solution (0.0115 g of indium acetate and 0.0352 g of myristic acid dissolved in 3 mL 1-octadecene) was then injected into the InP core solution, and the temperature was increased to 300°C. After 20 min, the mixture was cooled 230°C, additional phosphorus solution (0.015 mL tris(trimethylsilyl)phosphine and 0.3 mL 1-octylamine in 1 mL ODE) was mixed into the InP core solution, and the mixture was brought to 300°C. After 20 min, the mixture was cooled to 230°C. These additional precursors increased the diameter of the InP core.

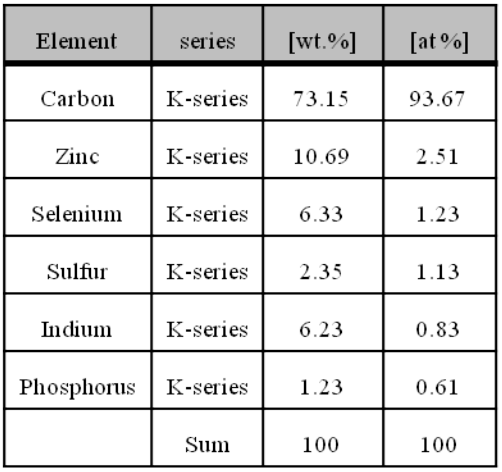
For the ZnS shell coating, a mixture of 4.2 mL of zinc oleate solution and 0.1 mL of 1-octanethiol solution was injected into the InP core solution at 300°C. After 20 min, the mixture was cooled to 230°C.

For the ZnSe shell coating, a mixture of 4.2 mL of zinc oleate solution and 0.1 mL TOPSe solution was injected into the InP/ZnS solution at 300°C. After 20 min, the solution was cooled to room temperature. The nanoparticles were washed and redispersed as described above.

Preparation of white LED lamp

A GaN LED chip without a phosphor coating was purchased from Trikaiser LED Co. The blue-emitting chip was attached to the bottom of the LED base with no overcoat material above the chip. In general, the conventional cup-shaped void was filled with color-converting material. The peak wavelength of the blue LED chip was 456 nm at an operating current of 60 mA. A thermo-curable resin (silicone, Dow-Corning Co.) was mixed with QDs and phosphor at a ratio of 0.5 g (resin) to 0.015 g (YAG phosphor) to 0.02 g (InP/ZnS/ZnSe). The nanocomposite was thermally cured at 125°C for 2 h. Spectrum was measured in the integrating sphere using the CSLMS LED 1060 LED spectra light measurement system under 3.25 V, 60 mA controlled by the Keithley 2400 digital source meter. The operating current and voltage operated the GaN LED chip and emitted 442 nm blue light to stimulate the YAG phosphor and QDs. Stimulated phosphor and QD emitted yellow and red light. Part of blue light penetrated resin. Mixed three colours generated white light. The ratio of three light changes CRI value.

Table S1. Elemental analysis by EDS



Element	series	[wt.%]	[at%]
Carbon	K-series	73.15	93.67
Zinc	K-series	10.69	2.51
Selenium	K-series	6.33	1.23
Sulfur	K-series	2.35	1.13
Indium	K-series	6.23	0.83
Phosphorus	K-series	1.23	0.61
	Sum	100	100

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Figure S1. PL spectrum and color coordination of white LED lamp made from a YAG phosphor.