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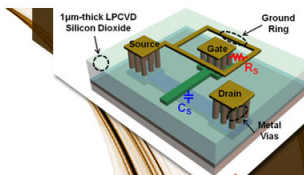
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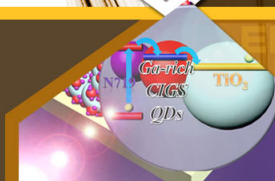
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Highly luminescing multi-shell semiconductor nanocrystals InP/ZnSe/ZnS

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We design, synthesize, and characterize multi-shell quantum dot structure of an indium phosphide core surrounded by zinc chalcogenide shells. A simple mathematical model describing the wave function of electronhole pairs enabled us to design ZnSe and ZnS shells to confine the carriers inside the core region effectively. The result indicates that the designed multi-shell quantum dots show improved optical properties that are more robust against chemical and photo-environmental changes. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4745844>]

Colloidal semiconductor nanocrystals, or quantum dots (QDs), with size-tunable bandgaps are applicable to a number of technologies such as biomedical fluorophores, light-emitting diode emitters (LEDs), and photovoltaic devices.¹⁻⁹ The optical properties of QDs are dependent on their individual surface chemistry and also chemical environment, which presents challenges for certain applications.¹⁰ Efforts to address this performance challenge include applying thick shells or creating shells with compositional gradients from the core to the outer shell.¹¹ However, most efforts toward nanoparticle shell engineering have focused on systems containing a II-VI nanocrystalline core, which often contain toxic elements such as cadmium or lead.¹² In contrast, III-V QDs are generally considered to be “greener” because metals like gallium, indium, and aluminum have low to negligible toxicity in an ambient environment.¹³ Despite the lower toxicity, QDs systems have not been widely studied because they are more difficult to chemically synthesize. When III-V QDs are chemically synthesized, they suffer from poor optical performance due to both a high number of nonradiative surface recombination sites and high activation barriers for carrier detrapping.^{14,15} Several research groups have recently reported synthetic strategies for preparing III-V QDs that show improved optical properties by adapting core-shell approaches similar to those used for II-VI nanocrystal synthesis.^{13,16} In particular, the indium phosphide (InP) core-shell nanocrystals reported in the literature that have employed ZnS or ZnCdSe₂ outer shells do not exhibit optical properties comparable to II-IV compounds.¹⁷

Here, we report enhanced optical properties of a multi-shell QD structure with an InP core and its design and synthetic strategy. As shell materials with lattice parameters similar to the core nanocrystal passivate the core more uniformly with minor atomic-level lattice disorder at the interface, we chose ZnSe as a shell material due to its close lattice match (3.2%) to InP and the ZnSe shells were grown on the InP core up to 3-nm thick with minimal impact to the InP photoluminescence (PL) spectrum. The results revealed in strong and narrow band-edge emission measurement indicate that QD carriers are strongly confined by the Zn/Se and

ZnS outer shells of the radial wavefunctions for electronhole pairs in their lowest energy levels, and the shell-thickness dependence on the carrier confinement is clearly observed.

The quantum wave functions of electron and hole and their energy eigenvalues are calculated using the effective mass approximation.¹⁸ For a stepwise potential with spherical symmetry, the Schrödinger equation for the radial part $R_{nl}(r)$ of electron or hole, which is given by

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + k_{nl}^2 \right] R_{nl}(r) = 0, \quad (1)$$

can be numerically solved in each radial region, where $k_{nl} = \sqrt{2m^*E_{nl}/\hbar^2}$ is the wave vector and m^* is the effective mass of either electron or hole. By imposing the boundary conditions, $R_{nl,i}(r_i) = R_{nl,i+1}(r_i)$ and $m_{i+1}^* dR_{nl,i}(r)/dr|_{r_i} = m_i^* dR_{nl,i+1}(r)/dr|_{r_i}$ on Eq. (1) at each i th regional boundary r_i , the whole radial wave function is constructed as a system of linear equations. When we restrict the calculations to only ground states, or $l=0$, the Coulomb interaction between electron and hole can be treated as the helium-like atomic interaction as

$$E_c = \frac{-e^2}{4\pi\epsilon_0} \frac{|R_e(r_e)|^2 |R_h(r_h)|^2}{\max(r_e, r_h) \epsilon(r_e, r_h)} r_e^2 r_h^2 dr_e dr_h, \quad (2)$$

where the interpolated relative dielectric constant $\epsilon(r_e, r_h)$ is used for a simplified calculation.¹⁹ Then, the PL photon energy is given by

$$E_{PL} = E_e + E_h + E_c + E_{\text{band}}, \quad (3)$$

where E_e and E_h are the electron and hole energies, respectively, E_c is the Coulomb interaction energy, and E_{band} is the bulk material bandgap. Figure 1(a) shows the calculated probability distributions of electron and hole of the QD structure, of which the material parameters²⁰⁻²² and the band alignment are summarized in Table I and Fig. 1(b), respectively. The estimated PL wavelength is 534 nm.

InP/ZnSe/ZnS multi-shell nanocrystal QDs has been synthesized in stepwise fashion using a modified version of the successive ion layer adsorption reaction (SILAR) method. Control of the interfacial layer formation between

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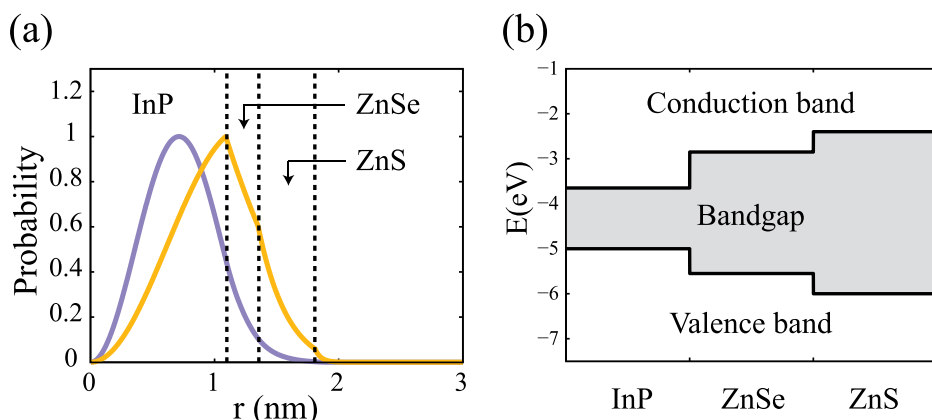


FIG. 1. (a) Calculated probability distribution of electron (yellow line) and hole (purple line) of InP/ZnSe/ZnS QDs. (b) Schematic diagram of InP/ZnSe/ZnS band alignment (see Refs. 13 and 23). $E = 0$ corresponds to vacuum level.

III-V and II-VI materials has been found to be the key to creating thick shells, improving optical properties and chemical stability. Zinc oleate $[\text{Zn}(\text{CH}_{17}\text{H}_{33}\text{COO})_2]$ has been synthesized and used as the Zn source for the shell formation. InP nanocrystals have been synthesized using a previously reported method.¹⁶ Zn oleate has been injected into the InP colloidal solution and incubated at 230 °C, which has passivated the surface phosphorus atoms. It is noted that recent studies on multi-layer QDs compared the effects of one-step and two-step synthetic ZnS shell formation routes on the optical properties of an InP core, in which the QDs prepared with one-step shell formation routes is found to exhibit better optical properties than those prepared with two-step techniques.¹³ In this work, we have created the QD shell in a step-wise process in an attempt to control formation of the ZnSe interfacial layer.

All reagents, indium(III) acetate $[\text{In}(\text{OAc})_3, 99.99\%]$, myristic acid (95%), octadecene (ODE, 90%), and octylamine (OcA, 97%), were purchased from Sigma-Aldrich (St. Louis, MO) and used as received without further purification. Trioctylphosphine (TOP) was purchased from Sigma-Aldrich and was degassed prior to use. Selenium shot was purchased from Alfa Aesar (Ward Hill, MA). Tris(trimethylsilyl)phosphine (99%) was purchased from JSI silicon (Sungnam, Korea). Oleylamine passivated InP/ZnS dispersed in toluene was purchased from NN-Labs (Fayetteville, AR). All techniques were carried out using a standard Schlenk and glovebox techniques under ambient nitrogen. All moisture/air sensitive chemicals were stored under nitrogen atmosphere.

Synthesis of multi-shell InP nanocrystals has been carried out as following: indium acetate (0.0230 g, 0.079 mmol) and myristic acid (0.0703 g, 0.26 mmol) were dissolved in 6 ml of ODE at 188 °C under a N_2 atmosphere. This solution was degassed for 2 h at 110 °C. A solution of 0.029 ml of tris(trimethylsilyl)phosphine (0.079 mmol) in 0.3 ml of OcA and 1 ml of ODE was rapidly injected into the indium solu-

tion at 200 °C. In order to create the ZnSe shell layer, the InP colloid was cooled to 150 °C after 30 min. Zinc oleate solution (2.8 ml, 1.2 mmol) in ODE was injected into the InP solution at a rate of 1 ml/min by a syringe pump at 230 °C. After 20 min, the solution was then cooled to 150 °C, 0.14 ml of a 2 M TOP Se solution and 1 ml of TOP were injected into the reaction at a rate of 1 ml/min, the solution was heated to 230 °C for 20 min and cooled to 150 °C. For ZnS shell formation on InP/ZnSe, 2.8 ml of the zinc oleate solution was injected into the reaction at a rate of 1 ml/min and heated to 230 °C. After 20 min, the reaction was cooled to 150 °C, and 2.8 ml of a 0.1 M sulfur solution in ODE was injected at a rate of 1 ml/min. The reaction was held for 20 min and cooled to room temperature. This solution was washed and centrifuged using a mixture of acetone, chloroform, butanol, and methanol. The finished, decanted powder was dispersed in hexane for further characterization.

The microstructure and crystallographic structures have been investigated by field-emission transmission electron microscopy (FEI, Tecnai F30 Super-Twin). Figure 2 shows the high-resolution transmission electron microscopy (TEM) image of the synthesized InP/ZnSe/ZnS QD layers. The average of the QDs InP core diameters is measured to be 2.1 ± 0.4 nm, and the total diameter of the QDs ZnSe shell coating and InP core is 2.6 ± 0.2 nm. The lattice of the ZnSe shell exhibits more ordering than the InP core. Upon addition of the final ZnS layer, the average QD diameter is increased to 3.3 ± 0.4 nm.

Absorption spectra have been obtained by a SD-1000 UV-VIS spectrometer (Scinco, Korea). Photoluminescence experiments have been performed on a Fluorolog-3 spectrometer (HORIBA Jobin Yvon, Inc., NJ) at room temperature with a 1-nm slit width for both excitation and emission monochromators. The absorption and emission spectra of the core-shell QDs are shown in Fig. 3. The uncoated core exhibits the first excitonic transition at 460 nm. When excited with a 350-nm Xe lamp, weak and broad low-energy radiative recombination is observed with no band-edge emission.²⁴ After the ZnSe shell formation, the 1S absorption peak shifts to 519 nm due to electron delocalization over the InP/ZnSe structure, while the hole is localized mainly within the core. The shell appears to prevent defect-related emission, resulting in a cleaner spectrum.

Strong luminescence from narrow band-edge emission suggests monodisperse QDs and efficient surface

TABLE I. Material parameters of InP, ZnSe, and ZnS.

	Bandgap (eV)	m_e^*	m_h^*	ϵ
InP	1.35	0.08	0.6	9.6
ZnSe	3.6	0.21	0.6	9.1
ZnS	2.7	0.34	0.58	8.9

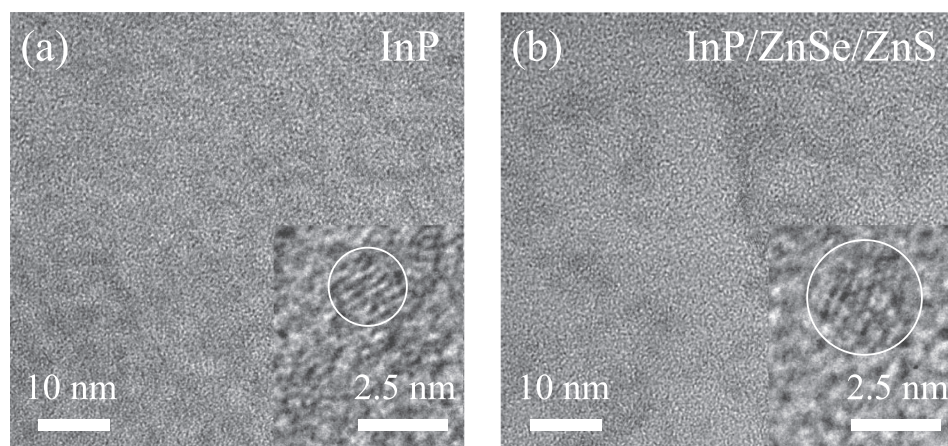


FIG. 2. TEM images of (a) InP and (b) InP/ZnSe/ZnS. Circles in the insets denote the nanocrystals.

passivation. When a ZnS outer shell is formed over the InP/ZnSe structure, the maximum wavelength of the excitonic transition shifts to a lower energy transition of 525 nm. The band-edge emission spectra are shifted to longer wavelengths after the coating of the zinc chalcogenide shells, as expected. ZnSe shell formation over the InP core causes red shifting of the InP emission spectrum due to the small bandgap between the InP core and ZnSe shell.

Quantum yield²⁵ has been measured using a C-9920-02 quantum yield measurement system (Hamamatsu, Japan) with a composed integral sphere, photomultiplier tubes, monochromator, and Xe lamp. As synthesized, the quantum yields of the excitation-emission process for the InP QD core are found to be 2% (uncoated InP core), 46% (InP/ZnSe), and 55% (InP/ZnSe/ZnS), respectively. The quantum efficiency of the InP spectral transition is greatly enhanced by shell encapsulation. The photostability of the QDs has been determined by exposing the InP QDs to 365-nm light from a UV lamp for several days followed by comparison with commercially available InP/ZnS core-shell QDs under the same conditions (see Fig. 4). It is noted that commercial QDs showed rapid degradation of the quantum efficiency after 24-h exposure, and no emission was observed after 48 h. The InP/ZnSe/ZnS multi-shell, however, continued emitting yellow-green light after more than 72 h of exposure. Photo-enhanced luminescence has been suggested in CdSe/ZnS core/shell systems in solution²⁶ and CdSe multishells in polymer composites,⁶ for which trap recharging and/or photo-chemical bond restructure at interface are considered to play a possible role.

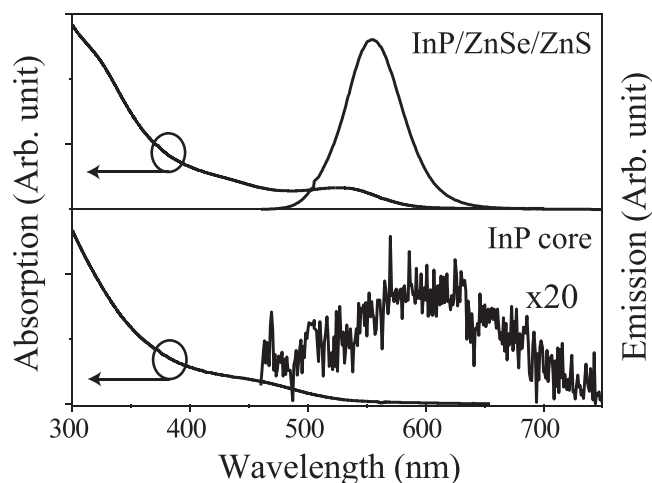


FIG. 3. Absorption and emission spectra of InP/ZnSe/ZnS (top) and pre-encapsulated InP core (bottom). The small emission signal of InP core is enlarged by a factor of 20.

In summary, this work has demonstrated that InP/ZnSe/ZnS multi-shell QDs are synthesized through a modified SILAR method. When using III-V structures, the interfacial layer design is crucial for the enhanced optical properties and environmental robustness. Additional control of the interfacial layers through compositional variation is expected to further improve the optical characteristics of III-V core-shells, thereby allowing them in various applications such as LEDs.

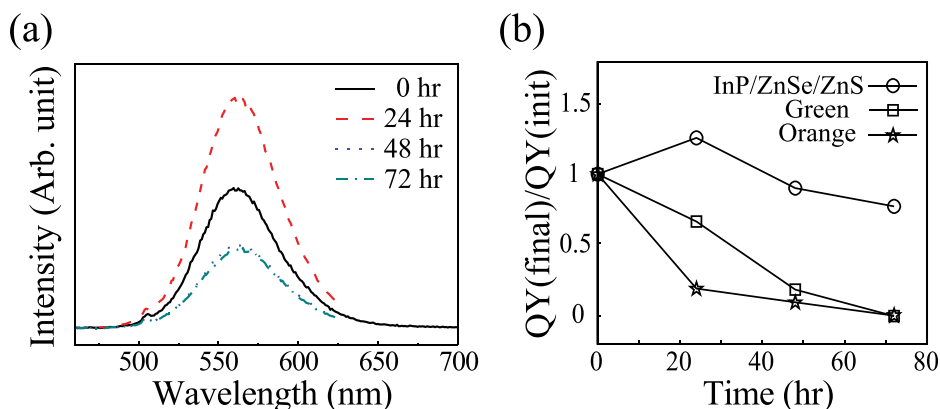


FIG. 4. (a) Spectral stability of InP/ZnSe/ZnS multi-shell quantum dots after exposure to 365-nm UV light and (b) its quantum yield compared with commercial green and orange InP/ZnS core-shell quantum dots.

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