

PbSe/PbSe_xS_{1-x} core-alloyed shell nanocrystals

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Abstract

This work describes a novel synthetic method for the formation of PbSe core-shell nanocrystals. The PbSe show a special interest due to their strong quantum size effect and activity in the near IR spectral regime. Common colloidal procedure of semiconductor core-shell structures includes an initial preparation of the core, isolation of the NCs from the mother solution, dissolving in a new solution with a post injection of the shell constituents. This paper discusses an alternative procedure, utilizing a single-injection of the core and shell constituents, simultaneously. The faster reactivity of selenium to a lead precursor, directs a nucleation of a PbSe core, while the sulfur reagent participate at a later stage as a PbSe_xS_{1-x} shell. PbSe core-shell NCs, prepared by the discussed single-injection process, were compared with those prepared via a two-step injection, containing equimolar reagents and NCs size. Both cases showed a strong fluorescence (with quantum efficiency 30–60%), but with a pronounced red-shift of the band edge (30–120 meV), with respect to the core, upon an increase of the shell thickness. This red-shift was substantially larger for core-shell NCs prepared via a one-step injection. The red-shift corresponds to the formation of type II transition between $E_{c,PbSe}$ and $E_{v,PbS}$. While the extra red-shift, upon preparation by a single injection, corresponds to the formation of shells with a tunable alloy composition.

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1. Introduction

Semiconductor nanocrystals (NCs) exhibit size dependent electronic properties due to a quantum confinement effect. The IV–VI (e.g., PbSe, PbS) NCs are a focus of a special interest, due to their unique intrinsic properties [1]. A bulk PbSe and PbS materials have a cubic (rock salt) crystal structure and a narrow direct band gap (0.13–0.27 eV at 300 K) at the L point of the Brillouin zone. The high dielectric constant (ϵ^∞ 18–24.0) and the small electron and hole effective mass ($<0.1 m^*$; m^* : free electron mass) create an exciton with a relatively large effective Bohr radius ($a_{B(PbSe)}=46$ nm), eight times larger than that of CdSe. Recent interband optical studies of colloidal PbSe NCs exhibited well-defined band-edge excitonic transitions tuning between between 1.1–0.5 eV, small Stokes shift, and

sub-microsecond lifetime [2–4]. Recently, an amplified spontaneous emission was demonstrated [5] from PbSe NCs with gain parameters similar to those observed in CdSe NCs [6]. These findings indicate the feasibility of using the PbSe and PbS NCs in telecommunication [7], eye-safe lasers [5] and biological markers with blood transparency [8,9].

Various colloidal syntheses have been developed in the last couple of years, producing PbSe NCs with size mono-dispersity ($<5\%$ size distribution), uniform shape and high crystallinity. Murray et al. [10] synthesized spherical core PbSe NCs, with narrow size-distribution and band-gap tuning at the near IR spectral regime. Sashchiuk et al. [11] reported a two-step colloidal procedure for the preparation of spherical PbSe/PbS core-shell NCs, with average size ranging between 2.5–7 nm. Lifshitz et al. [12] also reported a unique colloidal procedure, using alkyl-diamine solvent as a coordinating molecular template, which led to the formation of wires (20 nm \times 1 μ m) rods (20 \times 100 nm), and cubes (100 nm). The use of specific coordinating solvent molecules and adjustment of the temperature and duration of the reaction governed the morphology of those quantum structures. Recently, Sash-

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chiuk et al. [13] reported the formation of spherical and wire-like assemblies of core PbSe NCs, reserving the quantum size properties of individual NCs, accompanied by collective conductivity properties of an assembly.

The aforementioned colloidal procedures varied mainly by the use of surfactants with different molecular lengths and attraction forces to the NCs surface. Alternatively, core-shell structures consist of a NCs covered by an epitaxial layer of another wide-band semiconductor. The current growth of core-shell structures proceed by a post-exchange of the organic surfactant capping at the NCs' surface, by the precipitation of an epitaxial shell, with the appropriate stoichiometry. However, this procedure occasionally results in broadening of size distribution, and the existence of an abrupt change of a potential and crystallography at the interface. The current paper discuss a unique technique for the growth of PbSe core-shell NCs, by a single injection of the precursors, lead, selenium and sulfur in oleic-acid/trioctylphosphine/phenyl-ether solution, into a pre-heated phenyl-ether mother solution. As will be shown below, the faster nucleation of PbSe component permits the creation of the core constituent, followed by the formation of a $\text{PbSe}_x\text{S}_{1-x}$ alloyed shell, with $\sim 1\%$ crystalline mismatch. The crystallographic properties of the core and core-shell NCs were examined by a high-resolution transmission electron microscopy (HR-TEM), X-ray and selected area electron diffraction (SAED), while the optical properties are investigated by an absorption and photoluminescence (PL) spectroscopy.

2. Experimental

2.1. Materials

The investigated research compared the structure, composition and optical properties of the following samples: (A) Core PbSe NCs capped with organic ligands; (B) $\text{PbSe}/\text{PbSe}_x\text{S}_{1-x}$ core-shell NCs, prepared in a single-step process; (C) PbSe/PbS core-shell NCs, prepared in a two-step process. Detailed description of the synthetic procedures is described below at the indicated order.

(A) Synthesis of core PbSe NCs included the preceding stages: (1) 0.71 g of lead(II) acetate trihydrate [Pb-ac] ($\text{Pb}[\text{CH}_3\text{COO}]_2 \cdot 3\text{H}_2\text{O}$, GR, Merck) were dissolved in a solution composed of 2 mL phenyl-ether ($\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$, 99%, Aldrich), 1.5 mL oleic-acid [OA] ($\text{CH}_3(\text{CH}_2)_7\text{CHCH}(\text{CH}_2)_7\text{COOH}$, 99.8%, Aldrich) and 8 mL trioctylphosphine [TOP] ($(\text{C}_8\text{H}_{17})_3\text{P}$, Tech, Aldrich), under standard inert conditions in the glove box, and were inserted into a three-neck flask (no. I); (2) 10 mL of phenyl-ether was inserted into a three-neck flask (no. II) under the inert conditions of a glove box; (3) Both flasks were taken out of the glove box and were placed on a Schlenk line and heated under a vacuum to 100–120 °C for an hour; (4) Flask I was cooled to 45 °C, while flask II was heated to 180–210 °C, both under a fledging of an argon-gas; (5) 0.155 g of selenium

powder (Aldrich, 99.995%) was dissolved in 2.0 mL trioctylphosphine, forming a TOP:Se solution, under standard inert conditions of a glove box. Then, 1.7 mL of this solution was injected into flask I, on the Schlenk line; (6) The content of flask I, containing the reaction precursors, were injected rapidly into the phenyl-ether solution in flask II, reducing its temperature to 100–130 °C, leading to the formation of PbSe NCs within the first 15 min of the reaction; (7) The NCs growth was terminated by cooling the solution in flask II to room temperature. Aliquots were taken out of the reaction mixture periodically for determination of the NCs size and elemental composition. The NCs were isolated by their precipitation from the reaction solution upon an addition of methanol and centrifugation. All NCs were purified by dissolving them in chloroform and filterization with 0.02 μm membrane for several rounds. The described procedure produced nearly mono-dispersed NCs with $<8\%$ size distribution, with average size between 3 and 9 nm, controlled by the temperature and the time duration of the reaction. In order to perform optical measurements, colloidal NCs were either embedded in a polymer film or dissolved in a glassy solution (2,2,4,4,6,8,8,-heptamethyl-nonane). The polymer was prepared by mixing PbSe NCs in chloroform solution with poly-methyl-methacrylate [PMMA] ($[-\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)-]_n$, analytical grade, Aldrich) polymer solution. The resultant mixture was spread on a quartz substrate and dried to a uniform film over 24 h.

(B) The preparation of $\text{PbSe}/\text{PbSe}_x\text{S}_{1-x}$ core-shells structures was nearly identical to that of the core NCs, using a single injection of the precursors into a single round flask. However, step A(5) was altered by the use of an alternative chalcogen precursor solution. A stock solution of Se, S was prepared by mixing 0.15 g Se dissolved in 1.4 mL TOP, with 0.03–0.10 g S dissolved in 0.3 mL TOP. The amount of S in the new stock solution corresponded to a stoichiometric amount of 1–2 monolayers of the PbS compound. Thus, the mole ratio of the precursors Pb : Se : S ranged between 10 : 9 : 5 and 7 : 6 : 14. Periodic removal of aliquots during the reaction was followed by a purification and examination of the species by HR-TEM and absorption spectroscopy. The results discussed below suggest a fast nucleation of PbSe core, resumed by a slower precipitation of $\text{PbSe}_x\text{S}_{1-x}$ shell with gradual change of the chemical composition.

(C) The preparation of PbSe/PbS core-shell NCs by a two-step procedure begins with formation of core PbSe NCs and their isolation from the initial reaction solution, according to the procedure given in (A). Those core NCs were re-dissolved in chloroform solution, to lead a solution of 50 mg/mL concentration. A 1.4 mL of TOP was then added to the NCs solution, while the chloroform molecules were removed by distillation under vacuum and heating at 60 °C. In parallel, a 0.2 g of a lead precursor, Pb-ac, were dissolved in a mixer of 2 mL phenyl-ether, 1.5 mL of OA and 8 mL of TOP, was heated to 120 °C for an hour, and then cooled to 45 °C. Also, a 0.03–0.10 g of S were dissolved in 0.3 mL of TOP and was pre-mixed with a PbSe core NCs in a TOP solution. This mixer

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