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Role of ZnS Segment on Charge Carrier Dynamics and Photoluminescence Property of CdSe@CdS/ZnS Quantum Rods

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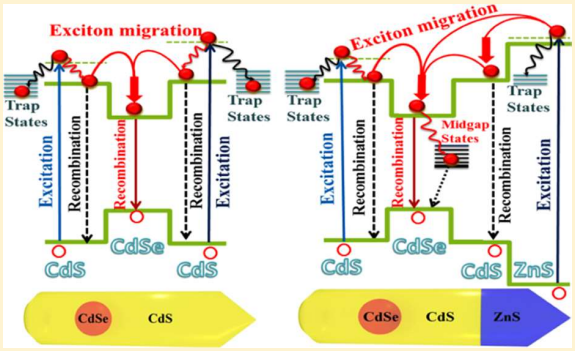
Supporting Information

ABSTRACT: Growing a wide band gap shell on bare core and/or core@shell materials is a fascinating idea for improving the photoluminescence (PL) efficiency and stability. An epitaxially grown shell adds another degree of complexity to the system and modulates the excited-state relaxation dynamics, which remain poorly understood. Employing time-resolved PL and femtosecond transient absorption (TA) spectroscopy, we present a thorough study on charge carrier dynamics of CdSe@CdS and CdSe@CdS/ZnS quantum rods (QRs). Various excitation wavelengths were used to identify the contribution of individual segment toward the optical properties of the QRs. Our femtosecond TA measurements provide a clear evidence of excitation migration from CdS as well as ZnS to CdSe core within few picoseconds of photoexcitation. The excitons recombine faster in the CdSe moiety of the CdSe@CdS/ZnS than that of the CdSe@CdS QRs via an extra decay path. The interband trap states that are created via the formation of extended defects because of lattice strain relaxation (or ion exchange during the formation of ZnS segment) in CdSe@CdS/ZnS QRs could provide the additional decay channel leading to low PL intensity and quantum yield. We believe that our study will help to develop a strategy for enhancing the PL efficiency through energy funneling across semiconductor heterojunctions and to understand the charge carrier dynamics in nanoheterostructures.



1. INTRODUCTION

Developing a thin shell of a wide band gap semiconductor on the outer surface of the emitting nanocrystals allows substantial improvement of their stability and tunability of the photoluminescence (PL). Such types of core@shell nanocrystals exhibit efficient PL with stability superior to single-phase nanoparticles and organic dyes and are of practical interest for light-emitting devices and biological imaging.[1,2] Because of the visible PL from CdSe, a continuous attention was paid to CdSe-based colloidal heteronanostructures in the past decades to understand their optical and electrical properties. The optoelectronic properties of these materials are strongly dependent on their composition, shape, and dimensions.[3,4] A number of materials are available for designing shells around CdSe core, but a greater attention has been devoted to CdS because it provides a high flexibility to the shell growth because of the small lattice mismatch between CdSe and CdS (~4%).[5] Tetrapod,[6] plate,[7] and rod[8]-shaped CdS shells surrounding a CdSe spherical core have been reported in the recent past. The core/shell CdSe/CdS structures enable electron−hole wave function overlap engineering because of the small conduction band (CB) offset between CdSe and CdS.[9,10] It is reported in the literature[11,12] that CdS shell on CdSe core helps to remove the surface states, and, with increasing shell thickness, the PL quantum yield (QY) increases tremendously.[13,14] These structures were used as fluorescent reporters in bioanalysis and microscopy[15,16] and as optoelectronic components in photovoltaics, light-emitting diodes, and liquid crystal displays.[17−20]

An interesting class of nanocrystals is the dot-in-a-rod (QD@RD or QD@QR), in which a spherical seed of a semiconductor nanocrystal is embedded within another rod-shaped semiconductor material. A spherical CdSe core embedded closer to one end in CdS rods across the rod length shows improved PL QY.[21] Furthermore, the QD@QRs emission is anisotropic or polarized, whereas the PL from quantum dots (QDs) is isotropic.[22,23] Therefore, in the last few years, QD@QRs have increasingly replaced QDs in many of the commercially available II/VI semiconductor nanocrystal-based products.[24] CdSe@ZnS and CdSe@CdS heterostructures show type-I band

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