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Facile synthesis of water-soluble $Zn_xCd_{1-x}Se$ nanocrystals *via* a two-phase cation exchange method

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HIGHLIGHTS

- A two-phase cation exchange method was developed to prepare aqueous $Zn_xCd_{1-x}Se$ nanocrystals.
- The new method allows $Zn_xCd_{1-x}Se$ formation and MPA functionalization simultaneously.
- The obtained $Zn_xCd_{1-x}Se$ nanocrystals have good crystallinity and stability.
- The mechanism involved in the formation of $Zn_xCd_{1-x}Se$ nanocrystals has been studied.

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ABSTRACT

In this paper, a facile two-phase method was developed to synthesize water-soluble $Zn_xCd_{1-x}Se$ nanocrystals through cation exchange reaction of the pre-synthesized ZnSe nanocrystals (in organic phase) with Cd^{2+} (in water phase) and by adding 3-mercaptopropinonic acid (MPA). High-quality alloy nanocrystals with desired emission wavelengths (ranging from 412 to 570 nm) can be synthesized precisely and reproducibly by varying the reaction temperature and time. For the first time, this new strategy allows the simultaneous execution of $Zn_xCd_{1-x}Se$ formation and MPA functionalization. It overcomes the poor crystalline shortcomings in the water-phase synthesis. The obtained alloy nanocrystals not only have high quantum yields (QYs) and stability, but also have good crystallinity. It is expected that the reported simple synthetic strategy can be developed into a very practical approach to produce high-quality water-soluble nanocrystals.

1. Introduction

Colloidal semiconductor nanocrystals are of tremendous fundamental and technical interest due to their applications in photonic devices [1–4], biological detection, and especially biolabelling and biomedical imaging [5,6], which require nanocrystals with both excellent photoluminescence (PL) properties and good stability in water. Owing to their size-dependent tunable PL across the visible spectrum, CdSe nanocrystals have been extensively investigated [7–9]. However, the most advanced CdSe-based binary semiconductor system does not work well for emission in the short wavelength spectral region from 450 to 500 nm, which is of special interest for optoelectronic devices and multi-color biomedical imaging. This is because the short-wavelength emissions require extremely small particle size (<2 nm), which not only greatly lowers the stability of nanocrystals but also increases the difficulties of passivation, and this also leads to low emission efficiencies and broad emission widths [10]. In contrast, alloying of CdSe and ZnSe to produce composition-tunable $Zn_xCd_{1-x}Se$ nanocrystals are proven to be an attractive alternative as their emission color can be tuned from blue region to the red region by changing the composition of the Zn/Cd molar ratio in the alloy [10–13]. Up to date, the synthesis of highly fluorescent $Zn_xCd_{1-x}Se$ alloy nanocrystals has been accomplished by pyrolyzing organometallic reagents in hot coordinating solvents; this approach utilizes oil-soluble ligands, such as tri-*n*-octylphosphine oxide (TOPO) or oleic acid (OA) [10–12,14], which make the obtained nanocrystals insoluble in aqueous solution. Although the organic-phase syntheses ensure good optical properties and crystallinity, extra phase transfer treatments are required since the demanding of water-soluble nanocrystals for biological applications [15]. However, the phase transfer method still faces some problems, such as the stability of aqueous nanocrystals and the complexity of the transfer process. As for the direct water-phase synthesis of $Zn_xCd_{1-x}Se$ nanocrystals, due to the inherent shortcomings of this method (the maximum reaction temperature of the aqueous phase method cannot exceed 100 °C), very few reports have been found on the success synthesis

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