Biologically programmed synthesis of core-shell CdSe/ZnS nanocrystals†

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Here we report a biomimetic method to synthesize core-shell CdSe/ZnS semiconductor nanocrystals using a bi-functional peptide; the resulting nanocrystals had a defect free crystallinity and a clearly observed core-shell structure; the results are significant as this is the first report of core-shell semiconductor nanocrystal synthesis using a peptide template.

Type II–VI semiconductor nanocrystals (e.g., ZnS, CdS, CdSe, CdTe) or quantum dots (QDs) have been shown to possess unique optical, electrical and optoelectronic properties for a wide range of applications.1 These properties can be controlled effectively by tuning the sizes, compositions, and crystal structures of the nanocrystals.2 For most biological applications, core-shell CdSe/ZnS QDs have played a particularly important role because they can be created to span the whole optical spectrum suitable for imaging.3

A wide range of nanoparticles that selectively self-organize via the use of peptides templates have been demonstrated.4 The use of peptides not only directs the nucleation in inorganic materials, but also controls the crystal structure and size, all in aqueous and ambient conditions. Methods have been developed based on phage display technology to select peptide sequences to guide the growth of ZnS and CdS nanocrystals with different crystalline structures at room temperature.5 However, the feasibility to guide the growth of core-shell nanocrystals using peptide templates has not been demonstrated. Recently, hybrid Au–Pd nanoparticles have been generated using a bi-functional peptide containing an Au-binding domain and a Pd-binding domain.6 By exploiting the selectivity of the two peptide domains, sequential deposition of Au and Pd resulted in bimetallic nanoparticles with a 10 nm Au nanoparticle core and smaller 1–2 nm Pd nanoparticles decorated on the surface. This result clearly indicated that the peptide templates are fully functional at the interface and the oriented peptide domain on the Au nanoparticle surface can be used to guide the nucleation and growth of additional materials.

Herein, we demonstrate that this approach can be generalized to guide the growth of core-shell CdSe–ZnS semiconducting nanocrystals using layer-by-layer deposition programmed by tailoring the specificity of a bi-functional peptide template. Binding peptides with exquisite specificity towards either ZnS or CdS crystals have already been generated via phage display selection.7 We speculate that the CdS-specific peptide may also be exploited for CdSe formation. These highly selective peptides offer the possibility for layer-by-layer deposition to synthesis core-shell hybrid nanocrystals without any cross contamination (Fig. 1).

To promote core-shell nanocrystal formation, a bi-functional peptide (Fig. 2A) containing a CdSe domain (Cys-Thr-Tyr-Lys-Cys) and a ZnS domain (Lys-Arg-Arg-Ser-Ser-Glu-Ala-His-Asn-Ser-Ile-Val) bridged by a proline linker was synthesized. Inclusion of a proline linker is essential as it has previously been reported to help maintain the functionality of these peptides at interfaces.8 The ability of the bi-functional peptide to promote CdSe nanocrystal formation was first investigated. Addition of 5 mM CdCl2 and 2.5 mM freshly prepared NaHSe to 20 μM bi-functional peptide resulted in fluorescent materials (Fig. 2B), which exhibited a broad absorption spectrum (Fig. 2C) with a shoulder at 400 nm. A corresponding photoluminescence peak was detected at 470 nm, which lies within the visible range typical for CdSe nanocrystals.8 In contrast, no fluorescence was detected in the absence of the peptide. HR-TEM imaging (Fig. 3) revealed the formation of fairly uniform CdSe nanocrystals around 4–5 nm diameter. A lattice spacing of ~0.37 nm was observed across the entire crystals, indicating ability of the Cd-specific peptide domain to initiate nucleation and growth with a precise control over the crystal size. Furthermore, an elemental analysis of these nanocrystals confirmed a 1 to 1 ratio between Cd and Se.

Similarly, the ability of bi-functional peptides to guide the nucleation of ZnS nanocrystals was tested by adding 1 mM

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ZnCl₂ and 1 mM freshly prepared Na₂S to 0 mM bi-functional peptide. UV-visible spectra of as synthesized ZnS nanocrystals revealed a broad absorption and a shoulder at 285 nm, which correlate well with the photoluminescence peak at 340 nm typical of ZnS nanocrystals (Fig. 4A). The presence of ~5 nm zinc-blend nanocrystals was further confirmed by TEM imaging (Fig. 4B). Elemental analysis also confirmed the 1:1 Zn to S content for the ZnS nanocrystals. In comparison, no nanocrystals were detected without the addition of the bi-functional peptides (data not shown).

Once the ability of each domain to promote the growth of either CdSe or ZnS nanocrystals was confirmed, the bi-functional peptide was further evaluated for its ability to synthesize the proposed core-shell CdSe/ZnS nanostructures. The CdSe core was first synthesized as described above. The 4–5 nm CdSe nanocrystals were then allowed to interact with 0.5 mM ZnCl₂ for 1.5 h before the addition of 0.5 mM Na₂S. HRTEM imaging revealed the formation of some larger nanocrystals in the range of 12 nm (Fig. 5A). These nanocrystals contained a clear core-shell structure (Fig. 5B) with the size of the CdSe core consistent with the expected 4–5 nm, demonstrating the possibility of growing a ZnS shell over the CdSe core. Elemental analysis confirmed the expected ratio of 1:1 for Zn/S or Cd/Se, respectively. The ZnS shell growth also resulted in a 1.5-fold increase in photoluminescence while the spectral properties were similar to the CdSe nanocrystals (Supporting information). This relatively low improvement in photoluminescence can be partially attributed to the relative modest fraction of nanocrystals containing the fully grown ZnS shell. Another possibility is the thickness of the ZnS shell in the range of 2–3 nm. It has been previously reported that only one or two monolayers of ZnS shell are desirable for maximum improvement in photoluminescence. The shell thickness may be modulated if another capping peptide is added to control the ZnS shell growth. This possibility will be explored in the future.

In summary, we report a facile method for the synthesis of semiconductor CdSe/ZnS core-shell nanocrystals. The specific sequences of the bi-functional peptide guide the synthesis with control over size and composition. Most importantly, this benign and flexible strategy can be generalized for other hybrid inorganic nanostructures since the required peptide

![Fig. 2 Formation of fluorescent CdSe nanocrystals. (A) The bi-functional peptide used in this study. (B) Fluorescent CdSe nanocrystals visualized under UV illumination. (C) The UV visible absorption spectrum and photoluminescence (excitation at 410 nm) of the synthesized CdSe nanocrystals.]

![Fig. 3 A TEM image showing uniformly distributed CdSe nanocrystals with an average size of 4 nm. The insert shows the HRTEM image of a nanocrystal with the 0.37 nm lattice spacing.]

![Fig. 4 Synthesis of ZnS nanocrystals using bi-functional peptides. (A) UV visible absorption spectra and photoluminescence data (excitation at 280 nm) for such synthesized ZnS nanoparticles. (B) TEM imaging of ZnS nanoparticle giving an average size of 5 nm. Inset shows a HRTEM image demonstrating lattice fringes.]

![Fig. 5 Biologically synthesized CdSe/ZnS core-shell nanocrystals. (A) A TEM image showing the formation of 12 nm CdSe/ZnS nanocrystals. (B) A HRTEM image showing a ZnS shell grown on top of the CdSe core for the CdSe/ZnS core-shell nanocrystal.]

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sequences can be selectively fine-tuned in a high-throughput manner to meet a wide range of industrial needs.

Notes and references


