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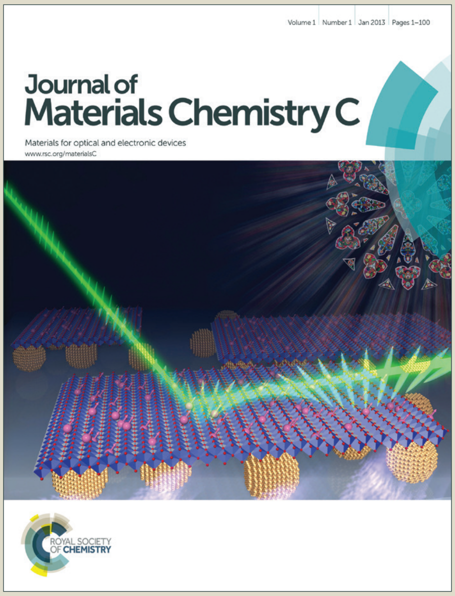

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Confined synthesis of CdSe quantum dots in the pores of metal-organic frameworks

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Ultra-small CdSe nanoparticles (~2 nm) were synthesised in the pores of a metal-organic framework, MIL-101(Al)-NH_2, using a stepwise injection-reaction protocol. Electron microscopy measurements showed that the nanoparticles were densely packed due to the highly ordered pores of the MOF.

Semiconductor nanoparticles; *e.g.* quantum dots (QDs),[1] are an intriguing class of materials for use in electronics and optics because their physical properties can be rationally tailored by varying the size and/or shape of the particles. In addition to tunable physical properties, assembly of QDs into well-ordered arrays results in electronic coupling among the QDs, which can be exploited to efficiently harvest light in a specified wavelength range.[2] Thus, the assembly of QDs into densely packed structures is an attractive method of fabricating fascinating optoelectronic devices. Conventional strategies for assembling QDs in liquid media have relied on interactions between the surfactants of adjacent QDs. However, the use of long-chain surfactants prevents close packing of QDs[3]. One way to overcome this issue is to synthesise the QDs in highly ordered cavities in porous materials. Although confinement of QDs in porous materials has been reported,[4] loading a single QD into each nanosized pore remains a key challenge in achieving a densely packed array.

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are potentially ideal for loading with a high density of QDs.[5] PCPs are microporous materials synthesized by assembling metal ions with organic ligands. The size, shape, and surface functionality of the pores in these materials can be rationally designed by a judicious choice of metal ions and organic linkers.[6] This designability allows for the fabrication of cage-typed pores suitable for the encapsulation of QDs. Chemical functionalisation of the pore surfaces can be used to initiate the nucleation of QDs within the pores.[7] Despite these prominent features, no general strategy has yet been reported that allows one to define the properties of QDs by restricting their formation to the interior of pores in MOFs. We describe herein a method for fabricating CdSe nanoparticles with diameters that match the pore sizes of MOFs and a means of creating densely packed QD arrays in MOF crystals.

$[Al_3OCl(DMF)_2(NH_2\text{-bdc})_3{\bullet}nH_2O]_n$, also known as MIL-101(Al)-NH_2,[8] was selected as the template MOF because it possesses two cage-type pores with diameters of 2.9 and 3.4 nm, respectively. These pores were deemed ideal because (1) the pore sizes are suitable for creating CdSe particles with high QD performance, (2) a cage-type, zero-dimensional pore configuration prevents the synthesised nanoparticles from self-aggregation, and (3) functionalisation of the pore surfaces with NH_2 groups helps adhere precursor Cd^{2+} ions and facilitates the infiltration of these precursors into the pores, which ultimately results in a dense configuration of aligned nanoparticles.[9]

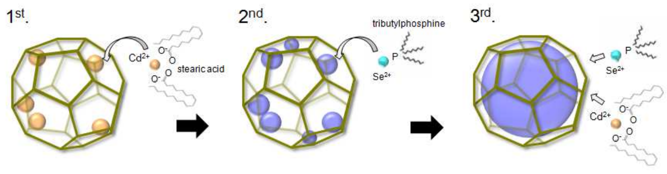

Figure 1. Schematic illustration of a stepwise injection-reaction protocol that confines the growth of CdSe nanoparticles to the interior of MOF cavities.

The stepwise injection-reaction protocol is key to the successful synthesis of CdSe nanoparticles. The nanoparticle precursors (ions or nuclei) were introduced into the MOF cavities, which confine the reaction and the growth of nanoparticles. The synthesis of QDs in MIL-101(Al)-NH_2 was performed as follows.[10] A Cd precursor solution, consisting of CdO and stearic acid as a complexing agent in octadecane, was added to powdered crystals of MIL-101(Al)-NH_2. The mixture was heated to 503 K to load Cd ions into the MOF cavities.

Next, a Se precursor solution, containing tributylphosphine as a complexing agent in octadecane, was injected into the reaction mixture, to form CdSe nuclei. The nanocrystalline nuclei were grown by maintaining the reaction temperature at 503 K (Figure 1). After the reaction, the solution was cooled to room temperature and composites of CdSe@MIL-101(Al)-NH_2 were obtained by washing and centrifugation.

The synthesis of QDs was confirmed, and the particles characterised, by scanning transmission electron microscopy (STEM). The STEM micrograph in Figure 2 shows the synthesised QDs on a crystalline face of MIL-101(Al)-NH_2. The particle diameter is approximately 2.0-3.0 nm, corresponding to the pore sizes of MIL-101(Al)-NH_2. STEM-EDS (energy dispersive X-ray spectroscopy) measurements showed a homogeneous distribution of both Cd and Se on the surface of MIL-101-NH_2. In each selected area, both elements existed in nearly equal amounts, implying the successful synthesis of CdSe nanoparticles (Figure S4).

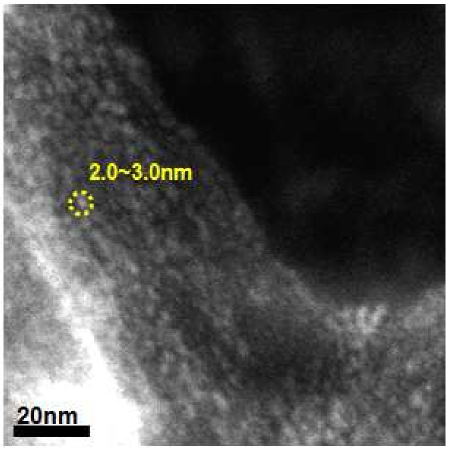

Figure 2. STEM micrograph of CdSe quantum dots supported on the surface of MIL-101 (Al)-NH2 crystals.

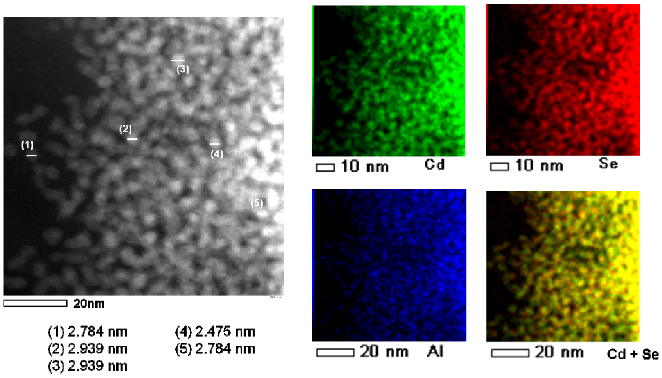

Figure 3. High-resolution STEM-EDS micrographs of the cross section of CdSe@MIL-101(Al)-NH_2.

The cross-sectional STEM micrograph of QD@MIL-101(Al)-NH_2 is consistent with the synthesis of CdSe in the MOF pores. The nanoparticles ranged in size from 1.5-3.0 nm, even in densely packed configurations (Figure S5). STEM-EDS measurements showed that CdSe nanoparticles were dispersed over the MOF crystal (Figure S6). The high-resolution STEM-EDS micrograph shown in Figure 3 shows CdSe quantum dots with diameters of 2.0 to 3.0 nm.

In contrast to the densely packed CdSe nanoparticles created in crystals of MIL-101(Al)-NH_2, another framework material with similar pore sizes, MIL-100(Fe) ($[Fe_3OCl(H_2O)_2(btc)_2•nH_2O]_n$ (btc = 1,3,5-benzene tricarboxylate),[11] allowed the formation of CdSe particles only on the surface of crystal (Figure S7 and S8). Although the pore sizes of MIL-100(Fe) (two distinct pores with diameters of 2.5 and 2.9 nm, respectively) are similar to those of MIL-101(Al)-NH_2, the pore windows of MIL-100(Fe) are considerably smaller than those of MIL-101(Al)-NH_2. The pentagonal windows measure approximately 5.5 Å for MIL-100(Fe) and 12 Å for MIL-101(Al)-NH_2, while the hexagonal windows measure 8.6 and 16 Å, respectively. Thus, pore window diameter is likely a dominant factor in restricting the diffusion of QD precursors with bulky complexing agents into the pores of the MOF.

Note that a similar packing effect, facilitated by pendant amine groups, in the formation of Au–Pd nanoparticles was reported with a MIL-101(Cr) MOF with ethylenediamine bound to coordinatively unsaturated metal centres.[9] This previous study also demonstrated efficient loading of metal nanoparticles in MOF pores, owing to strong interactions between the amine group and the metal precursors. This phenomenon is consistent with our observations of densely packed CdSe nanoparticles in this study.

Photoluminescence (PL) experiments on samples of QD@MIL-101(Al)-NH_2 at low temperature (12K) yielded four characteristic emission peaks at 436, 468, 585, and 660 nm after excitation at 325 nm (Figure 4). The diameters of the CdSe QDs in the samples, estimated from band-edge energies with effective mass approximations, were 1.7, 1.8, 3.3, and 6.2 nm, respectively. The emission peak at 585 nm is thought to originate from QDs attached on the outside of the MOF pores. This hypothesis is supported by the presence of the same emission peak from the supernatant of the CdSe QD synthesis solution (Figure S9). The largest of the synthesised QDs (λ = 660 nm, ϕ = 6.2 nm) is also most likely attached to the surface of the MOF crystals.

The two characteristic emission peaks at 436 and 468 nm are assigned to QDs synthesized in the pores of MIL-101(Al)-NH_2 with the estimated diameters of 1.7 and 1.8 nm (see also ESI), respectively. These calculated values fit particle diameters measured from electron micrographs.

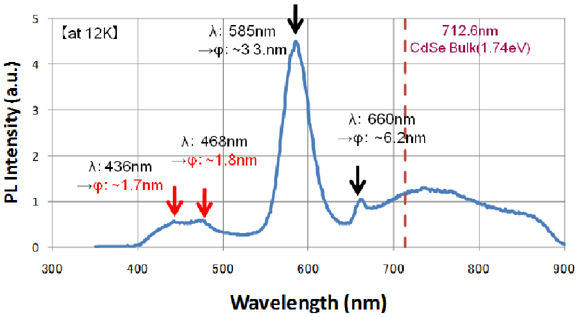

Figure 4. Photoluminescence at 12 K from QD@MIL-101(Al)-NH_2 after excitation at 325 nm.

The PL emission intensity from the synthesised QDs decreased with increasing temperature from 12 K to 300 K, as shown in Figure S10. In contrast to the diminished intensity observed at 436 nm, which can be assigned to QDs formed in the smaller cages, the emission at 468 nm remained, even at 300 K. Note that in conventional syntheses, the surface of such QDs would be passivated with protecting agents, such as trioctylphosphine oxide, octadecylamine. However, no such agents strongly coordinated with QDs were added to the reaction. This emission at 300 K is most likely due to the passivation of QDs that are held in large pores and the relatively large number of NH_2 groups on the interior surface of these pores. Amine groups are efficient passivating agents for cadmium-based nanoparticles.[12] In addition, the amino-benzene moiety of the linker can freely rotate into the pores, allowing for optimal positioning and coordination with cadmium atoms. The large and small MOF pores can have an estimated 42 and 30 amino groups, respectively, on their surfaces if all of the amino groups from the linkers are directed toward the pores. This estimate excludes the tetrahedral pores, which are too small to hold a CdSe particle. These numbers correspond to the numbers of cadmium atoms on the surface of CdSe nanoparticles with diameters of 1.8 nm (Cd:45, see also ESI).

Conclusions

This study demonstrated the direct fabrication of CdSe quantum dots, with diameters of only a few nanometres, in the pores of MIL-101(Al)-NH_2 by a stepwise injection-reaction protocol. This procedure resulted in the densely packed QDs over the entire MOF crystal. Pendant NH_2 groups on the pore surface support high loading of metal precursors and effectively passivate the surface of the resulting QDs. This method offers a novel means of tuning the size of QDs without using protecting agents. Improvements to the photoluminescent properties of QDs made via this technique are currently underway.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details for synthesis, encapsulating procedure, additional TEM and TEM-EDS data, and photoluminescence measurements. See DOI: 10.1039/c000000x/.

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