# Two-dimensional arrays of luminescent metal-selenide nanoparticle†

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**The direct synthesis of CdSe nanoparticles inside the core of PS-P4VP micellar structures has been utilized for the easy fabrication of 2-D CdSe nanoparticle arrays with variable sizes on a solid substrate.**

Luminescent semiconductor nanomaterials, such as metal-selenide (CdSe, ZnSe, PbSe), have been of great interest because of their unique quantization phenomena[1] and potential applications in optoelectronic devices and biology.[2] Synthetically, significant control over size and size distribution has been achieved in a number of nanoparticle compositions.[3] To harness the nanoparticles' full potentiality, for example in bulk-heterojunction solar cells[4] and photonic crystals,[5] spatial control of both the nanometer length scale of the particles as well as much larger length scales associated with arrays and assemblies is required. Several strategies including the use of templates based on self-assembled block copolymers[6] and biopolymers,[7] liquid crystalline[8] and solvent constraint evaporation technique[9] have been explored to control the position of the nanoparticles in thin films. However, finding techniques for fabricating 2-D arrays of metal-selenide nanoparticles with tunable size and interspacing remains a great challenge.

Block copolymer, which forms micellar structures in a selective solvent, provides an excellent platform for realizing highly ordered 2-D nanoparticle arrays with easy control of size and interparticle spacing. For example, polystyrene-*block*-poly(vinylpyridine) copolymer (PS-PVP) micellar structures have been successfully used to fabricate various metal and metal-oxide nanoparticle 2-D arrays.[10] The presence of a pyridine unit in PS-PVP enables easy and selective loading of various metal salts, as precursor for nanoparticles, into the core of the micelles.[11] If an approach were developed to prepare metal-selenide nanoparticles directly in the core of the micelles, it would be highly advantageous for 2-D nano-array fabrication. Metal-sulfide nanoparticles have already been prepared in the micelle core by taking advantage of the gaseous nature of sulfur precursor ($H_2S$), though 2-D array fabrication has not been demonstrated.[12] Although block copolymer templates[6] have been investigated previously, those strategies utilize the pre-synthesized CdSe nanostructures and therefore rely on the surface chemistry of the nanostructures or external forces such as an electric field to achieve the selective positioning of the nanoparticles in the nanodomain of the templates. Herein, we report the direct preparation of CdSe nanoparticles in polystyrene-*block*-poly(4-vinylpyridine) copolymer (PS-P4VP) micelle core and 2-D array fabrication with variable heights. Although we mainly focus on CdSe nano-arrays in this communication, the approach presented can also be extendable to other metal-selenide (ZnSe, PbSe) as well as metal-telluride nano-array fabrication.

The preparation of CdSe nanoparticles inside the PS-P4VP micelle core and fabrication of 2-D arrays are schematically shown in Fig. 1. PS-P4VP–$CdCl_2$ micellar solution was layered on top of the freshly prepared NaHSe[13] aqueous solution and stirred for more than 24 h at room temperature. To vary the height of CdSe nanoparticles, we used two different $CdCl_2$ concentrations (molar ratio of $CdCl_2$ to vinyl pyridine monomer = 1.0 and 20), which are referred to as PS-P4VP–CdSe-1 and PS-P4VP–CdSe-2, respectively.

Fig. 2(a and b) shows the transmission electron microscopy (TEM) images of PS-P4VP–CdSe-1 and PS-P4VP–CdSe-2 samples. CdSe nanoparticles were formed in the PS-P4VP micelle core and the size of $CdSe_2$ particle in each micelle core looks similar. However, a closer look at the micelle core reveals the formation of multiple nanoparticles in a single core (Fig. S1 in the ESI†). High resolution TEM (HR-TEM) investigation reveals that only amorphous CdSe nanoparticles were formed in PS-P4VP–CdSe-1 (inset in Fig. 2a). Interestingly, PS-P4VP–CdSe-2 shows well developed lattice fringes, indicating a high crystallinity of the CdSe nanoparticles (inset

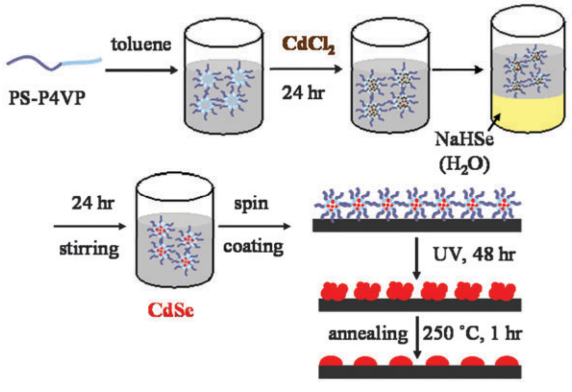

**Fig. 1** Schematic of CdSe nanoparticle preparation inside the core of the PS-P4VP micelles and fabrication of 2-D nano-arrays.

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† Electronic supplementary information (ESI) available: Detailed experimental methods, TEM image of PS-P4VP-CdSe-2 at a higher magnification, photoluminescence spectra of PS-P4VP-CdSe-1 and PS-P4VP-CdSe-2 excited at different wavelength, and SPM analysis of as fabricated and polymer matrix removed 2-D arrays CdSe nanoparticles obtained from PS-P4VP-CdSe-1 and PS-P4VP-CdSe-2 micellar solution, and HR-TEM and EDX of ZnSe and PbSe nanoparticles prepared in the micelles core. See DOI: 10.1039/b718232e

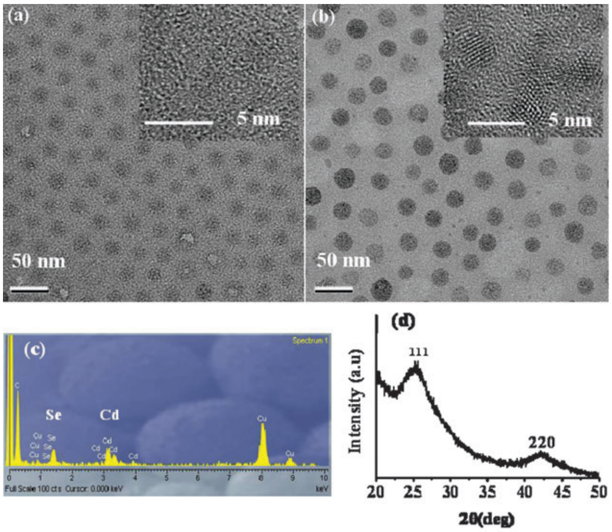

**Fig. 2** TEM images of (a) PS-P4VP–CdSe-1 and (b) PSP4VP-CdSe-2. (c) EDX spectrum of CdSe nanoparticles and (d) powder X-ray diffraction pattern of PS-P4VP–CdSe-2.

in Fig. 2b). Although TEM images exhibit good contrast difference between PS-P4VP–CdSe-1 and PS-P4VP–CdSe-2 nanoparticles, the particle height tuning is not very clear. However, the height variation is more evident from the optical studies in micelle solution and scanning probe microscopy (SPM) and field-emission scanning electron microscopy (FE-SEM) investigation of the fabricated nanoparticle arrays from the corresponding micellar solution (to be discussed later). The energy dispersive X-ray (EDX) spectrum (Fig. 2c) shows nanoparticles consisting of only Cd and Se and also confirms the equal elemental composition. The powder X-ray diffraction (XRD) pattern of PS-P4VP–CdSe-2 reveals that the formed CdSe nanocrystals are in the cubic phase (Fig. 2d).[14] Diffraction peaks at $2\theta = 25.4$ and 42.6 correspond to the (111) and (220) plane reflections of cubic CdSe. It is noted that the cubic phase is the most stable form at low temperature. The broad diffraction peaks indicate a smaller size of CdSe nanocrystals.

The CdSe nanoparticles from TEM images (Fig. 2a and b) appear to be too large to exhibit quantum confinement effects,[1] but the absorption spectrum of PS-P4VP–CdSe-1 shows strongly blue shifted multiple absorption peaks compared to bulk CdSe (716 nm) and a small peak appears at 500 nm for PSP4VP-CdSe-2 (Fig. 3a). In photoluminescence (PL), when PS-P4VP–CdSe-1 was excited at 390 nm, three broad, but distinct, emission peaks appeared at 466 nm, 480 nm and 492 nm (Fig. 3b). When the excitation wavelength was varied, the intensity of the three distinct peaks also showed slight variation between them (Fig. S2 in the ESI†). For PS-P4VP–CdSe-2, excitation at 550 nm exhibits a strong and broad emission band centered at 729 nm (Fig. 3b), which is nearly the same as that of bulk CdSe materials.[15] However, 490–520 nm excitation shows a deep red emission band centered between 703–715 nm, suggesting that smaller size nanoparticles are also present along with the major larger size nanoparticles (Fig. S2 in the ESI†). The absorption and PL studies suggest that the formed multiple CdSe nanoparticles in the micelle core are of different size. The observed broad PL peaks are commonly attributed to the recombination of charged carriers trapped in surface states and are related to the size of CdSe nanoparticles.[16]

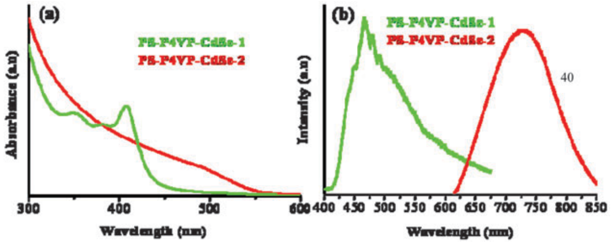

**Fig. 3** Optical absorption (a) and photoluminescence (b) spectra of PS-P4VP–CdSe-1 and PS-P4VP–CdSe-2 measured in solution phase.

The direct synthesis of CdSe nanoparticles inside the core of the PS-P4VP micellar solution offers easy fabrication of a 2-D array on a solid substrate by simple spin or dip coating. In our case, monolayer micellar films were fabricated by spin coating on a silicon wafer. To achieve the pure CdSe nanoparticle arrays, the composite monolayer films were exposed to deep UV light to remove the PS-P4VP polymer matrix.[17] We confirmed that the neat PS-P4VP film was completely removed when it was exposed to deep UV light.

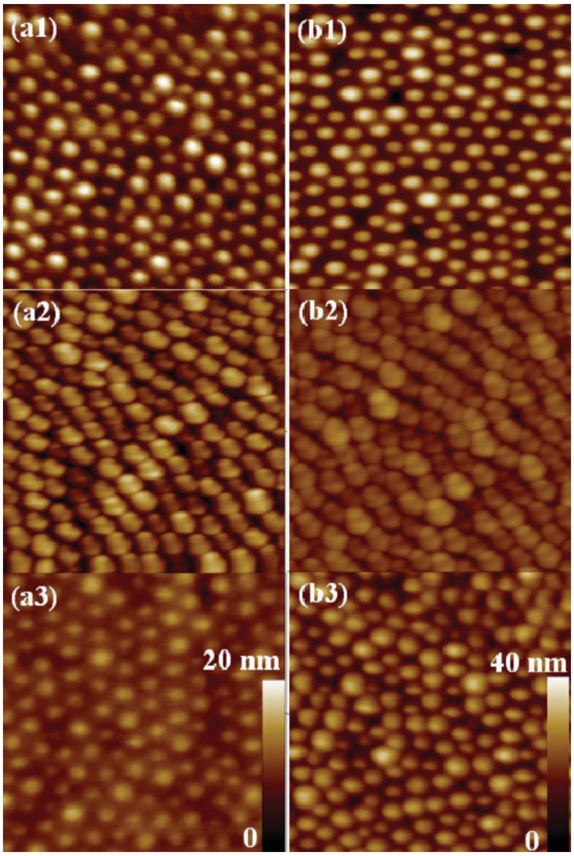

**Fig. 4** SPM height images of (1) as-fabricated monolayer thin film, (2) polymer matrix removed by UV exposure and (3) annealed CdSe nanoparticle arrays of PS-P4VP–CdSe-1 (a) and PS-P4VP–CdSe-2 (b). Image size: 500 nm × 500 nm.

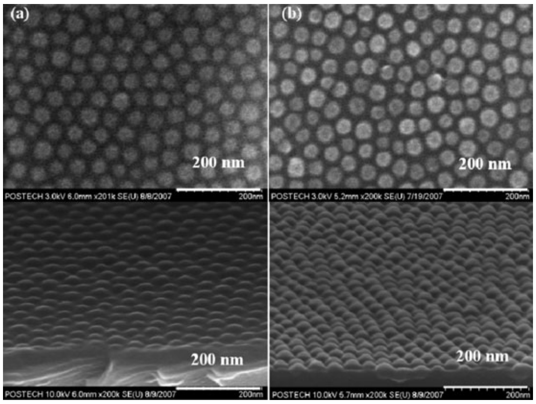

**Fig. 5** FE-SEM images of the top and 45° tilt views of two-dimensional arrays of pure CdSe nanoparticle prepared from (a) PSP4VP-CdSe-1 and (b) PS-P4VP–CdSe-2 micellar solution.

Fig. 4 shows the SPM height images of the as-fabricated monolayer films, polymer matrix removed by UV exposure and annealed pure CdSe nanoparticle arrays. The cross-sectional height profiles are given in the supporting information (Fig. S3 in the ESI†). The average height contrast between PS matrix and P4VP domain and the average diameter of P4VP core of the neat PS-P4VP micellar film are 3 nm and 23 nm (Fig. S4 in the ESI†). The inclusion of CdSe nanoparticles in P4VP core has increased the average height contrast to 8 nm and 15 nm for PS-P4VP–CdSe-1 and PS-P4VP–CdSe-2, respectively (Fig. 4a1 and b1). But both samples show the same average P4VP domain diameter (30 nm), which is larger than that of neat PS-P4VP (23 nm). The SPM investigation of the PS-P4VP matrix removed samples also clearly shows the coexistence of multiple nanoparticles in a single P4VP domain (Fig. 4 a2 and b2) and supports the observation of optical studies (Fig. 3).

Before the polymer matrix was removed, the P4VP core might have acted as a layer to hold together the multiple nanoparticles in spherical shape. Upon removal of the holding layer the unrestricted nanoparticles appear to fall down on the substrate surface and show pan-cake morphology. However, when the sample was annealed at 250 °C for 1 h under vacuum, the differently sized multiple nanoparticles of each domain moved closer and became single CdSe nanoparticles (Fig. 4 a3 and b3). The average height of CdSe nanoparticles obtained from PS-P4VP–CdSe-1 and PS-P4VP–CdSe-2 is 3 nm and 8 nm, respectively (see ESI† Fig. S3). However, CdSe nanoparticles fabricated from both the samples exhibit the same average diameter of 30 nm. The average interspacing between CdSe nanoparticles in the nano-array is 43 nm, which is nearly the same as that of the neat PS-P4VP micellar structure P4VP domain interspacing (40 nm). Fig. 5 shows the FE-SEM images of the top and 45° tilt views of the polymer matrix removed samples, which exhibit highly ordered, height tunable 2-D array of CdSe nanoparticles. The polymer matrix removed annealed samples exhibit brighter CdSe nanoparticles domains in FE-SEM due to change of domain density. By using a similar synthetic approach, we have prepared ZnSe and PbSe nanoparticles inside the PS-P4VP micelle core (Fig. S5 in the ESI†).

In conclusion, we have presented a simple micellar approach to fabricate 2-D arrays of CdSe nanoparticles on a solid substrate. The height of the CdSe nanoparticles varied by changing the concentration of metal salt in the micelle solution. Optical investigation of the CdSe nanoparticles in micelle solution demonstrates the bulk as well as quantized phenomena. The approach presented provides new opportunities for easy fabrication of highly ordered luminescent quantum dot arrays for numerous applications in photonics and electronics.

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