$Cd_2P_2Se_6$ nanolenses formed at a water–air interface

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Self-assembly offers an attractive approach for the organization of nanocrystals (NCs) into functional superstructures. Well-ordered arrays with various configurations have been produced upon solid substrates [1–6], but there are obvious advantages to be exploited if self-supporting films containing assemblies of functional NCs can be produced. To this end, the self-assembly behavior of NCs on liquid substrates, such as water surfaces, has been investigated. Lim *et al.* produced close-packed arrays of 5 nm silver NCs at a water–air interface by introducing a NC dispersion in the presence of polysterene [7]. Well-organized monolayer and bilayer regions were embedded in a continuous layer of the polymeric species. In a similar manner, Park *et al.* produced free-standing photonic bandgap crystals by developing 3-D assemblies of colloidal polysterene particles (∼240 nm in diameter) [8].

In the present letter we describe attempts to apply this approach to tri-*n*-octyl phosphine oxide (TOPO)-coated CdSe NCs. The authors have had considerable success in assembling such NCs into assemblies on solid substrates, even to the point of producing well-ordered monolayers with strong crystallographic texture [9]. Attempts to produce free-standing assemblies at a water–air interface, however, led to the serendipitous observation of nanoscale lens-shaped particles of the cadmium hexachalcogeno-hypodiphosphate phase $Cd_2P_2Se_6$. A summary of these observations is presented here together with an outline of possible routes by which this phase could form and how the morphology might develop.

The method for producing TOPO-coated CdSe NCs has been described in detail elsewhere [10]. Briefly, the precursors used are dimethyl cadmium and a solution of selenium in tri-*n*-octyl phosphine (TOP). The precursors were pre-mixed and subsequently introduced into a reaction flask containing a degassed mixture of TOPO and TOP under a nitrogen atmosphere at an elevated temperature (∼300 °C). The growth of the NCs in the reaction solution was monitored by ultraviolet visible spectrometry. The surfaces of the as-synthesised CdSe NCs were passivated by a layer of TOPO molecules in the presence of the TOPO/TOP solvent mixture. These solvents were then removed by precipitation and repeated rinsing with methanol. Fractionation was performed using a solvent/non-solvent pair (chloroform/methanol) to further narrow the initial size distribution of the CdSe NCs [11]. This procedure was used to produce NCs of various core diameters, corresponding to different luminescent wavelengths. The CdSe NCs used in this work had a core diameter of 6.20 ± 0.36 nm, i.e. a variation of $\pm 6.0\%$.

Dilute dispersions of these fractionated CdSe nanocrystals in toluene were slowly deposited onto the surface of water contained in a 100 mm diameter Pyrex petri dish. Since toluene and water are immiscible, the dispersion formed a smooth floating circular layer on the water surface. The petri dish was then covered and the toluene allowed to evaporate for a period of 4 days. When the evaporation was completed, a fragmented thin film remained on the water surface. These fragments were carefully transferred on to a TEM copper grid and examined in a Philips EM420T operating at an accelerating voltage of 100 kV.

Many regions of the thin film fragments were too thick for the electron beam to penetrate. In those regions that were electron-transparent, no assemblies of close-packed CdSe NCs were observed. Instead, large numbers of disc-like nanoparticles were present. These varied in diameter from 20 nm to 400 nm and were typically ∼100 nm in diameter. Fig. 1 is a bright-field TEM micrograph obtained from a representative area showing such particles. It was not possible to measure the thickness of the discs accurately but tilting experiments indicated that this was far less than the diameter of the discs in each case and probably <10 nm.

The composition of the particles was investigated using energy dispersive spectrometry (EDS) in the TEM. The spectra exhibited characteristic peaks corresponding to Cd L_α, Se L_α, and P K_α, together with K_α system peaks for Cu and Zn, which arose from the support grid and specimen holder. Accurate quantification was not possible in the absence of a suitable standard, but standard-less analysis indicated that the particles certainly contained far more Se and P than one would

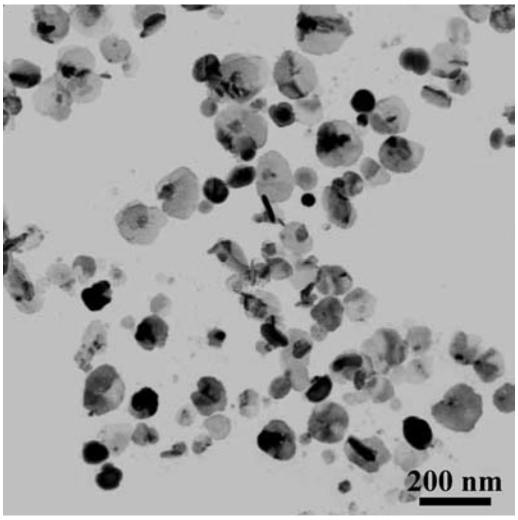
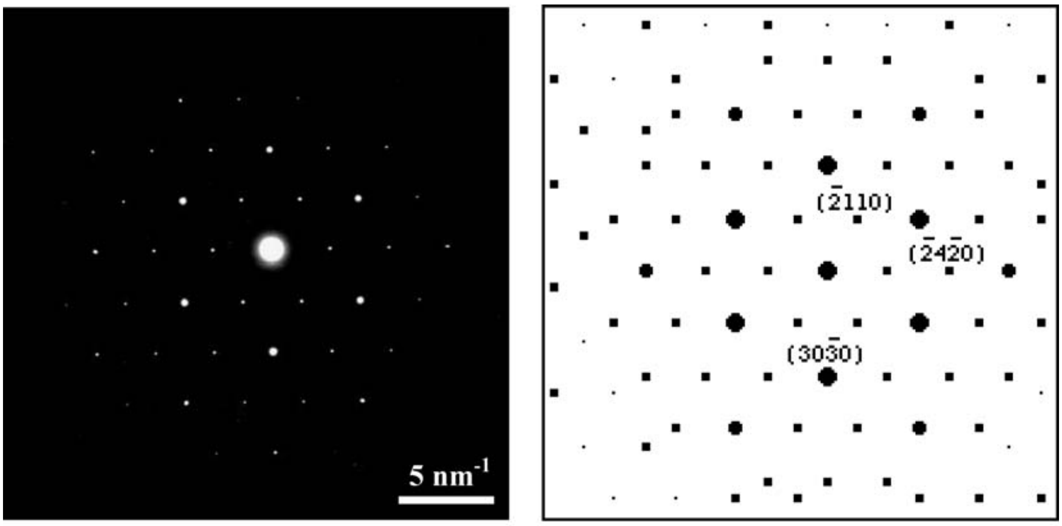


Figure 1 Bright field TEM micrograph of an area containing several of the disc-like particles which form in the fragmented film.

expect for TOPO-capped CdSe. A more conclusive identification was obtained from analysis of selected area electron diffraction (SAED) patterns obtained with the beam perpendicular to the plane of the particles and one such pattern is shown in Fig. 2a. The primary reflections in this pattern correspond to interplanar spacings of 0.324 and 0.186 nm. These match well with those expected for the compound $Cd_2P_2Se_6$ which exhibits the layered rhombohedral structure shown in Fig. 3 with lattice parameters $a = 0.649$ nm and $c = 1.997$ nm [12, 13]. Further confirmation was obtained by comparing patterns simulated for this compound using the software *Desktop Microscopist* with those obtained experimentally. The simulation shown in Fig. 2b was obtained using the structural parameters reported for $Cd_2P_2Se_6$ by Potoril *et al.* [13], with a beam direction of [0001], and an accelerating voltage of 100 kV. The spacings, symmetry, and the relative intensities of the diffraction maxima all match very well with those in experimental patterns such as Fig. 2a. From this we infer that the discs are (0001)-oriented plates of the $Cd_2P_2Se_6$ phase.

The metal hexachalcogeno-hypodiphosphates have the general formula $M_2P_2X_6$, where M is a transition or post-transition metal, and X is S or Se. This is an intriguing class of compounds both because they exhibit a wide range of optical [14], ferroelectric [15], electronic [16, 17] and magnetic [18] characteristics, and because the properties can be modified by the intercalation of atoms, ions, or molecules into the "Van der Waals gaps" between adjacent chalcogen layers [19, 20]. The compound $Cd_2P_2Se_6$ is a peritectic phase in the Cd-P-Se system and this complicates direct synthesis. As such, the compound is usually produced by high-temperature chemical vapor transport with iodine as the carrier medium [13, 19]. Our observations suggest that there may be a simpler and more scaleable low-temperature solution-based route to synthesize this phase. By referring to the $Cd_2P_2Se_6$ structure shown in Fig. 3, one can envisage the way in which these nanolenses might form. It can be seen that the structure is layered and that each layer consists of $P_2Se_6^{4-}$ anions with ethane-like staggered conformation and oriented with the P dimers parallel to [0001], and Cd^{2+} cations arranged in sheets parallel to (0001) bisecting these anions. It is plausible that oxidative decomposition of the surface passivating TOPO ligands, which occupy over one-third of the total Se surface sites, provides adequate P to transform all nanocrystal Se sites to PSe_3^{2-} anions: these could then dimerize to form $P_2Se_6^{4-}$ anions. Since the CdSe nanocrystals contain approximately equal amounts of Cd and Se atoms, the $P_2Se_6^{4-}$ anions would claim one-third of the Cd atoms in forming crystals of the $Cd_2P_2Se_6$ structure at the water/air interface. The remaining two-thirds of the Cd atoms would probably interact with water forming various cadmium hydroxide hydrated moieties $Cd(OH)_2(H_2O)_x$. Our prior research has shown that these moieties are partially soluble in aqueous media [21], which explains why



(a) (b)

Figure 2 Electron diffraction from the particles: (a) experimental pattern obtained with the beam direction normal to the plane of the particle; (b) simulated [0001] zone axis pattern for $Cd_2P_2Se_6$ at an accelerating voltage of 100 kV.

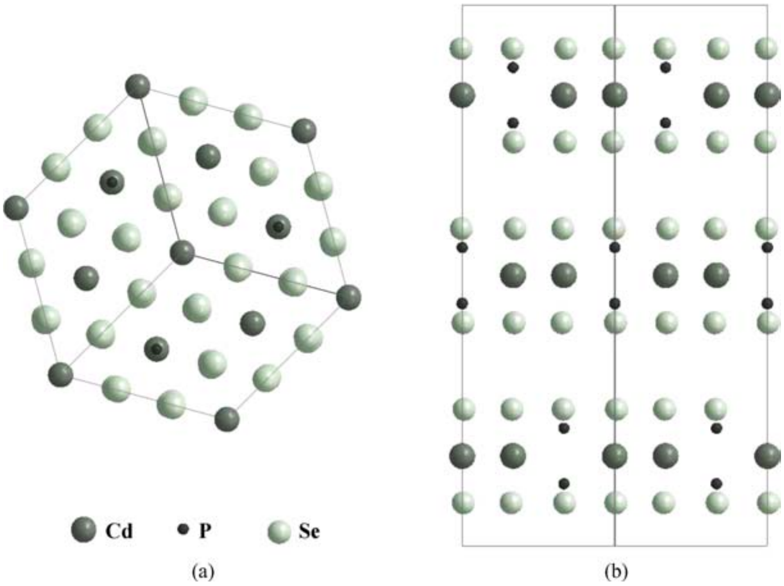


Figure 3 The non-primitive hexagonal unit cell for the crystal structure of $Cd_2P_2Se_6$ viewed along: (a) [0001]; (b) $[\bar{1}\bar{1}20]$.

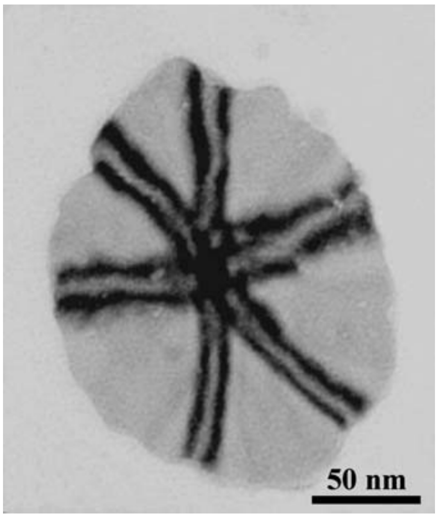


Figure 4 Bright field TEM micrograph of a single particle oriented perpendicular to the beam showing characteristic bend contour contrast.

no evidence for such oxides was detectable within the formed $Cd_2P_2Se_6$ nanostructures. Although this interpretation is rather speculative, we note that it would account for the formation of stoichiometric (0003) sheets of the $Cd_2P_2Se_6$ structure parallel to the water/air interface.

Finally, we note that the $Cd_2P_2Se_6$ plates exhibit bend contours in bright field TEM images and are, therefore, not flat. This is shown most clearly in images such as Fig. 4, which was obtained with a particle oriented perpendicular to the beam. In this orientation the particles exhibit three bands of contrast that intersect at $\approx 60^\circ$ to one another at the center of the particle. Dark-field imaging experiments have been used to show that these correspond to the $\pm 30\bar{3}0$-type bend contours. The contours arise due to curvature of the plates and appear along loci at which the Bragg condition is fulfilled for a particular reflection. Since the width of each band is approximately the same across the particle, the radius of curvature is constant, i.e. the plates are actually spherical caps or "nanolenses". Tilting experiments were used to show that the radius of curvature for the particle shown in Fig. 4 is approximately 1500 nm, and values of between 1000 and 2000 nm have been obtained for other particles. The most likely explanation for this characteristic morphology is differential intercalation, with the Van der Waals gaps closest to the water/air interface containing a lower concentration of intercalating species. We note, however, that it would be extremely difficult to verify this experimentally.

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