

Cl-capped CdSe nanocrystals *via in situ* generation of chloride anions†

Cite this: *Nanoscale*, 2014, 6, 6812

Cristina Palencia,^{‡*a} Koen Lauwaet,^a Leonor de la Cueva,^a María Acebrón,^a Julio J. Conde,^a Michaela Meyns,^b Christian Klinke,^b José M. Gallego,^{ac} Roberto Otero^{ad} and Beatriz H. Juárez^{‡*ae}

Halide ions cap and stabilize colloidal semiconductor nanocrystal (NC) surfaces allowing for NCs surface interactions that may improve the performance of NC thin film devices such as photo-detectors and/or solar cells. Current ways to introduce halide anions as ligands on surfaces of NCs produced by the hot injection method are based on post-synthetic treatments. In this work we explore the possibility to introduce Cl in the NC ligand shell *in situ* during the NCs synthesis. With this aim, the effect of 1,2-dichloroethane (DCE) in the synthesis of CdSe rod-like NCs produced under different Cd/Se precursor molar ratios has been studied. We report a double role of DCE depending on the Cd/Se precursor molar ratio (either under excess of cadmium or selenium precursor). According to mass spectrometry (ESI-TOF) and nuclear magnetic resonance (¹H NMR), under excess of Se precursor (Se dissolved in trioctylphosphine, TOP) conditions at 265 °C ethane-1,2-diylbis(trioctylphosphonium)dichloride is released as a product of the reaction between DCE and TOP. According to XPS studies chlorine gets incorporated into the CdSe ligand shell, promoting re-shaping of rod-like NCs into pyramidal ones. In contrast, under excess Cd precursor (CdO) conditions, DCE reacts with the Cd complex releasing chlorine-containing non-active species which do not trigger NCs re-shaping. The amount of chlorine incorporated into the ligand shell can thus be controlled by properly tuning the Cd/Se precursor molar ratio.

Received 22nd January 2014
Accepted 30th March 2014

DOI: 10.1039/c4nr00431k

www.rsc.org/nanoscale

Introduction

Colloidal semiconductor nanocrystals (NCs) show tunable and photostable luminescence properties along with broadband absorption and narrow emission, which makes them suitable for optoelectronic and photovoltaic applications.^{1,2} For these

purposes, fine control over the synthetic procedure to obtain monodisperse, robust and highly emissive semiconductor NCs is required. The development of the hot-injection method³ provides high control over size, shape, shape distribution and NCs surface composition for semiconductor materials such as CdSe,^{4,5} PbSe^{6,7} or PbS.^{8,9} This method also allows fine control over the NCs growth, which is achieved by the use of long alkyl chain surfactants acting as both metal complexing agents and ligands. These ligands form an insulating layer between NCs, restricting the charge transport between them and, as a consequence, devices containing such NCs (solar cells and photodetectors^{10,11}) may show low conversion efficiencies. A less insulating ligand shell is obtained by the exchange of these long alkyl chain molecules for shorter ones, including thiols^{12,13} or amines,^{14–16} in post-reaction treatments. The use of halides to perform ligand exchange reactions has recently been proposed.^{11,17–19} Halide anions can be considered as the shortest X type (ionic) ligands, facilitating charge transport among NCs. The passivating role of halide anions in PbS systems has been reported¹¹ and other reports have evidenced the passivation effect of chlorine in CdSe NCs, highlighting the possibility of using halogenated molecules to efficiently displace both L (coordinative) and/or X type ligands.^{18,19} Post-reaction treatments with chlorine-containing solutions seem to provide some benefits to certain colloidal NCs, such as more robust optical

^aIMDEA Nanoscience, c/Faraday 9, Campus de Cantoblanco, 28049 Madrid, Spain. E-mail: cristina.palencia.ramirez@chemie.uni-hamburg.de; beatriz.hernandez@imdea.org

^bInstitute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany

^cInstituto de Ciencia de Materiales de Madrid, ICMM, CSIC, Sor Juana Inés de la Cruz s/n, 28049 Madrid, Spain

^dDpto. de Física de la Materia Condensada and Instituto Nicolás Cabrera, Facultad de Ciencias, Universidad Autónoma de Madrid UAM, Avda. Fco. Tomás y Valiente 7, 28049 Madrid, Spain

^eDpto. de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid UAM, Avda. Fco Tomás y Valiente 7, 28049 Madrid, Spain

† Electronic supplementary information (ESI) available: Table S1 shows the molar amounts of the precursor used to prepare CdSe NCs from different Cd/Se precursor molar ratios. Fig. S2 shows TEM images of the control experiments. These consist of the synthesis of CdSe NCs from Cd/Se precursor molar ratios of 4, 2, 1, 0.5 and 0.25 in the absence of DCE. Table S3 shows the relative XPS peak areas of CdSe samples synthesized from different Cd/Se precursor molar ratios. See DOI: 10.1039/c4nr00431k

‡ Current address: Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany.



properties due to better passivation.²⁰ Furthermore, better performances of NC-based solar cells have been achieved upon chlorine-based treatments of the NCs followed by thermal annealing.²

On the other hand, chloride anions are known to form complexes of Cd chalcogenides and thus, nucleation and growth kinetics can be manipulated by the use of halides.²¹ Halides can be also used as etching agents, altering the initial shape of NCs.^{22–24} The re-shaping of CdSe rod-like into pyramidal NCs is another example in which the presence of chlorine in the ligand shell also shows some benefits to promote interactions with graphitic surfaces, allowing for the fabrication of composites made of graphitic carbon allotropes and semiconductor NCs.^{25–27}

In this work we have performed a systematic study on the size, shape and surface chlorine content of CdSe NCs synthesized using different Cd to Se precursor molar ratios in the presence of a chlorinated co-solvent (1,2-dichloroethane, DCE). Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) have been used to correlate the morphology and surface composition. Under excess Se precursor conditions, initial rod-like NCs modify their shape influenced by chloride anions, which are released through a reaction between TOP and DCE at the synthesis temperature (265 °C). These anions get incorporated into the NCs ligand shell and trigger the above mentioned re-shaping from rods to pyramids. The reaction between TOP and DCE has been evidenced by nuclear magnetic resonance (¹H NMR) and mass spectrometry (ESI-TOF). Density functional theory (DFT) calculations support the feasibility of the mechanism.

The incorporation of halogen anions as ligands during the NCs synthesis represents a versatile procedure, which may have advantages in solution processed optoelectronics.

Experimental section

Materials

Cadmium oxide (CdO, 99.998%) and octadecylphosphonic acid (ODPA, 97%) were purchased from Alfa Aesar and tri-octylphosphine oxide (TOPO, 98%) from Merck. Aldrich supplied trioctylphosphine (TOP, 90%), toluene (99.5%) and methanol (99.8%). 1,2-Dichloroethane (DCE, 99.5%) was purchased from Panreac. All these chemical reagents and solvents were used without further purification. XPS experiments were performed on NCs covering Highly Oriented Pyrolytic Graphite substrates (HOPG) ZYB quality, with a thickness of 2 mm purchased from NT-MDT.

In situ chlorine incorporation into the CdSe NCs ligand shell

Synthesis from different Cd/Se precursor molar ratios. CdSe NCs synthesis was performed following a variation of the method previously reported.²⁸ NCs obtained from a Cd/Se precursor molar ratio of 0.5 were prepared by stirring and heating (under nitrogen) 0.025 g (2×10^{-4} mol) of CdO (cadmium precursor) and 0.20 g (6×10^{-4} mol) of ODPA, using 2.9 g (8×10^{-3} mol) of TOPO as reaction medium. The solution turned clear at around

250 °C, evidencing the Cd(ODPA)₂ complex formation. Afterwards the temperature was decreased to 80 °C and 4 μL (5×10^{-5} mol) of DCE were injected with a Hamilton glass microsyringe 701SN with an 11 cm needle to assure reaching the level of the solution. After the addition of the chlorinated source, the temperature was increased to 265 °C and 0.43 mL of Se dissolved in TOP (selenium precursor) (1 M) (4×10^{-4} mol) were injected for nucleation. For the growth regime, the temperature was kept at 255 °C for 21 h. After this, the reaction was quenched by decreasing the temperature to 70 °C and adding 3 mL of toluene. The preparation of NCs from different Cd/Se precursor molar ratios was carried out analogously but with different relative Cd, Se and chlorine precursor concentrations. In order to facilitate the Cd(ODPA)₂ complex formation, the ODPA/CdO molar ratio was fixed to 3 in all cases. Detailed information about the corresponding amounts can be found in Table S1 (see ESI†). As previously mentioned, CdSe NCs with chlorine on their surface are prone to decorate graphitic surfaces.^{25–27} Thus, the CdSe synthetic reactions were carried out in the presence of HOPG substrates (1 cm²) included in the pot.²⁷ This methodology guarantees the coverage of one single layer of NCs on the surface, which turns out to be essential to prevent charging effects during XPS measurements. Once the reaction was finished, CdSe NCs attached to the HOPG substrates were purified by washing the substrates in toluene baths. NCs not attached to the HOPG substrates were purified by centrifugation/redispersion processes, using toluene as solvent and methanol as non-solvent. Finally, the purified NCs were redispersed in toluene and maintained in the dark at 4 °C. CdSe NCs were synthesized from Cd/Se precursor molar ratios of 4, 2, 1, 0.5 and 0.25 in the presence of DCE. Blank experiments were also carried out in the absence of DCE to discard the effect of the different Cd/Se molar ratios on the re-shaping of the NCs (images in Fig. S2 in the ESI†).

Chlorine incorporation into the CdSe NCs ligand shell in two steps

Synthesis from CdSe rods. Previously prepared and purified CdSe rods were used in all the cases as starting samples. They have been synthesized analogously to the one-step CdSe NCs in the absence of DCE. CdSe rods were purified by centrifugation/redispersion in toluene and methanol and kept in the dark at 4 °C. The resulting CdSe rods show an average diameter of 4.3 ± 0.5 nm, a length of 11.8 ± 1.3 nm and an absorption maximum of 623 nm. To perform the chlorine incorporation reactions, 2 mL of the CdSe rods (optical density 1.12) were loaded with 2.9 g of TOPO under a nitrogen atmosphere into a three-neck reaction flask and heated until 120 °C. The mixture was stirred under vacuum at this temperature to completely eliminate the toluene. To add the required amount of DCE, the temperature was dropped until 80 °C. Then, the mixture was heated until the TOP injection temperature (265 °C) was reached. Aliquots were taken at 2 h, 4 h, 5.3 h and 21 h to follow the re-shaping of the NCs with reaction time.

Experiments for the chloride generation study

To prevent oxidation of TOP, the direct mixing of DCE and TOP as well as the reaction at 265 °C and the samples preparation for



NMR and mass spectrometry experiments were carried out under nitrogen. In a three-neck flask coupled to a Schlenk line an equimolar mixture of DCE and TOP was stirred at room temperature for some minutes. Afterwards, a first aliquot was taken as a representative sample of the direct mixing of DCE and TOP at room temperature. A second aliquot was taken after keeping the temperature at 265 °C for 21 hours. NMR samples were prepared using deuterated chloroform (CDCl_3) as solvent. The NMR tubes, containing the precise amount of CDCl_3 were purged and filled under nitrogen. ^1H NMR spectra were recorded on a Bruker AMS-300 MHz. ^1H NMR spectra were acquired with a sufficient relaxation delay to allow complete relaxation between pulses. The samples for mass spectrometry were prepared analogously, using chloroform as the mobile phase. Mass spectral data were acquired in an ESI-TOF (6224, Agilent) mass spectrometer equipped with a 1200 Agilent HPLC. The data were acquired in a mass range of m/z 110–3200.

Characterization

Absorption measurements were carried out in a Varian Spectrophotometer Cary 50. Photoluminescence spectra were recorded in a spectrofluorometer Horiba Jobin Yvon Fluoromax-4. Transmission electron microscopy (TEM) images were obtained in a JEOL 1010 microscope, operating with an acceleration voltage of 100 kV. Size distribution data were obtained by measuring the NC sizes from TEM images. At least one hundred NCs were measured in each sample. XPS measurements have been performed using a monochromated Al-K α source ($h\nu = 1486$ eV) and a PHOIBOS 150 electron energy analyzer. Spectra for Cd 3d, Se 3d, and P 2p were recorded using a pass energy of 10 eV, whereas spectra for Cl 2p were recorded with 20 eV. Using these pass energies we obtained a FWHM for the Cd 3d $^{5/2}$ line of 1 eV and 1.3 eV, respectively. The binding energies were referenced to Cd 3d $^{5/2}$ at 405.2 eV. Charge neutralization was deemed to be unnecessary, since no movement of the Cd 3d $^{5/2}$ line with time had been detected. In order to evaluate the feasibility of the reaction between TOP and DCE, DFT calculations had been performed using the ORCA software.²⁹ The simulations were performed using the hybrid functional B3LYP with the Ahlrichs TZV basis set.³⁰

Results and discussion

Pyramidally shaped CdSe NCs synthesized in the presence of the chlorinated precursor DCE can be interpreted as a fingerprint of the chlorine incorporation into the ligand shell.²⁷ To survey the correlation between Cd, Se and Cl precursors in the chlorine incorporation into the NC ligand shell, we developed a series of experiments in which the Cd/Se precursor molar ratios were varied from 4 (excess of Cd precursor, CdO) to 0.25 (excess of Se precursor, Se@TOP), as stated in Table S1 (see ESI †). Representative TEM images of CdSe samples obtained for Cd/Se precursor molar ratios of 2, 1 and 0.5 are depicted in Fig. 1 along with size histograms both for the diameter and for the length of the NCs.

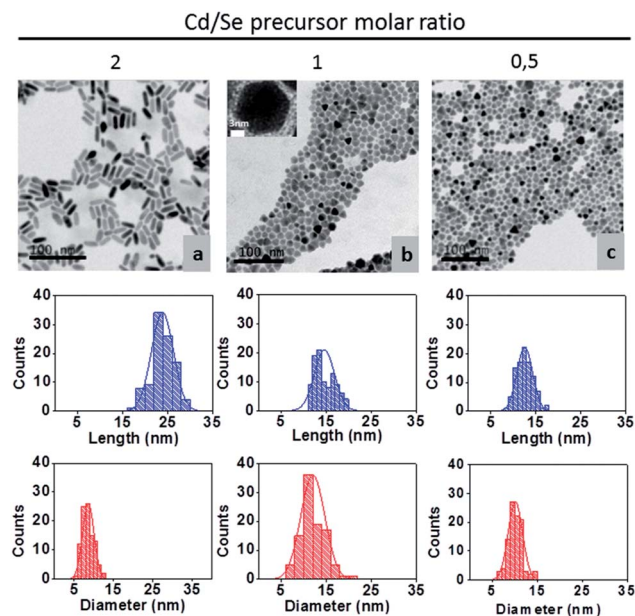


Fig. 1 TEM images of CdSe NCs obtained after 21 hours of reaction from Cd/Se precursor molar ratios of 2, 1 and 0.5 in the presence of DCE. The inset in (b) shows a pyramidal NC in the [001] direction. The histograms correspond to the length (blue) and diameters (red) of the NCs.

When the NCs synthesis is carried out in the absence of DCE, the shape of the NCs is rod-like regardless the Cd/Se precursor molar ratio (see TEM images of the control experiments in Fig. S2, ESI †). As it can be observed in the TEM images in Fig. 1, for stoichiometric Cd/Se conditions or under Se excess precursor conditions the addition of DCE during CdSe synthesis leads to a re-shaping from rods into pyramids. However, under excess Cd precursor conditions the addition of DCE does not trigger the re-shaping. Thus, the incorporation of chlorine might be driven by a chlorine-containing species (different from the precursor, DCE) which must be generated *in situ* under certain reaction conditions, in which the Cd/Se precursor molar ratio might play a crucial role. In order to quantify the effect of DCE in the shape evolution, the size of rod-like and pyramidal NCs has been measured for the samples shown in Fig. 1. As clearly seen in the histograms, the morphological anisotropy observed for samples obtained under excess of Cd precursor (Fig. 1a) turns into a more isotropic shape for samples with stoichiometric Cd/Se ratios or excess of Se precursor (Fig. 1b and c). Aspect ratios around 3 are observed for rods and close to 1 for pyramids. The width of the size distribution of the NCs does not exceed 10% of the mean radius for Cd/Se precursor molar ratios ranging from 2 to 0.5. The synthesis with molar ratios out of this range yields either bigger NCs and/or highly polydisperse ones (*i.e.* NCs obtained from Cd/Se precursor molar ratios of 4 and 0.25, images not shown). We attribute such polydispersity to the large difference between Cd and Se precursor concentrations, which might enable a high monomer saturation regime during nucleation and first growth stages, promoting further severe Ostwald ripening.²⁸ However, the Cl incorporation can be controlled so as to obtain smaller and highly monodisperse NCs, as it will be demonstrated below.



In order to obtain quantitative surface composition information and to investigate the integration of Cl in the ligand shell XPS analyses have been performed. Since the P 2p and Cl 2p XPS peaks are related exclusively to the NCs ligand shell,²⁷ we calculated the normalized areas Cl/Cd and P/Cd, between elements comprising the ligand shell (Cl or P) and a component of the NC core (Cd). Fig. 2 shows the XPS Cl/Cd and P/Cd normalized areas plotted as a function of the Cd/Se precursor molar ratio in the synthesis. The numeric data concerning the normalized areas studied for each sample are gathered in Table S3,[†] where the Se/Cd and the Cl/P normalized areas have also been included (ESI[†]). It is worth noting that these ratios do not correspond to quantitative concentration values of elements present in the samples but to qualitative amounts of different elements composing the shell relative to a given amount of Cd.

As it can be observed in Fig. 2, the Cl/Cd and P/Cd XPS normalized areas show noticeable variations as a function of the Cd/Se precursor molar ratio. For low Cd/Se values (Cd/Se < 1), low P/Cd and high Cl/Cd values are observed. This trend is the opposite for high Cd/Se values (Cd/Se > 1). In a previous work we proposed that the ligand shell of rod-like CdSe NCs is composed of octadecylphosphonic acid (ODPA) related species (both double deprotonated octadecylphosphonic acid and its anhydrides) whereas incorporation of chlorine as the ligand entails the substitution of ODPA anhydrides and further re-shaping of the initial rods.²⁷

The fact that the Cl/Cd and P/Cd ratios follow opposite trends as a function of the Cd/Se precursor molar ratio supports this mechanism. Based on these results, we observe that the minimum NC chlorine content (as Cl/Cd) necessary to perform the re-shaping from rods to pyramids is around 0.17. The fact that as the Cd/Se precursor molar ratio decreases (1 to 0.25), the Cl/Cd ratio obtained from the XPS data increases (0.17 to 0.22) indicates a more effective Cl incorporation into the ligand shell under excess Se precursor conditions. A tentative ligand distribution has been represented in the schemes of Fig. 2. Our results indicate that while an excess of Cd precursor does not favour the incorporation of Cl into the ligand shell, the excess of

Se precursor does, pointing to different pathways of DCE during the reaction depending on the Cd/Se precursor molar ratio. CdSe NCs synthesized under initial excess Cd conditions are rod-shaped even with the addition of relatively large DCE amounts (see Table S1[†]).

This can be rationalized assuming a reaction between the excess of the Cd complex (Cd(ODPA)₂) and the chlorinated precursor, forming compounds such as CdCl₂, that may modify both nucleation and/or growth processes.^{21,22,24,31} These chlorinated species, however, do not trigger a shape modification of the NCs (see Fig. 1). The reactivity between the Cd-ODPA complex and chlorine is further proved by a series of experiments in which DCE/CdO molar ratios exceeding 1.3 make the Cd precursor unable to react with Se@TOP. This result evidences the ability of DCE to displace ODPA ligands from the Cd complex, which may also lead to partial substitution of ODPA in the complex (*i.e.* Cl-Cd-ODPA). Therefore, under excess Cd precursor conditions, the Cd complex might mainly have evolved to CdCl₂ (not triggering the re-shaping), although a small amount may form Cl-Cd-ODPA complexes. The NCs obtained from the latter complexes are expected to have both ODPA related species and a small amount of Cl in the ligand shell. This could be the case of the low chlorine content found in rod-like CdSe NCs synthesized from Cd/Se precursor molar ratios of 2 and 4 (see ligand distribution schemes in Fig. 2 and numeric data in Table S3, ESI[†]).

In contrast to excess Cd precursor conditions, the incorporation of Cl into the ligand shell under excess Se precursor is clearly favoured. We performed a series of blank experiments to conclude that the reaction between TOP (or TOP@Se) and DCE is responsible for the incorporation of Cl into the NCs ligand shell, triggering the re-shaping of the NCs. As a result of this knowledge, controlled incorporation of chlorine into the ligand shell of CdSe NCs can be obtained at will, either *in situ* or in a two-step process by post-treatments of previously synthesized NCs (see Experimental section).

A representative sample is shown in Fig. 3 where previously synthesized rod-like CdSe NCs have been used to carry out systematic experiments. This two-step synthesis was designed with the double aim of obtaining smaller and highly monodisperse chlorine-containing CdSe NCs and to confirm the possibility to perform the chlorine incorporation over previously synthesized CdSe NCs. Fig. 3a corresponds to the initial 4.3 nm rod-like CdSe NCs used as the starting material and Fig. 3b depicts the TEM images of the CdSe NCs obtained after mixing the starting rod-like CdSe NCs with DCE and TOP (see Experimental section). As evidenced by the images (Fig. 3b), this procedure leads to quasi-monodispersed pyramidal shaped CdSe NCs after 2 hours of reaction. Longer reaction times did not produce observable differences in shape, size or size distribution (images not shown). However, DCE/TOP molar ratios higher than 0.29 point to a severe etching effect (dissolution of NCs after 30 minutes of reaction), driven by a higher concentration of the generated chloride anions, which should be eventually responsible for the NCs dissolution. The absorption and emission properties of the initial rods and pyramids obtained by the two-step procedure are depicted in Fig. 3. An

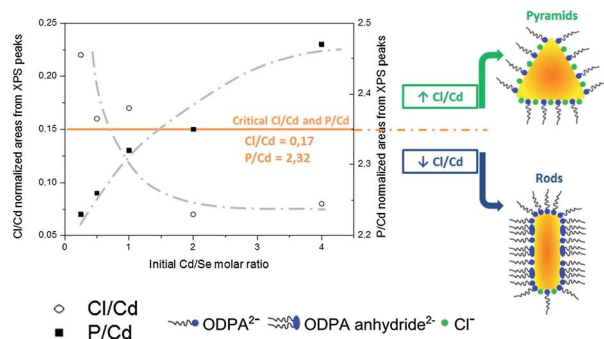
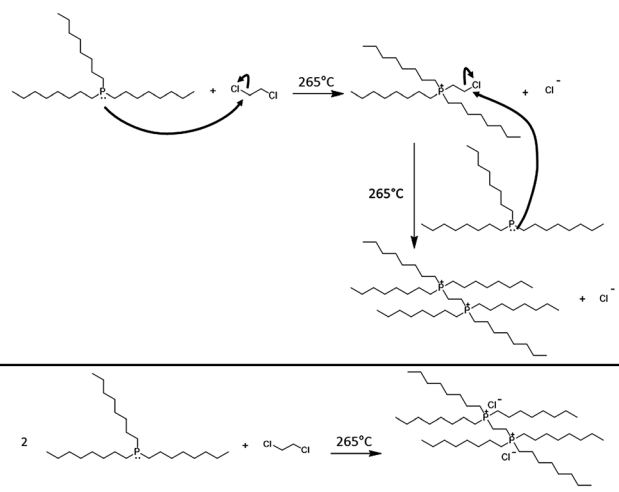


Fig. 2 Cl/Cd (circles) and P/Cd (dark squares) normalized areas calculated from XPS data and plotted versus the Cd/Se precursor molar ratios. The horizontal continuous line indicates the minimum Cl value to promote the re-shaping of rod-like to pyramidal-like NCs. The discontinuous curved lines are only a guide for the eyes. The experimental error associated with the relative peak areas is around 10%.



Fig. 4c shows the ESI-TOF spectrum of the reaction product. The main peak dominating the spectrum is situated at m/z 384.39. This peak can be unambiguously attributed to ethane-1,2-diylbis(trioctylphosphonium)dichloride. This assignment is also supported by the fact that the $M + 1$ and $M + 2$ peaks of ethane-1,2-diylbis(trioctylphosphonium)dichloride are separated by a difference of 0.5, according to a doubly charged product (a zoomed spectrum can be found in the ESI, Fig. S3†). The intensity relations correspond to the abundance of the carbon isotopes. The peaks at 371.38 and 387.37 are assigned to TOP and TOPO, respectively, and correspond to the singly charged species which have peaks of $M + 1$ and $M + 2$ separated by a difference of 1. The presence of unreacted TOP and a small amount of TOPO is also supported by ^1H NMR. The peak in the ESI-TOF spectrum ($m/z = 384.39$, Fig. 4c), together with the disappearance of the DCE peak after mixing with TOP at high temperature (Fig. 4a) evidences the ethane-1,2-diylbis(trioctylphosphonium)dichloride generation. This reaction may occur through a substitutional mechanism, as depicted in Scheme 1. It is clear that the proposed reaction mechanism in Scheme 1 only occurs at relatively high temperatures, since the simple mixing of TOP and DCE at RT does not produce any ^1H NMR peaks different from the ones characterizing the individual species. In order to support the proposed mechanism of reaction between DCE and TOP we employed DFT simulations (B3LYP/TZV). For that, we calculated the enthalpy for the reaction shown in Scheme 1 by subtracting the calculated enthalpy of formation of the products from the ones of the initial reagents. Two molecules of TOP react with one molecule of DCE to form ethane-1,2-diylbis(trioctylphosphonium)dichloride. This results in a reaction enthalpy of -0.88 eV indicating the feasibility of the mentioned reaction.

According to the literature, chloride anion generation could be achieved either by chemical or photochemical routes. Anderson and Owen have reported the possibility to exchange carboxylate ligands with chloride ligands in CdSe NCs by mixing them with chlorotrimethylsilane in Bu_3P solution at RT.¹⁹ In a



Scheme 1 Proposed mechanism for the chloride anions generation as products of the reaction between DCE and TOP at 265 °C.

recent paper by Lim *et al.*²³ the generation of chloride anions is suggested as the main driving force for the anisotropic etching of phosphonic capped CdSe NCs, which is in accordance with our results. However, they did not observe pyramidal shapes, which might be due to the short reaction time in their case. These two studies report on the generation of chloride anions at room temperature. However, as shown in Fig. 4, only at high temperatures the rupture of the DCE molecule is apparent. The role of other halogen-containing sources (*i.e.*, bromine, iodine) in the shape evolution of the NCs has also been recently reported.³²

Conclusions

The addition of a chlorinated solvent (DCE) in the synthesis of CdSe NCs produces different NC sizes and shapes depending on the Cd/Se precursors concentration. While NCs produced under excess Cd precursor conditions show rod-like shape and a comparatively low amount of Cl on their surface, NCs produced under excess Se precursor conditions modify their shape from rods to pyramids containing higher amounts of the halogen on their surfaces. This effect is produced by the presence of chloride anions, released *in situ* upon reaction between TOP and DCE at 265 °C. We propose that this reaction proceeds through the formation of ethane-1,2-diylbis(trioctylphosphonium)dichloride. The chloride anions generation *in situ* allows high versatility to incorporate halogen anions as ligands to a wide range of samples, which may have advantages in solution processed optoelectronics.

Acknowledgements

CP acknowledges financial support from the European Commission under the Seventh Framework Program by means of the grant agreement for the Integrated Infrastructure Initiative N. 262348 European Soft Matter Infrastructure (ESMI). CK and MM acknowledge the Deutsche Forschungsgemeinschaft (DFG) for financial support (KL 1453/5-1). Financial support from the Ministerio de Ciencia e Innovación (FIS2010-18847, FIS2012-33011 and Consolider-Ingenio en Nanociencia Molecular, ref CSD2007-00010), Comunidad de Madrid (grant S2009/MAT-1726) and EU (SMALL, PITN-GA-2009-23884) is gratefully acknowledged. The authors thank Dr Emilio M. Pérez, Alberto de Juan and Alejandro López for fruitful discussions about NMR experiments. JJC acknowledges Fundación Iberdrola for his scholarship.

Notes and references

- 1 R. Debnath, O. Bakr and E. H. Sargent, *Energy Environ. Sci.*, 2011, **4**, 4870–4881.
- 2 B. I. MacDonald, A. Martucci, S. Rubanov, S. E. Watkins, P. Mulvaney and J. J. Jasieniak, *ACS Nano*, 2012, **6**, 5995–6004.
- 3 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706–8715.



- 4 D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase and H. Weller, *Nano Lett.*, 2001, **1**, 207–211.
- 5 L. Liang-shi, J. Hu, W. Yang and A. P. Alivisatos, *Nano Lett.*, 2001, **1**, 349–351.
- 6 J. M. Pietryga, R. D. Schaller, D. Werder, M. H. Stewart, V. I. Klimov and J. A. Hollinsworth, *J. Am. Chem. Soc.*, 2004, **126**, 11752–11753.
- 7 I. Moreels, K. Lambert, D. De Muynck, F. Vanhaecke, D. Poelman, J. C. Martins, G. Allan and Z. Hens, *Chem. Mater.*, 2007, **19**, 6101–6106.
- 8 M. A. Hines and G. D. Scholes, *Adv. Mater.*, 2003, **15**, 1844–1849.
- 9 L. Cademartiri, J. Bertolotti, R. Sapienza, D. S. Wiersma, G. von Freymann and G. Ozin, *J. Phys. Chem. B*, 2006, **110**, 671–673.
- 10 D. V. Talapin, J. S. Lee, M. V. Kovalenko and E. V. Shevchenko, *Chem. Rev.*, 2010, **110**, 389–458.
- 11 J. Tang, K. W. Kemp, S. Hoogland, K. S. Jeong, H. Liu, L. Levina, M. Furukawa, X. Wang, R. Debnath, D. Cha, K. W. Chou, A. Fischer, A. Amassian, J. B. Asbury and E. H. Sargent, *Nat. Mater.*, 2011, **10**, 765–771.
- 12 J. M. Luther, M. Law, Q. Song, C. L. Perkins, M. C. Beard and A. J. Nozik, *ACS Nano*, 2008, **2**, 271–280.
- 13 D. A. R. Barkhouse, A. G. Pattantyus-Abraham, L. Levina and E. H. Sargent, *ACS Nano*, 2008, **2**, 2356–2362.
- 14 D. V. Talapin and C. B. Murray, *Science*, 2005, **310**, 86–89.
- 15 M. Law, J. M. Luther, Q. Song, B. K. Hughes, C. L. Perkins and A. J. Nozik, *J. Am. Chem. Soc.*, 2008, **130**, 5974–5985.
- 16 R. Li, J. Lee, B. Yang, D. N. Horspool, M. Aindow and F. Papadimitrakopoulos, *J. Am. Chem. Soc.*, 2005, **127**, 2524–2532.
- 17 A. H. Ip, S. M. Thon, S. Hoogland, O. Voznyy, D. Zhitomirsky, R. Debnath, L. Levina, L. R. Rollny, G. H. Carey, A. Fischer, K. W. Kemp, I. J. Kramer, Z. Ning, A. J. Labeller, K. W. Chou, A. Amassian and E. H. Sargent, *Nat. Nanotechnol.*, 2012, **7**, 577–582.
- 18 J. S. Owen, J. Park, P. E. Trudeau and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2008, **130**, 12279–12281.
- 19 N. C. Anderson and J. S. Owen, *Chem. Mater.*, 2013, **25**, 69–76.
- 20 W. K. Bae, J. Joo, L. A. Padilha, J. Won, D. C. Lee, Q. Lin, W. K. Koh, H. Luo, V. I. Klimov and J. M. Pietryga, *J. Am. Chem. Soc.*, 2012, **134**, 20160–20168.
- 21 M. R. Kim, K. Miszta, M. Povia, R. Brescia, S. Christodoulou, M. Prato, S. Marras and L. Manna, *ACS Nano*, 2012, **6**, 11088–11096.
- 22 M. Saruyama, M. Kanehara and T. Teranishi, *J. Am. Chem. Soc.*, 2010, **132**, 3280–3282.
- 23 S. J. Lim, W. Kim, S. Jung, J. Seo and S. K. Shin, *Chem. Mater.*, 2011, **23**, 5029–5036.
- 24 S. J. Lim, W. Kim and S. K. Shin, *J. Am. Chem. Soc.*, 2012, **134**, 7576–7579.
- 25 B. H. Juárez, C. Klinke, A. Kornowski and H. Weller, *Nano Lett.*, 2007, **7**, 3564–3568.
- 26 B. H. Juárez, M. Meyns, A. Chanaewa, Y. Cai, C. Klinke and H. Weller, *J. Am. Chem. Soc.*, 2008, **130**, 15282–15284.
- 27 F. Iacono, C. Palencia, L. de la Cueva, M. Meyns, L. Terracciano, A. Vollmer, M. J. de la Mata, C. Klinke, J. M. Gallego, B. H. Juárez and R. Otero, *ACS Nano*, 2013, **7**, 2559–2565.
- 28 Z. Peng and X. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 3343–3353.
- 29 F. Neese, The ORCA program system, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73–79.
- 30 A. Schafer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577.
- 31 L. H. Qu, A. Z. Peng and X. G. Peng, *Nano Lett.*, 2001, **1**, 333–337.
- 32 M. Meyns, F. Iacono, C. Palencia, J. Geweke, M. D. Coderch, U. E. A. Fittschen, J. M. Gallego, R. Otero, B. H. Juárez and C. Klinke, *Chem. Mater.*, 2014, **26**, 1813–1821.

