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Synthesis of CdSe nanoparticles using various organometallic cadmium precursors

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Investigations into replacing Me_2Cd as a common precursor for the synthesis of CdSe nanoparticles by pyrolysis in a hot coordinating solvent have proven that more stable, less volatile or even crystalline organometallic cadmium compounds can be used instead of Me_2Cd. Dineopentylcadmium, bis(3-diethylaminopropyl)cadmium and (2,2′-bipyridine)dimethylcadmium have been used successfully as cadmium sources for the preparation of tri-*n*-octylphosphine oxide (TOPO)-capped CdSe nanoparticles. The resulting nanocrystallites have been characterized by UV–VIS and IR spectroscopy, photoluminescence spectroscopy (PL), mass spectrometry and transmission electron microscopy (TEM). They consist of separated, well defined spherical particles and show a small size distribution as well as a characterisitic blue shift due to quantum confinement in their optical spectra. The replacement of Me_2Cd by less dangerous organometallic precursors thus results in nanocrystallites that show no reduction in quality when compared to the standard method.

Introduction

Without doubt quantum dots have been among the most exciting research topics in recent years, both because of the underlying fundamental theoretical aspects, particularly quantum confinement, and a vast variety of applications.[1–4] CdSe semiconductor nanoparticles represent a particularly well-understood system: their physical and chemical properties have been thoroughly studied along with their synthetic and manufacturing details. Furthermore, possible applications such as in diodes[2] and in biological labeling[3] have emerged. The key issue for manipulations of any kind, however, is the synthesis of sufficient quantities of high quality particles with well-defined properties, *i.e.* high crystallinity, uniform shapes and sizes within the quantum confinement, stability through effective surface passivation and a high degree of monodispersity. A number of synthetic routes have been developed to prepare small particles of CdSe including arrested precipitation,[4] sol–gel processes,[5] gas-phase synthesis,[6] heterocumulene metathesis[7] and the use of organometallic[8,9] or single source precursors.[10,11] Among these, the injection of organometallic cadmium precursors into a hot coordinating solvent provides a simple route to produce particles with the desired properties as mentioned above. Dimethylcadmium (Me_2Cd), a volatile and highly toxic substance, is used almost exclusively as the organometallic cadmium source in the high-temperature procedure. A synthesis of CdSe particles using Me_2Cd has to take place under very controlled conditions for reasons of safety. One possibility to overcome this drawback is the single-source-precursor approach. However, such single source compounds are still not commercially available and their synthesis requires working with very toxic and volatile selenium compounds such as CSe_2. Recently, Peng and Peng described the formation of high-quality CdSe nanocrystals using simply CdO as a precursor,[12] together with hexylphosphonic acid (HPA) or tetradecylphosphonic acid (TDPA), that led to the intermediate formation of a cadmium HPA/TDPA complex. By injection of selenium dissolved in tributylphosphine, this approach yields nearly monodisperse quantum rods and dots. Due to a slow initial nucleation (tens of seconds after the injection) the reaction is not only reproducible, but can be performed at lower temperatures and does not depend on the injection rate (a very critical parameter in the organometallic Me_2Cd approach). Hence, this method based solely on inorganic precursors, meets all criteria for high-quality CdSe nanoparticles. However, systematic studies on altering the cadmium source are still very rare in the literature and there is a clear need for safe and convenient preparative routes to CdSe nanoparticles starting with easily accessible precursors. We herein describe our studies on a selection of oxygen-free organometallic cadmium compounds, *i.e.* dineopentylcadmium, bis(3-diethylaminopropyl)cadmium and (2,2′-bipyridine)dimethylcadmium, as alternative and safer precursors than Me_2Cd for the preparation of CdSe semiconductor nanocrystallites by thermolysis in hot tri-*n*-octylphosphine oxide (TOPO).

Experimental

Chemicals

$CdCl_2$ (Sigma), selenium (Merck), tri-*n*-octylphosphine oxide (TOPO, 90%) (Aldrich), tri-*n*-butylphosphine (95%) (Acros), 2,2′-bipyridyl (Fluka) and MeMgI (3 M in diethyl ether) (Fluka) were commercially available and used without further purification.

$(CH_3)_3CCH_2MgBr$ and $[Et_2N(CH_2)_3]Li$ were prepared using standard procedures. Dimethylcadmium and (2,2′-bipyridine)-dimethylcadmium were prepared according to the method described by Foster and Cole-Hamilton.[13]

The solvents used for preparation were distilled, deoxygenated under an argon flow and stored over molecular sieve (type 4 Å) before use.

UV–VIS and IR spectroscopy

A Perkin Elmer Lambda 9 UV/VIS/NIR spectrophotometer was used to carry out the optical measurements. Samples were dissolved in toluene and were placed in special optical glass cuvettes (1 cm path length). The optical measurements were referenced against toluene. The band edges of the different samples were determined by extrapolation after performing a

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linear regression on the absorption band edge data. Infrared spectra were recorded as pressed KBr-discs on a Perkin Elmer FT-IR spectrometer 1720 X.

Photoluminescence spectroscopy

A Fluoro Max-2 instrument with a continuous ozone-free xenon lamp (150 W) and a R928P photomultiplier tube as a detector was used to measure the photoluminescence of the particles. The slits were set to 2.5 nm and the integration time was 1 s. Toluene solutions of the samples were placed in special optical glass cuvettes (1 cm path length). The excitation wavelength was 350 nm.

Mass spectrometry

A VG Instruments AutoSpec was used to carry out the FAB MS. The matrix for the powder samples was *m*-nitrobenzylalcohol.

Electron microscopy

A Hitachi H-8100 scanning and transmission electron microscope operating at accelerating voltages up to 200 kV with a single crystal LaB_6 filament was used for the TEM studies. X-Ray energy-dispersive spectra (EDS) were obtained from an attached EDX analysis system (Oxford Link with Si(Li) crystal and ultrathin window ATW 2). The specimens were prepared by placing a drop of a dilute solution of a sample in toluene on a carbon-coated copper grid and allowing to dry at room temperature.

Syntheses

Dineopentylcadmium. A suspension of $CdCl_2$ (1.68 g, 9.16 mmol) in Et_2O (20 mL) was stirred vigorously and a solution of $(CH_3)_3CCH_2MgBr$ (21 mL, 1.08 M in Et_2O) was added dropwise. After stirring for 14 h at room temperature the solution was removed from the precipitate using a cannula and the Et_2O was removed *in vacuo*. The remaining solid was sublimed and 1.5 g (64%) of dineopentylcadmium was obtained as a crystalline white, air-sensitive, light-stable solid. Analytical data were in agreement with the literature.[14,15]

Bis(3-diethylaminopropyl)cadmium[16]. A suspension of $CdCl_2$ (0.54 g, 2.95 mmol) in Et_2O (25 mL) was stirred vigorously and a solution of 3-(diethylamino)propyllithium (0.71 g, 5.86 mmol) in Et_2O (25 mL) was added dropwise. After heating to reflux for 5 h and stirring overnight at ambient temperature the solution was removed from the precipitate using a cannula. Distillation (turbomolecular pump) yielded 0.76 g (76%) of a colorless oil.

^1H NMR (C_6D_6): δ 0.52 (t, 2H, $CdCH_2$), 0.89 (t, 6H, NCH_2CH_3), 2.03 (m, 2H, $CdCH_2CH_2$), 2.25 (m, 2H, CH_2NEt_2), 2.37 (q, 4H, NCH_2CH_3). ^{13}C NMR (C_6D_6): δ 11.1 (s, NCH_2CH_3), 12.5 (s, $CdCH_2$), 27.3 (s, $CdCH_2CH_2$), 46.6 (s, NCH_2CH_3), 57.9 (s, CH_2NEt_2).

Method for the preparation of quantum dots

Tri-*n*-octylphosphine oxide (TOPO, 4 g) was dried and degassed by heating to about 200 °C *in vacuo*. The temperature was then stabilized at 350 °C under about 1 atm of argon. 0.2 mL of a solution of selenium (0.4 g, 5 mmol) in tri-*n*-butylphosphine (10 g) was combined with 0.2 mL of a solution of the cadmium precursor (7 mmol) in tri-*n*-butylphosphine (10 g) and quickly injected into the rapidly stirring, hot TOPO solution. The temperature was lowered due to the injection and the reaction mixture kept at 315 °C for 10 min. After cooling to room temperature an excess of dry methanol (*ca.* 20 mL) was added to precipitate the nanocrystals. The particles were washed several times with methanol using ultrasound and then redissolved in toluene.

Results and discussion

CdSe nanoparticles were prepared by modification of a method initially investigated by Bawendi and coworkers.[8] Four different cadmium sources were subjected to the above mentioned procedure: dimethylcadmium (Me_2Cd), dineopentylcadmium (Np_2Cd), bis(3-diethylaminopropyl)cadmium ($(RN)_2Cd$) and (2,2′-bipyridine)dimethylcadmium (BipyCd). Dimethylcadmium represents the standard organometallic cadmium precursor. The colorless liquid is thermally unstable depositing cadmium metal within minutes when exposed to daylight, it fumes upon exposure to air and decomposes in water. While not pyrophoric, it is highly toxic and detonates spontaneously at temperatures above 90 °C. Dineopentylcadmium is a similar alkylcadmium compound, but offers various advantages over dimethylcadmium. The neopentyl group is known to stabilize metal alkyl complexes by preventing a β-elimination reaction: dineopentylcadmium is a crystalline, waxy, white solid with a melting point of 40 °C *cf.* −4.5 °C for Me_2Cd. It decomposes only slowly at elevated temperatures (>90 °C), can be distilled without decomposition (50 °C at 10^{-2} Torr) and is less volatile than dimethylcadmium (3 Torr at 52 °C compared to 78 Torr for Me_2Cd). Thus, the thermal and photolytic stability is improved which facilitates storage, handling and safety precautions. Another possibility to chemically stabilize the cadmium source is *via* intramolecular adduct formation as in bis(3-diethylaminopropyl)cadmium. This type of alkyl ligand is often used for organometallic precursors suitable for deposition of thin films and epitaxial layers of metals or semiconductors in MOCVD because it leads to less sensitive and more easily manageable compounds which also provide good leaving groups. Bis(3-diethylaminopropyl)cadmium, in contrast to liquid Me_2Cd, is a colorless oil with low volatility. It can be distilled without decomposition but it is less stable to heat and light than dineopentylcadmium. Finally, the Lewis base adduct (2,2′-bipyridine)dimethylcadmium is a crystalline and non-pyrophoric solid (mp 75–78 °C) in sharp contrast to Me_2Cd. It is still very air-sensitive as indicated by a color change from orange to white within minutes on contact with air. However, compared to the other cadmium sources, the solid exhibits the lowest volatility in the series and is therefore the compound of choice with respect to manageability and safety. Tri-*n*-butylphosphine selenide (TBPSe) was used as the selenium source throughout the whole work. The ratio of selenium to cadmium to tributylphosphine was kept constant. Since the injection temperature, growth temperature and growth time strongly influence the size, as well as the size distribution of the nanocrystallites, they were closely monitored and also kept constant. The red precipitates obtained after the addition of methanol were centrifugated from the solvent and washed several times. Depending on the analytical technique, the particles were then either dried *in vacuo* or redispersed in toluene, to investigate their structural and optical behavior. The samples were labeled according to the precursors employed, *i.e.* Me_2Cd-CdSe, Np_2Cd-CdSe, RN_2Cd-CdSe and BipyCd-CdSe, respectively.

Optical properties

The electronic situation in bulk semiconductors can be described in terms of valence and conductivity bands and a gap between these bands. However, as the particles become smaller, the wavelength of the electrons is closer to the range of the particle sizes and the laws of classical physics (continuous bands of extended solids) have to be substituted by quantum mechanical rules (discrete electronic levels as in molecules). The consequence is a larger band gap for quantum confined semiconductors compared to that of the bulk material and hence a blue shift in the absorption spectra. Conversely, it is possible to determine the "optical band gap" (E_g) from absorption spectra by fitting the absorption edge data to a direct transition process and to estimate the particle size using a simple model based on the geometry of the semiconductor sphere *via* eqn. (1):[17]

$$\Delta E_g = \frac{h^2}{8a^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) \qquad (1)$$

The absorption spectra of the CdSe nanocrystallite samples are shown in Fig. 1. All absorptions are shifted from the 1.74 eV (713 nm) bulk band gap clearly showing the effect of quantum confinement. The band edges of the different samples (and the corresponding absorption maxima) are as follows: 617 nm/2.01 eV (560 nm) for Me_2Cd-CdSe, 624 nm/1.99 eV (568 nm) for Np_2Cd-CdSe, 602 nm/2.06 eV (545 nm) for RN_2Cd-CdSe and 621 nm/2.00 eV (567 nm) for BipyCd-CdSe. The estimated particle sizes using eqn. (1) are 3.7 nm (Me_2Cd-CdSe), 3.9 nm (Np_2Cd-CdSe), 3.4 nm (RN_2Cd-CdSe) and 3.8 nm (BipyCd-CdSe).[18] Hence all of the selected cadmium precursors provide nanosized CdSe particles. It can be seen that the blue shift differs slightly for the different samples. If one takes into account that it is very difficult to keep all relevant parameters exactly constant, and that the variation in sample preparation may alter the wavelength of the absorption by a few nanometers, the results show that the size regime of CdSe nanocrystallites is very likely independent of the cadmium source. In a series of preparations using dimethylcadmium under practically the same conditions we observed an erratic deviation in the UV–VIS absorption maximum of 5%. In the series of the different cadmium sources reported here the observed deviation is only 2.5%. Moreover, the absorption width is similar for all four spectra indicating a similar size distribution.

Fig. 2 shows the photoluminescence spectra of the CdSe particles at room temperature. The peak of the emission is shifted by about 30 nm towards the red of the absorption maximum due to the size distribution and its width is equal to that observed for the absorption band.

Surface properties

The synthesis of nanoparticles requires a coordinating solvent that chemically passivates the semiconductor surface and stabilizes the resulting crystallites with respect to aggregation. The dispersions can, for example, be stabilized by the lyophilic coat of alkyl groups stemming from TOPO. Upon the complexation of a ligand the corresponding bond will show a shift in its IR spectra providing an indication of the surface composition.

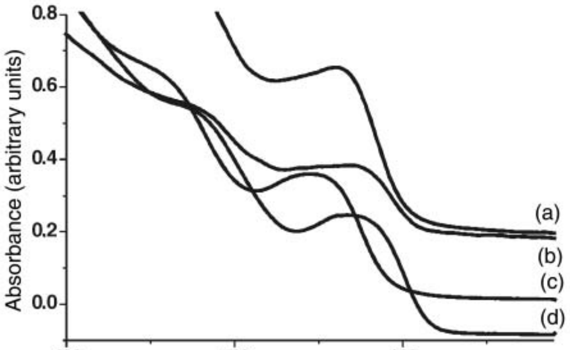

Fig. 1 UV–VIS spectra of different solutions of nanoparticles: (a) Me_2Cd-CdSe, (b) Np_2Cd-CdSe, (c) $(RN)_2Cd$-CdSe and (d) BipyCd-CdSe.

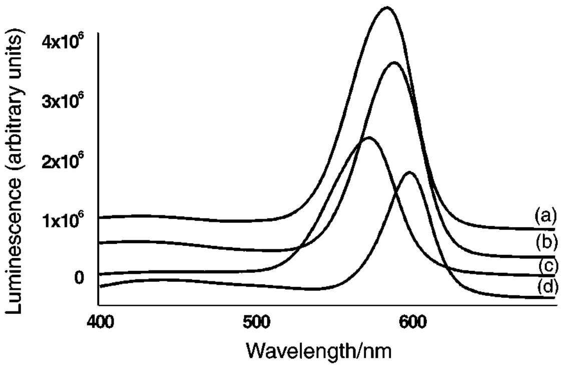

Fig. 2 Luminescence spectra of different solutions of nanoparticles: (a) Me_2Cd-CdSe, (b) Np_2Cd-CdSe, (c) $(RN)_2Cd$-CdSe and (d) BipyCd-CdSe.

All IR spectra (Fig. 3) exhibit the same peaks both in terms of wavenumber and relative intensity. The P–O-stretch of TOPO is shifted to lower wavenumbers compared to that of free TOPO and proves the anchoring of TOPO to the surface of the nanocrystals. No aromatic C–H-stretch is observed when BipyCd is used as the cadmium precursor, indicating that Bipy is not present on the surface. These data indicate that the surface of the CdSe nanoparticles obtained from different cadmium precursors are very similar and consists mainly of TOPO (especially BipyCd). This result is further confirmed by mass spectrometry: the FAB spectrum of all nanoparticles shows a peak for TOPO but no peaks for 2,2′-bipyridine or diethylpropylamine.

Transmission electron microscopy

TEM allows the direct imaging of nanoparticles and provides more information on the quality of individual particles, *e.g.*, their size, size distribution, shape and, for crystalline samples at high magnification, lattice parameters.

The TEM images of the nanoparticles (Fig. 4) further illustrate the similarity of the four samples. Particles were found to be uniform in size and size distribution with a mean diameter of approximately 4 nm. This is in good agreement with the calculated particle sizes using the experimental data derived from UV–VIS absorption spectroscopy and eqn. (1). Despite the simple underlying model, the agreement with experimental observations is surprisingly good suggesting a facile alternative for the estimation of the particle size. Imaging at high magnification (see insets of Fig. 4(a)–(d)) shows clear lattice fringes for each sample corresponding to the (100) or

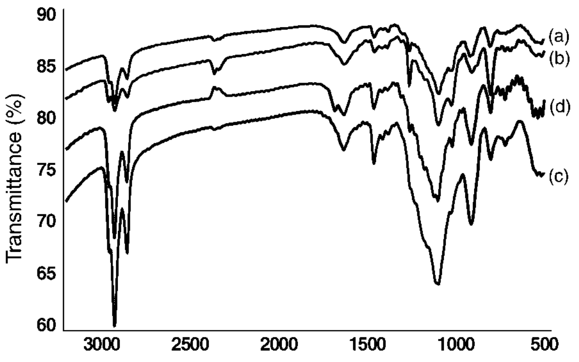

Fig. 3 IR spectra of different nanoparticle samples dispersed in KBr: (a) Me_2Cd-CdSe, (b) Np_2Cd-CdSe, (c) $(RN)_2Cd$-CdSe and (d) BipyCd-CdSe.

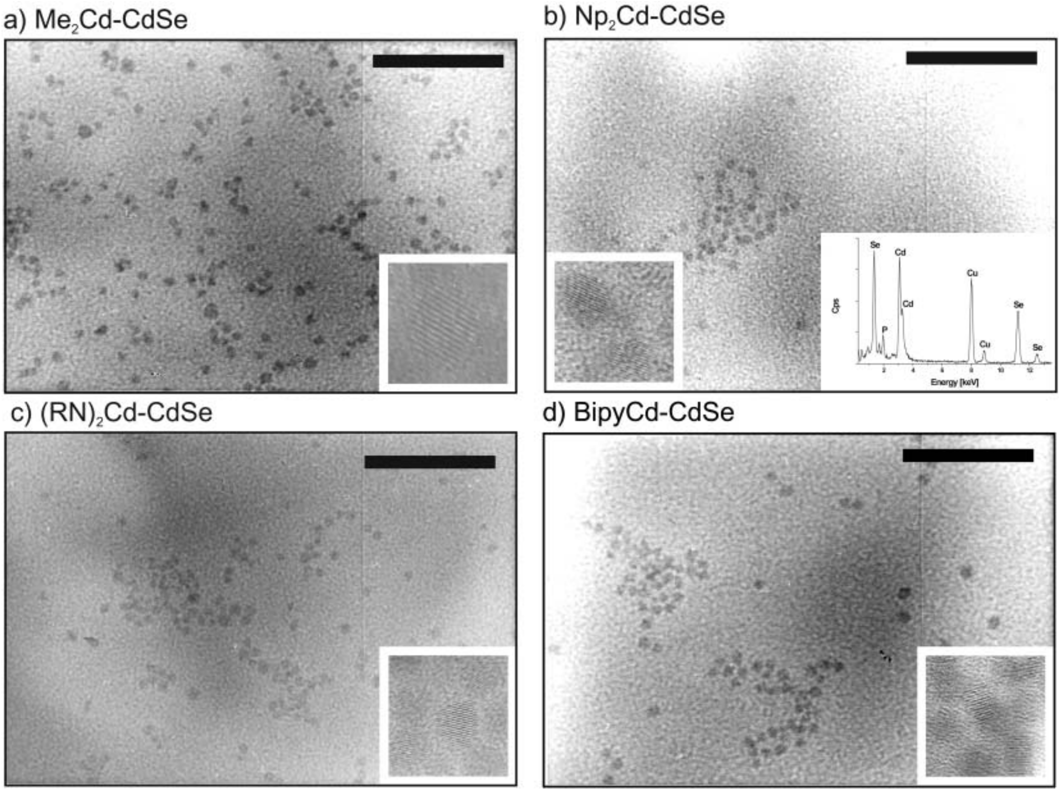

Fig. 4 TEM images of different solutions of nanoparticles: (a) Me_2Cd-CdSe (inset 8.2 nm^2), (b) Np_2Cd-CdSe (inset 14.8 nm^2), (c) $(RN)_2Cd$-CdSe (inset 16.6 nm^2) and (d) BipyCd-CdSe (inset 12.1 nm^2). Bar = 56 nm.

(002) lattice planes of the hexagonal phase of CdSe. An EDX analysis performed on the nanoparticles results in a spectrum with peaks for Cd and Se, confirming that each precursor used indeed produces CdSe nanocrystallites (see inset of Fig. 4(b)). Additional peaks for P, O, Cu and C have been detected, stemming from tri-*n*-octylphosphine oxide on the surface of the particles and the support grid..

From studies on CdTe organometallic vapor-phase epitaxy (OMVPE) using dimethylcadmium and dimethyltelluride it is known that thin film deposition occurs by a free-radical mechanism involving surface reactions that lead to alkyl radicals in the gas phase.[19] If no surface is available, the thermal decomposition of the vapor is believed to be homogeneous as well as heterogeneous giving several products including cadmium metal, alkanes (methane, ethane) and alkenes (ethylene).[20] Since the Cd–C bond dissociation energy D_0 for dimethylcadmium is only 281 kJ mol^{-1} [21] it is very likely that the first reaction step after the injection of the precursor into TOPO at $T = 350$ °C is the rupture of the Cd–C bonds. The precursors we used as substitutes for Me_2Cd all have Cd–C bonds, some with additional ligands that coordinate *via* nitrogen atoms (the Cd–N bond is weaker than the Cd–C bond, *e.g.*, 144 kJ mol^{-1} in $Cd[(NSiMe_3)_2]$[22]). The weakness of the Cd–C bonds leads to the expected independence of the reaction on the choice of precursor and demonstrates that it is possible to avoid the use of the dangerous and toxic dimethylcadmium without loss in quality.

Conclusions

We have demonstrated that Me_2Cd, the most common cadmium source in the synthesis of CdSe semiconductor nanocrystallites through colloidal chemistry, can be successfully substituted by other organometallic precursors without loss in quality of the observed TOPO capped CdSe nanoparticles. We have used three compounds, dineopentylcadmium, bis(3-diethylaminopropyl)cadmium and (2,2′-bipyridine)dimethylcadmium, to elaborate on their potential as substitutes for Me_2Cd and observed no change in the size of the particles or their size distribution and surface coverage. The advantage lies in being able to work with less toxic, more stable and crystalline cadmium precursors. In particular, the BipyCd-source (2,2′-bipyridine)dimethylcadmium is easily accessible and is the suggested substitute for the dangerous Me_2Cd.

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18 Parameters of eqn. (1): ΔE_g is the bandgap shift, a is the particle size and m_e and m_h are the effective electron and hole mass, respectively; $m_h = 0.13m_0$, $m_h = 0.44m_0$ (data from bulk CdSe), where $m_0 = 9.1095 \times 10^{-31}$ kg is the electron rest mass
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