Improved photovoltaic performances by post-deposition acidic treatments on tetrapod shaped colloidal nanocrystal solids

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Abstract
The ligand exchange reaction with pyridine is the standard procedure for the integration of colloidal semiconductor nanocrystals (NCs) in photovoltaic devices; however, for large sized and irregularly shaped branched NCs, such as CdSe@CdTe tetrapods, this procedure can lead to a considerable waste of materials and the aggregation of NCs in the colloidal solution, therefore resulting in the formation of an inhomogeneous film and low device performances. Here, we report on alternative post-deposition treatments with carboxylic acids on films of CdSe@CdTe tetrapod shaped NCs. This approach guarantees the removal of the insulating surfactant, necessary to obtain good charge transport among NCs, while preserving the film integrity. We perform a complete characterization of the nanocrystalline films treated with different carboxylic acids and demonstrate the successful integration of such films in photovoltaic devices, showing a doubled efficiency with respect to the standard ligand exchange procedure. Our approach represents a general route towards the development of NC based devices with improved performances and minimized waste of material.

1. Introduction
Nanocrystal (NC) solids are considered to have a great potential as prospective materials for photovoltaic and photodetector applications [1–4]. The tunable and broad band absorption and the possibility to prepare NC films by means of low cost solution processing methods have motivated numerous studies on photovoltaic devices made by colloidal nanorods [5, 6], hyperbranched NCs [7–9] and tetrapods [10–13]. In these reports it has been demonstrated that the elongated or branched shape provides a more extended active area for charge separation and, in principle, could lead to efficient charge transport [14]. Despite all the advantages, the integration of such materials in photovoltaic devices is challenging because colloidal NCs typically possess electrically insulating ligand shells that must be shortened or removed to convert nanocrystalline solids from insulators to conductors. The common approach to improve the electronic coupling between adjacent NCs is to replace the long hydrocarbon chains with smaller molecules such as pyridine, a short and weakly coordinating ligand which was demonstrated to be effective in the case of CdSe nanorods [15]. However, even if the surfactant exchange with pyridine is widely used for the fabrication of photovoltaic cells, it can have negative...
effects in the case of NCs with a large size and an irregular shape, such as CdSe@CdTe tetrapods. In particular, branched structures coated with pyridine tend to aggregate in solution, thus resulting in inhomogeneous films [16, 17]. Moreover, the ligand exchange is a time consuming procedure which involves a considerable waste of material.

Recently several approaches, alternative to ligand exchange, based on post-deposition chemical treatments on lead salt quantum dots have been developed. The exposure of NC films to a dilute solution of hydrazine has been exploited to improve the conductivity of PbSe colloidal quantum dots [18–22]. This approach has been proven effective for the fabrication of both photovoltaic devices [23, 24] and transistors [18]. An alternative method consists of the use of ethanedithiol [25, 26], benzenedithiol [27–30] or mercaptotripropionic acid [31] used as bidentate ligands to exchange the original insulating ligands and cross link PbS or PbSe nanodots after thin film deposition. Metal chalcogenide and atomic ligands have also been exploited to enhance electronic transport and to passivate surface defects in nanocrystal solids [32, 33].

Despite the extensive work on photovoltaic devices based on branched CdSe and CdTe NCs, there are no reports on post-deposition treatments of such materials. In this work, we explore the possibility to use dilute carboxylic acid solutions on heterostructured CdSe@CdTe tetrapods to achieve effective inter-particle charge transfer and to improve the photovoltaic performance of tetrapod based solar cells. The type II energy level alignment at the CdSe/CdTe interface ensures an efficient charge separation in solar cells. The type II energy level alignment at the CdSe/CdTe interface ensures an efficient charge separation in solar cells. The CdSe/CdTe interface ensures an efficient charge separation in solar cells.

2. Experiment

2.1. Synthesis of tetrapod shaped colloidal NCs

All the reagents and chemicals for the synthesis of colloidal NCs, trioctylphosphine oxide (TOPO, 99%), triocetylphosphine (TOP, 97%), cadmium stearate (90%), tellurium (Te 99.999%), and selenium (Se 99.99%), were purchased from Strem Chemicals. Octadecylphosphonic acid (ODPA) and hexylphosphonic acid (HPA) were purchased from Polycarbon Industries. Cadmium oxide (CdO, 99.5%), pyridine (Py, >99%), acetic acid (99.7 + %), and 1.0 M hydrazine anhydrous solution in tetrahydrofuran were purchased from Sigma-Aldrich. All solvents used were anhydrous, and they were purchased from Sigma-Aldrich, and used as received without further purification.

The synthesis of colloidal CdSe/CdTe tetrapods was carried out in a standard Schlenk line setup under a nitrogen flow, and all following reactions and manipulations were carried out under nitrogen in a glove box. The synthesis of the CdSe@CdTe tetrapods was carried out via a seeded growth approach following a previously reported procedure as follows [35]. A solution was prepared which contained Te in TOP (Te/TOP, 0.6 g total weight, 10 wt% in Te) and previously synthesized spherical CdSe NCs (~2–3 nm in diameter) having a sphalerite structure. This solution was injected into a reaction flask containing a mixture of surfactants (TOPO, HPA, and ODPA) and CdO heated at 340°C. After the injection, the resulting solution was kept at 340°C for 3 min, after which it was cooled to room temperature. This solution was then washed by repeated precipitation (via the addition of methanol) and re-dissolution in toluene. After the last washing step, the tetrapods were dissolved in 5 ml of anhydrous toluene.

2.2. Surfactant exchange with pyridine

A batch of as-synthesized tetrapods precipitated by methanol was mixed with 2 ml of pyridine. The mixture was refluxed at 120°C under stirring for 24 h to allow the exchange of the surfactants on the tetrapod surface. The NCs were then precipitated with hexane, separated from supernatant by centrifugation and were re-dispersed in a mixture of chloroform and pyridine (the chloroform/pyridine volume ratio was equal to 9:1).

2.3. Preparation and characterization of NC solids

Films of tetrapods were deposited by spin-coating the solution of the as-synthesized nanoparticles capped with phosphonic acid onto ITO–glass substrates coated with 30 nm PEDOT:PSS. The reference sample was deposited under the same conditions starting from NCs that first underwent a surfactant exchange procedure with pyridine. For the post-deposition treatments, the film prepared with tetrapods capped with phosphonic acid was immersed in a 1 M solution of hydrazine, acetic, trifluoroacetic or formic acid in anhydrous methanol. The samples were soaked for 10 min, then rinsed with methanol, and annealed at 120°C for 10 min on a hot plate. The deposition and immersion was repeated twice to obtain a crack free film. The morphological inspection of all the samples was carried out by a Veeco Nanoscope V atomic force microscope (AFM). The high resolution scanning electron microscopy (SEM)
measurements were performed with a SEM–FEG microscope FEI NOVA NanoSEM 200. Images were typically acquired at an accelerating voltage of 10 kV.

Infrared spectroscopy measurements (FTIR) in the 4000–1000 cm\(^{-1}\) spectral range were carried out on tetrapod samples deposited on silicon substrates using a Jasco FT/IR 6300 spectrophotometer in transmission mode at a resolution of 4 cm\(^{-1}\). For the FTIR measurements the samples were prepared either by spin-coating following the former procedure, or by drop-casting to obtain a thicker sample and a stronger signal.

For the transport measurements, films of NCs were deposited by spin-coating onto silicon substrates patterned by standard photolithography and lift off procedures. To evaluate the resistivity, TLM patterns were employed consisting of similar gold electrodes with increasing separation (from 5 to 20 \(\mu\)m). After the spin-coating deposition of CdSe@CdTe tetrapods on such samples, the films were treated with dilute solutions of hydrazine, acetic, trifluoroacetic, or formic acid.

2.4. Fabrication and characterization of solar cells

The photovoltaic devices were fabricated in a bi-layer geometry with the following structure ITO/PEDOT:PSS/CdSe@CdTe tetrapods/C60/Al. For the reference device, a highly concentrated solution of pyridine-exchanged CdSe@CdTe tetrapods was deposited by spin-coating onto ITO–glass substrates coated with 30 nm PEDOT:PSS. For the fabrication of post-deposition treated devices, as-synthesized CdSe@CdTe tetrapods were employed and deposited using a similar procedure, but the NC films were then soaked with dilute solutions of hydrazine, acetic, trifluoroacetic, or formic acid, repeating this procedure twice in order to form a uniform CdSe@CdTe film. All the NC films (pyridine standard and treated with acids) then underwent a gentle annealing at 150 °C for 20 min on a hot plate in a nitrogen glove box without exposing the samples to air. Finally, a 30 nm thick layer of C60 was deposited on the CdSe@CdTe films, followed by a 130 nm Al cathode by thermal evaporation. All processing steps, except for the PEDOT:PSS deposition, were performed in a glove box under nitrogen atmosphere.

The device performances were evaluated under simulated AM 1.5G illumination set to 100 mW cm\(^{-2}\) using a Spectra Physics Oriel 150W Solar Simulator. The integrated intensity was set to 100 mW cm\(^{-2}\) using a thermopile radiant power meter (Spectra Physics Oriel, model 70260) with a fused-silica window. The current density–voltage (J–V) characteristics were measured using a Keithley 2400 source-measure unit. All the measurements were performed on encapsulated devices, sealed using a glass lid attached by a bead of UV-cured epoxy resin. The photon to current efficiency (IPCE) was measured by using a 300 W Xe arc light source coupled to a monochromator to create the scanning light. A dual channel Merlin lock-in amplifier was utilized for the sensitive optical power and current measurements.

3. Results and discussion

3.1. TEM and morphology characterization of tetrapods

In hybrid organic colloidal NC devices, the presence of long chain organic surfactants severely reduces the transfer of charge between adjacent NCs or NCs and organic species. As a consequence, the efficient integration of colloidal NCs in organic solar cells relies on the ability to remove their long chain insulting ligands to ensure good charge transport in the device [36]. In this respect, the ligand exchange with pyridine is a standard procedure for the preparation of colloidal NCs for organic photovoltaic devices. Pyridine is a weak-binding Lewis base with a relatively low boiling point (116 °C), and is often chosen with the aim of facile removal [15]. However, as a result of the weakly coordinating character, colloidal NCs treated with pyridine are very unstable and tend to form aggregates and precipitate in solutions [37]. This effect can be observed in figure 1, where we report two transmission electron microscopy (TEM) images of tetrapod shaped NCs as-synthesized and after pyridine treatment. It can be readily observed that the sample treated with pyridine shows a considerable aggregation whereas well defined tetrapod nanostructures can be easily recognized in the as-synthesized sample.

In order to assess how tetrapod aggregation and film morphology affect the photovoltaic performances of devices, we perform AFM studies on films prepared by spin-coating.
the tetrapod shaped NCs on a glass/ITO/PEDOT:PSS substrate. In figure 2 we compare topography images of NCs from an as-synthesized colloidal solution, after pyridine exchange and after post-deposition treatments with hydrazine, acetic, trifluoroacetic and formic acid, respectively. The film made from the as-synthesized tetrapods (figure 2(a)) exhibits a homogeneous morphology, with a roughness of about 4 nm; while clusters and agglomerates can be observed when pyridine-exchanged tetrapods are employed (figure 2(b)). Then, in the case of hydrazine treated films (figure 2(c)), still larger aggregates with a size of hundreds of nanometers are visible, suggesting that this treatment considerably damages the NC film. This is in accordance with previously reported data, which demonstrated that the exposure of a colloidal solution of CdSe@CdTe tetrapods to hydrazine induces a severe etching of their surface [13]. AFM images are also acquired on carboxylic acid treated samples (figures 2(d)–(f)). It is worth noting that a branched motif can be observed in the untreated sample (figure 2(a)) due to the presence of organic surfactants, whereas this morphology cannot be distinguished on the samples treated with carboxylic acids (figures 2(d)–(f)). Differences in the morphology can also be attributed to a film shrinkage due to a reduced distance between NCs caused by the removal of the surfactant [18, 34].

In order to verify that the NC structure is preserved after the post-deposition treatments, we have also performed SEM characterization. SEM images show clearly that tetrapods have retained their original shape after post-deposition treatments with carboxylic acids (figures 3(d)–(f)), while after pyridine exchange (figure 2(b)) and hydrazine (figure 2(c)) treatment NCs seem partially fused into bigger aggregates.

3.2. FTIR, transport and optical absorption measurements on NC films

To further clarify the impact of acetic, trifluoroacetic and formic acid treatments on CdSe@CdTe NC solids, we perform Fourier transform infrared (FTIR) spectroscopy experiments. For comparison untreated, after pyridine exchange and hydrazine treated nanocrystalline films are measured. The loss of phosphonic surfactant is monitored though the characteristic absorption bands in the IR spectrum at 2929 and 2857 cm$^{-1}$, which are ascribed to the antisymmetric and symmetric C–H stretching vibrations, respectively, of the –CH$_2$– groups of the hydrocarbon moiety. In figure 4(a) we report the FTIR spectra of the different samples prepared by drop-casting tetrapods on silicon substrates. The samples treated with hydrazine are all left overnight in a dilute solution of hydrazine in methanol; despite the prolonged treatments the FTIR spectra show the presence of intense C–H peaks, which attest that this treatment is not sufficient to remove the surface ligand. According to a previous study, the tips of the tetrapod arms, compared with other regions of the tetrapods surface, have a higher reactivity under various chemical treatments, which leads to a preferential removal of surfactants from these regions [13]; most probably the hydrazine treatment in our sample removes and partially etches the surface of the tips, leading to an incomplete removal of the surfactant and damage of the NC...
The broad band above 3000 cm$^{-1}$ can be attributed to NH$_2$ stretching bands (3100–3400 cm$^{-1}$) and is an indication that hydrazine adsorbs molecularly onto the nanocrystalline film during the treatment [22]. The FTIR spectra of the film treated with hydrazine was monitored during 24 h, for instance after 10 min and 12 h (data not shown), but we could not observe differences among the spectra in the time course. From this observation, we can conclude that even the prolonged soaking with hydrazine does not lead to an effective removal of the surfactant. On the other hand, the C–H peaks are absent in the acid treated samples. All these data indicate that the treatments with carboxylic acids successfully remove the insulating surfactant. Thus, this is expected to result in a reduced distance between the NCs and an improved conductivity. To provide direct evidence of this effect, we carry out transport measurements on films of untreated tetrapods and on films treated with acetic, trifluoroacetic and formic acid. Specifically, films of NCs are deposited by spin-coating onto silicon substrates patterned by standard photolithography and lift off procedures in order to fabricate TLM patterns consisting of similar gold electrodes with increasing separation (from 5 to 20 µm). The resistivity of each film is then evaluated from the plot of the resistance as a function of the electrode distance. As shown in figure 3(b), the untreated film clearly exhibits the higher resistivity ($10.1 \times 10^5$ Ω cm$^{-1}$), which decreases in the films treated with acetic acid ($8.7 \times 10^5$ Ω cm$^{-1}$), trifluoroacetic acid ($8.0 \times 10^5$ Ω cm$^{-1}$) and formic acid ($6.0 \times 10^5$ Ω cm$^{-1}$). To allow a better comparison of the resistivity values (extrapolated from the slope), the contact resistance (corresponding to the intercept) was removed in figure 4(b).

An effect of treatments on the states confined in the NCs is also observed. Figure 4(c) shows the absorption spectra of CdSe@CdTe tetrapod solids, untreated, after pyridine exchange, and treated with hydrazine and with different acids. It can be observed that the spectra of the NC thin film after carboxylic acidic treatments still show the excitonic features (peak at ~720 nm); therefore, the tetrapods are still distinct and the nanocrystalline structure is preserved. On the contrary, the sample treated with hydrazine shows an evident broadening of the first exciton peak that, along with a more pronounced blue shift, can be attributed, according to previous reports, to a more severe etching of the NC surface [38] and to a possible reshape of the tetrapods caused by the exposure to the aggressive hydrazine chemical [22, 39].

### 3.3. Tetrapod based solar cells

To test the photovoltaic properties of the acid treated tetrapod films, we fabricate and characterize a device structure consisting of a NC layer sandwiched between an ITO/PEDOT:PSS anode and a C60 electron acceptor/transport layer; an aluminum cathode completes the device stack (inset of figure 5(a)). After light absorption and exciton formation, the charge separation can occur either at the interface between CdSe@CdTe tetrapods and C60 (which act respectively as electron donor and acceptor) or in the tetrapod heterostructure, where the electrons can be trapped in the CdSe core and holes in the CdTe arms; thus, electrons segregate in the CdSe...
Figure 4. (a) FTIR spectra of tetrapod films on silicon substrates. The spectra refer to the samples treated overnight with hydrazine, after pyridine exchange and to the samples treated for 10 min with different carboxylic acids; as a reference, the FTIR spectrum of the as-prepared sample (no treatments) is also reported. (b) Plot of the measured resistance as a function of the electrode distance. The resistivity can be evaluated from the slope. (c) Comparison between the absorption spectra of NC solids untreated, after pyridine exchange, and treated with hydrazine and different carboxylic acids. Both the FTIR and UV–vis spectra are shifted vertically for clarity and the contact resistance is removed in the resistance plots to allow an easy comparison of the sample resistivities (related to the slope).

cores in contact with C60, due to its strong electron acceptor character, and can be extracted. Upon the charge separation, the electrons and holes diffuse through the aluminum cathode and the ITO anode respectively.

Figure 5 shows the current density–voltage ($J$–$V$) characteristics under dark and illuminated conditions for devices fabricated with treated and untreated NC films. The corresponding photovoltaic performances are listed in Table 1.

The results indicate that post-deposition treatments with carboxylic acids improve both the electrical and photovoltaic characteristics. In particular we measure an almost doubled short current density ($J_{sc}$) in the case of treatment with acetic and trifluoroacetic acids compared to devices prepared using the standard pyridine exchange procedure. The $J_{sc}$ is also improved for devices treated with formic acid. On the other hand, the device made from the as-synthesized tetrapods shows a very low short circuit current ($J_{sc} = 0.09$ mA cm$^{-2}$).
and power conversion efficiency ($\eta = 0.01\%$) as expected. A very low power conversion efficiency, $\eta = 0.07\%$, is also measured for devices made from NC films treated with hydrazine, most likely due to the very bad morphology of the tetrapod layer (figure 2(c)). The best performing devices are fabricated by means of post-deposition treatments with acetic and trifluoroacetic acids, which show a power conversion efficiency (PCE) of $\eta = 0.58\%$ and $\eta = 0.51\%$, respectively.

The series resistance, evaluated by fitting of dark current curves for the positive bias region, is $R_s = 87.5 \times 10^3 \, \Omega \, \text{cm}^{-2}$ for the untreated device, $R_s = 4.6 \times 10^3 \, \Omega \, \text{cm}^{-2}$ for the device treated with hydrazine, $R_s = 1.3 \times 10^3 \, \Omega \, \text{cm}^{-2}$ for the device made from tetrapods with pyridine exchange, and $R_s = 1.2 \times 10^3 \, \Omega \, \text{cm}^{-2}$, $R_s = 1.9 \times 10^3 \, \Omega \, \text{cm}^{-2}$, and $R_s = 0.6 \times 10^3 \, \Omega \, \text{cm}^{-2}$ for devices treated with acetic, trifluoroacetic and formic acids respectively. The series resistance of a photovoltaic device arises from the resistance of the cell materials to the current flow, and consequently the lower series resistances for the cells made by post-deposition acidic treatments denote an improvement in the transport properties of the treated tetrapod films.

The differences in PCE between the diverse acidic treatments can be ascribed to differences in the active layer morphology. As a matter of fact, smaller grains are present in the sample treated with acetic or trifluoroacetic acid (figures 2(d) and (e)), while larger grains can be observed for the sample treated with formic acid (figure 2(f)). The root mean squared (rms roughness) is 2.91 nm for the acetic acid, 2.88 nm for the trifluoroacetic acid, and 2.28 nm for the formic acid treated NC solids. The higher roughness of the acetic and trifluoroacetic acid treated films offers a larger interface between tetrapods and C60, and consequently the effective area for charge separation is bigger; this is reflected in a higher PCE for the device made with tetrapods treated with acetic or trifluoroacetic acid. Indeed, in the film treated with formic acid the average size of the grains is larger and consequently, regardless of the smaller series resistance, the device prepared with such a film shows a lower PCE.

In order to verify that the photocurrent is generated by the CdSe/CdTe tetrapods, incident photon to current efficiency (IPCE) measurements are performed on the devices made by post-deposition treatments with carboxylic acids (figure 6). The IPCE profile closely follows the absorption spectrum of the tetrapods, demonstrating that the spectral response is dominated by the nanocrystal contribution.

Considering the results on device performances and nanocrystalline film morphology, it appears that less aggressive chemical treatments are effectively improving the charge transport across multiple tetrapods and hence creating pathways for carriers, without apparent disruption of the chemical structure of the NCs and of the other components of the device. More aggressive treatments with hydrazine appear instead to be detrimental for the performance of the photovoltaic devices.

4. Conclusions

In summary, we investigate the impact of post-deposition treatments with different carboxylic acids to improve the performance of NC based photovoltaic devices. We demonstrate that the treatments with acetic and trifluoroacetic acids on CdSe@CdTe tetrapod solids lead to a doubled photovoltaic performance when compared to the standard pyridine exchange procedure. Through a complete characterization of the treated NC solids (FTIR spectroscopy, AFM inspection and transport measurements) we prove that the improved photovoltaic performance can be attributed to a complete removal of the insulting organic ligand from the NC surface, which results in better electronic coupling, and to an optimized morphology. Moreover, we show that a device based on a tetrapod film treated with hydrazine shows a tremendous drop in the power conversion efficiency, which is attributed to damage of the film and to an incomplete removal of the insulting organic ligand.

Finally, our strategy can be considered as an effective alternative route to the standard ligand exchange procedure, which involves a considerable waste of materials. The carboxylic acids gently and effectively remove the insulating surfactant while preserving the nanocrystalline structure of the CdSe@CdTe tetrapods. Our method can be generalized and applied to disparate NC based electronic and optoelectronic devices.

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References

[1] Nozik A J 2002 Physica E 14 115–20
[2] Gledhill S E, Scott B and Gregg B A 2005 J. Mater. Res. 20 3167–79
[3] Milliron D J, Gur I and Alivisatos A P 2005 MRS Bull. 30 41–4
[4] Hillhouse H W and Bread M C 2009 Curr. Opin. Colloid Interface Sci. 14 245–59
[5] Huynh W, Dittmer J J and Alivisatos A P 2002 Science 295 2425–7
[6] Gur I, Fromer N A, Geier M L and Alivisatos A P 2005 J. Mater. Res. 20 3167–79
[7] Milliron D J, Gur I and Alivisatos A P 2005 MRS Bull. 30 41–4
[8] Huynh W, Dittmer J J and Alivisatos A P 2002 Science 295 2425–7
[9] Sun B Q, Dittmer J J, Libby W C, Whiting G L, Whiting G L and Alivisatos A P 2003 Adv. Funct. Mater. 13 73–9
[10] Zhou Y F, Eck M and Kruger M 2010 Energy Environ. Sci. 3 1851–64
[11] Talapin D V and Murray C B 2005 Science 310 86–9
[12] Murphy J E, Beard M C and Nozik A J 2006 J. Phys. Chem. B 110 25455–61
[13] Luther J M, Beard M C, Song Q, Law M, Ellingson R J and Nozik A J 2007 Nano Lett. 7 1779–84
[14] Williams K J, Tisdale W A, Leschkes K S, Haungstad G, Norris D J, Aydil E S and Zhu Y Y 2009 ACS Nano 3 1532–8
[15] Law M, Luther J M, Song O, Hughes B K, Perkins C L and Nozik A J 2008 J. Am. Chem. Soc. 130 5974–85
[16] Leschkes K S, Beatty T J, Kang M S, Norris D J and Aydil E S 2009 ACS Nano 3 3638–48
[17] Kim S J, Kim W J, Cartwright A N and Prasad P N 2008 Appl. Phys. Lett. 92 191107
[18] Tang J, Wang X H, Brzozowski L, Barkhouse D A R, Debnath R, Levina L and Sargent E H 2010 Adv. Mater. 22 1399–402
[19] Luther J M, Law M, Beard M C, Song Q, Reese M O, Ellingson R J and Nozik A J 2008 Nano Lett. 8 3488–92
[20] Tsang S W, Fu H, Wang R, Lu J, Yu K and Tao Y 2009 Appl. Phys. Lett. 95 183505
[21] Zhou Y F, Fu H, Wang R, Lu J, Yu K and Tao Y 2009 Appl. Phys. Lett. 95 183505
[22] Zhou Y F, Eck M and Kruger M 2010 Energy Environ. Sci. 3 1851–64
[23] Talapin D V, Scheele M and Talapin D V 2009 Science 324 1417–20
[24] Tang J et al 2011 Nature Mater. 10 765–71
[25] Zarghami M H, Liu Y, Gibbs M, Gebremichael E, Webster C and Law M 2010 ACS Nano 4 2475–85
[26] Fiore A et al 2009 J. Am. Chem. Soc. 131 2274–82
[27] Lee J-S, Kovalenko M V, Huang J, Chung D S and Talapin D V 2011 Nature Nanotechnol. 6 348–52
[28] Radychev N, Lokteva I, Witt F, Kolny-Olesiak J, Borchert H and Parisi J 2011 J. Phys. Chem. C 115 14111–22
[29] Talapin D V, Rogach A L, Kornowski A, Haase M and Weller H 2001 Nano Lett. 1 207–11
[30] Vercelli B, Zotti G and Berlin A 2011 J. Phys. Chem. C 115 4476–82