

# Heterogeneous deposition of noble metals on semiconductor nanoparticles in organic or aqueous solvents†

Jun Yang,<sup>a</sup> Larissa Levina,<sup>b</sup> Edward H. Sargent<sup>b</sup> and Shana O. Kelley\*<sup>a</sup>

Received 25th August 2006, Accepted 14th September 2006

First published as an Advance Article on the web 27th September 2006

DOI: 10.1039/b612255h

We describe a versatile approach for synthesizing heterogeneous semiconductor/noble metal nanostructures both in organic and in aqueous solvent at room temperature. The deposition is based on the preferential nucleation and growth of noble metals (Au, Ag) at a single nucleation site on semiconductor (PbS) nanocrystals. The synthesis of multifunctional heterogeneous nanostructures of PbS–Au and PbS–Ag was demonstrated. The self-assembly of the heterogeneous structures into ordered arrays was observed by transmission electron microscopy (TEM), which may lead to semiconductor–metal nanostructures with potential for self-assembly, geometric complexity, and multifunctionality. Also, the successful deposition of Au on PbS in the aqueous phase may find use in biological applications.

An important frontier in nanocrystal synthesis is the incorporation of different materials within the same nanostructure as a means of increasing functionality.<sup>1–10</sup> A combination of materials of particular interest consists of noble metals and semiconductors contained within the same nanocrystal, with noble metal tips providing anchor points for electrical connections and for self-assembly.<sup>2,11</sup> However, the selective growth of noble metals on semiconductors remains a challenge, and the generation of heterostructures featuring extended order and hierarchy is particularly important.

Recently, the growth of gold tips on the apexes of semiconductor rods (CdSe) was reported, forming ‘nano-dumbbells’ (NDBs).<sup>2</sup> The architecture of these nanostructures is qualitatively similar to bi-functional molecules such as dithiols that provide two-sided chemical connectivity. Methods also exist to grow a gold tip on one side of CdSe dots and rods; for these structures, the mechanism of growth was explained using the process of Ostwald ripening.<sup>11</sup> Importantly, the limited examples of noble metal growth on semiconductor nanostructures involve growth within organic solvents, and thus produce materials not suitable for biological application.

In this work, we present a simple approach that enables noble metal (Au, Ag) deposition on PbS nanoparticles in organic and aqueous environments at room temperature. This method involves the synthesis of PbS nanoparticles in the organic phase and a series of phase-transfer processes (from toluene to water for PbS

nanoparticles and from water to toluene for noble metal precursors). Given the general utility of transferring metal precursors from water to toluene, this method provides an opportunity to systematically investigate the deposition of a variety of noble metals on semiconductor nanoparticles. We selected PbS as the target semiconductor because of its wide application in solar cell construction<sup>12–14</sup> and because it can easily be produced in controlled shapes and sizes.<sup>15–22</sup> The self-assembly of the resulting heterogeneous nanostructures into ordered arrays on TEM grids was also demonstrated in this work.

To generate the semiconductor portion of our heterostructures, PbS nanoparticles were synthesized by a previously reported method,<sup>17</sup> in which oleic acid was used as stabilizer. These nanocrystals are soluble in toluene. A method was also developed to transfer PbS nanoparticles from toluene to water for the deposition of Au in the aqueous phase. Briefly, mercaptopropionic acid (MPA) and dimethylaminopyridine (DMAP) were used to replace oleic acid from starting PbS nanoparticles to make them dispersible in water. (See the ESI for detailed descriptions of experimental protocols.†) The phase transfer of metal (Au, Ag) precursors from water to toluene relies on a method mediated by ethanol and an amine.<sup>23,24</sup> All of the depositions were carried out with a fixed 1 : 1.25 molar ratio of noble metal–PbS semiconductor. Other ratios did not yield optimal deposition.

Fig. 1 shows the representative TEM images and energy dispersive X-ray analysis (EDX) spectra of PbS nanocrystals and the PbS–Au heterogeneous nanostructures prepared in toluene. The TEM image under low magnification (Fig. 1a) shows that the PbS nanocrystals were spherical with an average diameter of approximately 5 nm. The high resolution TEM (HRTEM) images (Fig. 1b) shows clear and perfect crystal lattices throughout the entire crystal, indicating that the nanocrystals were single-crystalline.

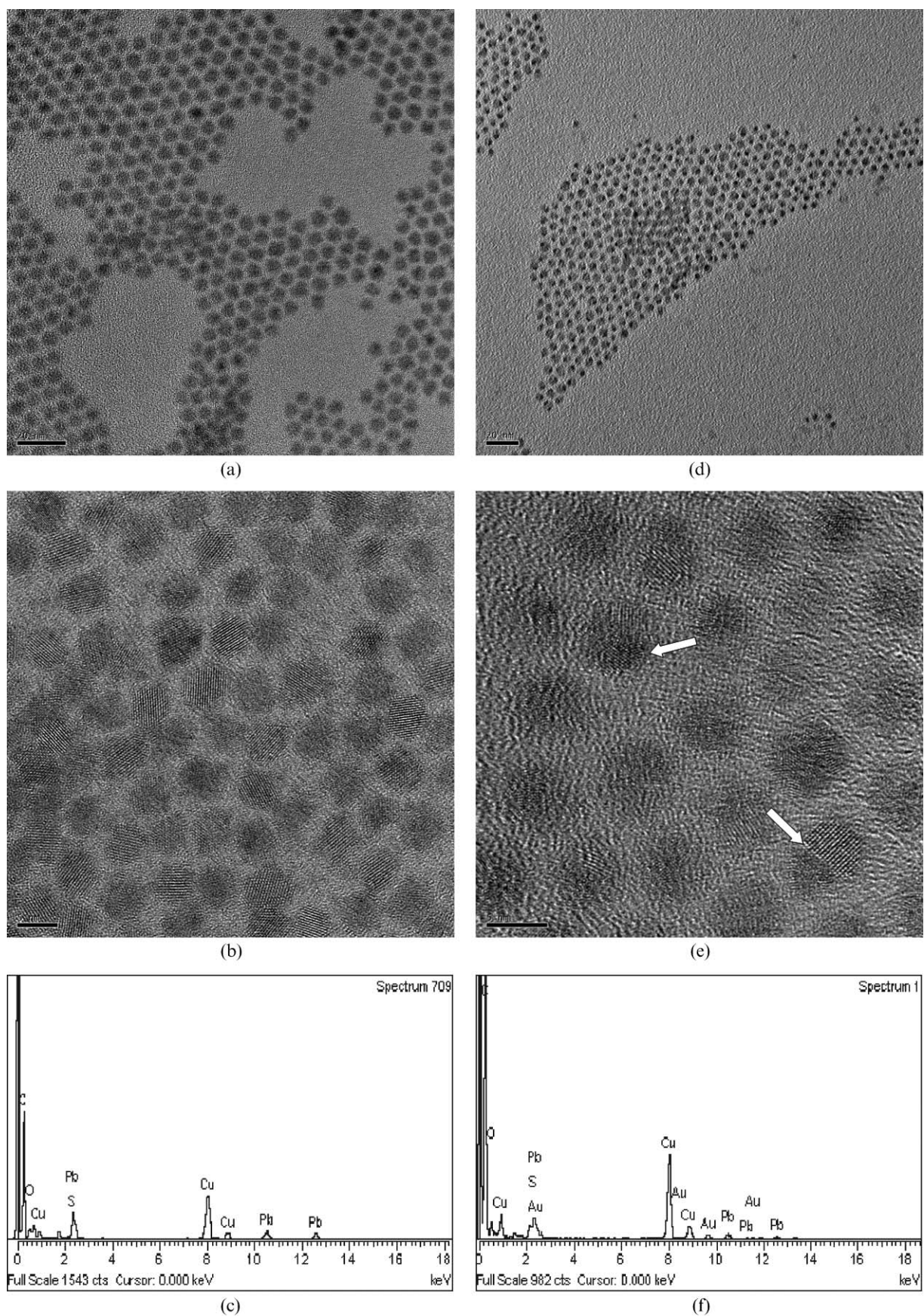
After aging the mixture of PbS and HAuCl<sub>4</sub> in toluene for 3 h in the presence of dodecylamine, uniform PbS–Au heterogeneous nanostructures were the dominant product, as shown in Fig. 1d. Isolated gold nanocrystals were not observed. This result indicates that gold nucleates preferentially on the existing PbS nanoparticles (rather than homogeneously) under the experimental conditions used here. It is noteworthy that in the absence of PbS nanoparticles, the reduction of HAuCl<sub>4</sub> by dodecylamine needs several days, showing that the presence of a semiconductor can catalyze this reduction process. Since gold has strong imaging contrast, the heterogeneous PbS–Au composites could be easily identified. It is interesting to note that gold is deposited only at a single site on each PbS nanocrystal. The diameter of the deposited gold structures was about 2 nm. EDX analysis (Fig. 1f) confirms that the nanostructure was composed of PbS and Au. The

<sup>a</sup>Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts, 02467, USA. E-mail: shana.kelley@bc.edu;

Fax: +1 (1)617 552 2705; Tel: +1 (1)617 552 3121

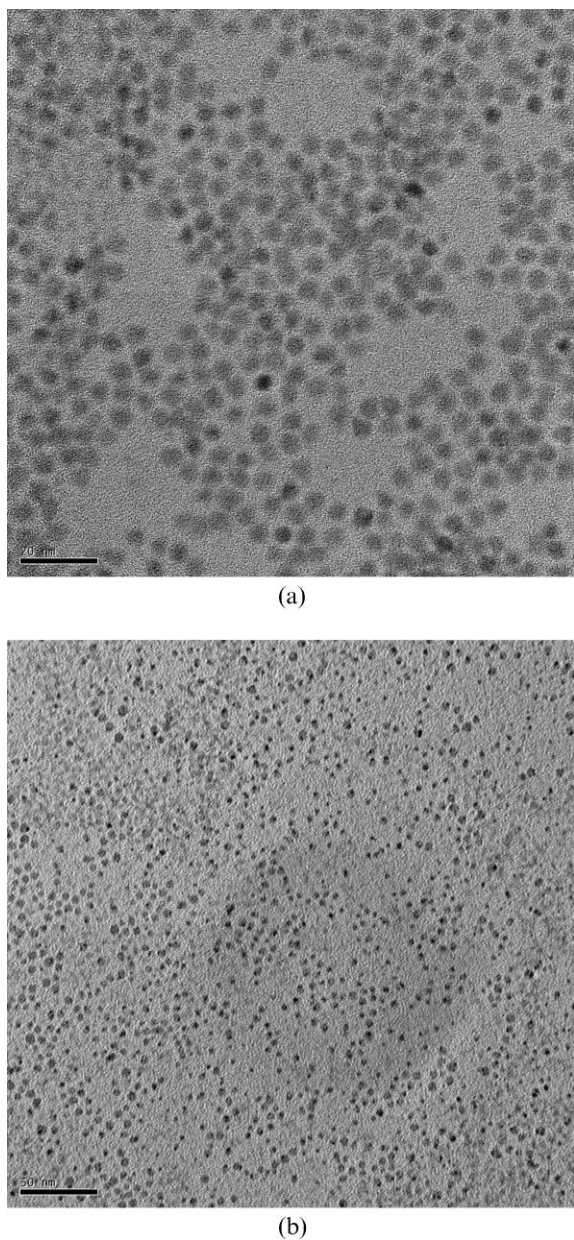
<sup>b</sup>Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Canada M5S 3G4

† Electronic supplementary information (ESI) available: Experimental protocols. See DOI: 10.1039/b612255h

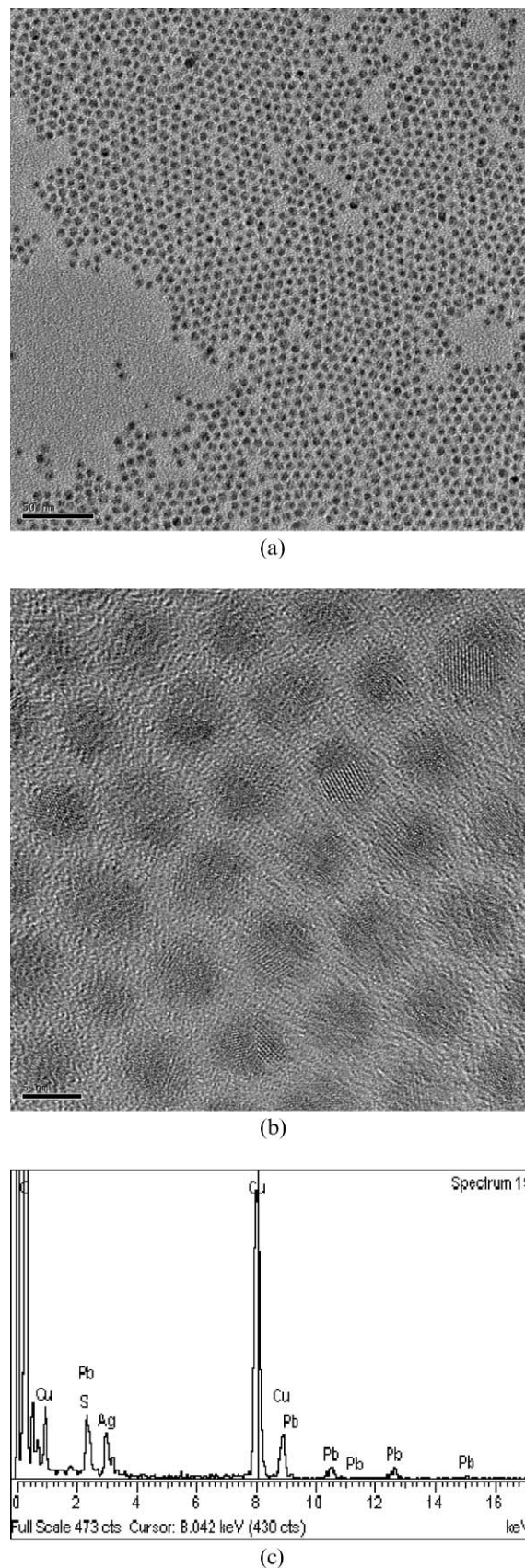


**Fig. 1** (a) TEM image, (b) HRTEM image and (c) EDX spectrum of the PbS nanoparticles before metal deposition; and (d) TEM image, (e) HRTEM image, and (f) EDX spectrum of PbS-Au heterostructures.

crystalline nature of PbS and Au were also confirmed by the HRTEM image shown in Fig. 1d (several particles with clear lattice contrast are indicated using red arrows). The lattice fringes were identified as the (200) crystal planes of PbS and the (111) crystal planes of Au. However, these crystal planes of gold were not parallel to those of PbS in each heterogeneous nanostructure, and the angles between them varied from one nanocrystal to the next, indicating that the growth of gold took place in different orientations. This result is similar to previous observations of the CdSe–Au nanostructure,<sup>2</sup> but is different from the recent report of a peanut-shaped PbS–Au nanostructure where the (200) crystal planes of PbS were parallel to the (111) crystal planes of gold.<sup>25</sup> This indicates that there was no epitaxial growth between the (200) planes of PbS and the (111) planes of Au.



**Fig. 2** (a) TEM image of PbS nanoparticles transferred from toluene and (b) PbS–Au heterogeneous nanostructures in the aqueous phase.



**Fig. 3** (a) TEM image, (b) HRTEM image and (c) EDX spectrum of PbS–Ag heterogeneous nanostructures prepared in toluene.

The final morphology of the heterostructured particles depends on whether the surface of substrate particles allows only a single nucleation site or multiple ones.<sup>25</sup> Our results here showed that only a single site on the PbS nanoparticle surface facilitated the nucleation of gold clusters. The mechanism responsible for the observed morphology formation may be broadly similar to that of Au-Fe<sub>3</sub>O<sub>4</sub> hybrid nanoparticles.<sup>7</sup> Upon nucleation of Au on the PbS surface, electron density from the PbS nanoparticle is drawn to the polar PbS/Au interface. Free electrons in the PbS nanoparticle may also catalyze the Au nucleation, which eventually grow to form dots on PbS surface.

This heterogeneous deposition of Au on PbS nanoparticles can also be performed in aqueous phase. In the presence of MPA, DMAP and NaBH<sub>4</sub> (necessary because a weak reducing agent such as citrate ions cannot effectively reduce HAuCl<sub>4</sub> at room temperature), phase transfer and gold deposition is achieved. Fig. 2 shows the TEM images of the starting PbS nanoparticles transferred from toluene into water using the MPA/DMAP-mediated method and the resulting PbS–Au heterogeneous nanostructures. As indicated, after transfer from toluene to water, no change in particle size and distribution of PbS nanoparticles was observed. The deposition of Au on PbS in water also results in the formation of PbS–Au heterogeneous nanostructures. The size and shape of PbS–Au were similar to those formed in toluene, as shown in Fig. 2b and Fig. 1d. The results here can provide the opportunity for the heterogeneous PbS–Au nanostructures to be used in biological systems because of their water solubility.

Hydrophobic metal, semiconductor or metal oxide nanoparticle colloids can form ordered superlattice structures on substrates or at interfaces due to pinning effects and entropy-driven ordering that occurs upon solvent evaporation.<sup>26–30</sup> However, for water-soluble nanoparticles, because this solvent has a slow evaporation rate, large-scale area assembly with ordered features is typically hard to obtain. Here, the PbS–Au heterogeneous nanostructures dispersed in toluene generated a local superlattice on a TEM copper grid after solvent evaporation, as shown in Fig. 1d. Although the sizes and shapes of the nanoparticles are preserved in water, the ordered structure is not maintained (Fig. 2b).

We experimentally found that in addition to AuCl<sub>4</sub><sup>–</sup>, other metal ions including Ag<sup>+</sup>, Rh<sup>3+</sup>, PtCl<sub>6</sub><sup>2–</sup>, Ru<sup>3+</sup>, Ni<sup>2+</sup>, Pd<sup>2+</sup>, Ir<sup>4+</sup> and Os<sup>3+</sup> could also be transferred from water to toluene using the ethanol mediated method we mentioned in the ESI.† For example, we deposited Ag on PbS nanoparticles in organic solution. The experimental conditions for depositing Ag on PbS was similar to those used to depositing Au. The only difference was the reaction time, which was 6 h for silver. Fig. 3 shows the TEM image and EDX spectrum of the PbS–Ag heterogeneous nanostructures. The heterogeneous nanostructures and self-assembly into ordered arrays were again observed. The lattice contrast between silver and PbS could be seen clearly at the HRTEM image in Fig. 3b. The similarity of these results with those obtained with PbS–Au nanostructures supports the idea that there is only a single nucleation site on the PbS nanoparticles used in this work for the deposition of noble metals.

In summary, we have demonstrated a versatile approach for synthesizing semiconductor–noble metal heterogeneous

nanostructures with different materials combinations both in organic and in aqueous solvents. The self-assembly of the heterogeneous structures into ordered arrays was also observed, which may lead to the use of heterogeneous semiconductor nanoparticles in applications that require self assembly. Also, the successful deposition of Au on PbS in aqueous phase may find use in biological systems.

## Notes and references

- 1 D. V. Talapin, R. Koeppel, S. Goetzinger, A. Kornowski, J. M. Lupton, A. L. Rogach, O. Benson, J. Feldmann and H. Weller, *Nano Lett.*, 2003, **3**, 1677.
- 2 T. Mokari, E. Rothenberg, I. Popov, R. Costi and U. Banin, *Science*, 2004, **304**, 1787.
- 3 C. Paholski, A. Kornowski and H. Weller, *Angew. Chem., Int. Ed.*, 2004, **43**, 4774.
- 4 D. J. Milliron, S. M. Hughes, Y. Cui, L. Manna, J. Li, L.-W. Wang and A. P. Alivisatos, *Nature*, 2004, **430**, 190.
- 5 S. Kudara, L. Carbone, M. F. Casula, R. Cingolani, A. Falqui, E. Snoeck, W. J. Parak and L. Manna, *Nano Lett.*, 2005, **5**, 445.
- 6 T. Teranishi, Y. Inoue, M. Nakaya, Y. Oumi and T. Sano, *J. Am. Chem. Soc.*, 2004, **126**, 9914.
- 7 H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. Sun, *Nano Lett.*, 2005, **5**, 379.
- 8 Y. Li, Q. Zhang, A. V. Nurmikko and S. Sun, *Nano Lett.*, 2005, **5**, 1689.
- 9 H. Gu, R. Zheng, Z. Zhang and B. Xu, *J. Am. Chem. Soc.*, 2004, **126**, 5664.
- 10 C. Sanchez, B. Lebeau, F. Chaput and J. P. Boilot, *Adv. Mater.*, 2003, **15**, 1969.
- 11 T. Mokari, C. G. Sztrum, A. Salant, E. Rabani and U. Banin, *Nat. Mater.*, 2005, **4**, 855.
- 12 S. A. McDonald, P. W. Cyr, L. Levina and E. H. Sargent, *Nat. Mater.*, 2005, **4**, 138.
- 13 A. Maria, P. W. Cyr, E. J. D. Klem, L. Levina and E. H. Sargent, *Appl. Phys. Lett.*, 2005, **87**, 1.
- 14 S. Hoogland, V. Sukhovatkin, I. Howard, S. Cauchi, L. Levina and E. H. Sargent, *Opt. Express*, 2006, **14**, 3273.
- 15 S. M. Lee, Y. W. Jun, S. N. Cho and J. Cheon, *J. Am. Chem. Soc.*, 2002, **124**, 11244.
- 16 J. Joo, H. B. Na, T. Yu, J. H. Yu, Y. W. Kim, F. Wu, J. Z. Zhang and T. Hyeon, *J. Am. Chem. Soc.*, 2003, **125**, 11100.
- 17 M. A. Hines and G. D. Scholes, *Adv. Mater.*, 2003, **15**, 1844.
- 18 L. Levina, V. Sukhovatkin, I. Howard, S. Cauchi, R. Nisman, D. P. Bazett-Jones and E. H. Sargent, *Adv. Mater.*, 2005, **17**, 1854.
- 19 X. Fang and L. Zhang, *J. Mater. Sci. Technol.*, 2006, **22**, 1.
- 20 L. Xu, W. Zhang, Y. Ding, W. Yu, J. Xing, F. Li and Y. Qian, *J. Cryst. Growth*, 2004, **273**, 213.
- 21 X. Fang, C. Ye, L. Zhang, Y. Wang and Y. Wu, *Adv. Funct. Mater.*, 2005, **15**, 63.
- 22 H. Zhang, B. Chen, B. Gilbert and J. F. Banfield, *J. Mater. Chem.*, 2006, **16**, 249.
- 23 J. Yang, J. Y. Lee, T. C. Deivaraj and H. P. Too, *Colloids Surf., A*, 2004, **240**, 131.
- 24 J. Yang, J. Y. Lee, H. P. Too and S. Valiyaveetil, *J. Phys. Chem. B*, 2006, **110**, 125.
- 25 W. Shi, H. Zeng, Y. Sahoo, T. Y. Ohulchanskyy, Y. Ding, Z. L. Wang, M. Swihart and P. N. Prasad, *Nano Lett.*, 2006, **6**, 875.
- 26 C. B. Murray, C. R. Kagan and M. G. Bawendi, *Science*, 1997, **270**, 1335.
- 27 C. J. Kiely, J. Fink, M. Brust, D. Bethell and D. J. Schiffrin, *Nature*, 1998, **396**, 444.
- 28 L. Motte, E. Lacaze, M. Maillard and M. P. Pileni, *Langmuir*, 2000, **16**, 3803.
- 29 J. M. Petroski, T. C. Green and M. A. El-Sayed, *J. Phys. Chem. A*, 2001, **105**, 5542.
- 30 V. Santhanam, J. Liu, R. Agarwal and R. P. Andres, *Langmuir*, 2003, **19**, 7881.