

# Synthesis of cerium/cobalt phosphate nanostructures in catanionic reverse micelles

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Nanofilaments/nanorods of cerium phosphate or cobalt phosphate are produced by reaction of aqueous hexadecyltrimethylammonium phosphate [(CTA)<sub>3</sub>PO<sub>4</sub>] micelles with either [Ce(AOT)<sub>3</sub>] or [Co(AOT)<sub>2</sub>] reverse micelles prepared in isooctane. The nanostructures are hydrophobic, highly uniform in width (4–5 nm) and variable in length (up to 1200 nm). Whereas the particle width is constrained by the size of the catanionic reverse micelles, changes in the reaction conditions such as the concentration of the surfactant salts and [Ce(AOT)<sub>3</sub>]/[(CTA)<sub>3</sub>PO<sub>4</sub>] molar ratio, markedly influence the length of the inorganic nanostructures. The CePO<sub>4</sub> nanofilaments are crystalline and morphologically invariant with regard to changes in the reaction conditions, whereas the Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> nanorods are amorphous and more sensitive to modifications in the surfactant salt molar ratio. The results are consistent with a mechanism based on the slow uni-directional aggregation/crystallization of nanoscale surfactant-coated inorganic building blocks.

## Introduction

The synthesis of high aspect ratio inorganic nanostructures is an important and emerging field in various aspects of materials science. Anisometric small-scale structures exhibit novel properties that often differ from the bulk state, and therefore should be of technological value in numerous applications.<sup>1–3</sup> Although there are well established high temperature routes to many types of high aspect ratio nanostructures, more economic and environmentally benign approaches are of immediate consideration. In this regard, the use of complex fluids as organized reaction media for controlled inorganic nucleation and growth appears to be a promising approach. A number of different anisometric nanostructures have been prepared in reverse micelles and microemulsions,<sup>4,5</sup> and in most cases this involves a single amphiphilic component usually in the form of either a cationic or anionic long chain surfactant. In contrast, very limited work has been done using complex fluids prepared in the presence of both cationic and anionic surfactants. Lisiecki *et al.* synthesized copper nanoparticles in water-in-oil microemulsions prepared using sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT), and added cetyltrimethylammonium chloride (CTAC) to control the size of the crystals.<sup>6</sup> In similar studies, hexadecyltrimethylammonium bromide (CTAB) was added to AOT microemulsions to increase the stability of silver halide nanoparticles.<sup>7</sup> Recently, a few studies on the synthesis of high aspect ratio nanostructures using water-in-oil microemulsions prepared from combinations of two surfactants have been reported. For example, Simmons *et al.* described the synthesis of highly acicular cadmium sulfide particles obtained from a water-in-oil microemulsion containing an equimolar mixture of anionic

AOT and the zwitterionic lipid, lecithin.<sup>8</sup> In other work, Qi *et al.* prepared BaWO<sub>4</sub> nanowires<sup>9</sup> and hierarchical superstructures consisting of BaCrO<sub>4</sub> nanobelts<sup>10</sup> using catanionic reverse micelles prepared from water, decane, and an equimolar mixture of anionic (undecylic acid) and cationic (decylamine) surfactants.

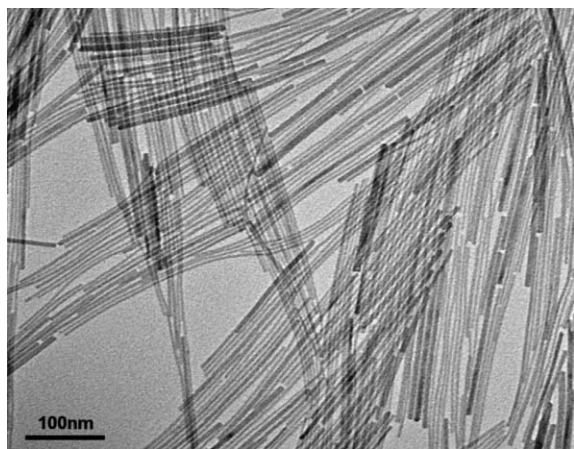
In this paper, we report a new method for the synthesis of nanofilaments/nanorods of cerium phosphate or cobalt phosphate by reaction of aqueous hexadecyltrimethylammonium phosphate [(CTA)<sub>3</sub>PO<sub>4</sub>] micelles with either [Ce(AOT)<sub>3</sub>] or [Co(AOT)<sub>2</sub>] reverse micelles prepared in isooctane. On mixing the reaction solutions, hydration of the reverse micelles occurs by influx of water molecules and phosphate ions, and in order to maintain electroneutrality the cationic and anionic surfactants spontaneously associate, with the consequence that inorganic precipitation is mediated within the oil phase by a surrounding sheath of mixed amphiphilic molecules. Our results indicate that this process produces hydrophobic nanofilaments/nanorods of highly uniform width and variable size up to 1200 nm in length. The highly constrained width of the nanostructures is commensurate with the size of rod-like reverse micelles, whereas the length is markedly influenced by changes in the reaction conditions, such as the concentration of the surfactant salts and [Ce(AOT)<sub>3</sub>]/[(CTA)<sub>3</sub>PO<sub>4</sub>] molar ratio. We show that whereas the CePO<sub>4</sub> nanofilaments are crystalline and morphologically invariant with regard to changes in the reaction conditions, the Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> nanorods are amorphous and more sensitive to modifications in the surfactant salt molar ratio. Our results are consistent with a mechanism based on the slow uni-directional crystallization or aggregation of nanoscale surfactant-coated inorganic clusters of cerium or cobalt phosphate, respectively, and suggest that coupling the *in situ* formation of catanionic micelles with inorganic deposition is a promising strategy for the room temperature preparation of a wide range of high aspect ratio nanostructures.

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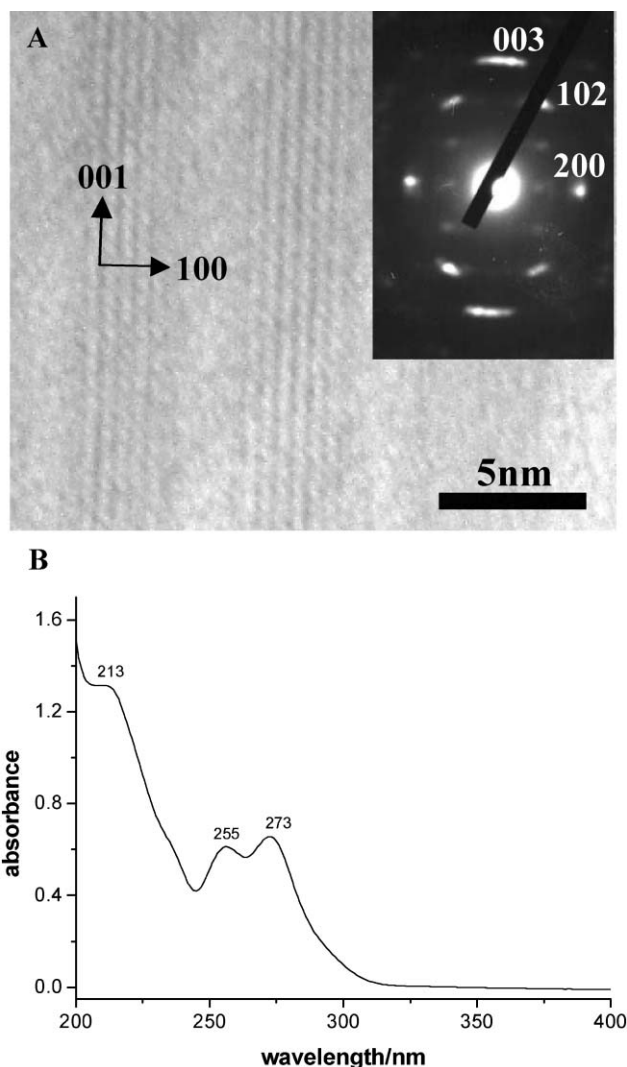
## Results and discussion

Addition of aqueous  $(\text{CTA})_3\text{PO}_4$  to an isooctane dispersion of  $\text{Ce}(\text{AOT})_3$  reverse micelles at a concentration of 10 mM,  $[\text{Ce}(\text{AOT})_3]/[(\text{CTA})_3\text{PO}_4]$  molar ratio of 1 : 1 and pH 2.2 produced three phase-separated layers. TEM images of samples extracted from the upper oil layer after 24 h revealed aggregates of partially coaligned nanofilaments (Fig. 1). The filaments were straight with smooth edges and flat ends, variable in length (typically > 120 nm and up to 1200 nm), and highly uniform in width ( $3.5 \pm 1.2$  nm). Co-aligned filaments were not in contact but spatially separated, often by a distance of *ca.* 2 nm. SAED data indicated that the filaments were crystalline with a hexagonal structure (space group  $P6222$ ,  $a = 7.055$  Å,  $c = 6.439$  Å), observed  $d$  spacings/ $(hkl)$  values; 3.06 Å (200), 2.87 Å (102) and 2.18 Å (003). The diffraction patterns suggested that the nanofilaments grew preferentially along the  $c$  axis, which was confirmed by HRTEM images that showed distinct (100) lattice fringes with a spacing 0.59 nm (Fig. 2a). EDX analysis on the washed nanofilaments showed peaks for cerium (4.84, 5.26, 5.61 keV), phosphorus (2.01 keV) and sulfur (2.22 keV), the latter suggesting that AOT molecules were strongly associated with the inorganic nanostructures. This was confirmed by FTIR spectra of washed materials (data not shown), which showed bands at 2854, 2925 and 2961  $\text{cm}^{-1}$ , and a peak at 1731  $\text{cm}^{-1}$  corresponding to the alkyl chains and ester group carbonyl of AOT, respectively, along with phosphate bands at 1047, 614, and 542  $\text{cm}^{-1}$ . In addition, the presence of CTA in the washed nanofilaments was confirmed by the increased intensities of the alkyl chain bands as well as a weak shoulder peak for the C–N stretching mode at 1384  $\text{cm}^{-1}$ . UV–vis absorption spectra of the crystalline  $\text{CePO}_4$  nanofilaments showed three peaks with maxima at 213, 256 and 273 nm (Fig. 2b) that were consistent with reported data for f–d electron transitions in  $\text{CePO}_4$ .<sup>13</sup>

A series of other studies was undertaken to investigate the influence of reaction conditions on nanofilament formation. At pH 2.2 and  $[\text{Ce}(\text{AOT})_3]/[(\text{CTA})_3\text{PO}_4] = 1 : 1$ , reducing the surfactant salt concentrations from 10 to 5 mM produced similar nanofilaments, whereas only limited numbers of short



**Fig. 1** TEM image showing bundles of coaligned cerium phosphate nanofilaments isolated from the oil layer of a  $(\text{CTA})_3\text{PO}_4/\text{Ce}(\text{AOT})_3$  reaction mixture. Scale bar = 100 nm.

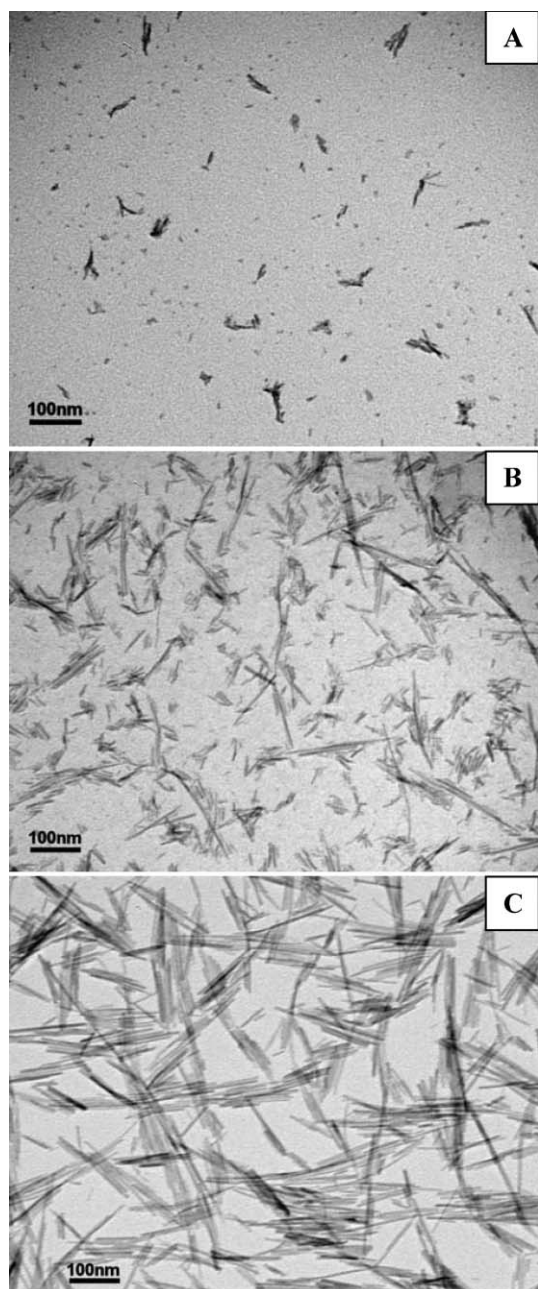


**Fig. 2** (a) HRTEM image of two  $\text{CePO}_4$  nanofilaments showing (100) lattice fringes running parallel to the morphological long axis. Inset: corresponding electron diffraction pattern. (b) UV–visible absorption spectra of  $\text{CePO}_4$  nanofilaments.

crystalline  $\text{CePO}_4$  nanorods were observed at 0.5 mM. In comparison, high yields of shorter filaments with a mean width of  $4.0 \pm 0.8$  nm and lengths less than 200 nm and 100 nm were produced at surfactant salt concentrations of 50 and 100 mM, respectively. Similarly, changes in the  $[\text{Ce}(\text{AOT})_3]/[(\text{CTA})_3\text{PO}_4]$  molar ratio between values of 1 : 20 and 20 : 1 tended to decrease the length of the nanorods without significantly changing the particle width. For example, lengths between 40–450 nm and 30–120 nm were observed when the molar ratio was adjusted between 1 : 5–1 : 20, and 5 : 1 to 20 : 1, respectively.

TEM studies were undertaken to investigate the growth stages associated with formation of the  $\text{CePO}_4$  nanofilaments at a  $[\text{Ce}(\text{AOT})_3]/[(\text{CTA})_3\text{PO}_4]$  molar ratio of 1 : 1. Samples extracted 5 min after mixing the reagents consisted of electron dense rods with a relatively uniform width (mean width,  $4.5 \pm 0.6$  nm) and variable length (range, 12–55 nm), along with spherical nanoclusters of mean diameter,  $3.6 \pm 0.6$  nm (Fig. 3a). No evidence for crystallinity was obtained from





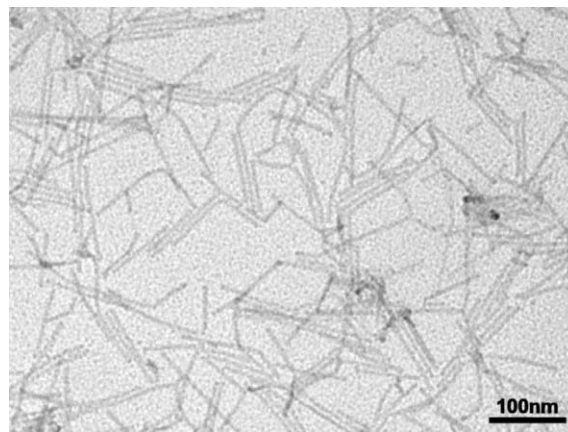
**Fig. 3** TEM images of  $\text{CePO}_4$  samples after (a) 5 min, (b) 30 min, and (c) 6 h.

electron diffraction analysis. After 30 min, the nanofilaments increased unidirectionally in length to values between 20 and 200 nm, whilst the width remained essentially unchanged (Fig. 3b). Electron diffraction analysis showed powder diffraction rings indicating that the cerium phosphate nanofilaments were at least partially crystalline at this stage. By 6 h, the filaments grew to 100 to 500 nm in length (Fig. 3c), and reached their maximum length within 24 h, after which the samples remained effectively unchanged up to 3 weeks in the reaction mixture.

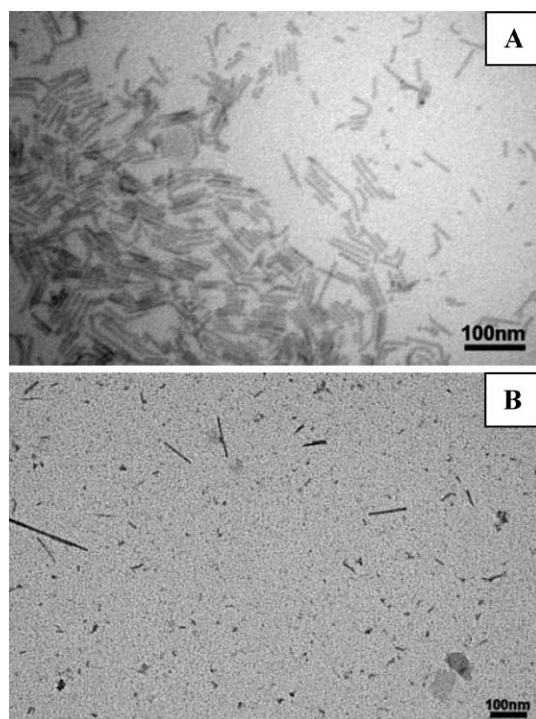
Similar studies were undertaken to prepare cobalt phosphate nanostructures by addition of aqueous  $(\text{CTA})_3\text{PO}_4$  to an isooctane dispersion of  $\text{Co}(\text{AOT})_2$  reverse micelles at

concentrations of 10 mM and  $[\text{Co}(\text{AOT})_2]/[(\text{CTA})_3\text{PO}_4]$  molar ratio of 1 : 1. TEM images of samples extracted from the upper oil layer after 3 weeks revealed well-defined nanorods that were straight or kinked in morphology (Fig. 4). The nanostructures had a mean width of  $5.0 \pm 0.6$  nm and lengths in the range of 30–280 nm. Interestingly, selected area electron diffraction indicated that the anisometric particles were amorphous. EDX analysis of washed samples showed peaks for cobalt (6.93 keV), phosphorus (2.01 keV) and sulfur (2.22 keV), and FTIR spectra of washed materials showed bands corresponding to the presence of AOT (2858, 2927, 2958  $\text{cm}^{-1}$ , 1731  $\text{cm}^{-1}$ ), phosphate (1048, 610, and 530  $\text{cm}^{-1}$ ) and CTA (1384  $\text{cm}^{-1}$ ), indicating that the cobalt phosphate nanorods were strongly associated with surfactant molecules.

Reducing the surfactant salt concentrations from 10 to 5 mM produced similar nanorods, whereas limited numbers of very short  $\text{Co}_3(\text{PO}_4)_2$  nanorods (mean width =  $6.0 \pm 0.6$  nm, length, 20–50 nm) were observed at 0.5 mM. High yields of progressively shorter rods were produced as the surfactant salt concentration was increased to 25, 50 and 100 mM (mean lengths,  $52 \pm 10$ ,  $33 \pm 7$  and  $25 \pm 9$  nm), although the mean width remained unchanged. A decrease in the lengths of the nanorods was also observed when the  $[\text{Co}(\text{AOT})_2]/[(\text{CTA})_3\text{PO}_4]$  molar ratio was changed from 1 : 1 to 20 : 1 (typical mean lengths; 44 nm (10 : 1) and 21 nm (20 : 1)) (Fig. 5a). Significantly, when the  $[\text{Co}(\text{AOT})_2]/[(\text{CTA})_3\text{PO}_4]$  molar ratio was changed from 1 : 1 to 1 : 20, only cobalt phosphate nanofilament networks were observed. TEM studies on the time-dependent formation of the cobalt phosphate nanorods in the oil layer showed that spherical nanoparticles (mean diameter =  $5.8 \pm 0.8$  nm) along with very short nanorods (mean width and length,  $5.5 \pm 1.0$  nm and  $30 \pm 15$  nm, respectively) were produced during the initial 24 h after mixing the reagents (Fig. 5b). After 2 days, the nanorods were heterogeneous in size with mean lengths and width of  $52 \pm 14$  nm and  $5.4 \pm 0.6$  nm, respectively. The nanorods progressively increased in size without significant change in width to lengths of  $80 \pm 6$  and  $113 \pm 45$  nm after 4 and 14 days, respectively.



**Fig. 4** TEM image showing 5 nm-wide cobalt phosphate nanorods isolated after 3 weeks from the oil layer of a  $(\text{CTA})_3\text{PO}_4/\text{Co}(\text{AOT})_2$  reaction mixture at molar ratio = 1 : 1. Scale bar = 100 nm.



**Fig. 5** TEM images showing (a) cobalt phosphate nanorods prepared at  $[\text{Co}(\text{AOT})_2]/[(\text{CTA})_3\text{PO}_4] = 10 : 1$  after 3 weeks, and (b) cobalt phosphate nanoparticles obtained after 24 h at  $[\text{Co}(\text{AOT})_2]/[(\text{CTA})_3\text{PO}_4] = 1 : 1$ .

The above results illustrate the potential of catanionic reverse micelles to control the nucleation and growth of hydrophobic high aspect ratio cerium or cobalt phosphate nanostructures. In both cases, increasing the surfactant salt concentrations produces higher yields of shorter nanofilaments/nanorods, which is consistent with a nucleation controlled process. For the formation of  $\text{CePO}_4$  nanofilaments, changes in molar ratio have minimal effect, suggesting that strong binding of  $\text{Ce}(\text{III})$  ions to the sulfonated AOT headgroups even in the presence of excess phosphate may dominate the nucleation process, with the consequence that the crystallization mechanism does not change markedly with modifications in the reaction conditions. In contrast, the formation of cobalt phosphate nanorods is more sensitive to changes in the molar ratio, particular in the presence of excess phosphate ions, which is consistent with the weaker binding of  $\text{Co}(\text{II})$  ions to the AOT headgroups. Significantly, both reaction systems produce nanofilaments ( $\text{CePO}_4$ ) or nanorods ( $\text{Co}_3(\text{PO}_4)_2$ ) with extremely uniform widths of 4–5 nm, suggesting that the crystallization or aggregation processes, respectively, are confined by the dimensions of the catanionic reverse micelles. As shown by the time-dependent studies, uni-directional growth occurs progressively from the tips of the initially formed nanorods until the reactants are depleted. Moreover, whilst these processes are strongly associated with the AOT molecules, the incorporation of CTA into the reverse micelles has a significant influence on controlling the regularity of the nanofilaments. For example, when control experiments based on the above synthesis method but in the absence of CTA at  $\text{pH} = 1.7$  and  $[\text{Ce}(\text{AOT})_3]/[\text{Na}_2\text{HPO}_4] = 1 : 1$  were

undertaken, only highly disordered and morphologically indistinct short nanofilaments were obtained. Similarly, addition of  $\text{Co}(\text{AOT})_3$  reverse micelles in isooctane with aqueous  $\text{Na}_2\text{HPO}_4$  solutions at  $[\text{Co}(\text{AOT})_2]/[\text{Na}_2\text{HPO}_4] = 1 : 1$  did not produce nanorods. Instead, mixtures of irregular plate-like cobalt phosphate particles were observed.

## Conclusions

This paper describes the formation of high aspect ratio nanostructures of cerium phosphate or cobalt phosphate by reaction of aqueous  $[(\text{CTA})_3\text{PO}_4]$  micelles with either  $[\text{Ce}(\text{AOT})_3]$  or  $[\text{Co}(\text{AOT})_2]$  reverse micelles prepared in isooctane. On mixing the reaction solutions, nucleation and growth of crystalline  $\text{CePO}_4$ /amorphous cobalt phosphate nanofilaments/nanorods are mediated within the oil phase by a surrounding sheath of cationic and anionic surfactant molecules. The nanostructures are hydrophobic and have a highly uniform width (4–5 nm) and variable lengths (up to 1200 nm), consistent with a growth mechanism involving the uni-directional aggregation/crystallization of nanoscale surfactant-coated inorganic clusters. Changes in the concentrations of the surfactant salts and  $[\text{Ce}(\text{AOT})_3]/[(\text{CTA})_3\text{PO}_4]$  molar ratio, markedly influence the length of the inorganic nanostructures, and whereas the  $\text{CePO}_4$  nanofilaments are morphologically invariant the cobalt phosphate nanorods are more sensitive to modifications in the reactant molar ratio. The results suggest that coupling the *in situ* formation of catanionic micelles with inorganic deposition is a promising strategy for the room temperature preparation of a wide range of high aspect ratio nanostructures.

## Experimental

### Materials

All chemicals were of analytical grade and used without further purification.  $\text{Ce}(\text{AOT})_3$  and  $\text{Co}(\text{AOT})_2$  were prepared by ion exchange using NaAOT and cerium or cobalt nitrate, respectively.<sup>11</sup> A saturated aqueous solution (50 mL) of the metal nitrate was filtered and added to 25 mL of a 1.0 M NaAOT solution in absolute ethanol. 10 mL of diethyl ether was added to the mixture in a separating funnel to produce two phases; the upper organic phase contained the  $\text{Ce}(\text{AOT})_3$  or  $\text{Co}(\text{AOT})_2$  salt, and the lower aqueous phase, which contained  $\text{NaNO}_3$  and excess cerium or cobalt nitrate was removed. The organic phase was washed repeatedly with water until the extracted aqueous phase contained no nitrate ions as determined by the brown ring test. The surfactant-containing phase was then evaporated to dryness on a Buchi rotary evaporator, left in a vacuum oven at 35 °C for 48 h, and stored over  $\text{P}_2\text{O}_5$ .

$(\text{CTA})_3\text{PO}_4$  was prepared from hexadecyltrimethylammonium bromide (CTAB) by metathesis using solid silver phosphate in methanol followed by recrystallization from acetone–methanol.<sup>12</sup> CTAB (7.290 g, 0.2 M) was dissolved in 100 mL of methanol in a light-protected flask to give a colorless transparent solution, and powdered  $\text{Ag}_3\text{PO}_4$  (4.186 g) then added under stirring to immediately produce a yellow precipitate of  $\text{AgBr}$ . The reaction mixture was sonicated for

2 min, and then kept under stirring for a further 2 h, followed by standing at room temperature overnight. The product was filtered and the AgBr precipitate removed. Acetone was then added to the clear solution until a white precipitate of  $(\text{CTA})_3\text{PO}_4$  appeared. The precipitate was removed by filtration and dried under vacuum for 1 day. The product was dissolved in water and titrated against aqueous  $\text{AgNO}_3$  or  $\text{BaCl}_2$  solution to confirm the absence/presence of  $\text{Br}^-$  and  $\text{PO}_4^{3-}$  ions, respectively.

#### Preparation of cerium phosphate and cobalt phosphate nanostructures

Cerium phosphate nanofilaments and cobalt phosphate nanorods were synthesized at a molar ratio of  $[\text{M}(\text{AOT})_x]/[(\text{CTA})_3\text{PO}_4] = 1 : 1$ . In a typical synthesis, 1 mL of aqueous  $(\text{CTA})_3\text{PO}_4$  solution (10 mM) was added to 1 mL of a 10 mM solution of  $\text{Ce}(\text{AOT})_3$  (or 1.5 mL of 10 mM solution of  $\text{Co}(\text{AOT})_2$ ) reverse micelles prepared in isooctane. The mixture was left without shaking to separate into three phases; a clear organic top layer, a milk-like emulsion middle layer, and a water-rich clear lower layer. Samples formed in the upper oil layer were predominantly studied. The water–oil emulsion middle layer and aqueous bottom layer of the reaction systems contained only low yields of inorganic nanofilaments/nanorods.

#### Characterization

Samples for transmission electron microscopy (TEM) were collected separately from each layer of reaction solution and deposited onto carbon-coated copper grids. For samples extracted from the top and middle layers, the grids were washed with pure isooctane after being air-dried. For samples isolated from the bottom layer, grids were washed with water. TEM was performed in bright field mode using a JEOL 1200 and 2010 electron microscopes operating at 120 and 200 kV, respectively. Energy dispersive X-ray analysis (EDXA) was used to confirm the presence of certain/cobalt elements and selected area electron diffraction (SAED) used to identify the

cerium/cobalt phosphate phases. For FTIR spectroscopy, samples were precipitated by ethanol or methanol and washed extensively with isooctane, air dried and then analyzed using KBr disks.

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#### References

- 1 G. Fasol, *Science*, 1998, **280**, 545.
- 2 J. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435.
- 3 Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353.
- 4 (a) L. M. Qi, J. M. Ma, H. M. Cheng and Z. G. Zhao, *J. Phys. Chem. B*, 1997, **101**, 3460; (b) M. Li, H. Schnablegger and S. Mann, *Nature*, 1999, **402**, 393; (c) D. Kuang, A. Xu, Y. Fang, H. Ou and H. Liu, *J. Cryst. Growth*, 2002, **244**, 379; (d) S. Sadisivan, D. Khushalani and S. Mann, *Chem. Mater.*, 2005, **17**, 2765; (e) C. E. Fowler, M. Li, S. Mann and H. C. Margolis, *J. Mater. Chem.*, 2005, **15**, 3317.
- 5 (a) J. D. Hopwood and S. Mann, *Chem. Mater.*, 1997, **9**, 1819; (b) G. D. Rees, R. Evans-Gowing, S. J. Hammond and B. J. Robinson, *Langmuir*, 1999, **15**, 1993; (c) M. Li and S. Mann, *Langmuir*, 2000, **16**, 7088; (d) M. H. Cao, C. W. Hu and E. B. Wang, *J. Am. Chem. Soc.*, 2003, **125**, 1119; (e) J. Zhang, L.-D. Sun, X.-C. Jiang, C.-S. Liao and C.-H. Yan, *Cryst. Growth Des.*, 2004, **4**, 309; (f) Z. H. Li, J. M. Du, J. L. Zhang, T. C. Mu, Y. N. Gao, B. X. Han, J. Chen and J. W. Chen, *Mater. Lett.*, 2005, **59**, 64.
- 6 I. Lisiecki, M. Bjorling, L. Motte, B. Ninham and M. P. Pileni, *Langmuir*, 1995, **11**, 2385.
- 7 L. Jeunieu and J. B. Nagy, *Colloids Surf., A*, 1999, **151**, 419.
- 8 B. A. Simmons, S. Li, V. T. John, G. L. McPherson, A. Bose, W. Zhou and J. He, *Nano Lett.*, 2002, **2**, 263.
- 9 H. Shi, L. Qi, J. Ma and H. Cheng, *Chem. Commun.*, 2002, 1704.
- 10 H. Shi, L. Qi, J. Ma, H. Cheng and B. Zhu, *Adv. Mater.*, 2003, **15**, 1647.
- 11 J. Eastoe, G. Fragneto, B. H. Roninson and T. F. Towey, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 461.
- 12 E. A. Lissi, E. B. Abuin, L. Sepulveda and F. H. Quina, *J. Phys. Chem.*, 1984, **88**, 81.
- 13 Y. Fang, A. Xu, R. Song, H. Zhang, L. You, J. C. Yu and H. Liu, *J. Am. Chem. Soc.*, 2003, **125**, 16025.