Self-assembly of uniform hexagonal yttrium phosphate nanocrystals†

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We report a facile chemical route for the synthesis of uniform hexagonal yttrium phosphate hydrate nanocrystals and their assembly into close-packed regular superstructures through noncovalent interactions of long chain molecules attached to the surfaces of inorganic nanocrystals.

Inorganic nanocrystals (NCs), which exhibit many interesting novel shape- and size-dependent phenomena and properties, have been extensively investigated for both their scientific and technological applications.[1] Due to their many potential applications,[1,2] NCs with distinct sizes and shapes will be promising building blocks for a bottom-up approach to form complex superstructures.[3] With the growing interest in building advanced materials using nanostructured building blocks, the development of a facile synthetic method towards these high quality NCs with uniform size and shape appears to be of key importance for the exploration of new research and application fields.[3,4] Apart from a synthetic system, assembly of discrete nano-building blocks into controllable architectures and materials with advanced functions is of ever increasing importance in chemistry and materials science.[5] By utilizing noncovalent interactions, self-assembly and self-organization provide feasible tools to generate advanced and functional nanometre and micrometre superstructures from various nano-objects.[6] During the past several years, although considerable effort has been placed on the development of various chemical synthetic methods to readily fabricate high quality NCs and consequent self-assembly,[4–6] it is still a challenge to effectively couple the controllable synthesis of uniform NCs with the consequent organization of discrete NCs into regular superstructures.

Herein we report the hydrothermal synthesis of uniform hexagonal yttrium phosphate hydrate ($YPO_4{\cdot}0.8H_2O$) NCs *via* an attractive method owing to the higher yield and simplicity. Research into nanostructured $LnPO_4$ became an active field due to their wide use in light-emitting, low-threshold lasers, optical amplifiers, fluorescent labelling of cells, agglutination assays and *in vitro* detection assays.[7–9] Recently, in a particularly important work, Haase and co-workers prepared dispersible $LnPO_4$ colloidal nanoparticles in boiling organic solvent which exhibited multicolor emission and had a strong potential application in biosensors.[10] In our synthetic system, a solution synthetic pathway is introduced to fabricate high quality NCs. The whole synthetic process is accomplished in mixed ethanol and water solvent using long chain oleic acid molecules. As a result, the synthetic process endues the individual NCs with a hydrophobic surface that lead to good dispersity in apolar solvents. More importantly, long chain molecules attach to the surfaces of the as-obtained NCs in this synthetic system, which induce the self-assembly of these discrete hexagonal NCs to form high-order superstructures through the noncovalent interactions of the long chain molecules and stabilize organized architectures.

The preparation involves the direct precipitation of $Y^{3+}$and PO_4^{3-} in a mixed water–ethanol solvent system and consequent hydrothermal treatment at the designed temperature. A given quantity of oleic acid (OA), as well as NaOH, is introduced into the above systems. NaOH can readily react with OA to form sodium oleate (NaOA) which is used to cap Y^{3+} through an ion exchange process in the mixed solvent, and then phosphate (aqueous solution) is added to react with Y^{3+} to form basic monomers. These monomers interact and then aggregate together; subsequently the NCs grow and crystallize in these conditions. In the end, OA, proved an efficient reagent to prevent the growth of NCs, terminate their growth and absorb on the NC surfaces.[11,12] Due to a large amount of ethanol and water in the system, the final products spontaneously separate at the bottom of the autoclave without further treatment.

The size and morphology of yttrium phosphate hydrate NCs were determined by low-and high-resolution transition electron microscopy (TEM). Fig. 1a shows a typical image of NCs which have uniform shapes, with each side *ca.* 16 nm in length, and a very narrow size distribution. An HRTEM image of an individual NC, given in Fig. 1b, shows the crystalline structure with lattice fringes of *ca.* 5.9 Å corresponding to the {100} lattice plane. In TEM images, it is noteworthy that the as-obtained NCs tend to assemble together spontaneously to form close-packed 2D-superstructures. In fact, uniform NCs with hexagonal structure can self-assemble to form high-order superstructures due to their shape, consistent with some natural phenomena. In nature, the self-assembly of hexagons is rather common, *e.g.* in beehives, snowflakes and tortoise shells. Hexagons, with high symmetry,

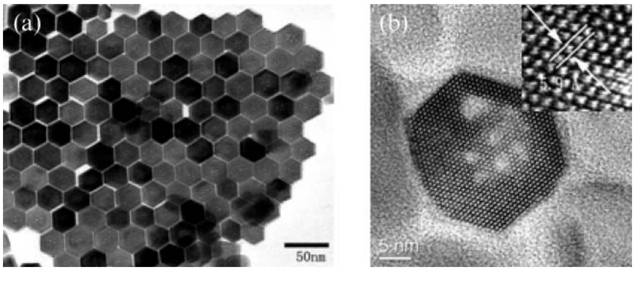

Fig. 1 (a) TEM images of yttrium phosphate hydrate NCs. (b) HRTEM image of an individual NC.

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can utilize minimum materials to occupy maximum area and spontaneously assemble to form close-packed architectures. Meanwhile, in our case, if the assembled patterns contain some defects, other hexagonal NCs or pieces will come into the patterns more easily and perfect the structures after a little adjusting.[13] On the other hand, these assemblies also require the narrow size-distribution. The products with different shapes and sizes are rather difficult to self-assemble into high-order superstructures. So, in that system, more uniformity of NCs will bring more spontaneity and order in self-assembly.

In the synthetic process, *in situ* generated OA absorbed on the surfaces of the NCs, which endowed the NCs with hydrophobic surfaces and led to good dispersibility in apolar solvents. OA molecules also offer the unique possibility of the post-synthesis grafting of other functional molecules onto yttrium phosphate hydrate NCs.[9b,14] OA, as a component of cooking oil and emulsifying agents in foods, is fully safe *in vivo* which reveals their good biocompatibility. More importantly, the formation of the specific surfaces, linked with long alkyl chains, does not play an important role in the synthetic process but also induces self-assembly. Traditionally, self-assembly is a natural and spontaneous process occurring mainly through interactions such as van der Waals, hydrogen bonding, hydrophilic/hydrophobic, electrostatic and metal–ligand coordination networks.[5] Herein mainly, by utilizing the noncovalent interactions of long chain molecules, the regular close-packed superstructures could be obtained from the uniform discrete NCs. Experimentally, the self-assembly of large superstructures was achieved using drops of uniform yttrium phosphate hydrate NCs solution of varying concentration. When the drops of NCs were deposited onto a TEM grid and left to dry, NCs would assemble spontaneously to form regular patterns through the noncovalent interactions of long chain molecules associated with hydrophobic interactions and a siphonic effect.

The surfaces, as an important matter in the total process, were paid additional attention. A corresponding HRTEM image (Fig. 2a), taken from the edge of the NCs, shows that an obvious uncrystallized layer surrounds a crystallized core. The thickness of the uncrystallized layer is 1.7 ± 0.1 nm, nearly consist with a contracted monolayer of OA molecules. More information about the surfaces was obtained by FT-IR analysis, Raman spectrum and electron energy loss spectrum (EELS) (see ESI†) The characteristic results reveal the uncrystallized layer may be formed from a great many close-packed OA molecules absorbed on the surfaces of the NCs. The length of an OA molecule is *ca.* 2 nm, so the absorbed OA molecules may happen to tilt at a certain angle or contract by several angstroms under the irradiation of an electron beam. In Fig. 2b, it can be evidenced that the assembled NCs are separated by an interparticle spacing of (2.6 ± 0.2 nm). Since the spacing is smaller than the double thickness of a contracted OA monolayer (1.7 nm), it indicates that either a considerable overlap of aliphatic tails or a certain tilt angle might be present. The first case, the OA molecules interdigitating each other to form an "arm to arm" interaction as described in Fig. 2c, is more favorable to self-assembly. The interparticle spacing (2.6 ± 0.2 nm) is nearly 1.5 times the size of the OA monolayer (1.7 nm) indicating that maybe half of each OA molecule alkyl chain (nearly 9 C atoms) overlaps.[2a] Furthermore, relative primary molecular mechanics calculations prove that the interdigitating of OA will efficiently minimize the energy of system.[15] These results reveal that several proposed factors contribute to the success of self-assembly in this process. First, the uniform assembled superstructures are more stable than the dissociated NCs or disordered aggregates. Second, OA did not only prevent the growth of NCs to obtain high quality NCs with uniform shapes, but also gave the NCs a hydrophobic surface, and these hydrophobic sides are attracted to one another over long distances resulting from minimization of the interfacial free energy which leads to relatively rapid assemblies rather than dissociates. Finally, multiple interactions of long-chain alkyls comes from long chain molecule induced assembly, stabilising the complex superstructural systems.[2,3,13,16]

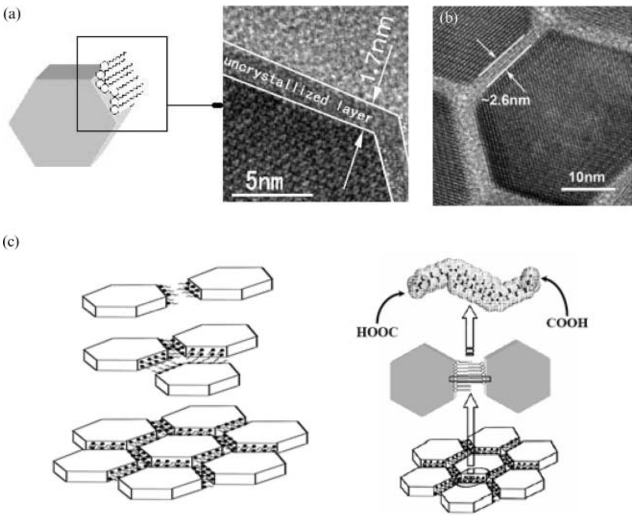

Fig. 2 (a) HRTEM image on the edge of an yttrium phosphate hydrate NC. (b) HRTEM image of NCs shows the interparticle spacing is *ca.* 2.6 nm. (c) Proposed models for the self-assembly process and the interdigitation of OA molecules between the NCs induced self-assembly. (For clarity, OA molecules were magnified individually).

Lanthanide phosphates have been shown to be a useful host lattice for other lanthanide ions, generating phosphors emitting various colors.[8,10] The fluorescence of rare earth ions mainly originates from electron transitions within the 4f shell. In our case, the 4f shell of Y^{3+} is empty with an electron configuration of ($3d^{10}4s^24p^64f^0$). No f–f transitions are possible, hence yttrium phosphate hydrate is transparent in the visible spectral region and can serve as a host lattice for Eu^{3+} which is always adopted as a doping ion to probe structural differences for its emission spectrum is very sensitive to the local chemical environment. Here the yttrium phosphate hydrate NCs doped with Eu^{3+} were prepared by the same hydrothermal treatment as the undoped products and the doping alters neither the crystal structure nor the morphology of the host materials. A room temperature emission spectrum of $YPO_4\cdot0.8H_2O$: Eu(10%) NCs is presented in Fig. 3. The emission spectrum of hexagonal $YPO_4\cdot0.8H_2O$: Eu(10%) NCs was located mainly in the red spectral area (from 570 nm to 700 nm), and it proved europium ion had been doped in the NCs successfully. These lines correspond to transitions from the excited $^5D_0$ level to the ^7F_J levels of the $4f^6$ configuration of Eu^{3+} due to the electron–electron interaction and spin–orbit coupling.[8,17] Luminescence of the uniform hexagonal structured NCs coupled with their good biocompatibility reveals their potential applications in related fields.

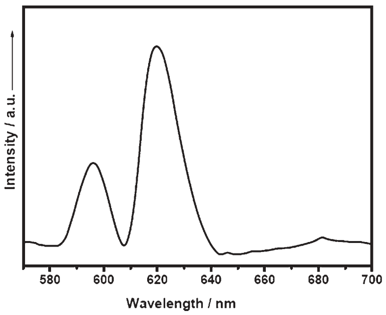

Fig. 3 Photoluminescence spectrum of $YPO_4 \cdot 0.8H_2O$: Eu(10%) NCs (λ_{exc} = 258 nm).

In conclusion, a facile synthetic method performed in mixed water and ethanol solvent to obtain high quality NCs as ideal building blocks with uniform shapes is demonstrated here. Interaction of long-chain alkyls and the uniformity of the NCs give us the ability to assemble these promising building blocks to fabricate functional close-packed superstructures by a bottom-up approach. It is believed that the effective and successful combination of controllable synthesis and assembly may provide a feasible method for manipulating various uniform nanostructures to form complex advanced architectures with tailored composition.

Notes and references

1 A. P. Alivisatos, *Science*, 1996, **271**, 933.

2 (*a*) C. C. Chen, A. B. Herhold, C. S. Johnson and A. P. Alivisatos, *Science*, 1997, **276**, 398; (*b*) X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59.

3 (*a*) M. Li, H. Schnablegger and S. Mann, *Nature*, 1999, **402**, 393; (*b*) W. D. Luedtke and U. Landman, *J. Phys. Chem. B*, 1998, **102**, 6566; (*c*) E. Rabani, D. R. Reichman, P. L. Geissler and L. E. Brus, *Nature*, 2003, **426**, 271; (*d*) W. D. Luedtke and U. Landman, *J. Phys. Chem.*, 1996, **100**, 13323.

4 (*a*) X. F. Duan, Y. Huang, Y. Cui, J. F. Wang and C. M. Lieber, *Nature*, 2001, **409**, 66; (*b*) Y. H. Gao and Y. Bando, *Nature*, 2002, **415**, 599; (*c*) Z. H. Zhong, F. Qian, D. L. Wang and C. M. Lieber, *Nano Lett.*, 2003, **3**, 343; (*d*) T. Kuykendall, P. J. Pauzauskie, Y. F. Zhang, J. Goldberger, D. Sirbuly, J. Denlinger and P. D. Yang, *Nat. Mater.*, 2004, **3**, 524.

5 (*a*) G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418; (*b*) C. B. Murray, C. R. Kagan and M. G. Bawendi, *Science*, 1995, **270**, 1335; (*c*) C. B. Murray, S. H. Sun, W. Gaschler, H. Doyle, T. A. Betley and C. R. Kagan, *IBM J. Res. Dev.*, 2001, **45**, 47; (*d*) M. M. Maye, I. S. Lim, J. Luo, Z. Rab, D. Rabinovich, T. B. Liu and C. J. Zhong, *J. Am. Chem. Soc.*, 2005, **127**, 1519; (*e*) C. P. Collier, T. Vossmeyer and J. R. Heath, *Annu. Rev. Phys. Chem.*, 1998, **49**, 371.

6 (*a*) H. M. Chen, R. S. Liu, H. L. Li and H. C. Zeng, *Angew. Chem., Int. Ed.*, 2006, **45**, 2713; (*b*) W. Lu, J. Fang, K. L. Stokes and J. Lin, *J. Am. Chem. Soc.*, 2004, **126**, 11798; (*c*) C. T. Black, C. B. Murray, R. L. Sandstrom and S. H. Sun, *Science*, 2000, **290**, 113; (*d*) M. P. Pileni, *Langmuir*, 1997, **13**, 3266.

7 (*a*) K. Riwotzki, H. Meyssamy, H. Schnablegger, A. Kornowski and M. Haase, *Angew. Chem., Int. Ed.*, 2001, **40**, 573; (*b*) G. S. Yi, H. C. Lu, S. Y Zhao, Y. Ge, W. J. Yang, D. P. Chen and L. H Guo, *Nano Lett.*, 2004, **4**, 2191; (*c*) R. Si, Y. W. Zhang, L. P. You and C. H. Yan, *Angew. Chem., Int. Ed.*, 2005, **44**, 3256; (*d*) Y. P. Fang, A. W. Xu, R. Q. Song, H. X. Zhang, L. P. You, J. C. Yu and H. Q. Liu, *J. Am. Chem. Soc.*, 2003, **125**, 16025.

8 R. X. Yan, X. M. Sun, X. Wang, Q. Peng and Y. D. Li, *Chem.–Eur. J.*, 2005, **11**, 2183.

9 (*a*) F. Meiser, C. Cortez and F. Caruso, *Angew. Chem., Int. Ed.*, 2004, **43**, 5954; (*b*) L. Y. Wang, R. X. Yan, Z. Y. Huo, L. Wang, J. H Zeng, J. Bao, X. Wang, Q. Peng and Y. D. Li, *Angew. Chem., Int. Ed.*, 2005, **44**, 6054.

10 (*a*) H. Meyssamy, K. Riwotzki, A. Kornowski, S. Naused and M. Haase, *Adv. Mater.*, 1999, **11**, 840; (*b*) K. Riwotzki, H. Meyssamy, A. Kornowski and M. Haase, *J. Phys. Chem. B*, 2000, **104**, 2824; (*c*) O. Lehmann, K. Kömpe and M. Haase, *J. Am. Chem. Soc.*, 2004, **126**, 14935.

11 X. Wang, J. Zhuang, Q. Peng and Y. D. Li, *Nature*, 2005, **437**, 121.

12 W. W. Yu and X. G. Peng, *Angew. Chem., Int. Ed.*, 2001, **41**, 2368.

13 (*a*) J. M. Lehn, *Acc. Chem. Res.*, 1978, **11**, 49; (*b*) G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; (*c*) N. Bowden, A. Terfort, J. Carbeck and G. M. Whitesides, *Science*, 1997, **276**, 233; (*d*) J. H. Warner and R. D. Tilley, *Adv. Mater.*, 2005, **17**, 2997.

14 (*a*) P. Schuetz and F. Caruso, *Chem. Mater.*, 2002, **14**, 4509; (*b*) W. J. Li, X. Wang and Y. D. Li, *Chem. Commun.*, 2004, 164.

15 Computations were mainly carried out using GAUSSIAN 03 and a few instances using SYBYL 6.6 molecular modeling software. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision B.02)*, Gaussian, Inc., Pittsburgh, PA, 2003 (http://www.gaussian.com/); *SYBYL molecular modeling system*, Tripos, Inc., St Louis, MO, 2005 (http://www.tripos.com/).

16 (*a*) J. Huang, A. R. Tao, S. Connor, R. He and P. Yang, *Nano Lett.*, 2006, **6**, 524; (*b*) A. Javey and H. J. Dai, *J. Am. Chem. Soc.*, 2005, **127**, 11942; (*c*) X. Qiu, C. Wang, Q. Zeng, B. Xu, S. Yin, H. Wang, S. Xu and C. Bai, *J. Am. Chem. Soc.*, 2000, **122**, 5550; (*d*) C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annu. Rev. Mater. Sci.*, 2000, **30**, 545.

17 B. R. Judd, *Phys. Rev.*, 1962, **127**, 750.