

# One-pot synthesis of monodisperse CeO<sub>2</sub> nanocrystals and superlattices†

Ziyang Huo, Chen Chen, Xiangwen Liu, Deren Chu, Haohang Li, Qing Peng and Yadong Li\*

Received (in Cambridge, UK) 25th February 2008, Accepted 6th May 2008

First published as an Advance Article on the web 19th June 2008

DOI: 10.1039/b803215g

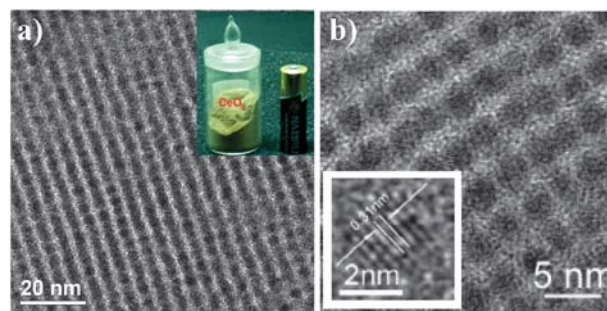
**Monodisperse CeO<sub>2</sub> nanocrystals and superlattice-like colloidal particles have been successfully synthesized in ethanol–water mixed solvent by adopting a one-pot approach using icosahedral (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> as precursor.**

Over recent decades, monodisperse nanocrystals (NCs) have drawn wide attention from researchers in broad areas for both their unique size-dependent properties and many potential applications in related fields.<sup>1</sup> At the same time, these NCs with narrow size distributions, controllable shapes and tunable compositions have also been seen as ideal building blocks for a bottom-up approach in forming various two-dimensional (2D) or 3D superstructures and advanced functional materials.<sup>2</sup> Due to considerable efforts placed on the synthetic strategy for these NCs, several facile and efficient methods have been built up successfully.<sup>3</sup> Among these classical examples, organometallic compounds and metal-surfactant complexes, especially, metal oleates or metal oleylamine complexes are always the preferred precursors to prepare high-quality monodisperse oxide NCs in bulk weakly polar organic solvents at high temperature under inert atmosphere.<sup>4</sup> Although it seems that both the metal–organic complexes and organic solvent are quite indispensable for synthesis of monodisperse oxide NCs,<sup>5</sup> establishing a convenient and reliable method to prepare large-scale monodisperse oxide NCs, by using simple inorganic salts as precursors and avoiding large amounts of organic solvent, is still a challenge and an important issue, due to the solubility limit of inorganic species in organic solvents and the lower controllability of inorganic chemical reactions in aqueous solutions.

Herein, we develop a novel pathway to multi-gram synthesis of ultrafine monodisperse CeO<sub>2</sub> NCs in water–ethanol mixed solvent by using (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> as precursor. (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> releases Ce(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> in water–ethanol mixed solvent, which will retain its stable icosahedral structure and is the basis of the synthesis. The decomposition of the (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> might take place with the formation of the Ce–oleate complex simultaneously in the synthesis process. The combination of this precursor and appropriate reaction rate is the basis of the final uniform products. In our systems, the whole preparation was free from a large amount of inert

nonpolar organic solvents, and there are no organometallic compounds and metal-surfactant complexes used as direct precursors. Furthermore, these as-obtained monodisperse NCs can be spontaneously assembled towards submicrometer colloidal particles with highly ordered superlattice structures in one step without further treatment, when a suitable concentration of reactant was employed. In a typical experiment, 0.5 g NaOH was dissolved in 10 ml of distilled water, and then 15 ml of ethanol and 4 ml oleic acid were added to form a clear solution under vigorous stirring. 8 mmol (4.4 g) (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> was dissolved in 5 ml of water and added dropwise to the mixed solvent to form a yellow precipitate. The reaction mixture was then transferred into a 40 ml Teflon-lined autoclave and heated at 120 °C for 8–12 h. After the autoclave was cooled to room temperature naturally, the multi-gram scale monodisperse brown CeO<sub>2</sub> NCs were directly collected at the bottom of the vessel, without any further size selection process. The yield was >90% as calculated according to conversion of Ce<sup>4+</sup> after annealing at 450 °C to remove all the organic molecules. The inset of Fig. 1(a) shows a digital image of the as-obtained products adopting the one-pot approach after drying at 60 °C. In the preparation, *in situ* generated oleic acid will absorb on the surface of the CeO<sub>2</sub> NCs, which will endow the individual NC with a hydrophobic surface and lead to spontaneous separation from the polar bulk solution. Further, these as-obtained NCs could be readily dispersed in nonpolar solvents such as hexane or toluene and have an excellent ability to form large area films.

Transmission electron microscopy (TEM) images show that these oxide NCs are monodisperse, nearly spherical particles with a diameter of *ca.* 2.9 nm (Fig. 1(a) and (b)). These NCs are observed to aggregate to form regular arrays after



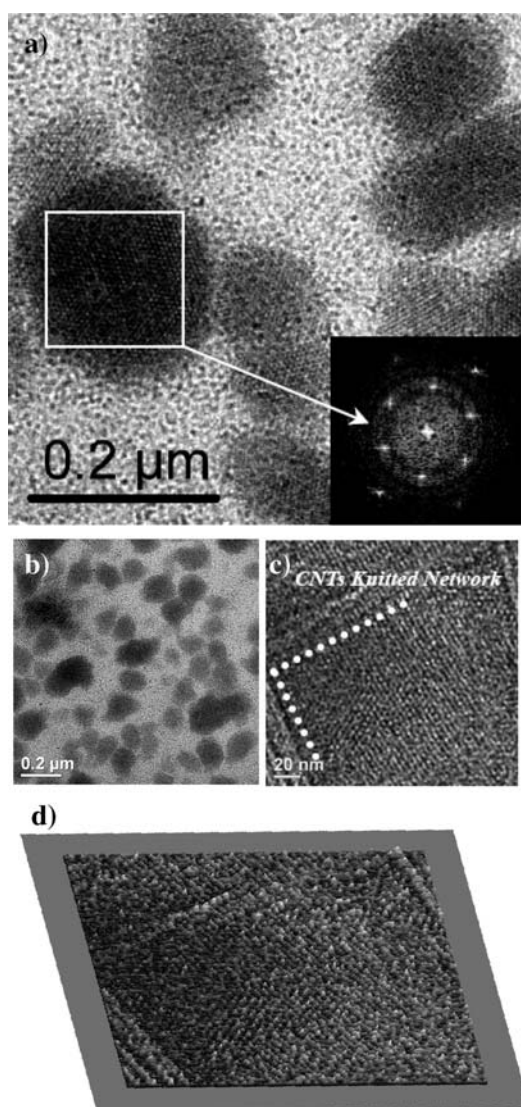
**Fig. 1** (a) TEM image of as-obtained monodisperse CeO<sub>2</sub> NCs at low magnification; the inset shows a digital camera image of the product in relation to an AA battery. (b) TEM image of the products at high magnification; the inset shows a HRTEM image of the individual NC.

Department of Chemistry, Tsinghua University, Beijing, P.R. China.  
E-mail: ydli@tsinghua.edu.cn; Fax: 86-10-62788765; Tel: 86-10-62772350

† Electronic supplementary information (ESI) available: Details of experiments, XRD pattern, EDXA, TG curve, UV-Vis spectrum, TEM images, IR spectrum. See DOI: 10.1039/b803215g

evaporation of organic solvent. A high-resolution TEM (HRTEM) image of individual CeO<sub>2</sub> NCs (inset of Fig. 1(b)) show that the products are highly crystalline, and the lattice spacing is calculated as *ca.* 0.31 nm corresponding to the (111) lattice plane for bulk CeO<sub>2</sub> (JCPDS 43-1002), which is in good agreement with the results from X-ray powder diffraction (see ESI†) According to the Scherrer equation ( $d = 0.89\lambda/B\cos\theta$ ), the calculated size of the products is *ca.* 4.1 nm, which is quite close to the corresponding result measured from the TEM image. Energy dispersion X-ray analysis (EDXA) of the CeO<sub>2</sub> NCs is shown as ESI.† Ce and O signals can be readily detected (Cu signal is from the copper grid. C signal is from the carbon membrane and OA molecules which are absorbed on the surface of the NCs).

In our systems, it is noteworthy that a mass of agglomerated NCs submicrometer-sized colloidal particles with highly



**Fig. 2** (a) TEM image of self-assembled colloidal particles with highly ordered secondary structures; inset shows the FFT of the selected area; (b) a broad range TEM image of the as-obtained colloidal particles; (c) TEM image of NCs-assembled membranes supported by a CNT knitted network; (d) *in situ* surface plot of (c).

ordered secondary superstructures also appeared in the bottom of the vessel (Fig. 2(a)), when more (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> (18 mmol) was used. Fast Fourier transformation (FFT) of the selected area shows a typical regular matrix, which indicates all the NCs are organized regularly within the colloidal particles (inset of Fig. 2(a)). Fig. 2(b) shows that the colloidal particles have irregular shapes and very broad size distributions. It is obvious that these particles are generated from the corresponding assembly of original NCs. In contrast with previous reports on the formation of superlattice structures,<sup>2</sup> no additional steps were employed. In this process, the formation of colloidal particles is quite slow, and the reaction time needs to be extended. Due to the high dispersibility and uniformity of these NCs, highly ordered membranes (Fig. 2c) could be readily formed through a self-assembly process, and these NC-integrated superstructures could cover large areas, such as carbon nanotube (CNT) knitted networks (as marked in Fig. 2(c), see also ESI†). Fig. 2(d) shows an *in situ* surface plot of the planar image (Fig. 2(d)), which revealed the high-order of the membrane with only a few abnormal peaks. The generated noncovalent interactions of organic molecules, which were absorbed on the surface of NCs, will make the colloidal particle or the superstructures more stable.<sup>6a</sup>

IR analyses indicate that some of oleic acid molecules are absorbed on the surface of individual NCs which prevents continued growth efficiently<sup>6</sup> (see ESI†). This implies that the absorption is occurring with the decomposition of (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> in the synthesis, namely, a coordinated competition between oleate ion and nitrate ion will take place,<sup>7</sup> and this process is strongly related to the crystal structure of the selected precursors Ce(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> dissociated from (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>. The Ce(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> complex has a stable icosahedral structure as shown in Fig. 3. The 12 apical oxygen atoms of the icosahedron are from six nitrates (each NO<sub>3</sub><sup>-</sup> provides two oxygen atoms), and Ce<sup>4+</sup> is located at the centre of the icosahedron. Such a natural cage constructed by oxygen atoms could slow down the hydration of Ce<sup>4+</sup>, and keep the reaction at an appropriate rate continuously. We believe that this is the most important reason why the synthesis can be well performed in aqueous systems and so distinct from the traditional methods. Compared with traditional metal-organic complexes, the new precursor we have chosen is quite stable and not sensitive to aqueous surroundings which will avoid the use of excess organic solvent. More importantly, oleate ions would cap the CeO<sub>2</sub> NCs through ion exchange during dismantling of the icosahedral structure. The appropriate reactive rate and effective capping lead to high quality NCs



**Fig. 3** Schemes of the icosahedral structure of Ce(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> and the synthesis process (for details see ESI†).

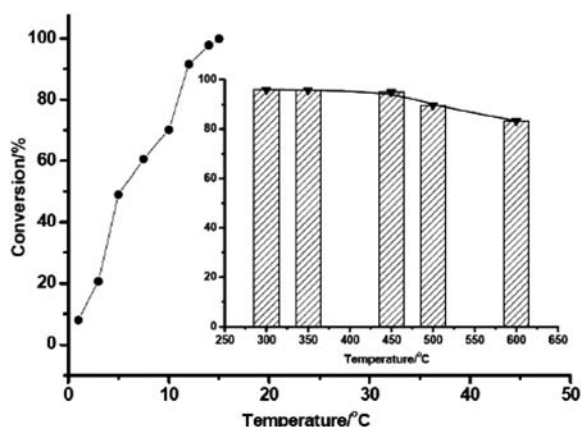


Fig. 4 Percentage conversion vs. temperature plots; inset shows the conversion at 293 K after annealing at different temperatures.

even when very high concentration of precursor was used. Taking advantage of this process, these nonpolar uniform NCs will precipitate from the bulk polar solution and aggregate together gradually. At the same time, some high-ordered superlattices also form from the above aggregates, and consequently, larger colloidal particles will be formed when higher amounts of NCs are present.

Harnessing the catalytic properties of the nanostructured CeO<sub>2</sub> is another appealing goal. Nanostructured CeO<sub>2</sub> with small sizes has been considered to have a great potential to become high-activity catalysts.<sup>8,9</sup> Here, we also investigate the catalytic activities of Au particle deposited NCs for CO oxidation. In the case of Au-supported catalysts, the choice and structure of the supports play a very important role in the CO oxidation.<sup>8a</sup> Fig. 4(a) shows that the resulting (2%)Au/CeO<sub>2</sub> catalyst gave 99.5% conversion of CO when the reaction was performed at 289 K and no catalyst deactivation was observed during 10 h of continuous running of the catalytic process. Although CeO<sub>2</sub> has been reported to be inadequate for preparing active gold catalysts for CO oxidation at low temperature previously, the as-prepared catalyst exhibits excellent activity at room temperature. In spite of its high activity, Au/CeO<sub>2</sub> catalyst also shows re-activable stability after annealing at different temperatures. The inset of Fig. 4 shows the histogram of CO conversions of Au/CeO<sub>2</sub> samples at 20 °C after heating at 300, 350, 450, 500 and 600 °C, respectively. With increased annealing temperature, the corresponding conversion is decreased, but the resulting conversions are still >90% up to the sample treated at 600 °C. Here, the size effect of the Au nanoparticles seems to be the main reason for the decrease of catalytic activity. When the catalysts were heated at high temperature, the size of Au nanoparticles

would expectably become larger than in the original samples (the original size of Au nanoparticles was 3–4 nm, see ESI†). On the other hand, we also observed that the supports show a higher degree of aggregation which will decrease the surface area of the supports.

In summary, high quality monodisperse CeO<sub>2</sub> NCs and superlattice-like colloidal particles could be readily prepared in ethanol-water mixed solvent by adopting a one-pot approach. The key factor of the successful gram-scale synthesis is the use of icosahedral (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> as precursor. The Au/CeO<sub>2</sub> catalyst exhibits stable catalytic property for CO oxidation at room temperature. NC fabrication in large amounts fulfils the important requirement for their potential use as building blocks in nanotechnology. It is also believed that this established method can significantly be expanded to controlled growth of other oxides NCs and solid solutions.

## Notes and references

- (a) X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59; (b) S. H. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
- (a) C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annu. Rev. Mater. Sci.*, 2000, **30**, 545; (b) H. Y. Fan, K. Yang, D. M. Boye, T. Sigmon, K. J. Malloy, H. F. Xu, G. P. Lopez and C. J. Brinker, *Science*, 2004, **304**, 567; (c) L. Motte, F. Billoudet, E. Lacaze, J. Douin and M. P. Pileni, *J. Phys. Chem. B*, 1997, **101**, 138.
- (a) K. Kompe, H. Borchert, J. Storz, A. Lobo, S. Adam, T. Moller and M. Haase, *Angew. Chem., Int. Ed.*, 2003, **42**, 5513; (b) X. Wang, J. Zhuang, Q. Peng and Y. D. Li, *Nature*, 2005, **437**, 121; (c) F. Bai, D. S. Wang, Z. Y. Huo, W. Chen, L. P. Liu, X. Liang, C. Chen, X. Wang, Q. Peng and Y. D. Li, *Angew. Chem., Int. Ed.*, 2007, **46**, 6650; (d) J. P. Ge, Y. X. Hu, M. Biasini, W. P. Beyermann and Y. D. Yin, *Angew. Chem., Int. Ed.*, 2007, **46**, 4342.
- (a) S. E. Habas, H. Lee, V. Radmilovic, G. A. Somorjai and P. Yang, *Nat. Mater.*, 2007, **6**, 692; (b) D. P. Liu, G. D. Li, Y. Su and J. S. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 7370; (c) Z. Li, Q. Sun and M. Y. Gao, *Angew. Chem., Int. Ed.*, 2005, **44**, 123.
- (a) J. Park, K. J. An, Y. S. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang and T. Hyeon, *Nat. Mater.*, 2004, **3**, 891; (b) C. K. Chan, X. F. Zhang and Y. Cui, *Nano Lett.*, 2008, **1**, 307; (c) H. Meyssamy, K. Riwotzki, A. Kornowski, S. Naused and M. Haase, *Adv. Mater.*, 1999, **11**, 840.
- (a) Z. Y. Huo, C. Chen, D. R. Chu, H. H. Li and Y. D. Li, *Chem.-Eur. J.*, 2007, **13**, 7708; (b) Z. Y. Huo, C. Chen and Y. D. Li, *Chem. Commun.*, 2006, 3522.
- (a) Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim and Y. Q. Yan, *Adv. Mater.*, 2003, **15**, 353; (b) X. G. Peng, *Adv. Mater.*, 2003, **15**, 459.
- (a) S. Carrettin, P. Concepcion, A. Corma, J. M. L. Nieto and V. F. Puntes, *Angew. Chem., Int. Ed.*, 2004, **43**, 2538; (b) G. C. Bond and D. T. Thompson, *Catal. Rev.-Sci. Eng.*, 1999, **41**, 319; (c) K. B. Zhou, X. Wang, X. M. Sun, Q. Peng and Y. D. Li, *J. Catal.*, 2005, **229**, 206.
- K. B. Zhou, Z. Q. Yang and S. Yang, *Chem. Mater.*, 2007, **19**, 1215.