Self-organized ultrathin oxide nanocrystals

Ziyang Huo, Chia-kuang Tsung, Wenyu Huang, Melissa Fardy, Ruoxue Yan, Xiaofeng Zhang, Yadong Li, Peidong Yang*

Department of Chemistry, University of California, Berkeley, CA 94720, USA
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
Department of Chemistry, Tsinghua University, Beijing, P. R. China 100084
Nanotechnology Systems Division,, Hitachi High Technologies America, Inc., Pleasanton, CA 94588

E-mail: p_yang@berkeley.edu

Abstract

Sub 2 nm (down to one-unit cell) uniform oxide nanocrystals and highly-ordered superstructures were obtained in one step using oleylamine and oleic acid as capping and structure directing agents. The cooperative nature of the nanocrystal growth and assembly resulted in mesoscopic 1-dimensional ribbon-like superstructures made of these ultrathin nanocrystals. The process reported here is general and can be readily extended to the production of many other transition metal (TiO_2, ZnO, Nb_2O_5) and rare earth oxide (Eu_2O_3, Sm_2O_3, Er_2O_3, Y_2O_3, Tb_2O_3, and Yb_2O_3) systems.

In the past two decades, inorganic colloidal nanocrystals have been intensively investigated due to their broad range of potential applications.[1-4] These nanocrystals[5-10] represent ideal nanoscale building blocks for various nano-enabled devices and systems. A fundamental challenge, however, still remains in the production of uniform ultrathin nanocrystals with sizes of 1-2 nm and down to the one unit-cell limit. Here we report a simple process for the synthesis of highly uniform ultrathin oxide nanocrystals. These nanocrystals can have thicknesses as thin as one unit-cell of the corresponding crystal lattice. Appropriate surfactants were used in this process both as nanocrystal capping and structure directing agents. The cooperative nature of the nanocrystal growth and assembly resulted in mesoscopic 1-dimensional ribbon-like superstructures made of these ultrathin nanocrystals. The process reported here is general and can be readily extended to the production of many other transition metal and rare earth oxide systems.

Typical nanocrystal studies reported in the literature deal with features of 4-5 nm and above.[11-15] Reports on 1-2 nm nanocrystal syntheses have been rare due to the increased difficulty to control the growth at such an atomic level. TiO_2 nanorods (NRs) are used here as an example to illustrate the effectiveness of our simple method in generating high-quality ultrathin nanostructures and their corresponding self-assembled superstructures. In a typical synthesis, 0.5~0.6g of titanium isopropoxide or titanium butoxide (reagent grade, 97% from Aldrich) was dissolved in a mixed solvent of dry octadecene (18g) and oleic acid (16g) under vigorous stirring at 80^{o}C for ~4h. To this transparent yellow solution, 6~7g of oleylamine (≥70%, Technical Grade from Aldrich) were added and then the entire solution was heated at 260~280^{o}C under a nitrogen atmosphere. After the reaction was cooled to room temperature, the gel-like product could be readily separated from the bulk solution by centrifugation at 3000 rpm for 10min (Fig 1a, inset).

Figure 1 shows typical transmission electron microscopy (TEM) images of the as-obtained product at different magnifications. As seen in Figures 1a and 1b, the product is composed of many well-defined, uniform, ribbon-like structures ~20 nm in width and ~600 nm in length. The corresponding energy dispersive X-ray spectroscopy (EDS) analysis (Fig 1b, inset) reveals that the structures contain only oxygen and titanium. Interestingly, upon further increase of the magnification (Fig 1c), it is clear that these ribbon-like structures are actually composed of many ultrathin TiO_2 NRs, ca. 2 nm x 20 nm, which are stacked side-to-side in a highly ordered fashion. High resolution TEM (HRTEM, Fig 1d) images of these individual building blocks show that the TiO_2 NRs are single crystalline with lattice fringes of 3.50 Å and 2.38 Å corresponding to the spacings between the (101) and (004) lattice planes, respectively. From this HRTEM study, it can also be concluded that these nanorods grew along with *c* axis. It should be noted here that the self-assembly of these highly uniform ultrathin TiO_2 NRs into oriented ribbon-like superstructures occurred spontaneously during the initial synthesis of TiO_2 NRs without additional post-processing steps.

The composition and crystal structure of the reaction products were examined by X-ray diffraction (XRD) at both low and high angles. The high-angle diffraction pattern of the final product (Fig 2) clearly demonstrates that the NRs were composed of pure anatase TiO_2 (JCPDF 21-1272) and that no other crystalline phases or impurities were present. The apparent broadening of the diffraction peaks is indicative of the small size of the TiO_2 nanocrystals. The 004 diffraction peak, on the other hand, exhibits a relatively narrow peak width, which implies the formation of TiO_2 NRs with a preferred growth orientation along the [004], namely, the *c* axis direction of the anatase crystal structure. This is consistent with the HRTEM analysis.

Low-angle XRD was recorded from the gel-like sample after the reaction was aged at 260°C for 1h (Fig 1a inset, 2). The XRD pattern shows four well-resolved peaks with d spacings of 23.48, 15.73, 11.84 and 9.52Å, which could be readily indexed to the $00l$ reflection series for a layered mesostructure with layer spacing of ca. 47.2 Å. This 4.7 nm value corresponds well with the thickness of the long chain alkyl molecule bilayer plus the width of the TiO_2 nanorods.[16-18] This low-angle diffraction clearly suggests that mesoscopic ordering of the nanorods could occur spontaneously[18] during the synthetic process.

Based on these TEM and XRD experimental observations, a cooperative[19,20] nanocrystal growth and self-assembly mechanism is hypothesized (Fig 3). First, inorganic precursor species were complexed with surfactants to form metal-surfactant complex monomers. These complex monomers and excess surfactants were organized into layered mesostructures (Fig 3b, also see supporting information for an example of low-angle XRD pattern for the initial layered mesostructures) which contained many nanoscale reactive pockets for oxide nanocrystals to nucleate and grow. The inorganic portion of the monomers was largely restricted in the hydrophilic reactive pockets, and the metal-surfactant complexes were decomposed in situ at high temperature to produce a metal-oxygen network through an ester elimination process.[15,21] After the reaction was heated at a given temperature for 4h, crystalline NRs evolved from the layered mesostructures. The layered mesostructures was then disrupted and the nanorods spontaneously self-assembled into 1D superstructures (Fig 3c,d). This type of ribbon-like 1D superstructure ensures the largest side-to-side contact area between the nanorods and therefore effectively decreases the interfacial energy.[18,22]

To test this cooperative growth/assembly hypothesis, this synthetic method was applied to a number of other metal oxides. Significantly, many other transition metal oxide nanostructures were prepared with a sub 2 nm dimension. A majority of these oxide nanocrystals spontaneously formed ribbon-like mesoscopic superstructures. For example, Figures 4a and 4b show as-synthesized Nb_2O_5 NRs with diameters of 1.3~1.6nm. Again, these uniform NRs self-assembled into ribbon-like superstructures. XRD and HRTEM studies confirmed the single crystalline nature of these Nb_2O_5 NRs (Supplementary Information, Fig S1 a-d).

Additionally, uniform ZnO NRs of 1.1~1.4nm in width could be readily generated from ordinary acetate precursors using this simple strategy. There is an earlier report on the synthesis of ZnO quantum rods, but with diameters of 2.2 nm.[23] Figures 4c and 4d show typical TEM images of ZnO NRs and their ribbon-like superstructures at different magnifications. The side-to-side assembled superstructures can have lengths up to ~1.6 μm with aspect ratios of ~80.

Apart from the ultrathin nanorods, uniform disk-like nanostructured oxides with thicknesses on the order of a single unit cell were also be prepared using the same method. Figure 4f shows as-obtained Eu_2O_3 nanodisks with thicknesses of 1.2~1.4nm, which is close to it's cubic lattice constant of 10.868Å. These rectangular nanodisks with 20~30nm in length of a side (Supplementary Materials Part II) were close-packed into 1D superstructures via face-to-face interaction as shown in Figures 4e and 4f. Again, according to our TEM and XRD studies, these oxide nanocrystals are all single crystalline. Interestingly, this same simple procedure can be readily applied to many other rare earth oxide systems, including Sm_2O_3, Er_2O_3, Y_2O_3, Tb_2O_3, and Yb_2O_3 (Supplementary Materials Part III, IV). The authors note that Cao et al. previously reported Gd_2O_3 nanocrystals with similar dimensions.[24]

In summary, sub 2 nm (down to one-unit cell) uniform oxide nanocrystals and highly-ordered superstructures were obtained in one step using oleylamine and oleic acid as capping and structure directing agents. Through the interaction between surfactants and inorganic species, well-organized layered mesostructures with arrays of nanoscale reactive pockets could be formed. The nanoscale reactive pockets limited the growth of oxide nanocrystals, leading to mesoscopic ordering in the final assemblies. This simple synthetic strategy could be applicable for the synthesis of many other functional nanocrystals with similar dimensions and down to the strongly quantum confined region that is not easily accessible with previously reported synthetic protocols. Meanwhile, the well-defined assemblies of these building blocks could offer more opportunities for investigating their collective properties, as well as open the door for other technologically important applications.

ACKNOWLEDGMENT

This work was supported by the Office of Basic Science, Department of Energy. We thank Professor A.P. Alivisatos for the use of the TEM and X-ray diffractometer. P.Y. would like to thank NSF for the A.T. Waterman Award.

Z.H. would like to thank the Chinese Scholarship Council (CSC) for financial aid.

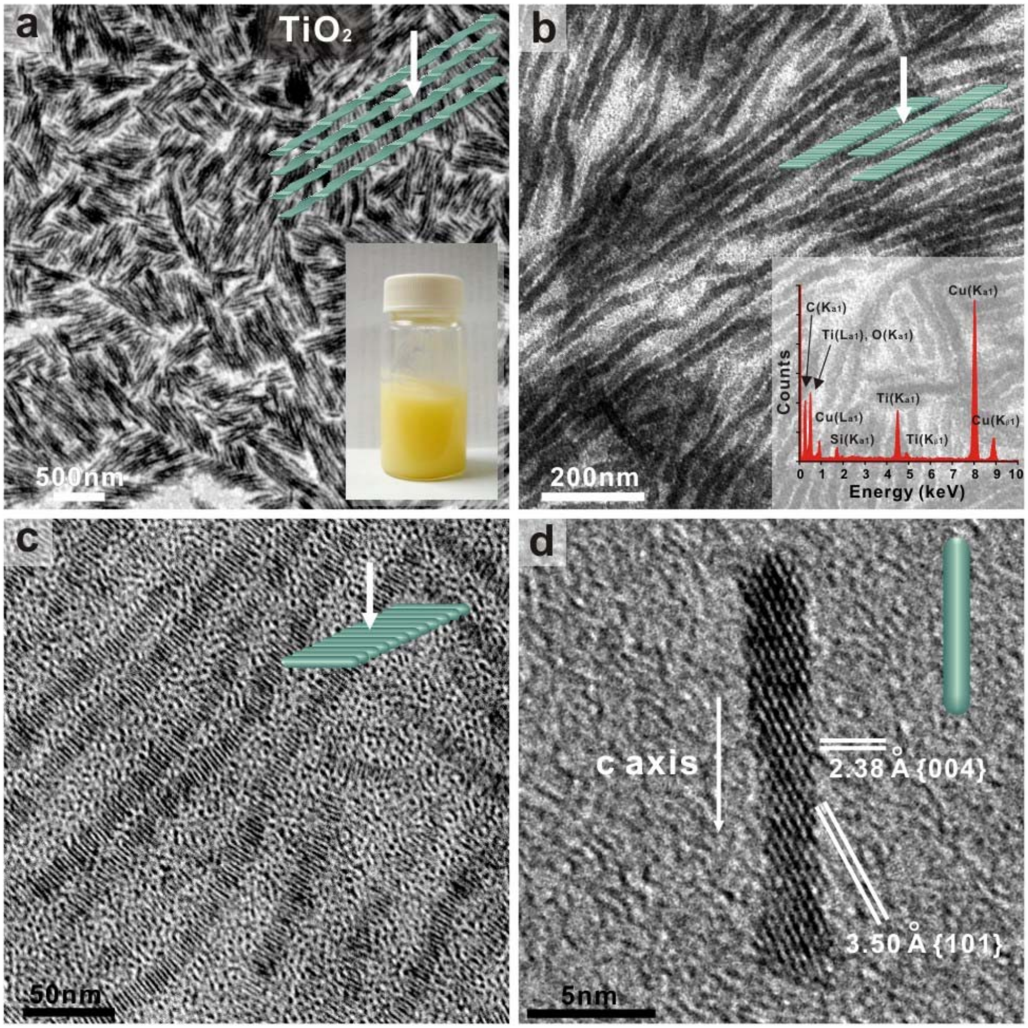

Figure 1 a-c, TEM images of the as-prepared TiO_2 NRs and their superstructures. Inset in fig a is an image of the as-prepared gel-like product; inset in fig b is the EDS spectrum of the TiO_2 NRs. The copper and silicon signals come from the copper TEM grid and EDS detector, respectively. The carbon signal is present due to the carbon film on the TEM grid and the organic molecules absorbed on the surface of the TiO_2 NRs. **d**, HRTEM image of an individual TiO_2 NR.

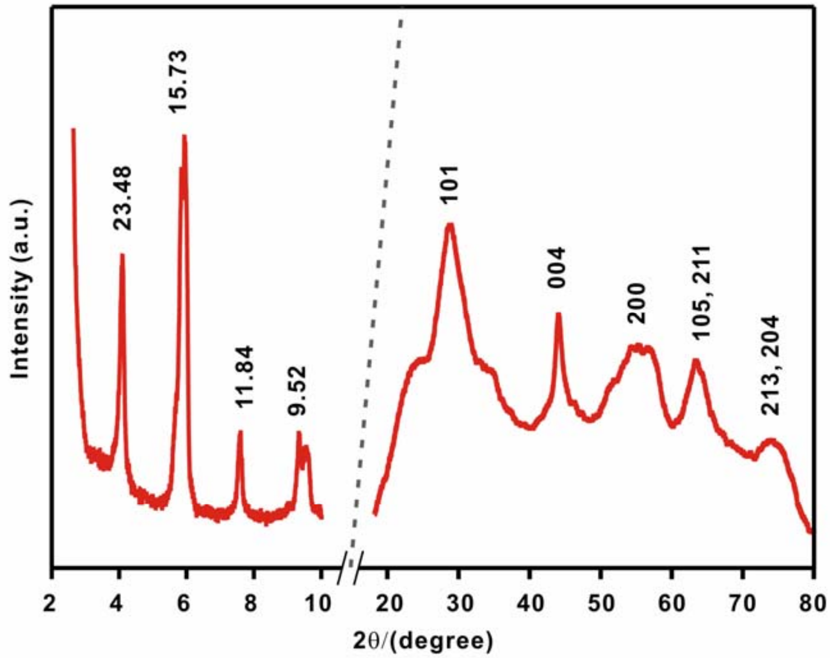

Figure 2 Low-angle and high angle XRD pattern of the TiO_2-surfactant mesostructures and the final TiO_2 nanorods. Peak labels indicate the corresponding d spacings in Å (for low angle) and diffraction index (for high angle).

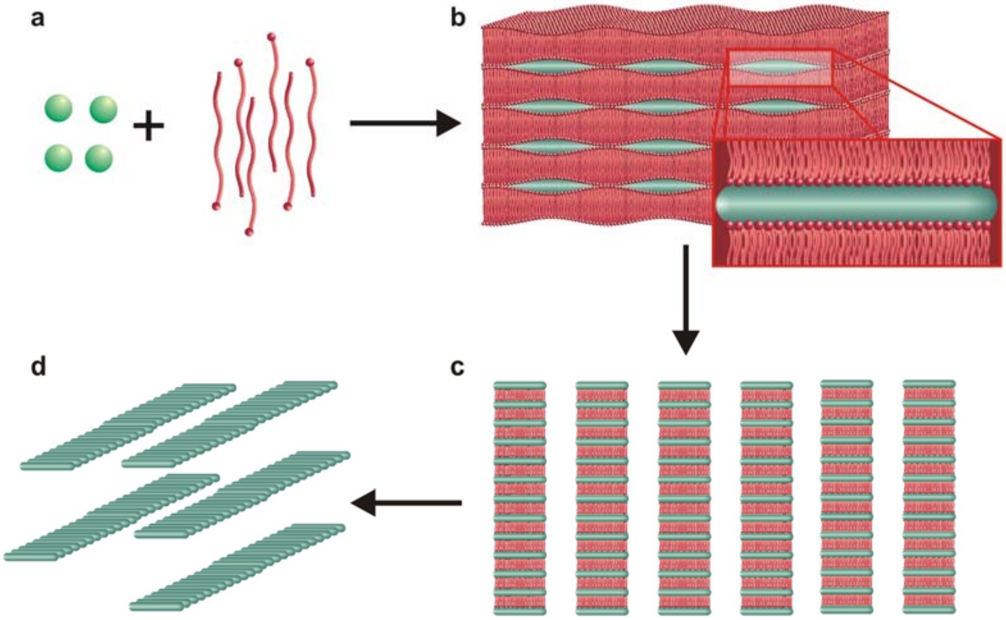

Figure 3 Schematic illustration for the synthesis of ultrathin nanostructures and their assembly.

prepared oxide nanocrystals. **a,b,** Nb_2O_5 NRs. **c,d,** ZnO NRs. **e,f,** Eu_2O_3 nanodisks.

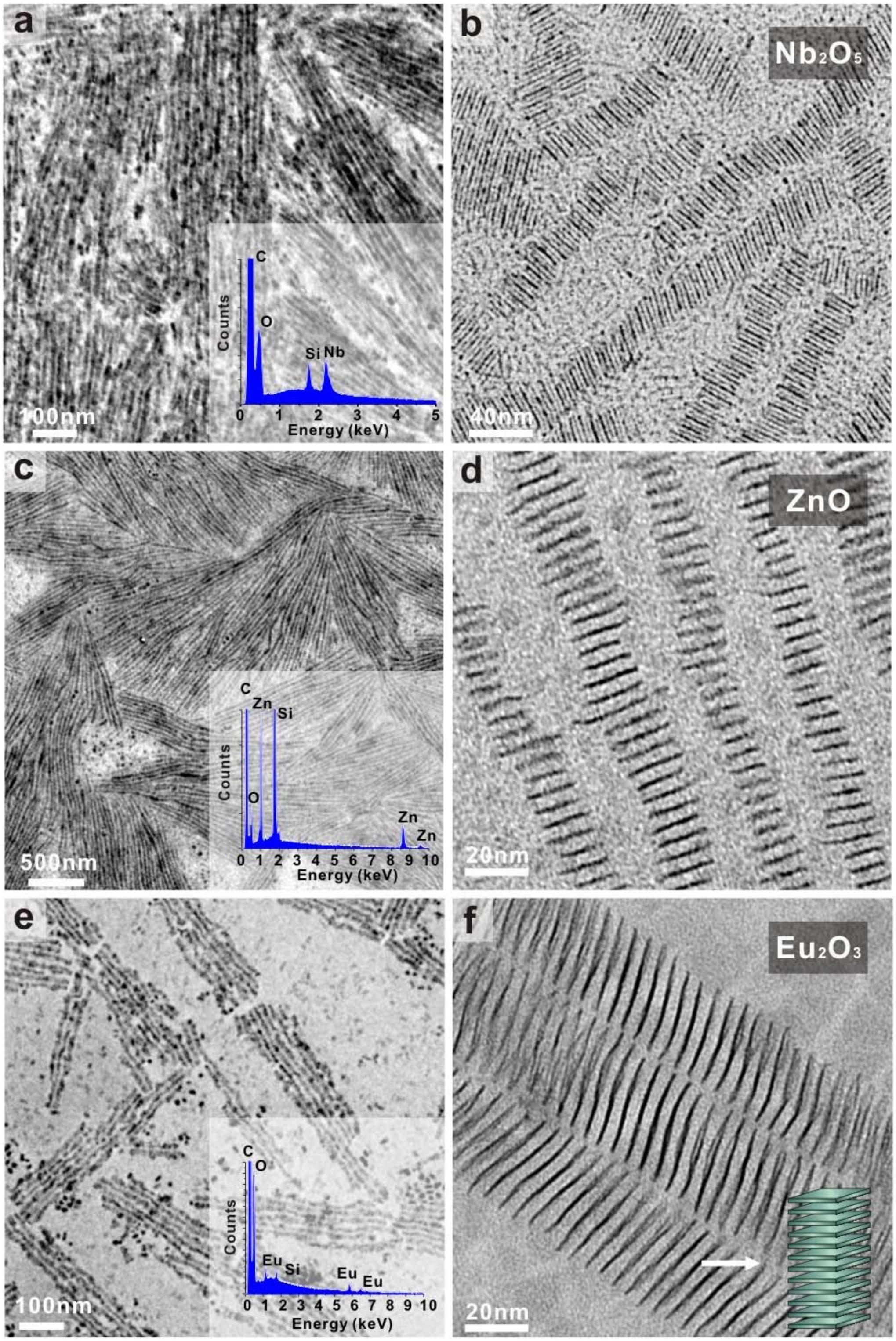

Figure 4 TEM images and the corresponding EDS spectra (inset) of the as-prepared oxide nanocrystals. **a,b,** Nb_2O_5 NRs. **c,d,** ZnO NRs. **e,f,** Eu_2O_3 nanodisks.

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Acknowledgements: This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Material Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We thank the National Center for Electron Microscopy for the use of their facilities.