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1

A general method for ultrathin 1D oxide nanomaterials

Yuxin Zhao, Bing Sun, Shucui Zhang, Lin Wang, Xin Gao, Quanzhen Liu, Shanjun Mu, Miao Zhang, Shi Hu* and Ziyang Huo*

A series of oxide ultrathin nanomaterials are prepared via a general method and the catalytic property is demonstrated in CeO₂.

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By utilizing the interaction between inorganic species and organic surfactants, the ordered layered mesostructures were generated for the synthesis of the one-dimensional oxide nanomaterials. The oxide nanomaterial products evolved from the above layered structures were demonstrated as ultrathin (less than 2 nm) one-dimensional structures with superior catalytic performance. The synthetic method based on layered structures can be extended to prepare other one-dimensional oxide nanomaterials with the same ultrathin structures.

During the past decade, much effort has been devoted to the synthesis of one-dimensional (1D) nanostructures, because of the importance of understanding the dimension-confined transport phenomena and fabricating nano-devices and nano-sensors.^{1–3} Many synthetic methods, such as thermal evaporation, laser-assisted catalytic growth, and solution-based chemical reaction, have been successfully established for the preparation of a wide range of 1D nanostructures, such as Ag, Si and ZnO.^{3–6} However, the size of the generated products derived from the present methods is always relatively large (above 5 nm). Moreover, the ultrathin 1D nanostructures with size of 1–2 nm is rarely studied due to the lack of preparation methods for such materials.^{7–12} In this work, we report a universal method through the construction of inorganic-surfactant mesostructures to synthesize such ultrathin 1D nano-

structures, including transition metal oxides and rare earth oxides.

In the synthesis, inorganic salts and surfactants were dissolved together in organic solvents, followed by a subsequent treatment at high temperature for thermal decomposition. Herein, we select 1D CeO₂ nanoribbons as an example to demonstrate the effectiveness of our facile strategy in producing high quality ultrathin nanostructures. In a typical procedure, 0.45 g of cerium acetate hydrate was dissolved in a solvent mixture of 20 mL of dry oleylamine and 5.7 mL of oleic acid under vigorous stirring at 85 °C for more than 30 min. Here, oleylamine is used both as solvent and surfactant, which has already been demonstrated to generate ordered layered structures.^{13–15} The small amount of oleic acid helps the inorganic salts to dissolve in the organic solvent. During this procedure, an appropriate number of organic surfactant molecules bond with inorganic species to yield organic-inorganic complexes, which will be organized into layered mesostructures. The formation of the ordered structures can be evidenced by the appearance of some lyotropic liquid crystal phase in the solvent mixture (see the movie in the ESI†). The solution was then heated to 240 °C and kept at this temperature for 6 h in order to let the products further crystallize. A light yellow solution was obtained after cooling the reaction products to room temperature (see ESI movie†). Ultrathin 1D product was separated from the bulk solution by centrifugation.

Fig. 1 shows the X-ray diffraction (XRD) pattern of the as-prepared intermediate layered structures and the ultrathin 1D CeO₂ nanoribbon products. As shown in the small-angle range, the lamellar nature of the intermediate complexes is verified. The corresponding pattern shows one intense diffraction peak with *d* spacing of 2.40 nm and three weak peaks with *d* spacing of 1.57 nm, 1.19 nm and 0.96 nm, which are readily attributed to the (001) reflection series for a typical layered mesostructure with an average layer spacing of 4.76 nm. This spacing value is close to the combined thickness of the surfactant molecule bi-layer and the inorganic species, suggesting that the ultrathin nanostructures may evolve from

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†Electronic supplementary information (ESI) available: Details for synthesis and characterizations, supporting TEM images of as-prepared CeO₂ nanostructures under different experimental conditions, XRD patterns for the other ultrathin oxides. See DOI: 10.1039/c7nr03659k

Fig. 1 XRD patterns of as-generated intermediate layered structures (low angle), and as-prepared crystalline CeO₂ nanoribbons.

the ordered mesostructures *via* a cooperative interaction between the surfactant molecules and inorganic species, as we proposed in our previous work.^{4,16,17} As shown by the high angle XRD result, the crystal phase of the as-obtained CeO₂ nanoribbons is undisputedly indexed to cubic structured CeO₂ with a lattice constant $a = 5.4 \text{ \AA}$ (JCPDF 75-9470). The broadening of the reflection peaks is indicative of the small size of the products. Furthermore, it is noteworthy that the reflection peak of (200) with the relative higher intensity is obviously sharper than others, which also reveals the preference of the growth direction, and is consistent with the following high resolution transmission electron microscopy (HRTEM) analysis.

The morphologies of the as-prepared products are shown in Fig. 2. On the basis of the transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images, the proportion of the 1D nanostructures is estimated to be about 80%. As shown in Fig. 2(a) and (b), well-organized 1D nanomaterials were always found among the ultrathin products. The as-prepared 1D nanostructures tend to assemble in bundle-like superstructures in a “side to side” mode, which indicates that the inorganic 1D crystal may have evolved from ordered mesostructures. Higher magnified images in Fig. 2(c) and (d) illustrate that the as-obtained 1D CeO₂ is around 3–4 nm in diameter and over 200 nm in length. Fig. 2(e) shows that some CeO₂ nanoribbons have smaller thickness (less than 2 nm), as labeled by the blue ring, whereas the ribbons labeled by the red ring are relatively thicker. By carefully analyzing these TEM images, we propose that the as-prepared ultrathin 1D CeO₂ is a ribbon structure. The narrow cross section of the products could be observed when the ribbons are stacked up. The HRTEM image was taken on the narrow section of the CeO₂ nanoribbons. As shown in Fig. 2(f), the ultrathin nanoribbons are *ca.* 1.2 nm thick, which is close to twice the size of CeO₂ unit cell. Moreover, the spacing of lattice fringes is approximately 2.7 Å, which indicates that the as-prepared products are (001) oriented. Based on the above structural information, the nanoribbon structure is illustrated in Fig. 2(g).

Fig. 2 Structure analysis of as-prepared ultrathin CeO₂ nanoribbons. TEM and STEM images of as-prepared 1D products at low (a, b) and high (c, d) magnification; TEM image (e) reveals the ribbon structure in the products. The narrow and wide cross sections are labeled by blue and red rings respectively. HRTEM image (f) shows the crystalline structure of the ultrathin ribbons. The schematic illustration of the crystal-line ultrathin CeO₂ ribbons (g). Red and yellow balls are oxygen and cerium atoms, respectively.

The thickness of the uniform nanoribbons is composed of two layers of the CeO₂ unit cell while the width equals to 5–6 unit cells. Due to the small crystal size, the as-prepared nanoribbons contain a large amount of surface oxygen vacancies, as a considerable amount of Ce³⁺ at the surface is detected by X-ray photoelectron spectroscopy (XPS). The enrichment of

active surface oxygen vacancies could enable the ultrathin oxides to be both promising catalysts and support materials for oxidation reactions because the high concentration of surface oxygen vacancies can significantly enhance the oxygen diffusion at the ceria surface and thus promote the catalytic activity. Furthermore, the well-defined exposed crystal faces such as (100) on the 1D ultrathin materials could provide deeper insight into the relationship between surface atom arrangements and catalytic performances.

The TEM and XRD analysis suggest that the formation of layered mesostructures has played an important role in producing ultrathin nanomaterials. During the reaction, inorganic species and surfactant were coupled together and then organized into ordered layered mesostructures through the cooperative assembly process.^{18,19} Therefore, the subsequent crystal growth is confined in the space organized by inorganic-surfactant complexes and excess surfactant. Meanwhile, the inorganic crystal growth also strongly depends on crystal structures under the experimental conditions. In our experiments, the inorganic concentration can affect the sizes and the shapes of the final products. An appropriate concentration of the inorganic salts in the synthetic system is necessary for the formation of the layered mesostructures.^{16,17,20,21}

Reaction with low concentration of Cerium precursor only produces uniform small nanoparticles, which imply the unsuccessful formation of ordered mesostructures.²² At higher concentration, the ordered layered structure is still obtained, but the ribbons become wider although the thickness is still less than 2 nm (see Fig. S1†). The phenomena suggest that the as-generated mesostructures, as soft templates, cannot prevent the growth of inorganic nanocrystals partly because of the increasing concentration of the inorganic species. By using dramatically higher concentration, large 2D crystalline flakes of 6–8 nm thickness were achieved, which confirms that the layered mesostructures cannot confine the inorganic crystal growth any further. More importantly, the as-prepared flakes have an interesting screw structures with the height of 2 nm, which reveals the growth process in our synthetic system.^{23,24} Once the appropriate amount of inorganic species is introduced to the organic solution to form the layered mesostructures, this synthetic strategy could be used for the synthesis of other 1D nanomaterials with ultrathin structures, independent of the composition of the materials.

In order to prove the generality of this synthetic method, the procedure was extended to some other oxides. Significantly, many other 1D metal oxide nanostructures with similar size were successfully prepared with the same synthetic strategy. As shown in Fig. 3(a), the ultrathin rare earth oxides (La_2O_3) nanoribbons were readily obtained with the same size and morphology as CeO_2 . As the lattice constant of cubic structure La_2O_3 is 11.4 Å, the thickness of nanoribbons is close to the size of a single unit crystal cell, which means the as-prepared La_2O_3 nanoribbons are single unit-cell dimensional products. These as-prepared 1D La_2O_3 could be up to several hundred nanometers long. Apart from the rare earth oxides, some ultrathin nanoribbons of transition metal oxides includ-

Fig. 3 TEM images of as-prepared 1D ultrathin oxides. (a) Lanthanum oxide, (b) niobium oxide, (c) vanadium oxides, (d) tungsten oxide, (e) titanium oxide, (f) indium oxyhydroxide.

ing niobium oxide, vanadium oxide, and tungsten oxide have also been prepared *via* the same solution-based synthesis at a higher temperature. The typical TEM images in Fig. 3(b)–(d) show the ultrafine structures of as-obtained oxides and XRD patterns shown in Fig. S2.† Besides the ribbon structure, some 1D nanowires with a similar size could also be prepared using the same method. Uniform titanium oxide and indium oxyhydroxide nanowires with small diameters (less than 3 nm) were readily synthesized by constructing the corresponding mesostructures. The morphology of the as-prepared ultrathin products is also commonly determined by the crystal structure and self-limitation growth, although the crystal sizes are strongly confined by mesostructures.

The as-prepared ultrathin nanomaterials were assembled into catalyst to further understand the surface properties. One of the most important features of the ultrathin structure is the abundance of surface atoms derived from the large surface area. Those large amounts of surface atoms will also deliver the unstable coordination atoms and dangling bonds at the surface which is favorable in adsorption of reactant molecules

Fig. 4 X-ray photoelectron spectra of CeO₂ ultrathin nanoribbons and CeO₂ nanorods. The composition of as-made oxides and oxygen plasma treated samples are illustrated by peak fitting in (a), and the composition ratio of Ce³⁺/Ce⁴⁺ from above samples are summarized in Table-1. (b) The summary of turnover frequencies (TOF) and activation energy of the CO oxidation reaction measured on CeO₂ catalysts before and after oxygen plasma surface treatment.

and transformation of intermediates. CeO₂ nanomaterials were selected as an instance to examine the ultrathin surface feature through the analysis of X-ray photoelectron spectroscopy (XPS) results and CO oxidation catalytic reaction, as is shown in Fig. 4 and Fig. S4.† To remove the surface capped organic ligands completely and expose the active crystal face to the reaction molecules, we introduce oxygen plasma treatment process to generate ozone and superoxide radical to etch the surface organics locally (the plasma treated samples are noted as CeO₂ (p) in Fig. 4). The uniform CeO₂ nanorods (NR) with were also involved as reference samples to investigate and compare with the as proposed ultrathin materials (Fig. S3†). These CeO₂ NRs with (110) crystal surface have been widely suggested as the highly active catalyst in CO oxidation reaction.^{25–28} As shown in Fig. 4(a), the XPS results revealed that both ultrathin nanoribbons and highly active NRs have a considerable amount of Ce³⁺ and accompanying oxygen vacancies, which can create effective pathways for CO oxidation through the redox of Ce³⁺/Ce⁴⁺.²⁶ Through XPS peak fitting, the concentration of the corresponding valence states in these CeO₂ catalysts was confirmed. The ultrathin nanomaterials based catalysts have the higher concentration of Ce³⁺ compared to NR catalysts, which also indicate the higher density of oxygen vacancy and potential active sites. After oxygen plasma surface treatment, the surfaces of those catalysts were partially oxidized by generated oxygen species. The ratios of Ce³⁺ in both samples were slightly decreased, but the catalyst with ultrathin structure still showed the higher concentration of over 30% of Ce³⁺ in the frame which can guarantee the stable catalytic performance. Its catalytic performance suggests a consistent result with the XPS. The catalyst with ultrathin structure showed superior performance in oxidation reaction in both turn-over frequency (TOF) and activation energy. By utilization

of plasma surface treatment, the catalytic activity was further promoted since the organic molecules were removed from the surface, although some Ce³⁺ and oxygen vacancies vanished during this oxidation process. The catalytic results and the surface-state analysis indicate that the oxides materials with the ultrathin structure and uncommon coordinate states could be potentially organized into highly efficient catalyst and catalytic supporting materials.

Conclusions

In conclusion, a series of 1D oxide nanomaterials with similar ultrathin structures have been successfully prepared *via* a solution based method. Through the cooperative interaction between inorganic salts and surfactants and the consequently formed mesostructures, the anisotropic crystal growth was well-controlled. These typical experimental results demonstrate the general applicability of our synthetic method, which suggests that the established method could be rationally selected for synthesis of many other functional 1D nanostructures. Meanwhile, the ultrathin 1D nanomaterials could be ideal objects for investigation of dimensionally confined phenomena and the underlying physics. Such ultrathin oxides nanomaterials with significantly increased surface atoms can provide abundant active sites and facilitate the catalytic reaction, making them promising materials for catalytic applications.

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