FACILE AND LARGE-SCALE ROUTE TO THE FABRICATION OF CuO NANOSHEETS FROM A LAMELLAR MESOPHASE AND THEIR REVERSIBLE SELF-ASSEMBLY

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Received March 19, 2009. Revised Manuscript Received April 20, 2009

CuO and ZnO nanosheets were conveniently synthesized on a multigram scale under ambient conditions by using a surfactant lamellar mesophase as a soft template. The fabricated nanosheets were found to exhibit reversible self-assembling properties. By using the nanosheets as a basic building block and surfactants as structure-directing agents, highly ordered lamellar mesostructures were reassembled on the substrate.

Metal oxide nanostructures have been extensively studied in recent decades because of their novel physical and chemical properties, which are related to their nanoscale dimensions. Diverse methods have been developed for the synthesis of 0D and 1D nanostructures with various morphologies and properties such as nanocrystals, quantum dots, and crystalline nanorods and nanowires. However, the development of facile and efficient synthetic methods for crystalline 2D nanosheets faces considerable challenges because of their colloidal instability.

The most frequently used process for the preparation of metal oxide nanosheets is the exfoliation of multilayered oxides. In previous studies, in order to obtain nanosheet crystallites such as nanocrystals, quantum dots, and crystalline nanorods and nanowires, metal oxide nanosheets is the exfoliation of multilayered oxides. Diverse methods have been developed for the synthesis of 0D nanostructures by using surfactant mesophases as templates is an important challenge. In this study, to obtain a crystallized CuO nanosheet/surfactant mesophase, we used an anionic surfactant, sodium dodecyl sulfate (SDS), as the template material and KOH as the crystallization agent. Metal ions and anionic surfactants form a lamellar mesophase in aqueous media. In the lamellar layers, the metal ions undergo ionic interactions with the anionic heads of the surfactants, and are crystallized without structural collapse as a result of the addition of KOH. When CuCl2 was dissolved in the SDS solution, the solution turned sky-blue, indicating the formation of Cu(H2O)62+(aq). When KOH solution was added, a bright blue precipitate of Cu(OH)2 was formed, indicating the formation of Cu(OH)2 precipitate. This method is a facile one-step method for the spatially confined crystallization without structural collapse of crystalline nanostructures by using surfactant mesophases as templates is an important challenge.

In this Letter, we report the preparation of highly ordered CuO nanosheet/surfactant lamellar layers in an aqueous solution at room temperature. The hybrid multilayers are easily delaminated by washing with water to form single layer crystallites with a thickness of ~0.8 nm. The delaminated colloidal nanosheets can reversibly reassemble into nanosheet/surfactant lamellar layers. The single crystalline CuO nanosheets were conveniently synthesized on a multigram scale under ambient conditions within a few hours without special equipment. To the best of our knowledge, this is the first report of a facile and efficient multigram scale synthesis of metal oxide nanosheets with reversible self-assembly and disassembly properties. Copper oxide nanostructures have received much attention because of their potential applications in many areas, in particular as catalysts and electrodes of lithium-ion batteries.

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formed. The precipitate color gradually turned dark-brown undervigorous stirring. Cu(OH)$_2$ is unstable in aqueous solution, so it loses water and forms CuO.

Figure 1a shows the low-angle X-ray diffraction (XRD) pattern of the as-prepared CuO nanosheet/SDS lamellar mesophase. The three peaks with $d$-spacings of 3.33, 1.69, and 1.11 nm correspond to the (100), (200), and (300) reflections of an ordered lamellar mesophase with an interlayer spacing of 3.33 nm. These XRD peaks indicate the lamellar ordering of the CuO nanosheets. The crystallized nanosheets are located between surfactant bilayers. It was reported that AgBr nanosheets were synthesized between bilayers of cationic surfactants. It was experimentally calculated that the surfactants were compactly packed, forming interdigitated arrangements between the inorganic layers. The SDS molecules are expected to form tail-to-tail bilayer arrangements. Because the SDS bilayer thickness is larger than the molecular length of SDS but smaller than twice the length, the SDS molecules might form a tilted tail-to-tail bilayer similar to the dried bilayers of SDS.

To remove the surfactant bilayers, the samples were washed with water several times and dried. After washing, the periodic structures were delaminated and discrete CuO nanosheets were obtained. Thermogravimetric analysis (TGA) measurements showed that the weight of the sample is unchanged up to 600 °C, which indicates that SDS was entirely removed by washing (Supporting Information Figure S1). SDS adsorbed on the metal oxide surface could also be analyzed by IR spectrum analysis. Bands of CH bending, CH stretching, and SO$_4$ stretching were not observed in the IR spectrum of the CuO nanosheets (Supporting Information Figure S2).

Figure 1b shows the wide-angle XRD pattern of the delaminated CuO nanosheets and reference XRD data from JCDPS 41-0254 (CuO, tenorite). The XRD reflection peaks can be indexed as (100), (−111), (111), (−202), (020), (202), (−113), (−311), (220), (311), (004), and (222), and matches those of the monoclinic phase of CuO. Thus, the XRD pattern indicates that the CuO nanosheets are highly crystalline without any other phases.

The morphology and microstructure of the CuO nanosheets were investigated with transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). A typical TEM image of the nanosheets is shown in Figure 2a. The lateral size of the nanosheets is in the range of a few hundred to several hundred nanometers. A representative HRTEM image and the selected area electron diffraction (SAED) pattern of the nanosheets are shown in Figure 2b. The lattice image and SAED pattern can be indexed to the [001] zone axis of monoclinic CuO, which indicates that the sample has a single-crystalline structure. To investigate the thickness of the nanosheets, an atomic force microscopy (AFM) analysis was performed (Figure 2c). This height profile analysis shows that the prepared nanosheets are fairly flat with a thickness of about 0.8 nm.

One important advantage of the method reported here is that it makes possible large-scale syntheses with simple and nontoxic low-cost processing. In one reaction with 300 mL of solvents, that is, water and ethanol, 14.7 g of CuO nanosheets was obtained (Supporting Information Figure S3). The overall synthetic yield was calculated to be 92.4%, which demonstrates the high efficiency of this synthetic procedure.

We have also fabricated ZnO nanosheets with the same method by using ZnCl$_2$ and TMAOH instead of CuCl$_2$ and KOH, respectively. Figure S4 in the Supporting Information shows the low-angle XRD pattern of the as-prepared ZnO nanosheet–SDS nanosheets.
lamellar mesophase. The reflection peaks indicate the presence of an ordered lamellar structure with an interlayer spacing of 3.31 nm. After the removal of the surfactants with water, discrete ZnO nanosheets were obtained. Figure S5 in the Supporting Information shows the wide-angle XRD pattern of the delaminated ZnO nanosheets and reference XRD data from JCPDS 79-0207 (ZnO, zincite). The XRD reflection peaks can be indexed as (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104), and (203), and matches those of the hexagonal phase of ZnO. Figure S6a in the Supporting Information shows a TEM image of a typical ZnO nanosheet. The lateral size of the prepared ZnO nanosheets is in the range of several tens of nanometers to a few hundred nanometers. An ultrathin crystalline layer is shown in Figure S6b in the Supporting Information. Figure S6c in the Supporting Information shows a representative HRTEM image and a fast Fourier transform (FFT) pattern of the ZnO nanosheets. The lattice image and FFT pattern can be indexed to the [010] zone axis of crystalline ZnO. An AFM analysis of the ZnO nanosheets was also performed (Supporting Information Figure S7). The height profile analysis indicates that the prepared ZnO nanosheets are fairly flat with a thickness of about 0.9 nm. We expect that this method for the synthesis of CuO and ZnO nanosheets can be extended to other metal oxide nanosheets.

Figure 2. (a) TEM image, (b) HRTEM image and SAED pattern, and (c) AFM image and height profiles of the CuO nanosheets.

Anisotropic crystal growth with surfactant templates is limited by the dynamic properties of the templates. In general, spherical crystallization is preferred over soft template-directed crystallization. However, our experimental results demonstrate the templating effect of the surfactant mesophase during nanosheet crystallization. The ionic interactions between the SDS molecules and the metal ions mean that the former cannot move freely in highly concentrated mesophases. The metal ions are concentrated on the heads of SDS by the ionic interactions in the water layer of the lamellar mesophase. The nucleated crystals become attached to the head parts of the SDS bilayers to decrease their surface energy. The growing crystals are fixed by the SDS bilayers, and crystallization preferentially occurs along the lateral direction due to the geometrical confinement and the complexation of the metal ions and SDS.

By using the nanosheets as a basic building block, highly ordered architectures can be self-assembled on the substrate. The nanosheets are well-dispersed in aqueous poly(acrylic acid) (PAA) solution. Such aqueous colloidal dispersions are kinetically stable even at nanosheet concentrations over 100 mg/mL. It is reasonable to assume that PAA is preferentially absorbed onto the surface of the nanosheets because of its highly negative


charge, which enhances their dispersion stability. To estimate the absorbed amount of PAA, TGA analysis was performed. Prior to the measurements, the dispersion was centrifuged and the precipitate was dried. From the weight loss of 15.1% obtained during heating (Supporting Information Figure S1), we estimate that 0.178 g of PAA was absorbed on 1 g of CuO nanosheets. SDS was used as a structure-directing agent. As a result of adding SDS to the nanosheet dispersion and spin-coating the dispersion onto the substrate, the nanosheets reassemble into a lamellar structure.

Figure 3a shows the low-angle XRD pattern of the CuO nanosheet-PAA/SDS lamellar mesophase spin-coated onto a silicon wafer. The four peaks with d-spacings of 4.0, 1.96, 1.30, and 0.98 nm correspond to the (100), (200), (300), and (400) reflections of an ordered lamellar mesophase with an interlayer spacing of 4.0 nm. The XRD peaks indicate that the PAA absorbed CuO nanosheets are located between the SDS bilayers, which is consistent with the as-prepared state of the nanosheets. The delaminated nanosheets can reversibly reassemble into ordered lamellar structures. The lamellar layers self-assembled on a silicon wafer were directly observed with AFM. The layered structure with a single-layer thickness of about 4 nm is shown in Figure 3b. The edges of the single layers are marked by asterisks (*) in the height profile. The film thickness was measured to be in the range of 1.1–1.5 μm in the cross section scanning electron microscopy (SEM) image (Supporting Information Figure S8). By controlling the amount of nanosheets, PAA, and SDS correspondingly, the film thickness was controlled in the range of 600 nm to 2 μm. The optimized conditions for the highly ordered layer structures and their self-assembling mechanisms are subjects of our ongoing studies.

In summary, we fabricated CuO and ZnO nanosheets with thicknesses of 0.8 and 0.9 nm, respectively, by using surfactant lamellar mesophases. In aqueous media, metal ions and anionic surfactants form a lamellar mesophase. In the lamellar layers, metal ions crystallize without structural collapse. In one reaction using 300 mL of solvents, that is, water and ethanol, 14.7 g of CuO nanosheets was conveniently synthesized under ambient conditions within a few hours without special equipment. It is expected that this method could be a facile and large-scale route to the fabrication of metal oxide nanosheets. The fabricated nanosheets have reversible self-assembly and disassembly properties. By using the nanosheets as a basic building block and surfactants as a structure-directing agent, highly ordered lamellar mesostructures were reassembled on the substrate.

Acknowledgment. This work was supported by the Center for Ultramicrochemical Process Systems of the Korea Science and Engineering Foundation.

Supporting Information Available: Experimental details, TGA curves, IR spectra, XRD pattern, TEM images, AFM image, and SEM image. This material is available free of charge via the Internet at http://pubs.acs.org.