Hydrothermal Synthesis of Highly Crystallized Lepidocrocite Nanosheets of TiO_2 under Low Temperature

Fumin wang,[†,††] Jinting Jiu,[††] Lihua Pei,[††] Keizo Nakagawa,[††] Seiji Isoda,[†††] and Motonari Adachi*[†††]
[†]*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China*
[††]*Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011*
[†††]*Institute of Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011*

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The highly crystallized lepidocrocite nanosheets of TiO_2 was synthesized by hydrothermal methods at low temperature by using dodecanediamine (DDA) as a surfactant. The above structural features of the titanium oxide nanosheets were confirmed by transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD) and UV–vis optical spectra analysis.

Bottom-up techniques have been an integral method in nanotechnology and materials manufacturing. In order to make some functional and multifunctional materials with different shape, size and structure, it is necessary to make some basic building blocks first, and then build them into larger units. Nanosheet crystallites have been regarded as new classes of nanosized materials which can be used as building blocks for constructing various functional materials with different structure such as thin flaky particulates,[1] multilayer films,[2] core/shell composites, and hollow microspheres as well as hollow shells.[3] Many kinds of novel functionalized systems have been constructed by layer-by-layer manipulation of nanosheets based on self-assembly techniques.[4] Among the various nanosheets materials, titania nanosheet is the most interesting and useful as a relative form of a versatile material of titanium dioxide, which is attracting much attention for various applications such as photocatalyst, basic materials for dye-sensitized solar cell and luminescent materials. The titania nanosheets are usually derived by delamination of a polycrystalline sample of layered titanates,[5] in which complicated process and very high temperature (1073–1273 K) are needed. In this letter we report a new process for fabrication of titania nanosheets in low temperature by hydrothermal method.

The process is based on the interaction and self-assembly between titania precursors and soft templates, DDA surfactant. Because of the highly hydrophobic property of this diamine under basic condition, the lamellar structure composed of surfactant and titanium oxide can be easily formed. The condensation reaction occurred in this confined space of thin water layer and the interplay between the Ti–OH group and DDA result in the formation of titania nanosheet. In a typical process, the titanium isopropoxide (TIPT) was mixed with triethanolamine (TEOA) at a molar ratio of [TIPT]:[TEOA] = 1:2 to form a compound of Ti(IV) which is stable against hydrolysis of Ti(IV) at room temperature and then distilled water was added to make an homogeneous stock solution. The DDA solution was added into the above stock solution of Ti(IV), and pH of the mixed solution was adjusted to 12.8 by adding 1 M NaOH solution. The mixed solution was then transferred into a Teflon autoclaves, and aged at 373 K for 24 h and then kept at 413 K for 96 h. The resulting white solid products were then centrifuged, washed with distilled water and ethanol to remove the ions possibly remaining in the final products, followed by drying at 353 K in air.

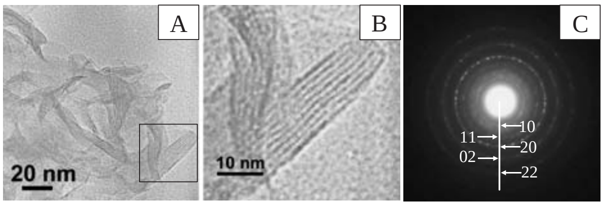

Figure 1. (A) TEM image of the sample, (B) magnified image of selected square area indicated in (A), (C) SAED patterns of the sample.

TEM images of the prepared sample was given in Figure 1. The multilayer structures of the sample can be clearly seen in this TEM image (Figure 1a). Figure 1b shows a magnified image of selected square area indicated in Figure 1a, from which the multilayer structure can be seen more clearly. In this case the nanosheets are still pinned by DDA, the black stripes correspond to the TiO_2 nanosheets and the white stripes correspond to the surfactant in the gallery. It should be pointed out that TEM is inevitably concerned with dried products, which may not be a perfect reflection of the natural state in hydrothermal solution. The gallery between two layers can also shrink during the TEM measurement due to the vacuum condition. The selected area electron diffraction patterns of the samples (Figure 1c) were composed of a series of diffraction rings. The spacings for rings are 0.38, 0.24, 0.19, 0.15, and 0.12 nm, respectively, which corresponds to the indices of 10, 11, 20, 02, 22 for the two-dimensional (2-D) unit cell (0.38×0.30 nm) of nanosheet structure[6] very well.

In our case of nanosheet titania formation, the overall reaction under hydrothermal condition can be written as:

$$\mathrm{Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH} \tag{1}$$

$$\mathrm{Ti{-}OH + XO{-}Ti \rightarrow Ti{-}O{-}Ti + XOH (X = H,R)} \tag{2}$$

$$\mathrm{2Ti{-}OH + DDA \rightarrow Ti{-}OH{\cdot}DDA{\cdot}HO{-}Ti} \tag{3}$$

$$\mathrm{Ti{-}OH + OH^- \rightarrow Ti{-}O^- + H_2O} \tag{4}$$

Eqs 1 and 2 expressed the hydrolysis reaction and condensation processes. Eq 3 indicates the interplay between the nanosheet titania and surfactant DDA. Eq 4 indicates the role of some possible presenting cations which also play a role in preventing further condensation. If DDA was removed from the multi-nanosheet structure and there is not any cation present, the nanosheet

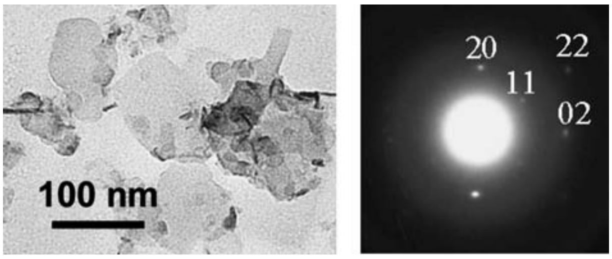

Figure 2. TEM image of exfoliated sample (A) and its electron diffraction pattern (B).

structure can not be expected to be in existence steadily because of the facility for condensation reaction (2) in hydrothermal solution.

From the analysis above, it can be seen that the nanosheet titania formed in our system prefers to present as multi-sheets structure. In order to separate the multilayered structure into individual molecular nanosheet, we need to remove DDA from multilayer by alcohol, and also to replace two amino group of DDA with some cations under basic condition, because cations cover the monosheet of TiO_2 and stabilize the monosheet. From Sasaki's research,[6] it was shown that the tetrabutylammonium hydroxide (TBAOH) is the best candidate. After we put our prepared solids sample in the mixture of alcohol and TBAOH solution, the transparent colloid suspension was formed at once which is the evidence for mono nanosheet formation. The sample for TEM measurement was prepared by placing one drop of the colloid suspension onto a carbon-coated Cu grid. The TEM image of the mono nanosheet and its electron diffraction are shown in Figure 2. It should be noted that the mono nonosheet is not so regular and flat as those prepared by exfoliating layered titanate, which may be due to our soft-template synthesis method. The observed very faint contrasts showed the very thin thickness of the sample, which can be expected to be mono-sheet. From the TEM image some curled sheets on their edge can also be seen. The electron diffraction patterns of this sample give more information about its monocrystalline property. The diffraction spots from the Figure 2b displayed an orthogonal array of sharp spots, which indicates single-crystal quality of the nanosheet. The diffraction spots can be indexed as 11, 20, 02, 22 reflections, respectively, for a two-dimensional lattice of 0.38 × 0.30 nm, being compatible with the nanosheet structure.

The XRD patterns of the sample were shown in Figure 3a. The sample were prepared by depositing the above colloid suspension on quartz glass and placed at room temperature for one day. Then the sample which has not been dried completely was subjected to XRD diffraction. Two noticeable features can be discerned. One is the faint reflections at the 2θ values of 23.6°, 48.1° and 61.2°. These three peaks can be indexed as 10, 20, and 02 diffractions for the unit periodicties of TiO_2 nanosheets structure. This XRD result agrees very well with the SAED result. The other feature is a series of sharp peaks in low angular range at 5.04°, 10.1° and 15.2°. These diffractions are assignable as 010, 020, 030 reflections, respectively, of a spacing of 1.75 nm which can be identified as the TBA intercalated nanosheet compound. This XRD pattern characteristic of layer-to-layer restacking of nanosheets agreed quite well with the results shown in detail by Sasaki et al.[5]

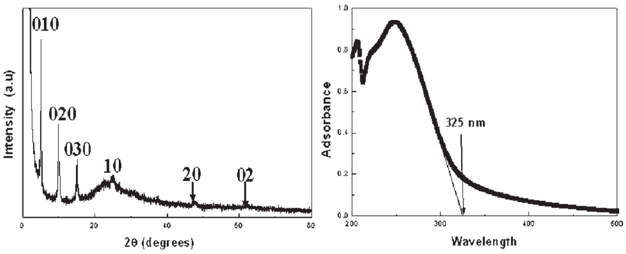

Figure 3. (A) XRD patterns of the sample; (B) Optical absorption spectra of the colloidal suspension of the sample.

According to Sasaki et al.,[7] the well-crystallized molecular nanosheet of titanium oxide should have novel optical properties. Figure 3b dipicts room-temperature absorption spectra for the colloidal suspension that were recorded on a Shimadzu UV-2200 spectrometer. The absorption for the colloidal nanosheets was significantly blue-shifted compared with those for bulk TiO_2 crystals (anatase and rutile). The absorption peak centered at 256 nm may be the characteristic feature of nanosheets. The onset wavelength of 325 nm corresponds to a photon energy of 3.82 eV. It means that the band gap of the titania nonosheet we prepared is about 3.82 eV, which is very similar and almost the same as that of the nanosheet prepared by Sasaki et al.[7] As it is well known, the bandgap energy shift by exciton confinement in anisotropic 2-D crystallites is determined by the crystallite dimensions. In other words, the blue-shift is predominantly governed by the sheet thickness. The similar or almost the same bandgap energy shift of our sample with Sasaki's means that the nanosheet structure we make is the same as those prepared by delamination of a polycrystalline sample of layered titanates.[5]

In summary, we have demonstrated a simple and versatile approach to the fabrication of titania nanosheets. Although the present work has been mainly focused on titania, we believe that the procedure described here could be extended to provide a generic route to nanosheets made of other oxides such as GeO_2, SiO_2, CeO_2, and Nd_2O_3 because the hydrolysis of metal alkoxide has been a general process for metal oxide nanopreparation. By carefully controlling the hydrolysis and condensation reaction in the lamellar restrained space, various ceramic oxide can be expected to be formed via this route.

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