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Preparation of Nanoleaf-like Single Crystals of Anatase-type TiO_2 by Exfoliation and Hydrothermal Reactions

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Nanoleaf-like single crystals of anatase were prepared by hydrothermal treatment of a layered titanate nanosheet colloidal solution at 135 °C. The single crystals have high crystallinity and prefer to expose (010) or (100) plane. The surface of the nanocrystals showed a high photocatalytic activity for degradation of Methylene Blue.

Anatase-type TiO_2 nanomaterials have received much research attention because of its unique photocatalytic properties which have wide applications to photosplitting of water,[1] decomposition of organic species for environmental cleaning system,[2] photovoltaic cells,[3] sensors,[4] medical treatment for cancer tissues,[5] etc. The photocatalytic activity is dependent mainly on the surface area and the crystallinity of the materials. A larger surface area and higher crystallinity of the photocatalysts correspond to more effective photocatalysis.[6]

Exfoliation techniques for layered compounds are interesting and useful for the preparation of the two-dimensional nanomaterials.[7] Nanosheets of elementary host layer of the layered compounds with uniform thickness can be obtained by using the exfoliation process. We think that the exfoliated nanosheets are not only useful nanomaterials, but also promising precursors in the nanomaterial synthesis, because the nanosheets can be transformed easily to other nanomaterials by slightly changing their morphology and structures. In our previous study, we have found that exfoliated layered manganese oxide nanosheets can be transformed to manganese oxide nanofibers under hydrothermal conditions.[8] In the present paper, we report the preparation of anatase-type TiO_2 nanocrystals by using the exfoliation and hydrothermal techniques. This novel process provides TiO_2 nanocrystals with nano-leaf-like morphology which are difficult to be prepared by using normal process.

In the synthesis process, first a layered titanate of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (KTLO) with a lepidocrocite-like layered structure[9] was prepared by a hydrothermal method. 5.1 g of KOH, 0.6 g of $LiOH\cdot H_2O$, 6.9 g of TiO_2 (anatase), and 25.0 mL of H_2O were sealed in a Hastelloy-C-lined vessel and then heated at 250 °C for 24 h under stirring conditions. After the hydrothermal treatment, the sample was washed with distilled water and dried at room temperature to obtain KTLO. KTLO (10 g) was treated with a 0.2 M HNO_3 solution (1 L) for 1 day under stirring conditions to exchange K^+ and Li^+ in the layered structure with H^+. After 2 times of the acid-treatment, an H^+-form layered titanate $H_{1.07}Ti_{1.73}O_4\cdot nH_2O$ (HTO) was obtained. HTO (10 g) was treated in a 0.1 M *n*-propylamine solution (1 L) under stirring conditions at room temperature for 1 day to exfoliate the layered titanate into its structural elementary nanosheets.[10,11] After the exfoliation treatment, HTO nanosheet colloidal solution was obtained.

The TiO_2 nanocrystals were prepared by hydrothermal treatment of the HTO nanosheet colloidal solution. The HTO nanosheet colloidal solution was sealed in a Teflon-lined stainless steel vessel and was hydrothermally treated at a desired temperature for 24 h. After the hydrothermal treatment, the product was separated from the solution by centrifuge, then washed with distilled water, and finally dried by a freeze drier.

The crystal structures of products were investigated by powder X-ray diffraction analysis (SHIMADZU XRD-6100 X-ray diffractometer). Figure 1 shows the XRD patterns of HTO and samples obtained after exfoliation treatment and hydrothermal treatment. HTO has a lepidocrocite-like layered structure with H_3O^+ and H_2O in the interlayer space.[9,10] When HTO was treated in propylamine solution, the propylamine molecules intercalated into the interlayer, which cause the exfoliation of the layered structure into the HTO nanosheets. When the nanosheet colloidal solution was dried, the nanosheets restacked to layered structure again, and propylamine-intercalated layered titanate was formed (Figure 1b). This sample has a larger basal spacing (1.06 nm) than that of HTO (0.922 nm). The layered phase transforms to anatase phase under the hydrothermal conditions above 100 °C. A small amount of anatase phase was observed in the sample prepared, but the main composition is the layered phase at 100 °C (Figure 1c). The layered phase transforms completely to the anatase phase at 135 °C (Figure 1e). In the transformation

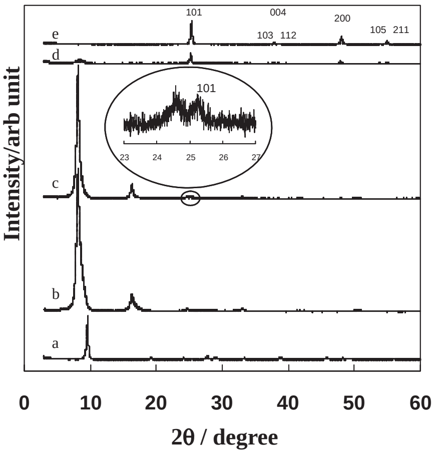

Figure 1. XRD patterns of (a) HTO, (b) propylamine-intercalated HTO, and products obtained by hydrothermal treatment of the nanosheet colloidal solution at (c) 100, (d) 130, and (e) 135 °C, respectively.

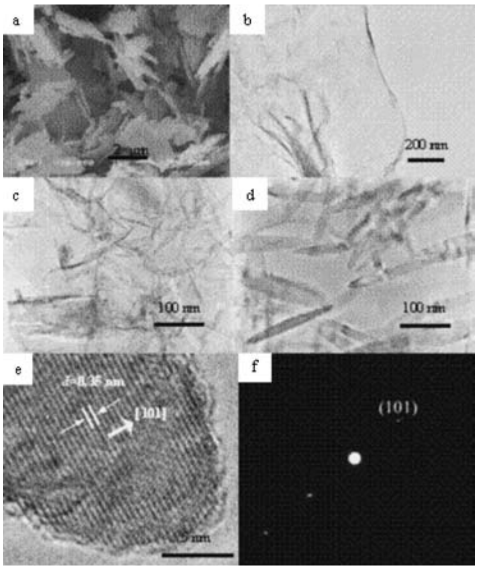

Figure 2. SEM (a) and TEM (b)–(e) images of the products: (a) HTO, (b) exfoliated HTO nanosheets, and products obtained by hydrothermal treatment at (c) 130, (d), (e) 135 °C, (f) SAED pattern of sample (e).

reaction, the amount of residual layered phase decreased while that of anatase phase increased with increasing the reaction temperature. This result suggests that the HTO nanosheet has a high reactivity and easily transforms to anatase phase under the hydrothermal conditions.

The particle size and morphology were characterized by TEM (JEOL JEM-3010) and SEM (JEOL JSM-5500S). The particle morphology of the products changed dramatically in the reaction process (Figure 2). HTO shows plate-like particle morphology of about 2 μm in width (Figure 2a). HTO was exfoliated into the nanosheets in the propylamine solution (Figure 2b). The nanosheet-like particles were split into nanobelt-like particles after the hydrothermal reaction at 130 °C (Figure 2c). The XRD analysis indicated the main composition of this sample was anatase phase with a small amount of the layered phase (Figure 1d). The nanobelt-like particles changed to nanoleaf-like particles at 135 °C (Figure 2d). The nanoleaf-like particles have a particle size of 25–40 nm in width, 200–250 nm in length, and the thickness is larger than that of the nanobelt-like particles. The XRD result indicated the nanoleaf-like particles are the single phase of anatase (Figure 1e). It has found that if the plate-like HTO particles without exfoliation treatment were hydrothermally treated, plate-like anatase particles were obtained.[9] These facts suggest that the nanosheet presorcur is necessary to prepare the nanoleaf-like particles.

A high-resolution transmission electron microscopy (HRTEM) image and selected area electron diffraction (SAED) of the nanoleaf-like particle are shown in Figures 2e and 2f, respectively. Lattice image was very clearly observed, indicating that the nanoleaf-like particle has a single-crystalline structure with high crystallinity. In the SAED pattern, only the spots of (101) plane were observed, which also revealed the single-crystalline structure and high crystallinity. The lattice spacing of 0.35 nm was determined from the SAED pattern, which corresponded to the lattice spacing of the (101) plane of anatase phase. We observed that the basal plane of the nanoleaf-like particles is always vertical to the (101) plane. This result suggested that the nanoleaf-like single crystals prefer to expose the plane parallel to [101] direction. These results suggested that the basal plane of the nanoleaf-like crystals corresponds to (010) or (100) face of anatase and most possibly is (010) face.[12] It has reported that anatase nanocrystals showed a high ability for adsorbing N3 and N719 dyes for the dye-sensitized solar cell (DSC), when the lattice fringes of (101) plane were observed most frequently in the TEM image.[13] This suggests that the nanoleaf-like anatase crystals have a potential application to the DSC.

Preliminary measurement of photocatalytic activity was carried out on the sample prepared at 135 °C by degradation of a Methylene Blue solution with irradiation by an incandescent source. For comparison, the same measurement was also carried out on a commercial Ishihara ST-01 sample as the reference. The degradation ratios for the both of samples are almost the same in the range of 660 min studied here. BET surface area measurements indicated that the surface area of sample prepared at 135 °C (34.8 $m^2 \cdot g^{-1}$) was much smaller than that of ST-01 (349 $m^2 \cdot g^{-1}$). The result of same activity and small surface area suggests that the nanoleaf-like anatase has a higher photocatalytic activity surface than that of ST-01. The high-activity surface may be due to the high crystallinity and high activity of (010) surface.

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