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Synthesis of Anatase Titania via Surfactant-assisted Hydrothermal Process: Nanosheet to Nanotube

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Nanomaterials with different shape and structure usually have varied chemical, optical and electrical properties. Shape control has been significant concern in nanotechnology. In present work, by controlling concentration of titanium sources and molar ratio of titanium to dodecanediamine(DDA), we obtained anatase titania with different shapes as nanosheets, nanorods and nanotubes. The formation mechanism of titania with different shapes can be elucidated by our experimental results.

In a typical experiment, titanium isopropoxide(TIPT) was mixed with triethanolamine(TEOA) with molar ratio of 1:2, then distilled water was added to make a aqueous solution with concentration of Ti^{4+} fixed at 0.5M(solution 1). Another solution(sulution 2) was prepared by mixing DDA with distilled water and the concentration of DDA was fixed at 0.1 M throughout the experiment. Then solution 1 was mixed with solution 2 by different ratio of volume (indicated as $R=V_{solution1}:V_{solution2}$). The pH of the mixed solution was adjusted to 12.8 by adding NaOH solution. The mixed solution was moved into a Teflon-lined stainless steel autoclaves, sealed, and aged at 100 ℃ for 24 hours and then increased to 140 ℃ for another 72 hours to nucleate and grow the titania particles. And then, the resulting white solid products were centrifuged and washed with distilled water and ethanol to remove the ions possibly remaining in the final products, followed by drying at 80℃ in air.

Figure 1 shows the SEM and TEM images of the anatase product prepared under R=1.0 and R=0.5. Under R=1.0, it can be seen that the samples show defined nanotube structures. The selected area electron diffraction (SAED) shown in figure 1C indicated the single crystalline nature of the nanotube. The unique morphology of 2-D nanosheets was observed as main product under R=0.5 as shown in Figure 1D. From the SEM image shown in figure 1B, some nanotubes show their multilayer structure very clearly. It should be noted that some sheets are rolling and forming tubes(indicated by an arrow), which gave us some clue that the nanotubes were formed from the rolled sheets. XRD analysis shows that the products are anatase titania with high purity and crystallinity.

In order to elucidate the rolling mechanism of formation of nanotube, we depart the sample with nanosheet structure which prepared under R=0.5 into two parts. One was treated in hydrothermal solution at 160℃ for 24 hours and another was treated in solvothermal solution of alcohol at same temperature for same time. Figure 2A shows the TEM image of sample treated in hydrothermal solution, in which it can be seen the nanosheet structure remains in this sample. Figure 2B shows the TEM image of sample treated in solvothermal solution, in which it can be seen that some nanosheets have rolled into needlelike structure(Figure 2C). The SAED pattern of the nanoneedle indicated its single crystalline nature.

The contrast of light-coloured center and black edges shown in the HRTEM image (figure 2D) suggests that the nanoneedle is hollow, which reminds us that the nanoneedles may result from the rolled nanosheets. From figure 2C , it also can be seen that nanoneedles was formed from the rolled nanosheets. From this we can conclude that the alcohol plays important role in the rolling of nanosheets.

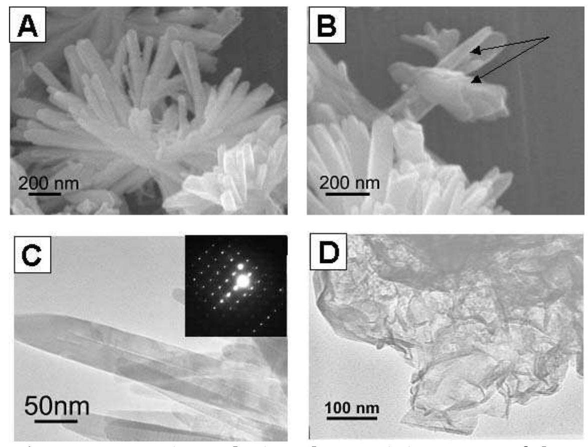

Figure 1 SEM(A and B) and TEM(C) images of the sample prepared under R=1.0 and TEM(D) image of the sample prepared under R=0.5

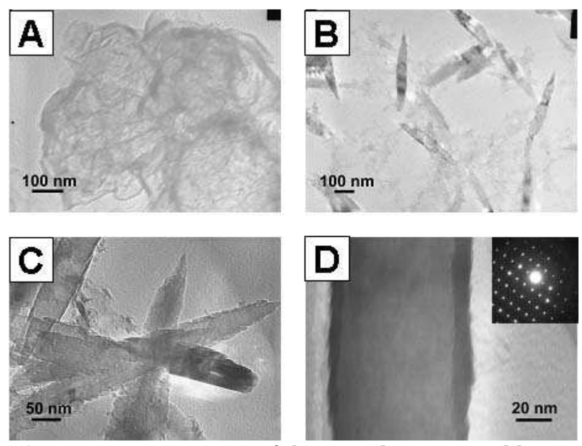

Figure 2 TEM images of the samples prepared by treating the nanosheet structure in different method: (A) hydrothermal at 160℃, (B,C,D) solvothermal at 160℃

In conclusion, the procedure for the formation of nanotubes can be divided into two steps, one is the formation of 2-D nanosheets bonded by DDA; the other is the rolling of the nanosheets. The isopropanol generated in the hydrolysis reaction of TIPT acts as the deintercalating agent by dissolution.

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