

In-Situ Structural Investigations of Nanocrystalline Titania from Titanate Nanotubes

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Titania (TiO₂) has received considerable attention in heterogeneous photocatalysis due to its high chemical stability, low cost, and potential applications to environmental remediation, chemical synthesis as well as energy production and storage. Recently the research on preparation of TiO₂ with mixed phases of anatase and rutile was motivated since the synergetic effect between the two phases was believed to be advantageous to reduce the re-combination rate of photoinduced electrons and holes. The activity enhancement is found to depend on the contents of anatase/rutile.

Since the pioneering works conducted by Kasuga *et al.*[1], nanotubes that obtained from hydrothermal treatment of TiO₂ in concentrated-base environment have stimulated substantial interests for their unique tubular morphology and high surface area. Although much efforts have been devoted, hitherto the controversy for the crystallographic structure of the nanotubes still existed. Currently it is reasonably accepted that the structure of hydrothermal-obtained nanotubes are of layered titanate nature. Recently titanate nanotubes were found to be highly reactive in aqueous acid solution to proceed phase-transformations to rutile and anatase. In this report, we found that nanocrystalline titania with tunable mixed-phase of anatase and rutile can be prepared from titanate nanotubes in acid environment. The contents of anatase/ rutile phases were found to be readily and effectively controlled by adjusting the acid concentration and treatment temperature.

Titanate nanotubes (Tnt) were prepared *via* a hydrothermal method by modifying our previous procedures [2]. Briefly, TiO₂ powders (Degussa P25) were mixed with 10 M NaOH_(aq) and then autoclaved at 130 °C for 24 hours. After the hydrothermal treatment, the white solid was retrieved by centrifugation, washed with deionized water and dilute HNO₃, and followed by drying to yield titanate nanotubes. The acid treatment for nanotubes to proceed phase transformation was carried out by dispersing nanotubes in HNO_{3(aq)} of designated molar concentration at specific temperature for 24 hours. The products were recovered by centrifugation and then dried.

It was indicated that the lower treatment temperature requires higher acid concentration for phase transformations. Meanwhile, the ratio of anatase/rutile decreases gradually as increasing in acid concentration at specific treatment temperature. As exemplified at 80 °C, when HNO_{3(aq)} was at 0.05 M, apparent phase-transformation from nanotubes to anatase can be observed. As acid concentration increased, rutile also

appeared and resulted in the progressive decrease of anatase/rutile ratio. The decrease was more pronounced when HNO_{3(aq)} concentration was less than 0.5 M. Pure rutile titania was eventually obtained at 2.5 M HNO_{3(aq)} concentration. All phase identifications obtained from XRD results were consistent with Raman spectra.

Dependence of treatment time on phase-transformations was *in-situ* monitored by treating these nanotubes in 1.5 M HNO_{3(aq)} within a quartz capillary by synchrotron x-ray diffraction at energy of 20 keV ($\lambda = 0.619 \text{ \AA}$). The temperature was controlled using a gas-flow heater. The results were presented in Figure 1. At room temperature, nanotubes exhibited diffraction peaks at $2\theta = 3.5^\circ, 9.7^\circ, 11.1^\circ$ and 18.9° . The broad background from *ca.* 6° to 18° was attributed to the quartz capillary. The d-spacing deduced from the diffraction peak at $2\theta = 3.5^\circ$ is *ca.* 0.8 nm, which is very close to the interlayer distance of the multi-walled nanotubes observed in HRTEM images. After heating to 80 °C, no apparent change can be observed. As time went on, the structure of the nanotubes disappeared gradually and the diffraction peaks of anatase and rutile emerged. When time proceeded to 85 min, no diffraction peak corresponding to nanotubes can be observed.

The prepared nanocrystalline titania with anatase and/or rutile phase were expected as promising candidates for photocatalysts. The photoanodes made of the pre-prepared pure anatase titania were found to exhibit higher conversion efficiency than those of Degussa P25 and sol-gel TiO₂ in dye-sensitized solar cells application.

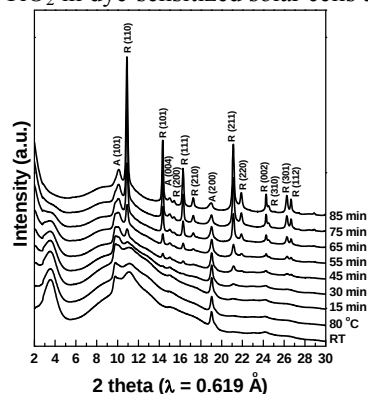


Figure 1. In-situ synchrotron x-ray diffraction patterns of the titanate nanotubes in 1.5 M HNO_{3(aq)}.

References

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- [2] S.-H. Chien, Y.-C. Liou, and M.-C. Kuo, *Synthetic Met.* **152**, 333 (2005).