EFFECT OF PRECURSOR MATERIALS AND HYDROTHERMAL TIME ON THE MORPHOLOGY, MICROSTRUCTURE AND PHOTOCATALYTIC ACTIVITY OF TiO_2 NANOTUBES

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ABSTRACT

In this study, effects of precursor materials and hydrothermal reaction time on the morphology, microstructures and photocatalytic activity of TiO_2 nanotubes (TNTs) were investigated. Results show that the selection of nanopowder TiO_2 precursors and hydrothermal time has significantly affected the morphology, microstructure and photocatalytic property of TiO_2 nanotubes. TNTs–Merck was fabricated from TiO_2–Merck precursor at 130 °C for 22 h possesses a uniform structure with a range of the diameter of ~ 10 nm and length of ~ 100 nm.

Keywords: TiO_2, nanotubes, hydrothermal, precursor, photocatalytic

1. INTRODUCTION

TiO_2 nanotubes have recently attracted a considerable interest of their photocatalytic properties for environmental cleaning and antibacterial activities. So far, many different methods have been used to fabricate the TiO_2 nanotubes including: templating [1], sol-gel [2], electrochemical anodization [3], and hydrothermal synthesis methods [4, 5]. A review of these methods was presented in the report of N. Liu et al. [6]. Hydrothermal method is a simple and environmentally friendly approach to fabricate large scale production of nanotubes with simply, cost-effectively experimental facilities [7]. Moreover, TiO_2 nanotubes fabricated by this method possess highly uniform morphology. However, there are many factors that affect the formation

of nanotube structures: the precursor powder, acid washing steps, calcination temperatures, hydrothermal temperature and time. Vuong et al. [8] investigated the effect of three different precursor materials on the formation of TiO_2 nanotubes: (a) the wet gel-TiO_2, (b) commercial TiO_2 nanopowders (P25-anatase) and (c) the annealed wet gel-TiO_2 powders at 500 °C. Results showed that TiO_2 nanotubes produced from the third precursor possesses the more uniform morphology than those of the first and second samples with a length of a few hundred nanometers and a diameter of 25 nm. Recently, a study of P. V. Viet et al. [9] on the influence of hydrothermal temperature and the acid pH value on the formation of TiO_2 nanotube structure was carried out. Results showed that the morphology of TiO_2 nanotubes was uniform at the hydrothermal temperature of 135 °C and pH = 4. Various studies and research groups have focused on the effects of hydrothermal temperature, annealing temperature, the acid pH value or choosing precursor materials on the formation and photocatalytic activities of TNTs. However, to the best of our knowledge, the investigation of effects of precursor materials and hydrothermal time on morphology, microstructure and photocatalytic activity of TiO_2 nanotubes has not been studied up to date. In this paper, the fabrication of TiO_2 nanotubes (TNTs) by hydrothermal method with various nanopowder precursors was presented. The influence of precursors and hydrothermal time on morphology, microstructure and photocatalytic activity of TiO_2 nanotubes were also investigated.

2. EXPERIMENTAL

2.1. Materials

Four types of TiO_2 nanopowders: TiO_2 – P25, TiO_2 – Merck, TiO_2 – Roha and TiO_2 – Rutile were chosen as precursors for the fabrication of TNTs by hydrothermal method. Details of parameters of these precursor materials were presented in Table 1.

Table 1. The manufactured parameters of nanopowder TiO_2 Precursors.

Type of nanopowders	Origin	Purity	External
TiO_2 – P25	Germany	> 99 %	White, impalpable
TiO_2 – Roha	India	> 96 %	White, fine
TiO_2 – Merck	Germany	> 99 %	White, fine
TiO_2 – Rutile	Russia	> 96 %	White

2.2. Synthesis of TiO_2 nanotubes (TNTs)

The production process of TNTs was followed by TiO_2 nanopowders were mixed with 10 M NaOH aqueous solution; the mixture was then heated at 130 °C for 22 h in Teflon autoclave. After carrying out the filtration and centrifugation, the white powder was washed with distilled water until pH~9; then 2 M HNO_3 acid solution was slowly added into and final washing in distilled water boiled at 80 °C until the desired pH ~7. The obtained products were filtered and dried at 60 °C for next 4 h and then, these white powders were annealed at 450 °C for 2 h. To investigate the influence of hydrothermal time, the synthesis with various hydrothermal time: 6 h (TNTs – 6), 12 h (TNTs – 12), 22 h (TNTs – 22), 36 h (TNTs – 36) and 48 h (TNTs – 48) at 130 ºC.

2.3. Characterization methods

The phases and crystallinity of nanopowder TiO_2 precursors and TiO_2 nanotubes were characterized by X-ray diffraction (Bruker D8-ADVANCE), transmission electron microscopy (TEM, JEM-1400), respectively. The photocatalytic ability of TNTs was measured using the photoluminescence (PL) (Horiba iHR320) spectra of the terephthalic acid (AT) solution at 435 nm.

3. RESULTS AND DISCUSSION

3.1. Effect of precursors on formation of TNTs

3.1.1. Analysis and evaluation of precursors

Figure 1 shows the different range of particle sizes of TiO_2 precursors. For instance, the average particle size of TiO_2 – P25 is 10 ÷ 30 nm; those of TiO_2 – Merck and TiO_2 – Roha are 70 ÷ 250 nm whilst that of TiO_2 – Rutile is 2 ÷ 4 μm.

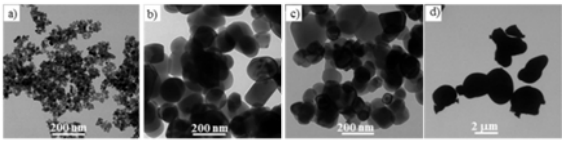

Figure 1. TEM images of various nanopowder TiO_2 precursors: a) TiO_2 – P25, b) TiO_2 – Roha, c) TiO_2 – Merck and d) TiO_2 – Rutile.

Figure 2 shows XRD patterns of nanopowder precursors. The XRD pattern of TiO_2 – P25 exhibits the main components of sample were rutile phases (111) while those of the anatase phase (101) were minor phases. On the other hand, TiO_2 – Roha and TiO_2 – Merck were

crystallized in anatase phase with prominent peaks of (101), (004), (200), (105), and (204). The XRD of TiO_2 – Rutile showed only peaks of rutile phase at diffraction angles of 2θ = 27.47 ° (110), 36.11 ° (101) and 54.35 ° (211).

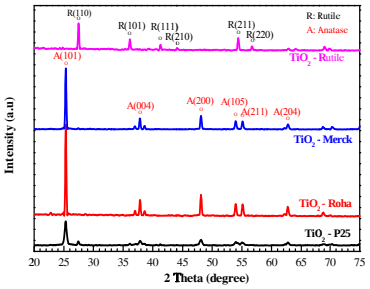

Figure 2. XRD patterns of nanopowder TiO_2 precursors.

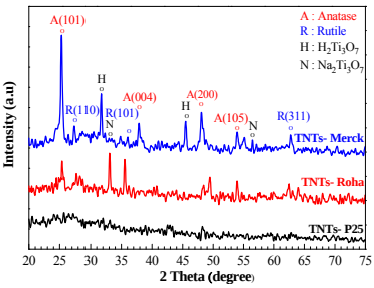

Figure 4. XRD patterns of TNTs fabricated from various nanopowder TiO_2 precursors.

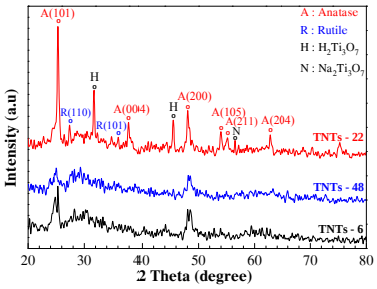

Figure 6. Powder XRD patterns of TNTs fabricated with various hydrothermal times.

3.1.2. Effect of the initial precursor on the formation of TNTs

Figure 3 shows TEM images of TNTs fabricated by various precursors. The result shows that TNTs – P25, TNTs – Roha and TNTs – Merck samples exhibit tube structure while TNTs – Rutile sample was not formed the tube structure. TEM image of TNTs – Merck sample indicates that this sample possesses the highest uniform structure, resulting from the high purity of TiO_2 – Merck with the main peaks of anatase phase. Besides, it is noted that TEM images of TNTs – Rutile showed that the hydrothermal reaction of this precursor does not form the tube structure, which caused by the micrometer-size particles of TiO_2 – Rutile (Figure 1d). It indicates that the nanometer-size particle of the precursors plays an important role in the formation of TNTs which is consistent with other reports [10 - 12].

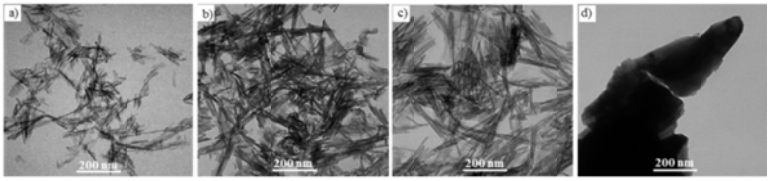

Figure 3. TEM images of TNTs fabricated from various nanopowder TiO_2 precursors: a) TNTs – P25, b) TNTs – Roha, c) TNTs – Merck and d) TNTs – Rutile.

The crystal structure of TNTs fabricated from nanopowder precursors (TiO_2 – P25, TiO_2 – Roha and TiO_2 – Merck exception of TiO_2 – Rutile) are shown in Figure 4. Results showed that the TNTs – Roha, and TNTs – Merck possess the anatase phases with characteristic peaks of TiO_2 at 2θ = 25.08 °, A (101); 37 °, A (004); 48.05 °, A (200); and some rutile phases with characteristic peaks of 2θ = 27.47 °, R (110); 35.89 °, R (101) and 41.02 °, R (111), respectively.

However, only TNTs – P25 does not exhibit characteristic diffraction peak of anatase. A small amount of impurity phases was indexed as $H_2Ti_3O_7$ and $Na_2Ti_3O_7$, respectively. In summary, with different nanopowder TiO_2 precursors, TiO_2 – Merck, is profitable for the fabrication of TNTs by hydrothermal method.

3.2. Effect of the hydrothermal time on TNTs

The nanopowder TiO_2 – Merck precursor was used for investigating the effect of hydrothermal time on the TNTs formation. Figure 5 shows that the morphology of TNTs in various hydrothermal times is different, indicating that the critical hydrothermal treatment time plays an important role in the formation of tubular structure. For instance, with a short period of treatment time (t = 6 h), TNTs were formed with non-uniform morphology. When increasing reaction time from 12 to 22 h, the crystalline TNTs grows with the more uniform size of $8 \div 11$ nm in diameter and a few hundred nanometers in length. At 22 h, TNTs has a uniform structure. However, when increasing the hydrothermal time up to $36 \div 48$ h, the diameter of the tube increases with the un-uniform length of a few tens to a few hundreds of nanometers. This result is entirely consistent with the report of Sheng Jiang et al. [13]. It is suggested that when the hydrothermal reaction time is too long (over 36 h), the stable state of TNTs would be damaged in the boiling NaOH aqueous solution, according to: (i) a portion of TNTs will be dispersed into the solution and acting as nutrients for the growth of nanoribbon structure; (ii) a portion of TNTs would link together to form rafts through a multistep attachment process in order to reduce the surface energy; (iii) or they grow spirally into nanowires along the inner (200) surface.

XRD patterns of TNTs – 6, TNTs – 22 and TNTs – 48 were carried out to investigate the process of TNTs formation (Figure 6) The structural analysis indicates that all samples crystallize in anatase phases with prominent peaks at (101) and (200), respectively. When reaction time increases from 6 h to 22 h, the intensity of the peaks significantly increase at A (101), A (200), and A (004) faces and R (110), R (211) faces, whilst the intensity of impurity peaks ($H_2Ti_3O_7$, $Na_2Ti_3O_7$) also increase. However, when the hydrothermal reaction time increases to a longer time of 48 h, the characteristic peaks of anatase, rutile, and impurity phases were not observed. It is indicated that in the short term synthesis, the reaction of the hydrothermal process occurs incompletely, which is not enough time for the formation of complete crystallization of materials [14]. On the contrary, with the longer time synthesis, the TNTs would be dispersed in NaOH aqueous solution and formed TiO_2 nanosheets arrays instead of tubular structures, which is consistent with TEM results (Figure 5e). This suggests the

hydrothermal treatment time is critical in the crystal structure and formation of TNTs [15].

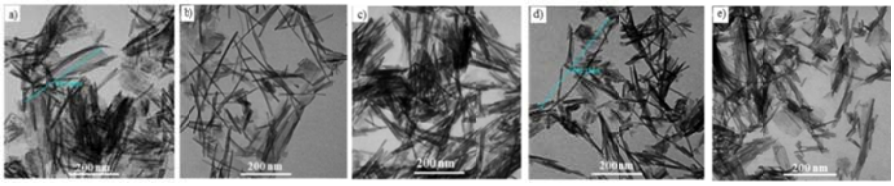

Figure 5. TEM images of TNTs fabricated at various hydrothermal times: a) TNTs – 6: 6 h; b) TNTs – 12: 12 h; c) TNTs – 22: 22 h; d) TNTs – 36: 36 h and e) TNTs – 48: 48 h.

3.3. Photocatalytic activity of TNTs

Figure 7a shows the PL spectra of terephthalic acid solution under 80 mins UVA irradiation of TNTs – Roha, TNTs – Merck and TNTs – P25. Samples were all luminescent At 435 nm (AT could readily react with •OH to product 2-hydroxyl acid terephthalic, with a fluorescence signal characterizing peak around 435 nm). The intensity of this fluorescence peak arranges in the ascending order: TNTs – Merck, TNTs – Roha and TNTs – P25, respectively. This indicates that TNTs – Merck possesses the higher photocatalytic activity than the those of other samples according to the better crystallinity of TNTs – Merck. The high photocatalytic activity is controlled by the high crystallinity of the precursor material in which the formation of electron traps is reduced while the recombination of electron-hole pairs is limited [15].

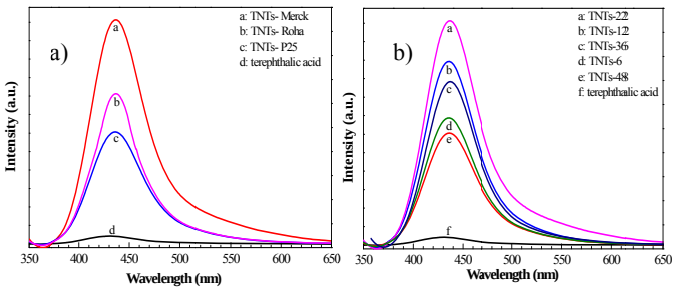

Figure 7. PL spectra of TNTs fabricated from a) various precursors and b) various hydrothermal time in terephthalic acid aqueous solution under 80 mins UVA irradiation.

Figure 7b shows the effect of hydrothermal treatment time on the photocatalytic activity of TNTs. Results show that the intensity of fluorescence peak of TNTs fabricated with various hydrothermal time is changed. TNTs – 22 sample shows the higher photocatalytic activity than those of other samples. In other words, the optimal hydrothermal time is 22 hours, a decrease or increase of the hydrothermal time would lead to the decrease in photocatalytic ability of TNTs. It suggests that TNTs are fabricated from high crystalline precursor powders and with a critical

reaction time would obtain the high performance of photocatalytic activities. However, this is only the initial research to find the hydrothermal time points to determine the best tube structure, the time period from 12 to 22 h and 22 to 36 h need to be examined more smooth. This content will be focused on the future of group.

4. CONCLUSIONS

The selection of nanopowder precursor and hydrothermal time has significantly affected the morphology, microstructure and photocatalytic property of the hydrothermally synthesized TiO_2 nanotubes. The fabricated TNTs from nanopowder precursor with anatase phase (TiO_2 – Merck) shows more uniform morphology and better crystallinity of TiO_2 TNTs than those of other precursors with rutile phase. In this work, the critical reaction time was at 130 ºC for 22 h with the selection of TiO_2 – Merck as the precursor material. The optimized hydrothermal time plays a critical role in the formation and photocatalytic activities of TNTs.

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