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Effect of Calcination Temperature on the Physical Properties and Photocatalytic Activity of TiO2 Nanotubes Synthesized by Simple Hydrothermal Method

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ABSTRACT

Titanium dioxide (TiO_2) nanotubes was synthesized by hydrothermal method and calcined at different temperature (300, 400, 500, 700°C) for 2 hours to study the effect of different calcination temperature on the physical properties and photocatalytic activity of TiO_2 nanotubes was studied. The anatase phase structure of the TiO_2 nanotubes is remained even after calcination at highest temperature studied of 700 °C. However, their morphological structure transformed from nanotubes into nanoparticles after calcination at higher temperature. Hence, reduces the photocatalytic activity of TiO_2 material in degrading methyl orange due to the decreases in surface area and porosity of the materials.

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INTRODUCTION

Recently, nanostructured TiO_2 materials including nanoparticles, nanorods, nanowires and nanotubes have been developed because they show novel chemical and physical properties, being different from their bulk forms. Nanotubes structure is particularly interesting due to their larger surface areas and pore volumes [Adachi *et al*., 2000]. They also have high interfacial charge transfer rate, resulting in the carriers being free to move throughout the length of these nanostructures, which is expected to reduce the e^-/h^+ recombination probability [Macak *et al*., 2007]. Subsequently, various methods such as the assisted– template method [Li *et al*., 2005], the sol–gel process [Brnardic *et al*., 2013], electrochemical anodic oxidation [Perillo and Rodriguez, 2014] and hydrothermal treatment method [Jioa *et al*., 2014], have been applied to prepare titanium dioxide nanotubes (TiO_2-NT's). In the last few years, hydrothermal method has caught interest of researchers because of its ease in handling of nanotubes production and the simple preparation method. The hydrothermal method is also environmentally friendly than other synthesis methods, which can be attributed in part to energy-saving low processing temperature, ability to recycle waste, safe and convenient disposal of waste that cannot be recycled. In addition, the hydrothermal method is conducted through an aqueous process, enabling satisfactory solubility, uniform dispersion of doping metal-ions, and control of stoichiometry (Rashad *et al*., 2013). Hydrothermal treatment can also be used to change the morphology, microstructure, and phase composition of materials by varying the reaction parameters such as temperature and pressure. The hydrothermal method can be defined as a versatile heterogeneous chemical reaction in the presence of solvent, aqueous or non-aqueous conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and pressure [Byrappa and Yoshimura, 2001]. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced. Under the hydrothermal condition it is possible to grow nanotubes of metal oxides by dissolution and crystallization thereby creating distinctive difference in their characteristics at the nano-scale level [Byrappa and Yoshimura, 2007]. Therefore, in this work we employ the hydrothermal method to synthesize TiO_2 nanotubes and explore the effect

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of different calcination temperature on the structure and function of the TiO_2 nanotubes. It is known that, the calcination process has a significant affects on the surface morphology, crystalline phase composition, and photocatalytic properties of the synthesized TiO_2. Therefore, it is necessary to investigate the effect of calcianation temperature on the synthesized TiO_2 nanotubes.

Experiments Preparation:

Titanium dioxide nanotubes were prepared using hydrothermal method. 5 g of commercial TiO_2 powders (Fluka) was dispersed in 10 M NaOH (200 ml) and subjected to hydrothermal treatment at 150°C for 24 h in autoclave. The sample was taken out and washed with HCl followed by distilled water until pH 7 of solution was obtained. The precipitate was collected from solution by filtering using vacuum suction filter with Whatman Grade 40 used as filter paper. Finally, the white precipitate was dried at 80°C for 24 hours and calcined at 300, 400, 500 and 700 °C in atmosphere air for 2 hours.

Characterization:

X-Ray diffraction (XRD) analysis was performed using Bruker D8 Diffractometer with Cu-Kα (λ = 1.54021 Å) and scans were performed in step of 0.2^o/second over the range of 2θ from 10 up to 90^o. TEM and FESEM micrograph was captured using Philips CM12 TEM and ZEISS SUPRA^{TM} 35VP FESEM respectively.

Photocatalytic Study:

The photocatalytic degradation experiment was carried out by adding 0.1 g of samples into 100 ml of 20 ppm MO dye solution. The suspension was subjected to UV irradiation for 3 hours. The UV light source was provided by an UV bench lamp (302 nm, 230V ~ 50 Hz). The aqueous suspension was magnetically stirred throughout the experiment. At every 30 minutes of time intervals 5 ml of aliquot was taken out using syringe and then filtered through 0.45 µm millipore syringe filter. Then absorption spectra were recorded via UV-Vis spectrophotometer (Perkin Elmer Lambda 35 UV-Vis) and the percentage of MO degradation was calculated using the formula in Equation 1 (Razali *et al*. 2009).

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \qquad \text{Equation 1}$$

Where C_0 is the initial absorption of dye and C_t is the absorption of dye after the reaction at *t* time.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of TiO_2 nanotubes calcined at various temperatures. For all studied samples, anatase TiO_2 was formed as indicated by XRD peak appeared at 2θ = ~25.57°, 38.05°, 48.28°, 54.10°, 55.29°, 62.90°, 68.92°, 70.45°, 75.24°, and 82.83°. As the calcination temperature increases the degree of crystallinity of anatase TiO_2 increases which is reflected by their peaks being sharper and narrower. This is because at higher calcination temperature, it may enhance the atomic mobility and causes crystallite growth, resulting in higher crystallinity of anatase TiO_2 (Chang *et al*., 2002). The degree of crystallinity of TiO_2 is an important factor in obtaining active TiO_2. Indeed, amorphous titania is poorly active. An optimum calcination temperature of amorphous samples presumably corresponds to a compromise between an enhanced crystallinity, together with a decreased density of lattice defects, and limited decreases in surface area and coverage by OH groups.

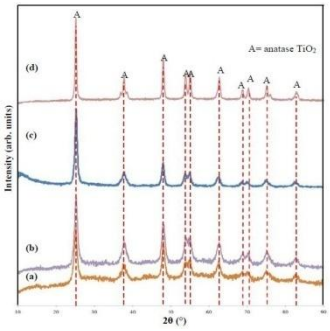

Fig. 1: XRD patterns of TiO_2 nanotubes calcined at (a) 300 °C (b) 400 °C (c) 500 °C (d) 700 °C for 2 hours.

In order to support the XRD result, Raman spectroscopy was carried out. The Raman spectra of TiO_2 nanotubes calcined at 300, 400, 500 and 700 ^oC are illustrated in Figure 2 (a), (b), (c), (d), respectively. It can be seen that similar Raman spectra was obtained with the presence of the peaks at 147cm^{-1}(Eg), 197 cm^{-1}(Eg), 399 cm^{-1} (B1g), 516 cm^{-1} (A1g/B1g unresolved doublet) and 640 cm^{-1}(Eg) which is assigned to TiO_2 in the form of anatase. As reported by Berger *et al*. (1993) and Zhang *et al*. (2000) the strongest peak at 143 cm^{-1} (Eg mode) was attributed to the external vibration of the anatase structure, therefore confirming the XRD analyses that the TiO_2 is an anatase phase.

It has been reported anatase phase exhibits better photocatalytic activity than other phases of TiO_2 (Tanaka *et al*., 1991). Several reasons have been proposed to explain that the most photocatalytically active samples have been found within the series of anatase samples. For instance, higher energy position of the anatase conduction band could be the reason because it increases the

driving force for the electron transfer to O_2 to form active superoxide radicals. This radical are extremely reactive and readily attack organic pollutant molecules and degrading them into CO_2 and H_2O (Razali *et al*., 2009). Furthermore less dense structure of anatase, caused higher mobility of the charge carriers to proceed with further reaction for the formation of active radical.

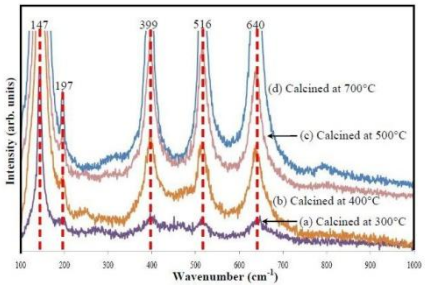

Fig. 2: Raman spectra of TiO_2 nanotubes calcined at (a) 300 °C (b) 400 °C (c) 500 °C (d) 700 °C for 2 hours.

Figure 3 shows the FESEM micrographs of the TiO_2 nanotubes which were calcined at various temperatures. At calcinations of 300 and 400 °C, the fibrous-like structures were observed and tend to stick together (Figure 3(a) and (b)). However at 500 °C, the isolated fibrous-like structure appeared to have broken into small particles (Figure 3(c)). The small particles that constitute the fibrous structure were more visible at higher magnification of FESEM (Figure 4). The tubes were severely sintered and consolidated, the tubular architecture gradually disappeared. Further calcination at higher temperature of 700 °C, had resulted in complete breaking down of fibers to form agglomerated particles (Figure 3 (d)).

Further analyses on morphological transformation of TiO_2 nanotubes were studied using TEM. The TEM micrographs of the TiO_2 nanotubes calcined at 300, 400, 500 and 700 ^oC are shown in Figure 5. At 300 ^oC, the formation of nanotubes structure had been proven with the existence of a hollow space inside the fibrous (~4 nm and ~10 nm for inner and outer diameter, respectively) (Figure 5(a)). After calcination at 400 °C, the nanotubes structures remain in their shape. Previously, An *et al*. (2008), also reported the treated nanotubes can maintained a tubular structure when calcined at 400 ^oC. Nevertheless, in this study the aggregation of nanotubes had occurred due to heat treatment thus slightly increases the inner diameter of nanotubes (Figure 5(b)). They transformed into nanoparticle after calcination at higher temperature (500 and 700 °C). At 500 ^oC, the size of the nanoparticle produced was about 14 nm (Figure 5(c) and became larger after cacination at 700°C (Figure 5(d)). The transformation of the morphology from nanotubes to nanoparticles, as a result from dehydration of inter-layered OH groups which accelerate the crystal growth and induce the change of crystallinity thus, destroy the nanotubes structure to produce irregular nanoparticles (Razali *et al*., 2014).

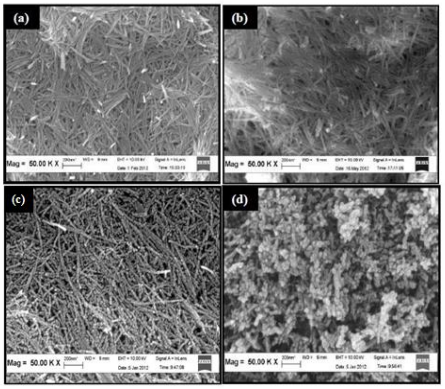

Fig. 3: FESEM micrographs of TiO_2 nanotubes calcined at (a) 300 °C (b) 400 °C(c) 500 °C (d) 700 °C for 2 hours.

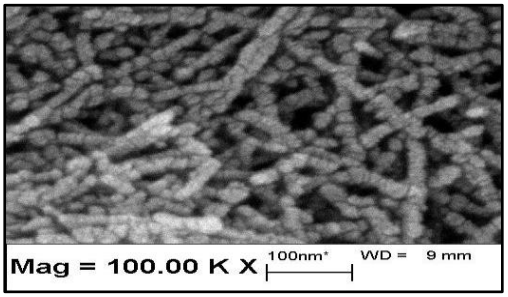

Fig. 4: FESEM micrographs of TiO_2 nanotubes calcined at 500 °C for 2 hours with higher magnification (100.00 K X)

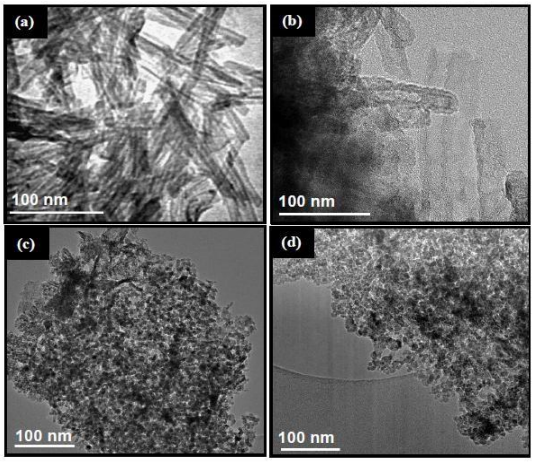

Fig. 5: TEM micrographs of TiO_2 nanotubes calcined at (a) 300°C (b) 400°C (c) 500°C (d) 700°C for 2 hours.

It can be concluded that at calcination temperature of 300°C, nanotubular structure was observed and still preserved at 400 °C, however their inner and outer diameter increases resulted from crystallite growth in the tube walls during the high temperature annealing thus promoted nanotubes agglomeration. At 500 °C, the tubular structure had broken into small particles due to destruction of nanotube, but the particles were still attached to each others. At 700 °C, the nanotube structure was totally degraded and subsequently transformed to isolated nanoparticles having an irregular shape. The schematic of nanotubes transformation to nanoparticle after calcination at higher temperature was illustrated in Figure 6.

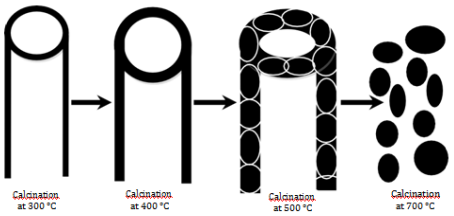

Fig. 6: Illustration of morphology transformation of nanotubes into nanoparticles after calcination at different temperatures for 2 hours.

Figure 7 shows the photocatalytic activity of the as-synthesized pH 7 sample which was calcined at various temperatures. After calcination at 300 °C, the sample showed the highest degradation of MO (81.90 %) after 3 hours under UV irradiation. This could be attributed to their tubular morphology and anatase TiO_2 phase. The formation of anatase after calcination has high amount of oxygen vacancy sites which would contribute to the high degradation of MO (Ding *et al*., 2000; Song *et al*., 2010). The present of more oxygen vacancy sites were produced more active radical for degradation of MO because the oxygen vacancy will reacts with oxygen to produce active radical. Meanwhile, the tubular morphology promotes diffusion of reactants and products, thus enhancing the photocatalytic activity by facilitating access to the reactive sites on the surface of the photocatalysts. The nanotube structure can also help rapid mass transfer of the adsorbed molecules form bulk solution onto the catalyst surface, and therefore causing the photocatalytic process to be accelerated (Wang *et al*., 2005). The explanation justify the large degradation of MO was observed from sample calcined at 300 °C. After calcination at 400 °C the photocatalytic activity of the sample slightly decreases. That is probably due to the agglomeration process which leading to thicker tube walls and destruction of nanotubes structure, thus significant decrease of the surface area after calcination at high temperature (Lin *et al*., 2015). Further calcination at higher temperature studied of 500 and 700 °C, results in the performance of the TiO_2 for MO degradation to be further reduced. It could be explained by the transformation of the morphology of the samples into the small irregular particle rather than tubular structure which would reduce the surface area and porosity of the materials and thus photocatalytic activity.

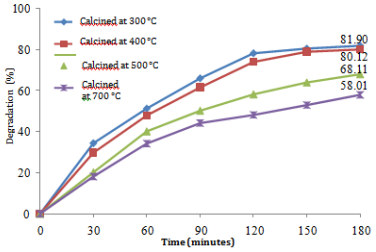

Fig. 7: Photocatalytic degradation of MO using TiO_2 materials calcined at different temperature for 2 hours.

Conclucion:

The effect of calcination temperature on physical properties (morphology and phase structure) and photocatalytic activity TiO_2 nanotubes was investigated. The morphology of nanotubes structure was observed at 300 °C and retained after calcination at 400°C. However their diameter became larger due to nanotubes agglomeration. At calcination temperatures of 500 °C the nanotubes undergo a transformation to nanoparticles gradually. At 700 °C, the nanotubes were completely transformed into nanoparticle. Somehow, the phase structure of anatase TiO_2 retained even after calcination at highest temperature studied (700 °C). Even though the anatase TiO_2 remained their photocatalytic activity reduces after calcined at higher temperature due to the morphology transformation from nanotubes to nanoparticles which would reduce the surface area and porosity of the materials.

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