International Journal of Engineering & Technology, 7 (2.23) (2018) 455-458

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Hydrogen Production Through Water Splitting Reaction Using Titanium Dioxide (Tio_2) Nanotubes Photocatalyst

Mohdhasmizamrazali*, Nurarifah Ismail, Khairulanuar Mat Amin

School Of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia
**Corresponding Author E-Mail:Mdhasmizam@Umt.Edu.My*

Abstract

Nowadays, the most ideal process for hydrogen production is to use water as a hydrogen source through water splitting reaction with the present of the titanium dioxide photocatalysts. Titanium dioxide nanotubes (TiO_2-NT's) was synthesized using facile hydrothermal method. TEM micrograph shows that the synthesized TiO_2-NT's had tubular structure with "hair-like" nanoscopic filaments with large specific surface area, which is needed to be a high performance photocatalyst. The saiz of nanotube are 4 nm and 10 nm for inner and outer diameters, respectively. Meanwhile, their surface area was found to be 226.52 m^2/g. XRD pattern revealed that the phase structure of synthesized TiO_2-NT's was anatase TiO_2. Synthesized TiO_2-NT's was tested for hydrogen gas production managed to produce 80 µmol after 5 hours reaction.

Keywords:*Hydrogen; nanotubes; photocatalyst; titanium dioxide.*

1. Introduction

Hydrogen energy is expected to become as a carbon free energy carrier in the future, because of their efficiency and complete absence of toxic emissions. However, main subject for realization of hydrogen energy is to find out the best way for cheap bulk hydrogen gas production.
Hydrogen can be produced using different process such as methanol decomposition (MD) [1], steam reforming (SRM) and partial oxidation (POM) [2-5]. Commercially, hydrogen gas was produced through water gas shift reaction (Equation 1.1).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(Equation 1.1)}$$

Although this reaction could be used for hydrogen gas production, however high temperatures is needed make it highly costing. Nowadays, the efficient route to produce hydrogen gas is via water splitting reaction. In this photochemical reaction, hydrogen is produced from water with presence of light and TiO_2photocatalyst. The TiO_2photocatalyst uses energy from light to dissociate water molecule into hydrogen and oxygen (Equation 1.2).

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \text{(Equation 1.2)}$$

TiO_2photocatalyst, especially TiO_2 nanotubes are attractive attributed to their non-toxicity, inexpensive, stable against photocorrosion and chemical corrosion [6]. TiO_2 nanotubes was explored as a photocatalyst for energy generation such as methane and methanol through carbon dioxide (CO_2) photo-reduction [7] and was widely used in electrochemical devices, photovoltaic dye sensitized solar cells and gas sensors application [8-10]. This is due to their large surface area, large surface to volume ratio and with uniform inner and outer diameters of the nanotubes make these elongated hollow structures an excellent candidate as photocatalyst [11]. Furthermore, the high sedimentation rate of the nanotubes facilitates the used as the photocatalyst due to their easy separation, collection and recycling the nanotubes powders from a suspension [12-14]. TiO_2 nanotubes photocatalyst can be synthesized by numerous methods including templating, anodization and chemical vapour deposition. The requirement of controlling nanostructure dimension is vital for specialised applications. Regarding to that, the hydrothermal process has proven to be effective methods to synthesize elongated TiO_2 nanotubes with uniform dimensions. Preparation using this method also avoids the use of organic precursors, which can lead to contamination of the product and environmental pollution. Thus, TiO_2 nanotubes was synthesised using hydrothermal method using commercial TiO_2 powder as precursor. The synthesised nanotubes was tested for hydrogen gas production via water splitting reaction.

2. Experimental

2.1. Preparation of TiO_2 Nanotubes

2 g of TiO_2 powders (Fluka) was dispersed in 10 M NaOH (100 ml) and heated at 150°C for 24 h in teflon-lined autoclave. After that, the sample was washed with HCland distilled water until pH 7. In order to the product, the precipitate was filtered using vacuum suction filter The collected precipitate was dried at 80°C in oven for 24 hours and called as synthesized sample. Finally, as-synthesized sample was calcined at different temperature (300, 400, 500 and 700 °C) for 2 hours.

2.2. Characterization

X-Ray diffraction (XRD) was carried out using Bruker D8 Diffractometer with Cu-Kα (λ = 1.54021 Å) and scannedfrom 10-80^o of 2θ. TEM micrograph was captured using Philips CM12 TEM and Micromeritics ASAP 2000 instrument was used for the nitro-

gen gas adsorption analysis at the temperature of -196 °C for surface area and porosity measurements.

2.3. Photocatalytic Study for Hydrogen Gas Production Via Water Splitting Reaction

The reaction was done in a closed gas-circulation system. 1g of prepared photocatalyst samples was suspended in water and stirred continuously in an irradiation reactor made of Pyrex glass showed in Figure 1. A high-pressure Hg lamp was utilized as the ultraviolet (UV) light source. The reaction was run for 5 hours and the produced hydrogen gas was measured for every 30 minutes using hydrogen gas detector.

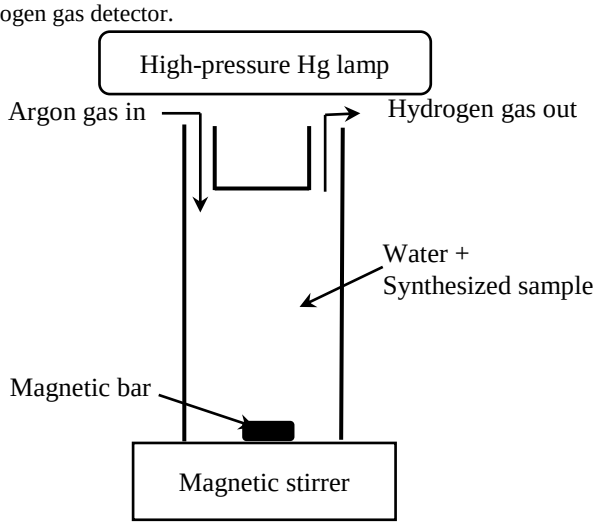

Figure 1: Photocatalytic testing reactor.

3. Results and Discussion

As-synthesized sample is assigned to hydrogen trititanate ($H_2Ti_3O_7$) ascribed to the peaks appeared at 2θ = 25.43° and 48.40° (Figure 2(a)). The hydrogen titanate was retained after calcination at 300 °C (Figure 2(b)), somehow their peaks became broader due to the dimensionality changes [15]. After calcination at 400, 500 and 700 °C, hydrogen trititanate was decomposed to produced TiO_2 with anatase phase 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° (Figure 2(c)-(e)). TiO_2anatase was formed via simple decomposition reaction of hydrogen trititanate as in equation 1.3.

$$H_2Ti_3O_7 \rightarrow TiO_2 + H_2O \qquad \text{(Equation 1.3)}$$

The formation of TiO_2anatase is interesting, as it has been reported that exhibited better photocatalytic activity than other phases and amorphous TiO_2 [16-18].

TEM analysis was carried out the study the morphology of TiO_2anatase obtained. Only 2 samples was selected which are calcined samples at 400°C and 700°C. At 400 °C, the nanotubes sample was obtained as the elongated hollow nanostructured was observed in the TEM image. The inner and outer diameters of nanotube was found to be ~4 nm and ~10 nm, respectively (Figure 3(a)). The nanotubes was destroyed and altered into nanoparticle at 700°C. This alterationoccurred because the dehydration of interlayered OH groups which accelerate the crystal growth and induce the change of crystallinity thus, perished the nanotubes structure to produce irregular nanoparticles [19,20]. The size of anatase TiO_2 nanoparticles obtained was within 20-30 nm.

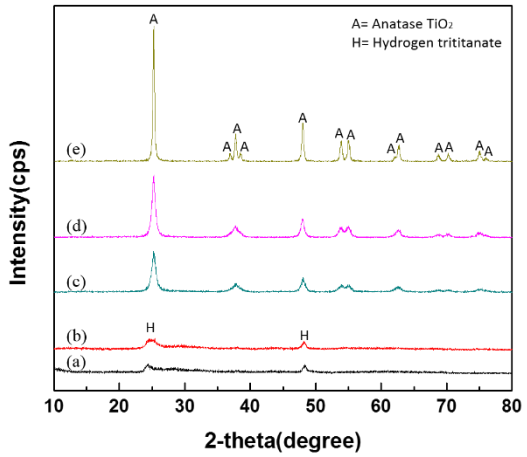

Figure 2: XRD patterns of (a) as-synthesised sample and after calcination at (b) 300 °C (c) 400 °C (d) 500 °C and (e) 700 °

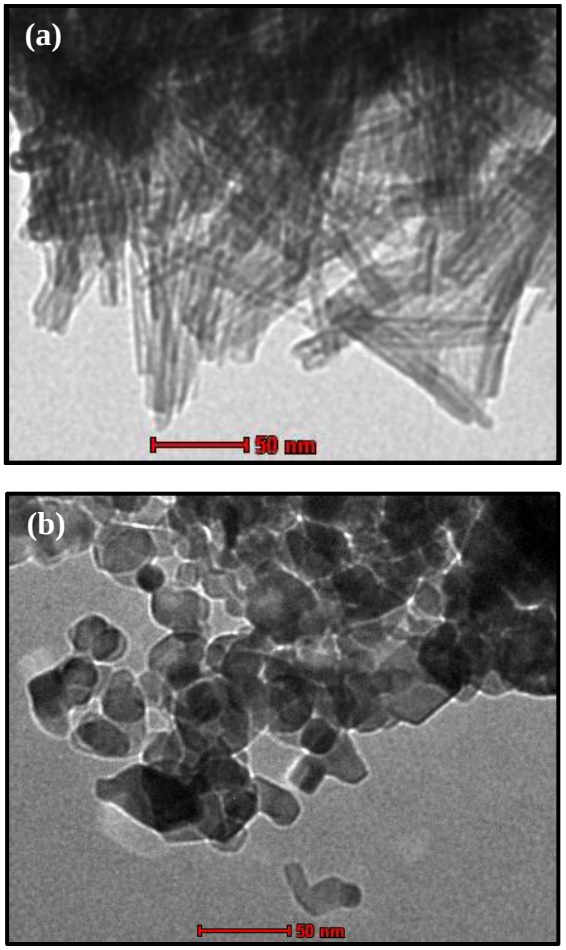

Figure 3: TEM micrographs of synthesized samples after calcination at (a) 400 °C (b) 700 °C for 2 hours.

As shown in Table 1, the surface area of TiO_2 precursor powder was only 9.28 m^2/g. Nevertheless, calcined sample at 400°C which is TiO_2 nanotube possessed large surface area which is 226.52 m^2/g. It is believed that the inner and outer surfaces of the nanotube structure were the major reason for their large surface area [21]. However, after calcination at 700 °C, the BET surface area of the sample was reduced to 60.47 m^2/g. This is due to the morphology transformation and proved the destruction of tubular structure in this sample. Moreover, the coarsening of particles and pore coalescence at higher temperatures (700 °C), resulted in a significant lower surface area [21].

Figure 4 shows the isotherm plot of calcined samples at 400 °C and 700 °C, which are TiO_2 nanotubes and TiO_2 nanoparticles, respectively. Both studied samples exhibit similar types of isotherm, having a type IV mode, indicating the presence of mesopore in the system. Mesopore materials having pores sizes generally in the range of 2 to 50 nm. For type IV isotherm, it could be observed that the adsorption of the nitrogen gas is low at the initial relative pressure (P/P_o), but then increase markedly at higher values of P/P_o where pore capillary condensation takes place. A hysteresis effect associated with the pore condensation and studied samples display closely with Type H3 hysteresis loops, implying the slit shaped mesoporous characteristics of materials.

Figure 5 displays that the TiO_2 nanotubes, the synthesized sample calcined at 400°C produced the highest amount of hydrogen gas with 80 µmol/g after 5 hours irradiation. Meanwhile, TiO_2 nanoparticles (sample calcined at 700 °C) and sample calcined at 500 °C only managed to produce 42 and 60 µmol/g of hydrogen gas, respectively. The loss in photocatalytic activity of calcined-samples at 500 and 700 °C, were due their low surface area. Low surface area will be resulted in less active sites. Less active side will lead to the less accessibility of water molecule to react with the photogenerated electron on photocatalyst surface for H_2 production. Commercial TiO_2 precursor gave the lowest photocatalytic activity due to the lowest surface area. Meanwhile, the photocatalytic activity of
as-synthesised sample and sample calcined at 300 °C were very low attributed to their amorphous state as proved by XRD analysis. The amorphous phase, which usually comprises numerous defects such as impurities act as recombination centers thus reduces the photocatalytic performance [18].

Table 1: BET surface area of TiO_2 precursor and synthesized sample after calcination at 400 and 700 °C.

Sample	BET surface area (m^2/g)
TiO_2 precursor	9.28
Calcined at 400 °C (TiO_2 Nanotubes)	226.52
Calcined at 700 °C(TiO_2 Nanoparticles)	60.47

4. Conclusion

TiO_2 nanotubes was produced using hydrothermal method. The nanotubes was obtained after calcination at 400 °C. In general, hydrogen gas was successfully produced through water splitting reaction using synthesized TiO_2photocatalyst and commercial TiO_2. TiO_2 nanotubes photocatalyst gave the highest catalytic activity with 80 µmol/g hydrogen gas after 5 hours irradiation because of larger surface area and high crystallinity.

Acknowledgement

The authors are grateful to Universiti Malaysia Terengganu (UMT) for providing the facilities to carry out this project and Ministry of Higher Education of Malaysia for the financial support vote FRGS 59358.

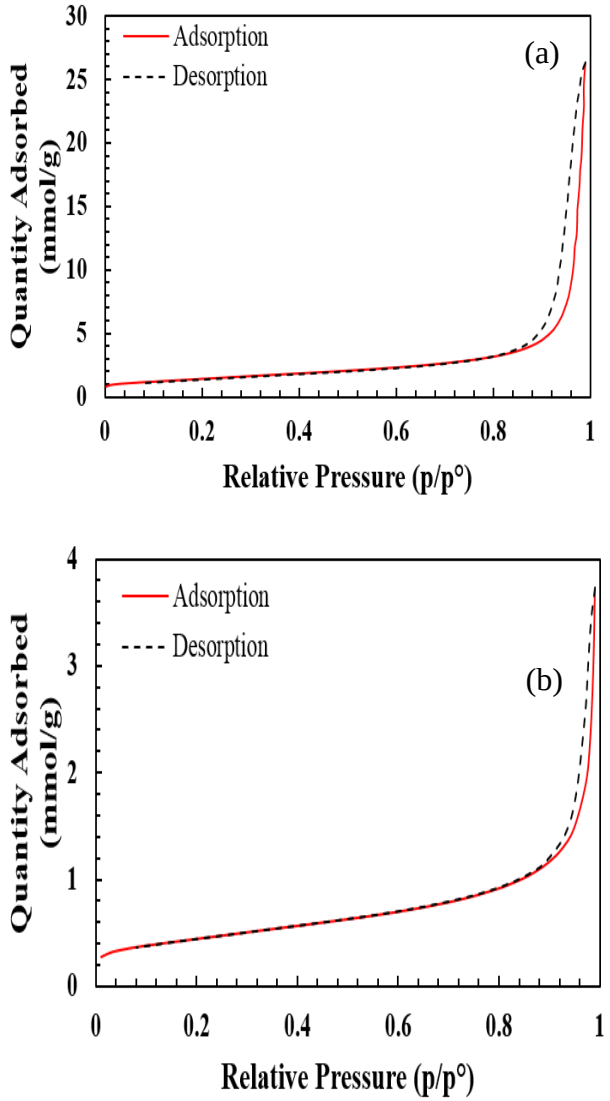

Figure 4: Nitrogen gas adsorption isotherm plot of synthesised samples after calcination for 2 hours at (a) 400 °C (TiO_2 nanotubes) and (b) 700 °C (TiO_2 nanoparticles)

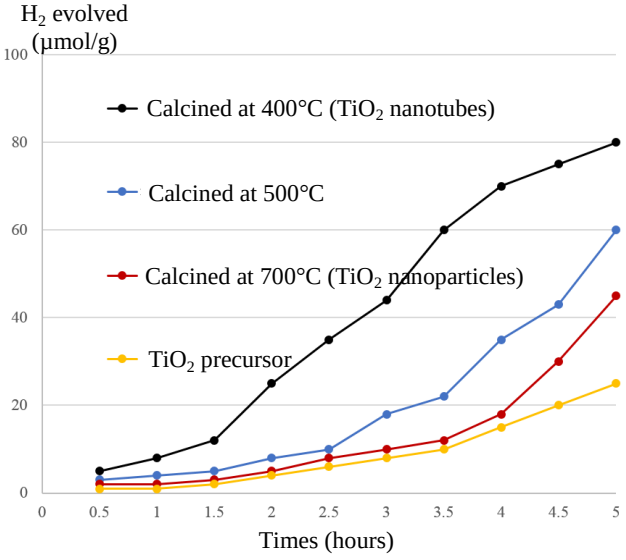

Figure 5: Hydrogen production through water splitting reaction using TiO_2 precursor and synthesised sample calcinedat different temperature.

References

[1] Fan M, Xu Y, Sakurai J, Demura M, Hirano T, Teraoka Y, Yoshigoe A. Spontaneous activation behavior of Ni3Sn, an intermetallic catalyst, for hydrogen production via methanol decomposition. International Journal of Hydrogen Energy. 40 (2015)12663-12673.

[2] Chen YF, Lee CY, Yeng MY, Chiu HT. Preparing titanium oxide with various morphologies. Materials Chemistry and Physics. 81 (2003) 39-44.

[3] González-Cobos J, Ruiz-López E, Valverde JL, de Lucas-Consuegra A. Electrochemical promotion of a dispersed Ni catalyst for H2 production via partial oxidation of methanol. International Journal of Hydrogen Energy. 41 (2016) 19418-19429.

[4] Czylkowski D, Hrycak B, Jasiński M, Dors M, Mizeraczyk J. Microwave plasma-based method of hydrogen production via combined steam reforming of methane. Energy. 113 (2016) 653-661.

[5] Roselin LS, Chiu HW. Production of hydrogen by oxidative steam reforming of methanol over Cu/SiO2 catalysts. Journal of Saudi Chemical Society. 2017 1-13

[6] Lei Y, Zhang C, Lei H, Huo J. Visible light photocatalytic activity of aromatic polyamide dendrimer/TiO_2 composites functionalized with spirolactam-based molecular switch. Journal of Colloid and Interface Science. 406 (2013) 178-185.

[7] Li FT, Zhao Y, Hao YJ, Wang XJ, Liu RH, Zhao DS, Chen DM. N-doped P25 TiO_2–amorphous Al_2O_3 composites: One-step solution combustion preparation and enhanced visible-light photocatalytic activity. Journal of Hazardous Materials. 239. (2012):118-127.

[8] Perillo PM, Rodríguez DF. The gas sensing properties at room temperature of TiO_2 nanotubes by anodization. Sensors and Actuators B: Chemical. 171 (2012) 639-643.

[9] Shen PS, Tai YC, Chen P, Wu YC. Clean and time-effective synthesis of anatase TiO_2nanocrystalline by microwave-assisted solvothermal method for dye-sensitized solar cells. Journal of Power Sources. 247 (2014) 444-451.

[10] Xiang C, She Z, Zou Y, Cheng J, Chu H, Qiu S, Zhang H, Sun L, Xu F. A room-temperature hydrogen sensor based on Pd nanoparticles doped TiO_2 nanotubes. Ceramics International. 40 (2014) 16343-16348.

[11] Chen WT, Jovic V, Sun-Waterhouse D, Idriss H, Waterhouse GI. The role of CuO in promoting photocatalytic hydrogen production over TiO_2. International Journal of Hydrogen Energy. 38 (2013) 15036-15048.

[12] Li XH, Liu WM, Li HL. Template synthesis of well-aligned titanium dioxide nanotubes. Applied Physics A. 80 (2005) 317-20.

[13] Rashad MM, Elsayed EM, Al-Kotb MS, Shalan AE. The structural, optical, magnetic and photocatalytic properties of transition metal ions doped TiO2 nanoparticles. Journal of Alloys and Compounds. 581 (2013) 71–78.

[14] K. Byrappa, Yoshimura, M. (2001). Handbook of hydrothermal technology, Noyes Publications, New Jersey, USA.

[15] Weng LQ, Song SH, Hodgson S, Baker A, Yu J. Synthesis and characterisation of nanotubulartitanates and titania. Journal of the European Ceramic Society. 26 (2006) 1405-1409

[16] Tanaka K, Capule MF, Hisanaga T. Effect of crystallinity of TiO2 on its photocatalytic action. Chemical Physics Letters. 187 (1991) 73-76.

[17] Chang YS, Chang YH, Chen IG, Chen GJ, Chai YL. Synthesis and characterization of zinc titanatenano-crystal powders by sol–gel technique. Journal of Crystal growth. 243 (2002) 319–326.

[18] Rao, C.N.R.,Rao, K.J. 1978. *Phase Transitions in Solids: An Approach to the Study of the Chemistry and Physics of Solids*, McGraw-Hill, New York, London,

[19] Razali MH, Ahmad-Fauzi MN, Mohamed AR, Sreekantan S. Effect of Calcination Temperature on the Morphological andPhase Structure of Hydrothermally Synthesized Copper ion Doped TiO_2 Nanotubes. *Advanced Materials Research*, 1024 (2014) 7-10.

[20] Dris, M.R.M., Sheng, C.K., Isa, M.I.N. and Razali, M.H., A study of cadmium sulfide nanoparticles with starch as a capping agent. *Int J Tech*, *1* (2012) pp.1-7.

[21] Razali, M.H., Noor, A.F.M. and Yusoff, M., Hydrothermal Synthesis and Characterization of Cu^{2+}/F^{-}Co-Doped Titanium Dioxide (TiO_2) Nanotubes as Photocatalyst for Methyl Orange Degradation. Science of Advanced Materials, 9(2017) 1032-1041.