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Degradation of Rhodamine B Dye by TiO_2 Nanotubes Photocatalyst Synthesized via Alkaline Hydrothermal Method

T MAZLINA Mat Darus [a] and JUSMAN Muktar [b]

Department of Physics, Faculty of Science and Mathematics, Sultan Idris Education University, 35900, Tg. Malim, Perak, Malaysia

Abstract. Titanium dioxide (TiO_2) nanotubes have successfully been synthesized by using one step approach of hydrothermal method. Commercial TiO_2 (anatase) powder was used as precursor to synthesize the TiO_2 nanotubes. The TiO_2 nanotubes were synthesized at 120 ^oC/20 hrs in an alkaline solution of NaOH. The photocatalytic study of the as-synthesized samples was conducted by analyzing the degradation of Rhodamine B (Rh B) dye under UV light irradiation. Rh B is a toxic dye which is commonly used in textile industry. It is the one of the most common pollutants in the effluents and highly soluble in water. A comparison study was carried out in order to investigate the photocatalytic activity between the synthesized TiO_2 nanotubes and the commercial TiO_2 nanoparticles. Results show that the TiO_2 nanotubes exhibits better photocatalytic activity in the degradation of Rh B as compared to the TiO_2 nanoparticles.

1 Introduction

Photocatalysis is use of light to activate a catalytic material which has tremendous potential for environmental application. Titanium dioxide (TiO_2) nanosized particles are the most popular photocatalyst which attract much attention for both fundamental research and water treatment technology [1]. Enormous research is going on with TiO_2 materials to produce some promising applications in the areas of photovoltaic and photocatalysis to photo electrochromics and sensors [2, 3]. The term photocatalysis means that TiO_2 uses energy from light (photo) to help chemical reactions to occur (catalysis). This involves the generation of hydroxyl radicals used as the primary oxidant for degrading organic pollutants [1].

TiO_2 belongs to the family of transition metal oxides. There are four commonly known polymorphs of TiO_2 found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO (B) (monoclinic). The most common forms are anatase and rutile. Anatase is used in photocatalysis and photon electron transfer [4]. Brookite however, is uncommon and unstable due to the most dense structure and smallest unit cell [5] and rutile is usually used in light scattering.

The extensive use of dye and pigment in textile, plastic, food, paper printing, pharmaceutical and cosmetic industries has arouse environmental issues in dealing with the effluent [6-7]. The release of the organic pollutants into the water will colour the water and inhibit the penetration of sunlight to the lower layer and affect the aquatic life. Currently, the conventional method used to degrade the dye of the contaminated water include primary (adsorption, flocculation), secondary (biological methods), and chemical processes (chlorination, ozonization) [8-9]. However, the drawback of these methods is that they only transfer the non-biodegradable matter into sludge, giving rise to a new type of pollution, which needs further treatment [10-11]. Among various oxide semiconductor photocatalysts, TiO_2 photocatalyst is found to be a more efficient catalyst for photocatalytic degradation of pollutants due to faster electron transfer to molecular oxygen [12]. Apart from that, TiO_2 is the most suitable catalyst for widespread environmental application because of its biological and chemical inertness, strong oxidizing power, non-toxicity and long-term stability against photo and chemical corrosion [13-14].

In this study, TiO_2 nanotubes were synthesized by using hydrothermal method in alkaline solution. The method employed in this study is an easy and economical approach as compared to the conventional methods. The morphologies of the TiO_2 nanostructure can be controlled by changing the concentration of alkaline solution, hydrothermal reaction temperature and time [15]. TiO_2 nanotubes structure was chosen to be synthesized in this study due to its excellence properties compared to the common nanoparticles in photodegradation of organic dyes [16]. The high rate of electron hole combination on TiO_2 particles (within nanoseconds) results in low efficiency of photocatalysis. TiO_2 nanotubes morphology can provide direct electron transferring pathway for photo generated electrons and decrease the carriers' recombination rates. The photo generated electrons and holes are essentials for the degradation process through redox reaction.

Corresponding author: [a] mazlina.md@fsmt.upsi.edu.my; [b] mazeq22@yahoo.com.

2 Experimental

All chemical reagents used in this study were of analytical grade from Sigma-Aldrich. TiO_2 nanotubes were synthesized via hydrothermal method in sodium hydroxide (NaOH) solution. In a typical procedure, 2 g of anatase TiO_2 was added into 50 ml of 10 M NaOH solution and stirred on the magnetic stirrer for 45 minutes. The mixture was then transferred to a Teflon-line stainless autoclave which was heated at 120 ^oC for 20 hrs. The sample was then rinsed for several times and dried. The morphology of the as-synthesized sample was analyzed by Hitachi SU 8020 UHR field emission scanning electron microscope (FESEM) and JEOL 2100 transmission electron microscope (TEM).

For photocatalytic measurement, 80 ml of 1×10^{-5} M of Rh B dye was transferred into the crystallization dish followed by the addition of 7 mg of TiO_2 nanotubes photocatalyst into the solution. The solution was allowed to reach an adsorption–desorption equilibrium for 30 min before UV-light irradiation. A 100W UV lamp with 254 nm wavelength was used as light source to trigger the photocatalytic reaction. The average light intensity striking the surface of the reaction solution was about 9.75 mW/cm^{-2}. For every 10 mins of time interval, 2.2 ml of the mixture was taken out by using pipette and filled in the small vial. The UV absorbance intensity of the degraded solution was then analysed by using UV-Vis spectrophotometer (Agilent Technology). The method was repeated for TiO_2 nanoparticles photocatalyst for comparison.

3 Results and discussion

The morphology of the commercial anatase TiO_2 used as precursor is shown in Fig. 1 (a). The anatase TiO_2 has the nanoparticles structure with diameter between 40-50 nm. Well-defined nanotubes structures TiO2 have successfully been synthesized from TiO_2 nanoparticles by using hydrothermal method. Fig. 1 (b) shows the morphology of the as-synthesized TiO_2 nanotubes. The external diameter of the nanotubes is about ~ 8 nm and length between 1.0 to 1.5 µm. From BET measurement, the surface area of the TiO_2 nanoparticles is 58.57 m²/g and 19.80 m²/g for the TiO_2 nanotubes.

The photocatalytic activity of both samples was evaluated by means of photocatalytic degradation of Rh B in aqueous solution at ambient temperature under UV-light irradiation. The major peak of UV absorbance for Rh B is at 550 nm as shown in Fig. 2 (a). The UV absorbance of the dye mixed with the photocatalyst was measured for every 10 minutes of time interval after being exposed to the UV light. The intensity of the peak decreases when the mixtures were exposed to the UV light. The decreasing in UV absorbance implies the reduced of Rh B concentration. This can also be observed visually by the decreasing in the intensity of the pink colour of Rh B into colourless solution. The results of the UV absorbance are shown in Fig. 2 (b) and 2 (c) respectively.

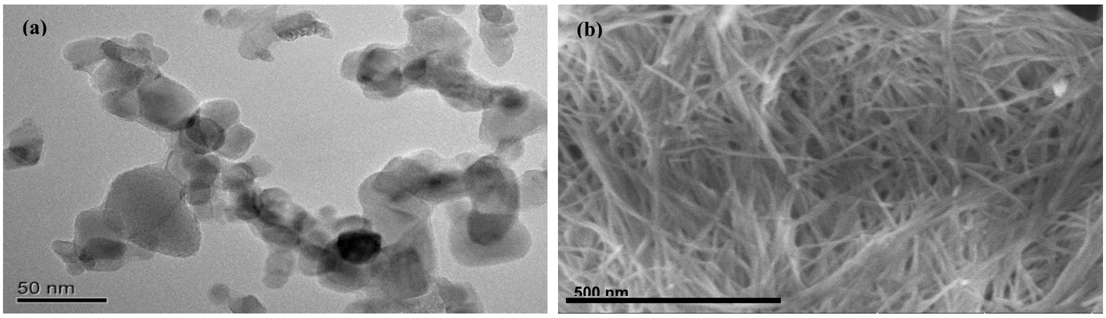

Figure 1. (a) Commercial anatase TiO2 nanoparticles used as precursor and (b) uniform TiO2 nanotubes synthesized using (a) by hydrothermal method

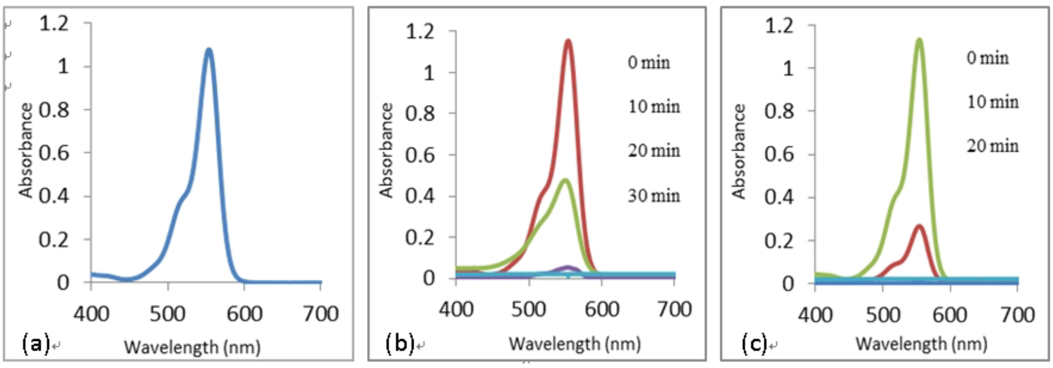

Figure 2. (a) Major peak of UV absorbance for pure Rh B. UV absorbance of Rh B when exposed under UV light added with photocatalysts; (b) commercial TiO2 nanoparticles (c) TiO2 nanotubes.

Fig. 3 shows the reduced of Rh B concentration degraded by both photocatalysts in less than one hour. It is found that, the commercial TiO_2 nanoparticles degraded Rh B completely in 30 minutes. In comparison, the TiO_2 nanotubes degraded Rh B in just 20 minutes. The result shows that TiO_2 in the form of nanotubes structure has much better photocatalytic activity in degrading Rh B compared to the nanoparticles. Despite of having smaller surface area as compared to the nanoparticles, the nanotubes structure facilitates efficient interfacial charge-transfer for Rh B degradation. A study by Zheng et.al. found that, ZnO nanocrystals with smaller BET surface area has higher photocatalytic activity since it is not only relates to the surface adsorption ability but also relates to the type and concentration of oxygen defects on the surface and/or surface layer [17].

The photocatalytic reaction kinetics is generally described by a classic model Langmuir-Hinshelwood (LH) adsorption kinetic model as shown by Eq. 1. The photocatalytic degradation reaction follows the linear relationships of *ln* (C_o/C) versus time:

$$ln\,(C_o/C) = kt + A \qquad (1)$$

where C is the concentration, C_o denotes the initial concentration, the slope k is the apparent reaction rate, and the intercept A is the value of ln(Co/C) when irradiation was initiated.

Fig. 4 shows the linear fit between the *ln* (C_o/C) and irradiation time. From this relation, the photocatalytic rate constant for the photocatalysts can be determined. The value of the apparent photocatalytic reaction kinetics for TiO_2 nanoparticles and TiO_2 nanotubes are 0.095 min^{-1} and 0.121 min^{-1} respectively. Higher rate constant corresponds to higher photocatalytic activity of the photocatalyst, which reflects to faster degradation processes of Rh B dye. The linear relationship of the Rh B degradation exhibits first order kinetics, matching well with the classic LH model. In the LH model, the reaction of degradation follows a rate determining step where an adsorbed molecule reacts with a reactive transient such as a OH radical formed on the surface by oxidation of H_2O or a surface OH group.

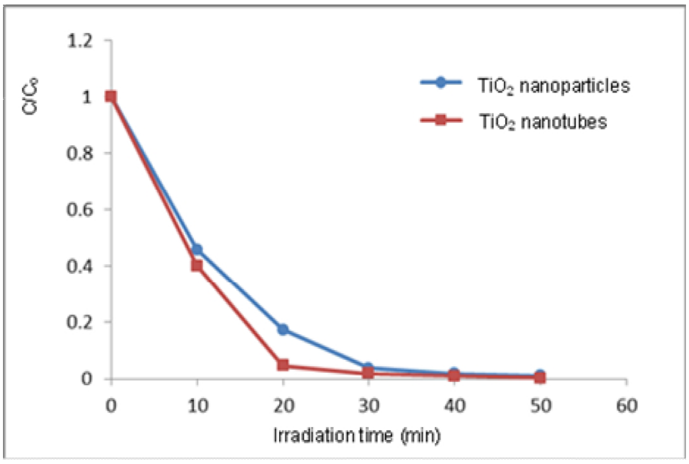

Figure 3. Degradation of Rh B by both photocatalysts.

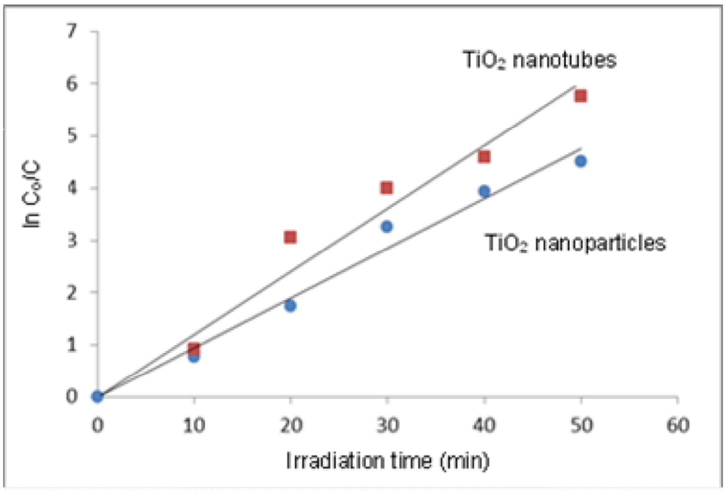

Figure 4. The apparent photocatalytic reaction kinetics for both photocatalysts.

4 Summary

In this study, TiO_2 nanotubes have successfully been synthesized by using commercial TiO_2 nanoparticles via alkaline hydrothermal method. The optimum condition to synthesize the TiO_2 nanotubes is by using 10 M NaOH heated at 1200 ^{o}C for 20 hours. The synthesized TiO_2 nanotubes demonstrated superior photocatalytic activity in the degradation of Rh B under UV light as compared to the TiO_2 nanoparticles. The morphology difference between TiO_2 nanotubes and TiO_2 nanoparticles has significant effects in the photocatalytic reaction kinetics. The ability in the degradation process is closely related to the reactive electron-hole pairs into interfacial charge-transfer. The reduction of the recombination rate of the photo-electron promotes direct electron transferring pathway for photo generated electrons, hence increasing the electron-hole utilization efficiencies to produce hydroxyl ions.

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