Direct synthesis of mesoporous TiO2 using PVA as surfactant template and assessment of their photocatalytic activity

by Ridhawati Thahir

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Abstract. Mesoporous TiO_2 with the high photocatalytic activity in methylene blue adsorption and Cu(II) were effectively synthesized using PVA as a surfactant template through hydrothermal treatment. The preparation of mesoporous TiO_2 was identified by X-ray diffraction (XRD), nitrogen adsorption, scanning electron microscopy (SEM) with EDX, differential scanning calorimetry (DSC), and fourier transform infrared (FTIR). The results of TiO_2 by nitrogen adsorption were indicative of mesoporous materials type IV with H2-type hysteresis loop with specific surface area 106 m^2/g, pore volume 0.18 cc/g, and pore diameter 11 nm. XRD analysis was obtained anatase phase with tetragonal structure. It was observed that the SEM morphology indicated of mesoporous TiO_2 were successful. In addition, the performance of a photocatalytic activity in methylene blue adsorption and Cu(II) was 96 mg/g and 1620 mg/g, it is a surprise to clear environment the by decomposition treatment of wastewater

Keywords:mesoporous TiO_2, PVA, photocatalytic activity, adsorption

1. Introduction

The porous materials are the most potent simply accessible hollow space and used in many application in the word of the synthesized scientific researcher. The International Union Pure Applied Chemistry (IUPAC) has classifiedporous material based on the pore diameter, i.e. macroporous (d > 50 nm), mesoporous (50<d>2) and microporous (< 2 nm) materials[1]. Investigating the mesoporous materials are a continuing concern within the synthesis of TiO_2 mesoporous and assessment of their potential application. The varied application includes photocatalyst, dye-sensitized solar cell, remediation of Pb(II), sensor, antimicrobial activity and photodegradation of organic and inorganicpollutants in water and air[2–9].

Recent evidence suggeststhat synthesis and photocatalytic activity of mesoporous TiO_2have attracted much practical in recent years. To acquire a right mesoporous material for photocatalyst, many structural parameters are crucial such as large pore diameter, high specific surface area, particle size, and phase structure [10]. Therefore, there are many factorsaffect the properties of mesoporous

TiO_2materials to improve their photocatalytic activity. In addition, some methods such as sol-gel route [5,7,11], ultrasonic irradiation [12], hydrothermal route [13], and solvothermal route [14] have been reported for synthesis mesoporous TiO_2. Furthermore, another strategy had been investigated for improving characteristic mesoporous TiO_2 such as a various surfactants template as a structure directing agent, which consist of P123 copolymer [15], polyacrylamide [11], soluble starch[16], hexadecyltrimethylammonium bromide[17], combination surfactant CTAB/PEG/sodium dodecyl sulfate [4], polyethylene [18], and bulky organic acid [19].

More recent attention has focused on the provision of design and fabrication of mesoporous TiO_2. It was explored that the high surface area and large pore volume can be synthesized with a green template-free method. The result of mesoporousanatase TiO_2 with high surface area 119 m^2/g, pore volume 0.3 cc/g and photocatalytic decomposition of methyl orange 47.8% in aqueous solution 10 mg/L [6]. The other study that the various surfactant template via the sol-gel method has found the specific surface area 23.27-51.06 m^2/g, pore volume 0.0894-0.2108 cc/g, and higher adsorption capacity of Pb(II) are 420.5 mg/g at 1000 mg/L of lead soil solution [4]. One observer has already drawn attention to the paradox in mesoporous TiO_2 powders was prepared via a template-free method with large surface area 353 m^2/g, pore volume 0.3 cc/g, and adsorption capacity by degradation of rhodamine B of 35 mg/g [20].

A considerable amount of the previous studies have been observed on preparation route and surfactant template. The major objective of this study is to evaluate a novel synthesis method for arrangement properties of mesoporous TiO_2 to enhance their photocatalytic activity using polyvinyl alcohol as direct surfactant agent and modified technique via sol-gel, ultrasonic and hydrothermal treatment. In this paper, I argue that this project provided an important opportunity to advance the understanding of high the performance mesoporous materials as a photocatalyst to degradeof methylene blue and Cu(II) pollutants in water.

2. Materials and methods

2.1. Materials

The chemicals and reagents utilized during this preparation are analytical graded and used as received, they are titanium(IV) isopropoxideas a precursor of titania(TTIP, analytical reagent; Sigma Alrich), polyvinyl alcohol as a surfactant agent (PVA,M_{wt} = 89,000-98,000 g/mol, analytical reagent; Sigma Alrich), aceticacid (analytical reagent; Merck), ethanol (analytical reagent; Merck), $CuSO_4.5H_2O$ (analytical reagent; Merck), methylene blue (analytical reagent; Merck), and distilled deionized water

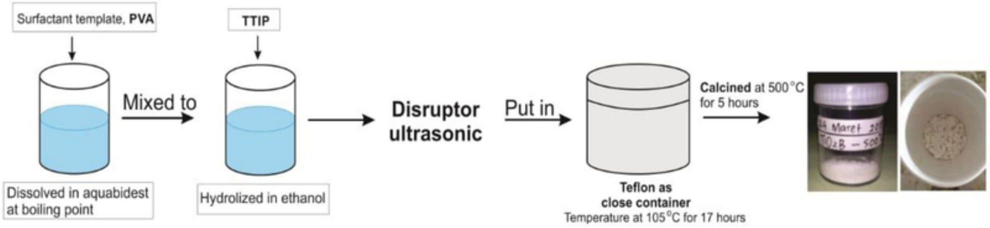

Figure 1. Diagram of preparation pathway of mesoporous TiO_2

2.2. Experimental method

The mesoporous TiO_2 were prepared via sol-gel, ultrasonic, hydrothermal treatment, and calcination method. 2.4 g PVA dissolved in deionized water at boiling point and stirred for 30 min. Afterward, this solution wasadded to another solution containing 15 ml of TTIP hydrolized in 60 ml of ethanol and 6 ml of acetic acid. The sonication of the solution was performed by an Ultrasonic Disruptor UD-211until the complete solution for 60 min at ambient condition. The intermediate products were then loaded into a teflonclose container for hydrothermal treatment at 105ºC for 17 hours. Finally, the products were calcinated at 500ºC for 5 hours. The corresponding diagram of preparation pathway of mesoporous TiO_2 in Figure 1.

2.3. Characterization

X-ray diffraction (XRD) was carried out using a Bruker D2 Phaser Diffractometer System with Cu Kα radiation source 1.5406 Å run at 40 kV, 30 mA. For XRD analysis in the range of 2θ from 10º to 80º, with scan step size of 0.02º. The measurements of nitrogen sorption isotherms at -196ºC were carried out using a Quantachoma NovaWin instrument version 11. The specific surface area (S_{BET}) of the sample was calculated with the Brunauer, Emmett and Teller method [21], using the adsorption data in the range of relative pressure [22]. The total pore volume was also estimated experimentally as the volume adsorbed at $P/P_o = 0.95$. The sample was previously degassed at 300ºC at approximately under vacuum for 3 hours. The morphology and defined areas of the samples were characterized using a scanning electron microscope (SEM with EDX) SU3500 with a working distance of 4940 µm and an electron voltage of 10 kV. EDX is based on the detector of characteristic x-ray emitted of an element as a result of the de-excitation of core electron holes created by a high energy electron beam. Instrument SU3500 EDX spectrum Ti and spectrum O were measured with beam 15 kV for 30 seconds.

2.4. Photocatalytic activity experiments

Methylene blue (MB) was chosen as a model organic pollutant and Cu(II) as an inorganic pollutant to investigate the photocatalytic activity of the mesoporous TiO_2 with a 150W mercury lamp. In the initial 100 mL pollutant (P1 = MB = 100 ppm; P2 = Cu(II) = 500 ppm). Afterward, 0.1 g TiO_2 powders were added, then the solutionswere stirred in the dark for 60 min until adsorption/desorption stability. A fixed quantity of each P1 and P2 solution was taken at a regular interval 10 min. The solutions were filtered andanalyzed the amount of MB or Cu(II) with UV-Vis absorption spectra. The filtrates were calibrated by 5 control solutions (for P1; 20, 40, 60, 80, 100 mgL^{-1} and P2; 50, 100, 200, 300, 500 mgL^{-1}). The adsorption amount, q_e (mg/g), was calculated as follows:

$$q_e = \frac{(Co - Ce)V}{m}$$

Where C_o and C_e (mgL^{-1}) in this case were estimated to be the amount of MB and Cu(II) at initial and equilibrium state, m is the mass adsorbent (g), and V is the solution volume. The adsorption removalefficiency was calculated

$$RE(\%) = \frac{(Ci - Ct)}{Ci}$$

Where C_i and C_t set as the initial and final of P1 or P2 concentration (at a certain time t), respectively.

3. Result and discussion

3.1. Crystal structure and morphology

The crystalline structure was determined using XRDand morphology structure by SEM with EDX. XRD patterns were indicated to evaluate the phase of the sample. Figure 2 presents that the XRD patterns of mesoporous TiO_2 were indicated anatase phase in all sharp peaks observed from the XRD pattern. Noticeable diffraction peaks positioned at 2θ = 25.29º, 37.94º, 48.76º and 53.95º which observed on the spectra attribute to (011), (004), (020), and (121) orientation plane of tetragonal structure and anatase phase of TiO_2. The results of this study will now be compared to the finding of previous work [16,19]. The anatase phase of TiO_2 is the most active crystalline for photocatalytic activity [6].

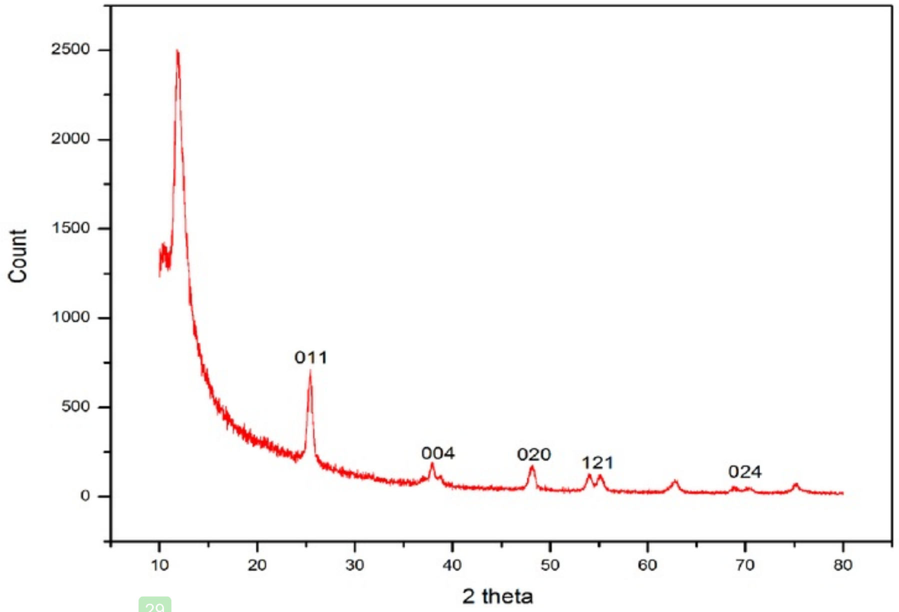

Figure 2. X-ray diffraction pattern of mesoporous TiO_2

In most recent studies, it is generally believed that characteristic of mesoporous materials is dependent on the specific surface area, pore volume and pore diameter of the particle. Scanning electron microscopy (SEM) of the TiO_2 materials were implemented for the sample which indicated better porous materials to evaluate the morphology. Figure 3 shows the intercorrelation among the porous of TiO_2 sample. The more surprising image from the using PVA as surfactant template can enhance the pore diameter until 11 nm. These results are consistent with those of other studies and suggest that the surfactant agents were created of mesoporous materials [15]. There are similarities between the attitudes expressed by PVA in this study and those described by Sadatlu M.A.A, 2016.

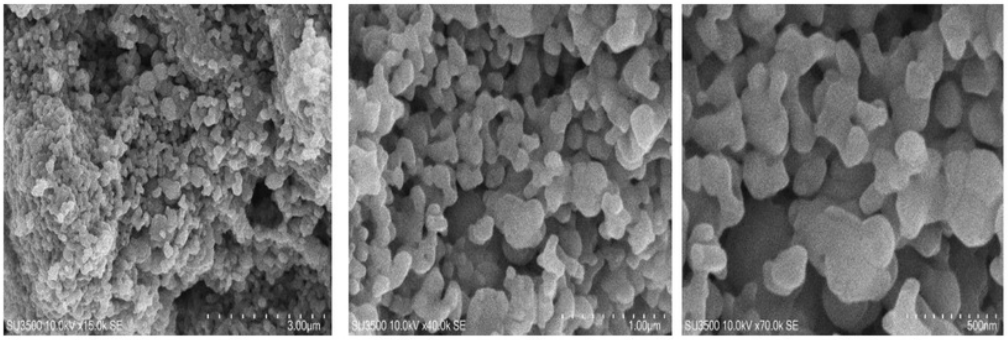

Figure 3. SEM image of mesoporous TiO_2 for macro (3 µm) and micro-morphology (500 nm)

The results obtained from the preliminary analysis of mesoporous TiO_2 are presented in Figure 4. In addition, all SEM images show that the obtained surfaces are porous. On the basis of EDX peaks, it can be concluded that the amount of Ti = 39.91% and O = 60.91%

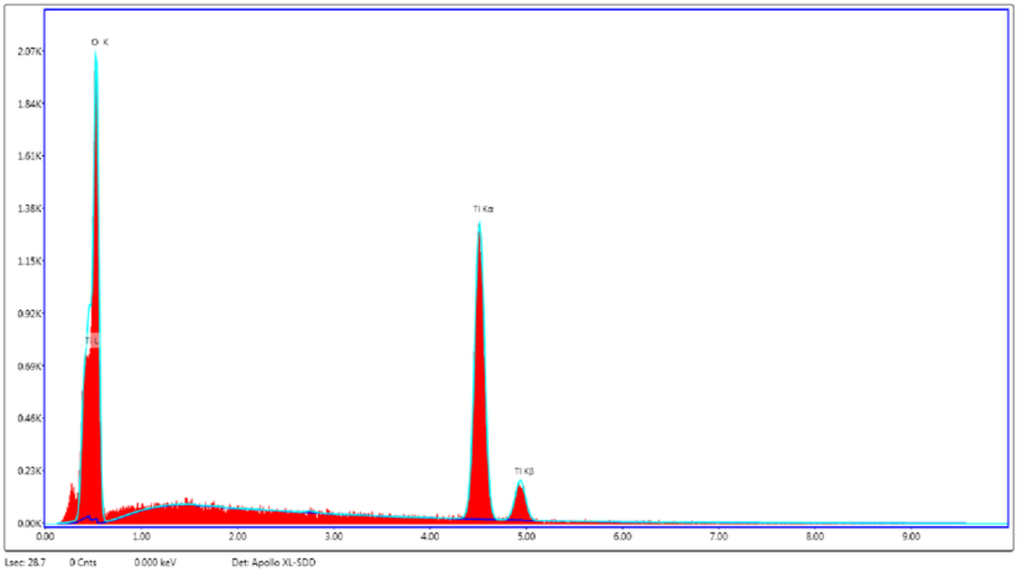

Figure 4. SEM-EDX micrographof mesoporous TiO_2 with

Surface area and pore analysis of mesoporous TiO_2were obtained with nitrogen adsorption-desorption isotherm. Using the BET method, the surface areas were calculated 106 m^2/g. The average pore size distributions were evaluated with the BJH method. The pore sizes were 11 nm and pore volume 0.18 cc/g.

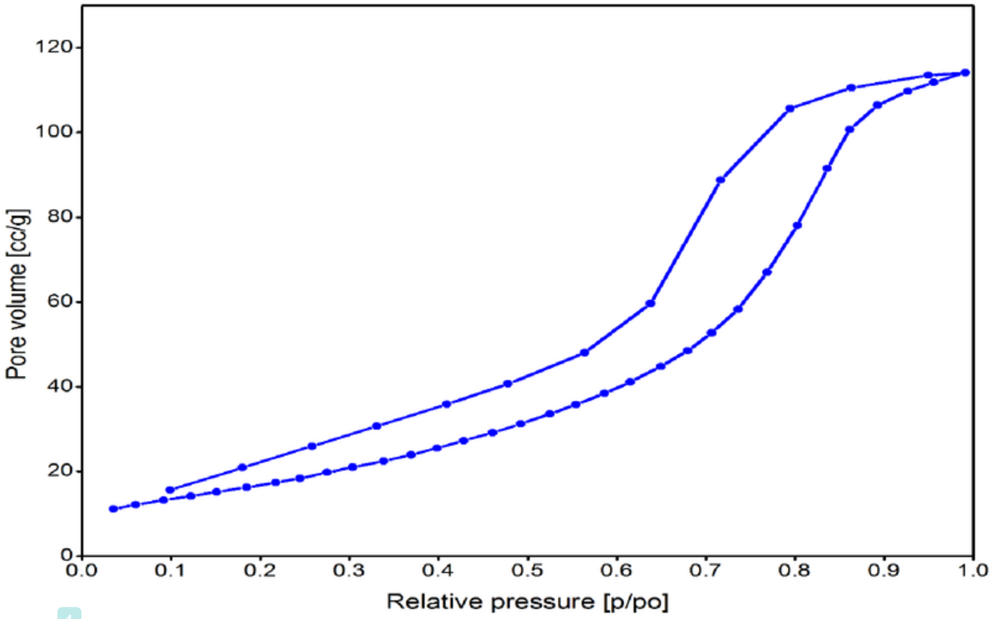

Figure 5. Nitrogen adsorption-desorption isotherm of mesoporous TiO_2

This observed pore size around 11 nm indicates a void space between the one-dimensional tetragonal of the TiO_2 sample. This finding has important implications for developing properties of the photocatalytic activity of mesoporous TiO_2. Typical type IV isotherms are observed for TiO_2 sample, showing a hysteresis loop H2-type with capillary condensation. These study produced results which corroborate the findings of a great deal of the previous work in this field [19].

3.2. Photocatalytic activity

The morphology and pore size analysis of the mesoporous TiO_2 have a great influence on the adsorption capacity. The photocatalytic activity was investigated by degradation of methylene blue as a model organic pollutants and Cu(II) as an inorganic pollutant. From the data on Figure 6 shows, it is observed that the degradation of MB shows lower adsorption capacity (96 mg/g) than the degradation of inorganic Cu(II) (1620 mg/g). There are several possible explanations for this result.

The particle size of Cu(II) is bigger than the pore diameter of mesoporous TiO_2. The interaction of Cu(II) between adsorbent of TiO_2occurred on surfaces of the adsorbent. The high surface area can support interaction Cu(II) between adsorbent of TiO_2. It is different for the degradation of MB. However, with a small sample size, caution must be applied, as the finding might not be available interaction on the surface of adsorbent but adsorbable into the pore volume. This is an important issue for future research.

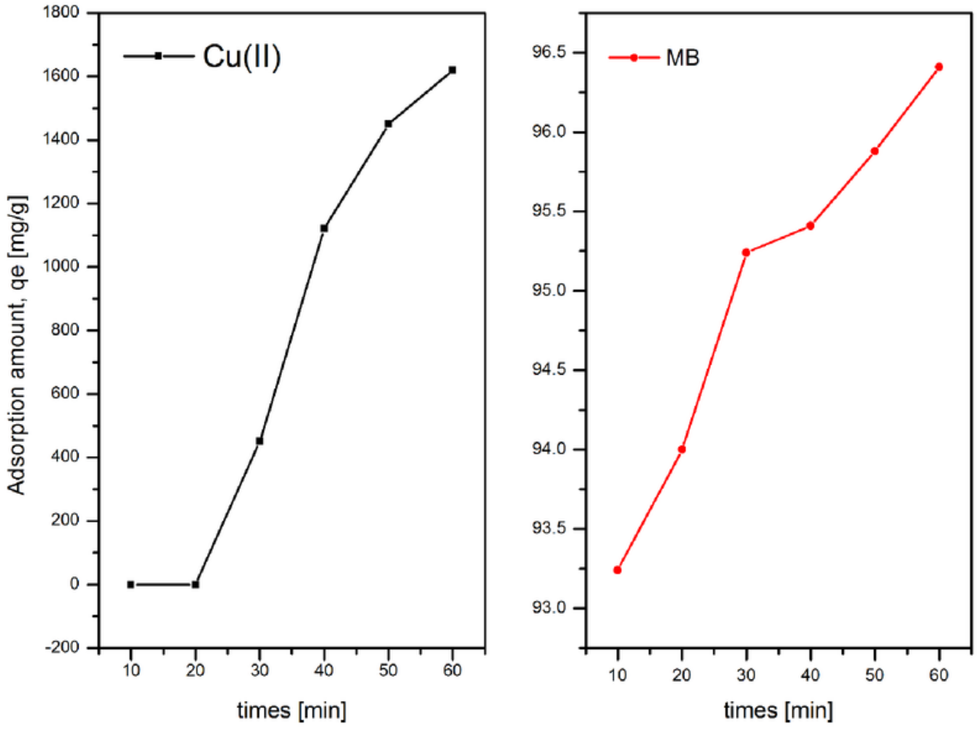

Figure 6. The amount of adsorption capacity of mesoporous TiO_2

The adsorption removal efficiency (RE, %) for degradation of Cu(II) and MB were maximized at 99% and 96.4% respectively at initial concentration 500 ppm and 100 ppm. The abilityuse of the mesoporous TiO_2 as potential adsorbents will be assessedforremoval organic and inorganic pollutants in water and air. The finding of this study has a number of important implication for future practice.

4. Conclusions

Mesoporous TiO_2 materials were synthesized using PVA as a surfactant direct agent via sol-gel, ultrasonic, and hydrothermal treatment. In this investigation, the aim was to asses the photocatalytic activity of mesoporous TiO_2 for degradation of methylene blue and Cu(II) as a model organic and inorganic pollutants. This information can be used to develop targetted intervention aimed at the high surface area of adsorbent has potential contributed for removal inorganic pollutants and the large pore volume and pore diameter have contributed to remove organic pollutants.

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