The Effect of pH and Aging Time on The Synthesis of TiO_2–Chitosan Nanocomposites as Photocatalyst by Sol-Gel Method at Room Temperature

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ABSTRACT

The synthesis of TiO_2–chitosan nanocomposite photocatalyst using Titanium(IV)-Isopropoxide (TTIP) as precursors and chitosan as host material has been conducted. The synthesis was carried out using a sol-gel method at room temperature and aging to grow crystal seeds and generate nanoparticles. The success of forming nano-sized anatase phase TiO_2 nanocrystal was strongly influenced by the sol pH system during hydrolysis and the aging time. The effect of sol pH system and aging time to the crystallinity level and particle size were examined using X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Diffuse Reflectance UV-Spectroscopy (DR-UV). The results showed that TiO_2 produced in acidic pHs (pH 2-4) tended to have higher crystallinity level than that produced in weakly alkaline (pH > 6), which prone to be amorphous. The longer aging time (> 14 days) also tended to produce the amorphous phase. Furthermore, chitosan as a host material had a notable influence in determining the crystallinity level and particle size of TiO_2 in TiO_2–chitosan nanocomposite.

Keywords: TiO_2-chitosan nanocomposite, host material, sol-gel method.

INTRODUCTION

TiO_2 nanoparticles have attracted the interest of many researchers because it can be applied widely, for instance, as photocatalyst, solar cells, gas sensors and optoelectronic devices (Chen and Mao, 2007). The physicochemical properties of TiO_2, such as crystal structure, particle size, specific surface area, porosity and thermal stability, are studied to support such applications.

As photocatalyst, TiO_2 has been applied widely for wastewater treatment because it is not only capable of breaking down organic compounds toxic but also reduces the toxicity of heavy metals and deactivates microorganisms. TiO_2 photocatalyst is non-toxic, cheap and quite stable in some conditions such as in varied pH and temperature. Photocatalytic activity of TiO_2 is relatively high because of the wide band gap of energy. With the right source of light, TiO_2 photocatalyst generates electron and hole pairs to start a chemical reaction chain of pollutants demineralization (Janus et al., 2011; Nguyen-Phan and Shin, 2011).

However, the use of pure TiO_2 powder has been reported to have some weaknesses, such as produces turbidity in water hence makes photocatalyst recovery difficult. Thus for photocatalytic application, TiO_2 has been modified into a layer of film or immobilized on inorganic materials such as zeolite (Wijaya et al., 2006), silica (Shiraishi et al., 2009), resins (Wahyuni et al., 2010), activated carbon (Andayani and Sumartono, 2007) and glass fiber (Pandiangan and Simanjuntak, 2013), as well as organic material such as polyurethane (Burgess, 2007) and chitosan (Chen et al., 2010; Qian et al., 2011; Zainal et al., 2009; Nawi et al., 2012).

Synthesis of metal oxide nanoparticles, in general, can be carried out in situ in a host material with a porous or hollowed structure or containing space between layers that can limit the growth of oxide particles. Chitosan can serve as a host material because the scrolled, layered, stretched and double twisted structure of long molecules contained in chitosan generate space and gaps that can confine the growth of metal oxide particles. (Chang et al., 2011; Wang et al., 2011; Cheng et al., 2010). Chitosan is also favored as a host material because its optical and electronic properties support the metal oxide functions of photocatalyst (Guibal, 2005), as well as diffuse the charge to the target compound (Nawi et al., 2012). Economically, chitosan is also relatively cheap because it is abundantly obtainable from exoskeleton of shrimp (*crustacea*), crab, clams (*mollusc*) and insects.

Chitosan has been successfully used as a host material for the synthesis of anatase phase

TiO_2 nanoparticle, as well as forming TiO_2-chitosan nanocomposite (Fajriati et al., 2013). The chitosan function as the host has also increased the photocatalytic activity in dyes degradation due to the synergy effects of chitosan adsorption ability against pollutants (Fajriati et al., 2014a). The synthesis of TiO_2–chitosan nanocomposite as photocatalyst has been conducted at room temperature using a sol-gel method with the aging process to generate the crystal phase of TiO_2. Unlike the regular synthesis of metal oxide in general, calcination process is not applied in the synthesis because chitosan is decomposed at high temperatures. In addition, room temperature can improve the purity and homogeneity of its nanocrystal particles (Hosseingholi et al., 2011).

Several factors can affect the synthesis result during the sol-gel process, among which is the concentration and the type of precursor compounds that can determine the character of crystals phase and size (Fajriati et al., 2014b). The solution pH system can also determine the particle size and crystalline phase, as well as the stability and morphology of TiO_2 particles since the pH affects the hydrolysis ability of alkoxide compounds in forming sol during sol-gel process. In addition, the aging time is also influential in determining the size and the stability of crystal phase since aging time is the gelation phase within the seed particles growth phase, thus enhancing the formation of anatase single crystal phase of TiO_2 (Behnajady et al., 2011).

Therefore, pH and aging time are the crucial factors in the formation of photocatalyst TiO_2–chitosan nanocomposite since the characteristic of crystal phase and size, morphology, and stability of photocatalyst materials are controlled in those conditions. As a result, pH control and timing of aging are indispensable in determining the optimum conditions for preparation of TiO_2–chitosan nanocomposite as photocatalyst. This research uses Titanium(IV)-Isopropoxide (TTIP) as precursor compound, HCl and NaOH to adjust pH, various pH and aging time are studied through determining the particles size, crystal phase, as well as optical and morphological properties of nanocomposite surface.

EXPERIMENTAL SECTION

Research Tools and Materials

The tools used include standard laboratory glassware, oven (Thermoline Electric Heraeus),analytical balance (110 BP Sartorius), magnetic stirrer (Cimarec Barnstead Thermolyne), centrifuge (Boeco C-28) desiccator, X-Ray spectrophotometer (Shimadzu x-ray Diffractometer 6000), Transmission Electron Microscope (JEOL JEM-1400) and Spectrophotometer Diffuse Reflectance UV-Vis(Shimadzu UV 1700 Pharmaspec).

The materials used include Titanium(IV)-isopropoxide from Aldrich ($Ti\{OCH(CH_3)_2\}_4$; BM 284.215 g/mol, density: 0.96 g/mL), Chitosan with purity of 87% from Biotech Surindo, acetic acid from Merck (CH_3COOH), HCl and NaOH from Merck, aqua bidest from UD. Organic Yogyakarta and mineral free water from Pharmaceutical Lab. No further purification or early treatment applied to all materials used.

Research Methods

Sol synthesis of TiO_2 nanoparticles

The sol synthesis of TiO_2 was performed by mixing 10 mL of TTIP solution with 100 mL of acetic acid 10%. The mixture was stirred for approximately 24 hours using magnetic stirrer to form a white colored sol. TiO_2 sol was incubated for 7 days at ambient temperature and pressure, resulting in clear solution with white deposits.

Sol synthesis of TiO_2 nanoparticles with various pH

Sol synthesis of TiO_2 nanoparticles with various pH was conducted by mixing 10 mL of TTIP solution with 100 mL of acetic acid 10%. The initial pH of the solution was 2,7. Then, the pH was adjusted to 2; 3; 4 and 5 with 0,1 M HCl or 0,1 M NaOH followed by agitation for ± 24 hours. The white colored sol was incubated for 7 days at ambient temperature and pressure. The clear solution with white deposits obtained afterward was then mixed in chitosan to form TiO_2–chitosan nanocomposite.

The synthesis of TiO_2–chitosan nanocomposite with various aging time

A total of 3 g chitosan was dissolved in 100 mL acetic acid 1% and stirred for 24 h. Afterwards, the TiO_2 sol, which had undergone aging for 7 days, was added to get the concentration of 0,65 mol/LTTIP. The mixture was then stirred for 24 hours to obtain a white homogeneous solution to be subsequently incubated variously for 7, 14, and 21 days for aging process.

After the aging process, nanocomposite materials were heated in oven at temperature of 80°C for 3 hours to get the dried material nanocomposite. Nanocomposite was then washed with aquades (neutral pH), followed by drying in oven at the same temperature. Lastly, the nanocomposite properties and photoactivities were examined.

RESULTS AND DISCUSSION

In the sol-gel process, TiO_2 nanoparticles are formed through hydrolysis and condensation of titanium(IV)-isopropoxide (TTIP) precursor in acetic acid solvent. TTIP is preferred as a precursor compound because the alkoxide is slower in forming TiO_2 crystals than using precursor from titanium salts. In a solvent that also functions as acetic acid modifier, hydrolysis of alkoxide compound can be stifled because acetic acid may suppress the amount of TTIP that hydrolyzed through the replacement of isopropyl group by acetate to form complex Ti–acetate. The replacement of isopropyl group is a nucleophilic substitution reaction, which happened competitively between acetate group and water molecules.

Hypothetically, there are two possible reaction mechanisms. First, esterification reactions accompanied by hydrolysis to produce ≡Ti-OH, and second, substitution reactions on some or all isopropyl groups by acetate ligands to form titanium-oxo-acetate complexes along with the elimination of alcohol molecules (Doeuff, et al., 1990). The formation of titanium-oxo-acetate group is the early stages of TiO_2 crystal seed formation, followed by condensation to form TiO_2 particles (Doeuff et al., 1990).

Mechanism of **Reaction 2** is more likely to occur because the presence of water molecules in the reaction system can damage the oxo bridge in Ti-oxo-acetate complex, thus leading to the formation of soluble and associated small groups (Birnie III and Bendzkob, 1999).

Association of Ti-O molecule occurs through the following reaction steps (Lima, 2010):

$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH$ (hydrolysis) … (1)

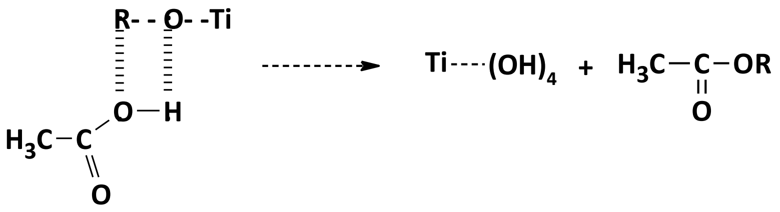
$Ti(OH)_4 \rightarrow TiO_2 \cdot xH_2O + (2-x)H_2O$ (condensation) … (2)

The reaction continues in chitosan matrix until TiO_2–chitosan nanocomposite is formed.

The effect of pH

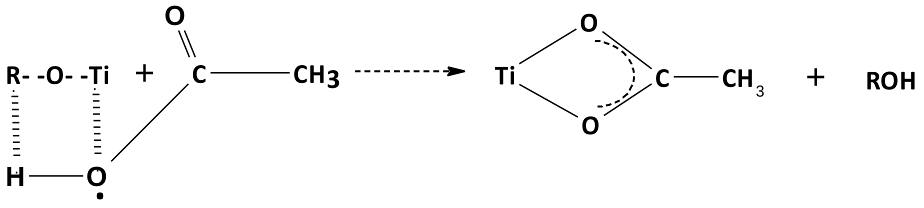
The effect of pH sol system in acidic pH 2; 2,7 (initial pH); 3; 4; 5, to the crystallinity level and particle size of TiO_2–chitosan nanocomposite, is shown in **Figure 1**. At pH 2-3, the intensity of diffraction pattern is relatively sharp, indicating the increasing number of TiO_2 crystals in nanocomposite. Meanwhile, at pH 3-5 the intensity of diffraction patterns is weaken, indicating that the number of TiO_2 crystals in nanocomposite reduced. These results are corroborated by the TEM-SAED profile on pH 2,7 (initial pH) and pH 5 in **Figure 2**, showing that the TiO_2 nanoparticles on pH 2,7 or 5 have spherical shape (**Figure 2A-2B and 2C-2D**).

Reaction 1: Esterification reaction



... Equation (1)

Reaction 2: The reaction of oxo-acetate complex formation



... Equation (2)

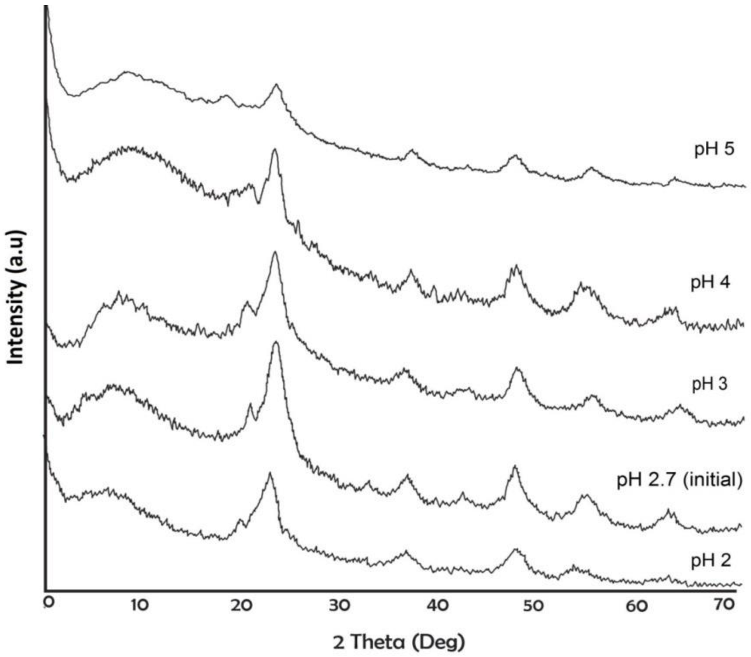


Figure1. X-ray diffraction of TiO_2–chitosan nanocomposite at pH 2; 2,7 (initial) 3; 4; 5; 7 and 9.

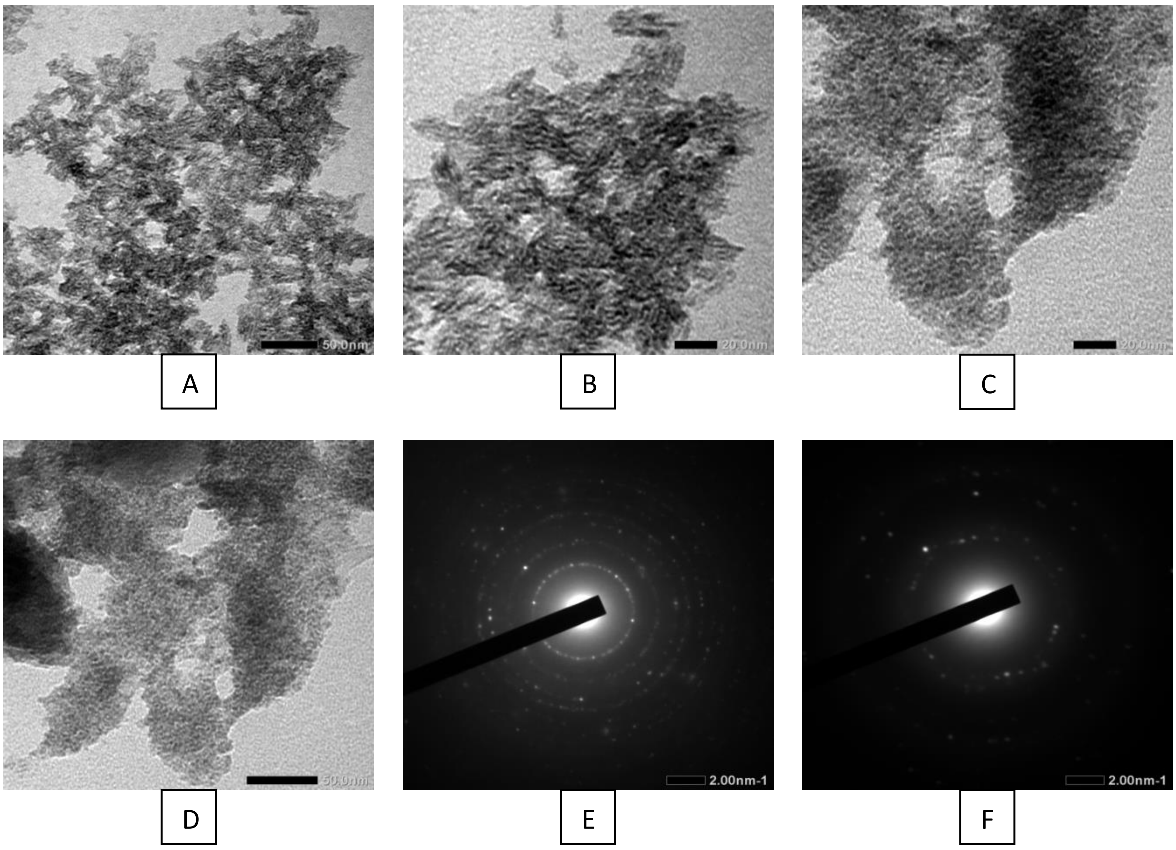


Figure 2. TEM images of TiO_2–chitosan nanocomposite at magnification scale of 20 and 50 nm, on conditions: (A) and (B) pH 2,7 (initial), (C) and (D) at pH 5, and (E) and (F) from the selected area electron diffraction (SAED, consecutively at pH 2 and pH 5,7.

At pH 5 (**Figure 2C and 2D**), the lattice fringe is not clearly visible and crystalline aggregation that forms amorphous phase is obvious. It can be seen that the ring spot on the same diffraction field from the selected area of electron diffraction (SAED) has weakened (**Figure 2E**). At an acidic pH, the more restrained hydrolysis occurs because of the protonated $Ti(OH)_4$ form $Ti(OH)_2^{2+}$ species at pH < 2 and $Ti(OH)_3^+$ at pH 2-4 (Sugimoto et al., 2002). The protonated species tends to undergo depolymerization and produces small hydrophilic oligomers in titanium complex hydroxo due to the increasing repulsion force between positive charges. Hence polycondensation happens more slowly and forms smaller TiO_2 particles (Simonsen and Søgaard, 2010; Yanasigawa and Ovenstone, 1999). At basic pH, the entire H_2O ligands in $Ti(OH)_4$ have been replaced by the hydroxyl group, at least 6 hydroxyl groups bonded in the same length. Therefore the polycondensation reaction occurs from all sides at the same speed and tends to produce amorphous particles.

Figure 3 shows the size of TiO_2 particles formed at pH 2,7 (initial), pH 3 and pH 5, calculated based on the peak fields (101) from XRD data following Debye Scherrer equation:

$$D = 0.9\lambda/\beta\ (\cos\theta) \quad ... \quad (3)$$

Where the value of λ is the wavelength of the of CuKα radiation (1.5405 Å), whereas θ states the angle of Bragg, which is determined from crystal field 101. Meanwhile, β is the Full Width at Half Maximum (FWHM), which is determined based on the difference between sample β and standard β. Particle size TiO_2 is obtained at the range of 8 – 10 nm. These results are in accordance with the optimum pH range in the synthesis of anatase phase TiO_2 nanoparticle, at pH 2,7-4 (Sugimoto et al., 2002).

The Effect of Aging Time

The effect of aging time for 0; 7; 14 and 21 days on TiO_2 crystallinity level and particle size in chitosan matrix is shown by diffraction pattern in **Figure 4**.

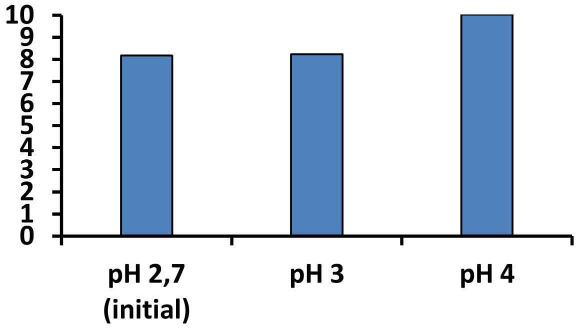


Figure 3. The effect of pH on TiO_2 particle size in TiO_2–chitosan nanocomposite

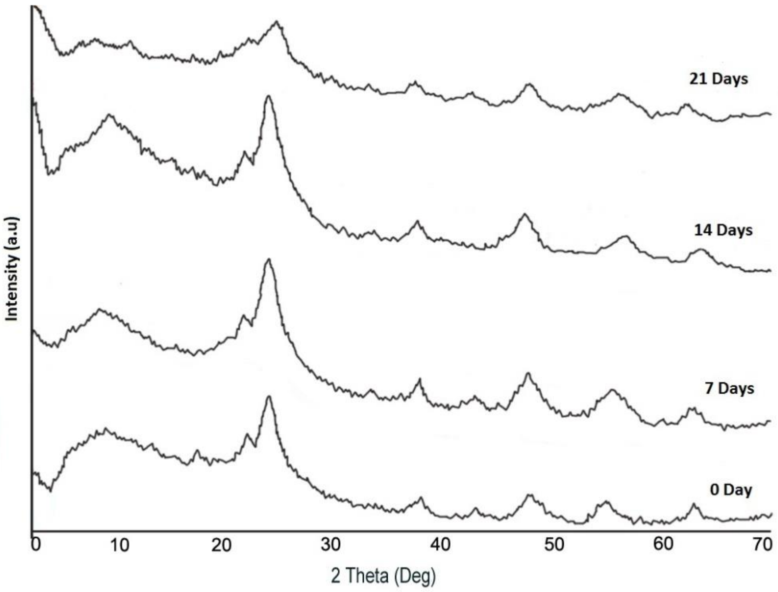


Figure 4. X-ray diffraction of TiO_2–chitosan nanocomposite on various aging time for: 0; 7; 14; and 21 days.

Figure 4 shows that the intensity of diffraction pattern is sharper at the time aging of 14 days, indicating a higher level of crystallinity. The aging period of 14 days as an optimum time for raising crystal phase is related to the process when the sol physical properties will turn into a coarsen phase through the stage of polymerization, coarsening and transformation (Wong et al., 2014).

Figure 4 also shows that only anatase phase single crystal is formed, since the synthesis at room temperature, the formation of TiO_6 octahedral molecules is structurally more easily led to the formation of anatase phase than rutile phase (Nie et al., 2009). But thermodynamically, the formation of anatase is faster because anatase has lower Gibbs free energy than rutile (Hanaor and Sorrell, 2011).

Furthermore, at the aging time of 14 days, chitosan viscosity increases due to evaporation of water molecules that causes the loss of polyamide chain and the formation of layers in chitosan film (Silva, et al., 2012). As a result, increasing viscosity lead to polycondensation of O-Ti-O and transformation into crystal phase are more difficult, thus damage the formed crystal phase system into amorphous phase. It is shown by lower diffraction intensity of nanocomposite after the aging period of 21 days (**Figure 4**).

The viscosity change during the aging process is given in **Table 1**, which shows that the longer the aging time, the lower the nanocomposite flow rate. However, TiO_2 bulk has relatively constant water flow, since the aging process of TTIP sol at room temperature does not alter the viscosity of 60 days aged sol (Wong et al., 2014).

The particle size calculated based on the Debye-Scherrer at the field peak (101) (**Figure 4**), is shown in **Figure 5**, with particle size of TiO_2 obtained by 8-10 nm. This result is confirmed by the absorption of TiO_2 particle with UV wavelengths since a red shift occurred in the TiO_2 formed through longer aging time Optical properties of TiO_2 particles are further used to determine the band gap energy (E_g) based on the absorption edge wavelength of each nanocomposite summarized in **Table 2**.

Table 1. The viscosity of TiO_2–chitosan nanocomposite in varied aging time, as well as the viscosity of the TiO_2 bulk and chitosan bulk as comparison

Various aging time	Kinematic flow rate at 28.0 °C (mm^2/s)		
	TiO_2–chitosan nanocomposite	TiO_2 bulk	Chitosan bulk
0 day	463,6	1,498	*)
7 days	392,2	1,494	*)
14 days	333,5	1,491	*)
21 days	243,5	1,488	*)

**) the too thick samples cannot flow at the capillary pipe S 600*

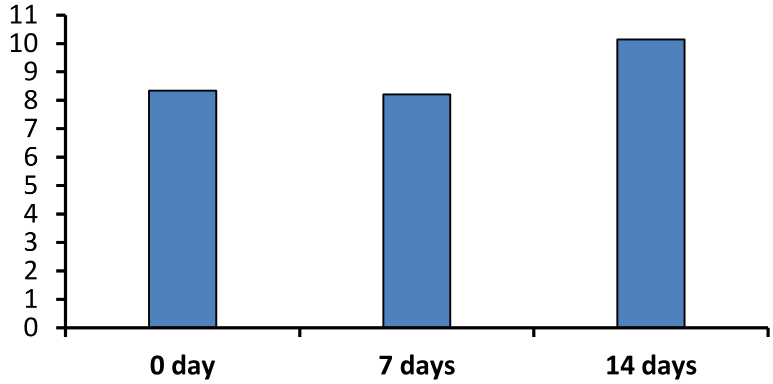


Figure 5. The effect of various aging time on TiO_2particle size in TiO_2–chitosan nanocomposite

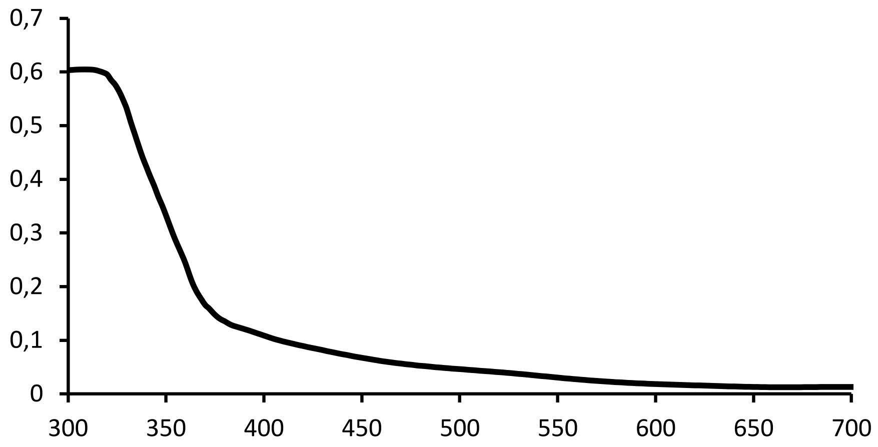


Figure 6. DRUV spectra of TiO_2–chitosan nanocomposite with aging time for 0; 7; and 14 days.

Table 2. The effect of aging time to the absorption edge wavelength (λ, nm) and band gap energy (E_g, eV) from TiO_2–chitosan nanocomposite

Aging time (day)	Absorption edge wavelength(nm)	Band gap energy (E_g) (eV)
0	392,18	3,15
7	388,48	3,17
14	402,75	3,07

The red shift observed in **Figure 6** causes the difference in E_g of each nanocomposites on various aging time. The result of E_g is given in Table 1, which shows that the shorter the aging time, the smaller the particle size. Therefore, the nanocomposite with the smallest E_g (aging time of 14 days) has the biggest particle size. The particle size tends to increase with increasing time of aging since the time available for crystal seed to grow is longer. However, the limit of crystal growth is also influenced by chitosan viscosity obtained no longer than 14 days, as has been discussed on previous paragraph.

CONCLUSION

The photocatalyst TiO_2 had been successfully synthesized using chitosan as host material to produce anatase phase TiO_2 nanocrystal as well as TiO_2-chitosan nanocomposite. The synthesis was carried out using TTIP as precursor through sol-gel method at room temperature and aging process. The pH and aging time significantly influenced the properties of synthesis product. At acidic pH (pH 2-4), TiO_2 was produced with higher crystallinity level than that in basic pH (pH > 6), which tended to be amorphous. The longer aging time (> 14 days) also tended to produce amorphous phase TiO_2.

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