Asian Journal of Chemistry; Vol. 27, No. 11 (2015), 3983-3987

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19027

Effects of Doped Dodecyl Trimethylammonium Bromide Surfactant on Synthesis and Performance of Nanoporous TiO_2-SiO_2/Chitosan

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Received: 16 January 2015; *Accepted*: 4 March 2015; *Published online*: 16 July 2015; AJC-17387

Nanoporous TiO_2-SiO_2/chitosan was synthesized *via* a sol-gel process under controlled sol-gel time. Titanium tetraisopropoxide (TTIP) and tetraethoxy ortho silicate (TEOS) were used as precursors with doped chitosan and dodecyl trimethylammonium bromide (DTAB) surfactant as a template of nanoporous in isopropanol solutions. The effects of various sol-gel times and surfactant DTAB were focused on investigated reviews that their nanoporous character and distribution were more homogeneous than without surfactant DTAB. The properties of these TiO_2-SiO_2/chitosan materials, characterized from the synthesis results in optimum sol condition during 5-8 h and gellation time during 10-15 h characterized with XRD showed that the crystal phase with hexagonal geometry (101) of crystal phase were anatase with their average crystal size to 9.6-18.2 nm. The FT-IR spectrum showed the interaction of Ti-O-Si occurred in the fingerprint was 960 cm^{-1}. SEM-EDX analysis showed spherical particles, porous and homogeneous distribution with different elements of the composition of the modified stoichiometry. BET and BJH analysis showed the specific surface area was 179.3 m^2/g, pore volume 0.2 cm^3 g^{-1} and pore diameter was 45.40 Å. Analysis of UV-visible spectroscopy revealed the values of energy gap (E_g) were 1.7-1.9 and thus showed that the material was effective to be applied in tropical environments where visible light is usually dominant.

Keywords: TiO_2-SiO_2/Chitosan, Nanoporous, Dodecyl trimethylammonium bromide.

INTRODUCTION

Titanium dioxide (TiO_2) is a photocatalyst which has attracted great attention of researchers and industries because it has a wide field of applications. Several researches have been carried out on modifications to the morphology, crystal size, crystal phase, specific surface area and porosity to improve the performance of the catalyst[1]. To improve the photocatalytic activity of the material, small size and high crystallinity and large surface area can lead to quantum effect in semiconductor[2,3]. For the application of TiO_2 on a tropical environment with visible energy source, it is therefore necessary to modify the morphology with the addition of doped metal ions or metal oxide compound semiconductor with a band gap lower than the precursors used[4-6]. Several authors[7,8] reported that TiO_2 modified with SiO_2 can lower E_g (energy gap), increased the stability of the crystal structure of anatase TiO_2 at high temperatures to 900 °C, because TiO_2 at 500 °C transformed into a rutile structure. TiO_2-SiO_2 is a very effective photocatalyst to environmental pollution reductors[7]. Being in the tropical area Indonesia is blessed with almost daily continuous solar radiation. Therefore it can be used as a source of radiation that is very practical and economic when the semiconductor photocatalyst TiO_2-SiO_2/chitosan is applied to the environment[9,10].

TiO_2-SiO_2 is a metal oxide clusters semiconductor obtained through a process of synthesis. Therefore, photocatalytic activity depends on how the catalyst is prepared. Several methods are known and practiced in the synthesis of TiO_2-SiO_2, including a sol-gel method. This method has several advantages as the process is simple, homogeneous and through setting process conditions such as temperature change calcination temperature, set the precursor stoichiometry, aging time, can modify the desired product specifications[3,10].

Rilda *et al.*[11] reported the addition of the chitosan in TiO-SiO_2 increased of the porosity of the surface of the catalyst. Porosity can also be reproduced if the optimization sol-gel time conditioned and addition of surfactant DTAB. Chitosan has a specific functional group *i.e.*, NH_2 and OH and these groups can serve to facilitate the molar amount of TiO_2 with

SiO_2 interacted through hydrogen bonding and covalent, so it can increased the amount of the metal oxide dispersion[12]. Chitosan is a biopolymer organic compounds that, can be used as a printing template pores. However, the distribution of pores on the surface is not homogeneous and furthermore, it is agglomerated.

In this study, we report the synthesis of TiO_2-SiO_2/chitosan with the addition of dodecyl trimethylammonium bromide (DTAB) as a surfactant. Surfactant in the sol-gel process will be used as a template for the growth of nanoporous crystal so as not to restrict the growth of agglomerated particles[13-16].

EXPERIMENTAL

The materials used were titanium isopropoxide ($Ti(OC_4H_9)_4$ (purity 97 %, Sigma-Aldrich), tetraethoxy silicate ($Si(OC_2H_5)_4$ (purity 97 %, Sigma-Aldrich), diethanol amine (DEA) (Merck), Isopropanol (purity 98 %, Merck), dodecyl trimethylammonium bromide [$C_{12}H_{25}N(CH_3)_3Br$] (Sigma-Aldrich), acetic acid (CH_3COOH) (Merck), ammonium hydroxide (Merck) and commercial chitosan purchased locally. All of these chemicals were used as received without further purification.

Synthesis of nanoporous TiO_2-SiO_2/chitosan is outlined below:

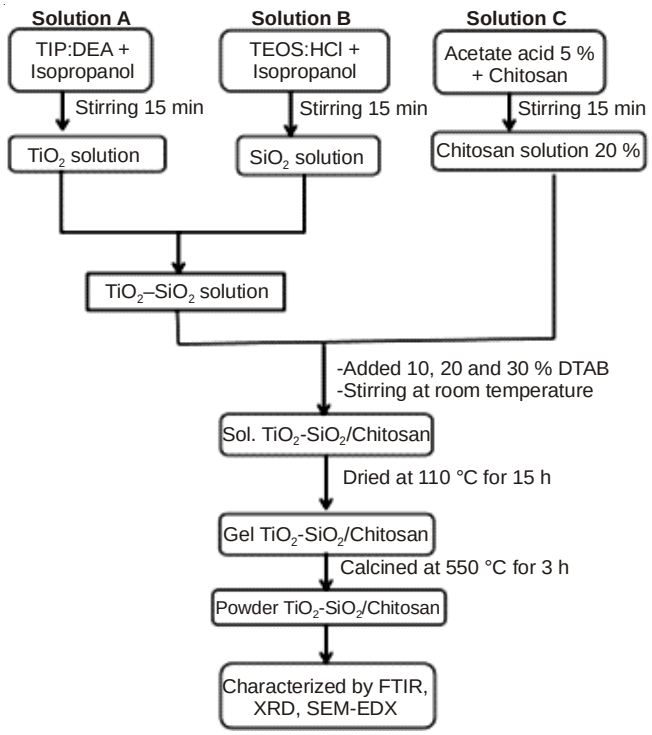

Fig. 1. Synthesis of nanoporous TiO_2-SiO_2/chitosan with addition of DTAB surfactant by sol-gel methods

The physical properties of synthesized TiO_2-SiO_2/chitosan were characterized by X-ray Diffraction (XRD) (X, Port PAN Analytical) to survey the crystal compositions, sizes and structure of TiO_2-SiO_2/chitosan. The crystal size was calculated using Scherers equation ($D = K\lambda/\beta\cos 2\theta$), where D is the crystal size, K is usually taken as 0.89, λ is 0.154 nm, the wavelength of the X-ray radiation, β is the Full-width at half maximum intensity (FWHM) and θ is the diffraction angle of the (101) peak for anatase ($2\theta = 25.3°$). Scanning electron microscopy and electron diffraction X-ray (SEM-EDX) (Model AS-68 SEM (Field Emission Leosupra 50 VP SEM Oxford INCA Energy 400) was used to reveal the surface morphology and composition of nanoporous TiO_2-SiO_2/chitosan. The specific surface area and pore size distribution were investigated with Brunauer-Emmett-Teller (BET) and Barrett, Joyner, Halenda (BJH) (Quantachrome, Serial 1089111903, Micrometrics ASAP 2000 apparatus). Spectrophotometer UV-visible data were used for the determination of the band gap.

RESULTS AND DISCUSSION

SEM-EDX characterization: The TiO_2-SiO_2/chitosan powders prepared by sol-gel method, the effect of doped surfactant DTAB and the variation of the sol-gel times observed in this process. This effect as shown in Fig. 2; SEM pattern of TiO_2-SiO_2/chitosan, the particles produced were spherical. Meanwhile, if the addition of chitosan can enhance particle growth, pore distribution is more focused. The spherical shape of nanoporous TiO_2-SiO_2/chitosan can be expected to induce the surface tension of surfactant DTAB through sol-gel process[14-17].

The EDX characterization (Fig. 3) shows the existence of differences in the composition of the compounds in both samples when varied stoichiometry. EDX pattern shown in Fig. 3b. TiO_2-SiO_2/chitosan wherein the composition has increased mass percent of TiO_2 with the addition of chitosan at a concentration of 10 % DTAB, which is 77.6 %. If correlated with the XRD pattern of TiO_2-SiO_2/chitosan with addition surfactant reviews these conditions has a narrow and sharp peaks indicated crystallinity occurs process more perfect.

BET/BJH characterization: BET/BJH can be used for the characterization of the specific surface area and porosity of the TiO_2-SiO_2/chitosan were investigated the catalyst by using the N_2 adsorption and desorption isotherms. Data analysis of BET/BJH are shown in Table-1. Mechanisms sol formation begins from the hydrolysis of long-chain precursors of isopropoxide in isopropanol. Stable sol obtained if perfect precursor hydrolysis in the solvent in the presence of doped chitosan and surfactant DTAB. The homogeneous sol affects the morphology of the result of crystalline product[18,19]. Formation of TiO_2 sol-need a stable SiO_2 additive compounds to prevent the formation of deposits diethanolamine. Titanium isopropoxide (TIP) precursor to $Ti(OH)_4$, whereas the precursor TEOS as a source of SiO_2 is less reactive than titanium isopropoxide, so that the catalyst necessary to accelerate the reaction of the formation of acid sol. The formation of a stable and homogeneous sol takes a long time.

Table-1 indicated that the sol is homogenized at a time of 8 h gives the product a porous catalyst with a more homogeneous distribution of particles with a surface area of 179.3 $m^2\ g^{-1}$ is bigger and 45.50 Å pore size, pore volume 0.20 $cm^3\ g^{-1}$ greater than the homogenization sol for 5 h. Large surface area and porosity showed correlation with the size of the nanoscale[15]. The longer the time of homogenization sol, sol hydrolyzed with perfect and crystal growth is getting smaller, because the addition of surfactant DTAB crystal growth can be controlled with the directional. While doped chitosan can

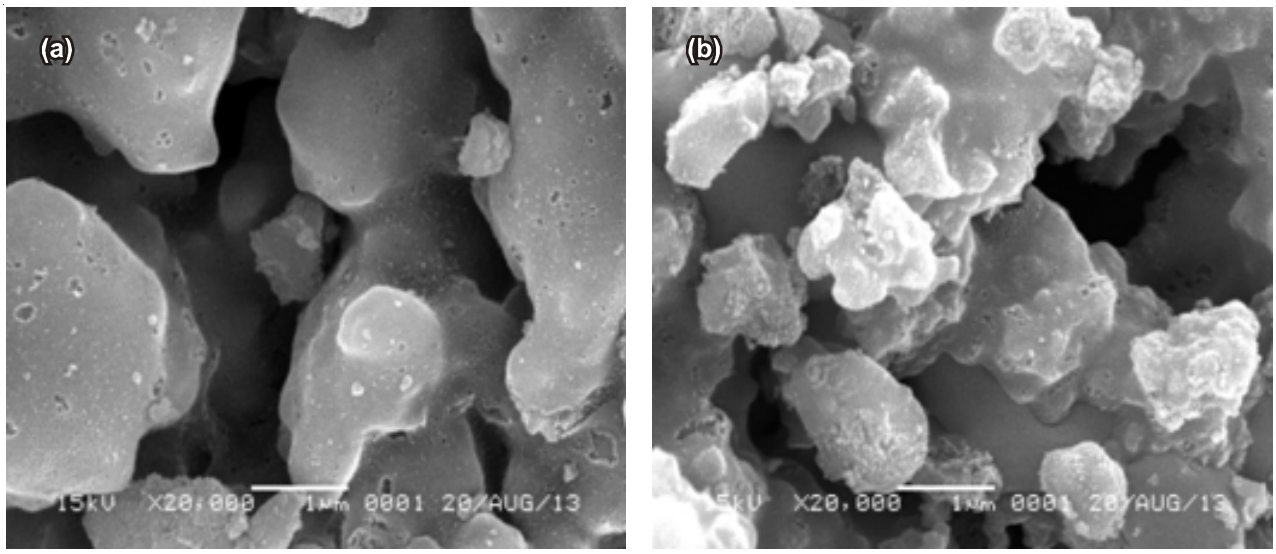

Fig. 2. SEM images of TiO_2-SiO_2 powder (a) TiO_2-SiO_2, DTAB 10 %; (b) TiO_2-SiO_2/chitosan, DTAB 10 %

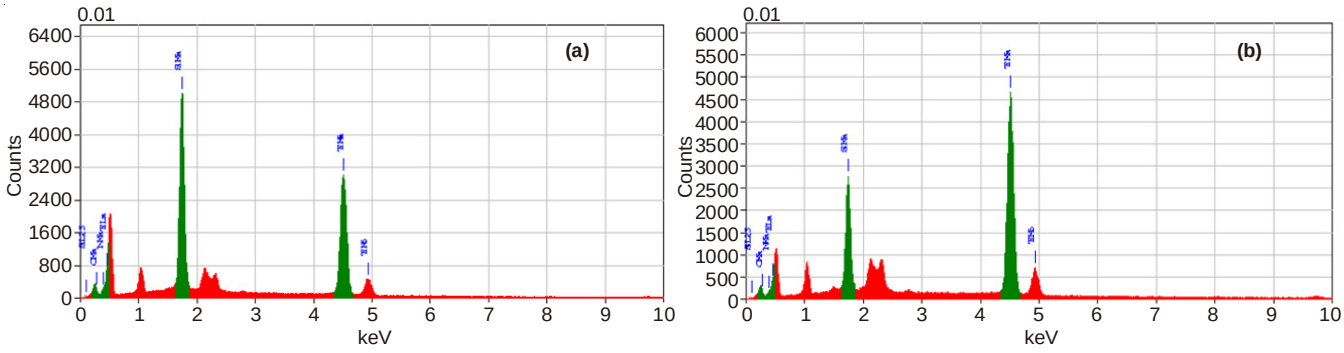

Fig. 3. EDX images of TiO_2-SiO_2 powder (a) TiO_2-SiO, DTAB 10 %; (b) TiO_2-SiO_2/chitosan, DTAB10 %

TABLE-1
SURFACE MORPHOLOGY OF TiO_2-SiO_2/CHITOSAN CATALYST IN DIFFERENT COMPOSITION AND SOL TIMES

Sample	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pores diameter (Å)
TiO_2-SiO_2, DTAB10 %, sol 5 h	26.6	0.03	33.9
TiO_2-SiO_2/chitosan 20 %, DTAB 10 %, sol 5 h	95.6	0.12	38.2
TiO_2-SiO_2/chitosan 20 %, DTAB 10 %, sol 8 h	179.3	0.20	45.4

also increase the surface area and porosity of the particles. When compared to the composition without chitosan sol, in Table-1 obtained a smaller surface area when compared with without chitosan 26.6 m^2 g^{-1}, 33.9 Å pore size, the pore volume of 0.03 cm^3 g^{-1} at the same time the homogenization sol 5 h.

Gellation is the initial formation of crystal core that begins with the gradual evaporation of the solvent, thus forming a three-dimensional network to develop into a crystal lattice unit cell. Gellation curing time can affect crystal morphology. Table-2 indicated that the curing of the gel made at the time of 10-15 h the data obtained showing crystals have different morphological physical properties. The longer the curing time obtained with the crystal morphology of specific surface area, pore size and pore volume of the larger and effect of chitosan can also influence the crystal morphology with longer curing gel. Performance of the catalyst is effective if the specific surface area of large particles, so it can be concluded for performance gel particles required curing time for 15 h with a large specific surface area 154.7 m^2 g^{-1}, 0.19 cm^3 g^{-1} pore volume, pore size 65.3 Å, required. The conditions of the sol-gel were the optimum condition of the sol-gel process.

Brunauer-Emmett-Teller characterization can provide information about the type and shape of the pores of the catalyst. Fig. 4 showed that all the isotherms of samples revealed the stepwise adsorption and desorption of type IV curve, indicating the presence of mesoporous material.

TABLE-2
SURFACE MORPHOLOGY OF TiO_2-SiO_2/CHITOSAN CATALYST IN DIFFERENT COMPOSITION AND GEL TIME

Sample	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore diameter (Å)
TiO_2-SiO_2/chitosan 20 %, DTAB 10 %/gel 10 h	102.3	0.17	33.8
TiO_2-SiO_2/chitosan 20 %, DTAB 10 %/gel 15 h	154.7	0.19	65.3
TiO_2-SiO_2 (2:1), DTAB 10 %, gel 15 h	13.1	0.03	33.9

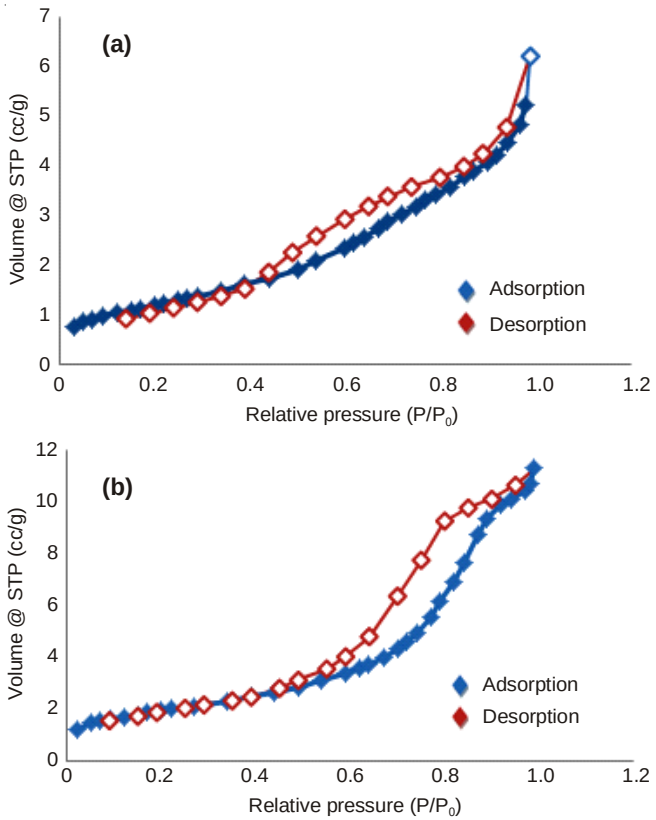

Fig. 4. Hysteresis curve of TiO_2-SiO_2/chitosan variation in composition, TiO_2-SiO_2/chitosan (a); long time sol 8 h (b); long time gellation 15 h; calcination 550 °C, 3 h

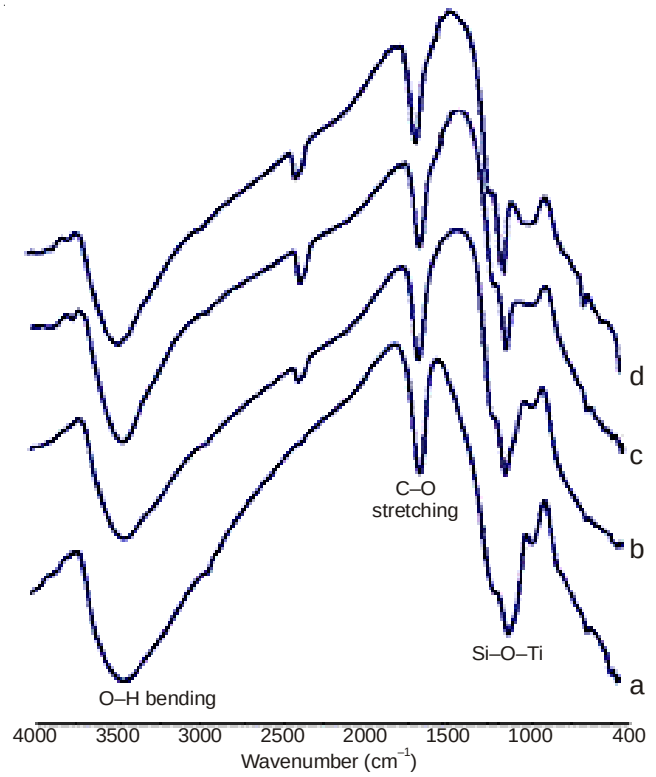

Fig. 5. FT-IR spectra of TiO_2-SiO_2/chitosan in various composition (a) TiO_2-SiO_2 (b) TiO_2-SiO_2/chitosan, DTAB 10 % (c) TiO_2-SiO_2/chitosan, DTAB 20 % (d) TiO_2-SiO_2/chitosan DTAB 30 %

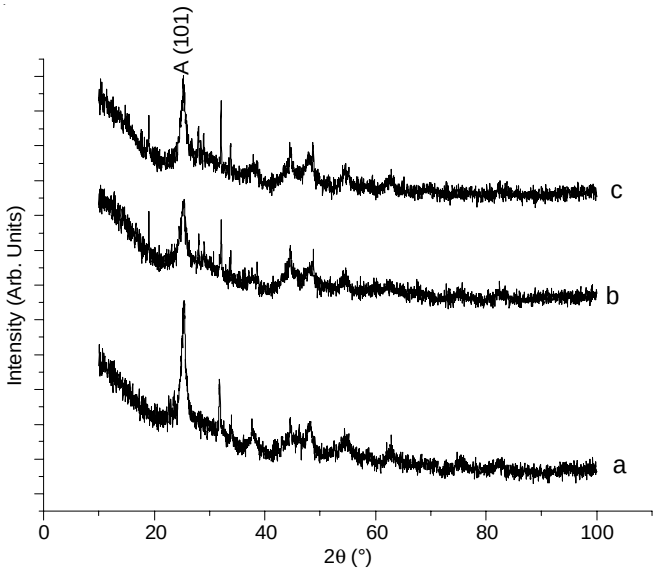

Fig. 6. XRD patterns of TiO_2-SiO_2/chitosan crystal in differences in the composition, gelation 15 h, calcination 550 °C for 3 h (a) TiO_2-SiO_2/chitosan, DTAB 20 %, sol 8 h (b) TiO_2-SiO_2, DTAB 20 %, sol 8 h, (c) TiO_2-SiO_2/chitosan, DTAB 20 %, sol 5 h

FT-IR characterization: FT-IR characterization shows the spectrum of TiO_2-SiO_2/Chitosan composition variations (Fig. 5). The peaks at 1100-956 cm^{-1} wave number is assumed as asymmetric stretching vibration from Si-O-Si and Si-O-Ti bond. The intensity of Si-O-Ti of TiO_2-SiO_2/chitosan is lower than TiO_2-SiO_2 without chitosan. It because of the higher intensity of anatase TiO_2 crystal is known by XRD characterization. Then, FT-IR spectra of TiO_2-SiO_2/chitosan with various concentration of DTAB show the peaks at 3500-3000 cm^{-1}indicate there is hydroxyl (OH) and 1600 cm^{-1} wave number indicates chemisorbed water (H-O-H) on each sample. From the FT-IR characterization, it can be concluded that TiO_2-SiO_2/chitosan preparation with addition SiO_2 and Chitosan, DTAB indicate the more amount of OH that can be adsorbed. It is caused by the addition of doped increases the acidity of material surface, so it is easier to catch OH in the air[12]. Then, modification of a stoichiometric composition with the addition of chitosan and surfactant variation can increase of intensity. If it is correlate by XRD characterization, the increasing of Ti-O-Si.

XRD characterization: XRD patterns were used to investigate the phase structure of the prepared TiO_2-SiO_2/chitosan. The effect of chitosan to crystallinity growth of TiO_2-SiO_2 powder by sol-gel methods showed to Fig. 6. Chitosan is a biopolymer compounds, are non-toxic, easily degraded when heated, so it can be used as a template steering mesoporous structure. Besides, chitosan has a functional group OH and NH_2, functional group can serve as an intermediary occurs of hybridization and dispersion of TiO_2 and SiO_2[19,20].

The crystallinity of anatase structure of TiO_2 was identified from the highest intensity peak (peak at 2θ: 37.5°, 47.5°, 53°, 55°, 62°, 75° and 83°) based on JCPDS No. 03-065-571. Anatase phase can be maintained at temperature (400-800 °C) in the presence of chitosan[5,13]. The crystallite size was determined from XRD peaks using the Scherer equation.

UV-visible characterization: The UV-visible spectrum of TiO_2-SiO_2/chitosan shows the value of the band gap as a catalyst morphology modification effect with the formation

of oxide clusters between TiO_2 and SiO_2. Value of the band gap can describe the basis for selecting the right light for the reaction mechanism of photocatalytic TiO_2-SiO_2/chitosan in its application[20]. UV-visible analysis of patterns can describe that SiO_2 to TiO_2 substituted into the matrix can affect the absorption band of TiO_2-SiO_2/chitosan[21].

The interaction between TiO_2 and SiO_2 interface bonding occurs in the presence of chitosan as cross-links, thus causing a change in the electronic structure of TiO_2 molecules. And causes a shift-blue at the maximum wavelength in the region $\lambda \geq 400$ nm or visible region. Beam is used to excite the electrons in the valence band to the conduction band[22].

Conclusion

Doped surfactant DTAB on synthesized catalyst can improve the crystallinity of TiO_2-SiO_2/chitosan, spherical crystal form, porous with a large specific surface area in optimum condition of sol-gel process, a longer time of sol gel *i.e.* 8 h and 15 h. The addition of DTAB and chitosan can simultaneously improve the performance of the catalyst TiO_2-SiO_2/chitosan, evenly distributed particles with crystal size in the nanoscale (9.6-18.2 nm), with specific surface area is 179.3 m^2/g, pore volume of 0.2 $cm^3\ g^{-1}$ and pore diameter is 45.4 Å. Analysis of UV-visible spectroscopy of the data gives the values of E_g = 1.7-1.9 and shows that the material is effective to be applied in tropical environments where visible light is dominant.

ACKNOWLEDGEMENTS

This study was funded through a grant scheme funded by the Fundamental Grant DIKTI through the DIPA (Budget Implementation List) Andalas University Number: 02/UN.16/PL/D-FD/I/2014, date 10 March 2014.

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