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Synthesis of mesoporous TiO_2 template-free and photocatalytic activity for azo dye degradation

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Abstract

Nanoporous titanium dioxide was prepared by sol-gel technique. To control the surface area, pore size and pore volume of the prepared TiO_2, a catalyzed hydrolysis was carried out using different concentrations of silicotungstic acid (SWA) as a template. A fixed molar ratio of H_2O/Ti was used. The prepared TiO_2 was calcined at 400 or 600^oC. Samples were characterized by nitrogen physic-sorption, X-ray powder diffraction (XRD), selected scattered electron diffraction, scanning and transmission electron microscopy (SEM and TEM). The photocatalytic activity of the prepared samples was evaluated by the degradation of alizarin yellow under UV light. The results showed that the crystallinity increases as the concentration of SWA decreases. The presence of SWA during the precipitation of TiO_2 prevents the formation of rutile phase and suppresses the crystal growth. The results showed also that the surface area increases as the concentration of SWA decreases. The samples prepared using 0.05M SWA and calcined at 600 ^oC showed a higher activity.

Keywords: mesoporous TiO_2, photocatalytic degradation, alizarin yellow, azodye.

1. Introduction

The dyeing wastewaters discharge a large number of hazardous pollutants, in which, the percentage of azo dyes accounts for about 70% of all dyestuffs by weight (Singh & Arora 2011). Azo dyes and their intermediates, e.g., aromatic amines, are toxic, carcinogenic and mutagenic, which may pose a potential health hazard tohumans (Turesky 2005; Dumont *et al.* 2010). Now adays, the dyeing wastewaters are mostly treated by biological processes. However, the biological degradation of azo dye is difficult. Furthermore, azo dye could inhibit the microbial activity and cause cell death at high concentration. Moreover, the effluent of biological treatment of dyeing wastewater was proved to be carcinogenic and mutagenic (Lima *et al.* 2007). To improve the biodegradability of azo dyeing wastewaters, combining advanced oxidation processes (AOPs) with biological process was pursued in recent years (Wang & Xu 2012). AOPs, defined as those technologies that utilize the hydroxyl radical ($OH^·$) for oxidation, including ozonation (Fu *et al.* 2011), Fenton oxidation (Tantak & Chaudhari 2006; Lodha & Chaudhari 2007), electrochemical oxidation (Guo 2006), or UV/H_2O_2 (Sudarjanto *et al.* 2006), followed by aerobic process are efficient for azo dyes degradation. Ionizing radiation (e.g., gamma radiationan delectron beam) is a special kind of AOP (Sudarjanto et al. 2006), which can produce approximately equal amounts of oxidizing species (d_{OH} and H_2O_2) and reducing species (ea_q and Hd) through water radiolysis. This technology has been receiving more and more attention for removal and/or pretreatment of azo dyes and other toxic pollutants (Jianlong & Jiazhuo 2007; Sharma *et al.* 2003; Hu & Wang 2007; Ting & Jamaludin 2008; Wojnarovits & Takacs 2008; Vahdat 2010; Yu *et al.* 2010) but this technology is more expensive than chlorine or ultraviolet disinfection. Because of this gamma irradiation is unlikely to be applied.

Photocatalytic degradation and mineralization of organic and inorganic pollutants by means of semiconductor TiO_2 have been extensively studied in order to solve environmental problems relating to waste waters and polluted air (Hoffmann *et al.* 1995; Hogfelt & Gratzel 1995; Fox & Dulay 1993; Pelizzetti & Serpone 1989; Heller 1995; Anpo & Yamashita 1996; Kamat 1993; Ollis & Al-Ekabi 1993). Among various metal oxide semiconductors, TiO_2 has been in the focus of photocatalysis under UV irradiation because of its physical and chemical stability, low cost, ease of availability, non-toxicity and electronic and optical properties.

Azo-dyes are abundant class of synthetic, colored, organic compounds, characterized by the presence of one or more azo bonds (-N=N-). Synthetic textile dyes of the azo family represent an important part of the world production of synthetic dyes. They are degraded into potentially carcinogenic amines (Chung & Stevens 1993; Nerud *et al.* 2001). Moreover, their color causes an aesthetic problem in receiving waters. The degradation mechanism of dye using TiO_2 can be described by the following steps:

$$TiO_2 + h\upsilon \rightarrow h^+ + e^- \quad (1)$$

$$h^+ + OH^- \rightarrow {}^·OH \quad (2)$$

$$e^- + O_2 \rightarrow O_2^- \quad (3)$$

$$dye + h\upsilon(UV) \rightarrow dye^* \quad (4)$$

$$dye^{·+} + O_2 \text{ (or } {}^·OH \text{ or } O_2^{·-}) \rightarrow \text{smaller organic molecules, } CO_2\text{, etc.} \quad (5)$$

Nowadays, progress is focusing on to prepare anatase TiO_2 phase of high surface area and controlled pore size, aiming to enhance the charge transfer efficiency. Generation of these highly controlled materials can be achieved by combining sol–gel techniques with the evaporation process taking place in the presence of a surfactant templating agent (Soler-Illia *et al.* 2002; Soler-Illia *et al.* 2003). After elimination of the organic template and controlled crystallization of the network (Grosso *et al.* 2003), one ends up with an organized arrangement of anatase nanoparticles shaped in mesoporous framework with narrow pore size distribution adjusted by the conditions and the surfactant molecular weight (Sakatani *et al.* 2006). Previous studies published in the litreature emphasis the preparation of mesoporous TiO2 without using template as reported by (Li etal.,2012, 2013), (Liu etal., 2012), (Gao etal., 2014) and (Abdel-Azim et al., 2014). Other published litretures emphasis the preparation of mesoporous TiO2 using different templates such reported by (Chevallier et al., 2012), (Bawer et al., 2012), (Zhao et al.,2012), (Duan et al., 2013), (Zhou et al., 2014), (Park et al., 2014), (Kim et al., 2013) , (Xiong et al., 2011), (Di et al., 2006), (Faisal et al., 2014), (Wang et al., 2013) and (Qiona et al., 2013). Other researchers used mixed template during the preparation of mesoporous TiO2 as (Wang et al., 2014), (Onsuratoom et al. , 2011), (Jantawasu et al., 2009) and (Sreethawong et al., 2005).

Generally, a sol-gel method based on the hydrolysis of titanium alkoxide is widely used to synthesize TiO_2 nanoparticles (Lakshmi *et al.* 1997). However, this method encounters some problems, such as weak anatase crystallinity and poor monodispersity. In addition, nanocrystalline TiO_2 prepared by the sol-gel method undergoes both phase transformation and crystallite size growth even at relative low temperature (Zhang *et al.* 2006). To apply TiO_2 particles synthesized from the sol-gel process as photocatalytic catalysts, it is important to maintain high anatase crystallinity (Cao *et al.* 2011). A previous study reported that high degree of anatase crystallinity can be achieved without high temperature calcination when TiO_2 particles were synthesized at low temperature due to fast hydrolysis and slow condensation (Nikkanen *et al.* 2007). In addition, many studies regarding the evaluation of the photocatalytic activity of TiO_2 nanoparticles have been conducted (Fujishima *et al.* 2000; Chong *et al.* 2010; Yu *et al.* 2007); however, few focused on the correlation between parameters used in the synthesis process of TiO_2 nanoparticles and their photocatalytic activity (Chong *et al.* 2010; Yu *et al.* 2007; Li *et al.* 2006).

Therefore, in this study we pay attention to the effect of the synthesis condition using silicotungstic acid in different concentration as a template on the physical properties of mesoporous TiO_2, in particular on its crystal composition, thermal stability, pore size distribution, surface area, and photocatalytic activity. The prepared materials were calcined at various temperatures and their crystalline composition, thermal stability, pore size distribution, surface area and photocatalytic activity were compared.

2.Experimental

2.1. Materials

Titanium (IV) isopropoxide, silicotungstic acid $H_4[W_{12}SiO_{40}]$ and the absolute ethanol were provided from Sigma-Aldrich CO.USA. The analytical grade alizarin yellow $C_{13}H_9N_3O_5$ was used without further purification.

2.2. Preparation of titanium dioxide

Titanium dioxide was prepared using sol-gel method as follows: 3.6 g of titanium tetraisopropoxide was diluted by absolute ethanol with constant stirring in a weight ratio of 1/7. After 15 min, 0.48 ml of silicotungstic acid (SWA) was added. The resulting suspension was stirred for three hours at room temperature, followed by the addition of 26 moles of waters per mole of Ti with vigorous stirring for two hours followed by the evaporation of water and ethanol at 78 ℃. The resulting precipitate was washed with deionized water and ethanol, drying under vacuum at 80 ℃ overnight, and then calcined at 400 or 600 ℃ for three hours.

2.3. Characterization of TiO_2

Nitrogen physisorption isotherms were measured at -196 ℃ using Quantachrome Nova Win 2 apparatus. The average pore size and pore size distribution were calculated using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms.

Crystalline phase of the TiO_2 formed was determined applying a Philips RB diffractometer in reflection mode using MoKα radiation at 40 kV, 40 mA.

The crystalline phases of TiO_2 were also investigated by scattered electron diffraction using a MORGAGNI 268D type (100 kV; W filament; point-resolution = 0.5 nm).

Surface morphology of the prepared TiO_2 was performed on JEOL JEM 3500 electron microscope.

Transmission electron microscopy (TEM) studies were carried out using a JEOL JEM-1230 electron microscope operating at 120 kV.

The pore structure of TiO_2 was investigated by a MORGAGNI 268D type (100 kV; W filament; point-resolution = 0.5 nm) scanning electron microscope.

2.4. Photodegradation of Alizarin yellow

500 ccm of an aqueous solution containing 10 ppm of high purity Alizarin yellow was subjected to UV irradiation using a 6 watt lamp at a wavelength of 254 nm. All photodegradation experiments were conducted in a batch reactor. The UV lamp was placed in a cooling silica jacket and placed in a jar containing the polluted water. The catalyst (0.05 g) was stirred in the

solution using a magnetic stirrer at a controlled reaction temperature of 25 ℃ during the experimental period. At different irradiation time intervals, samples of the irradiated water were withdrawn for analysis and the dye concentration was determined by absorption mode (using calibration curve of absorbance & the concentration of the dye) 8500 series UV-Visible spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Effect of SWA concentration and calcination temperature on the physicochemical structure of TiO_2

Figure 1 (a&b) shows the nitrogen adsorption-desorption isotherms, and the pore size distribution of a TiO_2 sample calcined at 400^{o}C. The isotherms are of type IV with H2 type hysteresis loop classified by IUPAC (IUPAC reporting physisorption data for gas/solid system 1985) with closure point ranging between p/p0=0.3-0.4 and a quite steep condensation step indicating the mesoporous nature of the solid. The H2 type hysteresis loop is generally attributed to pores of narrow entrance and wider body, i.e. ink bottle like shape. The amount of adsorbed nitrogen increases simultaneously with decreasing in SWA content indicating increasing adsorption capacity of the samples. The decrease in surface area with increasing SWA content can be attributed to a lower cross-linking degree during the sol-gel synthesis process (Phonthammachat *et al.* 2003; Khalil *et al.* 1998). These features are reflected in surface parameters, pore volume and average pore radius especially for the samples embedded low SWA content. Figure 2/a&b also shows the widening of the hysteresis loop which is more pronounced after introduction of SWA, and increases with decreasing SWA content implying the successful role of SWA in creating mesoporous system. It should be emphasized that the surface parameters are related to SWA content and the crystalline features of the samples (Table 1). Figure 2/a shows the pore size distribution for the calcined samples at 400^{o}C. It is obvious that as the SWA increases bimodal pores are formed. This indicates highly incorporated SWA in the TiO_2 structure.

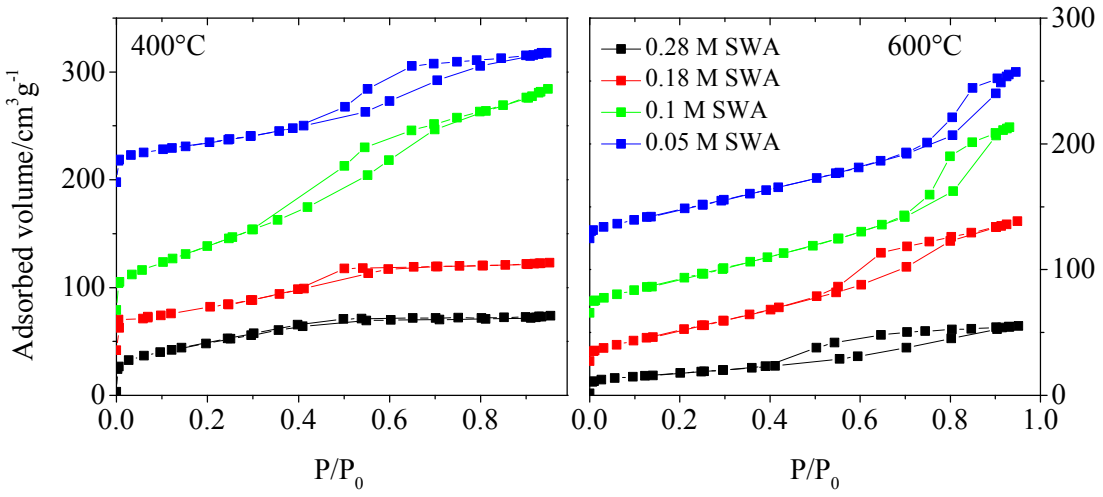

Figure 1:

Nitrogen physisorption isotherms for TiO_2 prepared by different concentrations of SWA calcined at 400 ℃ and 600 ℃ for 3 h.

Table 1

Textural properties of TiO_2 calcined at 400 ℃ using different concentrations of SWA.

SWA conc. (Mol/L)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	Crystallite size (nm)
0.28	140.0	0.11	10.9	18.2
0.18	153.0	0.12	18.2	15.0
0.1	173.7	0.18	18.1	12.1
0.05	256.6	0.31	21.6	9.1
Ref. a	93	0.10	5.8	-

[a]*Mesoporous TiO_2 was prepared using phosphotungstic acid assisted hydrolysis and polycondensation reactions of tetrabutyl titanate, followed by removal of the template via washing with water and ethanol. Luo, G.S. et al. (2006), Microporous and*

*Mesoporous Materials 96, 301–306***.**

The experimental results show that the surface area is influenced by the annealing temperature, whereas the mesopore size and the total pore volume are influenced by the amount of SWA and the annealing temperature (Table 2). The average mesopore diameter and the total pore volume decrease with increasing the concentration of SWA. Increasing the calcination temperature the surface area and the total pore volume are decreasing rapidly due to the growth of the crystallite size (Figure 2 a&b).

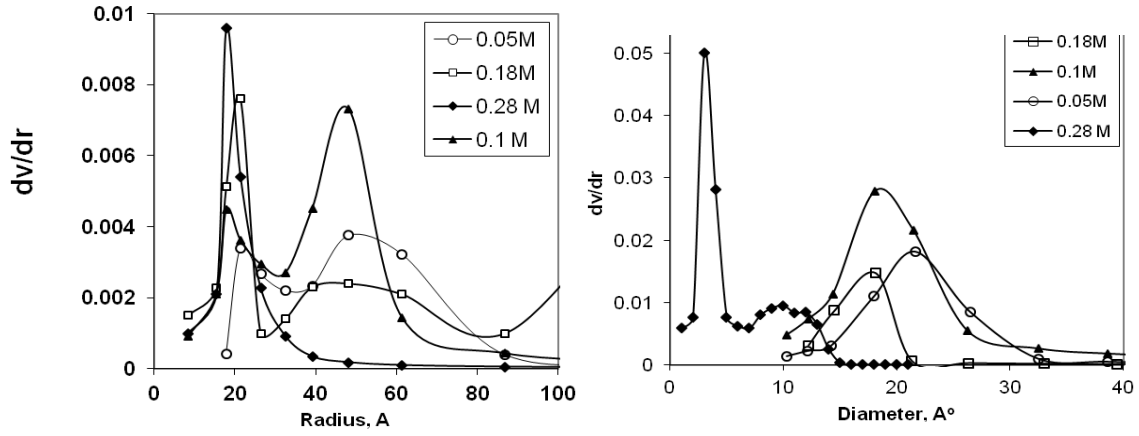

Figure 2
Pore size distribution for TiO_2 prepared by different amounts of SWA, calcined at (a): 400°C and (b) 600°C

Table2
Textural properties of TiO_2 calcined at 600 ℃ using different concentrations of SWA.

SWA conc. (Mol/L)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	Crystallite size (nm)
0.28	61.9	0.08	3.6	24.5
0.18	107.0	0.17	4.3	18.3
0.1	102.0	0.21	9.7	14.3
0.05	132.9	0.23	9.7	11.5

The X-ray diffraction (XRD) patterns of the calcined TiO_2 material prepared under various concentrations of SWA calcined at 400°C and 600°C are shown in Figure 3 a&b. All the reflections can be assigned to anatase phase without any indication the presence of any crystalline SWA. Hence, SWA was successfully incorporated into TiO_2 structure, rather than existing as a free solid acid. The peak found at 11.5 °2θ is the most intensive peak for the anatase phase. This peak is relatively broad due to the nano-sized dimension of the crystals. The particle sizes estimated by the Sherrer equation are varying between 9-18 nm, depending on the SWA concentration for samples calcined at 400°C and between 12-36 nm for samples calcined at 600°C. It should be emphasized that SWA plays a vital role in controlling the particle growth and the nature of crystalline phases. The addition of small amount of SWA is considered as a prime factor in stabilizing the anatase phase and hinders its transformation to the more stable rutile phase. Anatase appears to be the most photocatalytically and electrochemically active crystallographic form of TiO_2, opposed to the rutile and brookite forms; herein, the prepared mesoporous TiO_2 materials may have far-reaching implications for its use as a photocatalytic material.

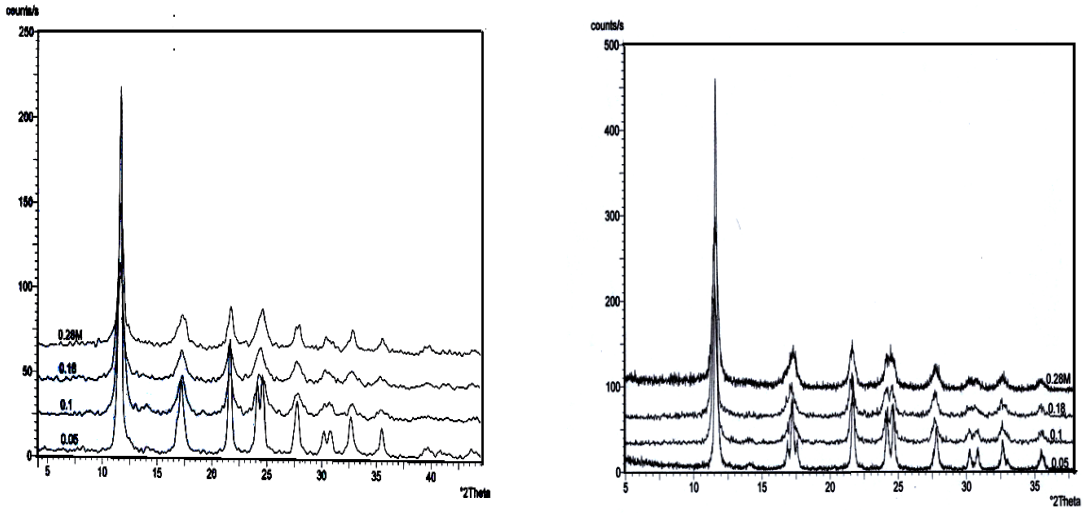

Figure 3

XRD patterns of TiO_2 prepared using different SWA concentrations, calcined at (a): 400°C and (b) 600°C for 3 h.

Selected area scattered electron diffraction (Figure 4) also supported that with increasing temperature the crystallinity of the anatase phase also increases. It is also obvious that the anatase crystallinity increases as the SWA content increases.

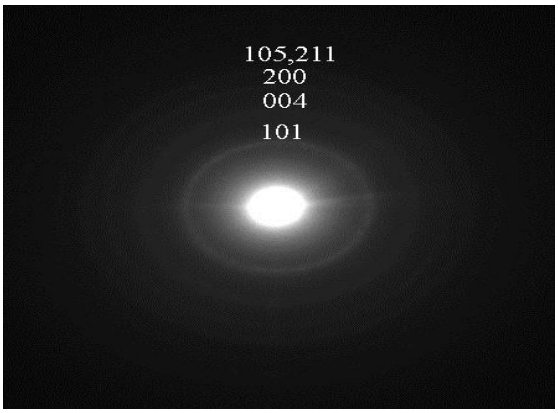

Figure 4

Electron diffraction pattern for TiO_2 prepared using 0.1 M SWA, heat treated at 600 ℃.

Surface morphology of the prepared TiO_2 samples calcined at 400 and 600°C are presented in Figure 5. The SEM images show that TiO_2 particles have well-defined spherical morphology, with a diameter range of 7–8 μm.

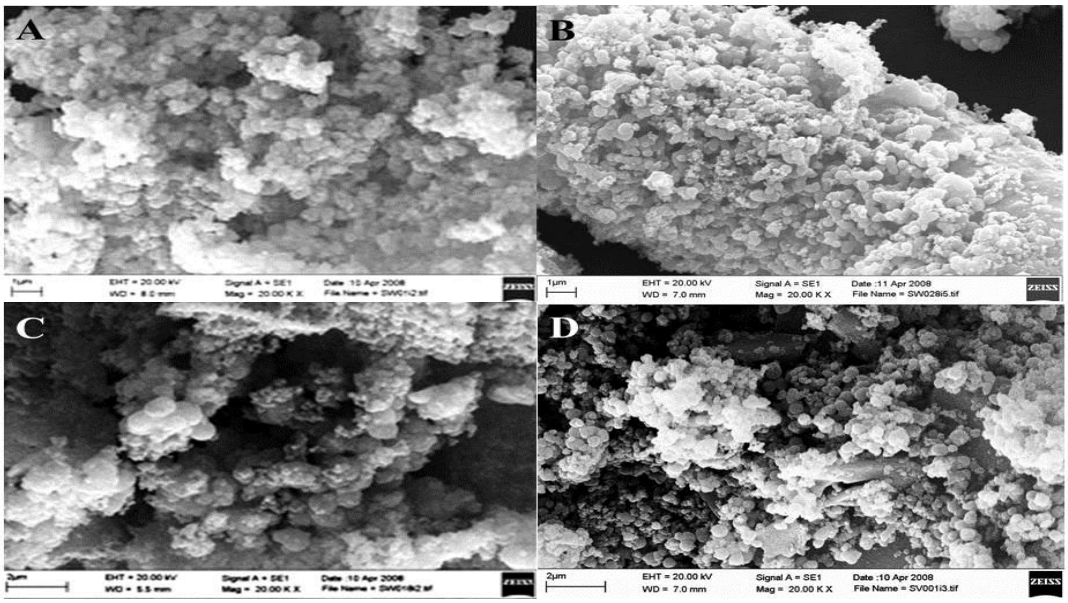

Figure 5
SEM images for TiO_2 prepared by different SWA concentrations: a) 0.28 M, b) 0.18 M, c) 0.1 M and d) 0.05 M and calcined at 400 ℃ for 3 h.

TEM images in Figure 6 show the aggregation of nanoparticles with particle size of 11-24 nm. A disordered wormhole-like pore structure can be observed, which is formed by the agglomeration of TiO_2 nanoparticles. The accessible pores are randomly connected, lacking discernible long-range order in the pore arrangement among the small TiO_2 particles. This indicates that the mesoporosity is mainly due to the inter-particle porosity rather than intra-particle porosity.

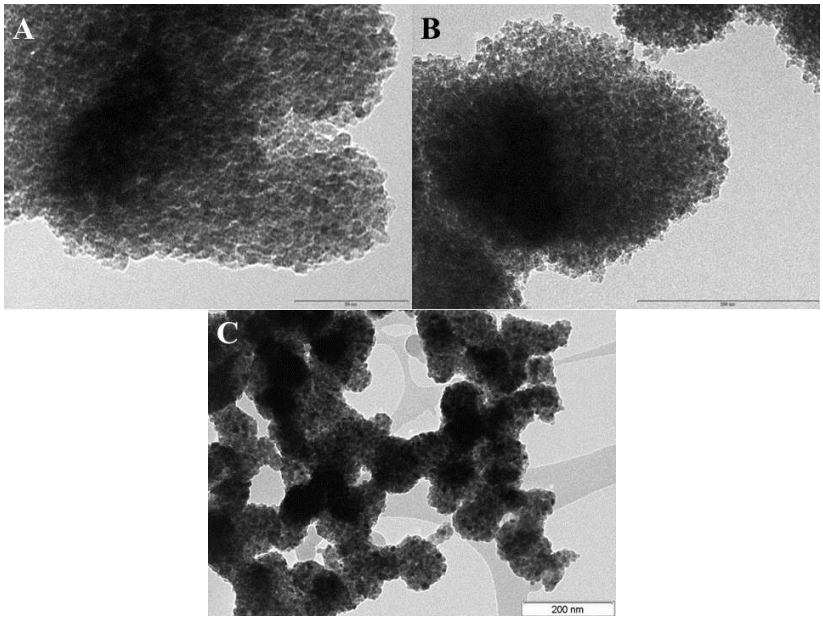

Figure 6:
TEM images for TiO_2 prepared by different SWA concentrations: a) 0.1 M, b) 0.05 M and c) 0.28 M and calcined at 600 ℃ for 3 h.

3.2. Mechanism of Formation Mesoporous TiO_2

A possible mechanism for the formation of well-dispersed mesoporous TiO_2 particles might be effective aggregation of the

TiO_2 particles in the presence of SWA. The SWA plays an important role in the formation of a stable sol–gel network with ordered array of Ti and O, without leading to the shrinkage and collapse of the network. The basic unit of SWA is the heteropolyanion of Keggin structure $H_4[W_{12}SiO_{40}]$, which is the most commonly studied heteropolyanions because of its great acid strength, stability, and availability compared to those of other polyoxometalates. A Keggin unit of SWA (Janik *et al.* 2003) is composed of a central SiO4 tetrahedron surrounded by twelve WO6 octahedra. There are four types of oxygen atoms in the Keggin unit: four oxygen atoms of the central tetrahedron, 12 oxygen atoms that bridge addenda atoms not sharing a central oxygen atom (corner-sharing, 12 oxygen atoms that bridge two addenda atoms sharing the same central oxygen atom (edge-sharing), and twelve terminal oxygen atoms associated with a single addendum atom (Janik *et al.* 2005). A hydrogen bond is easily formed between the proton on the Keggin unit and the oxygen atom of the water molecule. Bidentate water adsorption includes formation of a second hydrogen bond between a hydrogen atom of the water molecule and a second oxygen atom of the Keggin unit. Hydrogen bonds between SWA and hydroxylated tetrabutyl titanate are the essential factor to form this mesoporous structure. It is reported that mesoporous silica could be prepared by the hydrogen-bonding interaction of an alkylamine (S0) head group and hydroxylated TEOS (I0) (Tanev & Pinnavaia 1995). Similarly, surfactants with head groups that could interact with the titanium alkoxide will lead to TiO_2 mesostructures. This indicates that, without the formation of ordered micelles by hydrophilic and hydrophobic surfactants, SWA can be used successfully as a self-assembling template via formation of hydrogen bonds. Consequently, the titanium precursor is hydrolyzed and condensed around the self-assembled PWA structure combined with water at a controlled rate, resulting in the formation of highly porous crystalline TiO_2. The materials lack long-range ordering of pores and have higher amounts of interparticle mesoporosity, because the long-range effects of the electrostatic interaction that could control the packing of micellar rods are absent.

3.3. Photocatalytic degradation of Alizarin yellow

Titanium dioxide is considered as a promising photocatalyst extensively involved in partial or complete mineralization of various hazardous organic dyes through the active species on its surface. Once titanium dioxide is illuminated with UV light, electrons are excited from the lower energy valance band to the conducting band, which leads to the formation of positive holes and negative electrons on the catalyst surface. The holes react with water or hydroxyl ions producing hydroxyl radicals. Electrons in the conduction band (e_{CB}-) on the catalyst surface can reduce molecular oxygen to a superoxide anion. Hydroxyl (HO), hydrogen peroxide (HO_2), and superoxide ($\dot{O}_2^-$) radicals are considered the reactive species that oxidize the organic compounds adsorbed on the oxide surface (Hoffmann *et al.* 1995).

These generated radicals are usually react with the adsorbed dye molecules followed by the formation of several intermediates including radicals, and radical cations finally mineralized into carbon dioxide, water and inorganic nitrogen from nitrate ion.

The response mechanism of the electrons and holes of the Ti catalyst is expressed as follows:

$$\text{Ti (metal oxide)} + h\nu \rightarrow \text{Ti } (e^- + h^+) \quad (2)$$

$$\text{Ti } (h^+) + \quad \rightarrow \text{Ti} + RX^{\cdot+}_{ad} \quad (3)$$

$$\text{Ti } (h^+) + H_2O \rightarrow \text{Ti} + {}^{\cdot}OH + H^+ \quad (4)$$

$$\text{Ti } (h^+) + OH^- \rightarrow \text{Ti} + {}^{\cdot}OH \quad (5)$$

The electrons will, therefore, be transmitted via substances absorbed on the surface of the Ti catalyst such as H_2O, dye, and ${}^{\cdot}OH$. In addition, Organic compounds absorbed on the surface of Ti catalyst then oxidized by ${}^{\cdot}OH$.

$$Ti(\text{metal oxides})\ (e\text{-}) + O_2 \rightarrow Ti + O_2^{\cdot -} \quad (6)$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot}, \quad (7)$$

$$2\ O_2^{\cdot -} + 2\ H^+ \rightarrow 2\ {}^{\cdot}OH + O_2 \quad (8)$$

$$2\ {}^{\cdot}OH \rightarrow O_2 + H_2O_2 \quad (9)$$

$$Ti\ (\text{metal oxides})\ (e^-) + H_2O_2 \rightarrow Ti + OH^- + {}^{\cdot}OH \quad (10)$$

The photocatalytic activity of the prepared samples was determined by degradation of x M alizarin yellow solution under UV-light irradiation (Figure 7 a&b). For 0.28 M SWA sample no degradation of alizarin yellow was observed over a long period (180 min). For 0.18M SWA sample already a low degradation activity can be found. As the concentration of SWA decreases the photocatalytic activity increases to reach 100% after 180 min using 0.05M SWA. The photoactivity of TiO_2 in degradation process is influenced by several parameters such as the phase composition, band-gap energy, surface area, particle size, crystallinity and electron hole recombination rate (Boujday *et al.* 2004; Zhang *et al.* 2005; Ding *et al.* 2000). different Azo Dyes photodegradation were studied by several research groups; (Topkaya *et al.* 2014; Guo *et al.* ; Shariffuddin *et al.* 2013; Kalasin *et al.* 2011; Nešić et al., 2013 ; Lucˇic´ *et al.* 2014; Ilinoiu *et al.* 2013; Narayanasamy & Murugesan 2014; Jiao *et al.* 2014). High surface area mesoporous titania is considered a reactive photocatalyst in degradation process owing to the facility of alizarin yellow dye molecules to adsorb on the various active surface centers and its ability to diffuse through the large pore structure (Gopal *et al.* 1997; Lv *et al.* 2011; Han *et al.* 2012). Fig.10b represents the photocatalytic degradation of the prepared catalyst calcined at 600^{o}C. The same trend can be observed as for samples annealed at 400 ℃ but with higher activity. 100% degradation was obtained in 120 min using 0.05 M SWA. (Han *et al.* 2012; Tian *et al.* 2009) reported that, if specific surface area and pore volume of TiO_2 nanoparticles were dominant factors controlling the photocatalytic activity of TiO_2, the activity would have decreased with calcination temperature; however, the activity showed the maximum value at 700 ℃ in his study. The trend is likely attributed to the combined effect of anatase crystallinity which showed the highest value at 600 ℃, and to crystallite size which did not excessively increased up to 600 ℃.

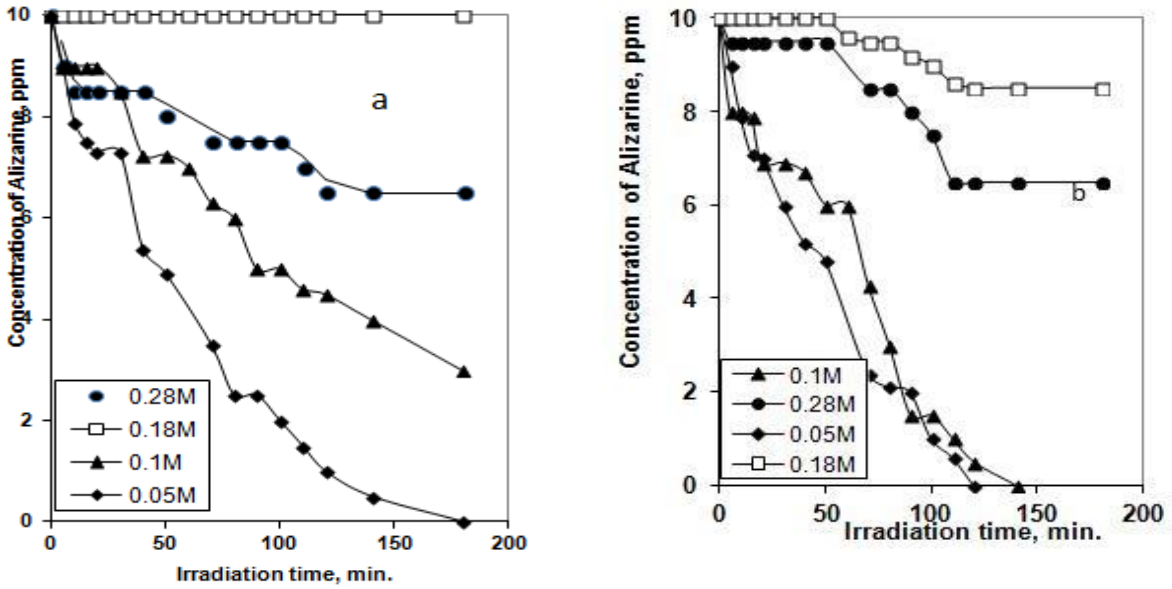

Figure7 a&b :

Photocatalytic degradation of alizarin yellow by using mesoporous TiO_2 at (a) 400 ℃ and (b) 600^{o}C.

5. Conclusions

In the present study the photocatalytic degradation of alizarin yellow by TiO_2 nanoparticles, synthesized under different concentrations of silicotungstic acid and calcination temperatures by sol-gel process, was investigated. The correlation between physical properties and photocatalytic activity of TiO_2 nanoparticles according to the different synthesis conditions is as follows:

- As the concentrations of silicotungstic acid increase the crystallinity of the anatase phase is slightly increases and the surface area decreases.
- Alizarin yellow degradation experiments revealed that the photocatalytic activity of TiO_2 nanoparticles was maximized at the calcination temperature of 600 ˚C.

However, surface area and pore volume of TiO_2 nanoparticles gradually decreases with increasing calcination temperature, indicating that textural properties are not critical for controlling the photocatalytic activity of TiO_2 nanoparticles. The trend is likely due to the combined effect of the anatase crystallinity, showed the highest value at 600˚C and the crystallite size did not excessively increase up to 600˚C.

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