PHOTOCATALYTIC DEGRADATION OF PHENOL OVER Ag-TiO_2-SiO_2 NANO POWDER UNDER SUNLIGHT IRRADIATION

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Abstract - Nanometric composite TiO_2, TiO_2-SiO_2 (TS10) and Ag-TiO_2-SiO_2 (A4TS10) powder photo-catalysts have been synthesized via sol-gel assisted with hydrothermal treatment method and employed for aqueous phenol decomposition under sunlight irradiation. Characteristics of those samples are analyzed by using X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), Energy dispersive X-ray (EDX), Transmission electron microscope (TEM), Brunauer-Emmett-Teller (BET) surface area and UV-Vis absorption method. The results of characteristic analysis show that all synthesized samples have the size of spherical nanostructures with the average nanoparticles size in range of 20 - 30 nm and pure anatase phase at a high crystalline degree. Moreover, the phenol degradation of TiO_2, TS10, A4TS10 samples increases significantly after 3 hours irradiation from 59%, to 68%, and 82%, respectively. These results demonstrate that Ag-TiO_2-SiO_2 is a promising candidate material for the wastewater treatment application in the future.

Key words - Ag-TiO_2-SiO_2; Photo-catalyst; Phenol Degradation; Nano Material; Sunlight Irradiation.

1. Introduction

Heterogeneous photo-catalysis could be used as a new method of wastewater treatment, which was a fast growing research area in the past decade due to a simple technique and high degradation efficiency. Titanium dioxide TiO_2 powder has been widely used as photo-catalytic materials to degrade organic pollutants in water and air owing to its nontoxicity, chemical and biological inertness, environmental friendly material and low cost. However, their commercial applications are hindered by serious disadvantages due to wide band gap of 3.2 eV, small surface area, agglomerations and difficulties of separation and recovery. Therefore, the enhancement of TiO_2 photo-activity is one of the most important issues in photo-catalytic field [1, 2].

Using the binary composite of TiO_2-SiO_2 can effectively decrease the aggregation and increase surface area, which lead to enhanced photo-catalytic activities. However, the addition of SiO_2 into TiO_2 matrix increases the band gap energy and most of TiO_2-SiO_2 mixed oxides are only active under UV light; therefore, doping is necessitated to use the photo-catalyst under visible or natural sunlight [3].

Recently, the noble metals such as Ag, Au, Pd and Pt have been incorporated into the TiO_2-SiO_2 materials to enhance the photo-catalytic activity due to the surface plasmon resonance (SPR). Among noble metals, Ag is the ideal metal for showing intense SPR at the desired wavelength (320-450 nm) [4]. Under visible light or sunlight irradiation, the electron-hole pairs are produced in Ag nanoparticles due to the SPR effect. These photo-excited electrons transfer into the conduction band of TiO_2 form superoxide radicals ($O_2^{\bullet-}$) with O_2 and then hydroxyl ($OH^{\bullet}$) radicals. The photo-catalytic TiO_2-SiO_2 modified by Ag deposition synthesized by sol-gel method exhibit high phenol degradation up to 57.2% after 6 hours UV radiation[5].

The sol-gel assisted with hydrothermal technique is the most effective method to produce homogenous materials with a high surface area. The synthesis of Ag-TiO_2-SiO_2 composite when using Ti and Si alkoxides as-precursors is usually accompanied with the limitations of the TiO_2 agglomeration because Ti alkoxides hydrolyze much faster than Si alkoxides. In order to overcome this problem, Acetyl acetone (AcAc) could be used as chelating agent in which the hydrolysis and condensation reactions occur more slowly even with the presence of water. In addition, the use of PEG + AcAc enhances small particles that improve the dyes absorbability.

In this work, the TiO_2, TiO_2-SiO_2 and Ag-TiO_2-SiO_2 photo-catalytic powder are synthesized via combining the sol-gel method assisted with hydrothermal technique, afterward the nanostructures and characteristics of synthesized samples are analyzed with TGA, XRD, FT-IR, TEM, BET, Band-gap and EDX. Besides, the phenol removal photo-activity under sunlight irradiation is investigated.

2. Materials and methods

2.1. Materials

Titanium n-butoxide (TNB, 99%) is obtained from Across Organics. Titanium dioxide Degussa (P25), Tetraethyl orthosilicate (TEOS, ≥99%), Silver nitrate ($AgNO_3$, 99.8%), Acetyl acetone (AcAc, ≥99%), Acid acetic (CH_3COOH, 100%), Polyethylene glycol 400 (PEG, 98%), Alcohol (99.5%) and Phenol (≥99%) were all purchased from Merck Chemical Company. Double distilled water was used in all experiments. TNB and TEOS were used as titanium and silicon precursors while AcAc was used as chelating agent.

2.2. Catalyst preparation

The TiO_2 and TiO_2-SiO_2 (TS10) photo-catalytic powder were synthesized by using sol-gel assisted with hydrothermal treatment method. The TS10 composite was prepared with the TiO_2:SiO_2 weight ratios of 90:10. The synthesis process involved two stages: in the first stage, the hydrolysis of TEOS in alcohol was performed by adding distilled water previously acidified with acetic acid to get the final molar ratio TEOS:Alcohol:Water:Acid of 1:10:5:0.3. This solution was agitated for 1 h at room temperature. In the second stage, TNB solution was prepared at room temperature by mixing with AcAc, Alcohol and PEG with the molar ratio

TNB:AcAc:Alcohol:PEG400 of 1:1:10:2. Subsequently, TNB solution was then mixed slowly into above TEOS solution for 2 h at room temperature. The mixture was hydrothermally treated in an autoclave at 120°C for 10 h, dried in oven at 110°C for 8 h to obtain the homogeneous TiO_2-SiO_2 ash and then calcinated in the air at 500°C for 3 h.

In order to synthesize Ag-TiO_2-SiO_2 (A4TS10) photo-catalyst with the Ag/TiO_2 weight percent of 4%, the silver nitrate was dissolved in alcohol and added into TNB solution and synthesized in the same manner with TS10 synthesized procedure.

2.3. Photo-catalytic reaction experiments

The decomposition of phenol in water was performed in a photo-reactor where 0.20 g powder catalyst suspended in 200 ml of 10 ppm phenol solution well mixed with magnetic bar. The suspension was stirred for 30 min in the dark before sunlight irradiation to ensure the adsorption/desorption equilibrium. During the process, the solution was stirred constantly and the temperature in photo-reactor was maintained at 31 ± 2°C by water-jacketed pyrex reactor. After a period of times, the aliquots of 2.5 mL solution were withdrawn and filtered through the syringe filters of size 0.45μm. The filtered solution after was reacted with 4-aminoantipyrine and potassium ferric cyanide at pH 8 to form a colored complex. This complex solution was determined by Spectro-2000 RS spectrophotometer with maximum absorbance wavelength of 500 nm according to the standard method for the examination of water and wastewater [6].

For the phenol degradation under natural sunlight, experiments were carried out on sunny day outdoors at Ho Chi Minh city University of Technology from 12:00 pm to 15:00 pm on 26 August, 2016. The sunlight intensity during the experiment time was measured by lux meter (FLM400, GEO-Fennel) with the average light intensity of 70 klux.

3. Results and Discussion

3.1. Characterization of the photo-catalyst

3.1.1. XRD studies

XRD patterns of the different samples are shown in figure 1. TiO_2 samples show distinct peak of anatase phase at 2θ = 25.3° (JCPDS No. 84-1286) at a high crystalline degree and no peak related to rutile (JCPDS No. 84-1286) at synthesized condition. The presence of 10% SiO_2 results in the broadening of distinct peaks and the reduction in their intensities. There is little change regarding the distinct peaks when 4% Ag is doped into the structure of the TS10. The average particle size calculated by using Scherer's equation at 2θ = 25.3° show that TiO_2 with particle size of 20 nm is larger than those of TS10 (15 nm) and A4TS10 (15 nm). The crystalline size depression could be attributed to the fact that SiO_2 structure blocks TiO_2 and inhibits the crystal growth of TiO_2 when adding silica[7].

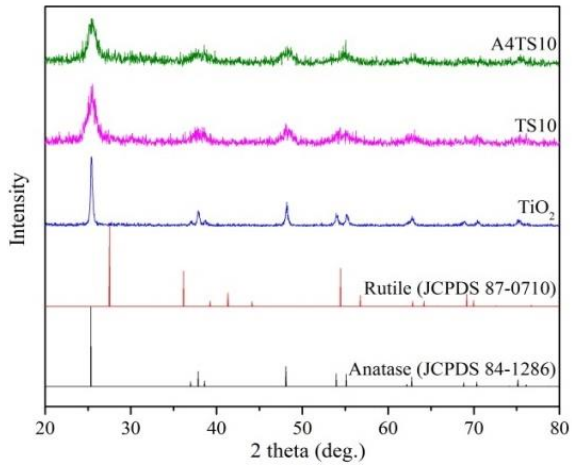

Figure 1. *X-ray diffraction patterns of TiO_2, TS10 and A4TS10*

3.1.2. FT-IR analysis

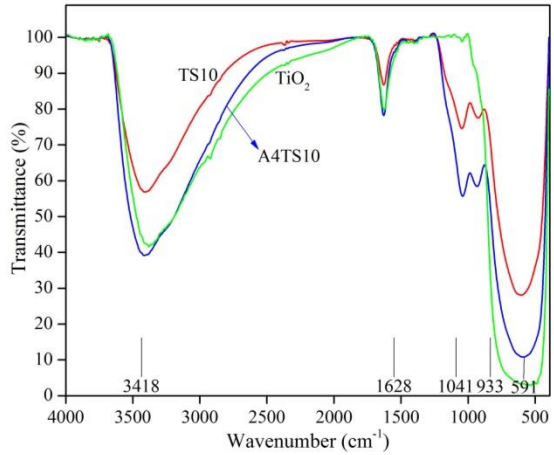

Figure 2. *FT-IR spectra of TiO_2, TS10 and A4TS10*

The FT-IR spectra are performed to analyze the composition of TiO_2, TS10 and A4TS10. In Figure 2, the observed peaks of all samples spectra at 591 and 3418 cm^{-1} are representative of the Ti-O-Ti and -OH bonds vibration which attributes to hydroxyl group of free water molecules, respectively [3]. The absorption bands at 1628 cm^{-1} are assigned to the M-OH bonds of the surface water molecules, which made the adsorption capability of TiO_2, TS10 and A4TS10 samples increase for varied hydrophilic compounds. The intended at 1041 cm^{-1} in the TS10 and A4TS10 samples assigned to the asymmetric vibration Si-O-Si [3]. Besides, the asymmetric Ti-O-Si hetero linkages with the most important peak at 933 cm^{-1} indicate the tight combination of TiO_2-SiO_2 nanocomposite and may enhance its adsorption capability [8, 9]

3.1.3. EDX analysis

Energy dispersive X-ray (EDX) analysis is used to determine composition in the sample. Figure 3 and Table 1 show that the A4TS10 mainly includes Ti, Si, O and small amount of Ag whose weight or atomic ratio percent conforms to the stoichiometric formula.

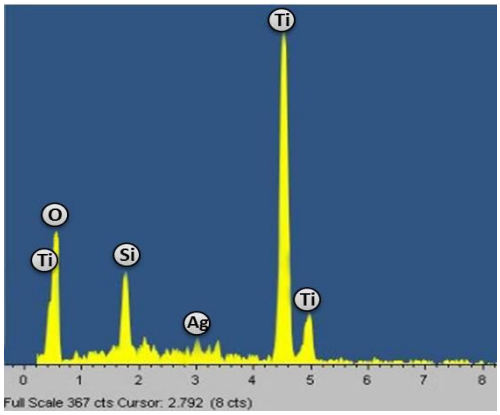

Figure 3. *EDX spectra of A4TS10*

Table 1. *The component of A4TS10*

STT	Element	Weight (%)	Atom (%)
1	Ti	46.54	24.96
2	Si	4.59	3.77
3	O	46.01	70.52
4	Ag	2.86	0.75
5	**Totals**	**100**	**100**

3.1.4. Band gap energy

The optical band gap can be determined by plotting $(\alpha h\nu)^2$ and photon energy ($h\nu$) based on the relation of equation (1):

$$\alpha h\nu = A(h\nu - E_g)^{1/n} \quad (1)$$

where, α is the absorption coefficient, A is a constant, E_g is the band gap energy (eV) and n is a parameter that depends on the electronic transition of the semiconductor; for indirect transition semiconductor such as TiO_2 anatase phase, $n = 2$ [10]. According to the above relation, the intercept of the tangent on the photon energy axis corresponds to optical band gap.

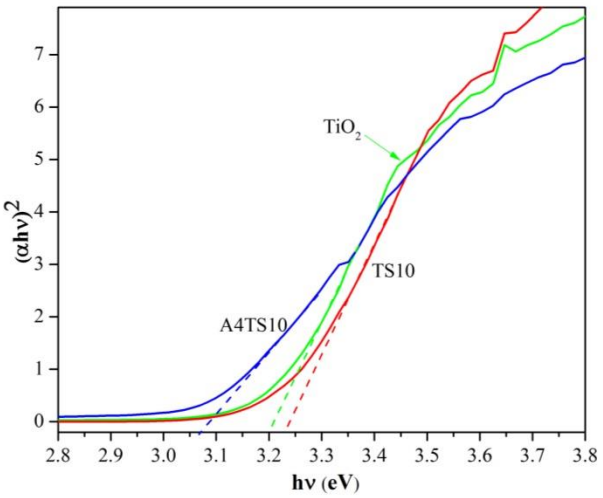

Figure 4. *The Tauc plots of TiO_2, TS10 and A4TS10*

As shown in Figure 4 and Table. 2, the band gap energy of pure TiO_2 is 3.20 eV, which is higher than that of P25 and equals to the reported anatase phase band gap 3.20 eV for anatase and 3.03 eV for rutile [2]. By raising the SiO_2 content up to 10%, the band gap of TS10 increases to 3.24 eV due to the decrease in particle size from 20 nm to 15 nm (Scherer's equation) and the stable Ti-O-Si linkages [3, 9]. Here, it is found that as the amount of SiO_2 in the nanocomposite increases, the band gap also increases. Corresponding to the band gap energy values, TiO_2 and TS10 samples exhibit absorption the UV region while the absorption edge is shifted towards visible light region when Ag is doped into the TiO_2-SiO_2 structure (A4TS10). The lower band gap is very effective to enhance photo-catalytic activity of Ag-TiO_2-SiO_2 nanocomposite.

Table 2. *The band gap energy (E_g) of different samples*

STT	Samples	Band gap E_g (eV)	
		E_g (eV)	Reference
1	P25	-	3.10 [11]
2	TiO_2	3.20	3.20 [2]
3	TS10	3.24	3.33 [12]
4	A4TS10	3.06	-

3.1.5. The specific surface area (SSA)

Table 3. *The specific surface area of different samples*

STT	Samples	BET (m^2/g)	
		BET	Reference
1	P25	-	49.2 [11]
2	TiO_2	38.9	31.8 [13]
3	TS10	191.4	164.5 [14]
4	A4TS10	218.4	-

The specific surface area (SSA) is one of the important parameters to enhance the photo-catalytic activity of the synthetic samples. The SSA values of pure TiO_2, TS10 and A4TS10 are shown in Table 3 which is 38.9, 191.4 and 218.4 (m^2/g) respectively. The results indicate that the SSA of TiO_2 prepared sample is lower than that of P25 due to the preparation method and phase composition; moreover, SSA increases significantly when adding the 10% SiO_2 (five-times higher than TiO_2) and rises lightly when doping 4%Ag into TS10 structure.

3.1.6. TEM

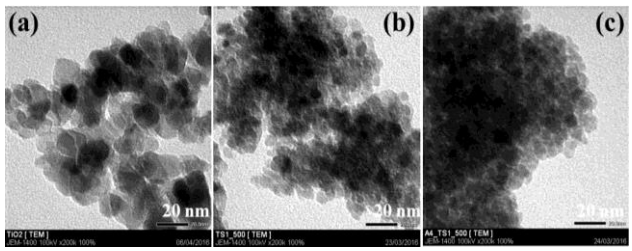

Figure 5. *TEM images of (a) TiO_2, (b) TS10 and (c) A4TS10*

TEM images presented in Figure5 show a significant difference in the surface morphology of TiO_2, TS10 and A4TS10. All the samples possess spherical shape with uniform particle size distribution. The average particle size of TS10 (about 20 nm) and A4TS10 (20 nm) are

much smaller than that of TiO_2 (30 nm). Thus, the silica matrix prevents the increase in particle size during the heat treatment.

3.2. Photocatalytic activities

3.2.1. Equilibrium isotherm models

In this study, the adsorption experiments of phenol from solution is performed at the initial concentration ranging from 10 mg/l to 80 mg/l with the A4TS10 dosage of 1 g/l and employed the Langmuir, Freundlich, Dubini-Radushkevich and Tempkin adsorption isotherm models to investigate the A4TS10 adsorption behavior. The relationship between the equilibrium adsorption capacity (q_e) and the equilibrium phenol concentration (C_e) of experiment data and these above model values is depicted in Figure 6.

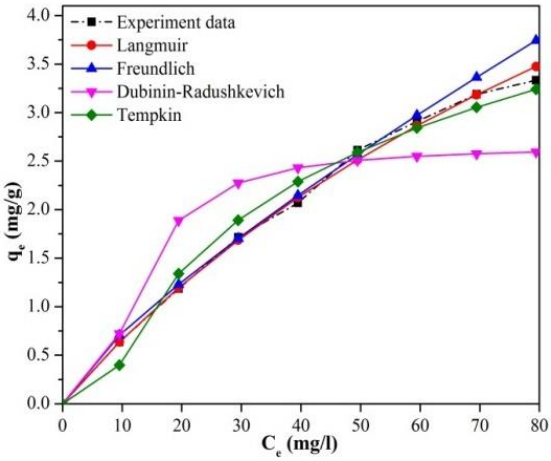

Figure 6. *The isothermal adsorption models between experiment and theory*

Figure 6 indicates that the isothermal adsorption of phenol on A4TS10 surface fits the Langmuir adsorption model well. According to that, equilibrium isotherm model of A4TS10 system can be described by Langmuir equation:

$$q_e = \frac{Q_{max}.K.C_e}{1+K.C_e} \quad (2)$$

The maximum adsorption capacity (Q_{max}) and Langmuir isotherm constant (K) are calculated to 9.166 mg/g and 0.008 (L/mg), respectively. Consider the Langmuir-Hinshelwood rate equation:

$$v = -\frac{dC}{dt} = \frac{k_r.K.C}{1+K.C} \quad (3)$$

At the initial low phenol concentration (10 mg/l) and K = 0.008 (l/mg) so K.C << 1, the equation (3) can be reduced to first order kinetic equation (4):

$$v = -\frac{dC}{dt} = \frac{k_r.K.C}{1+K.C} \simeq k_r.K.C = k_{app}.C \quad (4)$$

With k_{app} is the apparent rate constant (h^{-1}).

3.2.2. Photo-catalytic activity and chemical kinetics of phenol degradation

As shown in Figure 7 and Table 4, these results indicate that without the catalyst, under natural light irradiation with the average light intensity of 70 klux after 3 hours, phenol decomposed is 12.3% and the photo-catalytic activity of pure TiO_2 is lower than TS10 and A4TS10. The phenol removal efficiency (H%) of pure TiO_2, TS10 and A4TS10 are 58.8%, 67.5% and 81.6%, respectively. According to the above structure analysis (XRD, FT-IR, BET, Band gap and TEM), the result show that the specific surface area of TS10 are much larger than pure TiO_2 and the average particle sizes are smaller when SiO_2 is added, the simultaneous presence of Si-O-Ti linkages leads to enhanced adsorption capability and the photo-activity of TS10 sample [9]. Especially, the absorption edge is shifted towards visible light region when doping Ag into the TiO_2-SiO_2 structure lead to the increase in phenol degradation under sunlight irradiation.

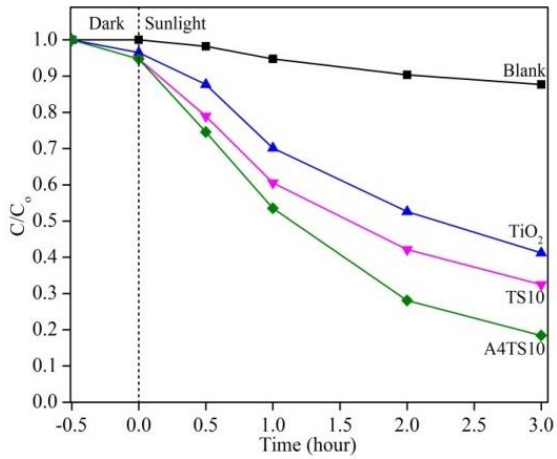

Figure 7. *The conversion of phenol degradation for different samples under sunlight irradiation*

Table 4. *The photo-activity efficiency and apparent rate constant for different samples under sunlight*

STT	Samples	H (%)	k_{app} (h^{-1})
1	Blank	12.3	-
2	TiO_2	58.8	0.293
3	TS10	67.5	0.364
4	A4TS10	81.6	0.564

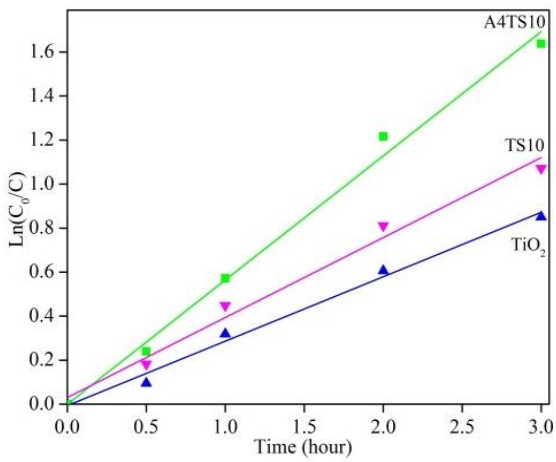

Figure 8. *The apparent rate constant of phenol degradation for different samples under sunlight*

The apparent rate constant of phenol degradation (k_{app}) under sunlight irradiation is shown in Figure 8 and summarized in Table 4. Obviously, these results give high

correspondence to pseudo-first order kinetic with high correlation coefficient ($R^2 > 0.9$); therefore, the Langmuir-Hinshelwood model isothermal adsorption model at low concentration suits well with the phenol adsorption. The decomposition rate constant and removal efficiency for 10 mg/l phenol aqueous solution of A4TS10 sample under sunlight irradiation are 0.564 h^{-1} and 81.6%, respectively, higher than that of Ag-TiO_2 photo-catalyst of 0.169 h^{-1} and 46% of which is conducted in the same experimental conditions [15].

4. Conclusions

In this study, the nanometric TiO_2, TS10 and A4TS10 powdered photo-catalyst are synthesized successfully with the average particle size of 30, 20, 20 (nm), and surface area of 38.9, 191.4, 218.4 (m^2/g), respectively. The optical absorption wavelength of A4TS10 is 3.06 eV and shifts photon absorption from ultraviolet region to visible region.

Besides, the absorption of aqueous phenol solution onto the surface of A4TS10 photo-catalyst suits the Langmuir absorption isothermal model. The photo-catalytic A4TS10 in the sunlight exhibits the highest activity by degradation of phenol solution, with the efficiency of 81.6% after 3 hours. The study reveals that the prepared nanocomposites could be widely applied to treat the contaminants in wastewater.

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