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A Study On Preparation And Application Of Ag/TiO₂ Complex Photocatalyst



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ABSTRACT

Based on a complex photocatalyst prepared by silver nitrate and butyl titanate under different pH values, this paper aims to explore the concentration and pH of silver nitrate and its influence upon the property of complex photocatalyst. Also, it intends to study the possible applications on dye decolouration and wastewater processing. The experimental results show that, photocatalysts prepared from acid sols present a filament-like appearance, and those prepared from alkali sols present blocklike particles. In the case of increasing concentration of silver nitrate, specific surface area and pore volume of complex photocatalyst are becoming bigger, but pore size becoming smaller. In the case of extremely high concentration of AgNO₃, mean particle size of TiO₂ increases conversely. When pH reaches 10, complex photocatalyst has a smaller specific surface area, pore volume and pore size. Photocatalyst prepared by acid sols has a longer wavelength of reaction and a good catalysis. In this test, catalysis of photocatalyst is improved with the growing concentration of silver nitrate.

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KEYWORDS

Butyl titanate;
Silver nitrate;
Sol;
Photocatalyst;
Specific surface area.

INTRODUCTION

Thanks to cost-effectiveness, high availability, nontoxicity, good stability and strong oxidizability which guarantee degradation of organic materials to

different degrees, titania photocatalyst has proved to have a bright future of applications in water processing^[1]. Photocatalytic oxidation method indicates that, under radiation of UV or sunlight, electrons within semiconductor catalyst particles will be activated af-

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ter absorbing photons of a certain energy, thus enabling a transition from low-energy valence band via a forbidden band to high-energy conduction band/valence band, where a cavity (h^+) is formed. The conduction band carries negative electron (e^-), while electron-cavity pair will shift towards the particle surface under the influence of electric field. After that, the electrons with strong reductibility can be combined with oxygen to generate O_2^- ion. With extremely strong electron absorption capability, photo-induced cavity enables directly oxidation of some organic materials, or allows for oxidation of OH^- into OH free radicals. The standard battery potential of OH free radical is $\Psi^0=2.80V$, which can dissolve almost all organic oxides into nontoxic substances such as CO_2 and H_2O . Currently, suspended phase titania photocatalytic oxidant most frequently applied is easily agglomerated in water without activity, and also acts as a barrier to optical penetration. In particular, the separation and recycling of processed catalyst is crucial to the availability of this technology^[2]. Also, the engineering applications of photocatalyst are limited owing to the following disadvantages: 1) Nano TiO_2 can only be activated by UV of $\lambda < 387nm$, which accounts for only 4%~6% of solar rays, leading to a lower utilization of solar energy; 2) Nano TiO_2 photo-induced electron-cavity pair of a higher recombination rate leads to lower activity of photocatalyst; 3) Nano TiO_2 is generally combined with wastewater to form suspending solution in an effort to make photocatalyst keep a full contact with materials to be degraded, but this place limitation on applications due to difficult separation. In recent years, the researchers made more efforts to study the mixing/modification for the former two disadvantages, and immobilization for the third disadvantage.

How to improve spectral response and catalysis efficiency of photocatalyst is a key to mixing load^[3]. At present, mixing loading refers to the means of surfaction, for example: deposit of precious metal, mixing of transition metal ions, mixing of negative ions and semiconductor composition, which can improve spectral response of TiO_2 , and reduce the combination of electron and cavity.

Deposit of precious metal

Owing to rapid combination of electron and cavity, nano TiO_2 affects negatively photocatalysis. So, photocatalysis activity can be improved by deposit of precious metals, such as Ag ^[4-5] or Pt ^[6-7].

Mixing of transition metal ions

Owing to multiple chemical valences in transition metal elements, mixing a little transition metal ions into TiO_2 can help prolong the combination time of electron and cavity, thereby improving photocatalysis activity of TiO_2 . And, solar energy can be utilized more efficiently since transition metal ions have a wider photoabsorption than TiO_2 ^[8-10].

Mixing of negative ions

R.Asahi^[11] initiated a new approach to mix negative ions recently. To ensure a higher photoabsorption for TiO_2 under visible light ($\lambda < 500nm$), negative ions can be mixed to replace some oxygen elements in TiO_2 by N, S, P, and then process into $TiO_{2-x}N_x$ photocatalyst, in addition to mixing of transition metal positive-ions.

Semiconductor composition

Soaking or sol-gel method can be applied to prepare binary or multiple compound semiconductors. According to the property of binary compounds, they are divided into semiconductor- TiO_2 semiconductor compound^[12-13] and insulator- TiO_2 semiconductor compound^[14-16].

In this test, Ag/ TiO_2 complex photocatalyst is prepared by mixing silver onto the surface of TiO_2 . This paper also tries to study the influence of silver nitrate of different concentrations or pH values upon the property of photocatalyst, and explore the feasible applications on dye/wastewater decoloration.

EXPERIMENTAL

Materials

Titanium n-butoxide (99%, TTB), 3-glycidoxypolytrimethoxysilane (gyptms), tetraethoxysilane (teos), all of extra grade, purchased from acros organics, USA); ethyl alcohol, acetic acid, nitric acid, sodium hydroxide, hydrochloric acid, sodium lauryl

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sulfate (SDS), at reagent grade (purchased from Shimadhisashi Pharmaceutical); ethyl acetoacetate (EAc), extra grade, purchased from Nihon Shiyaku Industries; silver nitrate, extra grade, purchased from Wako Pure Chemical Inc. Ltd.; methylene blue, at reagent grade, purchased from Wako Pure Chemical Inc. Ltd..

Methods

Preparation of complex photocatalyst

Fill 10ml Butyl titanate(TTB) into 30ml absolute ethyl alcohol after stirring, and then add 2 ml glacial acetic acid and 0.2ml acetylacetone. After a 30-minute stirring, a uniform and transparent solution is prepared (A). Mix 1ml distilled water with 15ml absolute ethyl alcohol, and slowly fill into 1M 0.1ml nitric acid, then proceed with 30-minute stirring to obtain solution (B). By adding slowly solution (B) into solution (A), it's possible to obtain uniform and transparent yellowish sol. After 1-hour stirring, 40ml distilled water is used to dilute it into white sol. Under different pH values (2~12), TiO_2 sol of above-specified concentration is added into AgNO_3 solution of proper volume, thus forming a reaction system. Continue to stir for 3 hours, and obtain Ag/TiO_2 complex sol. Place some sols into 100°C oven for 30-minute drying, and finally into a high-temperature furnace of $300 \sim 700^\circ\text{C}$, with a duration of 2 hour, thereby obtaining complex photocatalyst powder.

Various signs of complex photocatalysts are defined previous below:

Application of Ag/TiO_2 complex photocatalyst

Mix 1.5g complex photocatalysts with 20ppm methylene blue solution for 15-minute stirring. Then, make them exposed to long wave UV-light (367nm) for 2 hours, and make a sampling every 15 minutes. The samples at various stages are detected for their absorbancy, while the concentration of staining solution (C_n) is achieved from test curve. According to the concentration of stock solution C_0 , the conversion ratio of staining solution is obtained from the following formula:

$$E (\%) = C_n / C_0 \times 100\%$$

Analysis and measurement

The surface morphologies of the powders were observed with a JEOL Model JSM 6400 scanning electron microscopic. A gold coating was deposited on the samples to avoid charging the surface. The distributions of all atoms of the Ag/TiO_2 powders were analyzed by using energy-dispersive X-ray spectroscopy (EDS; SEM, Model EDSEM, JEOL, Tokyo, Japan). A Bruker-AXS D8 was used for X-ray powder diffraction (Parallel beam optics, Cu-target, scintillation counter, sampler changer with rotation). The samples were run with 40kV, 100mA, $5\text{-}60^\circ$ theta/ 2θ , 0.01° stepsize and 5sec counting time. The surface area and pore volume of the dried samples were determined through nitrogen physisorption analysis, using a Quantachrome Autosorb-1 system. The five-point BET calculation was used to determine the surface area. The UV-Vis analysis of Ag/TiO_2 and absorbancy of dyeing solution were measured with Hitachi U3010 model UV-Vis spectrometer.

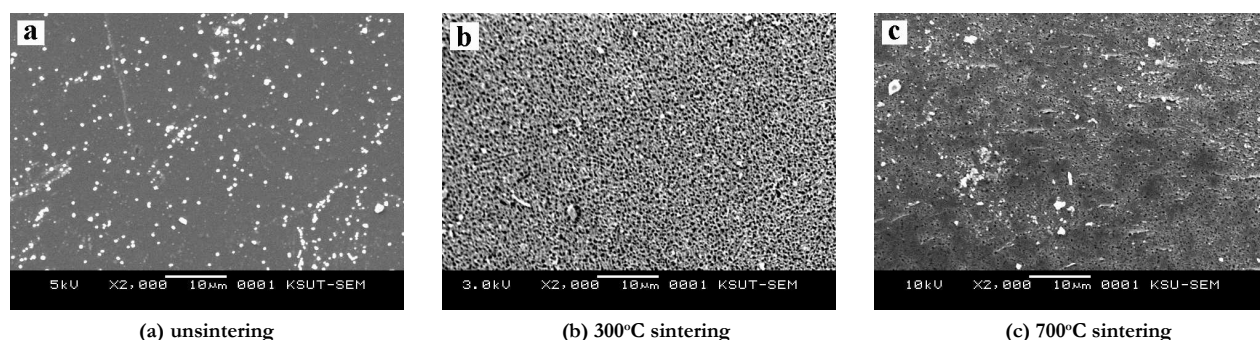
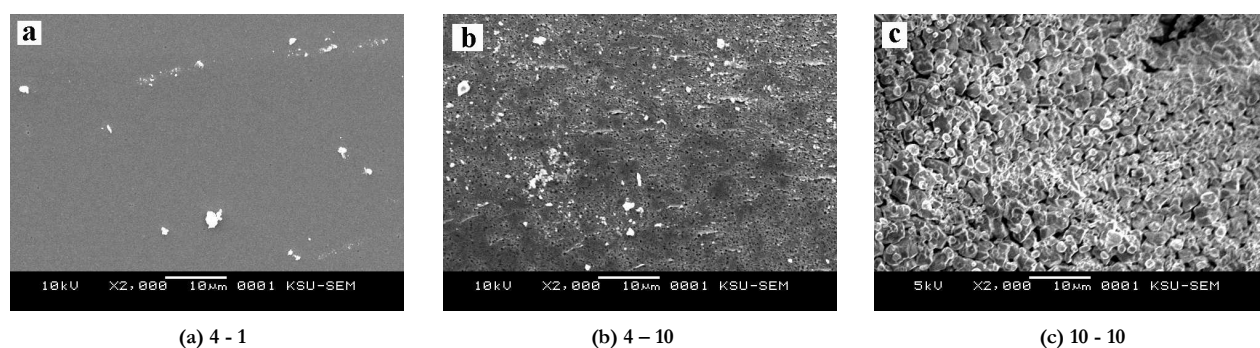
RESULTS AND DISCUSSION

SEM

As illustrated in figure 1a, complex photocatalyst particles sintered at 700°C are visibly observed, thus sintering temperature is set at 700°C . In this Figure, TiO_2 is represented by white section, and silver by black section. Silver particle or silver mirror reaction

Sign	Definition	Conc. of AgNO_3 (g/ml)
4-0	Complex photocatalyst prepared with 0ml AgNO_3 under pH4	0
4-10	Complex photocatalyst prepared with 1ml AgNO_3 under pH4	5.70×10^{-5}
4-30	Complex photocatalyst prepared with 3ml AgNO_3 under pH4	1.71×10^{-4}
4-60	Complex photocatalyst prepared with 6ml AgNO_3 under pH4	3.42×10^{-4}
4-10	Complex photocatalyst prepared with 10ml AgNO_3 under pH4	5.70×10^{-4}
6-10	Complex photocatalyst prepared with 10ml AgNO_3 under pH6	5.70×10^{-4}
8-10	Complex photocatalyst prepared with 10ml AgNO_3 under pH8	5.70×10^{-4}
10-10	Complex photocatalyst prepared with 10ml AgNO_3 under pH10	5.70×10^{-4}

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Figure 1a: SEM of Ag/TiO₂ complex photocatalysts. (4 - 10)Figure 1b: SEM of Ag/TiO₂ complex photocatalyst

can take place under alkali solution^[17]. In other words, silver ions are easily restored with increasing pH of sols. As the surface of TiO₂ can absorb easily OH⁻, negative charging density on surface of TiO₂ sol particles increase accordingly, thus contributing to deposit of Ag onto surface of TiO₂^[18]. Thus, bigger black spot silver is presented apparently. Figure 1-b-b and 1-b-c shows the different pH values, wherein photocatalysts prepared from acid sols present a filament-like smooth appearance reflecting metal materials, and those prepared from alkali sols present blocklike particles similar to sandstone. Figure 1-b-a and 1-b-b shows different AgNO₃ ml. The appearance of photocatalysts prepared from acid sols differs a little due to varied concentrations of silver nitrate, for example, only black spots are found to increase gradually, with the relevant data available from the following B.E.T.

B.E.T.

TABLE 1 is an analysis sheet of BET of Ag/TiO₂ complex photocatalyst. The filling concentration of AgNO₃ is changed in the event of acid sols.

TABLE 1: Specific surface area, pore size and pore volume of complex photocatalysts

Samples	Specific surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
04-1	4.5080	24.272	0.027354
04-6	5.1363	23.606	0.037274
04-10	6.9846	23.537	0.041099
10-10	1.5625	16.649	0.006504

With a growing concentration of silver nitrate, the surface area and pore volume of complex photocatalyst become bigger along with smaller pore size. When pH reaches 10, complex photocatalyst has a smaller specific surface area, pore volume and pore size. This is because acid sol has a better hydrolytic condensation capability than alkali sol, leading to smaller sol-gel particles; On the other hand, cavity makes sol-gel of bigger particles (alkali) collapse easily during sintering^[19], leading to a smaller pore size.

Secondly, during low-temperature sintering of TiO₂ powder that's mixed with a little portion of Ag, the mean particle size of anatase will decline, showing that mixing of Ag will inhibit the growing trend

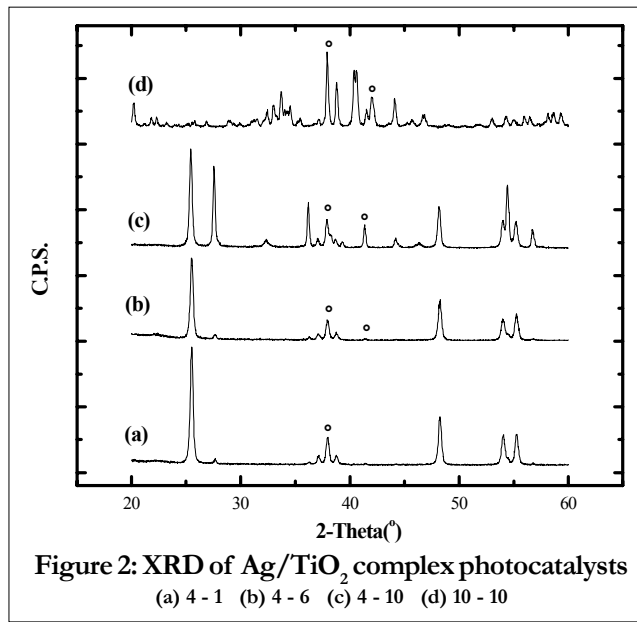
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of anatase particles. Thus, specific surface area of TiO_2 powder will grow. Since the radius of Ag^+ ion (126pm) is far more than that of Ti^{+4} ion (68pm), Ag^+ cannot enter crystal lattice of TiO_2 to form so-called solid solution, leading to diffusion or shift during sintering process. Instead, Ag diffusion layer or Ti-O-Ag bond exists at the surface of anatase particles. In this way, rearrangement of Ti and O ions on the surface of TiO_2 grains is held back for the growth of anatase particles during the process of sintering. Thus, TiO_2 particle size becomes smaller and specific surface area bigger. According to the references^[20-21], Ag-O bond is weaker than Ti-O bond or Ag-Ag bond. Since Ag has a higher surface free energy than TiO_2 , and also Ag has a higher diffusion rate on the surface of TiO_2 , Ag ions and atoms on the surface of anatase particles will gradually diffuse onto the particle surface, thus hindering the interaction and aggregation of TiO_2 particles, and leading to a declined particle size of anatase.

In the case of excessive concentration of AgNO_3 , i.e. excessive mixing of Ag, the mean particle size of TiO_2 will become bigger, possibly owing to easy aggregation of single Ag^[20]. Su and Martin et al.^[22-23] studied the growing mode of single Ag on the surface of TiO_2 grains. It's found that, in the event of little content of Ag, Ag is prone to grow on the surface of TiO_2 in a two dimensional way. In the case of excessive mixing of Ag after forming a two-dimensional Ag surface layer, excessive Ag is prone to form bigger three-dimensional needle-like clusters on the surface of TiO_2 . These Ag clusters are diffused onto TiO_2 surface, forming Ag particles of bigger size. Therefore, efficient distribution area of Ag on TiO_2 grain surface is reduced due to the presence of Ag clusters and particles of bigger size. As compared to Ag of higher diffusion rate without aggregation, such Ag has a poorer inhibitory effect for the growth and aggregation of TiO_2 particles, leading to bigger particle size of TiO_2 .

X-Ray

Figure 2 is a XRD analysis spectrum of Ag/TiO_2 complex photocatalyst. As for acid sol at 27°, 38° and 48°, an obvious absorption peak can be found, and becomes more obviously with the increasing content



of silver nitrate. When silver nitrate content has a difference of 10 times as shown in figure 2-a, 2-c, the difference of absorption peak can be observed, along with little change of peak location. This indicates that addition of AgNO_3 has little influence upon crystal structure of Ag/TiO_2 complex photocatalyst. As illustrated in figure 2-c and 2-d, if comparing photocatalyst prepared by acid-alkali sol, the absorption peak is much more complex under alkali conditions. Despite of obvious silver absorption peak at $2\theta=38.11^\circ$ and 44.12° , absorption peak of Ti differs a little, showing that acidity-alkalinity of sol has influence upon crystal structure of complex photocatalyst.

EDS

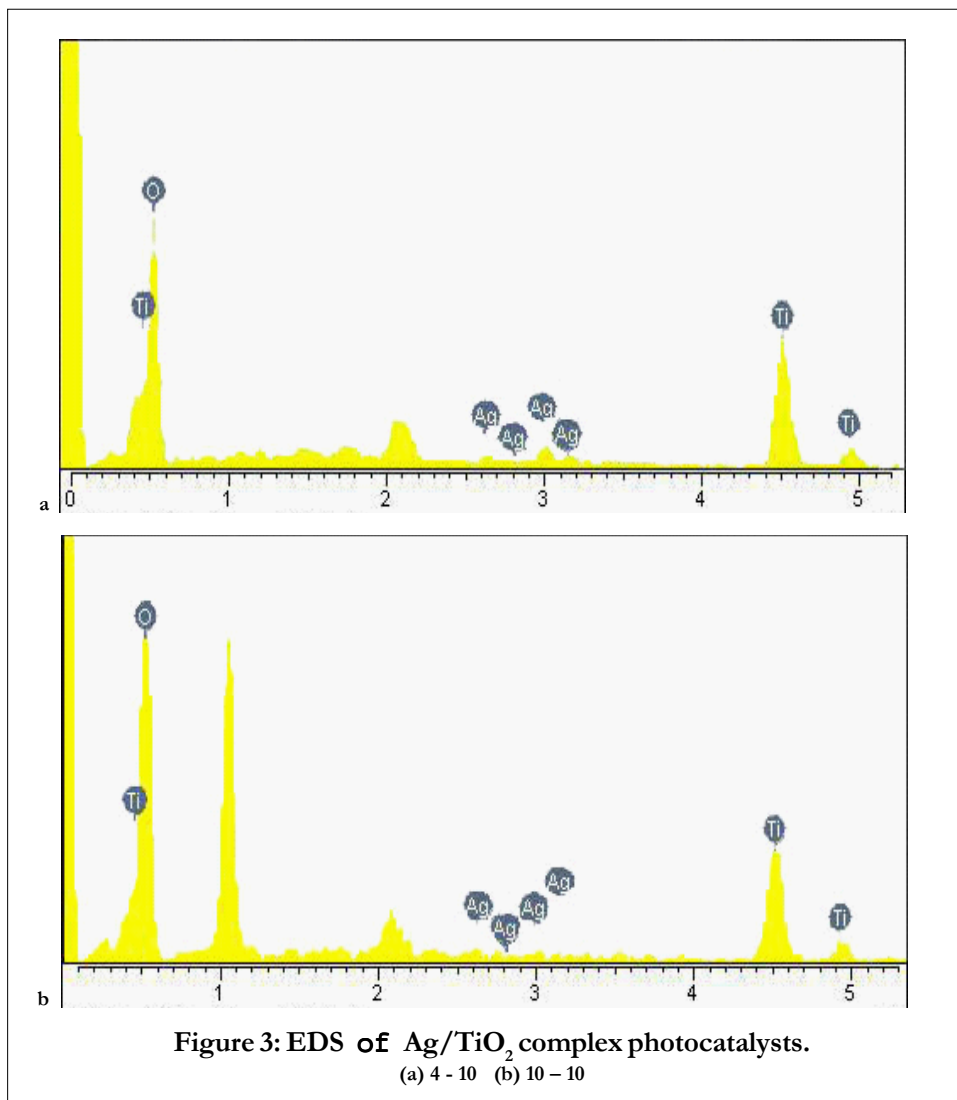
Figure 3 and TABLE 2 shows separately EDS analysis sheet of Ag/TiO_2 complex photocatalyst. Relative weight percentage of Ag in complex photo-

TABLE 2: EDS of Ag/TiO_2 photocatalysts

Elements	Properties							
	Weight (%) ¹				Atomic (%)			
	a ²	b	c	d	a	b	c	d
O	61.87	59.13	68.19	73.73	82.97	81.87	87.50	89.58
Ti	37.92	37.85	27.06	25.21	16.99	17.50	11.60	10.23
Ag	0.21	3.03	4.75	1.07	0.04	0.62	0.90	0.19
Totals	100	100	100	100	100	100	100	100

¹Relatively weight. ²a) 4-1, b) 4-6, c) 4-10, d) 10-10

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Figure 3: EDS of Ag/TiO₂ complex photocatalysts.

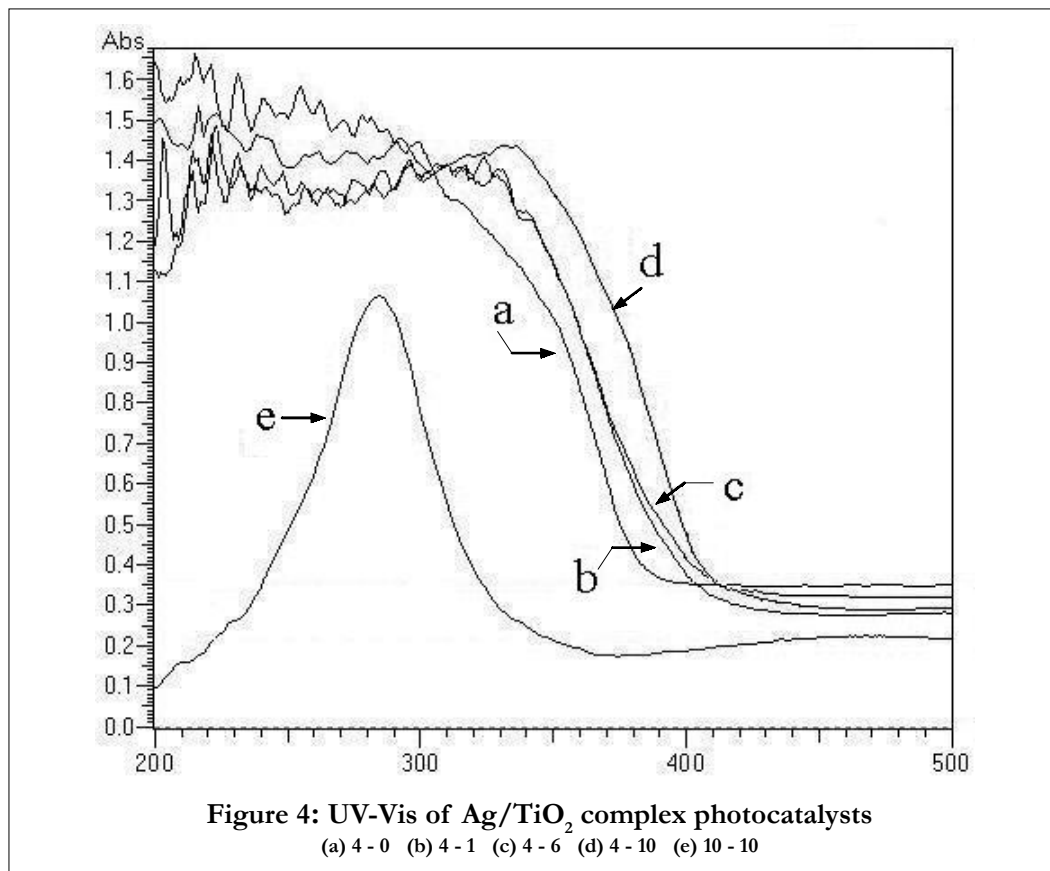
(a) 4 - 10 (b) 10 - 10

catalyst will increase with the addition of silver nitrate. In addition, figure 3-a, 3-b depicts separately EDS of photocatalyst prepared by changing Ph of sol. When pH value is represented by acidity, there is a higher amount of silver content; otherwise, silver content is relatively lower due to bigger particle size and difficult aggregation with TiO₂.

UV-Vis

Figure 4 is a UV-Vis analysis spectrum of Ag/TiO₂ complex photocatalyst. The reaction wavelength of TiO₂ photocatalyst is below 380nm. Mixing loading is generally required to prolong the reaction wavelength^[3]. At present, mixing loading refers to the means of surfaction, for example: deposit of precious metal, mixing of transition metal ions, mixing of negative ions and semiconductor composition, which can

improve spectral response of TiO₂, and reduce the combination of electron and cavity. In this test, this can be achieved by mixing precious metal Ag. Figure 4-c and 4-d depict the absorption of photocatalyst prepared from acid-alkali sols. It's clearly seen that, there is a nearly 0.5 absorbancy when the reaction wavelength of former is 400nm, otherwise, approx. 0.2 absorbancy. If the reaction wavelength of former one is below 400nm, there is an extremely high absorbancy, while the latter one has a good absorbancy at 280nm. It's thus proved that, photocatalyst prepared from acid sols has a longer reaction wavelength, thus proving a higher probability of application. In addition, notwithstanding photocatalyst prepared by acid sols as shown in 4-a, 4-b and 4-c, the reaction wavelength differs a little due to different mixed silver content. It's observed that the wave peak with more sil-



ver content is closer to the wavelength of visible light, and vice versa.

Application of complex photocatalyst

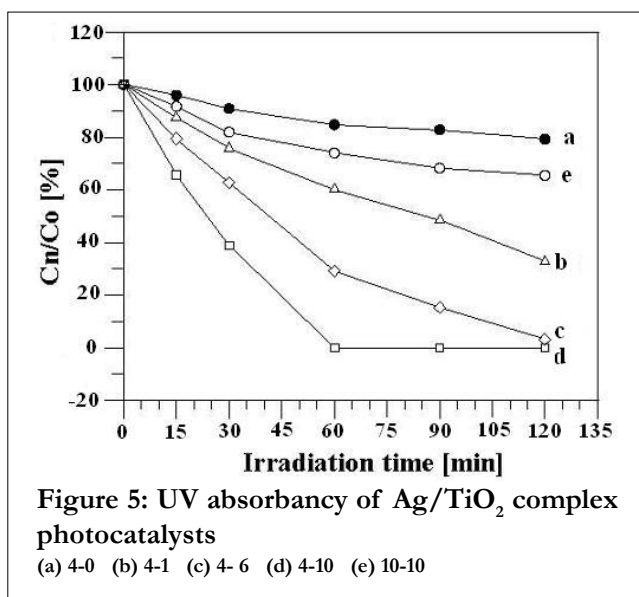
Figure 5-c and 5-d depicts separately the applications of photocatalysts prepared by acid or alkali sols. It's clearly seen that, when photocatalyst prepared by

acid sols is exposed to UV-light, methylene blue solution presents a transparent status during the 1st or 2nd hour, showing an excellent performance than photocatalyst prepared by alkali sols. This is possibly because little mixing of silver for the latter one leads to poorer photocatalysis. Notwithstanding photocatalysts prepared by acid sols as shown in 5-a, 5-b and 5-c, the concentration of silver nitrate is a decisive factor to the performance. The experimental results show clearly that, silver nitrate of a higher concentration has a better catalysis.

CONCLUSIONS

Based on complex photocatalysts prepared by silver nitrate of different concentrations and butyl titanate under different pH values, this paper aims to explore the property of photocatalysts and its influence upon catalytic decolouration of dyeing wastewater. The following conclusions are made from this test

(1) Photocatalysts prepared from acid sols present a



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filament-like smooth appearance, and those prepared from alkali sols present blocklike particles similar to sandstone.

- (2) In the case of increasing concentration of silver nitrate, specific surface area and pore volume of complex photocatalyst are becoming bigger, but pore size becoming smaller. In the case of extremely high concentration of AgNO₃, mean particle size of TiO₂ increases conversely. When pH reaches 10, complex photocatalyst has a smaller specific surface area, pore volume and pore size.
- (3) Acid-alkali sols have influence upon the crystal structure of complex photocatalyst, with the exclusion of the concentration of silver nitrate.
- (4) Photocatalysts prepared by acid sols has a longer reaction wavelength, while the reaction wavelength of photocatalyst with more silver mixing is closer to the wavelength of visible light.
- (5) Photocatalysts prepared by acid sols have a better catalysis, which is improved with the growing concentration of silver nitrate.

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