

## Synthesis of Ag-TiO<sub>2</sub> nanomaterial for treatment of organic pollutants under visible light

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### Abstract

In this study, the sol-gel synthesis method was employed for the preparation of silver-doped TiO<sub>2</sub> nanomaterial from potassium fluorotitanate and silver nitrate. The silver can be incorporated by direct calcination of the sol-gel material decomposing silver nitrate to silver. The visible light absorption ability of Ag-TiO<sub>2</sub> nanoparticles was investigated by means of UV-Vis measurement. Based on the UV-Vis spectra, the absorption in the visible light of the Ag-TiO<sub>2</sub> was found to be improved and was shifted to longer wavelength. The XPS spectra indicated that the elements detected were titanium, oxygen, and silver. Titanium and oxygen presented as Ti<sup>4+</sup> and O<sup>2-</sup> and silver Ag existed in Ag (0) form. It is attributed to the fact that the silver is homogeneously dispersed throughout the material. The experimental results showed that the photocatalytic efficiency of Ag-TiO<sub>2</sub> was better than prepared TiO<sub>2</sub> under the same conditions for the photodegradation of methylene blue.

**Keywords.** Potassium fluorotitanate, titanium dioxide, silver, photocatalysis, visible light.

### 1. INTRODUCTION

In the last decades, TiO<sub>2</sub> materials are most extensively studied owing to their stability, non-toxicity, and low cost. However, TiO<sub>2</sub> only exhibits photocatalytic activity under UV irradiation, because of its large band gap energy (3.2 eV) and fast recombination rate of photogenerated electron-hole pairs [1-5]. These drawbacks restrict the use of visible light or sunlight as the radiation source for photocatalysis of TiO<sub>2</sub>. The development of titania-based photocatalysts activated by visible light remains a great challenge. Non-metal doping of TiO<sub>2</sub> films and powders with elements like nitrogen, sulfur, carbon, and fluorine has been investigated in order to red-shift the absorbance to be achieved [5-8] or metal impurity in the TiO<sub>2</sub> lattice or to couple with lower band gap semiconductor [9-11]. The role of transition metal ion in TiO<sub>2</sub> is that transition metal ion offers a way to trap the charge carrier thus improving the efficiency of catalyst. Noble metal doped or deposited on TiO<sub>2</sub> shows enhanced photocatalytic activity of TiO<sub>2</sub> [1-3, 12, 13]. They enhance the electron hole separation by acting as electron traps, extend the light absorption into the visible range and enhance the surface electron excitation by plasmon resonance excited by visible

light. Among the noble metals, silver has been attracted by many researchers, because of their novel effects on the improvement of photoactivity of semiconductor photocatalysis. Silver could be doped into TiO<sub>2</sub> using chemical reduction of silver ion on TiO<sub>2</sub> nanoparticles, thermal deposition, sol-gel method,... [14-16].

In the present work, we use a simple approach for the synthesis of Ag-doped TiO<sub>2</sub> photocatalysts by sol-gel method by controlled hydrolysis of K<sub>2</sub>TiF<sub>6</sub> and AgNO<sub>3</sub> and investigate the comparative photocatalytic activity of TiO<sub>2</sub> and Ag-doped TiO<sub>2</sub> for the degradation of methylene blue as a model pollutant under visible light.

### 2. EXPERIMENTAL

#### 2.1. Chemicals and characterization of materials

The ilmenite used in the present study was supplied from Binh Dinh Minerals Joint Stock Company, Vietnam, HF 40 wt.%, NH<sub>3</sub> 25 wt.%, KCl (China) and silver nitrate (Merck).

Material surfaces were characterized by scanning electronic microscopy (SEM) (JEOL JSM-6500F). Chemical composition of catalysts was

revealed by Energy-dispersive X-ray spectroscopy (EDS) (Hitachi S-4700). Light absorption capability was evaluated by UV-Vis absorption spectroscopy (3101PC Shimadzu). X-ray photoelectron spectroscopy (XPS) spectra of the synthesized Ag-TiO<sub>2</sub> photocatalyst were obtained using a Thermo Fisher K-Alpha X-ray Photoelectron Spectrometer system. The Gaussian multi-peak shapes were applied to fit the Ag 3d and Ti 2p peaks in the obtained XPS spectra to determine the elemental states of the silver and titanium in the synthesized photocatalysts. Methylene blue concentration was determined by spectrometric method at 664 nm (UV 1800, Shimadzu).

## 2.2. Synthesis of Ag-TiO<sub>2</sub> catalyst

Ag-TiO<sub>2</sub> powders have been prepared by sol-gel route. K<sub>2</sub>TiF<sub>6</sub> was used as titanium source. 10 g K<sub>2</sub>TiF<sub>6</sub> were dissolved in deionized water under stirring at room temperature. After that, the reactor was heated under continuous stirring. When the temperature reached up to 80 °C, kept stable and a certain amount of 3.5 M NH<sub>3</sub>. Then, silver nitrate solution was added to the above mixture dropwise. The sols were stirred in closed beakers at room temperature for 24 hours for completion of the hydrolysis process. The obtained material after extensive washing was dried at 80 °C and calcinated at 550 °C in 5 hours (heating rate of 5 °C for per minute).

TiO<sub>2</sub> catalyst was synthesized in the same conditions without using silver nitrate solution.

## 2.3. Photocatalytic experiment

Photocatalysis experiments were carried out with an aqueous solution of methylene blue (10 mg/L) using solar/visible/filament lamp light (having an output of 60 W). 0.1 g of each sample was added to 200 mL of methylene blue solution. The above suspension was stirred for 2 hours in the dark to equilibrate and eliminate any error due to the initial adsorption effect. After the reaction time was 6 hours, 5 mL samples were taken and centrifuged at 6000 rpm for 20 min. Then, 1.5 mL of the supernatant was put in a disposable cuvette and analyzed. These aliquots were then analyzed using a UV-Vis spectrometer to measure their degradation properties.

## 3. RESULTS AND DISCUSSION

### 3.1. Materials characterization

To prove that silver is present, EDS analysis was employed. The EDS spectrum of Ag-TiO<sub>2</sub> material was shown in Fig. 1.

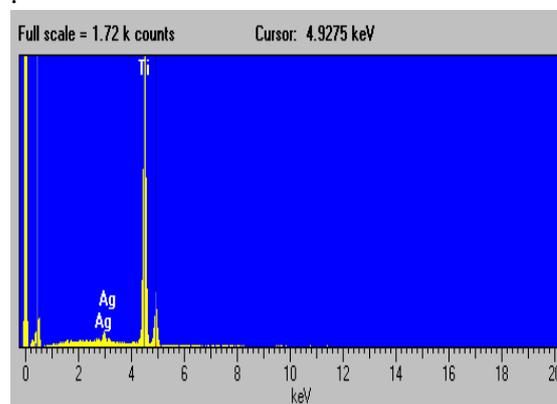


Figure 1: EDS spectrum of Ag-TiO<sub>2</sub>

It can be seen that TiO<sub>2</sub> modified by silver contained peaks of Ti, O and Ag elements; there are no peaks of other elements on the EDS spectrum. This proved the occurrence of silver in Ag-TiO<sub>2</sub> sample.

The samples were characterized by SEM to reveal their material surfaces. Fig. 2 shows the SEM images of TiO<sub>2</sub> and Ag-TiO<sub>2</sub> samples.

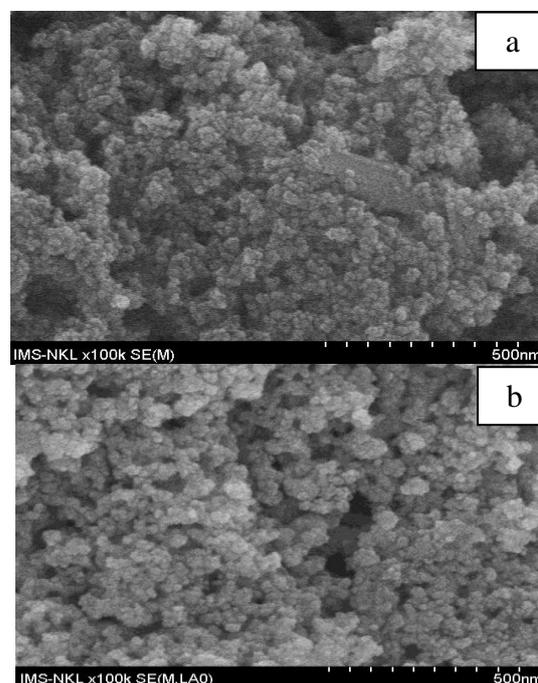


Figure 2: SEM image of TiO<sub>2</sub> (a) and Ag-TiO<sub>2</sub> (b)

From Fig. 2, it can be clearly seen that the Ag-TiO<sub>2</sub> samples exhibited a unique spherical structure

as compared to TiO<sub>2</sub>. It can also be seen that the particle size of Ag-TiO<sub>2</sub> is larger than TiO<sub>2</sub>, indicating that the size of Ag-TiO<sub>2</sub> can be regulated by silver during the catalyst preparation.

The diffuse reflectance spectra of the samples were used to assess the absorption of the photocatalysts in the UV-Vis region.

From diffuse reflectance spectra (Fig. 3), the absorption of Ag-TiO<sub>2</sub> is enhanced distinctly in both UV and visible light region compared to that of pure TiO<sub>2</sub>. This suggests that the introduction of the Ag can possibly cause modifications in the fundamental process of electron-hole pair formation during irradiation.

In order to examine the chemical states of elements involved in the as-prepared samples, XPS measurements were performed.

Fig. 4a illustrates XPS spectra of Ag-TiO<sub>2</sub> samples. The XPS spectra show that Ag-TiO<sub>2</sub> sample contained peaks of Ti and O elements, which can be attributed to composition of TiO<sub>2</sub>. It can be seen that TiO<sub>2</sub> modified by silver contained peaks of Ag elements. This proves that the occurrence of Ag in Ag-TiO<sub>2</sub> sample.

From the XPS spectra of O 1s in Fig. 4b, two peaks at the binding energy of 529.8 and 531.5 eV could be assigned for the O<sup>2-</sup> in TiO<sub>2</sub> and the -OH group on the surface of samples, respectively.

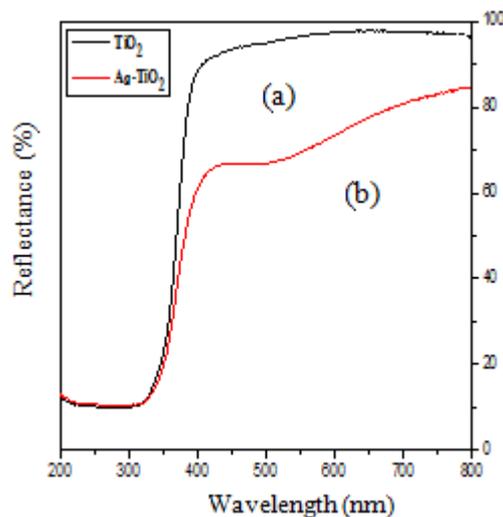


Figure 3: Diffuse reflectance spectra of TiO<sub>2</sub> (a) and Ag-TiO<sub>2</sub> (b)

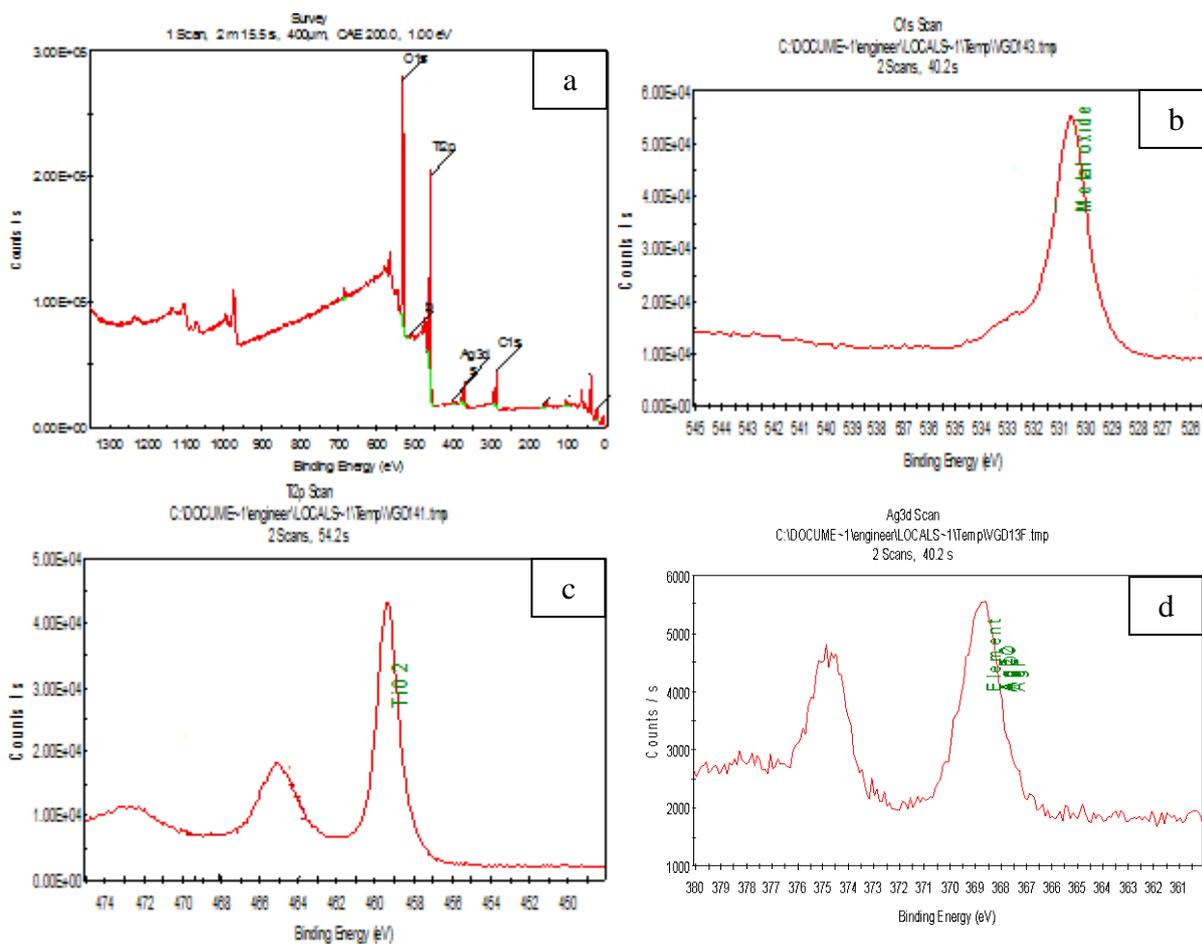
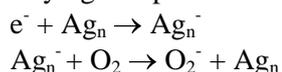


Figure 4: XPS spectra of Ag-TiO<sub>2</sub>

From Fig. 4c, Ti 2p peaks can be observed at binding energy of 464.1 (Ti 2p<sub>1/2</sub>) and 458.4 eV (Ti 2p<sub>3/2</sub>). This shows that there is no Ti<sup>3+</sup> in the sample; all Ti existed in Ti<sup>4+</sup> form. For silver (Fig. 4d), there are two peaks at about 374 and 368 eV, which can be attributed to Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub>, respectively. All Ag was in metallic form (Ag (0)), which means that AgNO<sub>3</sub> was reduced. Results obtained from this method agree with reports of other authors [16, 17].

XPS method proves that silver is in form of metallic silver (Ag (0)). Based on literature study, the radius of Ag<sup>+</sup> is 126 pm while the radius of Ti<sup>4+</sup> is only 64 pm. The difference in radius makes it impossible for silver to substitute titanium in its lattice. Therefore, doping silver cannot modify band gap energy of titania, and it might have no effect on catalytic efficiency on methylene blue degradation. However, in case of doping silver into titania, silver can play a role as intermediate step to facilitate electron transfer. Electrons transfer from conduction band of titania to silver cluster, then to oxygen, making the process much easier than without silver. Reactions underlying this process are shown below.



This has amazingly high capacity of degrading methylene blue of Ag-TiO<sub>2</sub>; it reaches near 93.06 % conversion rate after 6 hours under solar light, much higher than TiO<sub>2</sub> (table 1).

### 3.2. Photocatalytic experiments

The experiments were carried out simultaneously on Ag-TiO<sub>2</sub> and TiO<sub>2</sub> with different light sources (visible light, filament lamp and solar light). All other conditions were the same. Results are shown in table 1.

Table 1: Conversion of methylene blue using TiO<sub>2</sub> or Ag-TiO<sub>2</sub> under different light sources

Catalysts	Conversion (%)		
	Visible light	Filament lamp	Solar light
TiO <sub>2</sub>	20.15	30.25	75.32
Ag-TiO <sub>2</sub>	34.87	55.67	93.06

Results in table 1 indicate that efficiency of Ag-TiO<sub>2</sub> in methylene blue degradation is higher than TiO<sub>2</sub> under all light sources, which means that TiO<sub>2</sub> modified by silver can improve catalytic activity of TiO<sub>2</sub> material. The results show that after 6 hours, methylene blue removal efficiency on Ag-

TiO<sub>2</sub> reaches 93.06 % when using solar as light source, while it is only 55.67 % if experiments were carried out with filament lamp light. This observation is understandable because photon in solar light is stronger filament lamp light.

It is expected that Ag-TiO<sub>2</sub> photocatalyst would be activated under visible light. However, results in Tab. 1 indicate that efficiency of Ag-TiO<sub>2</sub> in methylene blue degradation under visible light source is just slightly higher than that in dark condition (34.87 % for visible light and 15.34 % for the dark). This observation is understandable because photon in visible region is not powerful enough to excite electrons in valence band to conduction band. A possible explanation is that photons in UV region of solar source give energy to electrons in valence band; then these electrons jump to conduction band of TiO<sub>2</sub>. In presence of silver cluster, surface plasmon surface is created, increasing photocatalytic activity of catalyst under visible light [18].

### 4. CONCLUSION

Silver doped titania is successfully synthesized from K<sub>2</sub>TiF<sub>6</sub> and AgNO<sub>3</sub>. The obtained results from XPS indicated that Ag existed as Ag (0), where silver can be deposited on the surface of TiO<sub>2</sub>. It is attributed to the fact that the silver is homogeneously dispersed throughout the material leading to its surface plasmon, which increased photocatalytic activity of the catalyst. The obtained experimental results showed that the photocatalytic efficiency of Ag-TiO<sub>2</sub> was better than prepared TiO<sub>2</sub> under the same conditions for the photodegradation of methylene blue.

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