

# Study on preparation and photocatalytic performance of Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts

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## Abstract

The chemical vapor deposition (CVD) and the photoreduction deposition method were used to prepare Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts. Surface characterization and photocatalytic degradation of salicylic acid were investigated. The results suggested that metal ion concentration had great influence on the properties of Ag/TiO<sub>2</sub> photocatalyst while the irradiation time had the most significant effect on the properties of Pt/TiO<sub>2</sub> photocatalyst. Results from surface and crystal structure analysis of the photocatalysts using powder X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectrometry clearly indicated the successful deposition of silver and platinum on the surface of the pure TiO<sub>2</sub> and that the crystal structure of the photocatalysts was anatase. Results of photocatalytic experiments indicated that high pH and low initial concentrations of salicylic acid led to high removal efficiencies. The formation of the intermediate products, 2,5-DHBA and 2,3-DHBA, was observed with 2,5-DHBA concentration being higher than that of 2,3-DHBA under all pH values except at pH 11.

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## 1. Introduction

Titanium dioxide has been proven to be an attractive and promising catalyst in heterogeneous photocatalysis and in advanced oxidation processes. TiO<sub>2</sub> has a wide band gap thus it only absorbs ultraviolet light, which constitutes only 3% of the solar light. The high recombination rate of electron/hole (e<sup>-</sup>/h<sup>+</sup>) pair limits the application of TiO<sub>2</sub> [1]. Therefore, several studies have attempted to modify the surface of TiO<sub>2</sub> as to improve its efficiency of photocatalytic activity and the use of solar energy [2,3].

Li and Li [4] indicated that Pt (0.75 wt%)-TiO<sub>2</sub> exhibited the best photocatalytic performance in the degradation of methyl blue and methyl orange and that the Pt-TiO<sub>2</sub> catalyst could be sensitized by visible light. They also confirmed the presence of Pt<sup>0</sup>, Pt<sup>2+</sup>, and Pt<sup>4+</sup> species on the surface of the Pt-TiO<sub>2</sub> and Ti<sup>3+</sup> in its lattice. The surface Ti<sup>3+</sup> and deposited silver particles provide additional sites for the photogenerated electrons which would enhance the reduction of O<sub>2</sub> to form reactive oxygen species of O<sub>2</sub><sup>•-</sup>.

Liu et al. [5] have observed that deposited silver particles on the TiO<sub>2</sub> surface acts as sites where electrons accumulate. The interaction of Pt impurity and the crystal surface of TiO<sub>2</sub> might form the Schottky barrier at the interface. This barrier facilitates electron capture and therefore hinders the recombination rate between electrons and holes [6].

In this work, Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts were deposited on the surface of pyrex glass tubes by a chemical vapor deposition technique and the photoreduction deposition method. The optimal conditions for the preparation of modified TiO<sub>2</sub> photocatalysts were obtained based on the Taguchi experimental design. Surface characteristics of the pure and modified TiO<sub>2</sub> were examined using scanning electron microscopy (SEM) and powder X-ray diffraction (XRD). Photocatalytic degradation of salicylic acid solution irradiated by 365 nm UV light for 8 h was used to model the photocatalytic performance of TiO<sub>2</sub> photocatalysts modified with silver and platinum.

## 2. Experimental

### 2.1. Preparation of photocatalysts

The photocatalytic reactor was prepared by depositing the TiO<sub>2</sub> film on the internal surface of the pyrex glass tubes by the

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modified CVD method as reported in our previous study [7]. Tetraisopropyl titanate (Merck, 98%) solution and de-ionized water were placed in two separate aeration flasks, and heated in a water bath at 60 °C. Highly pure nitrogen streams (>99.99%) were used to carry the organic titanium (flow rate = 0.5 NL/min) and water vapors (flow rate = 2.0 NL/min) to the pyrex glass tube in the tubular furnace that was kept at the oxidation temperature of 400 °C. The process of the CVD technique could be observed by the naked eye. Formation of a white mist indicated the beginning of TiO<sub>2</sub> crystallization. The tube reactor was being slowly rotated, thus the TiO<sub>2</sub> film was evenly covered over the inner wall of the tube reactor. Finally, the TiO<sub>2</sub> photocatalyst was calcined at 550 °C for 24 h to remove the impurities and to make sure a good crystallization was achieved.

The Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts were prepared by the photoreduction method. The TiO<sub>2</sub> deposited tube reactor was filled with solutions of AgNO<sub>3</sub> and H<sub>2</sub>PtCl<sub>6</sub> circulated with a peristaltic pump. The UV light lamp (365 nm, Spectronics, BLE-8T365) was placed in the center of the tube reactor to initiate the photoreduction, thus the reduced metals would deposit on the TiO<sub>2</sub>. The Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts were also calcined for 24 h to remove impurities and to make the metals fix on the wall firmly. The photocatalysts were characterized with XRD (Mac MXTHIII) and SEM (Topcon, ABT-150S, 15 kV). The analytical conditions of XRD were input energy of 40 kV, 150 mA and less than 4° min<sup>-1</sup> controlled condition.

For the modification of titanium dioxide photocatalyst, the experiments were carried out under Taguchi experimental design, which studied a large number of variables with a small number of experiments [8]. The L<sub>9</sub> array method proposed in Taguchi experimental methods was used to design the experiments on controllable factors such as metal ion concentration (0.5, 1.0, 1.5 mM), light intensity (2.0, 3.0, 4.0 mW cm<sup>-2</sup>) and irradiation time (4, 8, 12 h). The salicylic acid solution of 0.5 mM was injected into the photocatalytic reactor with a 365 nm wavelength UV lamp (3.0 mW cm<sup>-2</sup> of light intensity) prepared under various conditions to carry out the photocatalytic degradation. Based on the rate of conversion for aqueous salicylic acid in the 8 h photocatalytic experiments, the optimal preparation condition could be obtained.

## 2.2. Photodegradation experiments

The experiments were carried out in the reactors coated with Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> thin film. The reactor was equipped with a 365-nm wavelength UV lamp (3.0 mW cm<sup>-2</sup> of light intensity) which was placed in the center of the reactor. Salicylic acid solution was prepared by dissolving a given amount of the chemical (Riedel-de Haën Co., >99.5%) in de-ionized water in a pyrex cylinder (mixing) tank and circulated to the tube reactor at flow rate was controlled at 200 ml min<sup>-1</sup> by a peristaltic pump. The water temperature was kept constant at 20 ± 1 °C with the constant-temperature water bath. Samples were taken from the mixing tank for analysis of residual salicylic acid using HPLC (HP 1100) and TOC (O. I. Analytical Model 1010) analyses at pre-selected time intervals. The production of intermediates

(2,3-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid and catechol) was also analyzed by HPLC.

## 3. Results and discussion

In this study, the L<sub>9</sub> array method was used to determine the most influential controllable factors on the methodology for the preparation of the modified TiO<sub>2</sub> photocatalysts. Both Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> have nine sets of preparation conditions. Results of statistical analysis indicated that the metal ion concentration exhibited the greatest influence on the properties of Ag/TiO<sub>2</sub> whereas irradiation time was the major factor controlling the photocatalysis characteristics of Pt/TiO<sub>2</sub> photocatalyst. The Ag/TiO<sub>2</sub> photocatalyst prepared in the presence of 1.5 mM of silver ion, 3.0 mW cm<sup>-2</sup> of light intensity, and 4 h of irradiation time had the best photocatalytic performance on salicylic acid. Similar results were observed on Pt/TiO<sub>2</sub> photocatalyst, but the irradiation time was elongated to 8 h.

Fig. 1 shows respectively the SEM images of the pure TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts prepared under the optimal preparation condition. Fig. 1a indicates that the unmodified TiO<sub>2</sub> particle has a uniform particulate structure with porous agglomeration. Fig. 1b and c show Ag particles appear to be in the shape of rice grains deposited on the TiO<sub>2</sub> particles while agglomeration of Pt particles covered the TiO<sub>2</sub> particles.

The XRD analysis was carried out under input energy of 40 kV, 150 mA and less than 4° min<sup>-1</sup> controlled condition. In contrast with those for anatase (21-1276), rutile (21-1272), Ag (04-0783) and Pt (04-902) in JCPDS, the results indicated that the photocatalysts prepared by the CVD method were mainly in the anatase form of TiO<sub>2</sub> and silver and platinum indeed were deposited on the modified photocatalysts by the photoreduction deposition method. The particle diameter of TiO<sub>2</sub> was calculated to be around 30 nm. Additionally, the modification process did not alter the original crystal anatase structure of TiO<sub>2</sub>.

Fig. 2 shows the evolution of salicylic acid conversion with time over Ag/TiO<sub>2</sub> at various pH values. The TiO<sub>2</sub> and Pt/TiO<sub>2</sub> systems show the same evolution as the Ag/TiO<sub>2</sub> system. After 8 h photocatalytic reaction time, the conversion of salicylic acid is the best at pH 11 but shows a decreasing tendency when the solution pH drops. Fig. 3 shows the comparison of the photocatalytic degradation of TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> with various pH values. The main reason for the observed better salicylic removal efficiencies at higher pH levels is that the OH<sup>-</sup> ion may be excited by UV light to form free hydroxyl radicals that have high oxidation capability thus speeding up the removal of salicylic acid. Moreover, the pK<sub>a</sub> value of salicylic acid is 2.97. The species distribution of salicylic acid at high pH values is largely due to its being presence in ionic form, which has higher reactivity than molecular salicylic acid.

Amphlett et al. [9] suggested that 2,3-DHBA, 2,5-DHBA and catechol are the major intermediates at the first step of the pathway of salicylic acid degraded by hydroxyl radicals. When a benzene ring of salicylic acid is oxidized by free hydroxyl radicals, -COOH behaves as an electron-withdrawing group while -OH acts as an electron-donating group. Thus, the electron clouds at the ortho- and meta-positions are huge with brings

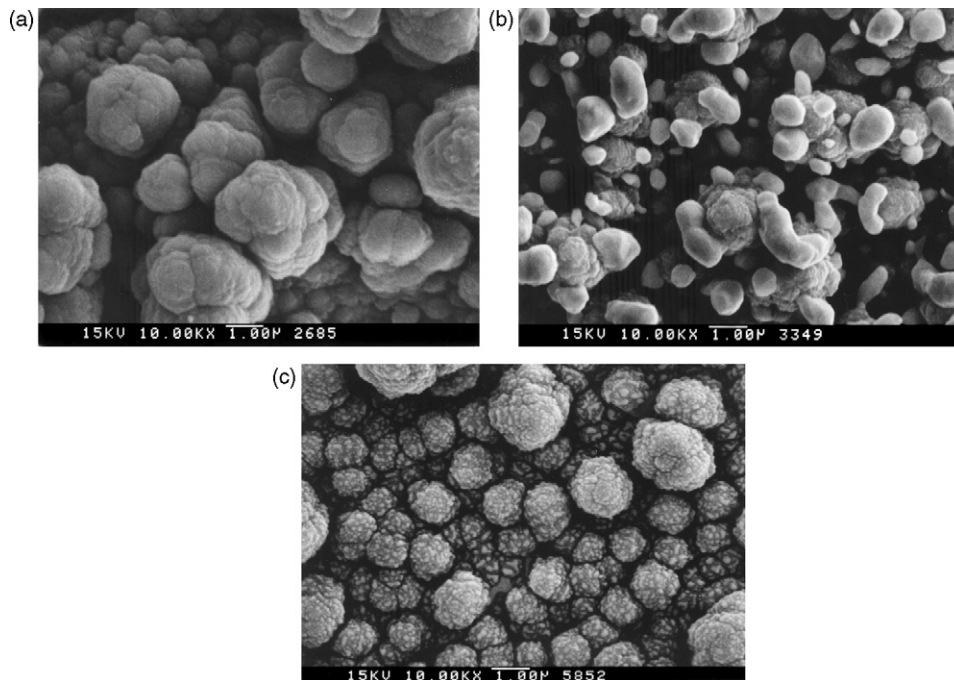


Fig. 1. SEM micrographs of photocatalysts: (a) TiO<sub>2</sub>; (b) Ag/TiO<sub>2</sub>; (c) Pt/TiO<sub>2</sub>.

about good reactivity. However, there was no catechol observed in this study. The mineralization of salicylic acid was less than 20%, which was speculated that a large number of the intermediates (2,3-DHBA and 2,5-DHBA) were degraded persistently by hydroxyl radicals to be low molecular organic acids but not mineralized in the end. In acidic and neutral conditions, 2,5-DHBA is the major intermediate and the concentration remains relatively constant at all pH values, but it is also found that 2,5-DHBA is easily to be photodegraded at pH 11. The quantity of 2,3-DHBA gradually increases with increase in pH values. Therefore, the amount of 2,3-DHBA is greater than that of 2,5-DHBA at pH 11.

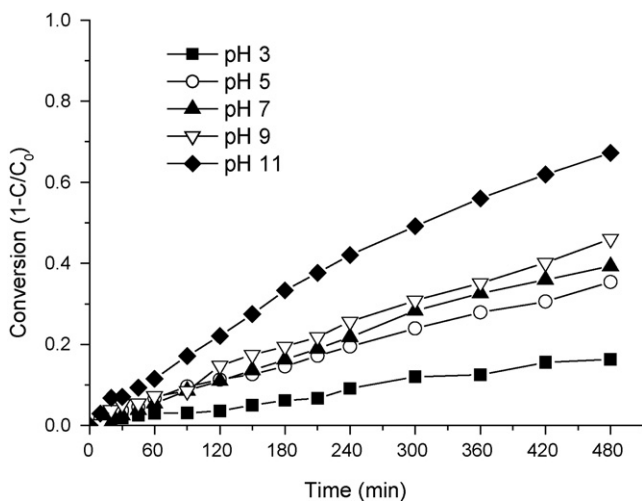


Fig. 2. Effect of pH on the conversion of salicylic acid over Ag/TiO<sub>2</sub> (experimental conditions: initial concentration, 0.5 mM; feeding rate, 200 ml min<sup>-1</sup>; temperature, 20 °C; light intensity, 3.0 mW cm<sup>-2</sup>).

Fig. 4 shows the effect of initial concentration on photocatalytic degradation of salicylic acid at pH 11 over Ag/TiO<sub>2</sub>. After being irradiated with UV light for 8 h, 80–90% of 0.1 mM salicylic acid was degraded. However, a decrease in removal efficiency is observed when the initial concentration of salicylic acid increases. Fig. 5 gives the comparison of the photocatalytic degradation of TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> with different initial concentrations. The Ag/TiO<sub>2</sub> system is less affected by initial concentration of salicylic acid than the Pt/TiO<sub>2</sub> system, i.e. the removal efficiency of salicylic acid is not sensitive to the variation of initial concentration. The results suggest that when the initial concentrations are 0.1 and 0.25 mM, there are 90 and 80%

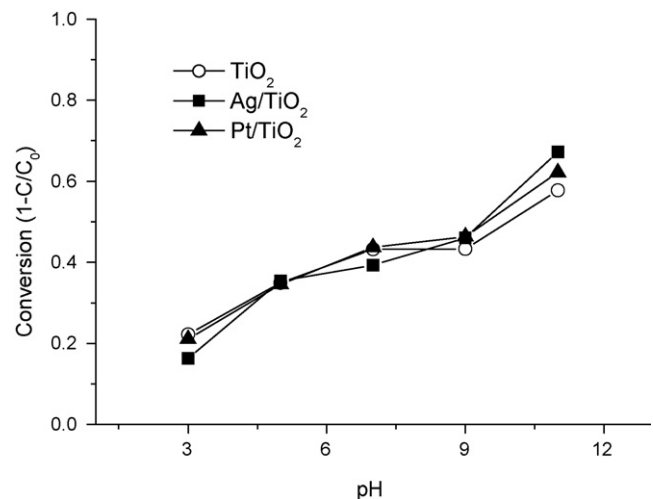


Fig. 3. The photocatalytic degradation of salicylic acid by TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> at various pH values (experimental conditions: initial concentration, 0.5 mM; feeding rate, 200 ml min<sup>-1</sup>; temperature, 20 °C; light intensity, 3.0 mW cm<sup>-2</sup>).

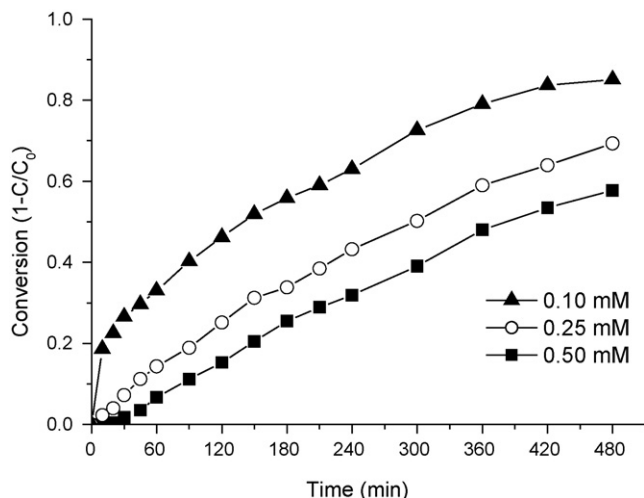


Fig. 4. Effect of initial concentration on the conversion of salicylic acid over Ag/TiO<sub>2</sub> (experimental conditions: pH 11; feeding rate, 200 ml min<sup>-1</sup>; temperature, 20 °C; light intensity, 3.0 mW cm<sup>-2</sup>).

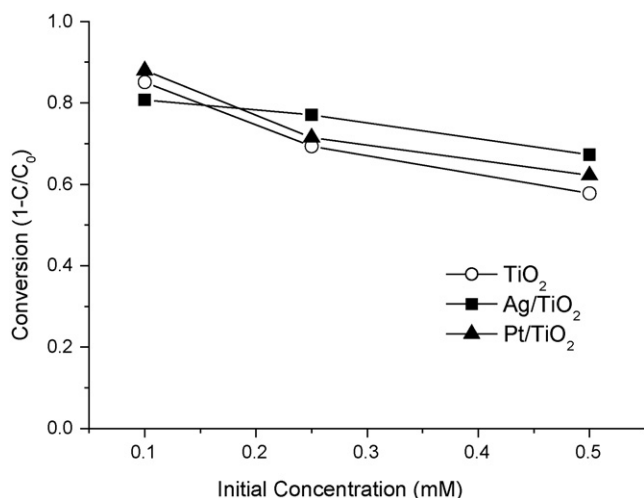


Fig. 5. The photocatalytic degradation of salicylic acid by TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> at different initial concentrations (experimental conditions: pH 11; feeding rate, 200 ml min<sup>-1</sup>; temperature, 20 °C; light intensity, 3.0 mW cm<sup>-2</sup>).

of salicylic acid being degraded, respectively. But when the initial concentration rises to 0.5 mM, only 60% of salicylic acid is photodegraded. It is speculated that the intermediates may compete with salicylic acid for activation sites on the surface of the photocatalysts, thus hindering the photocatalytic degradation. Augugliaro et al. [10] investigated the use of photocatalytic procedure to deal with nitrophenol isomers aqueous solution and indicated that higher initial concentrations of nitrophenol isomers lead to lower decomposition rates. Qamar et al. [11] indicated that as the initial concentrations of the dye increases, the color of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. As the initial concentration of salicylic acid is reduced, the quantity of intermediates is also reduced. Thus, more free surface activation sites are available and the intermediates are more easily adsorbed to the activation sites available

on the surface of photocatalysts; the adsorbed intermediates are then oxidized by the free hydroxyl radicals leading to higher mineralization rates.

#### 4. Conclusions

In this study, the TiO<sub>2</sub> film was deposited on the internal surface of the pyrex glass tubes by the CVD technique and then modified with the photoreduction method. Based on the results of the orthogonal array test, the optimal condition in terms of photocatalytic degradation efficiency of salicylic acid, for the preparation of both the Ag/TiO<sub>2</sub> and the Pt/TiO<sub>2</sub> photocatalysts were 1.5 mM of silver or platinum ion concentration, 3.0 mW cm<sup>-2</sup> of light intensity. But irradiation time were 4 h for the Ag/TiO<sub>2</sub> and 8 h for the Pt/TiO<sub>2</sub>. The results of XRD and SEM-EDX analyses suggested that the photoreduction deposition method did indeed deposit silver and platinum on the surface of the TiO<sub>2</sub> catalysts and that the crystal structure of the photocatalysts remained in the anatase form after modification. Results of photocatalytic experiments indicated that high pH and low initial concentrations of salicylic acid led to high removal efficiencies. The formation of the intermediate products, 2,5-DHBA and 2,3-DHBA, was observed. 2,5-DHBA concentration was higher than 2,3-DHBA concentration except at pH 11.

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