

ANTIBACTERIAL EFFICIENCIES OF Ag-TiO₂ (P25) CATALYST UNDER DIFFERENT LIGHT CONDITION

HIỆU QUẢ KHỬ KHUẨN CỦA VẬT LIỆU XÚC TÁC QUANG Ag-TiO₂ (P25) DƯỚI ĐIỀU KIỆN CHIẾU SÁNG KHÁC NHAU

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ABSTRACT

In recent years, the applications of Ag-TiO₂ nanomaterial in water purification process has gained wide attention due to its effectiveness in disinfection under UV light as well as the possibility of utilizing visible light spectrum. This paper aims to determine photocatalytic efficiencies of Ag-TiO₂(P25) catalyst in disinfection under UV light, visible light and in dark. Ag-TiO₂(P25) was synthesized by impregnation method with the mole percentage of Ag to TiO₂ at 0.5, 1, 2, 5 and 10% in batch experiments within 30 reacting - minutes. The presence of silver in 1%Ag-TiO₂(P25) nanomaterial increase the disinfection efficiencies under solar irradiation (5-log(10)) was higher than TiO₂(P25) under solar irradiation (2-log) or extremely higher than under solar light (1-log) and in dark (0%) after 20 minutes. Under UVC illumination, strong reduction on the survival number of E.coli cells with the presence of 1%Ag-TiO₂(P25). Meanwhile a combination of silver and TiO₂(P25) was found to significantly increase the disinfection efficiency.

Keywords: Ag-TiO₂ (P25); E.coli disinfection; dark; solar irradiation; UVC light.

TÓM TẮT

Trong những năm gần đây, vật liệu Ag-TiO₂ được ứng dụng nhiều trong xử lý nước vì có nhiều hiệu quả trong việc khử trùng vi khuẩn dưới điều kiện ánh sáng UV cũng như hiệu quả dưới ánh sáng nhìn thấy. Nghiên cứu này nhằm xác định hiệu quả xúc tác quang hóa của Ag-TiO₂(P25) trong khử trùng nước dưới điều kiện ánh sáng đèn UV ánh sáng nhìn thấy và điều kiện bóng tối. Vật liệu Ag-TiO₂(P25) được tổng hợp bằng phương pháp tẩm với tỉ lệ phần trăm mol của Ag:TiO₂ là 0,5; 1; 2; 5 và 10%. Kết quả cho thấy khi sau 20 phút chiếu sáng có mặt của 1%Ag-TiO₂(P25) dưới ánh sáng mặt trời (đạt log5) cao hơn rất nhiều so với TiO₂(P25) ở cùng điều kiện (đạt log2) và chỉ ánh sáng mặt trời (đạt log1) và trong điều kiện bóng tối (0%). Dưới điều kiện ánh sáng UVC, lượng vi khuẩn E.coli còn lại giảm rất nhanh. Điều này cho thấy sự kết hợp giữa bạc và TiO₂(P25) giúp nâng cao khả năng khử trùng của vật liệu.

Từ khóa: Ag-TiO₂(P25); khử khuẩn E.coli; bóng tối; ánh sáng mặt trời; ánh sáng đèn UVC.

1. INTRODUCTION

Nanocrystalline titania (TiO₂) becomes increasingly common due to its potential application such as catalysis/photocatalysis, antibacterial activity, photovoltaic applications and oxidation of toxic organic contaminants in water to carbon dioxide [1]. The range of applications of TiO₂ is wide

mainly because it is relatively efficient, cheap, non-toxic, chemically and biologically inert. However, due to the wide band gap of the TiO₂ (~3.2 eV), it can only be applied in the UV irradiation (a wavelength less than 387.5 nm) which was ~5% of the solar energy, while the visible light contains about 45% of the solar energy [2,3]. Therefore,

many researchers are interested in shifting the absorption spectrum of TiO_2 towards the visible region in order to increase the TiO_2 photocatalytic activity under UV irradiation [4,5] and to improve its visible light sensitivity [6].

Silver (Ag) has been known to exhibit strong cytotoxicity towards a broad range of micro-organisms. Ag^+ can bind, damage, and alter the functionalities of bacterial cell wall membrane, which are slightly negative [7–9]. It was reported that Ag strongly interacted with the thiol groups of proteins that were important for the bacterial respiration and the transport of significant substances through the cell [10]. In addition, the combination of Ag and TiO_2 was expected to improve photocatalytic inactivation of bacteria [11,12] and Ag nanoparticles enhanced photoactivity of TiO_2 by lowering the recombination rate of its photo-excited charge carriers and/or providing more surface area for adsorption [13].

In this study, Ag was doped in $\text{TiO}_2(\text{P25})$ by impregnation method to determine their disinfection activities under UVC light, solar light and in dark condition. This research examined antibacterial activity of suspended catalyst particles in water batch under each light condition. Photocatalytic efficiencies of catalyst on the disinfection process of *E.coli* bacteria were also determined with changing the mole percentage of Ag to TiO_2 .

2. EXPERIMENTAL

2.1. Preparation of Ag- $\text{TiO}_2(\text{P25})$ catalysts

To synthesize Ag- $\text{TiO}_2(\text{P25})$, 2g of commercial titanium dioxide (TiO_2 , Degussa-P25) were dispersed into 100 mL of deionized water by using ultrasonication for 30 min. After ultrasonic treatment, silver nitrate (Xilong, China) was added in TiO_2 suspension with the mole percentage of Ag to TiO_2 at 0.5, 1, 2, 5 and 10%. This solution was stirred for 1h and then centrifuged to obtain the Ag- $\text{TiO}_2(\text{P25})$ nanoparticles. The Ag- $\text{TiO}_2(\text{P25})$ nanoparticles were dried at

105°C in 24h and then calcined at 400°C in a muffle furnace for 6h before crushing.

2.2. Antibacterial test

Photocatalytic disinfection experiments of *Escherichia coli* (*E.coli*, ATCC®25922) was conducted in a reactor containing 300 mL of approximately 10^6 CFU (colony forming units) *E.coli* /mL in different conditions. The Ag- $\text{TiO}_2(\text{P25})$ catalyst with the concentration of 0.2 g/L was added after *E.coli* suspension was well mixed in 10 min by using a magnetic stirrer at approximately 200 rpm. The UVC lamp (15W-Aqua-Pro) was used in UVC condition (Fig.1) and reactor was explored under real sunlight in solar condition (90 Klux).

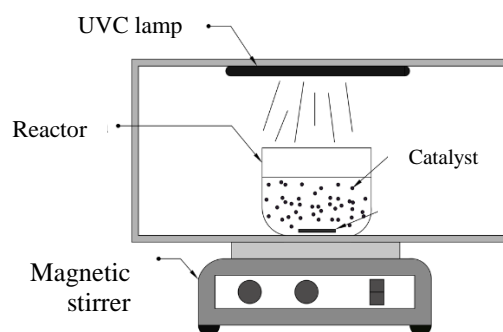


Figure 1. Batch reactor for photocatalytic experiments

Samples were taken at 5, 10, 15, 20 and 30 min. The antibacterial activity of the catalyst against *E.coli* was determined by quantitative evaluation methods. 1 mL of the treated solution was diluted with sodium chloride solution (NaCl 0.9%) to obtain the suitable environment for bacterial colonies. The diluted solution was then spread on Tryptic Soy Agar (TSA) plates and incubated at 37°C for 24 h before the bacterial colonies were counted. The obtained data were the average value of three parallel runs or the values showing the best fitting for an exponential reduction.

2.3. Characterization

The catalyst particle size and morphology were obtained by using transmission electron microscopy (TEM, JEM 1400, JEOL, Japan). The BET specific

surface area of catalyst was determined by nitrogen adsorption at 77K using a Chembet 3000. The band-gap energy and the optical absorption spectra were measured by UV-visible diffuse reflectance spectroscopy (UV-2401, Shimadzu, Japan)

3. RESULTS AND DISCUSSION

3.1. Characterization of Ag-TiO₂(P25) catalyst

Figure 2 shows TEM micrographs of impregnation-derived Ag-P25. Estimated from this figure, the particle size of the 1%Ag-TiO₂(P25) was approximately 22 nm, same as that of TiO₂(P25), approximately 21 nm. This agrees with other observations [14] that using Ag would decrease band gap of TiO₂(P25), from 3.24 to 3.02 eV. However, the specific surface area of the derived 1%Ag-TiO₂(P25) catalysts (approximately 22.02 m²/g) was lower than that of TiO₂(P25) (approximately 53.1 m²/g).

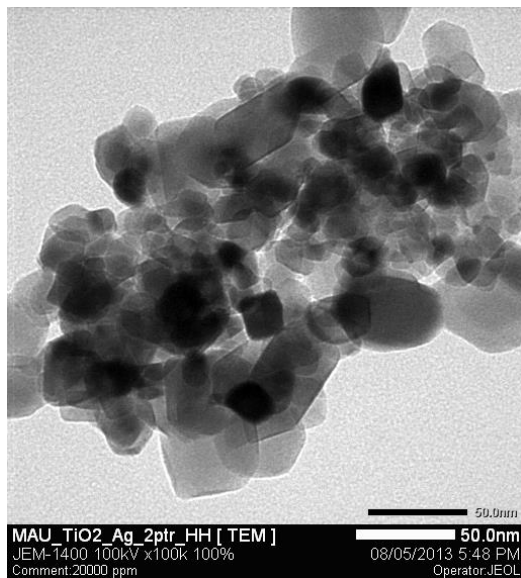


Figure 2. TEM micrographs of the impregnation-derived Ag-TiO₂(P25)

3.2. Disinfection of Ag-TiO₂(P25) against *E.coli* under different irradiations

Figure 3 shows the influence of the different irradiations on the number of survival *E.coli* cells, determined by bacterial counting on TSA agar plates and expressed in terms of logarithmic reduction. In the absence of light, the antibacterial

efficiencies of reactor with TiO₂(P25) and 1%Ag-TiO₂(P25) did not cause any reduction in cell viability. Obviously, dark was not sufficient to inactivate the bacteria, which was also confirmed by the previous studies [15,16]. However, the antibacterial efficiencies of Ag-TiO₂(P25) got 4-log when the mole percentage of Ag and TiO₂ was 10% in dark condition.

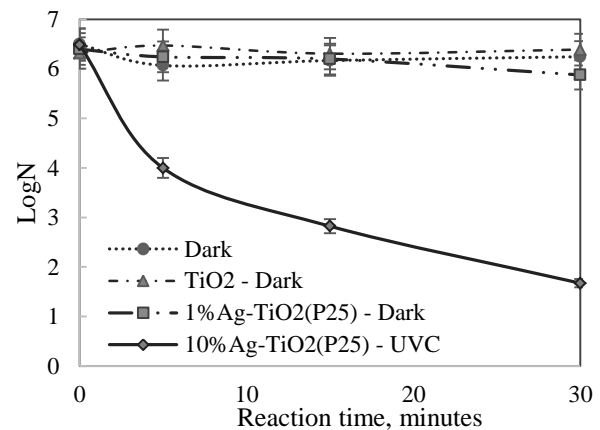


Figure 3. Antibacterial activity of 1%Ag-TiO₂(P25) (C=0.2 g/L) in dark condition

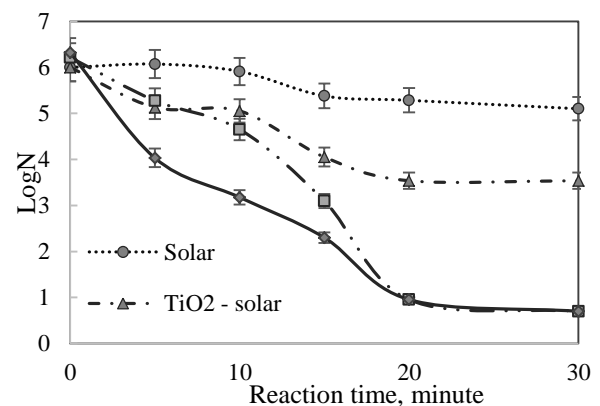


Figure 4. Antibacterial activity of 1%Ag-TiO₂(P25) (C=0.2 g/L) under solar light condition

Under solar illumination, slight reduction on the number of survival *E. coli* cells was observed whereas disinfection efficiencies was high in the presence of 1%Ag-TiO₂(P25) after 15 minutes (Fig 4). Within 20-minute exposure to solar light, 5-log(10) reduction of *E.coli* population was recorded with 1%Ag-TiO₂(P25) concentration of 0.2 g/litre. It is evident that silver has long been known to be one of the

most effective doping metals to change the intrinsic band structure of TiO_2 , and consequently, to improve its visible light sensitivity [17-18]. Therefore, the disinfection efficiency of solar light and 1%Ag- TiO_2 (P25) was increased compared to catalyst without silver (Fig. 4).

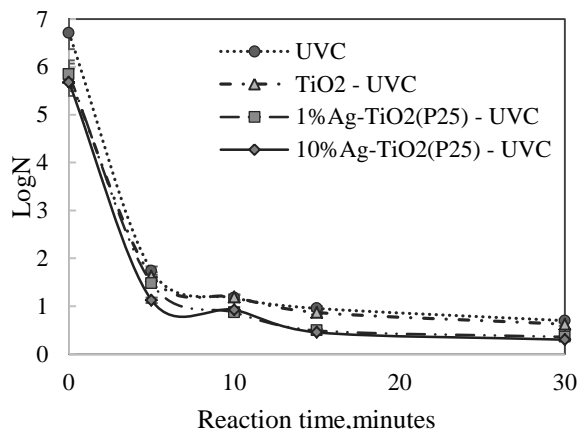


Figure 5. Antibacterial activity of 1%Ag- TiO_2 (P25) ($C=0.2 \text{ g/L}$) under UVC light condition

UVC light is a well-known traditional disinfectant as well as increases photocatalytic activity of photocatalysts [19]. Therefore, the photocatalytic properties of the catalysts were evaluated by conducting inactivation experiments of *E.coli* bacteria under UV irradiation. The presence of 1%Ag- TiO_2 (P25) under UVC was not observed to substantially improve the disinfection efficiency against *E.coli* of this catalyst (Fig. 5) since photocatalytic reaction occurred too fast to clearly perform the difference between reactor with UVC and the one with catalyst – UVC.

3.3. The effect of silver loading on disinfection of Ag- TiO_2 (P25) against *E.coli*

To further clarify the photocatalytic effect of catalyst, disinfection efficiencies of this catalyst against *E.coli* were investigated with the mole percentage of Ag to TiO_2 at 0.5, 1, 2, 5 and 10% under different light sources (Fig. 6 (a,b,c)).

Based on the reduction rate of *E.coli* colonies observed in Figure 6a, it could be

seen that disinfection efficiencies of these catalysts were not significantly different in the antibacterial activities when increasing the percentage of silver from 0.5%-to 10% of Ag- TiO_2 (P25) within 5-minute reaction under light condition. However, after 30-minute exploring under solar irradiation (Fig 6b,c), there was an increase in antibacterial activity according to the mole percentage of silver in catalysts from 0 to 1%. When the %Ag/ TiO_2 was more than 1%, the efficiencies did not significantly change.

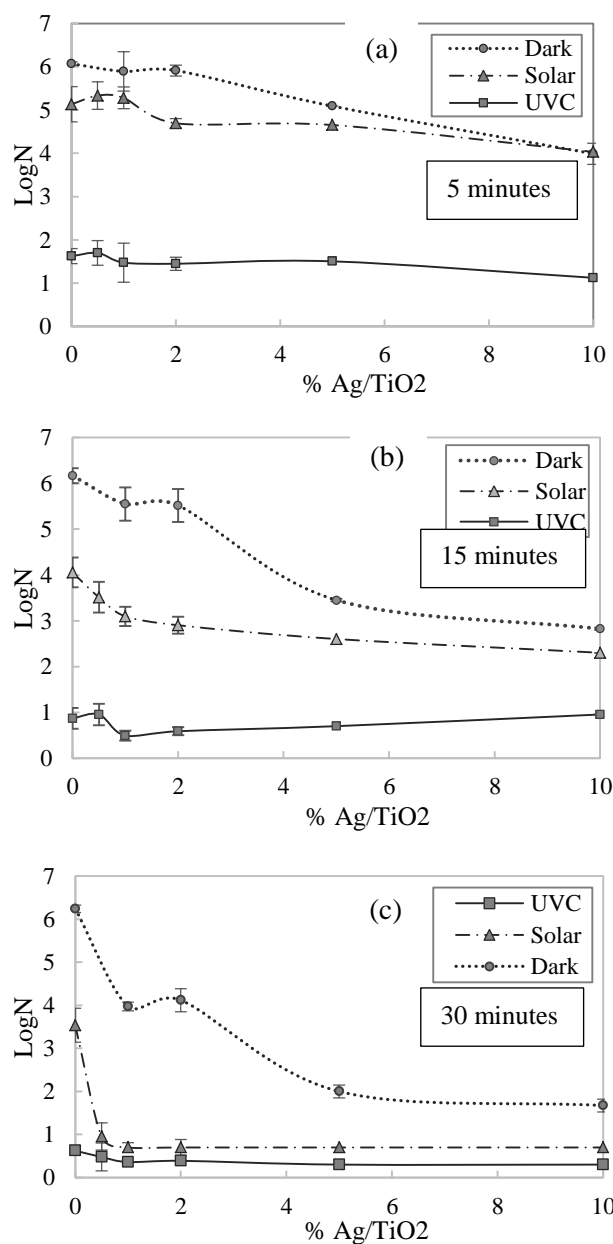


Figure 6. Antibacterial activity of Ag- TiO_2 (P25) ($C=0.2 \text{ g/L}$) with different mole percentage of Ag to TiO_2

In dark condition, antibacterial activities were remarkably affected by silver loading on Ag-TiO₂. The reduction of bacteria was from 1-log to 4-log within 30 minutes. Besides, the mole percentage of Ag and TiO₂ higher than 5% did not make the difference in killing *E.coli* bacteria.

4. CONCLUSION

Ag doped TiO₂ by impregnation method was synthesized to determine effect of the mole percentage of Ag and TiO₂ with

antibacterial activities. The band gap was found to be 3.02 eV for 1%Ag-TiO₂(P25) compared to 3.24 eV for TiO₂(P25). Disinfection efficiency of Ag-TiO₂(P25) samples was examined by the number of survival *E.coli* for 30 minutes under UVC, solar irradiation and in dark condition. It is found that the antibacterial activity depended on the ratio of Ag and TiO₂ under solar light and in dark condition while it was not clear under UVC light.

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