Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

A novel P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite film for water purification and antibacterial application under solar light irradiation

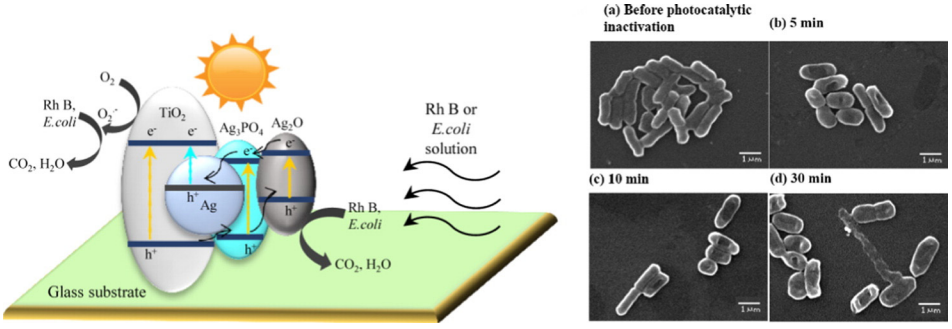
Qi Zhu [1], Xiaohong Hu [1], Mishma S. Stanislaus, Nan Zhang, Ruida Xiao, Na Liu, Yingnan Yang *

Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8577, Japan

HIGHLIGHTS

- P/Ag/Ag_2O/Ag_3PO_4/TiO_2 film showed great photocatalytic ability and stability.
- 10^7 CFU/mL of *E. coli* could be completely inactivated by this film within 5 min.
- Photo-generated holes and $O_2^{\bullet -}$ radicals were the major reactive species.
- This photocatalyst film could be a promising candidate for bacterial disinfection.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 July 2016
Received in revised form 20 October 2016
Accepted 21 October 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite film
Rh B photodegradation
Bacterial inactivation
Photocatalytic mechanism
Simulated solar light irradiation

ABSTRACT

TiO_2-based thin films have been intensively studied in recent years to develop efficient photocatalyst films to degrade refractory organics and inactivate bacteria for wastewater treatment. In the present work, P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite films on the inner-surface of glass tube were successfully prepared via sol-gel approach. P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite films with 3 coating layers, synthesized at 400 °C for 2 h, showed the optimal photocatalytic performance for rhodamine B (Rh B) degradation. The results indicated that degradation ratio of Rh B by P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite film reached 99.9% after 60 min under simulated solar light, while just 67.9% of Rh B was degraded by pure TiO_2 film. Moreover, repeatability experiments indicated that even after five recycling runs, the photodegradation ratio of Rh B over composite film maintained at 99.9%, demonstrating its high stability. Photocatalytic inactivation of *E. coli* with initial concentration of 10^7 CFU/mL also showed around 100% of sterilization ratio under simulated solar light irradiation in 5 min by the composite film. The radical trapping experiments implied that the major active species of P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite films were photo-generated holes and $O_2^{\bullet -}$ radicals. The proposed photocatalytic mechanism shows that the transfer of photo-induced electrons and holes may reduce the recombination efficiency of electron-hole pairs and potential photo-decomposition of composite film, resulting in enhanced photocatalytic ability of P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite films.

1. Introduction

As is known to all, water pollution is caused by not only the hazardous chemicals but also pathogenic microorganisms in the world. Therefore, it is very important to disinfect for water purification, because many water

* Corresponding author.
E-mail address: yo.innan.fu@u.tsukuba.ac.jp (Y. Yang).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.scitotenv.2016.10.170
0048-9697/

sources are polluted by virus, bacteria and parasitic worm (Mailler et al., 2016; Islam et al., 2015; Sukkasi and Terdthaichairat, 2015; Guerrant et al., 1990; Etchepare et al., 2015; Ortega-Gomez et al., 2016). However, traditional water disinfection methods (such as chlorination and ozonation) have some disadvantages due to the formation of potentially hazardous disinfection byproduct (DBPs) or complicated working to an external device (Bedner and MacCrehan, 2006; Bulloch et al., 2012; Buth et al., 2007; Dodd and Huang, 2007). Recently, photocatalysis has been found as an efficient technology to inactivate bacteria (Gan et al., 2013; Zhu et al., 2012; Thanh-Dong and Lee, 2015; Yu et al., 2016; Pham and Lee, 2015; Hossain et al., 2014; Wang et al., 2013), but more efficient photocatalysts are much needed to develop for water purification.

In our previous study, the solar-light-driven P/Ag/Ag_2O/Ag_3PO_4/TiO_2 photocatalyst was synthesized though sol-gel method, demonstrating extremely high photocatalytic ability and stability for rhodamine B (Rh B, a model of organic waste) degradation under simulated solar light (Hu et al., 2015). However, it was difficult to separate the powder from solution after the photocatalytic reaction, which caused the low efficiency of reusability. As such, it is necessary to improve the reusability efficiency and the possibility of practical application using the effective route, such as coating P/Ag/Ag_2O/Ag_3PO_4/TiO_2 thin film (Lee and Donahue, 2011; Li et al., 2015a). Surprising, there is few report on development of solar-light-driven photocatalyst film on the inner-surface of glass tube for circulatory water purification and antibacterial application. In view of this point, the current study was conducted to prepare P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite film on the inner-surface of glass tube in order to develop efficient approach for water purification and disinfection. Nowadays there is no report about any investigation of bacterial inactivation by P/Ag/Ag_2O/Ag_3PO_4/TiO_2 photocatalyst. Therefore, it's necessary for us to study sterilization of *E. coli* under solar light irradiation by using P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite film.

In this study, P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite film was firstly successfully synthesized by sol-gel method. Then, the influence of synthesis conditions on photocatalytic ability was explored by varying calcination temperature, calcination time and number of coating layers. The structure and optical properties of P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite films were analyzed, and also the photocatalytic ability of this composite film was investigated through Rh B degradation and sterilization of *E. coli* under solar light irradiation, in comparison with pure TiO_2 film. Further, morphology and microstructure of *E. coli* before and after photocatalytic inactivation were observed using SEM images. Finally, radical trapping experiments were conducted to propose a possible mechanism for Rh B degradation and sterilization of *E. coli* under solar light irradiation.

2. Experiment

2.1. Preparation of P/Ag/Ag_2O/Ag_3PO_4/TiO_2 thin film

All of the reagents purchased from Wako Pure Chemical Industries, Ltd' Japan were of analytical purity. Tetrabutyl titanate ($Ti(OC_4H_9)_4$), ethanol, HNO_3, $AgNO_3$ and Ag_3PO_4 were utilized as TiO_2 source, solvent, dispersing agents and dopants, respectively. Simulated solar light was taken as the irradiation source, and glass tubes (length: 15 cm, φ: 8 mm, Φ: 10 mm) were employed as thin film carrier.

The transparent P/Ag/Ag_2O/Ag_3PO_4/TiO_2 sol was prepared according to our previous study (Hu et al., 2015), and then obtained sol was coated on the inner surface of glass tubes. After coating, the films on glass tubes were dried under 105 °C for 24 h, and then calcined at different temperature ranging from 300 to 500 °C for varied time from 1 to 3 h in the muffle furnace. To prepare 1, 2, 3 and 4-layer films, the processes of coating and drying were repeated several times. Finally, the P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite films were successfully synthesized.

In order to compare the antibacterial activities between different photocatalysts, Ag, Ag_3PO_4, TiO_2, Ag/TiO_2, Ag_3PO_4/TiO_2 and Ag/Ag_3PO_4 thin films were prepared as controls by the same method. During the synthesis of Ag, Ag_3PO_4 and TiO_2 films, there was just addition of $AgNO_3$, Ag_3PO_4 and tetrabutyl titanate, respectively. For synthesis of Ag/TiO_2, Ag_3PO_4/TiO_2 and Ag/Ag_3PO_4 films, Ag_3PO_4, $AgNO_3$ or TiO_2 were not added, respectively. Certainly, the molar ratio of Ti to Ag was the same as that in P/Ag/Ag_2O/Ag_3PO_4/TiO_2. After the same heat treatments, Ag, Ag_3PO_4, TiO_2, Ag/TiO_2, Ag_3PO_4/TiO_2 and Ag/Ag_3PO_4 thin films were successfully prepared.

2.2. Analytical techniques

The photocatalytic degradation of Rh B was carried out under simulated solar lamp (XC-100, SERIC., Ltd.), and the concentration of Rh B solution was measured by a Shimadzu UV-1600 spectrophotometer. X-ray diffraction (XRD) patterns of thin films were characterized by using a Rigaku Altima III Rint-2000 X-ray diffractometer equipped with Cu Kα radiation (λ = 1.54178 Å). X-ray photoelectron spectra (XPS) were recorded using a Thermo VG Theta Probe (Thermo Fisher SCIENTIFIC), and all of the binding energies were calibrated to the C 1s peak at 284.6 eV. Scanning electron microscopy (SEM, Hitachi FE-SEM S-4800 EDX) was utilized to observe the morphology of thin films. UV–vis diffuse reflectance spectra of different samples were recorded in the range of 200–800 nm on a Shimadzu UV-3100PC Scan UV–vis-NIR spectrometer. The roughness of composite film was measured by AFM (MFP-3D-BIO, Oxford Instruments plc). The leakage of Ag^+ was measured by using a Leeman Prodigy Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, SPS3520UV-DD) system (SII Nano Technology Inc., Tokyo, Japan).

2.3. Photocatalytic reaction

The photoreaction system consisted of the glass tubes coated thin film, the rotary orbital shaker and simulated solar lamp, with the glass tubes fastened on the shaker. Photocatalytic degradation of Rh B was conducted through glass tubes coated thin films under simulated solar light with 50 mW/cm^2 light intensity, and the initial concentration of Rh B solution was 2 mg/L. The Rh B solution was collected at irradiation time intervals of 30 min, and analyzed to evaluate the concentration of Rh B by a spectrophotometer at a wavelength of 554 nm which corresponds to the maximum absorption wavelength of Rh B molecule.

2.4. Antibacterial activity tests

In this study, XM-G agar medium and Nutrient broth (Japan, BD) were used to isolate and culture the *E. coli*. Phosphate-buffered saline (PBS) (Wako, Japan) was utilized as carrier liquid in this study.

After isolated from Matsumi Lake (University of Tsukuba), *E. coli* was cultured and added into PBS with initial concentration of 10^7 CFU/mL. 50 mL of bacterial liquid was prepared in a beaker which was covered with para-film and used as a supply tank. Then liquid was circulated continuously through the composite film coated glass tube by pump at the flow rate of 24 mL/min. The film coated glass tube with 50.2 cm^2 of reaction surface was irradiated under the simulated solar light with intensity of 50 mW/cm^2. The schematic diagram and the parameters of this tubular cyclic system were shown in Fig. S1.

2.5. Radical trapping experiment

Radical-trapping experiments were conducted to investigate the major active species during the photocatalytic degradation of Rh B over P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite films. Benzoquinone, ethylenediaminetetraacetate (EDTA) and tBuOH were used as the superoxide anion radical scavenger, hole scavenger and hydroxyl radical scavenger, respectively. Prior to experiments, 1 mM scavenger was added into Rh B solution, and followed by dark condition to reach the adsorption-desorption equilibrium. After irradiation by simulated solar light, the solution was collected at given time intervals, and the concentration of Rh B was measured by a spectrophotometer.

Please cite this article as: Zhu, Q., et al., A novel P/Ag/Ag_2O/Ag_3PO_4/TiO_2 composite film for water purification and antibacterial application under solar light irradiation, Sci Total Environ (2016), http://dx.doi.org/10.1016/j.scitotenv.2016.10.170