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Gas phase photocatalytic bacteria inactivation using metal modified TiO_2 catalysts

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ABSTRACT

The present study describes the efficiency of heterogeneous photocatalytic reactor for the inactivation of three air born bacteria, *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus aureus* using metal modified TiO_2 photocatalysts and blacklight irradiation. The catalysts were prepared by photodeposition of silver, palladium or iron on commercial TiO_2, immobilized on glass plates. X-ray photoelectron spectroscopy analysis was applied to determine the atomic percentage and species of each metal on the TiO_2 surface, showing that 85% of silver, 73% of palladium and 45% of iron were present in metallic form on TiO_2 surface. The plates were positioned on the inner lateral walls of a chamber through which the contaminated air flow passed for disinfection. Irradiation of bare TiO_2 resulted in 50% inactivation of *E. coli* while 41% and 35% inactivation of *B. subtilis* and *S. aureus* were obtained, respectively. When metal modified TiO_2 was applied, the inactivation of *B. subtilis* was improved to 91% using Pd–TiO_2 while of *S. aureus* was improved to 94% with Fe–TiO_2, showing in this case no significant difference when compared to Ag–TiO_2 and Pd–TiO_2. In contrast, inactivation of *E. coli* was not significantly increased when metal modified TiO_2 was used, ranging from 47% to 57%.

1. Introduction

The indoor air tightness in buildings can lead to serious chemical and biological contamination. Sources of chemical contamination include combustion, building and furnishing materials emissions, house cleaning and personal care products, while common biological contaminants are microorganism like bacteria and viruses. Both types of contamination can have serious consequences to human health such as allergies and respiratory diseases. The available air purifying systems are usually based on filters to retain either chemical or biological contamination. Although this type of purification can be effective for short time use, the long-term utilization demands frequent replacement of filters and cleaning procedures to guarantee good air quality and prevent that they act as potential source of secondary pollution.

The heterogeneous photocatalysis, using TiO_2 in combination with UV irradiation, has been widely demonstrated to be very efficient for the degradation of air contaminants at ambient temperature in the presence of oxygen [1–5]. In this process, the photogenerated valence band holes of TiO_2, act as oxidation sites accepting electrons from hydroxyl ions or water and generating hydroxyl radicals, highly oxidizing species, which induce the degradation process of organic contaminant. Simultaneously, conduction band electrons increase the hydroxyl radical generation by reduction of molecular oxygen, metal ions or other electron accepting species, thus decrease the recombination rate of electron/hole pairs and maintain the valence band redox reactions.

Besides the degradation of organic contaminants, the heterogeneous photocatalysis is also applied to eliminate microorganisms, which constitute a much more complex system. The disinfection processes has been first demonstrated by Matsunaga et al. [6], who observed that bacteria cells were inactivated after exposure to TiO_2–Pt and near ultraviolet light. The proposed mechanisms for the photocatalytic inactivation of microorganisms are the alteration of respiratory activity by oxidation of intracellular Coenzyme A, leading to cell membrane damage and finally its death. The cell destruction was confirmed by potassium leakage, as well as by observations using transmission electron microscopy [7]. Other studies also indicate that cell membrane damage might be the cause of cell death [8–10]. Nevertheless, a detailed mechanism involved in the bactericidal effect of TiO_2 photocatalysis is still not completely understood. The peroxidation of membrane constituents mediated by reactive oxygen species including hydroxyl radical was demonstrated by the formation of peroxidation products such as aldehydes and ketones simultaneously to cell wall damage [11]. Independently of the details of the cell deactivation mechanism, the effectiveness of the application of photocatalysis for disinfection purposes is a consensus in the literature [12]. In particular, the fact that heterogeneous photocatalysis can promote

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simultaneously the degradation of organic contaminants and the inactivation of microorganisms is of great interest for the decontamination of indoor environments [13–16].

The increase of the photocatalytic activity by surface modification or substitutional doping of TiO_2 using metals has been shown in several studies [17–20]. The inhibition of the electron/hole (e^-/h^+) recombination process by catalyzing electron transfer to oxygen [4] and Fenton like redox processes on metal atom sites [21] has been demonstrated to be the main responsible for the improvement of the overall efficiency of the process. Furthermore, the metal incorporation in TiO_2 has been also used to extend the absorption range of the semiconductor to the visible region aiming mainly solar applications [18,21].

The aim of the present work was to evaluate the photocatalytic inactivation of three bacteria, *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus aureus* present in the gas phase using heterogeneous photocatalysis with metal modified TiO_2 immobilized on glass plates in a simple chamber flow reactor. The effect of silver, palladium and iron surface layers in comparison to bare TiO_2 on the bacteria inactivation was evaluated under blacklight irradiation.

2. Experimental

2.1. Photocatalysts preparation and characterization

Titanium dioxide (P25, Degussa), 70:30 anatase:rutile, BET surface area 50 $m^2\,g^{-1}$ with 30 nm mean particle size was used as photocatalyst. TiO_2 was immobilized on 24 (10×12 cm) glass plates, six for each series of experiments (bare TiO_2, Ag–TiO_2, Pd–TiO_2 and Fe–TiO_2). The plates were rough at the side where TiO_2 was immobilized, to allow a more homogeneous TiO_2 layer. In a first step, the plates were cleaned using a neutral surfactant followed by washing with tap and ultrapure water. Then they were immersed in 10% nitric acid for five minutes to remove any possible metal residue and then washed five times with ultrapure water. The plates were then dried at 100 °C and weighted. A volume of 500 mL of 1% (w/w) TiO_2 aqueous suspension was prepared where the glass plates were horizontally immersed for few minutes. Then they were withdrawn at 5 cm min^{-1} rate and dried in the air at an angle of 2.5° to allow a slow drain of the suspension and homogeneous deposition of the catalyst on the plates. This procedure was repeated 10 times and then the plates were dried at 100 °C. After removal of the catalyst from the sides and from the smooth back side of the plates, all plates were weighted to calculate the mass of the deposited photocatalyst.

Metal-modified TiO_2 plates were prepared by photoreduction of the corresponding metal salt solution ($AgNO_3$, $PdCl_2$ and $FeSO_4{\cdot}7H_2O$) onto TiO_2 under solar irradiation [22,23]. Aqueous solutions containing 2% methanol and each metal salt were prepared for the photodeposition of the metals. The amount of each salt in the solution was calculated to result in a 1% (at.%) metal addition to TiO_2 photocatalyst. The TiO_2 coated glass plates were immersed into the solution to a depth of 1.5 cm to allow a high light transmission toward the plates. Then the plates were then immediately exposed to solar irradiation during three hours, between noon and 3 p.m., under an approximate energy dose of 20 J cm^{-2} (measured with a PMA 2100, Solar Light Co radiometer in the 320–400 nm region). After photodeposition, the samples were dried in air, then heat treated at 100 °C and weighted to calculate the final mass of each photocatalyst. The remaining solutions were analyzed to determine residual metal concentration using atomic absorption spectrometry with argon plasma (Thermo Jarrel, IRIS/AP), with a detection limit of 0.01 mg L^{-1} for Ag and Pd and 0.05 mg L^{-1} for Fe.

Metal coated TiO_2 plates with an area of 1 cm^2 were analyzed by X-ray photoelectron spectroscopy (XPS) in order to determine the surface composition and the oxidation state of the metals. A UNI-SPECS UHV Analysis System equipped with Mg Kα ($h\nu$ = 1253.6 eV) radiation source was used. The high resolution photoemission spectra of Ti 2p, O 1s, Fe 2p, Ag 3d and Pd 3d were measured with a pass energy of 10 eV. The inelastic background of the peaks was subtracted using Shirley method. Charging effects were corrected using the C 1s hydrocarbon peak, fixed at a binding energy of 285.0 eV. The surface composition was determined with a precision of ±5% from the ratio of the relative areas of the peaks corrected by the atomic sensitivity factor of each element. The spectra were deconvoluted using Voigt profiles formed by the combination of Gaussian and Lorentz curves. The width at half height varied from 1.5 to 2.0 eV and the precision of the peaks position was ±0.1 eV.

In order to investigate the morphology of metal coated TiO_2 samples, field emission scanning electron microscopy (FEG-SEM) was used (JEOL 71500F) in the secondary electrons mode at 3 kV, including an energy dispersive X-ray spectroscopy (EDX) detector used for elemental mapping of the metal coated TiO_2 samples, operated at 15 kV.

2.2. Air disinfection photoreactor

For the construction of the photoreactor, wooden medium density fiber (MDF) plates of 15 mm thickness were used. The internal dimensions of the chamber were 42 cm × 10 cm × 4.5 cm, with an approximate volume of 1890 cm^3. Six glass plates (10×12 cm) coated with the catalyst were positioned at the lateral walls of the chamber (three at each side) together resulting in a 720 cm^2 photocatalyst area. Four 4 W blacklight lamps (UVA) (10.5 cm long and 1.5 cm of diameter) were positioned along the chamber as illustrated in Fig. 1. The central position of the lamps splited the air flow through the reactor in order to improve the contact of the microorganisms with the photocatalyst. Germicidal lamps (UVC) were only used for comparison in a blank experiment (absence of photocatalyst). An air compressor was used to nebulize the suspension of microorganisms into the chamber resulting in a 8000 $cm^3\,min^{-1}$ air flow rate and a 0.25 $cm^3\,min^{-1}$ microbial suspension flow rate, with a single pass through the reactor. Under these conditions, the air residence time was 14 s.

2.3. Microorganisms and experimental procedure of disinfection

The TiO_2 disinfection capacity was evaluated using three different bacteria as test microorganisms: *E. coli* (ATCC 25922), *Staphylococcus aureus* (ATCC 25923) and *Bacillus subtilis* (ATCC 6633). The cultures containing 10^8 colony forming units (CFU) mL^{-1} were preserved refrigerated and 24 h before the use they were dispersed in hydrated and sterilized brain heart infusion broth (Himedia) at 1:1000 ratio. Inactivation of the bacteria was studied in the following sequence of experiments:

(a) Control experiment in the dark and absence of catalyst (clean glass plates).
(b) Irradiation in the absence of catalyst (clean glass plates).
(c) Dark experiment with bare and metal modified TiO_2.
(d) Bare TiO_2 with irradiation.
(e) Metal coated TiO_2 with irradiation.

Firstly, each of the three suspensions of bacteria was nebulized into the reactor for three min for saturation of the reactor, which corresponds to 12 times de residence time in the reactor at the flow rate of 8 L min^{-1}. The purified air was then collected, also for 3 min, in a tube containing 10 mL sterile water. Three consecutive samples were collected for 3 min. The collected samples were then diluted 1:10 000 with sterile water and 1 mL of the diluted sample was applied to a 10 cm diameter Petri dish containing 25 mL agar