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Decomposition of ethylene in cold storage by plasma-assisted photocatalyst process with TiO_2/ACF-based photocatalyst prepared by gamma irradiation

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HIGHLIGHTS

- Modification of TiO_2/ACF-based photocatalyst films obtained by gamma radiolysis.
- EM, XRD and XPS techniques were used to characterize the photocatalyst films.
- Decomposition of ethylene by plasma-assisted photocatalyst (PAC) process.
- Higher the PAC process efficiencies of the films obtained than that of P25/ACF.
- Influence of the characterization of the photocatalysts on the efficiencies.

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ABSTRACT

A direct-current corona discharge plasma-assisted photocatalyst (PAC) system was developed for ethylene degradation in simulated cold-storage conditions. Titanium dioxide (TiO_2; P25 from Degussa) and TiO_2 treated by γ-irradiation (TiO_2^*), as well as TiO_2^* photocatalyst combined with Ag nanoparticles produced by reduction using γ-radiolysis [$Ag + TiO_2^*$], loaded on activated carbon fiber (ACF) were prepared. The changes in the crystallographic and physicochemical characteristics in the photocatalysts, induced by γ-irradiation and doping with Ag, were investigated using analytic techniques: electron microscopy (transmission electron microscope, scanning electron microscope and field emission scanning electron microscope), X-ray diffraction and X-ray photoelectron spectroscopy. We compared the performance of three photocatalyst films concerning ethylene decomposition, ozone formation and energy efficiency. The use of TiO_2^*/ACF and [$Ag + TiO_2^*$]/ACF as post plasma photocatalyst films led to a higher ethylene decomposition rate constant and a lower emission of the by-product ozone than for TiO_2/ACF. The PAC process with [$Ag + TiO_2^*$]/ACF had the highest performance of the three photocatalysts. The results could be explained by the impact of the crystallographic and physicochemical characteristics of photocatalysts, such as anatase and rutile relative amounts, crystallite dimension, hydroxyl radical groups and Ti^{3+} on the surface, and the Schottky barrier at the Ag-photocatalyst contact region.

1. Introduction

Ethylene (C_2H_4) gas is commonly present in the inside atmosphere of postharvest fruit and vegetable storage facilities. While C_2H_4 is invaluable due to its ability to initiate the ripening process in several types of fruit, it can also be very harmful to many fruits, vegetables, flowers, and plants by accelerating the aging process and decreasing shelf life. Even small amounts of C_2H_4 gas in the atmosphere in a storage facility can induce undesirable reactions in most fresh produce, such as development of senescence, bitter flavors, chlorophyll loss, disease susceptibility and physiological disorders. The major source of indoor C_2H_4 is postharvest horticultural products: these produce C_2H_4 within their tissues and release it into the surrounding atmosphere [1]. It is also a by-product of human activities, such as from the gaseous exhausts of internal combustion engines [2]. Conventional methods of controlling C_2H_4 (venting, potassium permanganate oxidation, adsorption onto brominated carbon, catalytic oxidizers and hypobaric storage) have not always proved to be economical or practical under cold-storage conditions [3]. Photocatalysis (PC) using titanium dioxide (TiO_2) as the catalyst is a promising alternative to the oxidation process used to degrade C_2H_4 in most conventional methods and has attracted considerable attention over the last 10 or more years

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[4,5]. Maneerat et al. [6] reported that C_2H_4 can by photocatalytically degraded using TiO_2 under high humidity at both room temperature and low temperature. The major advantage of this technology is the complete mineralization of undesirable organic contaminants in gas phases to CO_2 and H_2O, in addition to the non-toxic and inexpensive catalyst. However, recombination of photogenerated holes and electrons (H^+/e^-), low efficiency and photocatalyst deactivation still limit its widespread application [7,8]. Non-thermal plasma (NTP) are mixtures of heavy (molecules, atoms, free radicals and ions) and light (electrons and photons) species, generated by excitation of gas by electric discharges. NTP have high oxidation potentials and can directly initiate the oxidative reaction to decompose organic compounds. NTP technology has been investigated for the removal of C_2H_4 [2]. Its unique properties are quick response, system compactness and ease of operation. However, this technology alone has limitations such as incomplete oxidation, leading to formation of potentially toxic by-products [9–11].

The use of catalytic/photocatalytic films has been combined with NTP in attempts to overcome the limitations. Numerous studies have described advantages of using plasma-catalysis systems over plasma alone for degradation of low concentrations of pollutants, including enhanced conversion of pollutants, lower energy input giving improved energy efficiency for the plasma process, higher CO_2 selectivity and extended catalyst lifetime [12–14]. There are two types of arrangements for these plasma-catalysis systems: one- and two-stage configurations. In the one-stage configuration, the catalyst is placed directly in the discharge region allowing the plasma to directly activate the catalyst (IPC). In the two-stage configuration, the catalyst is placed downstream from the plasma reactor (referred to as plasma-assisted catalyst, PAC). NTP produces ozone (O_3) in the presence of oxygen, and this may provide a primary mechanism to reduce C_2H_4 in fruit, vegetable and floricultural environments, or conversely, O_3 can alter the quality, sensory attributes and acceptability of storage products [15,16]. An appropriate catalyst located after the discharge zone can increase the reaction time due to adsorption of intermediates and contaminants on the catalyst surface, resulting in a shift towards total oxidation, and a preferential consumption of undesired O_3 by surface reactions on the catalyst. Therefore, the PAC process has inherent desirable qualities for degrading C_2H_4. Increased adsorption and catalytic activity of photocatalysts would be very important for improving performance of the PAC process.

Activated carbon fiber (ACF) is a suitable carrier of TiO_2 as it has excellent characteristics of adsorption, conductivity and catalysis [17]. The enhancement of gas-phase toluene condensation as a result of the combined adsorption of ACF with TiO_2 has been reported [18,19]. Gamma radiation, also known as gamma rays (γ-rays), is electromagnetic radiation of high frequency and therefore high energy. The γ-irradiation can induce disruption and dislodgement of electrons and sometimes atoms within a crystal to create defects in the crystal structure. The transfers of generated carriers in a photocatalytic reaction are related to the surface properties of the TiO_2 photocatalyst, e.g. surface defects and surface chemical species [20]. In this respect, an understanding of the changes in catalytic activities that occur with treatment of TiO_2 with γ-irradiation is of a practical importance to achieve a high internal efficiency. Silver (Ag) has been observed to play an important role in increasing the photocatalytic stability of TiO_2 [21] and is known as an O_3-degrading catalyst – with the method of preparation playing a key role in its successful synthesis as a catalyst. Although there are many chemical routes available for production of shape- or size-controlled Ag nanoparticles, it is still desirable to design a rapid and large-scale synthesis for nanocrystals. Radiation-induced synthesis, which is generally fast, convenient and energy efficient, is considered one of the most promising strategies for preparation of Ag nanoparticles [22]. The PAC process for C_2H_4 degradation has been carried out using Pt/TiO_2 [23]. However, the PAC processing of C_2H_4 in a cold-storage environment using either an ACF-supported TiO_2^* photocatalyst (labeled TiO_2^*/ACF in the present study) or an ACF-supported TiO_2^* photocatalyst combined with Ag nanoparticle produced by reduction using γ-radiolysis (labeled $[Ag + TiO_2^*]$/ACF in the present study) as catalysts has rarely been reported.

In the present work, we studied the decomposition of C_2H_4 in simulated cold-storage conditions using a PAC reactor in a direct-current corona discharge plasma type with TiO_2 (Degussa-P25)/ACF, TiO_2^*/ACF and $[Ag + TiO_2^*]$/ACF as photocatalyst films. We compared the performance of three photocatalyst films in a PAC system concerning C_2H_4 decomposition, O_3 formation and energy efficiency. Results were explained by the impact of the crystallographic characteristics (e.g. anatase and rutile relative amounts and their crystallite dimension), analyzed by X-ray diffraction (XRD) pattern – and physicochemical characteristics, analyzed by X-ray photoelectron spectroscopy (XPS) – on the performance of the PAC system with the photocatalyst films. The aim of this study was to demonstrate the effectiveness of the γ-irradiation technique in facilitating catalytic reactions on the post plasma catalysts and to make the PAC process more attractive as a method of controlling C_2H_4 in cold-storage environments.

2. Materials and methods

2.1. Material and γ-ray source

A commercial form of TiO_2 (Aeroxide P25 from Degussa; primary size ~25–30 nm; BET area, ca. 50 m^2/g; agglomerate size ~100 nm) was used and labeled as TiO_2 in the present study. A viscose rayon-based ACF (STF1300, Sutong Carbon Fibers Co. Ltd., Jiangsu Province, PR China) in the form of a 3-mm thick felt was the supporting substrate. Ag nanoparticles were prepared from silver nitrate ($AgNO_3$). In the γ-irradiation process, polyvinyl pyrrolidone (PVP) K30 (MW = 50 000) was used as the stabilizer. Excess radicals were scavenged using 2-propanol (IPA). These chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. Distilled water was used throughout the experiment.

The ^{60}Co γ-ray source (Nordion International Co. Ltd., Ontario, Canada) was located at the Guangdong Center of Irradiation Technology, South China Agriculture University. The source strength was approximately 4×10^6 Ci and was applied at a dose rate of ~1 kGy/h at room temperature.

2.2. Post plasma photocatalyst films preparation and characterization

In the preparation of TiO_2^* (P25 treated with γ-irradiation), a 200-mL aqueous suspension containing 5 g of TiO_2 and 2.4% PVP by weight was agitated for 12 h using a magnetic stirrer. The quartz container was then sealed and irradiated with a total dose of 20 kGy at room temperature. Colloidal Ag nanoparticles were prepared as follows: first, an aqueous solution of 0.0012 M $AgNO_3$, 0.0013 M 2-IPA and a 2.4% PVP by weight was mixed for 30 min using a magnetic stirrer. Prior to irradiation, the solution was deaerated by bubbling a stream of pure nitrogen through it and was then sealed in a quartz container. Then the aqueous solution was irradiated with 40-kGy doses. The coating solutions were prepared by mixing the aqueous solutions described above in suitable proportions to give final molar ratios of Ag to Ti of 0% and 1%, respectively. TiO_2^*/ACF and $[Ag + TiO_2^*]$/ACF were prepared by dip-coating rectangular ACF (40 mm × 40 mm) in the coating solution for 1 min at a withdrawal speed of 0.42 cm/s. After coating, the resulting materials were dried at 100 °C for 1 h, and then