Building and Environment 142 (2018) 379–387

Contents lists available at ScienceDirect

Building and Environment

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

Performance of an innovative VUV-PCO purifier with nanoporous TiO_2 film for simultaneous elimination of VOCs and by-product ozone in indoor air

Tongzhou Xu[a,b,1], Hong Zheng[a,*,2], Pengyi Zhang[b,**,3]

[a] Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing, 100083, China

[b] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, China

ARTICLE INFO

Keywords:
VUV-PCO
Air purifier
Nanoporous TiO_2 films
VOCs
Ozone

ABSTRACT

An innovative vacuum ultraviolet photocatalytic oxidation (VUV-PCO) air purifier, consisting of a photocatalytic unit bearing nanoporous TiO_2 film, an ozone removal unit bearing Mn-Fe catalyst and a radial fan, was designed and constructed. The performance of the VUV-PCO air purifier in simultaneous elimination of VOCs and O_3 by-product was, for the first time, evaluated in a sealed actual room. The evaluation was conducted in both intermittent on/off and continuous operations. The results illustrated that the air purifier had high efficiency in removing formaldehyde and moderate efficiency in removing benzene, toluene, ofm-xylene, ortho-xylene, pentanal, octanal and nonanal, which were released from particleboard into the sealed room. During the removal of formaldehyde decomposition and TVOC in intermittent three-time on/off operation, the air purifier exhibited good stability. During the operation without heating, the air purifier had high formaldehyde and TVOC removal efficiencies, reaching values of about 48.00% and 78.71%, respectively after 90 min. During the continuous operation, the air purifier was able to continuously and effectively remove formaldehyde, benzene homologues, aldehyde and ketone compounds, while the ozone removal unit was able to effectively eliminate ozone generated during VUV photocatalysis. The removal of TVOC by 38.25% was reached after 240 min. In addition, heating the ozone removal unit was found to not only accelerate the release of VOCs from particleboard, but also promote the decomposition of ozone. The ozone removal unit operated with heating was able to reduce ozone content from 250 to 75 ppb.

1. Introduction

Volatile organic compounds (VOCs), such as formaldehyde, acetone and benzene homologues, are toxic air pollutants that can generally be found in indoor environments [1–6]. Long-term exposure to VOCs can greatly increase the risks of allergy, respiratory illness or even cancer [7,8]. Because people typically spend more than 80% of their time indoors, it is therefore necessary to effectively remove indoor VOCs so that the indoor air quality (IAQ) is improved and considered safe [9–11].

Air purifier can effectively remove VOCs and, in turn, improve IAQ by many measures; thus, it can be considered an indispensable means of controlling indoor air pollution. Moreover, unlike ventilation, air purifier can reduce the exposure of indoor air to outdoor air pollutants [12,13]. Adsorption filtration technology, which employs granular activated carbons [14] and zeolites [15] as adsorbents, has been widely studied because of its promising performance in the removal of VOCs. However, due to its disadvantages, such as generally large pressure drop and multiple regeneration of adsorbent, the applications of adsorption air purifiers are obstructed [16,17].

In recent years, an alternative method, heterogeneous photocatalytic oxidation (PCO), which has numerous advantages, such as simultaneous treatment of mixtures of diverse pollutants, complete reaction, ease of operation and maintenance, etc., has been considered as an energy efficient method that can improve IAQ by photocatalytic degradation of VOCs [18–20]. Moreover, vacuum ultraviolet (VUV) photocatalysis, which has higher removal efficiency than UV and visible light, has attracted wide attention for its applications in air treatment

* Corresponding author.
** Corresponding author.
E-mail addresses: tongzhouxurshdqch@163.com (T. Xu), zhengh@cugb.edu.cn (H. Zheng), zpy@tsinghua.edu.cn (P. Zhang).
[1] Full postal address: School of Materials Science and Technology, China University of Geosciences, Beijing 100083, P. R. China.
[2] Full postal address: School of Materials Science and Technology, China University of Geosciences, Beijing 100083, P. R. China.
[3] Full postal address: School of Environment, Tsinghua University, Beijing 100084, P. R. China.

https://doi.org/10.1016/j.buildenv.2018.06.047
Received 12 April 2018; Received in revised form 5 June 2018; Accepted 20 June 2018
Available online 21 June 2018
0360-1323/

[21]. VUV light can break most chemical bonds and generate strong oxidants, such as reactive oxygen species, hydroxyl radicals and ozone [21–23]. Nevertheless, the use of VUV light is limited because it generates toxic ozone [24]. Ozone is known to cause adverse health effects, thus ozone generated during VUV photocatalysis should be eliminated [22]. Furthermore, the performance of most air purifiers available in the market is evaluated under ideal reaction conditions, e.g. low volumetric air flow rates, tested only with one or a few VOCs, etc [25–29]. Therefore, the test results can be questionable, unreflecting air purifier performance in the removal of VOCs in actual room. Besides, the photocatalytic activity of catalyst should be further improved to meet the changing environments. Thus, it can be of theoretical and practical significances that the photocatalytic air purifier is achieved with small, practical and low-cost technology, and its performance in VOCs removal is reflected in actual environment.

Among different photocatalysts, titanium dioxide (TiO_2) has been proven to be the most preferred material owing to its high photocatalytic activity, long-term stability, non-toxicity and relatively low price [30,31]. Kim et al. reported that due to simultaneous reactions initiated by hydroxyl radicals and the enhancement of photocatalysis by ozone, the toluene removal rate of TiO_2/VUV photocatalysis was significantly higher than that of single VUV photocatalysis [32]. Anatase TiO_2 with dominant {001} facets and nanoporous TiO_2 materials with large surface areas have many promising applications in environmental and energy fields [33,34]. In our previous study, in which the degradation of typical organic contaminants of low concentration was conducted, TiO_2 films with exposed {001} facets and uniform nanopores in the crystal facets were found to exhibit superior UV [35] and VUV [36] photocatalytic activities compared with non-porous TiO_2 films and Pt-TiO_2 films. Consequently, employing TiO_2 films with exposed {001} facets and uniform nanopores to construct a VUV-PCO air purifier with improved air purification efficiency is promising.

Catalytic decomposition is most widely used for eliminating ozone because of its many advantages, including mild reaction conditions, high efficiency and low cost [37]. Numerous catalysts, including transition metal oxides [38–40], activated carbon [41,42] and noble metals [43], have been investigated. Among these catalysts, manganese oxides (MnO_x) have good catalytic performance in ozone decomposition. However, their catalytic activity tends to decrease with increasing amount of water vapor and prolonged reaction time [44]. Recently, Fe-modified manganese oxide with high content of oxygen vacancies has been demonstrated to be an efficient catalyst for the destruction of airborne ozone [37].

In this study, we developed a VUV-PCO air purifier, which can simultaneously remove VOCs and degrade residual ozone. The air purifier is composed of nanoporous TiO_2 film in photocatalytic unit, Mn-Fe catalyst in ozone removal unit, and radial fan. The air purifier performance in the removal of various VOCs, for the first time, in an actual room, was determined. The ability of VUV-PCO air purifier to remove VOCs (including formaldehyde, benzene homologues, aldehyde and ketone compounds) released from commercial particleboard was examined in an actual room. In addition, the effects of heating ozone removal unit on the release and the removal of VOCs, the regeneration of Mn-Fe catalyst, and the degradation of ozone were also investigated.

2. Experimental

2.1. Catalyst preparation

The fabrication of nanoporous TiO_2 film with exposed {001} facets has been described in our previously published report [35]. In brief, after Ti sheet (99.5% in purity) was pretreated by etching in boiled 10% oxalic acid solution, it was immediately dipped in 400 mL of 0.03 M HF aqueous solution containing isopropanol (the volume ratio of water/isopropanol was 2.2:1), and subsequently subjected to hydrothermal treatment at 180 °C for 3 h in a Teflon lined autoclave with total volume of 500 mL. After that, the treated sheet was rinsed gently with deionized water, air-dried at room temperature and finally subjected to calcinations at 600 °C for 2 h.

Mn-Fe catalyst was hydrothermally synthesized following the method reported by Jia et al. [37]. Briefly, $Mn(CH_3COO)_2{\cdot}4H_2O$ was mixed with $Fe(NO_3)_3$ at Mn/Fe molar ratio of 2:1 and was then added dropwise into a continuously stirred $KMnO_4$ solution containing cetyltrimethyl ammonium bromide (CTAB). After that, the slurry was placed in a Teflon lined autoclave, wherein it was hydrothermally treated at 140 °C for 2 h. After the slurry was cooled down to room temperature, the solid was isolated (by filtration), washed and finally dried at 85 °C.

Mn-Fe catalyst-coated aluminum sheet was prepared as follows. Firstly, aluminum sheet was pretreated by washing with ethanol to remove oil and then etched in $KMnO_4$ solution (60 g/L) containing 4% ammonia at 40 °C for 2 h. After that, the pretreated aluminum sheet was dipped three times in a Mn-Fe catalyst aqueous suspension containing acrylic acid (the mass ratio of water/Mn-Fe catalyst/acrylic acid was 15:2:1). Finally, the aluminum sheet was subjected to calcinations at 100 °C for 1 h.

2.2. Purifier design

The VUV-PCO air purifier was designed to consist of a photocatalytic unit equipped with nanoporous TiO_2 film, ozone removal unit equipped with Mn-Fe catalyst and a radial fan. The schematic diagram of the VUV-PCO air purifier is shown in Fig. 1A.

The photocatalytic unit, which has internal dimensions of 160 mm × 160 mm × 271 mm (length × width × height), consists of nine VUV lamps and nanoporous TiO_2 films with exposed {001} facets. The photocatalytic unit is divided into nine sections; each is separated by nanoporous TiO_2 films (Fig. 1B), which are supported by stainless steel brackets. The center of each section is placed with a 10 W low-pressure mercury lamp (VUV; main emission wavelength: 254 nm; minor emission wavelength: 185 nm), which is used as the light source. The distance between the lamp and the catalyst is 1.65 cm, and the total area of catalyst irradiated by VUV light is 4082 cm^2.

The ozone removal unit (Fig. 1C; dimensions: length = 191 mm, width = 165 mm, height = 130 mm), which is placed above the photocatalytic unit, is composed of Mn-Fe catalyst-coated aluminum sheet (dimensions: length = 144 mm, width = 100 mm, thickness = 2 mm), heating rods and temperature sensor (0–100 °C). Ozone generated by VUV lamps in the photocatalytic unit was directed to the ozone removal unit for degradation. Temperature of heating rods was controlled by temperature sensor and maintained at 80 °C for the regeneration of Mn-Fe catalyst as well as for the facilitation of ozone degradation.

The system is also equipped with a radial fan mounted at the top of air purifier. The fan controls air speed, providing air flow rate of up to 96 m^3/h. After air contaminated with VOCs enters into the air purifier at the bottom of the air purifier, it successively passes through photocatalytic unit, ozone removal unit, radial fan and then exits at the top of the air purifier.

2.3. Performance evaluation of purifier for simultaneous VOCs removal and ozone degradation

The air purifier performance in the removal of VOCs were examined in a large actual room with a volume of 11.29 m^3, a relative humidity range of 55%–65% and at a temperature of 30 °C (Fig.S1, Supplementary Information). Commercially available particleboard (dimensions: length = 600 mm, width = 600 mm, thickness = 6 mm) was used as the source of VOCs. The particleboards were dispersed on the ground of the room, where the VUV-PCO air purifier was placed in the center. The air purifier was supported by four stand bars (each with a 2-cm height) to provide space from the ground that is sufficient to allow VOCs to flow into the bottom of the air purifier. Twenty hours after the room was sealed, the VUV-PCO air purifier was turned on. Air sample was