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Mitigation of harmful indoor organic vapors using plug-flow unit coated with 2D g-C_3N_4 and metallic Cu dual-incorporated 1D titania heterostructure

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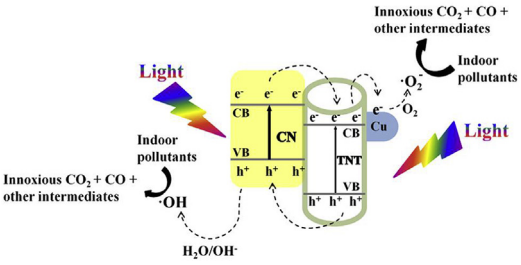
HIGHLIGHTS

- g-C_3N_4/Cu/1D TiO_2 composite had enhanced efficiency for indoor pollutant mitigation.
- Enhanced mitigation efficiency was ascribed to increased charge separation efficiency.
- Optimum g–C_3N_4–to-Cu/TNT percentage was determined for the synthesis of the composite.
- Operating parameters should be considered for better pollutant mitigation efficiency.
- Byproducts formed during mitigation process seem not to cause adverse health effect.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, a plug-flow reactor coated with one-dimensional (1D) TiO_2 nanotube (TNT) heterostructures incorporated with g-C_3N_4 (CN) and metallic Cu (CN/Cu/TNT) nanocomposite and irradiated by a daylight lamp was newly applied for the mitigation of harmful indoor organic vapors. The CN/Cu/TNT catalyst showed high mitigation efficiency for all target pollutants, followed by Cu-incorporated TNT (Cu/TNT), CN-incorporated TNT (CN/TNT), TNT, and TiO_2, in that order. The order of their photocatalytic activities agrees with that of the electron–hole separation rates determined from their photoluminescence emission spectra. The mitigation efficiency of the CN/Cu/TNT catalyst increased as the CN-to-Cu/TNT percentage was increased from 1% to 10%, but subsequently decreased as the CN-to-Cu/TNT percentage increased to 20%. The mitigation efficiencies of the CN/Cu/TNT catalyst decreased with increasing relative humidity, feed pollutant concentrations, and airstream flow rates. However, in most cases, the reaction rates of the target compounds increased when the feed concentration was increased from 1 to 5 ppm. The mineralization rates of all target pollutants were lower than the corresponding photocatalytic mitigation rates, which could be ascribed to the production of CO and organic intermediates observed during the photocatalysis of the target pollutants. Nevertheless, the intermediates formed during the photocatalytic mitigation process would not cause significant adverse health effects to building occupants, because their concentrations were far below their exposure or threshold limit values. A probable

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mechanism for the photocatalytic mitigation of the organic vapors by the CN/Cu/TNT catalyst under daylight illumination was also proposed.

1. Introduction

Air quality inside residential and commercial buildings is an important environmental issue for building occupants, since it is strongly related with their health and well-being (USEPA). Organic vapors are of particular concern because of their ubiquity in building interiors and their harmful health effects. Atmospheric organic vapors, which are emitted from a range of industrial activities, motor vehicles, and other combustion processes, can infiltrate into buildings and cause indoor air pollution (Kwon et al., 2016). These compounds also originate from a diverse array of indoor sources, including building finishing materials, furniture, household products, and cooking activities, further deteriorating indoor air quality (Bari et al., 2015). Inhalation exposure to organic vapors is closely associated with a variety of harmful health outcomes, such as short-term sick building syndrome symptoms and chronic carcinogenic and non-carcinogenic diseases (Ramírez et al., 2012; Doherty et al., 2017). These negative properties of organic vapors necessitate the development of tools to minimize indoor pollution levels.

The utilization of air cleaning devices was recommended as a control strategy for indoor air quality improvement by the (USEPA). Conventionally, indoor air cleaning devices, with adsorbents such as granular activated carbon and fibrous activated carbon, have been applied for the purification of organic vapors in indoor environments (USEPA, 2009; Popescu et al., 2013; Yoo et al., 2015). However, the use of adsorption methods has major drawbacks in that the contaminants are only transferred to a solid phase, and the adsorbent saturated with contaminants becomes noxious waste. To override this drawback, advanced oxidation techniques using metal oxide semiconductor photocatalysts, including TiO_2 and ZnO, have been applied for the treatment of a diverse array of airborne contaminants (Paz, 2010; Stucchi et al., 2018; Pozan and Kambur, 2014). However, these metal oxide semiconductors have limited quantum yields and visible light harvest capacity. Thus, a large number of modified metal oxide semiconductors have been developed for environmental remediation during the last a few decades (Etacheri et al., 2015; Lee and Jo, 2016; Alfieri et al., 2017). Especially, graphitic carbon nitride (g-C_3N_4) has received substantial attention as an excellent supporting nanomaterial for metal oxide semiconductors primarily because of its high adsorption capacity, retardation of charge carrier recombination, and harvest efficiency of visible light by serving as a sensitizer (Leary and Westwood, 2011; Ng et al., 2012). Several research groups have reported the improved photocatalytic performance of g-C_3N_4 (CN)-supported TiO_2 photocatalysts in degrading several environmental contaminants such as ciprofloxacin, clofibric acid, phenol, methyl orange, Rhodamine B, and N_2O (Chen et al., 2017; Li et al., 2015a, 2017; Jiang et al., 2016; Reli et al., 2016). The enhanced photocatalytic activity of CN-supported TiO_2 photocatalysts was primarily attributed to the fast charge transfer at the junction of CN and TiO_2. However, aforementioned studies investigated the photocatalytic degradation of water pollutants or inorganic gas.

Modification of metal oxide semiconductors with metals like Cu, Fe, Ni, and Co could also enhance photocatalytic activities by reducing charge carrier recombination due to the extraction of produced electrons and by enhancing the visible light absorption efficiency (Pelaez et al., 2012; Chen et al., 2015; Kerkez-Kuyumcu et al., 2015; Wang et al., 2017; Moradi et al., 2018). According to the Chen et al.'s study (Chen et al., 2015), the photocatalytic activity of Cu-modified TiO_2 for the photocatalytic degradation of aqueous perfluorooctanoic acid was higher than that of unmodified TiO_2. Kerkez-Kuyumcu et al. (2015) also reported that the TiO_2 catalysts modified with Cu, Ni, or Co displayed enhanced photocatalytic activities for the degradation of methylene blue under visible light illumination compared with that of pure TiO_2. However, several metal dopants may serve as recombination centers for charge carriers, which reduces quantum efficiencies of metal-modified metal oxide semiconductors (Pelaez et al., 2012). Moreover, one-dimensional (1D) TiO_2 nanotube (TNT) structures show high surface-area-to-volume ratios and charge carrier separation capacity compared to zero-dimensional spherical TiO_2 (Nakata and Fujishima, 2012; Ge et al., 2016). Accordingly, dual incorporation of two-dimensional (2D) CN and metals into 1D TNT architectures probably improve the photocatalytic activity further for the mitigation of environmental pollutants.

Herein, a plug-flow reactor coated with 1D TNT heterostructures incorporated with 2D CN and metallic Cu (CN/Cu/TNT) nanocomposite, irradiated by a daylight lamp, was applied for the mitigation of harmful indoor organic vapors. Cu was used as a metallic co-catalyst because of its lower cost than noble metals. The photocatalytic efficiency was tested using a plug-flow unit because it is facilely modulated with other units of indoor air cleaning devices. For comparison, four reference photocatalysts (TiO_2 particles, TNT, CN/TNT, and Cu/TNT) were examined for the mitigation of target compounds under fixed operational conditions. In addition, the effects of three important operational parameters (feed concentration of organic vapors, humidity, and airstream flow) on pollutant mitigation were evaluated using a representative CN/Cu/TNT nanocomposite. Monocyclic aromatic organic vapors (benzene, toluene, ethyl benzene, and *m*-xylene) were used as model organic vapors because of their toxicity and high concentrations in the interiors of residential and commercial buildings (Kwon et al., 2016; Bari et al., 2015; Ramírez et al., 2012; Doherty et al., 2017).

2. Experimental

2.1. Photocatalyst preparation and characterization

For the fabrication of TNT, P25 TiO_2 particles (0.7 g, Sanghyun Industry, Korea) were mixed with distilled water (50 mL) with stirring and NaOH (15 g, Alfa Aesar) was then added to the mixture. This solution was placed in an autoclave vessel and heated at 130 °C for 60 h. After cooling to room temperature, the resultant slurry was centrifuged and acid-treated with 0.1 M HCl (70 mL, Alfa Aesar), followed by washing with water. The cleaned precipitate was filtered, dried at 85 °C for 10 h, and then heated at 370 °C for 3 h to obtain the final TNT sample.

Cu/TNT was prepared by impregnating Cu into the as-synthesized TNT powder. In brief, copper(II) nitrate trihydrate (38 mg, 99%, Sigma-Aldrich) was added to deionized water (10 mL) with stirring for 1 h and then TNT powder (1 g) was added and stirred for 15 h. This mixture was aged for 10 h, dried at 80 °C for 12 h, and heated at 370 °C for 3 h. The calcined product was cooled