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Full Length Article

Application of recycled lanthanum-doped TiO_2 immobilized on commercial air filter for visible-light photocatalytic degradation of acetone and NO

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ABSTRACT

Herein, La-doped TiO_2 photocatalyst was synthesized by utilizing the recycled lanthanum from the waste fluorescent powder, and then was firstly immobilized on a commercial ceramic filter with porous structure and high surface area. Immobilized La-doped TiO_2 (La-TiO_2) was applied for photocatalytic degradation of acetone and NO at the ppb level under visible light region. It was found that 0.5 wt% La doping into TiO_2 exhibited an excellent photocatalytic performance. The photocatalytic removal efficiency of acetone and NO under visible light could reach up to 38% and 98% respectively, which were much higher than that of pure TiO_2 (28% and 65%, respectively). Moreover, the results of various physicochemical characterization showed that La-TiO_2 sol-gel could be uniformly immobilized on the ceramic filter by impregnation method and followed by a low-temperature calcination treatment process. The three-dimensional porous structure of ceramic air filter resulted in more adsorption sites and reaction contact between pollution gas and photocatalyst surface, which is superior to the powdered TiO_2 catalyst on substrates or thin film deposited on glasses. In order to the further application, the effect of relative humidity on photocatalytic performance was discussed. This work will provide a new perspective for promoting large-scale environmental application of immobilized photocatalysts.

1. Introduction

Modern people have been exposed to more risky indoor air pollution because of prolonged indoor inhabitation (more than 80% of time), which may cause a colossus extent of health problems and even be fatal [1]. Generally, these risky substances include nitrogen oxides (NOx), carbon oxides (CO and CO_2), volatile organic compounds (VOCs), and particulates, which emit from construction materials, human activities indoors (e.g., smoking, painting work, furniture, hygiene products, air fresheners printers or burning coal) and other pollutants from outdoors [2,3]. During the past years, considerable efforts have devoted to developing the remediation techniques such as adsorption [4,5], bio-filtration [6], biological treatment [7] and ozonation [8] et al. However, these conventional methods are expensive and inappropriate for a low-concentration pollutant of part-per-billion (ppb) level, which is a typical concentration for indoor air quality (IAQ) [9,10].

Photocatalytic oxidation (PCO) as a green technology has attracted more and more attention in view of its merits of utilizing natural sunlight or artificial indoor light to eliminate indoor air pollutants of low concentration at ambient condition, which provides an environment-friendly alternative to conventional approaches [11–13]. Titania (TiO_2), as a widely commercial photocatalyst, has attracted extensive attention in the past two decades due to its features of long-term photostability, strong PCO activity, non-toxicity and low cost [14,15]. Nonetheless, there are still two key aspects limiting the further practical environmental application for TiO_2. The first challenge is that TiO_2 can only harvest UV light with a wavelength < 380 nm because of its wide bandgap of 3.0–3.2 eV [16,17]. In order to take full advantage of 95% visible light from solar light, numerous strategies to broaden the spectral absorption range of TiO_2 have been proposed including doping, modification, co-catalysts, surface plasmon resonance (SPR) and other heterojunctions [18–22]. The second challenge is the immobilization of a photocatalyst on a proper support. Without the immobilization, the powdery TiO_2 is inappropriate for air purification because particles would be blown away and may cause respiratory problem [23]. Therefore, a variety of studies have immobilized TiO_2 particles on air purification materials which have the potential to commercialize applications, such as glass, stainless steel, porous subtract, fiber of active carbon and other fibers [24–33].

In this study, La-doped TiO_2 photocatalyst was synthesized through a facile sol-gel method by utilizing the recycled lanthanum from the waste fluorescent powder. And a commercial three-dimensional (3D)

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porous ceramic filter as the coating substrate was employed to immobilize the photocatalyst by a low-temperature calcination treatment process. For the following four reasons, porous ceramic filter was adopted to serve as substrate rather than flat films: (1) Due to the ceramic filter with porous structure, it is conducive to hydrodynamic properties for target pollutants (acetone and NO) passing. (2) It results in the low-pressure drop required by such filters because of a high bed porosity of structure [31]. (3) The mesoporous structure with the higher specific surface area can exhibit a higher photocatalytic capacity, because it provides abundant active sites. (4) This 3D porous ceramic filter as building materials, which has the resistance to high temperature and good mechanical properties, can be used as a building material for road side or tunnel wall material. Thus, it can be further conducted a commercial applications for the degradation of pollutant in enclosed or the semi-enclosed space, for instance parking lot.

In order to address the limitation of UV-light-driven TiO_2, La-doped TiO_2 photocatalyst mediated by rare earth metals (REMs) was synthesized in this study by utilizing the recycled lanthanum from the waste fluorescent powder. This method offered a facile approach to extend the light absorption range and suppress the recombination of electron-hole pairs [34]. According to previous researches, the doping of rare earth metals (REMs) showed that REMs having incompletely occupied 4*f* and empty 5*d* orbitals often act as promote catalysis. Doping TiO_2 with REMs can enhance the light absorption by tuning the phase structure, surface area and morphology [14,35]. Then, La-doped TiO_2 (La-TiO_2) immobilized on 3D porous ceramic filter was applied for photocatalytic degradation of acetone and NO at the ppb level. The results showed that 0.5 wt% La doping into TiO_2 exhibited an excellent photocatalytic performance under visible light region. The photocatalytic removal efficiency of acetone and NO under visible light could reach up to 38% and 98% respectively, which were much higher than that of pure TiO_2 (28% and 65%, respectively). The three-dimensional porous structure of ceramic air filter resulted in more adsorption sites and reaction contact between pollution gas and photocatalyst surface, which is superior to the powdered TiO_2 catalyst on substrates or thin film deposited on glasses. Moreover, the effect of relative humidity on photocatalytic performance was discussed. This work will provide a new perspective for promoting large-scale environmental application of immobilized photocatalysts.

2. Methods

2.1. Chemicals

The following chemicals used in this study were of analytical grade and were used directly without purification. All aqueous solutions were prepared using de-ionized water from Lab Water Purification Systems (ELGA LabWater, UK). The following chemicals were used as purchase: hydrochloric acid (35%) from ECHO Chemical CO.,LTD.; TBOT (97%) from Sigma-Aldrich; commercial TiO_2 Nano powders were obtained from Evonik Degussa (Aeroxide® P25); lanthanum extract (200 mg/L) was extracted by the waste fluorescent powder form Chung Tai Resource Technology CO.,LTD.; absolute ethanol from Nihon Pharmaceutical Industry CO.,LTD.; acetone gas (100 ppm) and nitric oxide gas(100 ppm) from Min-Yang Gas CO.,LTD; and ceramic filter (150 mm L × 150 mm W × 25 mm H) with 20 pores ceramic inch (ppi) from Ching-Huei ceramics CO.,LTD.

2.2. Preparation of photocatalytic ceramic air filter

Ceramic air filter was used as the substrate for immobilizing photocatalysts. Firstly, a series of La-doped TiO_2 sol was prepared by using lanthanum extract as the lanthanum source. The extraction method was based on the literature [36,37]. To investigate the effects of mass ratio of La on the photocatalytic performance, La/TiO_2 samples with various mass ratio of La^{3+} (wt% = 0, 0.25, 0.5 and 1.0) were synthesized in a typical process. Precursor solution for the titania sol reaction was prepared by the following method. In brief, 50 mL ethanol and 10 mL TBOT, were mixed simultaneously. Then, the sol-gel catalytic reagent, which was composed of 4.5 mL deionized water and different mass lanthanum extract containing 5 M hydrochloric acid, was added dropwise to the reaction precursors with vigorous stirring. And the transparent gel was gradually generated within a period of time. After reacting for two hours, the sol-gel solution was seal and kept in an oven, aging at 60 °C for 12 h. Secondly, the resulting gel-sol solution was evenly dip-coated onto the ceramic filter by impregnation method, and dried in the oven at 40 °C for 24 h. Finally, the porous ceramic air filter was calcined in the high temperature furnace at 400 °C for 2 h. After calcination, the recycled lanthanum-doped TiO_2 immobilized on commercial air filter was obtained. The coating mass of catalyst was kept 2 g in each experiment. The photographs of photocatalytic air filter and lanthanum-doped Titania sol were shown in Fig. S1 (Supplemental Information).

2.3. Characterization

The XRD characteristic of crystalline phase of as-obtained coating samples were determined by using an X-ray powder diffractometer (XRD; D8-ADVANCE-ECO, Bruker, the United States) with a Cu Kα radiation source (λ = 1.5419 Å) at a scan step size of 0.026° in the 2θ range of 20°–80°. Anatase-rutile fractions were calculated by taking into account the relative diffraction peak intensities using the following equation [38]:

$$\left(F_A(Anatasefractions) = \frac{0.79I_A}{0.79I_A + I_R}\right) \tag{1}$$

The optical properties of the coating catalysts at 350–800 nm was obtained using a UV–Vis Spectrophotometer system (UV–Vis; LAMBDA 650, Perkin Elmer Inc., the United States) with a film sphere diffuse reflectance accessory. Fourier transform infrared (FT-IR) spectra data was recorded on an FT/IR-6500 spectrometer (JASCO, Japan) with KBr as the diluent. Raman with the excitation wavelength at 532 nm and photoluminescence spectra with the excitation wavelength at 325 nm were also obtained to investigate the optical properties of the resulting samples via Micro-Raman & Micro-PL (ULVAC)/ Jobin Yvon/Labram HR.

The X-Ray Photoelectron Spectroscopy characteristic was performed by using a photoelectron spectrometer (XPS; K-Alpha, Thermo Fisher Scientific, the United States) with the sample being illuminated by monochromatic Al Kα X-ray source (hν = 1486.7 eV) under a pressure of 10^{-9} Torr. The morphology of the coating sample was characterized by scanning electron microscope (SEM, S-3000N SEM with Energy Dispersive Spectroscopy (EDS), Hitachi High-Technologies Corporation. Japan), and EDS mapping was recorded at the same time.

The adhesion of as-coated photocatalyst layers on porous filter was tested by sonication. Namely, the coated filter was placed in a beaker filled with de-ionized water and then treated with an ultrasonic bath (40 kHz, 500 W, UC-500, Enshine Scientific Corporation., Taiwan) [27]. After a certain time of sonication (0, 30, 60, 90, 120, 150, and 180 min), the layer was dried (60 °C, 4 h) and weighed to evaluate the mass loss during the test.

2.4. Photocatalytic activity assessment

Setup of air photocatalytic system Photocatalytic activities of the immobilized photocatalyst was investigated by the degradation of simulated gas acetone (1000 ppb) and nitric oxide (500 ppb) in a continuous flow reactor at ambient temperature under visible light. The simulated gas (acetone and nitric oxide) at an initial concentration of 100 ppm were diluted to 1000 and 500 ppb with an air stream supplied by a zero air generator (Model 1001, Sabio Instruments LLC,