Chemosphere 182 (2017) 174–182

Contents lists available at ScienceDirect

Chemosphere

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

Degradation of gaseous formaldehyde via visible light photocatalysis using multi-element doped titania nanoparticles

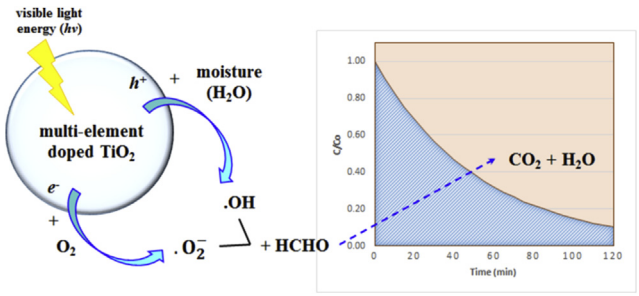
Maricris T. Laciste [a, b], Mark Daniel G. de Luna [c], Nolan C. Tolosa [d], Ming-Chun Lu [e, *]

[a] Environmental Engineering Unit, College of Engineering, University of the Philippines, Diliman, Quezon City, 1101, Philippines
[b] Research and Development Division, Environmental Management Bureau, Department of Environment and Natural Resources, Quezon City, 1101, Philippines
[c] Department of Chemical Engineering, University of the Philippines, Diliman, Quezon City, 1101, Philippines
[d] Office for Research Promotion and Coordination, Malayan Colleges Laguna, Cabuyao, Laguna, 4025, Philippines
[e] Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, 71710, Taiwan

HIGHLIGHTS

- Photoactivity of multi-element doped TiO_2 releases reactive species (OH^- and O_2^-).
- Hybridization of unoccupied Ti d(t_{2g}) with O 2p exist in conduction bands of TiO_2.
- Intense peak on XPS verifies the incorporation of Ag and W in the lattice of TiO_2.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 September 2016
Received in revised form
1 May 2017
Accepted 3 May 2017
Available online 5 May 2017

Handling Editor: Jun Huang

Keywords:
TiO_2 doping
Visible-light photocatalysis
Gaseous formaldehyde
Air purification
Multi-element

ABSTRACT

This study developed a modified titanium dioxide photocatalyst doped with multi-element synthesized via sol-gel process to productize a novel photocatalyst. The study includes degradation of gaseous formaldehyde under visible light using the synthesized novel titanium dioxide photocatalyst. Varying molar ratios from 0 to 2 percent ($\%_{mole}$ in titanium dioxide) of ammonium fluoride, silver nitrate and sodium tungstate as dopant precursors for nitrogen, fluorine, silver and tungsten were used. Photo-degradation of gaseous formaldehyde was examined on glass tubular reactors illuminated with blue light emitting diodes (LEDs) using immobilized photocatalyst. The photocatalytic yield is analyzed based on the photocatalyst surface chemical properties via X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared (FTIR) Spectrophotometry, Brunauer-Emmett-Teller (BET) and X-ray Diffraction (XRD) characterization results. The applied modifications enhanced the visible light capability of the catalyst in comparison to the undoped catalyst and commercially available Degussa P-25, such that it photo-catalytically degrades 88.1% of formaldehyde in 120 min. Synthesized titanium dioxide photocatalyst exhibits a unique spin orbital at 532.07 eV and 533.27 eV that came from the hybridization of unoccupied Ti d(t_{2g}) levels.

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1. Introduction

Various organic and inorganic compounds mainly formaldehyde, benzene, toluene and other VOCs, NOx and SOx contaminate

* Corresponding author.
E-mail address: mmclu@mail.cnu.edu.tw (M.-C. Lu).

http://dx.doi.org/10.1016/j.chemosphere.2017.05.022
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indoor air quality and pose significant health effects (Huang et al., 2016a). The prevalence of symptoms associated with these organic and inorganic compounds will include skin irritation, chest tightness, headache, fatigue, dullness and dehydration (Xiao et al., 2013). Most of our indoor air quality contaminates by the fumes from various indoor activities such as cooking and smoking and the influx of outdoor pollutants through openings from doors or windows and the fresh air of air-conditioners (Yu et al., 2009). When the outdoor air environment pose more risk, air dilution by ventilation (i.e. opening of doors and windows) may not be considered as an option for improving indoor air quality (Zhong et al., 2012; Photong and Boonnamnuayvitaya, 2009).

Volatile organic compounds, specifically formaldehyde (HCHO), is a simplest form of aldehydes that is commonly and naturally occur as major indoor air pollutants that can be found in some industrial resins such as the particle boards, coatings, adhesives and other wood-based materials (Fan et al., 2016; Huang et al., 2016e). Exposure of formaldehyde above acceptable level is hazardous to humans and animals which may cause serious pulmonary diseases (i.e. asthma, pneumonia, etc.), nasal sinus cancer and nasopharyngeal cancer (Fan et al., 2016; Huang et al., 2016a, 2016d). Reduction or elimination of the indoor HCHO emission has become the most vital aspect in the field of research (Fan et al., 2016).

There are several air treatment technologies that are currently employed and investigated to address indoor air quality issues. But there are two main categories of conventional air purification technologies and this includes: (a) one mainly utilizes filters and sorbents to capture pollutants, and (b) the other applies heating at elevated temperatures and/or light illumination to decompose or oxidize contaminants into CO_2 and H_2O in the presence of photocatalysts (Coutts et al., 2011; Huang et al., 2015; Huang et al., 2016e; Huang et al., 2016a). Semiconductors on the other hand are one of the most popular photocatalyst that has been known and attracted much attention in the field of research because of its potential solutions in chronic environmental pollution (Huang et al., 2016b). Most of the photocatalyst utilizes UV light that is only about 3–5% of the solar energy with poor visible-light activity due to wider band gaps (Huang et al., 2014; De Luna et al., 2016a, 2016b). This can be modified by structural designing and modulation, heterojunction, noble metal decorating, material hybridization, and doping with metal or non-metal elements to make it more active under visible-light irradiation by reducing its band gap energy and increase photocatalytic activity (Huang et al., 2014, 2015, 2016b). Metal ions during excitation, produces electron-hole pairs, separates and traps which occupies a regular lattice sites which produces reactive species of hydroxyl ion and super oxide for redox reactions (Huang et al., 2016c). Hereafter, it inhibits or reduces the rate of recombination occurrence and widens the available wavelength range, as a result it increases the utilization rate of the visible light (Wilke and Breuer, 1999; Wen et al., 2015). Consequently, metal ions can suppress the recombination of photo-induced electron-hole pairs thereby increasing the photocatalytic efficiency (Zhang and Liu, 2008). Whereas, non-metal ion as dopants can be incorporated in the lattice structure of titanium dioxide that creates mid-gap states which also decreases the band gap and increasing the visible light photocatalytic response of the titanium dioxide (Zhang and Liu, 2008).

Over the years, various visible-light active TiO_2 photocatalysts have been synthesized including N-TiO_2 (Nolan et al., 2012), C-TiO_2 (Chen and Chu, 2012), I-TiO_2 (He et al., 2012), Fe-TiO_2 (Cui et al., 2009), W-TiO_2 (Putta et al., 2011). In contrast to this, there were also study of co-doping performed by the researchers and this includes N:Ni-TiO_2 (Zhang and Liu, 2008), Ce:Si-TiO_2 (Chen et al., 2009), Zn:Fe-TiO_2 (Srinivasan et al., 2006), K:Al:S-TiO_2 (Tolosa et al., 2011), and K:Fe:C:N-TiO_2 (Gotostos et al., 2014). However, there were no studies attempted to conduct research on the photocatalytic performance of quadruple-elemental doped TiO_2.

Such that in this study, a multi-element doping of TiO_2 with W, Ag, N, and F was examined. According to Putta et al. (2011), a titanium dioxide synthesized using sol-gel method and doped with 0.5% W exhibited a 74% photodegradation of 2-chlorophenol under blue light irradiation is comparable to the same degree of reduction using commercial Degussa P-25 under UV irradiation (Putta et al., 2011). Whereas, according to the previous research by Barakat et al. (2011), the charge separation of electrons and holes of TiO_2 with silver nanoparticles deposited on surface that acts as an electron acceptors was also enhanced (Barakat et al., 2011). Page et al. (2007) reported that the presence of the silver oxide Ag_2O in conjunction with titania marked an increased in photocatalytic activity due to stabilization of photogenerated electron–hole pairs at the surface of titania by localization of the photogenerated electron on the silver oxide (Page et al., 2007).

Ananpattarachai et al. (2009) studied substitutional and interstitial N-doping of the TiO_2 structure and reported that nitrogen dopants effectively extended the light absorption of TiO_2 in the visible light range (Ananpattarachai et al., 2009; Bakar and Ribeiro, 2016). A narrowed band gap of the modified titania catalyst will facilitate more the excitation of electrons from the valence band to the conduction band even under visible light illumination, which results into higher photocatalytic activities. However, Li et al. (2005) reported that there are several advantages attributed to higher photocatalytic activity of F-doped titania in the degradation of gas-phase acetaldehyde which includes enhancement of surface acidity, creation of oxygen vacancies, and increased active sites (Li et al., 2005; Zhu et al., 2016). The high electronegativity of fluorine could stabilize the electron release upon oxygen depletion during calcination treatment. Although, the extrinsic absorption bands of the generated oxygen vacancies create free charge carriers that can take part in surface chemical reactions making a visible light photocatalytic excitation (Dozzi et al., 2011).

One of the main reason of quadruple doping in TiO_2 is to increase its photocatalytic activity in visible-light region. Doping with metals such as tungsten and silver will enhanced its adsorption capability. While doping with non-metal such as fluoride and nitrogen is to enhance TiO_2 activity that is not vulnerable to thermal instability and increase in carrier-recombination centers.

2. Materials and methods

2.1. Reagents

All chemicals used in preparation of catalysts and in photocatalytic activity were analytical grade. Tetra-*n*-butyl orthotitanate [$C_{16}H_{38}O_4Ti$] MW = 340.32 g mol^{-1} (98%, Merck, KGaA, Darmstadt Germany) is the titanium dioxide precursor. Ethyl alcohol MW = 46.068 g mol^{-1} (99.5%, Merck) as solvent. Ammonium fluoride MW = 37.037 g mol^{-1} (99%, Ferak GMBH, West Berlin), silver nitrate MW = 169.87 g mol^{-1} (99.8%, Ferak GMBH, West Berlin) and, sodium tungstate dihydrate MW = 329.86 g mol^{-1} (99%, Ferak GMBH, West Berlin) were used as dopants. Deionized water with resistivity value of 18.2 MΩ cm was used the step by step process as diluent and washing.

2.2. Synthesis of the multi-element/quadruple-element photocatalyst

The synthesis method used is based on a modified sol-gel method conducted by Tolosa et al. (2011). A 10 mL of tetra-*n*-butyl orthotitanate was added to 40 mL ethanol. The mixture was constantly stirred for 5 min at 400 rpm and 25 °C. Then additional

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