



Selective removal of polar VOCs by novel photocatalytic activity of metals co-doped TiO₂/PU under visible light



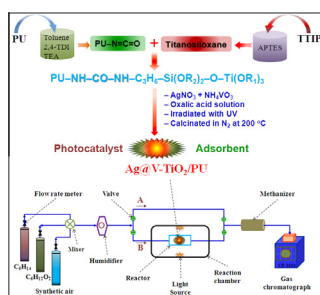
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HIGHLIGHTS

- Co-doping of TiO₂ with Ag and V gained all the advantages of both V and Ag doping.
- The optimal doping ratios of Ag/TiO₂ and V/TiO₂ were 4 and 2%, respectively.
- The Ag@V-TiO₂/PU exhibited very high electron-hole separation efficiency.
- The Ag@V-TiO₂/PU removed VOCs by both photocatalysis and adsorption.
- The photocatalysis preferentially oxidized the high polarity organic compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, Ag and V co-doped TiO₂ deposited on polyurethane (Ag@V-TiO₂/PU) was for novel photocatalytic removal of gaseous volatile organic compounds (VOCs). The combination of V doping, which enhanced internal electron transfer in the TiO₂ lattice, and Ag doping, which exhibited high internal electron transfer in the Ag₂O and enhanced exterior electron transfer among Ag particles, Ag₂O and TiO₂, increased the photocatalytic activity of Ag@V-TiO₂/PU for the removal of VOCs in aerosol. The surface area of this co-doped photocatalyst was also higher than that of the undoped and single-dopant photocatalysts. The optimal combination of weight ratios of Ag/TiO₂ and V/TiO₂ for maximizing the surface area and photocatalytic activity of TiO₂ was 4 and 2%, respectively. Under visible light, the removal efficiency of individual hexane and butyl acetate gas by 4Ag@2V-TiO₂/PU was 93.7 and 95.5%, respectively. The removed hexane and butyl acetate were mineralized into CO₂ with ratios of 93.2 and 96.2%, respectively. The individual removal of hexane and butyl acetate gas by Ag@V-TiO₂/PU was similar; however, in the mixture stream of both VOCs, much more butyl acetate than hexane was photocatalytically removed. This was associated with the much higher polarity of butyl acetate than that of hexane, so that the photocatalyst surface, where most of the oxy radicals were generated to oxidize the VOCs, was more occupied or covered by butyl acetate than by hexane.

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1. Introduction

Titanium dioxide (TiO₂) is a well known photocatalytic material because of its stable nature toward photo-corrosion, ease of preparation, non-toxicity, high ultraviolet absorptivity and strong oxidizing power toward great photocatalytic activity [1]. However,

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the major drawback of TiO₂ is that the photocatalyst only exhibits photocatalytic activity under UV irradiation because of its large band gap energy and fast recombination rate of photo-generated electron-hole pairs [2]. Doping TiO₂ with metals and non-metals is one of the most promising approaches to solve these problems [3]. Khan and Berk reported that doping could decrease the band gap energy of TiO₂, thereby extending the photo-response of TiO₂ from the ultraviolet into the visible region [4]. The doping could also improve the interfacial charge transfer and trapping of electrons, thereby reducing the recombination rate of the photo-generated electrons and holes [4]. In our previous studies, Ag and V were individually used as doping agents to enhance the photocatalytic activity of TiO₂ for removal of bacteria and benzene from aerosol, respectively. The photocatalytic activity of doped TiO₂ was much higher than that of the undoped one [5]. Recently, co-doping has been recognized as a novel approach to improve synergistically the photocatalytic activity of TiO₂ [6]. TiO₂ co-doped with two different atoms could exhibit higher photocatalytic activity and unique characteristics as compared to single-dopant TiO₂ [1]. Numerous studies have been done on co-doping TiO₂ by a combination of metal and non-metal including Mo-C, Mo-N, V-N, Fe-N, Ag-N, Pt-N and Sn-S [7–10]. However, very few studies have considered the combination of two different metals for co-doping TiO₂ [3,4]. The physiochemical properties and doping mechanism of metal-metal co-doped TiO₂ have been not well investigated. Therefore, the present study first aimed to use Ag and V as co-doping metals for synergistically enhancing the photocatalytic activity of TiO₂.

Powder photocatalysts have been widely applied for wastewater treatment because they can be easily dispersed or suspended in aqueous medium. However, the application of powder photocatalysts for air purification seems to be unsuitable because inhalation of the powders may lead to adverse effects on human health. Therefore, before being used in air purification systems, the powder photocatalysts should be immobilized on a suitable substrate. In our previous studies, porous polyurethane (PU) was used as a substrate to immobilize the V-doped TiO₂ and Ag-doped TiO₂ photocatalysts [5,11,12]. We hypothesized that the immobilization metals doped TiO₂ on PU foam, a 3D porous material, a high surface area material, which has honeycomb structure, would increase the adsorption ability of the photocatalyst. The obtained results indicated that the use of the PU substrate not only overcame the disadvantage faced by the powder photocatalyst but also increased the adsorption ability of the photocatalysts. Therefore, in the present study, we continued to use PU as the substrate to immobilize Ag@V co-doped TiO₂ (Ag@V-TiO₂/PU) to expand the potential applications of the synthesized photocatalysts to the air purification field.

Recently, the application of photocatalysts for the photocatalytic oxidation of volatile organic compounds (VOCs) has attracted much attention due to hazardous problems of these compounds to human health [13]. Photocatalyst can absorb a photon (hν), which has energy higher than the band gap energy of the photocatalyst, to generate an electron-hole pair. The generated electrons and holes can participate in reactions with O₂ and/or H₂O molecules to produce oxy radicals, including hydroxyl radicals and superoxide radicals, which are strong oxidative agents and which facilitate the oxidation of VOCs adsorbed on the photocatalyst surface into CO₂ and H₂O [14]. Pham and Lee reported that even under visible light irradiation, the V-TiO₂/PU photocatalyst could remove 80% of the toluene in 200-ppmV inlet gas, while 89.3% of the removed amount was mineralized into CO₂ and H₂O [11]. Banisharif et al. reported that Fe₂O₃-doped TiO₂ photocatalyst could remove 97% of trichloroethylene in 500-ppmV inlet gas with minor amounts of CO as a hazardous byproduct [13]. Most of the previous studies used only one VOC species in the inlet gas as a

pollutant target for photocatalytic removal process [15]. However, in real air purification applications photocatalysts usually must adsorb inlet gas streams containing many different VOCs species. The interactions among different VOC species in the gas mixture seem to adversely affect the removal efficiency [16]. Therefore, the third aim of the study was to use a gas mixture of *n*-hexane and *n*-butyl acetate, which have different chemical structures and different chemical properties, as the inlet gas for the photocatalytic removal process. Based on the obtained results, we report how the mixture of model pollutants is efficiently removed, especially considering the different removal efficiency and different polarity of the pollutant constituents.

2. Materials and methods

2.1. Material synthesis

According to our previous study, pristine PU was modified by a mixed solution of toluene, toluene-2,4-diisocyanate, and anhydrous triethylamine, to introduce isocyanate groups (NCO) onto its surface [5]. Amino titanilosiloxane, which contains Si-O-Ti bonds and an amine group (NH₂), was synthesized based on the reaction between titanium tetraisopropoxide (TTIP) and γ -aminopropyl triethoxysilane (APTES) [5,11,12]. Then, the modified PU was immersed into the amino titanilosiloxane solution for 1 h to immobilize the titanilosiloxane on PU. The titanilosiloxane was immobilized on PU by urea bond that was formed as a result of the reaction between the isocyanate groups of the modified PU and the amino group (NH₂) of the amino titanilosiloxane [5]. A mixture solution made from 0.1 M AgNO₃ and 0.1 M NH₄VO₃ solution was slowly added (drop-wise) onto the titanilosiloxane immobilized on PU. Then, 50 mL of a 1 M solution of oxalic acid was used to clean the obtained material. The cleaned material was irradiated with a UV-C light (60 W) for 5 h and then calcined under nitrogen at 200 °C for 5 h to produce Ag@V-TiO₂/PU. The added volume of AgNO₃ and NH₄VO₃ solutions were adjusted in order to synthesize seven Ag@V-TiO₂/PU photocatalysts with a total weight ratio of both dopants to TiO₂ fixed at 6 wt% constant and the weight ratio of each individual Ag and V dopant being varied among 0, 1, 2, 3, 4, 5 and 6 wt%. The synthesized materials were labeled XAg@YV-TiO₂/PU, where X and Y indicate the weight ratios of Ag/TiO₂ and V/TiO₂, respectively. The above procedure was repeated without drop wise of dopants precursors onto the titanilosiloxane to synthesize TiO₂/PU.

2.2. Material characterization

X-ray photoelectron spectroscopy (XPS) spectra of the synthesized Ag@V-TiO₂/PU photocatalysts were obtained using a Thermo Fisher K-Alpha X-ray Photoelectron Spectrometer system. The Gaussian multi-peak shapes were applied to fit the Ag 3d_{5/2}, V 2p_{3/2} and Ti 2p_{3/2} peaks in the obtained XPS spectra to determine the elemental states of the silver, vanadium and titanium in the synthesized photocatalysts. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images of Ag@V-TiO₂/PU were obtained using a JEOL TEM-2010F at acceleration voltage of 200 kV. A Bruker AXN model with a Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) source and operated at a scan rate of 0.02° s⁻¹ over a 2 θ range of 10–80° was used to obtain X-ray diffraction (XRD) spectra of Ag@V-TiO₂/PU. The surface morphology of Ag@V-TiO₂/PU was analyzed by a Hitachi S-4700 scanning electron microscope (SEM). Before the SEM analysis, the Ag@V-TiO₂/PU samples were coated with Pt to increase the conductivity of the photocatalyst surface. An Evolution 300 spectrophotometer (UV-1700 Shimadzu) was used to measure the optical absorption

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