



Photoelectrochemical characteristics, photodegradation and kinetics of metal and non-metal elements co-doped photocatalyst for pollution removal



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HIGHLIGHTS

- The co-doped photocatalyst of metal and non-metal elements is prepared.
- Photoelectrochemical solar cell is setup as well as its photocurrent is displayed.
- The photodegradation efficiency is about 99.99% using white light emitting diode.
- The kinetic parameters and photoelectrochemical characteristics are discussed.
- The photocurrent and power are related to the efficiency and kinetic parameters.

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ABSTRACT

Considering coordination effects, this study prepared a photocatalyst with a highly visible light response using co-doped titania with non-metal (nitrogen and sulfur) and lanthanide metal ions (cerium). As well, the photoelectrochemical characteristics and photocatalytic effects were tested. The feasibility was investigated on the power of the photoelectrochemical solar cell and the photodegradation of volatile organic compounds (VOCs) from indoor air pollution, taking toluene as a model compound. In this study, the different intensities of a light-emitting diode (LED) and the different initial concentrations (10–50 ppmv) were examined, and the kinetic model was addressed. The maximum power (P_m) at white light emitting diode (WLED) was 35.5 and 174.68 times that of the solar cell without cerium doping and without Ce, N and S doping, respectively. The decomposition efficiency (η_D) was more than 99.9% below 30 ppmv at 5050 WLED with 10 Ce/TiN_xS_yO_{2-x-y} (10 Ce/TNST). The photocatalytic decomposition was elucidated according to the Langmuir-Hinshelwood model. The reaction rate constant (k) and adsorption equilibrium constant (K_L) of 10 Ce/TNST with 5050 WLED in the range of 10–50 ppmv were 0.2637 ppmv min⁻¹ and 0.7008 ppmv⁻¹, respectively. This study succeeded in predicting optimum photodegradation conditions from the PECSC test. The photocurrent and power from the co-doped photocatalysts are related to the photodegradation efficiency.

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1. Introduction

In recent years, a modified photocatalyst to improve the catalytic efficiency of TiO₂ has received enormous attention. This is due to the advantages of using an inexpensive photocatalyst (TiO₂), operating under room temperature and atmospheric pressure [1]. Generally, a modified photocatalyst for visible-light application can be achieved from several methods. Most of these use a

low energy gap semiconductor, such as WO₃ [2] or CdS [3] as a direct photocatalyst. Adding transition or lanthanide ion metals, like Cr, Mo and Ce, to change the energy gap of TiO₂ not only can expand the absorption range from 380 nm to 620 nm, but also improve the TiO₂ photoelectrons-hole separation efficiency [4]. Tong et al. [5] pointed out that for cerium-doped titanium dioxide (Ce-TiO₂), electrons can be excited to the cerium valence band 4f layers under visible light irradiation electrons. Sidheswaran and Tavlarides [6] used CeO₂/TiO₂ in visible light illumination to destroy organic matter (toluene) and evaluate photocatalytic activity. Nevertheless, pure TiO₂ photocatalysts can be effectively

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utilized only under a UV ($\lambda < 365$ nm) light source, which accounts for merely 5% of the total solar energy or indoor visible light.

However, this also brings with it the serious problem of massive charge carrier recombination, which largely limits the photocatalytic activity of anion-doped titania. Numerous investigations have reported that the addition of Group VIII metals, transition metal ions and lanthanide ions to TiO₂-based photocatalytic systems to delay the carrier's recombination is an effective way to enhance photocatalytic activity [7,8]. Noble metals, including gold [9], platinum [10] and silver [11,12], are capable of creating the highest Schottky barrier among the metals facilitating the electron capture, as well as increasing the separation efficiency of photo-induced electron-hole pairs. The disadvantages of transition metal-doped materials are their thermal instability and the increase of carrier-recombination centers [13]. Furthermore, the impurities' energy level for Pd, V, Cr, Mn and Fe doped in single crystalline rutile TiO₂ was investigated by photocurrent measurement and theoretical calculations [14]. Considering the coordination effects, it would be helpful to obtain a photocatalyst with a high visible light response using co-doped titania with non-metal and lanthanide metal ions. In this respect, TiO₂ modification with rare earth metals, such as Ce, is considered an alternative since transitions of d and f orbital electrons affect absorption characteristics and assist in the reduction of the recombination rate of electrons and hole pairs in a semiconductor [15,16]. Matějová et al. [17] addressed the fact that the modification of TiO₂ with cerium also affected the spectral response of photocatalysts, shifting them to the visible light region. The absorption edge of photocatalysts decreased with the increase in Ce loading, from 3.19 eV (for TiO₂) up to 2.64 eV (for 10 mol% Ce/TiO₂). In order to overcome this limitation of TiO₂ absorption range, extending the absorption of TiO₂ into the wide visible light region is a possible solution since as much as 42% of the total sunlight or indoor visible light could then be utilized. Thus, many works have been devoted to improving the optical response of TiO₂ in the visible region. Furthermore, the location of oxygen vacancy formed in the TiO₂ crystals from non-metal doping increases the band gap energy [18]. Doping TiO₂ with different nonmetal elements, such as N [19–21], C [21,22], S [21,23], P [24], F [25] and Cl [26], substitute the oxygen vacancy in the TiO₂ [27,28]. Besides doping TiO₂ with nonmetal elements has provided promising results in visible light-induced (>400 nm) photocatalysis; for example, the UV-Vis absorption spectra results show that the absorption edge of un-doped composites is 390 nm while that of N, S co-doped-TiO₂ red shifts to 500 nm [29]. Nasir et al. [16] prepared Ce/N co-doped TiO₂ through a hydrothermal method by using cerium nitrate and tetrabutyl orthotitanate (TBOT). Photoluminescence spectroscopy (PLS) first showed a decrease in the recombination centers when Ce was introduced in co-doped TiO₂ with the maximum decrease for 0.05 Ce/N co-doped TiO₂ and then, an increase when Ce was increased in the samples. There is a direct relationship between the amount of recombination centers and the photoactivity of Ce/N co-doped TiO₂ [16]. Ferrari-Lima et al. [30] used N-doped TiO₂-Nb₂O₅ under UVA and visible light irradiation to treated solution which containing benzene, toluene and a mixture of o, m and p-xylene. Prabakar et al. [31] used single-cycle dip-deposited N-S doped TiO₂ thin films as visible light harvesters, as well as blocking layers, in dye-sensitized solar cells (DSSCs) and photoelectrochemical solar cells (PECSC). However, the connection and relationship between the results of PECSC and photocatalytic effect of the photocatalysts are seldom reported.

Metal (cerium) and non-metal (nitrogen and sulfur) element co-doped TiO₂ was prepared. The feasibilities for the removal of volatile organic compounds (VOCs) from indoor air pollution, taking toluene as a model compound, were tested in this study. As well, the photoelectrochemical characteristics, photodegradation and

kinetics were discussed and addressed. This study aims to predict the optimum photodegradation conditions from the PECSC test and it can be related to the photocurrent and photo-power. This means that the possibility of predicting the photodegradation efficiency or kinetics from the simple PECSC test can be achieved and it also can be applied to the design of air pollution control devices. Furthermore, in the near future, there will be a great tendency to replace traditional indoor lights with LEDs. Irradiation light sources use a visible-light light-emitting diode (VLLED), including a white light-emitting diode (WLED) with a different light intensity.

2. Materials and methods

2.1. Material preparation

2.1.1. Preparation process of TiN_xS_yO_{2-x-y} and TiN_xO_{2-x}

N- and S- doped TiO₂ (denoted as TiN_xS_yO_{2-x-y} or TNST) and N-doped TiO₂ (denoted as TiN_xO_{2-x} or TONT) were prepared by the incipient wet impregnation method with Ti(SO₄)₂ (20 wt%) (Kanto Chemical Co., Inc.), NH₃ (28%) (Fisher Chemical Co., Inc.) and Ti(OC₄H₉)₄ (99 wt%) (Alfa Aesar®, USA). The TiN_xS_yO_{2-x-y} was adjusted until the pH = 7 and centrifuged to remove water [4]. The wet impregnation method is a commonly used technique for the synthesis of a heterogeneous catalyst. Typically, an active metal precursor is dissolved in an aqueous or organic solution. Then, the metal-containing solution is added to a catalyst support containing the same pore volume as the volume of the solution that was added. Capillary action draws the solution into the pores. Any solution added in excess of the support pore volume causes the solution transport to change from a capillary action process to a diffusion process. The catalyst can be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst's surface. Therefore, in a container, 20 wt% Ti(SO₄)₂ was suspended in a pH = 7 solution using 28% NH₃ dipping to a certain pH. After being filtered and washed with distilled water to remove the SO₄²⁻, the samples were dried at 378 K for 30 min. The samples were calcined at 673 K for 1 h, milled in a mortar to prepare the TNST, and then, ground for use. The result of the elemental analysis of the TNST showed that the S and N contents were about 1.51 and 0.19 wt%, derived from Ti(SO₄)₂ and NH₃, respectively. For the TONT, the N content was only 0.04 wt %, and the S content was near 0 wt%. In a wet impregnation method, the maximum loading is limited by the solubility of the precursor in the solution. The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying.

2.1.2. Preparation process of Ce/TiO₂ and Ce/TiN_xS_yO_{2-x-y}

The Ce(NO₃)₃·6H₂O solution (99.5%) (Alfa Aesar®, USA) was added to the TiO₂ and TNST powders and irradiated under a 254 nm UV light for 24 h to transfer the Ce to a reduction type. Then, the sample was dried at 378 K in an oven for 30 min and milled in a mortar, calcined at 673 K for 1 h and ground for use (denoted as Ce/TiO₂ and Ce/TiN_xS_yO_{2-x-y} (Ce/TNST)).

2.2. Characteristic analyses of photocatalysts

An energy dispersive spectrometer (EDS) (LEO 1530, Germany), element analyzer (EA) (elementar VarioEL-III, Germany), high resolution scanning electron microscope (HRSEM) (Hitachi Tabletop TM-3000, Japan), Field Emission Gun Transmission Microscope (FEG-TEM) (FEI Tecnai G2 T20), X-ray single crystal diffractometer (XRD) (Rigaku TTRAX III, Japan), X-ray photoelectron spectroscopy analyzer (XPS) (VG MICROTECH, MT-500, UK), Brunauer Emmett Teller (BET) surface measurement device (Model ASAP 2100,

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