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Photocatalytic properties of nanocrystalline TiO_2 thin film with Ag additions

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Abstract

In the present study, nanocrystalline TiO_2/Ag composite thin films were prepared by a sol–gel spin coating technique. While, by introducing polystyrene (PS) microspheres, porous TiO_2/Ag films were obtained after calcining at a temperature of 500 °C. The as-prepared TiO_2 and TiO_2/Ag thin films were characterized by X-ray diffractometry, and scanning electron microscopy to reveal the structural and morphological differences. In addition, the photocatalytic properties of these films were investigated by degrading methylene blue under UV irradiation.

After 500 °C calcination, the microstructure of PS-TiO_2 film without Ag addition exhibited a sponge-like microstructure while significant sintering effect was noticed with Ag additions and the films exhibited a porous microstructure. Meanwhile, coalescence of nanocrystalline anatase-phase TiO_2 can be observed with respect to the sharpening of XRD diffraction peaks. The photodegradation of porous TiO_2 doped with 1 mol% Ag exhibited the best photocatalytic efficiency where 72% methylene blue can be decomposed after UV exposure for 12 h.

Keywords: Photocatalytic properties; TiO_2; Spin coating; Composite thin films

1. Introduction

Anatase-phase TiO_2 with its excellent photocatalytic properties has attracted extensive attentions during the last decades [1]. However, TiO_2 exhibits a relative high energy bandgap (~3.2 eV) and can only be excited by high energy UV irradiation with a wavelength shorter than 387.5 nm. Efforts have been made to extend the light absorption range of TiO_2 from UV to visible light or to improve the photocatalytic activity of TiO_2 further by adding transition and/or noble metals [1–4]. For example, Ag can serve as the electron traps aiding electron-hole separation, and also facilitate electron excitation by creating a local electric field [5,6]. Moreover, many researchers have tried to increase the attainable surface activation sites by either using nanocrystalline materials or making porous microstructure and, thus, the photocatalytic performance can be enhanced [7,8].

In the present study, the feasibility of preparing porous TiO_2 films with simultaneous Ag additions through a wet chemistry sol–gel route was investigated. The as-deposited TiO_2/Ag films were characterized by X-ray diffractometry, scanning electron microscopy, differential scanning calorimetry, and thermal gravimetric analysis. In addition, the photocatalytic properties of these films were evaluated by degrading methylene blue under UV irradiation.

2. Experimental procedures

The flowchart of the experimental procedures is shown in Fig. 1. The TiO_2 precursor sols were prepared by adding titanium n-butoxide ($Ti(OC_4H_9)_4$, ACROS Chem. Co., USA) into a dehydrated ethyl alcohol (99.5%) at room temperature. The silver contained solution was prepared by

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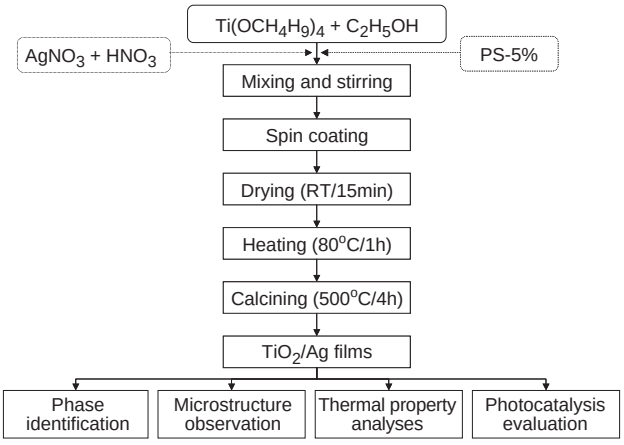

Fig. 1. Flowchart of the experimental procedures.

mixing the silver nitrate (99%, ACROS Chem. Co., USA) and ethyl alcohol into a diluted nitric acid (70%, SHOWA Chem. Co., Japan) for 5 min. Subsequently, various molar percentages (0, 1 and 5) of Ag-contained solution were added into the TiO_2 sols. After stirring at room temperature for 24 h, the Ag-added TiO_2 sols were spin coated on glass substrates (with a dimension of 5 cm^2). Moreover, in order to obtain porous microstructure, polystyrene (PS) microspheres (with a diameter ranged from 200 to 400 nm) in form of aqueous suspension (5% g/ml) were added into the precursor sols before the spin coating process. The spin-coated films were dried at room temperature for 15 min, heated at 80 °C for 1 h, and then calcined in air at 500 °C for 4 h to remove the PS spheres and residual organic materials. Thus porous TiO_2/Ag films with an average thickness of ~200 nm were prepared successfully.

The phase identification was performed using X-ray diffractometry (XRD, MAC-MXP3, Japan) with a Cu Kα radiation. The microstructure was observed using either scanning electron microscopy (SEM, HITACHI S3000N, Japan), or field-emission SEM (FE-SEM, HITACHI S4800, Japan), and transmission electron microscopy (TEM, JEOL 1200EX II, Japan). Thermal properties were examined by differential scanning calorimetry and thermal gravimetric analysis (DSC, TGA, 2960 SDT V3, TA Inst., USA). The heating rate was set at 10 °C/min in a temperature range of 30–600 °C.

The photocatalytic activity of the deposited films were evaluated by degrading methylene blue ($C_{16}H_{18}ClN_3S$, 2 ppm, 30 ml) in a reactor (C-70G, Chromato-Vue Cabinet, USA). The distance between the UV light source (365 nm) and deposited films was set as 10 cm. The variation of the methylene blue concentration, determined by the absorbance of the solution at 664 nm, was evaluated by a UV–Vis spectrophotometer (HP 8452A, USA).

3. Results and discussion

The spin coating technique can be easily employed as a fast and reliable process to produce TiO_2 films. Fig. 2 shows the SEM micrographs of heat-treated (a) pure TiO_2 film, (b) porous TiO_2 film, (c) porous TiO_2 containing 1% Ag, and (d) porous TiO_2 containing 5% Ag. The spin-coated films

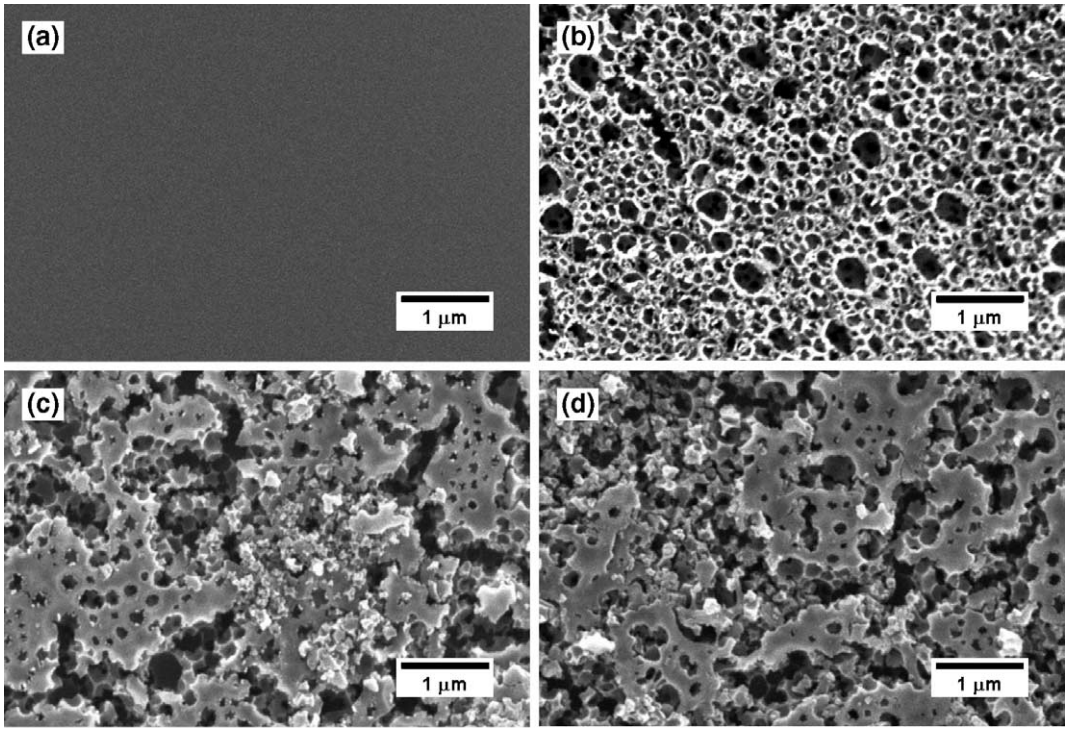

Fig. 2. SEM micrographs of (a) spin-coated TiO_2 film, (b) PS-TiO_2 film, (c) PS-TiO_2 film containing 1 mol% Ag, and (d) PS-TiO_2 film containing 5 mol% Ag. The porous TiO_2 specimens were obtained by removing the PS microspheres after the calcination at 500 °C.