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Enhancement of the photocatalytic performance of Ag-modified TiO_2 photocatalyst under visible light

Cheewita Suwanchawalit [a,*], Sumpun Wongnawa [b], Pimpaporn Sriprang [b], Pachara Meanha [a]

[a] Department of Chemistry, Faculty of Science, Silpakorn University, Sanam Chandra Palace Campus, Nakornpathom 73000, Thailand
[b] Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

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Abstract

A highly visible-light photocatalytic active Ag-modified TiO_2 (Ag–TiO_2) was prepared by a simple sol–gel process using $TiOSO_4$ as the starting material, $AgNO_3$ as a silver doping source, and hydrazine as a reducing agent. The prepared Ag–TiO_2 samples were characterized by several techniques such as X-ray powder diffraction (XRD), BET surface area measurement, scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductively coupled plasma optical emission spectroscopy (ICP-OES), energy dispersive X-ray spectrometry (EDX), X-ray absorption spectroscopy (XAS) and UV–vis diffuse reflectance spectroscopy (DRS). The Ag–TiO_2 photocatalyst, a mixture of amorphous and anatase phases, has a high surface area. The silver contents in the Ag–TiO_2 samples were determined by ICP measurements. The diffused reflectance UV–vis spectra indicated that the Ag–TiO_2 samples exhibited higher red shifts compared with the undoped TiO_2 sample. Indigo carmine degradation under visible irradiation indicated that the Ag–TiO_2 catalyst gave higher photocatalytic efficiency than those of commercial P25-TiO_2 and undoped-TiO_2 samples. The Ag–TiO_2 catalyst can be reused many times without any additional treatment.

Keywords: A. Sol–gel process; Titanium dioxide; Mesoporous titanium dioxide; Ag-modified TiO_2; Indigo camine; Dye decolorization

1. Introduction

Heterogeneous semiconductor photocatalysis is an attractive technology among the most promising technologies for solar energy conversion and environmental applications. Of the semiconducting materials employed, TiO_2 is the most effective because of its high photosensitivity, chemical stability, non-toxicity, easy availability, environmental friendliness, and low cost [1–4].

However, a major drawback of TiO_2 is the large band gap of 3.2 eV which limits its activity when sunlight is used. To overcome these limitations of TiO_2, many studies have been carried out to enhance the electron–hole separation and to extend the absorption range of TiO_2 into the visible region. These studies involved incorporation of metal ions or nonmetal ions into the TiO_2 lattice [5–8], dye photosensitization onto the TiO_2 surface [9–12], and deposition of noble metals onto the TiO_2 surface [13–15].

In particular, noble metal-modified TiO_2 particles have become the focus of many studies to maximize the efficiency of photocatalytic reactions. The noble metals deposited or doped on TiO_2 have high Schottky barriers among the metals and act as electron traps, facilitating the electron–hole separation and promoting the interfacial electron transfer process [16]. These noble metals may enhance the electron–hole separation, extend the light absorption into the visible range and enhance the surface electron excitation.

Among the noble metals used as electron traps, silver (Ag) is extremely suitable for industrial application due to its low cost and easy preparation. Ag-modified TiO_2 powders have become current interests due to its improvement of photocatalytic reactions and anti-microbial activity. There are several techniques for the preparation of Ag-modified TiO_2 such as sol–gel [16,17], photocatalytic deposition [13], and deposition precipitation [14].

In this work, undoped and Ag-modified TiO_2 samples were synthesized by the sol–gel process using $TiOSO_4$ and $AgNO_3$ as starting materials and hydrazine as a reducing agent. Herein, the synthesized Ag-modified TiO_2 catalyst was characterized

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* Corresponding author. Tel.: +66 3425 5797; fax: +66 3427 1356.
E-mail addresses: cheewita@su.ac.th, cheewita_31@hotmail.com (C. Suwanchawalit).

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by various physical techniques such as XRD, SEM, TEM, BET, DRS, EDX, ICP-OES and XAS techniques. The photocatalytic activity of the prepared catalysts was determined using indigo carmine as a model pollutant and the results compared with that of commercial Degussa P25-TiO_2 under visible irradiations.

2. Experimental

2.1. Synthesis of undoped-TiO_2 and Ag-modified TiO_2 catalysts

The undoped-TiO_2 was prepared by the sol–gel method. A 0.5 M $TiOSO_4$ aqueous solution was refluxed at 90 °C and then ammonia solution was added until the pH was 7 and then refluxed at 90 °C for 24 h to give TiO_2 precipitates. This precipitates were washed several times and dried at 105 °C for a day to give the undoped-TiO_2 powders.

In a typical preparation of Ag-modified TiO_2 catalyst, a 0.5 M $TiOSO_4$ aqueous solution was refluxed at 90 °C and then concentrated ammonia solution was added to the $TiOSO_4$ solution until the pH was 7. A 5.0 mmol% silver nitrate solution was added to the mixture followed by a 10.0 mmol% hydrazine solution and the mixture was refluxed at the same temperature for 24 h to give Ag–TiO_2 precipitates. The Ag–TiO_2 precipitates were washed several times until free of sulfate ion by the $BaCl_2$ solution test. The washed Ag–TiO_2 sample was dried at 105 °C for a day to give the Ag–TiO_2 catalyst.

2.2. Characterization of the catalysts

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku MiniFlex II X-Ray diffractometer with Cu K_α radiation (0.15406 nm) from 20° to 80° (2θ) to assess the crystallinity of the catalysts. The specific surface area and pore size distribution of the TiO_2 samples were determined by analyzing the N_2 adsorption isotherms obtained at 77 K using a Belsorp-Max automatic specific surface area analyzer. The particle morphologies were investigated using a scanning electron microscope (Quanta400) and transmission electron microscope (JEOL JSM 2010). The energy dispersive X-ray spectrometry technique (ISIS 300) was used to determine all elements in the samples. The Ag content was measured on a Perkin Elmer Optima 4300DV ICP-OES. Ag *L*3-edge XANES measurements were carried out using double crystal monochromator InSb (1 1 1) in the fluorescent mode with a 13-component Ge detector (Canbera) at the X-ray absorption spectroscopy beamline (BL-8) of the Siam Photon, National Synchrotron Research Center, Nakhon Ratchasima, Thailand. The band gap energies were determined using a Shimadzu UV-2401 spectrophotometer. The spectra were recorded in the diffused reflectance mode with $BaSO_4$ as a reference.

2.3. Evaluation of the photocatalytic activity of the Ag-modified TiO_2 catalysts

The experiments were performed by using 0.05 g TiO_2 sample dispersed in 50 mL of Indigo carmine (IC) solution. Prior to illumination, the suspension was stirred for 1 h to allow the adsorption equilibrium of the dye onto the surface of the TiO_2 sample. Then the mixture was irradiated under visible light irradiation (using a 18 W fluorescence TL-D 18 W/865 Philips tubelight as a visible light source). In all studies, the mixture was magnetically stirred during illumination. At given irradiation time intervals, samples were collected and centrifuged to separate TiO_2 powders. The residual concentration of IC was monitored by the change in absorbance of the dye at 610 nm using a UV-Vis spectrophotometer. Similar measurements were carried out on commercial P25-TiO_2. Controlled experiments either without light or TiO_2 were performed to ensure that degradation of the dye was dependent on the presence of both light and TiO_2. The disappearance of IC was analyzed by a Specord S100 UV–Vis spectrophotometer (Analytik Jena GmbH) over the 200–800 nm range.

3. Results and discussion

3.1. Characterization of the Ag-modified TiO_2

The XRD patterns of the undoped TiO_2 and the as-synthesized Ag–TiO_2 at different Ag contents are shown in Fig. 1 which all the synthesized Ag–TiO_2 and the undoped TiO_2 exist in the anatase phase. The peaks located at 25.4, 37.8, 48.0, 54.2, 62.7, 69.5, 75.2° respond to the reflections from the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 0 4), (2 2 0) and (2 1 5) planes of the anatase phase (JCPDS No. 21-1272). The average crystallite sizes of anatase in the samples were calculated by applying the Debye–Scherrer formula,

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \tag{1}$$

where *D* is the average crystallite size in angstroms, κ is a constant which is usually taken as 0.89, λ is the wavelength of

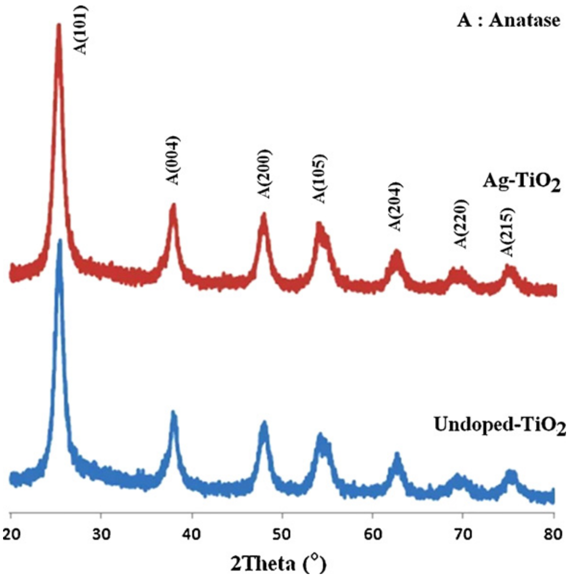

Fig. 1. XRD patterns of the undoped TiO_2 and prepared Ag-modified TiO_2 catalysts.