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Effect of tungsten-doping on the properties and photocatalytic performance of titania thin films on glass substrates

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ABSTRACT

Highly-transparent TiO_2 thin films with varying W-dopant levels (0.010–0.100 mol%) were deposited on soda-lime-silica glass substrates by spin coating, followed by annealing in air at 450 °C for 2 h. Characterization was by GAXRD, AFM, SIMS, XPS, UV–vis, and MB degradation. The films were comprised of single-crystal anatase grains. Increasing doping levels increased the crystallite sizes, grain sizes, and film thicknesses; they also changed the grain morphology from anhedral to euhedral. W^{6+} ions formed a substitutional solid solution in anatase and probably exhibited charge compensation by Ti vacancy formation, which led to lattice contraction. Contamination from the glass substrates was homogeneously distributed on the grain boundaries. Doping decreased the optical indirect band gap. However, at the highest doping level, it is not certain if this was an artificial effect of precipitation from overdoping or a true effect of lattice stress. The 0.010 mol% W sample showed the best performance probably owing to its formation of a homogeneous solid solution within the range of semiconducting properties, which could have narrowed the band gap or introduced mid-gap states. The 0.100 mol% W sample may have been overdoped and caused WO_3 precipitation. If so, the presence of the TiO_2–WO_3 couple may have enhanced charge separation and hence photocatalytic performance.

1. Introduction

Photocatalytic materials [1–3] are being used currently for self-sterilizing surfaces [4], air purification [5,6], water purification [7–9], self-cleaning surfaces [10–12], and solar cells [13–15]. Titanium dioxide (TiO_2) is one of the most promising photocatalysts owing to its low cost, non-toxicity, and chemical and thermal stability [16–18]. Work by Fujishima and Honda [19] on water splitting using single-crystal TiO_2 showed that high-energy radiation, such as UV, is required to excite electrons from the valence to the conduction band owing to the relatively large band gap (~3.2 eV [20]). This limits the efficiency of TiO_2 as a photocatalyst since UV radiation comprises only ~5% of the solar spectrum [21].

Several methods have been used to enhance both the spectral response of TiO_2 in the visible region and its photocatalytic activity [22–24]. The most common is the addition of dopants, which are intended to create mid-gap states in the electronic structure, thereby narrowing the band-gap [25,26]. The dopants also act as trapping centers that separate the hole and electron pairs, thereby extending the lifetime of these charge carriers and enhancing photocatalytic activity [26]. Several dopants, including metals [27–30] and non-metals [31–33], have been trialed for this purpose.

Doping with transition metal ions can help to retard the recombination of photogenerated electrons and holes, which thus increases the lifetime of charge carriers [34]. Moreover, tungsten (W) additions are believed to extend the spectral response of TiO_2 into the visible region through a positive shift in the conduction band [12,13]. However, the limited studies on W-doped TiO_2 have focused on powders. León-Ramos et al. [35] reported that 0.03 mol% W-doped TiO_2, produced hydrothermally, displayed higher photodegradation compared to undoped TiO_2. Li et al. [36] demonstrated that 3 mol% WO_3-doped TiO_2 powders, prepared by sol–gel, were most effective in degrading organic solutions, while Couselo et al. [37] suggested that the optimal performance of 3 mol% W-doped TiO_2 powders resulted from two competing factors, namely increasing surface area and decreasing specific activity per

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Table 1
Summary of experimental work on W-doped TiO_2 photocatalysts.

Material	Synthesis method	Dopant concentration	Reference
Powder	Sol–Gel	0.005–0.05 mol%	León-Ramos et al. [35]
Powder	Sol–Gel	3 mol%	Li et al. [36]
Powder	Sol–Gel	0.5–6.0 mol%	Couselo et al. [37]
Powder	Sol–Gel	0.4–1.2 wt%	Hua et al. [38]
Powder	Solvothermal method	0.6–9.6 mol%	Wu et al. [39]
Thin film	Aerosol-Assisted CVD	2–20 mol%	Sathasivam et al. [40]
Thin film	RF sputtering	3.83–15.84 at%	Ratova et al. [43]
Thin film	Dip coating	2–20 mol%	Rampaul et al. [44]
Thin film	Sol–Gel	1–8 wt%	Yang et al. [45]

adsorption site with increased doping. Recently, Hua et al. [38] reported that sol–gel-derived TiO_2 nanoparticles doped with 0.4–1.0 wt% W resulted in enhanced capability of degradation of methyl orange solution owing to the role of W ions in shifting the absorption edge of TiO_2 to the visible range. Wu et al. [39] showed that W-doped TiO_2 particles produced by the solvothermal method displayed enhanced near-infrared absorption performance and similarly enhanced photocatalytic activity to that of commercial Degussa P25 TiO_2 in the degradation of NO_x gas. Further, Sathasivam et al. [40] demonstrated that 2.25 at% W-doped TiO_2 films prepared by aerosol-assisted chemical vapor deposition were effective in degrading resazurin redox dye since the dopants contributed to an increase in the surface area and limitation in the relative grain boundary regions, which act as charge carrier recombination sites.

Prior studies have shown that doping with W^{6+} has the potential to modify the photocatalytic properties of TiO_2 since the similarity of its crystal radius to that of Ti^{4+} [41] suggests the potential for substitutional solid solubility. Further, the fact that its crystal radius is smaller than that of the two interstices adjacent to the central Ti ion in the elongated TiO_6 octahedron [42] suggests the potential for interstitial solid solubility. Both types of solid solubility would require charge compensation in the form of titanium vacancies or oxygen injection (with ionic compensation) or electrons (with electronic compensation); Frenkel defect formation also is possible. All of these would be expected to have significant effects on the photocatalytic performance.

Most prior work has focused on reducing the optical band gap of TiO_2 through W additions, without extended consideration of the effects of doping on the mineralogical, microstructural, and photocatalytic properties. Further, in other studies, the doping levels used have tended to be high (2–20 mol%) and well above the typical semiconducting addition range. This is particularly the case for W-doped thin films, as shown in Table 1 [35–40,43–45]. Previous work by the authors [46] has led to the observation that additions of transition metal dopants typically in excess of ~1 mol% (metal basis) are capable of exceeding the solubility limits, resulting in precipitation on the grain boundaries. This effect lowers the band gap of thin films but it cannot alter that of the doped TiO_2 further than that of the TiO_2 at the solubility limit. Hence, the band gap of the thin film and that of the TiO_2 comprising the film are different. Further effects may include lattice distortion and partial amorphization. All of these effects can alter the photocatalytic efficiency of the doped films, generally deleteriously.

There are many variables that affect the photocatalytic performance of doped TiO_2, including crystal structure, lattice deformation, defect equilibria (structural variables), grain size, surface area, and topography (microstructural variables) [46]. Since previous studies have taken a more focused approach to this range of variables, the present work aims to describe a more comprehensive investigation into the effects of doping on the mineralogical, microstructural, optical, chemical, and photocatalytic performance of TiO_2 thin films deposited on the common substrate soda-lime-silica glass. In the present case, doping with W in a compositional range (0.010–0.100 mol%) that is consistent with the formation of a homogeneous solid solution and semiconducting dopant levels is designed to systematize the structural variables while avoiding the effects of mechanistic changes in the microstructural variables, all of which affect the photocatalytic properties. In particular, since the band gap is used widely in the assessment of photocatalytic performance, in the absence of a WO_3-TiO_2 phase diagram or other solubility data, the low levels of dopant are intended to avoid precipitation, significant modification of the microstructure from precipitation and liquid formation, and artificial alteration of the band gap. In the present work, the recognized potential to influence the photocatalytic performance by W-doping of TiO_2, summarized above, has been investigated by the fabrication of thin films by spin coating, followed by annealing at 450 °C for 2 h. The thin films were characterized using different techniques to investigate the effects of W-doping on the mineralogical, morphological, topographical, chemical, optical, and photocatalytic properties.

2. Experimental procedure

2.1. TiO_2 thin film fabrication

To prepare sol-gel solutions for coating, titanium isopropoxide (TIP, reagent-grade, 97 wt%, Sigma-Aldrich) and isopropanol (reagent plus ≥99 wt%, Sigma-Aldrich) were mixed to obtain a titanium concentration of 0.1 M (2.84 g of TIP diluted in 100 mL isopropanol). The solution then was magnetically stirred on a hot plate at 90 °C for 10 min. Different amounts of tungsten hexachloride (WCl_6, ≥99.9 wt%, Sigma-Aldrich) were added to obtain W-dopant concentrations of 0.010, 0.025, 0.050, 0.075, and 0.100 mol% (metal basis to Ti).

Thin films were fabricated by spin coating (Laurell WS-65,052) involving the rapid deposition of ~0.2 mL solution onto a soda-lime-silica glass substrate (25 mm × 20 mm). Spinning was done at 2000 rpm in air for 20 s during deposition and the films were dried by additional spinning for 15 s. The overall process involved seven cycles of deposition to obtain thin films of identical thickness. Subsequent annealing was done in a muffle furnace at 450 °C for 2 h (heating rate of 0.5 °C/min from 25 °C to 200 °C and 1 °C/min from 200° to 450 °C; cooling rate of 1 °C/min).

2.2. Characterization

Film mineralogies were analyzed using glancing-angle X-ray diffraction (GAXRD, *PANalytical X'pert Materials Research Diffractometer*; 45 kV, 40 mA). Film topography was assessed using atomic force microscopy (AFM, *Bruker Dimension Icon Scanning Probe Microscope*; tapping mode, scan size: 1 µm × 1 µm). Film thickness and crystallography (including electron diffraction) were analysed using field emission gun transmission electron microscopy (FEGTEM, *Philips CM200*; 200 kV), the unit of which was equipped with an energy dispersive spectrometer (EDS, *Bruker Quantax*). Elemental distributions of dopants and contaminants were