



Effect of doping on the properties and photocatalytic performance of titania thin films on glass substrates: Single-ion doping with Cobalt or Molybdenum

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HIGHLIGHTS

- Increased recrystallization at low levels was owing to defect-related nucleation.
- Oversaturation leads to significant lattice distortion and reduced performance.
- Intervalance charge transfer effects leads to change in lattice structure.
- Reducing performance with increasing grain size owing to greater diffusion distance.

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ABSTRACT

TiO₂ thin films of varying Co and Mo individual doping levels (0.00–1.00 mol% metal basis) were fabricated on soda-lime-silica glass substrates by spin coating, followed by annealing at 450 °C for 2 h. Mineralogical analyses showed that all of the films were comprised only of anatase and suggested that both Co and Mo formed interstitial solid solutions. For the Co-doped films, the variation in anatase XRD peak intensities indicated three discrete stages of structural and nanostructural development: recrystallization (≤ 0.05 mol% Co), lattice distortion (0.05–0.60 mol% Co), and precipitation (≥ 0.60 mol% Co). For the Mo-doped films, Mo consistently enhanced nucleation, recrystallization, and lattice distortion within the solubility limit, which was not reached at 1.00 mol% Mo. Chemical analyses showed that Ti⁴⁺/Ti³⁺, Co³⁺/Co²⁺, and Mo⁵⁺/Mo⁴⁺ (and possibly Mo⁶⁺) were present in the films. The formation of non-equilibrium valences was considered in terms of the effects of crystal field stabilization energy (CFSE), intervallence charge transfer (IVCT), and electronegativity. Nanostructural analyses of the Co-doped films showed that, with increasing doping level, the grain size increased at the lowest level, followed by a decrease owing to changes in the structure (lattice destabilization) and nanostructure (localized liquid formation). In contrast, the grain size of the Mo-doped films increased with increasing doping level due to the maintenance of solid solubility, defect formation (and associated enhanced nucleation and recrystallization), and grain growth. Defect formation and charge compensation resulted in lattice contraction, which was confirmed by laser Raman microspectroscopy and resultant destabilization. Optical analyses showed that all of the thin films were flat, smooth, and nanostructurally homogeneous. The band gap data suggested that the governing effect derived from the lattice distortion associated with the lattice incorporation of both dopants. Photocatalytic testing showed that the lowest level of doping for both dopants (0.01 mol%) yielded maximal photocatalytic activity and that the performance decreased with increasing doping levels. This was attributed to the effects of nucleation and recrystallization, semiconducting effect, dopant size effect, and minimal lattice distortion.

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1. Introduction

Increasing global pollution and energy consumption have resulted in increased focus on technologies aimed at remediation of

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these issues [1,2]. Following the seminal work of Fujishima and Honda [3] on the use of titania (TiO_2) electrodes for photocatalytic water splitting, there has been an increasing amount of work on the use of photocatalytic titania for air and water purification [3–6], dye-sensitized solar cells [7,8], electrochromic films [9,10], optical coatings [11], and self-cleaning materials [12,13] owing to its advantageous properties, which include adequate performance levels, non-toxicity, chemical inertness, and low costs [14–16].

However, TiO_2 is an n-type semiconductor with a wide band gap of 3.2 eV (anatase) and thus only the UV range of the solar spectrum (<5%) has adequate energy to excite electrons from the conduction to the valence band [17]. To date, several methods, including compound semiconductors [18–20], dye sensitization [21–24], and metal and/or non-metal ion doping [25–35], have been investigated both to enhance the photocatalytic efficiency and to extend the absorption edge into the visible light region (400–800 nm). Previous studies have shown that doping with metals and non-metals can enhance the photocatalytic performance of TiO_2 thin films, with the majority of work being on transition metal dopants such as Mn [36–38], Cr [39–41], V [42–44], Ag [45,46], Zn [47–49], Fe [50–53], Co [54–56], and Mo [57–60].

Iwasaki et al. [54] reported that 0.03 mol% Co-doped TiO_2 nanoparticles exhibited enhanced photocatalytic efficiency under UV and visible light. Their work showed that the efficiency was dependent more on the Co valence state of 2+ rather than the specific surface area and crystallinity. Further, Barakat et al. [61] observed that 0.036 mol% Co-doped TiO_2 nanoparticles exhibited maximal photodegradation efficiency since Co solubility caused a significant absorption shift toward the visible region.

Another potential dopant is Mo since the sixfold crystal radius of Mo^{6+} (0.073 nm) [62] is similar to that of Ti^{4+} (0.0745 nm) [62], which increases the potential for substitutional solid solution formation. Yu et al. [63] analyzed the electronic and optical properties of Mo-doped TiO_2 by the density functional pseudopotential method and concluded that increasing the Mo doping level effectively lowers the band gap owing to the substitution of Ti by Mo. Khan et al. [64] reported that 0.10 at% Mo-doped TiO_2 nanoparticles synthesized by the hydrothermal method exhibited maximal visible-light photocatalytic activity due to reduced band gap and improved electron-hole pair separation.

Although there are numerous studies reporting TiO_2 doping, most of these report the examination of nanoparticulate powders at relatively high doping levels (>1 mol%). There is only a limited amount of work investigating the effects of the doping of TiO_2 thin films with low levels of transition metal ions (≤ 1 mol%) on the resultant photocatalytic performance. The present work reports a study of the effects of low-level doping (0.00–1.00 mol%) of Co or Mo on the photocatalytic properties of TiO_2 thin films deposited on soda-lime-silica glass substrates, fabricated by spin coating, followed by annealing at 450 °C for 2 h. The mineralogical, chemical, morphological, topographical, optical, and photocatalytic properties were investigated in order to understand the factors and mechanisms affecting the photocatalytic properties of these films.

2. Experimental procedure

2.1. Sample fabrication

The fabrication process for TiO_2 thin films using spin coating has been described in detail elsewhere [65–67]. Precursor solutions were prepared using titanium isopropoxide (TIP, Reagent Grade, 97 wt%, Sigma-Aldrich) dissolved in isopropanol (Reagent Plus, ≥ 99 wt%, Sigma-Aldrich) at 0.1 M titanium concentration (2.84 g of TIP was diluted to 100 mL volume with isopropanol). The Co or Mo dopant level was varied in the range 0.00–1.00 mol% (metal basis)

by adding CoCl_2 (Reagent Grade, 97 wt%, Sigma-Aldrich) or MoCl_5 (Reagent Grade, 95 wt%, Sigma-Aldrich), respectively, to the solution. The precursor solution was mixed by manual stirring for 10 min in a Pyrex beaker without heating. All of the objects used (glass substrates, beakers, stirring rods) were cleaned in an ultrasonic bath with ethanol, following by drying in air on a hot plate at 65 °C for 30 min. This was done in order to remove adsorbed water prior to all experimental work, thereby avoiding hydrolysis. Spin coating (Laurell Technologies WS-65052) was done by depositing ~0.2 mL (ten drops from a syringe) of precursor solution onto a soda-lime-silica glass microscope slide (Shanghai Machinery Import and Export Company, China) spinning at 2000 rpm in nitrogen over a period of ~10 s. The films were dried by spinning for an additional 15 s and the overall process was repeated six more times (~1.4 mL; seventy drops). Subsequent annealing in air was carried out in a muffle furnace at 450 °C for 2 h; the heating rates were 0.5 °C/min from room temperature to 200 °C and 1 °C/min from 200 °C to 450 °C, followed by natural cooling.

2.2. Characterisation

The mineralogies of the films were determined using glancing angle X-ray diffraction (GAXRD, 45 kV, 40 mA, beam diameter (1 cm) PANalytical Empyrean Thin-Film XRD) and laser Raman microspectroscopy (Raman, green argon ion laser (514 nm), 25 mW, 50X, spot size 1.5 μm , Renishaw inVia Raman Microscope). The surface composition of the films was analyzed using X-ray photoelectron spectroscopy (XPS, 13 kV, 12 mA, spot size 500 μm , 2–5 nm beam penetration, Thermo Scientific ESCALAB 250Xi X-ray Photoelectron Spectrometer Microprobe). Atomic force microscopy (AFM, tapping mode, scan size 1 $\mu\text{m} \times 1 \mu\text{m}$, Bruker Dimension Icon Scanning Probe Microscope) was used to analyze the surface topography and grain size. The optical transmission spectra of TiO_2 thin films in the visible wavelength region were obtained using an ultraviolet-visible spectrophotometer (UV-Vis, dual-beam, PerkinElmer Lambda 35 UV-Visible Spectrometer).

2.3. Photocatalytic performance

The photocatalytic performance of TiO_2 thin films was assessed in terms of the photo-bleaching of methylene blue (MB) solution. This test was done by immersing the TiO_2 thin films in MB solution while being irradiated under UV light for varying durations. The MB solutions were prepared using methylene blue (M9140, dye content ≥ 82 wt%, Sigma-Aldrich) dissolved in deionized water at 10^{-5} M concentration (0.0032 g of MB was diluted to 1 L volume with deionized water) [68]. The solutions were magnetically stirred in a beaker for 1 h without heating. Samples were placed in MB solution in a dark container for saturation for ~12 h prior to testing. Subsequently, the samples were placed in separate small beakers filled with ~10 mL of MB solutions and exposed to UV (365 nm) light provided by a UV lamp (3UV-38, 8 W, UVP) for different times. The vertical lamp-liquid and liquid-sample distances were ~6 cm and ~4 cm, respectively. After irradiation, the tested MB solutions were analyzed by UV-Vis spectrophotometry in order to determine the extent of degradation.

3. Results and discussion

3.1. Thermodynamics

Fig. 1 shows thermodynamic stability diagrams, which were prepared using FACT-Sage 6.2 (GTT Technologies, Germany). The Ti-O, Co-O, and Mo-O diagrams indicated that Ti^{4+} , Co^{3+} , and Mo^{6+} are the most likely species present in the films for the processing

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