



Titanium–vanadium oxide nanocomposite thin films: Synthesis, characterization and antibacterial activity



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HIGHLIGHTS

- Nanocomposite crystallinity was a function of sol composition.
- Silver was incorporated into the vanadia structure.
- A red shift was observed with an increase of vanadia concentration.
- Antibacterial analysis conducted on *Escherichia coli* and *Staphylococcus epidermidis*.

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ABSTRACT

A sol–gel based deposition method was successfully developed to produce a series of crack-free, spatially homogeneous undoped/silver doped titania–vanadia oxide nanocomposite thin films. Thin films were characterized using Glancing Incidence X-ray Diffraction (GIXRD), X-ray Photoelectron Spectroscopy (XPS), and Ultraviolet Visible Spectroscopy (UV–Vis). It was determined *via* both XRD and XPS that when calcined at 450 °C the nanocomposite crystallinity was a function of sol composition. Additionally, it was determined *via* GIXRD that upon silver doping, silver was incorporated into the vanadia structure or present in silver oxide form in crystalline films. A red shift within the UV–Vis spectra was observed with an increase of vanadia concentration from 0 to 100% respectively. Antibacterial analysis conducted on *Escherichia coli* and *Staphylococcus epidermidis* demonstrated that films exposed to light showed greater antibacterial properties.

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1. Introduction

Transition metal oxide (TMO) materials have a wide range of applications within the medical, energy, and environmental fields [1–6]. One particular TMO system which has garnered significant interest of late is titanium dioxide (TiO₂). Commercially, TiO₂ powders are used for water and air purification while TiO₂ thin films are used for a variety of self-cleaning surfaces including currently available self-cleaning glasses and ceramic tiles. Self-cleaning surfaces utilize the photocatalytic ability of TiO₂ to breakdown organic contaminants for cleaning and photoinduced superhydrophilicity to wash the contaminants from the glass surface. An additional photoinduced property of TiO₂, closely related to the breakdown of organic contaminants, yet considerably less studied than the above two, is its bactericidal activity [7–12]. There

are three proposed mechanisms that silver (Ag) exhibits its antibacterial effect. Ag nanoparticles can attach to the cell membrane causing structural/functional damage, in particular to sulphur sites that are intended for protein attachment. Ag is also a strong nucleic acid binder and can form complexes with DNA and RNA which can result in loss of replication ability. Also, the formation of free radicals, reactive oxygen species (ROS) on Ag particles has been found to lead to antimicrobial activities [13–17]. With respect to the photocatalytic activity of Ag, Ag incorporation is cited to increase the number of electron hole pairs which increases its photocatalytic activity [13]. Additionally, Ag has an electron accepting region at an energy just below the conduction band. After light absorption and charge separation the electron in the conduction band is trapped by the Ag. The hole oxidizes water and forms OH[−] radicals. This can be attributed to the dissolution of Ag and the photocatalytic characteristics of TiO₂–Ag [13].

TiO₂ is a wide band-gap semiconductor, and therefore when excited by photons with higher energy than the bandgap, photons are absorbed resulting in the production of an energetic, electron–

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hole pair (e^-/h^+). This electron–hole pair (e^-/h^+) can then be utilized for reaction catalysis (photocatalysis and/or bactericidal activity). Efficiency of the photoinduced properties/processes is dependent upon; (1) e^-/h^+ pair generation, (2) charge carrier trapping and recombination, and (3) interfacial charge transfer/oxidation [11,12,18]. Therefore optimization of any or all of these properties will increase TiO_2 photocatalytic performance. One major drawback of TiO_2 is related to its charge carrier generation ability; given the relatively large bandgap ($\sim 3.0\text{--}3.2$ eV), ultraviolet light is required for charge carrier generation. In attempts to make TiO_2 photocatalytically active with visible light illumination, there has been considerable work associated with lowering the bandgap energy of TiO_2 . Although numerous techniques have been applied, this study will focus on 2 methods the (1) preparation of TiO_2 -based nanocomposites with other TMOs having a lower bandgap than TiO_2 and (2) the doping of TiO_2 with noble metals [11,12,18–29].

Of particular interest here are nanocomposite thin films within the titania–vanadia (Ti–V) and Ag-doped Ti–V systems. To the best of the authors knowledge these systems have received little attention in the scientific literature and a combined study of the processing, characterization, and bactericidal activity across the undoped and Ag doped Ti–V compositional system has not been documented. However, numerous studies have been conducted on different materials/systems and light sources investigating TiO_2 and Ag in particular. Previous studies on $\gamma\text{-Fe}_2\text{O}_3@/\text{SiO}_2@/\text{TiO}_2\text{-Ag}$ nanocomposites developed by Cui et al. report the enhanced photocatalysis and antibacterial properties (>97%) under visible light radiation when tested in *Escherichia coli* [13]. Studies by Leung et al. reports increased photocatalytic bactericidal activity of TiO_2 films under fluorescent and UV light against two marine bacteria: *Alvinella alvinellae* and *Photobacterium phosphoreum* [30]. while Yao et al. investigated the photocatalytic effect of dye-modified TiO_2 thin films under visible light against phytopathogenic bacteria including *Enterobacter cloacae* SM1 and *Erwinia carotovora* [31]. Additionally metal oxide systems have been investigated by Thongsuirwong et al. ZnO thin films prepared by the sol–gel route demonstrated excellent bactericidal activity against *E. coli* [32]. The authors have previously investigated TiO_2 thin films doped with Ag, which proved to greatly reduce the proliferation of *E. coli* and *Staphylococcus epidermidis* on glass substrates. This work stems from this preliminary study with 1) the addition of vanadia within the substrate and 2) utilizes visible light as a photocatalytic activator [33].

TMO based thin films can be produced via; (1) sol–gel synthesis, (2) physical vapour deposition, (3) electrochemical deposition, and (4) chemical vapor deposition [2,8–12,18,34–37]. In this paper we will use a modified sol–gel based method given its established flexibility in controlling material properties as a function of processing parameters. In addition the sol–gel process is advantageous because of its ability to produce high purity and homogeneous materials and ease in dopant introduction. The objective of this study is to develop and characterize undoped and Ag-doped $\text{TiO}_2\text{-V}$ oxide [$(x)\text{TiO}_2 \cdot (100-x)\text{V}_2\text{O}_5$; where $x = 100, 75, 50, 25$ and 0 mol %] nanocomposite thin films which were deposited on glass

substrates via sol–gel spin coating. Additional objectives include determining any antibacterial effect in the absence of illumination and under visible light illumination with respect to two common bacteria; *E. coli* and *S. epidermidis*.

2. Materials & methods

2.1. Sample preparation

2.1.1. Preparation of glass substrates

The substrate used in this work was commercially-available soda lime silicate (SLS) float glass (Guardian Industries). The 3.2 mm SLS glass was cut into to 2.5 cm² sections and ultrasonically cleaned in acetone and blown with nitrogen gas. In addition, a SiO_2 barrier layer was deposited using the sol–gel method to inhibit unwanted ion diffusion. The reagents: tetraethyl orthosilicate (Aldrich reagent grade, 98%), denatured ethyl alcohol (Fisher A407P-4), hydrochloric acid (Fisher A142-212), and de-ionized water were mixed in a 1:11:0.06:5.1 M ratio. The reagents were added in the above order, magnetically stirred, and aged for 30 min. The solution was deposited on the cleaned SLS glass by a Chemat KW-4A spin coater (Northridge, CA). The barrier layer was produced by depositing 6 drops of the SiO_2 sol onto the SLS glass, followed by a 2500 rpm, 30 s spin cycle. The SiO_2 barrier layers were heat treated at 500 °C for 10 h. After the substrates cooled to room temperature, they were cleaned with ethanol, dried with nitrogen gas, and stored in a vacuum desiccator.

2.1.2. Preparation of titanium–vanadium thin films

The mixed oxide thin films were also prepared using the sol–gel method. The reagents consisted of: titanium (IV) isopropoxide (Aldrich, 97%), vanadium (V) oxytrisopropoxide (Aldrich), 2-propanol (Aldrich, 99.5%, anhydrous), hydrochloric acid (Fisher A142-212), and de-ionized water. The molar ratios of the reagents are reported in Table 1.

Two separate solutions were initially prepared; 1.) the titanium (Ti) and vanadium (V) precursors (6 wt%) were added to the 2-propanol and magnetically stirred for 5 min and 2.) hydrochloric acid (5 wt%) and de-ionized water (1 mol water: 1 mol titanium/vanadium precursor) were mixed with additional 2-propanol (10 wt%). Solutions 1.) and 2.) were then mixed and allowed to age for 5 min. Titanium/vanadium sols were added drop wise (approximately 6 drops) to the substrates (SiO_2 coated SLS). The thin films were produced by spinning at 2500 rpm for 25 s. The samples then underwent a two-step heat treatment (both in air): first to 150 °C for 10 min to remove the solvent and any organics, and then finally to 450 °C for 5 h. Following the heat treatments, the films were cooled to room temperature in air. The above methods resulted in a series of 5 thin films, denoted from this point forward as undoped 100Ti, 75Ti–25V, 50Ti–50V, 25Ti–75V, and 100V (Table 1).

2.1.3. Preparation of silver-doped titanium–vanadium thin films

An additional solution was required to introduce the silver into the thin films. The precursor reagent used was silver nitrate and

Table 1
Molar ratio used to produce mixed oxide thin films.

Reagents	100Ti	75Ti–25V	50Ti–50V	25Ti–75V	100V
Titanium isopropoxide	1.00	0.75	0.50	0.25	0.00
Vanadium oxytrisopropoxide	0.00	0.25	0.50	0.75	1.00
2-Propanol	81.81	79.04	76.27	73.50	70.75
Hydrochloric acid	8.14	7.87	7.59	7.32	7.04
De-ionized water	1.00	1.00	1.00	1.00	1.00
Silver nitrate	2.95×10^{-3}	2.95×10^{-3}	2.95×10^{-3}	2.95×10^{-3}	2.95×10^{-3}

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