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Silver loaded WO_{3-x}/TiO_2 composite multifunctional thin films

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ABSTRACT

Multifunctional WO_{3-x}–TiO_2 composite thin films have been prepared by sol–gel synthesis and shown to be good visible light photocatalysts whilst retaining a desirable underlying blue colouration. The WO_{3-x}–TiO_2 composite thin films were further enhanced using silver nanoparticles synthesised *in-situ* on the surface from the photo-degradation of silver nitrate solution. Thin films were characterised using X-ray diffraction, Raman, Scanning electron microscopy and UV–visible spectroscopy and shown to photo degrade stearic acid, using white light $\lambda = 420$–800 nm.

1. Introduction

The "value added glass" market now makes up a large proportion of total global glass sales and is geared towards the development of much technology that involves the functionality of thin films on sheet glass. One very prominent thin film that has spawned a $500 M per annum "value added glass" product is TiO_2 and has the benefits of self-cleaning glass [1,2]. There are however many other functionalities for which "value added glass" products do and should exist. In modern times a window needs to function as much more than simply a window. While outside surfaces can be self-cleaning [3–9], inside surfaces can be functionalised to reduce energy loss [10,11]. Furthermore, there are aesthetic factors to consider, such as colour tinting, with blue films in demand as they are the most aesthetically desirable.

Much research has been invested into the alteration of the properties of TiO_2, in attempts to shift the band onset from the UV into the visible to enable better and more versatile self-cleaning coatings with potential applications in the healthcare field [12]. TiO_2 can be modified in many ways [3,7] including methods of doping metals [11,13,14], or non metals, into the lattice such as nitrogen [13,15–25] and sulphur [26–33].

TiO_2 based films have superb self-cleaning properties when exposed to UV light, WO_{3-x} films have controllable colour tints towards the blue region of the colour spectrum [34,35] and silver nanoparticles have both an antimicrobial, sterilising effect and an influence on TiO_2 allowing it to utilise lower energy light than UV, making the films visible light photocatalysts [13,25,36].

In this paper two composite films are shown to have multi-functionality. These films contain two or three different composite systems that synergistically interact to improve desired functionality. A simple sol–gel technique was adopted to treat glass slides to deliver functionality from different nano-composite materials encased within the thin film structure. The mixing of properties and functionality often has detrimental effects on otherwise unconnected properties, *e.g.* preparing self-cleaning glass that works with indoor applications though the addition of nitrogen or sulphur to the lattice tends to produce a material that, while activated by visible light, has a yellow tint [15,16,26,37,38] which is unsuitable for aesthetic reasons. The problem here is that if a material's band-onset has been shifted to absorb visible light, then the surface is by virtue of that fact, going to appear coloured. N-doping leads to a shift in band onset to absorb visible light with the aim of capturing as much of the visible spectrum as possible but starting from the blue end, the highest energy component of visible light. Many N-doped TiO_2 samples are reported to have a yellow colour [15,16,37,38], and are therefore unsuitable for commercial, "value added" glass. In contrast, a blue self-cleaning glass is highly desirable. A degree of controllability between the blue and the yellow is even more desirable as this allows subtle tuning of the transmittance, while maintaining the desired colour. Blue tints are more absorbing, whilst yellow are more transmitting. We report here the first set of multi-functional thin films by sol–gel techniques that are good self-cleaning indoor photocatalysts and have tuneable colouration towards the blue region of the spectrum.

2. Experimental methods

2.1. Thin film deposition

Sample WO_{3-x}–TiO_2 was prepared by dip coating glass microscope slides (VWR International 76×26 mm) in a sol prepared as follows.

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Titanium-n-butoxide (16.64 g, 0.0489 mol) was added to a solution of acetylacetone (2.45 g, 0.0245 mol) dissolved in butan-1-ol (31 cm^3, 0.4182 mol) and stirred (1 h). Distilled water (3.56 g, 0.1979 mol) dissolved in propan-2-ol (8.81 g, 0.1466 mol) was added to the pale yellow stirred solution and this was stirred further (1 h). Acetonitrile (1.627 g, 0.0396 mol) was added to the stirred solution, followed by the immediate addition of tungsten (V) ethoxide (10 g, 0.02444 mol) after which the cloudy orange sol was further stirred (1 h), before left to age overnight. Ethanol (30 cm^3) was added to the aged sol and stirred until no further tungsten ethoxide dissolved. The microscope slides were dipped into the sol for 45 s and withdrawn at a uniform rate of 120 cm min^{-1}. The slides were allowed to dry (5 min) and the process was repeated to obtain a second coating. The slides were then annealed in a furnace (500 °C, 1 h), resulting in the formation of a transparent blue film upon the slide surface.

Sample Ag–WO_{3-x}–TiO_2 was prepared in the same way as sample WO_{3-x}–TiO_2 but post-calcination, the slides were immersed in $AgNO_3$ solution in methanol (5×10^{-3} mol) and withdrawn at a speed of 120 min^{-1}. The Ag-coated slides were then irradiated under UV light (254 nm, 30 min); this rendered the film an orange-brown colour.

2.2. Characterisation techniques

X-ray diffraction was achieved using a Bruker-Axs D8 (GADDS) diffractometer, utilising a large 2D area detector and a Cu X-ray source, monochromated ($K_{\alpha1}$ and $K_{\alpha2}$) and fitted with a Gobble mirror with the sample flat on the bed. The instrumental setup allowed 34° in both θ and ω with a 0.01° resolution and 3–4 mm^2 of sample surface illuminated at any one time. Multiple Debye–Scherrer cones were recorded simultaneously by the area detector with two sections covering the 65° 2θ range. The Debye–Scherrer cones were integrated along ω to produce standard 1D diffraction patterns of °2θ against intensity. Scan data was collected for 800 s to give sufficiently resolved peaks for indexing. Raman was achieved using a Renishaw inVia Raman microscope, and UV–vis; transmission and reflectance measurements were achieved using a Perkin Elmer λ950. Scanning electron microscopy was performed using secondary electron imaging on a JEOL 6301 field emission instrument with attached Oxford instruments energy dispersive X-ray analysis spectrometer. Samples were carbon coated prior to imaging to reduce charging effects and images were taken at 15 KV. A PerkinElmer Lambda 25 UV/visible spectrometer was used to measure UV–visible absorption and transmission spectra within the range of 1000–200 nm, yielding information on the band onset, the colour and the thickness of the films. Hardness tests were conducted using an HB pencil, stainless steel scalpel and diamond tipped pen and adhesion tests were performed using Scotch™ tape. Chemical durability was assessed by immersion in acetone, isopropyl alcohol, ethanol, dilute HCl (2 M) and NaOH (2 M), for a period of 2 h.

Functional testing was carried out using water contact angle measurements on a First Ten Angstroms, FTA 1000 contact angle measurement system. Samples were measured both prior to and post irradiation by white light with a drop of deionised water ~8.5 μL dispensed by gravity from a gauge 27 needle and photographed side on. The photo-destruction of stearic acid was used to assess the photocatalytic properties. A drop of saturated stearic acid (room temperature) in methanol was applied to the surface of the films and allowed to dry leaving a greasy residue. The carbon–hydrogen vibrational stretches in the stearic acid residue were monitored over time using IR spectroscopy using a PerkinElmer Fourier transform infra-red RX I Spectrometer within the range of 3000–2800 cm^{-1}. The substrates were exposed to different lighting conditions for a period of time between IR spectroscopy measurements. The lighting used was a UV light source (16 W Uvitec 2×8 W bulbs) and a white light source (GE Lighting 2D fluorescent GR10q-835 White 28 W), source details of which have been reported previously [15,26].

3. Results and discussion

The films appear to be blue in colour and have clean smooth surfaces except at the edge of the slide where the sol was absorbed. The silver loaded samples have a yellow/orange appearance on top of the underlying blue colour. All characterisation measurements were performed on the uniform central region of the films. The films were well adhered to the surface and resistant to scratching from all but a diamond tip pencil. The films were resistant to both acid and base at 2 M concentrations (Fig. 1).

3.1. UV–visible spectrometry

The transmission spectra, Fig. 2a, shows that both films have a high level of transparency. Sample WO_{3-x}–TiO_2 has a slightly higher transparency than sample Ag–WO_{3-x}–TiO_2 which is due to the presence of the silver nanoparticles on the surface of the films in sample Ag–WO_{3-x}–TiO_2. A high transmission is important for glass window coatings as is a fairly uniform response to visible wavelength light. Typical window glass has a transparency of >85% in the visible whilst bodytinted glass is typically between 60 and 80%.

Tauc plots, [39,40] Fig. 2b, allow for the estimation of the band onset and show a minimal shift in the band onset with the application of the silver nanoparticles to the surface of the WO_{3-x}–TiO_2 composite films. Silver has been shown in previous studies to shift the band onset of the titania, as well as having an antimicrobial effect leading to a synergistic relationship for antimicrobial applications [13,25].

Colour analysis showed Lab* coordinates as follows: sample WO_{3-x}–TiO_2, L = 89.00, a* = −1.69, b* = −10.49, dominant wavelength = 473 nm; sample Ag–WO_{3-x}–TiO_2, L = 77.14, a* = −0.31, b* = 2.47, dominant wavelength = 569 nm. The b coordinate that measures the blue/yellow colour shift shows a significant shift, from blue to yellow for the silver nanoparticle adorned films. The dominant wavelength is red shifted between the two samples. Thickness measurements showed that the films were 185(5) nm thick.

3.2. Scanning electron microscopy

The tungsten–titania composite film, sample WO_{3-x}–TiO_2, appeared to have a slightly mottled surface, with nodules which can be attributed to the tungsten (Fig. 3). This is in contrast to the unmodified titania film

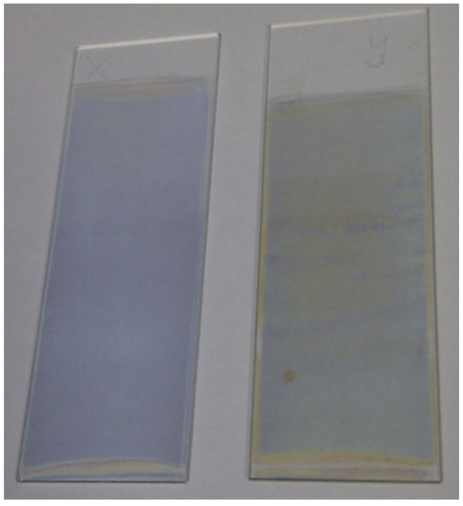

Fig. 1. Photograph of the two different films: on the left, calcined WO_{3-x}–TiO_2 composite films, on the right, Ag–WO_{3-x} TiO_2 composite films.