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Photoactive and antibacterial TiO_2 thin films on stainless steel

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Abstract

This paper describes an innovative method to achieve highly photoactive and antibacterial titania thin films on stainless steel by a novel combination of flame-assisted CVD (FACVD) – to deposit silica, and thermal APCVD – to deposit titania. We compare the chemical and structural characteristics, and photocatalytic activities of thin films of titania deposited onto stainless steel using APCVD from two different precursors. We show that the silica layer acts as a barrier to prevent the deleterious effect on photoactivity of iron and chromium from the substrate, and in particular, we show that the interaction of the precursor chemistry with the steel surface influences the structure of the films. The films were analysed using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and secondary neutral mass spectrometry (SNMS). Photocatalytic activity of the coatings was determined by the destruction of stearic acid layers, monitored using FT-IR spectroscopy. Studies show selected films to be effective as antibacterial coatings against *Escherichia coli*, with antibacterial performance comparable to reported values of TiO_2 on other substrates. The shape-forming capabilities and mechanical robustness of steel make it an ideal substrate for the exploration of new applications of photocatalysis. Applications of this technology include water purification, air cleaning, self-sterilizing and self-cleaning surfaces such as those used in hospitals or food preparation.

Keywords: Titanium dioxide; Photoactivity; Antimicrobial; Stainless steel; APCVD

1. Introduction

In recent years titania has received increasing attention as a photocatalytst due partly to the large-scale commercialisation of self-cleaning glazing products. These products utilise a well-adhered, nanocrystalline thin film of titanium dioxide – invariably deposited by an APCVD method – for the photo-oxidation of organic debris from the surface of the glass while also increasing the hydrophilic nature of the glass surface which aids the removal of contaminants via washing with water [1,2].

The use of titania as a biocide was first demonstrated by Matsunaga et al. in 1985 [3]. Subsequently there have been a number of papers reporting disinfection of bacteria, viruses and other pathogens by photoactive titania. Most of this early work utilised suspensions of titania to investigate its anti-pathogenic properties [4]. More recently titania as a thin film has been examined for biocidal activity with the substrate in variably glass [5–8].

Utilising stainless steel as the substrate for titania film growth, opens up many more potential applications owing to its physical properties, yet in comparison to coating on glass, the coating of steels with TiO_2 and related materials is still in its infancy. Reports of the deposition of titania onto stainless steels in the literature are limited, but include reference to techniques such as: electrophoretic deposition [9,10], anodic spark deposition (ASD) [11], the sol–gel method [12], low pressure metal organic CVD (MOCVD) [13], and atmospheric pressure MOCVD [14]. Only in some of this work was the photocatalytic activity of the films commented on [9,10,12].

Potential applications for photocatalytic titania on steel include self-cleaning surfaces for use in architecture and construction, water purification. The shape-forming properties of stainless steel also lend it to many further applications that may utilize another property of photocatalytic titania — as an anti-microbial coating making self-cleaning/sterilizing hospital equipment, anti-microbial coatings for inclusion in air-conditioning units and ducting or kitchen appliances a real possibility.

In this work we report the deposition of titania onto stainless steel by APCVD using two different precursors. Flame assisted CVD (FACVD) – still a relatively new and innovative

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technique – was used to investigate silicon dioxide layers as potential barriers to diffusion of contaminants from the stainless steel substrate. FACVD is an open air deposition process and as such requires little or no additional substrate heating, making it an attractive technique for deposition onto substrates that are effected by high temperatures [15] (such as stainless steel). It is also potentially compatible with continuous, high volume applications such as the coating of glass or steel.

2. Experimental

The titania deposition was carried out using a horizontal cold wall APCVD quartz reactor and precursors delivered via bubblers. Details of this system are reported elsewhere [16]. The titania thin films were deposited onto stainless steel 304 L substrates of dimensions (160 × 60 mm, 0.75 mm thickness). The stainless steel substrates were cleaned prior to use by washing with warm water and detergent, then rinsing with water, isopropanol and finally distilled water, before being dried in air. For TTIP film growth the deposition temperature was varied from 450–650 °C and for $TiCl_4$ from 550–650 °C. The thickness of the films was controlled using deposition time, and determined by the interference colour fringes exhibited (selected samples were confirmed using edge on SEM). A titania film thickness of 156 nm ± 10 nm was used for all measurements reported here.

The silicon dioxide coatings were grown in a flame assisted CVD (FACVD) reactor. The precursor used to deposit the silicon dioxide was tetraethylorthosilicate (TEOS). Details of the FACVD reactor and its operation have been previously reported elsewhere [15]. The thickness of the silicon dioxide layers were controlled by the number of passes of the substrate under the flame, two silicon dioxide thicknesses are reported here — 4 passes (30 ± 2 nm) and 16 passes (120 ± 8 nm).

Raman spectrometry was performed using a Renishaw 1000 spectrometer using a 514 nm wavelength. The surface morphology was investigated using scanning electron microscopy (Philips XL30 FEGSEM). X-ray photoelectron spectroscopy was performed on a Thermo VG Scientific spectrometer using aluminium radiation and the spectra interpreted using the XPS software package — Casa XPS. The photocatalytic activities were determined by monitoring the destruction of stearic acid layers using FTIR spectroscopy. The bioactivity testing used was a modification of the standard test described by BS EN 13697:2001. The procedure has been described in detail elsewhere [17]. In brief this involved pre-activation of the sample using UVA radiation (2.24 mW cm^{-2}, 24 h), application of the bacterium (in this case *Escherichia coli*) onto the samples, then exposure to the same UVA radiation for timed intervals. The bacteria were re-suspended in de-ionised water and a viability count performed by serial dilution and plating and incubation (37 °C, 48 h) on a nutrient agar in triplicate. Each experiment was performed in triplicate.

3. Results

Thin films of TiO_2 were deposited using $TiCl_4$ and ethyl acetate, and TTIP. Both precursors produced films of high quality, and demonstrated excellent adhesion to the substrate. The TiO_2 films were completely unaffected by the Scotch Tape test and maintained adhesion to the substrate after bending the substrate through 180°. Films grown using TTIP proceeded with a faster growth rate than those grown under similar conditions using $TiCl_4$ and ethyl acetate.

3.1. Structural determination

Fig. 1a shows the structures of the TiO_2 films deposited directly onto stainless steel — determined using Raman spectroscopy. It was found that the film deposited using TTIP yielded peaks at 144 cm^{-1}, 398 cm^{-1}, 515 cm^{-1} and 639 cm^{-1} corresponding to anatase TiO_2, and the $TiCl_4$ film yielded two peaks at 446 cm^{-1} and 610 cm^{-1} corresponding to rutile. XRD analysis also confirmed the TTIP film to be anatase and the $TiCl_4$ to be rutile. A further peak at around 670–700 cm^{-1} was observed in the $TiCl_4$ film. Previous studies have suggested that this peak could be due to iron and chromium oxides [18]. The Raman and XRD results interestingly suggest that the structure of the TiO_2 films deposited directly onto stainless steel may be determined by precursor selection and careful control of conditions; such that either anatase or rutile may be selectively deposited.

Of further interest is the occurrence of rutile at relatively low deposition temperatures, since thermal APCVD using glass substrates at these relatively low temperatures usually results in the growth of anatase exclusively. Rutile is commonly formed at much higher temperatures. The phase transition from anatase to rutile using thermal APCVD has been reported as occurring between 700–1100 °C [19].

Fig. 1b shows Raman spectra of a TiO_2 film after having deposited a SiO_2 layer using FACVD. Here it was observed that both films – i.e. regardless of precursor – were anatase. In both cases (for TTIP and $TiCl_4$ films) the Raman peaks for the TiO_2 deposited onto silica were noticeably more intense, sharper and smoother, and are indicative of better crystallisation [20]. These results suggest that by effectively ‘masking’ the influence of the substrate, the nucleation and growth characteristics of the film are altered enough to prevent the deposition of rutile from $TiCl_4$. Thus it seems that the observations are a careful interplay between precursor chemistry, our reaction conditions and perhaps the particular crystalline conditions present on the stainless steel surface.

3.2. Surface morphology

The morphologies of the films were examined using SEM. It was observed that the films deposited onto stainless steel had similar morphologies, in spite of being grown under different conditions using different precursors. The grains in both films were fairly spherical and relatively homogeneous in size. The TTIP film was more densely nucleated, but had a smaller grain size, whereas the $TiCl_4$ film had fewer, but larger nuclei. This fitted well with observations made during the growth of the films, where we observed a slower growth rate for the $TiCl_4$ films in spite of the deposition temperature being 150 °C higher than that employed when using TTIP (650 °C compared to