Aerosol assisted chemical vapour deposition of hydroxyapatite-embedded titanium dioxide composite thin films

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Abstract

This report describes the first Aerosol Assisted Chemical Vapour Deposition (AACVD) of photocatalytic titanium dioxide thin films embedded with synthetic hydroxyapatite, [$Ca_{10}(PO_4)(OH)_2$], nanoparticles. The hydroxyapatite nanoparticles were prepared using a low temperature continuous hydrothermal flow synthesis method; analysis of the hydroxyapatite powder showed that it was phase pure and that the as-prepared material was made up of nano-needles as expected. The nanoparticles were then embedded into TiO_2 coatings using the AACVD technique by suspending them in a solution of the titania precursor (titanium tetra-isopropoxide). Results showed that the hydroxyapatite, although present in very low concentrations in the coatings (not detectable by XRD or Raman spectroscopy), heavily affected their morphology, depending on their concentration in the precursor solution. Tests of the photocatalytic activity of the composite films showed that the inclusion of the hydroxyapatite led to an increase in the photodegradation (up to 50 % higher for methylene blue degredation) and that the materials were photostable.

This study shows that TiO_2 coatings embedded with hydroxyapatite nanoparticles have potential as highly efficient photocatalysts.

Keywords: hydroxyapatite, titanium dioxide, chemical vapour deposition, photocatalysis.

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Introduction

Photocatalytic materials are of interest due to their potential application for environment remediation and for self-cleaning structures. Under appropriate light irradiation, such materials can generate active species (electrons (e^-), holes (h^+), reactive oxygen species (ROS)), which can degrade organic molecules, including pollutants [Rauf, 2009]. Titanium dioxide (TiO_2) is the most common photocatalytic material and can exist in three different forms – anatase, rutile and brookite. The anatase form is particularly efficient as photocatalyst, with a band gap of 3.2 eV [Makwana, 2016]. TiO_2 can also be mixed / combined with different compounds, in multiphase systems as a route to achieving simultaneous multifunctional properties. For example, there are literature reports of TiO_2 combined with ZnO, PbO, SnO_2 or SiO_2 where the presence of the additional phase led to higher photocatalytic activity and/or photoactivity using a visible light source [Rajbongshi, 2014; Bhachu, 2014; Chadwick, 2014; de Chiara, 2015]. Improved and/or additional functional properties were also achieved with the incorporation of nanoparticles (NPs) into a titanium dioxide matrix; in the majority of cases, such composite systems were prepared using preformed metallic NPs, such as Au, Ag and/or other noble metals [Pedrueza, 2011; Kowalska, 2015; Li, 2016].

Hydroxyapatite (HAp), [$Ca_{10}(PO_4)_6(OH)_2$], is a calcium phosphate mainly known for its applications in bone replacement [Kolmas, 2016]. Literature data, however, suggests that some forms of HAp also have photocatalytic activity [Nishkawa, 2003; Piccirillo, 2013]; moreover, its combination with TiO_2 looks particularly promising; TiO_2-HAp biphasic composites have been shown to possess superior photocatalytic activities compared to the corresponding individual phases [Giannakopoulou, 2012; Anmin, 2006; Mitsionis, 2011]. Despite the large volume of literature on the photoactivity of titania-based multiphase films, to the best of our knowledge, no study has ever looked at photocatalytic properties of HAp-embedded TiO_2 films.

Hydroxyapatite can be made via a number of ways such as batch co-precipitation or flow methods [Sadat-Shojai, 2013]. In flow methods such as Continuous Hydrothermal Flow Synthesis (CHFS), supercritical water can be used as a reagent to drive the rapid synthesis of HAp [Chaudhry, 2013], as well as a wide range of metal oxides [Kriedemann, 2015; Naik, 2015; Litwinowicz, 2014; Dunne, 2014]. CHFS made HAp nanoparticles and doped variants were also prepared [Chaudhry, 2008; Chaudhry, 2013; Gimeno-Fabra, 2015]. More recently, lower temperature flow methods for HAp nanoparticle synthesis have also been developed which do not require high pressures [Anwar, 2014].

TiO_2 thin films for photocatalysis or other applications can be prepared using several methods [Blanco, 2015; Espino-Estévez, 2015; Lubas, 2014; Simonsen, 2012], including Chemical Vapour Deposition (CVD). The Aerosol Assisted Chemical Vapour Deposition (AACVD) technique in particular, is very versatile for the synthesis of TiO_2, as by using appropriate deposition solvents and process temperatures, it has been possible to tailor phase composition [Edusi, 2012]; moreover, different deposition precursors can affect the morphology of films [Romero, 2014]. NP-containing multiphasic TiO_2-based coatings can also be deposited using the AACVD process [Palgrave, 2006; Bhachu, 2014].

Herein, we report the synthesis of a composite coating of HAp-embedded in a TiO_2 matrix (HAp@TiO_2) using the AACVD technique. HAp nanoparticles were first prepared using a plastic flow reactor and then the freeze dried HAp powder was mixed at different loadings with a Ti-precursor (in toluene solution) that formed the feed for the AACVD process; this resulted in needle like HAp being embedded in TiO_2 films. The deposited thin films were characterised using several analytical techniques such as powder X-Ray Diffraction (XRD) and electron microscopy, to assess their composition and morphology. The photocatlytic activity of the coatings was also evaluated, to see whether the inclusion of HAp nanoparticles had any effect on such properties.

Materials and methods

Preparation of HAp NPs

HAp NPs were prepared using a continuous plastic flow synthesis (CPFS) reactor as described elsewhere by Anwar et al. (Figure 1) [Anwar, 2014]. This simple, single step synthesis method was used for HAp synthesis under near ambient conditions, with affordable and readily available reagents. The CPFS system consists of two HPLC Gilson pumps (Gilson Model 307 Pumps with 25 SC Pump heads). The first and the second pumps (P1 and P2) supplied the calcium and phosphate precursors respectively. The two feeds met in a 1/4’’ tee and the resulting mixture flowed through a first coil made of 9 m of 1/4’’ PTFE tubing (Polyflon, UK), which was submerged in a hot oil bath. Upon exiting the first coil, the product flowed through a second coil, made of 2 m of 1/4'’ PTFE tubing submerged in an ice bath. The product was collected at the exit of the second coil. Both pumps P1 and P2 were set at a flow rate of 12.5 mL/min, resulting in a combined outlet flow rate of 25 mL/min. The residence time in the first coil, i.e. the time between the mixing of the two precursor feeds and the entry of the product in the second coil in the ice bath, was 5 minutes. The residence time in the second coil was ca. 1 minute.

The samples were prepared by setting the oil bath temperature to 90 °C with P1 pumping a solution of 0.55 M calcium nitrate hexahydrate and pump P2 delivering a solution of 0.3 M ammonium phosphate dibasic. Ammonium hydroxide was added to both precursor solutions (2 vol% for calcium source and 7 vol% for phosphate source) to obtain a product with a pH > 9. All chemicals used were ACS reagent grade and purchased from Sigma Aldrich (Dorset, UK). The temperature at the outlet of the first coil was of 80 °C and of 15 °C for the second coil. The nanoparticles from the product slurry were recovered by centrifugation (model Sigma 4k-15) at 4300 RCF for 10 minutes. The concentrated sediment was re-dispersed in 50 mL of methanol and the centrifugation/re-dispersion steps were repeated twice. The cleaned wet solids were vacuum dried at 40°C overnight. A sample of the nanoparticles was then heat-treated at 1000 ^{o}C for 1 hour (heating ramp 10 ^{o}C/min) in order to then test it later via XRD for phase purity. Only the as-prepared samples were used to deposit films.

Film deposition

AACVD deposition experiments were performed using a cold-wall horizontal reactor; a detailed description of the apparatus was previously given [Piccirillo, 2007]. To deposit Titania coatings embedded with hydroxyapatite (HAp@TiO_2), the hydroxyapatite NPs were suspended in 40 mL of dry toluene (Aldrich); different quantities of NPs were used depending on the experiments (see Table 1). The suspension was sonicated with ultrasound for 2 hours, using a Sonic VCX 130 ultrasonic processor. After the sonication, titanium tetra-isopropoxide, TTIP (Aldrich), was added to the suspension.

An aerosol was generated from the suspension using an Asiamist 1308 ultrasonic humidifier; this was carried to the deposition reactor using N_2 (99.9 %, BOC) as inert carrier gas, with a flow rate of 1.0 L/min. As deposition substrate, float glass sheets were used (Pilkington Glass Plc.), with dimensions of 15 x 4.5 x 0.4 cm; the glass had a 50 nm thick SiO_2 layer to suppress the diffusion of the ions from the glass. The deposition temperature was 450 ^{o}C for all experiments; the substrates were heated through a Tempatron model 4800 thermostat, while the temperature was controlled by a Pt-Rh thermocouple. The depositions were continued until all the precursor solution was consumed, which normally took up to 50 minutes. The system was then cooled down to room temperature under a gentle N_2 flow. All experiments were performed in duplicate to check the reproducibility of the system.

Characterisation of powders and films

HAp powders were analysed with powder X-Ray Diffraction (XRD) and Raman spectroscopy to determine their composition. XRD was performed with a Bruker D4 Diffractometer (Cu Kα1, λ = 1.540598 Å). Raman spectra were collected with a Renishaw inViva Raman microscope, using a laser excitation at 514.5 nm. TEM images were taken using a JEOL JEM-2100 Transmission Electron Microscope (200 keV accelerating voltage).

The deposited coatings were characterised with XRD, using a Bruker D8 diffractometer, using filtered radiation on the reflection mode, with a glancing angle incidence of 1.5 ^{o}. Raman spectroscopy was also performed, using the same equipment described above. The crystallite size of the deposits was estimated from the full width half maximum (FWHM) of the (101) peak (2θ = 25.3 ^{o}) of the XRD patterns using the Scherrer equation [Dinnebier, 2008]; a shape factor of 0.9 was used. The morphology of the coatings was studies with Scanning Electron Microscopy (SEM), using a Hitachi S-4100, at 15 kV. Before the analysis, the films were covered with sputtered gold.

High resolution X-ray photoelectron spectroscopy (XPS) was performed on a Thermo monochromated aluminium k-alpha photoelectron spectrometer, using a monochromatic Al-Kα radiation. Survey spectra were collected at pass energy of 160 eV, whilst narrow scans acquired at pass energy of 40 eV. The data were analysed using CasaXPS^{TM} software and calibrated to the C(1s) signal at 284.1 eV, attributed to adventitious Carbon

Functional properties of the films

The photocatalytic activity of the deposits was tested by monitoring the degradation of methylene blue (MB) dye under UV light irradiation; a model XX-15 BL lamp (UVP, USA) (λ = 365 nm, irradiation density 1.86 mW/cm^2) was used as a UV radiation source. Samples of 1.0 cm^2 were placed in a 10^{-3} M methylene blue solution in closed transparent plates; samples were shaken in the dark for 30 minutes, to account for the MB adsorbed on their surface. At regular interval, the concentration of the MB in the solution was measured by monitoring the decrease in the UV absorption at λ = 660 nm, using a UV Nicolet Evolution 100 spectrometer. The degradation rate was expressed as C/C_0, i.e. the ratio of the concentration at a certain time (C) over the initial MB concentration (C_0). A control experiment was performed with a solution of MB only, to monitor the degradation of the dye due to just UV light exposure. To test the photostability of the coatings, two successive experiments were performed using the same films. To do this, at the end of the first test the sample was removed from the dye solution and washed using water and ethanol. It was then dried at room temperature and then reused for a second test.

Results

Characterisation of HAp NPs

Figure 2(a) shows the XRD patterns of the NPs, both as prepared and after a 1000 ^{o}C heat-treatment. Both patterns are similar to the HAp reference pattern (JCPDF 01-072-1243, see bottom of the figure); moreover, in both cases, no other phases apart from HAp can be detected. The data confirm that single-phase HAp was produced with the plastic flow system and that the 1000 ^{o}C heat-treatment did not lead to the formation of other phases, which suggests the material is stoichiometric (i.e. the Ca:P ratio of 1.67). As expected, PXRD data for the powder heat-treated at 1000 ^{o}C also suggested a much higher level of crystallinity.

In Figure 2(b) the Raman spectrum of the heat-treated powder is shown; peaks corresponding to 429, 590, 961 and 1045 cm^{-1} can be detected with that at 961 cm^{-1} being the most intense. These are signals are characteristic of HAp, due to the vibration of the PO_4 group [Demnati, 2012]. The data therefore confirm that HAp was the only phase present in the nanopowders.

TEM images of the HAp NPs are shown in Figure 3. They particles were found in the form of nanoneedles and nanoflakes, with diameters and lengths in the ranges ca.10 to 30 nm (average ca. 19 nm) and ca. 50 to 100 nm (average ca. 71 nm), respectively, the width increasing with length to maintain an elongated nature. The nanoflakes were polycrystalline in nature and formed along several elongated nanocrystals; some much smaller nanocrystals in the range 10 to 20 nm in length (average about 15 nm and a few nm thick) were also seen in the TEM images. It is suggested that HAp nanocrystals formed nanoflakes through a recrystallisation process (i.e., Ostwald ripening) and that the smaller nanocrystals were either from broken nanoflakes, or did not originally dissolve and recrystallize to form larger nanoflakes. In any case, there are only a few of these smaller nanocrystals, and they were a very small part of the total volume of HAp.

Characterisation of the coatings

Table 1 lists all the prepared samples. For all experiments, a uniform transparent and pale brown coating was formed on the bottom glass directly in contact with the heated graphite block and about three quarters of the substrate was coated. The films showed good adhesion, passing the Scotch tape test. The top glass, on the other hand, was uniformly covered by HAp NPs in a powdery form, which had no adhesion at all to the glass - indeed it could be removed by wiping with a towel. This was possibly due to thermophoresis taking place inside the deposition reactor, which has previously been reported for AACVD of NPs [Warwick, 2010]. Below the NP powder layer, film deposition could be observed only in some parts of the glass, with a very irregular pattern. Because of these characteristics, the coatings on top glass plates were not considered further, with all analyses and tests being performed on the bottom glass coatings.

Figure 4(a) shows the normalised XRD patterns of all deposits; it can be seen that in all samples, TiO_2 can be detected, in its anatase form (A). This is in agreement with literature, since deposition with TTIP under these experimental conditions leads to formation of anatase [Romero, 2015]. The data indicate that the presence of HAp NPs does not have an effect on the nature of the deposited compound. The only exception is sample **HAp1**, which does not show a clear diffraction pattern, suggesting that the deposit was amorphous. From Figure 4(a), no other phase could be detected in all samples. This, however, did not necessarily mean that NPs were not included in the coatings. Previous CVD experiments have shown that NPs can be incorporated in concentrations below the detection limit of XRD, and still affect the coating characteristics and properties [Qureshi, 2007; Warwick, 2010; Warwick, 2011].

The shape of the peaks of the diffraction patterns shown in Figure 4(a) indicates that the NPs present during deposition, had a significant effect on the crystallinity of the deposits. This was confirmed by the values of the crystallite sizes, estimated by application of the Scherrer equation to selected PXRD peaks [Dinnebier, 2008] and this is listed in Table 2. It can be seen that sample **HAp0** had crystallite size of ca. 36 nm, indicating a crystalline material. Sample **HAp1**, as already stated, had an amorphous structure; because of this, it was not possible to apply the Scherrer equation to the PXRD data. Sample **HAp2**, on the other hand, showed a more crystalline structure, but with much smaller crystallite than of sample **HAp0** (about 7 nm). Increasing the NP concentration in the deposition solution, led to a progressive increase to the crystallinity of the films; this could be seen by the higher values of the crystallite size for samples **HAp3**, **HAp4** and **HAp5** - 18, 19 and 27 nm, respectively.

All samples were also analysed with Raman spectroscopy to confirm their phase composition; the spectrum of sample **HAp3** is shown as an example in Figure 4(b). It can be seen that the peaks characteristics of TiO_2 (A) were detected, at 145, 198, 394, 513 and 636 cm^{-1}, in agreement with literature [Piccirillo, 2013]. The spectra of the other samples showed similar features (data not shown). As for the XRD data, the Raman measurement did not show the presence of any other phases; this confirmed that HAp NPs must be present in relatively low concentrations.

The microstructure of the films was studied using SEM, and Figure 5 shows the micrographs of all the coatings. It can be seen that the surface features of the deposits were heavily affected by the NPs used during the deposition, since there was a wide variation in microstructure between the coatings. The SEM image for sample **HAp0** (Figure 5(a)] showed a plate-like morphology, the plates appearing to be needles if viewed edge-on. The majority of these plates did seem to be edge-on to the surface, with the top and bottom faces perpendicular to the substrate. These plates had dimensions of hundreds of nanometres (400-600 nm) and thicknesses of around 100 nm. Growth / nucleation centres can be observed on the top and bottom faces of the plates, where new crystals can be seen to be growing. For sample **HAp1** [Figure 5(b)], a completely different morphology was observed, with rounded, irregular grains of dimensions in the range 300 to 600 nm, and no plate-like structure at all. Sample **HAp2** [Figure 5(c)] showed a completely different structure again, which was more similar to that of **HAp0**, with plates forming. However, these were much smaller in size (up to 300 nm long and tens of nm thick), and with a less-regular spatial arrangement – they were not all edge-on to the surface. Moreover, no smaller nucleation sites leading to the growth of smaller crystals on the upper and lower faces was observed. In sample **HAp3** (Figure 5(d)), a needle-like structure seemed to form, but these needles were in fact longer, thinner plates, and they appeared to be oriented with more faces perpendicular to the surface, leading to a more needle-like appearance. The plates formed herein were sharp and thin, with thickness similar to those seen for sample **HAp2**, but they were more elongated, up to 500 nm long.

Increasing the concentration of HAp NPs, led to further changes in the morphology, with a loss of the platy structure. Sample **HAp4** [Figure 5(e)] showed ovoid-shaped grains of ca 100-120 nm length, elongated in one axis but not plate-like, and with much smaller lengths. A similar morphology was observed for sample **HAp5** [Figure 5(f)], but with grains of an even smaller size in all dimensions.

These results suggested that in the pure TiO_2 films (**HAp0**), the grains formed as elongated plates, as is commonly seen in anatase, but that further grain growth occurred by crystallisation of smaller TiO_2 crystallites on the flat faces of these plates, and not on their edges. Hence, growth would be expected to continue in this axial direction, the plates becoming thicker rather than longer. It is not surprising that the flat nanoflakes of the HAp NPs would be attracted to these flat faces rather than the edges of the TiO_2 plates, depriving the TiO_2 of new nucleation sites for crystallisation and growth. This limits the growth of the TiO_2, and results in the small, irregular, non-platy grains as observed in sample **HAp1**. However, another effect was observed in samples **HAp2** and **HAp3**; it was suggested that in these samples, the HAp nanoflakes had completely covered the available nucleation sites on the faces of the TiO_2, causing crystallisation on the edges of the TiO_2 plates to now be favoured. This led to the extended thin plates as seen in these samples, with elongation in the plane of the plate, but no significant increase in thickness, as there was no growth allowed on the top and bottom faces. This process was more extreme in sample **HAp3**, with a greater quantity of HAp nanoflakes present. Then, finally there was another change in morphology, resulting the non-platy, smaller ovoid grains observed in samples **HAp4** and **HAp5**. The authours postulate that this was because the increased quantity of HAp nanoflakes that were now also blocking nucleation sites on the edges of the plates, preventing growth in this direction as well, effectively limiting growth in all dimensions and resulting the smaller grains as observed. No individual HAp nanoflakes were observed in any SEM images.

EDS data confirmed the presence of titanium and oxygen in all samples, but neither calcium nor phosphorus were detected; this indicated that HAp NPs may be present in the deposits with concentration below EDS detection limit.

To confirm the incorporation of HAp NPs into the TiO_2 coatings, XPS analysis were performed; samples **HAp1** and **HAp2** were not investigated further, considering their low crystallinity level. Figure 6 shows examples of the XPS spectra of samples **HAp0** and **HAp3**. Considering the titanium region [Figure 6(a)], two peaks can be observed for energies of 458.8 and 464.0 eV; these correspond to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ respectively [Yao, 2010; Luches, 1992]. No other peaks or shoulders were detected in this region, confirming a single titanium environment. Figure 6(b) reports the O1s region; it can be seen that two distinct environments are present: the first peak corresponds to the titanium dioxide, at 529.8 eV [Leinen, 1993]; a second peak, broader and with much lower intensity, was detected centred at 531.4 eV, could be attributed to the oxygen in phosphate group [Delichère, 1998]. This would confirm HAp presence. It has to be highlighted, however, that since the peak is so broad, it is likely to result from several different environments, including hydroxyls groups, both present in the HAp structure and/or from surface adsorbed water [Briggs, 1993].

Considering the Ca 2p energy region (Figure 6(c)), no signal at all can be observed for **HAp0**; for **HAp3**, on the other hand, two clear even if noisy peaks can be detected. These correspond to the binding energy of calcium in its +2 oxidation state – 347.4 and 350.8 eV, belonging to Ca $2p_{3/2}$ and Ca $2p_{1/2}$ respectively [Wang, 2015]. Samples **HAp4** and **HAp5** had profiles comparable to that of sample **HAp3**. Table 3 shows the elemental composition of such coatings. The phosphorus region was broad and very noisy (data not shown), indicating that small and unquantifiable amounts of the element were present. This is unsurprising, as it is known that phosphorous has a very low sensitivity factor in XPS and must generally be present in reasonable quantities (> ~2 at.%) in order to provide reliable quantification data [Briggs, 1993].

Photocatalytic activity

Figure 7(a) shows the results of the photocatalytic activity of some selected samples – **HAp0**, **HAp3**, **HAp4** and **HAp5**; the activity was measured by monitoring the degradation of MB. Sample **HAp0** was chosen as reference (i.e. unmodified TiO_2 prepared by AACVD), while samples **HAp3**, **HAp4** and **HAp5** were selected due to the detection of HAp NPs in the structure. Data in the figure showed that both samples **HAp3** and **HAp4** had higher photocatalytic activity than the unmodified TiO_2. Sample **HAp0**, in fact, only degraded about 50 % of the dye after 4 hour irradiation; both samples **HAp3** and **HAp4**, on the other hand, degraded 75% of the MB, a 50% increase in performance. In Figure 7(b) two successive tests with the sample **HAp3** are reported. It can be seen that the degradation efficiency is practically the same as for the first test, that the sample was very photostable and would be expected to be resuable and stable.

Discussion

The use of HAp NPs during TiO_2 deposition by AACVD showed to have a significant effect on the characteristics of the coatings; in fact, although the phase composition did not change, features such as crystallinity and morphology of the titania were heavily affected.

Regarding the crystal structure, overall the use of HAp NPs during the deposition led to a decrease in crystallinity of the titania coatings. It is interesting to highlight, however, that the effect was very different, depending on the concentration of the NPs. In fact sample **HAp1**, deposited with the lowest NP concentration, showed no crystallinity; this was in agreement with the more irregular structure shown by this film (Figure 5(b)). The use of higher NP concentrations corresponded to a higher level of crystallinity (see Table 2); even for sample **HAp5**, however, the average crystallite size was smaller than for unmodified TiO_2.

Such differences in morphology and crystallinity indicated different growth mechanisms taking place during the deposition. Without any NPs (sample **HAp0**), SEM showed smaller crystals nucleating on the top and the bottom of the platy crystals, but not on their edges; this led to them to grow thicker rather than longer and/or wider. The addition of a relatively small quantity of HAp NPs (sample **HAp1**) seemed to stop such nucleation and growth of TiO_2; a possible reason for that is that the NPs may have occupied the sites of TiO_2 nucleation / growth. This led to a coating with an irregular morphology and no preferential growth of TiO_2 along any particular direction. Higher NP concentrations (sample **HAp2**) seemed to prevent the nucleation even more and growth of TiO_2 on the top / bottom of the TiO_2 grains, but instead appeared to promote some growth of TiO_2 on the edges; this corresponded to the formation of thin elongated plates. This effect seemed even more enhanced with higher HAp NP concentrations; in fact, sample **HAp3** showed plates which were sharper and more aligned in the same direction. TiO_2 with similar morphology was previously observed in coatings prepared by AACVD (in presence of WO_3 nanoparticles) [Qureshi, 2007]. With even higher NP concentrations (sample **HAp4**), a structure with smaller grains of TiO_2 was observed; this could have been caused by an inhibition of the growth of TiO_2 in the lateral direction. This could be explained considering that all available sites for the HAp NPs on the top / bottom of the crystals are already occupied; hence, these NPs now also occupy sites at the edge, reducing the possibility for lateral growth of TiO_2. This occurrence seems even more enhanced for sample **HAp5**, which was prepared using higher HAp NPs quantities.

Although composite HAp-TiO_2 materials were previously prepared, this was the first time that HAp NPs were embedded into a TiO_2 matrix. The results herein showed that HAp@TiO_2 systems had better photocatalytic performance than single-phase TiO_2. This can be due the effect NPs have on titania structure, making it more textured; the synergic effect between the two materials, however, already observed in other biphasic systems, surely also played a key role [Anmin, 2006; Giannakopoulou, 2012]. It is interesting to note, however, that the improvement in the photocatalytic activity was never reported for such small amount of HAp in biphasic materials. This shows that HAp NPs in a TiO_2 coating was a very effective way to positively affect the photocatalytic activity. It is important to say, however, that the enhanced properties of the HAp@TiO_2 system were observed only in some cases, i.e. for samples **HAp3** and **HAp4**; this indicated that appropriate deposition conditions had to be selected to obtain materials with specific features.

XPS data show that calcium concentration, and hence also HAp NPs content, was comparable for samples **HAp3**, **HAp4** and **HAp5**. The different activities of the coatings, therefore, could be due to HAp concentration, but it was more likely to be linked to the way HAp NPs were included into the TiO_2 matrix. Indeed, literature reports suggest that for films including photocatalytic NPs, the photoactivity can be affected by several parameters and not just the concentration of the NPs [Warwick, 2011]. The smaller grains of sample **HAp5** may mean that HAp NPs were closer to each other; this may have favoured recombination of the e^-/h^+ charges and hence, have a detrimental effect on the photocatalytic activity [Liu, 2013]. Due to the low concentration of HAp NPs, it was not possible to detect them by SEM in the coating and see possible differences in their distribution in the films.

For a material to be used as a photocatalyst, its stability under light irradiation and possible loss in photocatalytic activity is a crucial parameter to be assessed. It is known that TiO_2 is generally a photostable material; in some cases, however, some decrease in the photoactivity has previously been seen where possible changes in titanium oxidation state and/or to the formation of oxygen vacancies on the surface of the material [Pan, 2013]. The results herein show that the incorporation of HAp NPs into TiO_2 coatings did not affect its stability; in fact the photocatalytic activity for sample **HAp3** did not decrease when the material was reused for a second test [Figure 7(b)].

Conclusions

Composite thin films of anatase titanium dioxide with needle-like hydroxyapatite nanoparticles incorporated in the structure were prepared using Aerosol Assisted Chemical Vapour Deposition. Characterisation of the films showed that the quantity of NPs in the precursor solution affected the morphology and crystallinity of the films. Choosing appropriate deposition conditions, allowed coatings with superior photocatalytic activity to be prepared; selected materials also showed photostability, i.e. no loss of photocatalytic activity was observed when reused. This work showed that the inclusion of HAp NPs into a TiO_2 matrix can improve performance as photocatalyst; hence the incorporation of HAp NPs with different shape/features should also be considered.

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Table 1. Description of the composition of the deposition solution of the samples.

Sample name	**HAp NPs quantity (mg)**	**TIIP quantity (mL)**	**HAp/Ti (mmol/mmol)**
HAp0	-	1	0
HAp1	50	1	14.75
HAp2	75	1	22.15
HAp3	100	1	29.50
HAp4	100	0.5	59.00
HAp5	120	0.46	77.95

N.B. In all cases the deposition solvent was dry toluene (40 mL).

Table 2. Crystallite size estimated with the Scherrer equation.

Sample name	**Size (nm)**
HAp0	36
HAp1	-
HAp2	7
HAp3	18
HAp4	19
HAp5	27

Table 3. Elemental composition of the coatings (atomic %).

Sample name	**Ti**	**Ca**
HAp0	17.58	-
HAp3	16.11	0.22
HAp4	16.36	0.12
HAp5	14.40	0.18