Hierarchically organized nanostructured TiO$_2$ for photocatalysis applications

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Abstract
A template-free process for the synthesis of nanocrystalline TiO$_2$ hierarchical microstructures by reactive pulsed laser deposition (PLD) is here presented. By a proper choice of deposition parameters a fine control over the morphology of TiO$_2$ microstructures is demonstrated, going from classical compact/columnar films to a dense forest of distinct hierarchical assemblies of ultrafine nanoparticles (<10 nm), up to a more disordered, aerogel-type structure. Correspondingly, the film density varies with respect to bulk TiO$_2$ anatase, with a degree of porosity going from 48% to over 90%. These structures are stable with respect to heat treatment at 400 °C, which results in crystalline ordering but not in morphological changes down to the nanoscale. Both as deposited and annealed films exhibit very promising photocatalytic properties, even superior to standard Degussa-P25 powder, as demonstrated by the degradation of stearic acid as a model molecule. The observed kinetics are correlated to the peculiar morphology of the PLD grown material. We show that the 3D multiscale hierarchical morphology enhances reaction kinetics and creates an ideal environment for mass transport and photon absorption, maximizing the surface area-to-volume ratio while at the same time providing readily accessible porosity through the large inter-tree spaces that act as distributing channels. The reported strategy provides a versatile technique to fabricate high aspect ratio 3D titania microstructures through a hierarchical assembly of ultrafine nanoparticles. Beyond photocatalytic and catalytic applications, this kind of material could be of interest for those applications where high surface-to-volume and efficient mass transport are required at the same time.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Nanostructured titanium oxide is a relevant material for a number of emerging energy and environmental technologies, such as dye sensitized solar cells (DSSC), organic photovoltaics (OPV), photocatalysis for direct hydrogen production and environmental remediation [1–4]. Two main research pathways have been followed, so far, in order to increase the efficiency of the above-mentioned technologies. Several studies have been devoted to shifting the absorption limit of the material in the visible range, searching for an increase in the reaction rate of photocatalysis and hydrogen production [5–7]. Another possible route is the maximization of the effective surface area as suggested by Rolison [8], underlying ‘the importance of nothing and the unimportance of periodicity’ in catalytic nano-architectures, where ‘nothing’ is the porosity at the nanoscale. The rationale behind these efforts resides in the basic argument that the efficiency of a surface mediated reaction increases with surface area. Ideally, one would like to have a full solar spectrum absorbing material with...
the highest specific surface area onto the smallest footprint. Photocatalysis is similar to photosynthesis in the conversion of photon energy to chemical, hence it seems reasonable to take inspiration from nature to enhance it, at least regarding the issue of maximizing the surface area. As an example, a forest possesses a hierarchical and self-organized structure starting from the single tree, with trunk, branches and leaves, up to the entire tight forest assembly. This superstructure maximizes the gaseous exchange with the atmosphere by maximizing leaf area, while at the same time optimizing leaf exposure to the sunlight. In a similar way, a hierarchical structure with a multiscale organization and with a large and accessible surface area would be desirable for photocatalytic applications. Neglecting dispersion-on-support methods [9], the most suitable approach is the assembly of nanoparticles, as small as possible, in a porous mesostructure. As far as titanium oxide is concerned, sol–gel synthesis of nanoparticles followed by sintering has been employed, generally yielding disordered films either with moderate porosity [10, 11], or in the form of an aerogel [12, 13]. Ordered structures, with an engineered pore architecture, have been obtained by using templating agents [14–17]. Besides the complexity of these approaches, the necessary removal of the templating agent may cause severe dimensional changes and surface area reduction [16]. Very recently, there have been reports on the template-free fabrication and photocatalytic activity of hierarchically organized nanostructured TiO$_2$ [18–21]. Although the employed techniques are very powerful in producing powders composed of highly engineered particles, characterized by a complex nanostructure, no reports have been issued on the growth of hierarchical TiO$_2$ thin films on surfaces for the functionalization of large scale areas. Typical thin film deposition techniques, such as CVD, sputtering and pulsed laser deposition (PLD), have also been tried with some excellent results in the doping issue but limited success in regards to surface area, since they tend to form essentially 2D films with limited surface area [22–25]. A few authors obtained columnar or sculptured thin films by sputtering [26], evaporation [27], or flame aerosol synthesis [28], with porosity determined by column diameter and spacing. In particular, Suzuki and Yang obtained high surface area TiO$_2$ and ZnO films, showing enhanced activity, by typical thin film techniques such as glancing angle deposition (GLAD) and MOCVD, respectively [27, 29]. Suzuki demonstrated an enhanced surface reaction efficiency of obliquely deposited TiO$_2$ thin films with variously shaped columns (e.g. zigzag, cylinder, and helix). He clearly showed that columnar thickness and spacing play an important role in the enhancement of the effective surface area. Notable examples of 3D film structure were demonstrated by Goosens et al., who obtained a fractal ‘forest like’ titanium oxide deposit by CVD [30]. In general, the active surface area of these films is limited to the sum of the exposed areas of individual columns or needles. Furthermore, inter-columnar spacing is hardly controllable to a large extent. We demonstrated, in the case of tungsten oxide [31], that PLD is a good candidate to address this issue thanks to its versatility in producing materials with defined structure and morphology. In a previous study [32], we performed comparative tests of photocatalytic activity of various surfaces, showing that PLD-produced TiO$_2$ films can be superior to anodized-annealed titanium surface and pure anatase powder.

In this communication we demonstrate the one-step, large scale and template-free production, by reactive PLD, of hierarchically organized nanostructured TiO$_2$. Our PLD bottom-up synthesis approach allows the assembling of ultrafine nanoparticles (<10 nm) in a hierarchical superstructure that resembles a ‘forest of trees’, without any use of templates or pre-patterning, over an area of more than 20 cm$^2$. By optimizing the PLD parameters, we were able to grow the single ‘tree’ structure and the entire ‘forest’ assembly, with tailored crystalline structure and morphology at the sub-micrometre scale. Noticeably, such architecture shows enhanced photocatalytic activity with respect to standard Degussa-P25 powder.

2. Experimental details

Pulsed laser deposition (PLD) of titanium oxide thin films was accomplished by ablating a pure Ti target with laser pulses from a KrF excimer laser (wavelength 248 nm, duration 10–15 ns, energy density 4 J cm$^{-2}$) at different dry air background pressures. PLD thin films were grown on both titanium and silicon substrates at room temperature. The effect of thermal treatment was investigated by 1 h annealing at a temperature of 400 ºC in air. X-ray thin film diffraction (Philips PW3020, Cu K$_\alpha$ radiation) and Raman spectroscopy (Renishaw InVia, excitation wavelength 514.5 nm) were used to characterize the oxide allotropic phases. Scanning electron microscopy images of the samples were acquired by a field emission SEM (Zeiss SUPRA 40). Photocatalysis tests on films deposited on Ti substrates were carried out by irradiating samples with a UV lamp (Xe 300 W HAMAMATSU Super Quiet). The light was focused by a converging lens; a quartz cell filled with water was used to absorb the IR component of radiation in order to avoid stearic acid sublimation. The radiation intensity was 0.2 mW cm$^{-2}$. Standardized tests were performed by covering the sample surface with a controlled amount of stearic acid diluted in hexane. The mineralization degree was determined at several irradiation times by FTIR (Nicolet 510P) measurements. Concentration abatement was measured by monitoring the IR peak corresponding to the asymmetric stretching mode (CH$_2$ group) at 2923 cm$^{-1}$. Optical microscope observations were performed to evaluate the distribution of stearic acid crystals and their time-dependent degradation. In order to elucidate how different hierarchical organizations affect film activity, care was taken to deposit a known mass of TiO$_2$. Precise control of sample mass was achieved by careful calibration of the deposition rate employing a quartz crystal microbalance (QCM) and HRSEM micrographs of the cross section of ‘ad hoc’ samples. In this way, the film density was calculated with respect to a bulk titanium oxide film of the same mass. Band gap energies were obtained by the Tauc Plot method from diffuse reflectance spectra acquired with a JASCO V570 (the spectrum of Degussa-P25 powder was used as reference). The BET surface area was analyzed by using the nitrogen-adsorption
method in a Micromeritics Tristar 3000 (USA). An ad hoc sample, about 10 mg in weight, was prepared for reliable measurements. All the samples were degassed at 120 °C for 4 h prior to the nitrogen-adsorption measurements. The BET surface area was determined by using the adsorption data in a relative pressure \((P/P_0)\) range of 0.05–0.3.

3. Results and discussion

Laser ablation in the presence of a reactive background gas pressure results in cluster formation in the ablation plume and thus in the production of nanostructured layers with a degree of porosity at the nano and mesoscale, which increases the specific surface area [33–35]. By controlling the deposition parameters it is possible to tune nanoparticle size [36] and chemistry up to the whole film mesostructure [37–39]. In order to explore the different hierarchical organizations attainable and their efficacy, nanostructured TiO\(_2\) thin films were deposited by PLD, ablating a pure Ti target in a synthetic air background pressure in the 10–100 Pa range. A decrease in film density of more than one order of magnitude with a consequent increase in surface area was observed (see below). In figure 1 we show SEM images of film cross sections at four different pressures. Film organization clearly changes passing from 10 to 40 Pa. While at the lowest pressure a 500 nm thick, dense columnar film develops, increasing the deposition pressure over 20 Pa causes cluster nucleation [34, 35] and the assembly of these in a characteristic ‘tree’ shape. This behavior is attributed to the interplay of gas-phase nucleation, reduced impact kinetic energy and an effective shadowing effect with increasing pressure. These findings suggest the possibility of varying ‘tree’ height (i.e. film thickness), diameter and spacing by changing deposition parameters, hereby defining film density and surface area.

The multiscale hierarchical organization of the film deposited at 40 Pa is clearly visible in SEM images at different magnification (figure 2), showing the whole film assembly (the ‘forest’) and the single columnar structures (the ‘trees’) composed of nanometric particles (the ‘leaves’). This same hierarchical organization is also observed in as deposited films revealing that annealing in air at 400 °C for 1 h does not significantly affect the film morphology at the meso and nanoscale (while it affects the film crystalline structure, as discussed below). An increase in film porosity occurs when increasing the deposition pressure; since the deposited mass was measured for each sample, we can calculate film density and porosity with respect to a film of the same total mass with bulk anatase density (100 μg over 1 cm\(^2\) would mean a 260 nm thick film). The sample deposited at 10 Pa shows about double the reference thickness indicating a 48% porosity. Increasing the deposition pressure yields a correspondent increase in porosity to 87% (20 Pa), 92% (40 Pa) and over 94% (100 Pa), i.e. void fractions typical of aerogels [11–13].

In figure 1 the dependence of film density on deposition pressure is shown (density of bulk anatase is 3.895 g cm\(^{-3}\)). Moreover, in contrast to randomly organized aerogels, our films exhibit a well defined vertical mesostructure persistent up to very high void fractions. Increasing the pressure up to 100 Pa yields a transition to disordered and mechanically non-stable samples (see figure 1(d)).

In parallel to the change in morphology, a well defined evolution in the film structure occurs. Raman spectroscopy indicates that as deposited films are prevalently amorphous or disordered, while after annealing in air at 400 °C for 1 h all spectra show crystalline signatures (figure 4(a)) over an amorphous background. The dominant TiO\(_2\) crystalline phase is anatase (Raman peaks at 143, 197, 399, 519 and 639 cm\(^{-1}\)), with an increasing rutile content (Raman peaks at 447 and 612 cm\(^{-1}\)) with increasing deposition pressure up to 100 Pa, where a predominantly rutile film is obtained. In this case, the intensity of the crystalline Raman peaks is very low and superimposed to large bands, suggesting a highly disordered structure and very fine grains (below 10 nm). From Raman spectra it is possible to identify the anatase-to-rutile relative content \((\text{AR} = \text{relative anatase percentage})\) in the film, as reported in [40]. No quantitative absolute estimation can be obtained due to the presence of
the amorphous phase. The estimations obtained confirm the
tendency from a mainly anatase film for low pressure deposited
films (10 Pa, AR = 100%), to a film with a predominantly
rutile crystalline content at high deposition pressure (100 Pa,
AR = 21.9%). In particular the sample deposited at 40 Pa
shows an anatase relative concentration of 86.7%, very close
to that of standard P25 powder. Moreover it is interesting
to note that 400 °C is well below the anatase–rutile transition
temperature, suggesting the presence of rutile nanocrystals
in as deposited samples, acting as nucleation centers even
at moderate temperature. X-ray diffraction (XRD) spectra
of annealed films confirm this evolution of the crystalline
structure (figure 4(b)). The XRD spectrum of the 100 Pa
sample did not show any significant signature due to the
reduced mass of the sample, nevertheless in [32] we showed
that in similar conditions a prevalently rutile phase is obtained,
in agreement with the Raman spectrum of figure 4(a). In
parallel to the morphology and crystalline structure, the grain
size also exhibits an evolution with deposition pressure. By
applying Scherrer’s formula to both (101) and (200) anatase
reflexes an average grain size was estimated of 20 nm for
the sample deposited at 10 Pa and of 10 nm for samples at
20 and 40 Pa. In the latter a weak and broad signal from the (110) rutile reflex is present, allowing a rutile grain size
estimate of about 6 nm. It has to be noted that a broader band
is present under the anatase (101) peak, also indicating the
presence of a distribution of much smaller, or very disordered,
crystalline domains. This is also witnessed by blue shift and
broadening of the anatase Eg Raman peak at 143 cm⁻¹ [40],
indicating a decreasing anatase crystalline domain size (ν =
143.6 cm⁻¹ and FWHM = 13 cm⁻¹ for 10 Pa versus ν =
146.3 cm⁻¹ and FWHM = 16 cm⁻¹ for 100 Pa), in good
agreement with the average grain size calculated from XRD
spectra. As already mentioned, comparison of SEM images
taken before and after annealing shows that no significant

Photocatalytic efficacy was tested by mineralization
(i.e. oxidation) of stearic acid. The reaction kinetics can
be described by a modified Langmuir–Hinshelwood model
in agreement with a surface reaction, as discussed, e.g. by

Figure 3. Nanostructured TiO₂ film density dependence on pressure.
Increasing deposition pressure causes a sharp drop in film density
due to gas-phase cluster nucleation, lower impact kinetic energy and
enhanced shadowing effect. Bulk anatase density is 3.895 g cm⁻³.
Figure 4. (a) Raman spectra of films deposited at increasing pressure and annealed in air at 400 °C for 1 h. A and R indicate anatase and rutile Raman peaks, respectively. A representative spectrum of the as deposited films is shown. (b) XRD spectra of films deposited at increasing pressure and annealed in air at 400 °C for 1 h. A, R and Ti indicate anatase, rutile and titanium (substrate) reflexes, respectively.

Al-Ekabi and Serpone [42],

\[
\ln \frac{C_0}{C} + k(C_0 - C) = k_r K t \quad (1)
\]

where \( C \) is the reactant concentration, \( C_0 \) the initial concentration, \( K \) is the adsorption coefficient of the reactant and \( k_r \) the reaction rate constant. Obviously, equation (1) is the sum of zero-order and first-order rate equations, and their contribution to the overall reaction depends essentially on the initial concentration \( C_0 \). When \( C_0 \) is very small, equation (1) reduces to the pseudo-first-order equation:

\[
\ln \frac{C_0}{C} = k' t \quad (2)
\]

where \( k' \) is the apparent first-order rate constant. Abatement curves are plotted in figure 5 for the various deposition pressures, both for as deposited (a) and annealed (b) films. Samples deposited at 100 Pa were not studied because their lack of mechanical robustness did not allow for repeated tests.

First-order rate constants for the as deposited and annealed films are calculated and plotted in figure 6. A sharp increase in degradation kinetics is evident going from 10 to 40 Pa deposition pressure, corresponding to the above-mentioned change in morphology. It is worth noting that the as deposited 40 Pa sample shows an activity comparable with that of P25 powder. Upon annealing, photocatalytic activity sharply increases in all cases, in particular that of the 20 Pa sample becomes comparable with P25’s, while even faster kinetics than P25 is observed for the 40 Pa annealed sample. Moreover, complete decomposition of the organic compound is achieved after as little as 5 h. In this case, plots of \( \ln(C/C_0) \) versus irradiation time (not shown) give a straight line for the 40 Pa film, while P25 powder and the 20 Pa film have an initial first-order character followed by a zero order; the 10 Pa film is not simply definable since it shows a mixed rate behavior. Annealing causes a net increase of activity of almost one order of magnitude for all samples. This effect may be ascribed to the increased crystalline order that has the beneficial effects of decreasing the number of defects,
Figure 7. SEM image of sample deposited at 40 Pa and annealed in air for 1 h at 400 °C after deposition of stearic acid, showing uniform wetting of the surface by the stearic acid.

4. Conclusions

A number of studies have been devoted to investigating the correlation between structural/morphological properties and the photocatalytic activity of titanium oxide films. As stated in the introduction, a hierarchically ordered assembly of nanoparticles is ideal for a number of reasons in photocatalytic and photovoltaic applications. In this study, we demonstrated the possibility to obtain, by proper control of pulsed laser deposition parameters, TiO₂ films with different organizations, density, particle size and specific surface area. Enhanced photocatalytic activity (stearic acid mineralization) was demonstrated with respect to standard P25 powder even for as deposited samples. Our ‘forest of trees’ arrangement favors deep penetration of organic molecules through the film and a very large surface area for light absorption and oxygen interaction. This is crucial, as the functional part of the light-absorbing material is the surface in direct contact with the molecules. Permeation of the organic compound through the film thickness is believed also to be fundamental for complete mineralization. This is interesting for TiO₂-based applications, since PLD allows deposition on inexpensive substrates, even plastics, kept at room temperature. Furthermore, single-step deposition of variable density films with good adhesion to the substrate is possible by PLD in a variable background pressure, an interesting perspective both for photocatalytic and advanced photovoltaic applications, substituting the time consuming deposition of different layers and lengthy annealing steps.

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