Preparation and photoactivity of nanostructured anatase, rutile and brookite TiO_2 thin films†

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Photoactive films consisting of pure anatase, brookite or rutile TiO_2 were prepared by dip coating from water dispersions obtained by using $TiCl_4$ as the precursor under similar mild experimental conditions.

TiO_2, both as a powdered photocatalyst or supported onto various types of materials, has been increasingly used in different environmental applications[1] and solar cell manufacture[2] because of its special physico-chemical properties. The immobilization of TiO_2 in the form of a thin film significantly reduces some of the drawbacks of practical application of heterogeneous photocatalysis; for instance the need to separate the powder or the tendency of the particles to agglomerate in aqueous dispersions.[3] Among the three polymorph TiO_2 phases, *i.e.* anatase, rutile and brookite, only the first two have been widely studied and their photoactivity tested and compared either as powders[4] or as thin films.[3,5] On the contrary, only a few recent papers dealing with the preparation of pure brookite powders[6] or films[7] can be found in the literature, and, to the best of our knowledge, no studies on the photocatalytic activity of brookite thin films have ever been published either in liquid–solid or in gas–solid systems. The scarcity of results is due to various reasons among which the most relevant is the difficulty of synthesizing pure brookite because it usually forms as a secondary minority phase along with rutile and/or anatase, depending on the experimental conditions used.

This work describes an easy way to prepare thin films of the three TiO_2 phases starting from aqueous dispersions of TiO_2 obtained by hydrolysis of $TiCl_4$. The photoactivity of the various samples was evaluated at room temperature by using the photodegradation of 2-propanol in a gas–solid regime as a probe reaction.

As described in previous work,[4c,d] photoactive powdered TiO_2 anatase samples were prepared under mild conditions by using an aqueous solution of $TiCl_4 : H_2O$ (1 : 50 v/v ratio) and boiling for 2 h. When the hydrolysis of $TiCl_4$ was performed by using a $TiCl_4 : HCl$ (37%) solution (1 : 50 v/v ratio), a mixture of rutile and brookite was obtained after 2 h boiling with a cooling reflux system. This mixture was allowed to decant and repeatedly washed with fresh water to separate rutile TiO_2 (**1**) as a precipitate. After sedimentation of the rutile, consisting of heavier and bigger particles, the surnatant dispersion (**2**) contained only

nanostructured brookite. The TiO_2 powders were dried under vacuum at 328 K and characterised by means of X-ray diffraction (XRD) and diffuse reflectance spectroscopy (see ESI,† Fig. S1 and S2).

Films of pure anatase, rutile or brookite were deposited on optically transparent microscopy glasses (75 × 25 × 1 mm) by immersing the supports in the corresponding dispersions and then withdrawing at a controlled rate (96 mm min^{-1}). It is worth noting that two different dispersions (containing a similar amount of solids) were used for rutile and brookite after their complete separation. The rutile film was obtained by immersing the support in a dispersion obtained after 0.5 h ultrasound treatment of the solid (**1**), while the brookite film was deposited using the dispersion (**2**). 10 deposition steps were performed in all three cases. After each coating, the films were dried at 298 K for *ca.* 0.5 h and subsequently calcined at 673 K for 3 h.

The films were characterised by XRD and scanning electron microscopy (SEM) observations. XRD patterns were obtained with a D8 Bruker X-ray diffractometer using Cu Kα radiation, a 2θ scan rate of 0.01° s^{-1} and a typical incident angle of 0.5°. SEM observations were performed using a Philips XL30 ESEM, operating at 25 kV, on specimens upon which a thin layer of gold had been evaporated. The thickness of the films was determined by an optical profilometer.

Fig. 1 shows XRD patterns of the three films. The diffractograms were recorded in the low angle incident mode to increase the sensitivity to the surface. The brookite film diffractogram shows
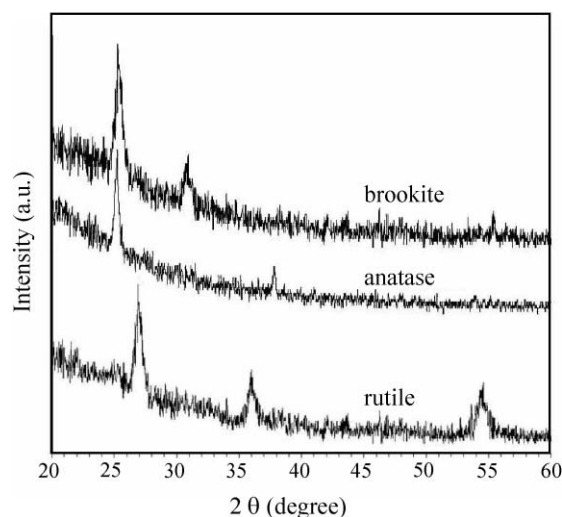
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Fig. 1 XRD patterns TiO_2 films, deposited in 10 steps, constituted of pure brookite, anatase and rutile phases.

peaks at 25.5° and 30.8° that are distinctive of the presence of brookite. The diffractogram of the anatase film shows peaks at 25.3° and 37.7°, due to diffraction from the (101) and (004) planes of anatase. The diffractogram of the rutile film shows characteristic peaks at 27.7°, 37.3° and 55.1°. The presence of some amount of amorphous TiO_2 in the films cannot be excluded.

Selected micrographs of anatase and brookite films are shown in Fig. 2. The anatase film (Fig. 2(a)) was more homogenous and the secondary particles were larger than those of brookite (Fig. 2(b)). The size of the particles was in the range 32–62 nm for anatase and 27–30 nm for brookite.

The thicknesses of the films were 40, 240, and 500 nm for rutile, brookite and anatase, respectively. It is worth noting that, although the experimental conditions under which the films were prepared were held constant as best possible (type of precursor, number of dip coating steps, kind of glass support, preparation temperature, *etc.*), the thicknesses of the three resulting films were very different. This finding could be related to the different properties of the dispersions used (adsorptivity onto the glass substrate and the self-coagulation property of TiO_2) and especially to the intrinsic physical and morphological characteristics (size, shape, specific surface area, surface hydroxylation, *etc.*) of the TiO_2 particles being supported (see ESI,† Table 1).

The photoactivity of the films was determined employing the photo-degradation of 2-propanol that has been widely described in the literature.[8a] The main reported intermediate product is propanone, which is furtherly oxidized to CO_2.[8b]

The photoreactivity runs were carried out in a gas–solid regimen in a cylindrical Teflon batch photoreactor (V = 0.05 l) equipped
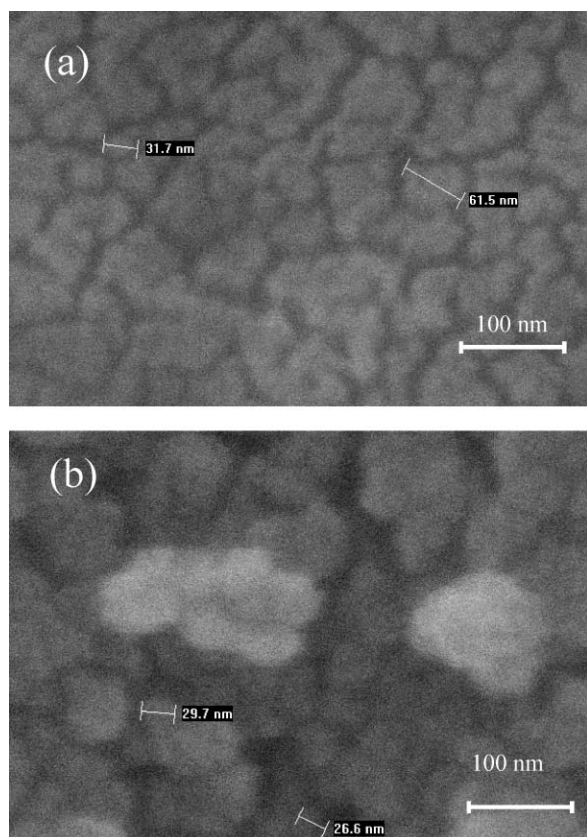
with a Pyrex window. The films were placed inside the photoreactor and were irradiated from the top using a 500 W medium pressure Hg lamp. The irradiance onto the surface of the films was 1.3 mW cm^{-2}. A water filter was interposed between the lamp and the reactor to cut the infrared radiation. The reacting mixture, obtained by bubbling O_2 in an aqueous solution of 2-propanol, was fluxed into the photoreactor. When the equilibrium concentration was reached the inlet and outlet valves were closed and the lamp was switched on. Samples of 500 µl were withdrawn at fixed intervals using a gas tight syringe. 2-Propanol and propanone concentrations were determined by means of a GC Shimadzu 17 A equipped with a HP-1 column and a FID detector using He as the carrier gas.

In Fig. 3 the ratio between the concentration of 2-propanol, C, at time t and the initial concentration, C_0, *versus* irradiation time is reported. The films based on anatase and brookite phases showed a good photoactivity and 2-propanol was completely degraded in *ca.* 4 h and 6 h for brookite and anatase, respectively. The rutile film revealed a scarce photoactivity and only *ca.* 40% of the initial concentration of 2-propanol was degraded after 7 h.

Fig. 4 shows the variation of the concentration of propanone during the photo-oxidation of 2-propanol. Studying the figure confirms that the brookite and anatase films were the most photo-active samples and propanone reached a maximum concentration after *ca.* 2–3 h before being subjected to degradation.

The presence of a less significant propanone concentration in the case of brookite suggests that propanone transforms more quickly into CO_2 and H_2O. It should be noted that, although the thickness of the anatase film was *ca.* twice that of brookite and the specific surface area of the powdered anatase supported onto the glass was significantly higher, the brookite film showed a higher photoactivity. This finding could be tentatively explained by hypothesising that only the very top surface photocatalyst particles are involved in the photoreaction and/or the light penetration depth is similar for both films.

In conclusion, despite the fact that one should be aware that it is very hard to present an accurate comparison among the three different phases, due to the difficulties of normalizing the quantity of photocatalyst onto the support and knowing the actual photoactive surface area of the films, the pure brookite film
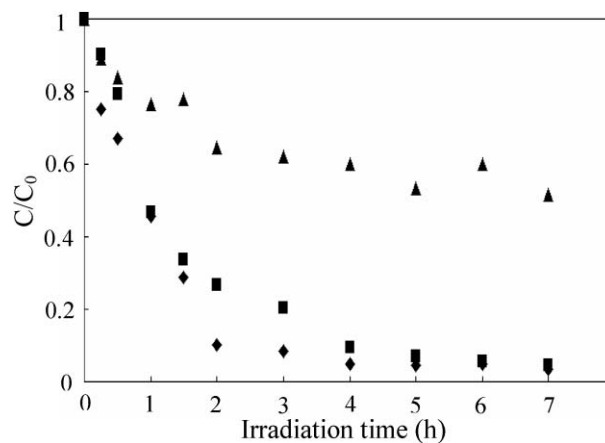
Fig. 2 SEM micrographs: (a) anatase film; (b) brookite film.

Fig. 3 Photocatalytic degradation of 2-propanol (C/C_0) in the presence of 10 step deposited films: (■) pure anatase; (♦) pure brookite; (▲) pure rutile. Initial substrate concentration: 60 mM.
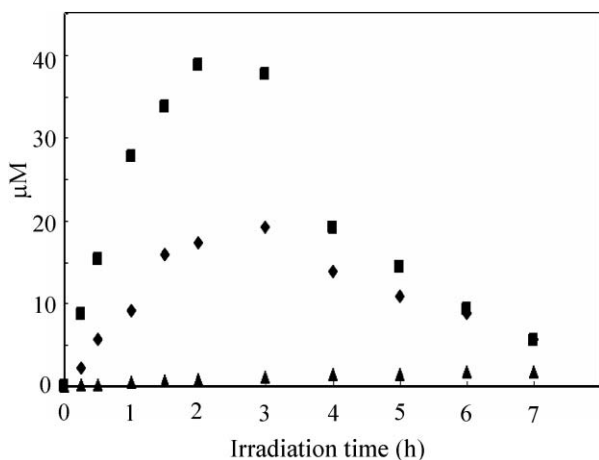
Fig. 4 Concentration changes of propanone in the presence of 10 step deposited films: (■) pure anatase; (♦) pure brookite; (▲) pure rutile. Initial 2-propanol concentration: 60 mM.

showed a significantly higher photoactivity, only partially justified by considering the lower size of the primary particles (see ESI†, Table 1).

Potentially useful future applications of these brookite films, prepared under very mild experimental conditions, can be foreseen because (i) the films did not deactivate even after long irradiation times and at least three runs showing similar results were carried out using the same sample, (ii) thermogravimetric analysis carried out on the brookite powders obtained from the dispersion used for the preparation of the film, showed a peak corresponding to the brookite–rutile phase transition at 1104 K (see ESI,† Fig. S3), indicating that brookite prepared with this method has a large field of thermal stability.

Further studies are in progress to characterize the brookite films better, optimizing some of the physico-chemical parameters influencing the photoactivity.

Notes and references

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