TITANIA INVERSE OPALS: AN INNOVATIVE PREPARATION METHOD WITH AN IMPROVEMENT IN THE MECHANICAL, OPTICAL AND PHOTONIC PROPERTIES

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Titanium inverse opals (IO) were prepared by two distinct infiltration approaches: (1) using a liquid precursor (LP-IO) and (2) with a suspension of TiO_2 nanoparticles (NP-IO). A characterization study was performed, including the study of the mechanical, optical and photonic properties. The samples were also characterized by SEM, TEM and X-ray diffractometry. The formation of a compact overlayer of TiO_2 in LP-IO samples, which was not seen in NP-IO samples, is assumed to contribute to detriment the optical properties. NP-IO samples showed also an improved mechanical stability.

Inverse opals have attracted considerable interest in the latest years due to their many interesting properties and applications, especially with the focus in electrochemistry [1] and photocatalysis [2]. Briefly, their structure can be described as the negative of opal colloidal crystals, face-centered cubic arrangements of sub-micron sized spheres. Because of the periodically variation in space of the refractive index of the material, they are a subclass of photonic crystals, materials with a stopband that forbids the propagation of photons within a certain energy range. Many materials are suitable for their preparation, but one of the most important ones is titanium dioxide, TiO_2, because of its high refractive index, low toxicity, low cost, among other desired properties [3].

The typical procedure for the production of inverse opals follows a bottom-up approach [4] and consists of a three steps process. First, an opal template is formed by the self-assembly of monodisperse spheres made commonly from polystyrene or polymethylmethacrylate. Then, if TiO_2 inverse opals are to be prepared, the template is usually infiltrated with a liquid TiO_2 precursor (LP-IO) such as titanium alkoxide; the precursor hydrolysis yields an opal in which the space between the spheres is filled with amorphous TiO_2 nanoparticles. In the last step, the sample is calcined to remove the polymeric template and crystallize the amorphous TiO_2. This method, however, involves the formation of a compact overlayer of titanium dioxide on top of the inverse opal structure, as shown in Figure 1, which disrrupts the photonic and photocatalytic properties, as it may block the light flow into the structure and impede the reactants, intermediates and products diffusion.

However, an improved method was developed, which uses a suspension of TiO_2 nanoparticles (NP-IO) in the infiltration step and shows many advantages.

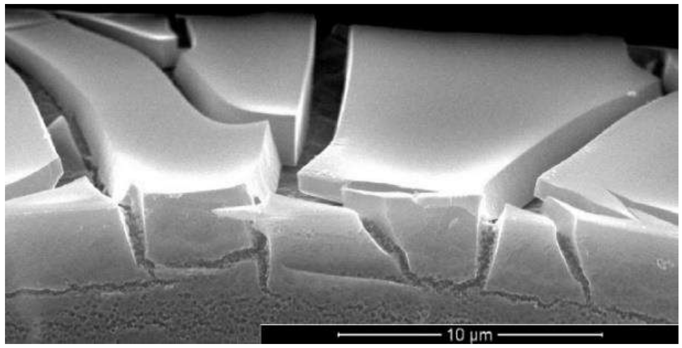

Figure 1: Scanning electron microscope micrograph (lateral view) showing the overlayer formed in TiO_2 inverse opals prepared by infiltration with a liquid precursor.

Therefore, TiO_2 inverse opals were prepared by two distinct infiltration approaches: one involved the use of a liquid precursor, and the other already synthesized nanoparticles. In both cases, the capillary deposition method [5] was used for the preparation of the opal templates.

To compare both types of preparation methods a thorough characterization study was performed, including the study of the mechanical, optical and photonic properties. The samples were firstly characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A rough surface texture and a thick overlayer were clearly visible in the LP-IO samples (Figures 2a and 3a), while the surface of NP-IO samples was more homogeneous and showed no overlayer (Figures 2b and 3b). TEM micrographies showed also a distinctive, elongated crystallite shape for NP-IO samples.

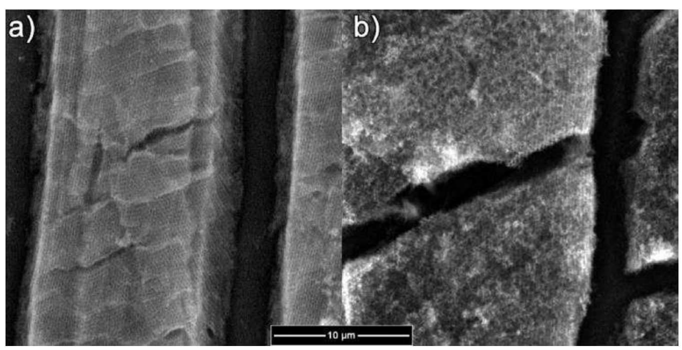

Figure 2: SEM micrographs of a top view for (a) a LP-IO sample and (b) a NP-IO sample.

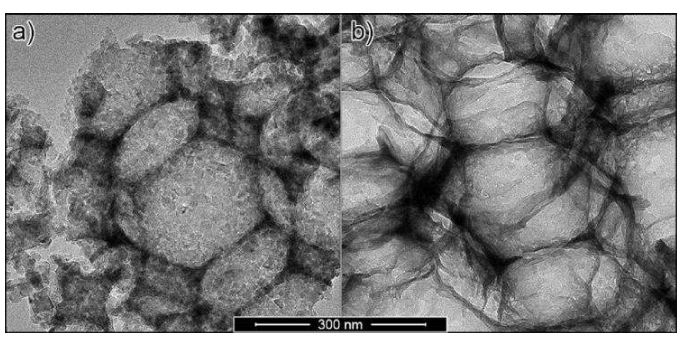

Figure 3: TEM micrograph at high magnifications of (a) a LP-IO sample and (b) a NP-IO sample.

X-ray diffraction patterns showed that anatase TiO_2 was the only crystalline phase present in both samples, and a slightly larger average crystallite size for LP-IO. Also, transmission spectra and reflectance spectra were obtained.

Adherence tests were performed according to an ASTM standard test, which assesses the adhesion of coating films to substrates by applying and removing pressure-sensitive tape over cuts made in the film. Figures 4a and 4b show a significant mass loss when performing the test over a LP-IO sample. Oppositely, it can be seen in Figures 4c and 4d, that the NP-IO sample results practically unaffected by the test, showing a highly improved mechanical stability, in particular, adhesion properties.

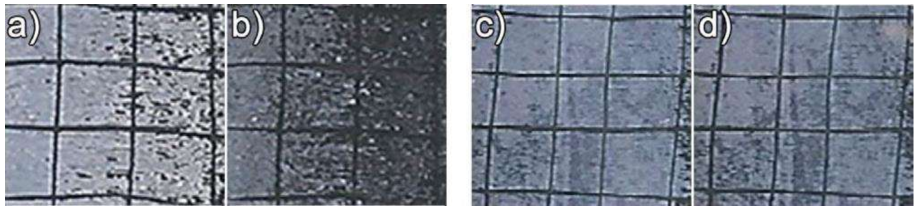

Figure 4: a) LP-IO sample before the test. b) LP-IO sample after the test. c) NP-IO sample before the test. d) NP-IO sample after the test. Each image encloses a circa 3.5×3.5mm^2 area.

To assess the photocatalytic activity of both samples, the degradation of methylene blue was evaluated. A remarkable increase in the rate constants was observed for NP-IO samples (Figure 5a), owing to the absence of the blocking overlayer, which may prevent a massive diffusion of methylene blue molecules towards the inverse opal structure. The result of performing consecutive degradation cycles can be seen in Figure 5b. NP-IO samples show a non-significant variation along three cycles. On the other hand, LP-IO samples show a considerable decrease, possibly due the poorly mechanical stability.

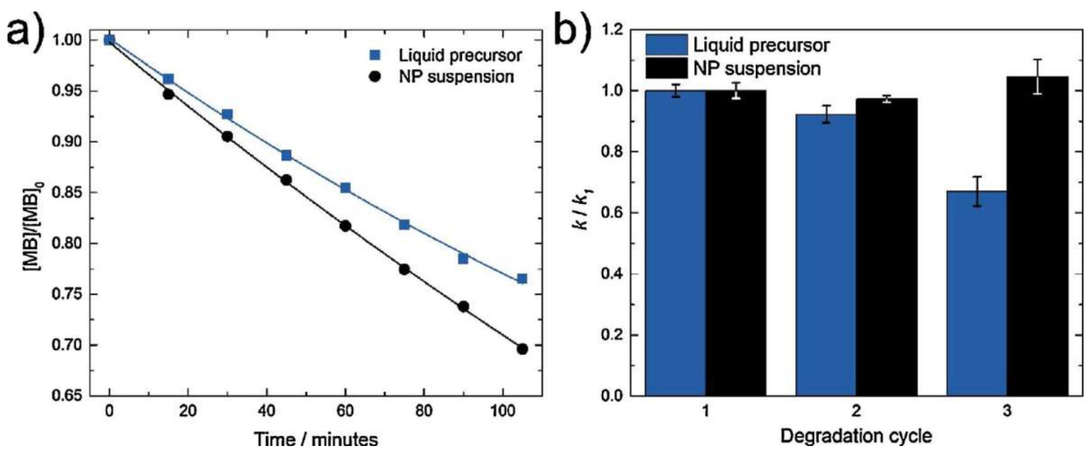

Figure 5: a) Photocatalytic degradation of methylene blue on both types of TiO_2 inverse opals. b) Three consecutive photocatalytic degradation cycles of both types of samples.

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