

Supplementary data

Photocatalytic performance of mesoporous TiO₂ films doped with gold clusters

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Porosity investigation:

Porous fractions of the templated films were obtained using the Bruggeman Effective Medium Approximation (BEMA) and optical properties of air and reference dense films. BEMA allowed the determination with very good accuracy of the relative volumetric fractions f_A and f_B of two A (air) and B (inorganic) mediums of known dielectric constants $\tilde{\epsilon}_A$ and $\tilde{\epsilon}_B$ within a volume unit of measured dielectric constant $\tilde{\epsilon}$ (porous film) as described in the following equation:

$$f_A \cdot \frac{\tilde{\epsilon}_A - \tilde{\epsilon}}{\tilde{\epsilon}_A + 2\tilde{\epsilon}} + f_B \cdot \frac{\tilde{\epsilon}_B - \tilde{\epsilon}}{\tilde{\epsilon}_B + 2\tilde{\epsilon}} = 0$$

This approach is only valid after the pyrolysis of the template. It also assumes that inorganic matrices of mesostructured films have optical properties similar to that of dense references, thus that they can be modelled with the dense reference film.

XPS measurements:

The working pressure was $< 5 \cdot 10^{-8}$ Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au4f_{7/2} line at 83.9 eV with respect to the Fermi level. The standard deviation for the BE values was 0.15 eV. The reported BE were corrected for the charging effects, assigning, in the outer layers where contamination carbon is still present, to the C1s line of carbon the BE value of 284.6 eV.^{1,2} Survey scans (187.85 pass energy, 1 eV/step, 25 ms per step) were obtained in the 0-1300 eV range. Detailed scans (58.7 eV pass energy, 0.05-0.1 eV/step, 100 ms per step) were recorded for the O1s, C1s, Au4f, Cl2p, Si2p, TiKLL and Ti2p regions. The atomic composition, after a Shirley type background subtraction³ was evaluated using sensitivity factors supplied by Perkin-Elmer.² Depth profiles were carried out by Ar⁺ sputtering at 3 kV with an Argon partial pressure of $5 \cdot 10^{-6}$ Pa. A specimen area of 2x2 mm² was sputtered. Samples were introduced directly, by a fast entry lock system, into the XPS analytical chamber. The assignments of the peaks was carried out by using the values reported in the reference textbook.^{2,4}

- (1) Briggs, D. & Seah, M. P. (1990) *Practical Surface Analysis - Second Edition*, ed. J. Wiley & Sons, New York, 543.
- (2) Chastain J. (1992) *Handbook of X-Ray Photoelectron Spectroscopy*, ed. Perkin Elemer Corp., Eden Prairie, MN.
- (3) Hirley, D. A. *Phys. Rev. B* **1972**, 5, 4709-4714.
- (4) NIST XPS Database, X-ray Photoelectron Spectroscopy Database 20, Version 3.0, National Institute of Standards and Technology, Gaithersburg.

Gold precursor influence on the mesostructure of crystallized TiO₂ films gold doped:

Assuming the films to be issued from a distorted bcc mesoporous lattice, it is possible to argue it is not the case as the 2D-SAXS pattern at low angle ($\beta = 10^\circ$) must present diffraction peaks, the TEM pictures present non-organized nanoporous structure and the SEM pictures (figure 9A) may present some hexagonal pores packing in contradiction to the supposed bcc mesophase.

A top-view mesopores ordination may not correspond to the mesophase present all over the film thickness.¹ Sanchez, Grosso and their collaborators presented the 2D-SAXS method to be the only straightforward and nonambiguous characterization technique of the mesoporous network structural periodic organization of thin films.² TiO₂ + 4 atom.% AuCl₃ is typical of an TiO₂ anatase distorted cubic structure (*Im3m*) annealed at 600°C with the typical (1-10) peaks in the [110] orientation with respect to the substrate (figure 6.D).³ The original 2D-SAXS pattern of TiO₂ + 4 atom.% Au₁₁³⁺ (figure 6.C) is attributed to the formation of an hybrid anatase/TiO₂ (B) from an amorphous TiO₂ matrix. Anatase and TiO₂ (B) are based on octahedral Ti^{IV} atoms but their respective lattice is different, the TiO₂ (B) phase is less compact (density 3.76 g cm⁻³) than the anatase lattice (3.89 g cm⁻³).⁴ It is reasonable to suppose that this difference of the lattice formation upon annealing involve a non-monodimensional shrinkage of the film to form a deformed cubic structure that differs to the commonly described *Im3m*. Additionally of the mesopore distortion induced by the crystal phase formation, the distortions induced by the migration of Au species and their aggregation to form Au nanoparticles occurs.⁵ The absence of peak on the 2D-SAXS pattern at low angle it is not the proof of the absence of bcc mesophase, a highly distorted bcc mesophase of HfO₂⁶ using KLE as template, developed by EISA method, and measured at low angle ($\beta \sim 5^\circ$) with a a synchrotron present 2D- SAXS pattern similar to the TiO₂ + 4 atom.% Au₁₁³⁺ one (figure 6.C) and correspond to disordered mesopores on TEM pictures. The 2D-SAXS pattern at high angle ($\beta = 90^\circ$) of TiO₂ + 4 atom.% Au₁₁³⁺ (figure 6.B) is a diffraction ring indicating a random orientation of mesostructure d domains parallel to the substrate plane, but this pattern presents a first ($S = 4.3 \text{ nm}^{-1}$) and a second ($S = 8.6 \text{ nm}^{-1}$) peaks that is the proof of an ordered mesostructure in the xy domain.⁷

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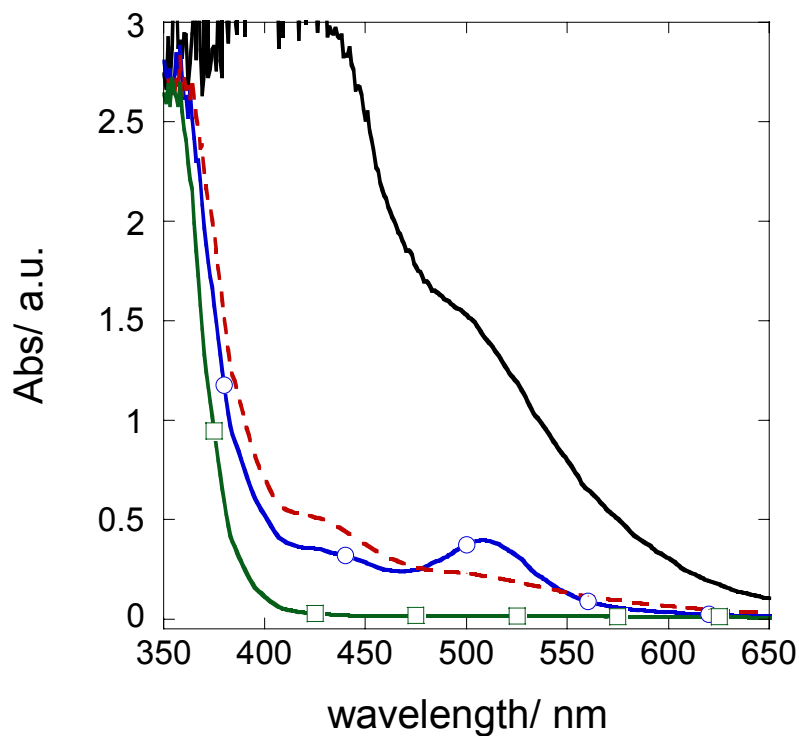


Fig. S1 UV spectra of solutions used for dip-coating to make pure TiO₂ (square), + 1 atom.% Au₁₁³⁺, (dashed line), 4 atom.% Au₁₁³⁺ (circles), + 10 atom.% Au₁₁³⁺ (virgin continuous line).