Hierarchical Porous TiO_2 thin films by soft and dual templating.

A quantitative approach of specific surface and porosity.

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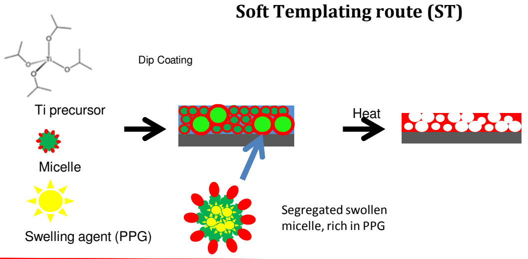
ABSTRACT

Hierarchical porous structures, with different pore sizes, constitute an important field of research for many applications. However, increasing the pore size results in the decrease of specific surface. There is a need to quantify and predict the resulting porosity and specific surface.
We have prepared hierarchical porous TiO_2 thin films either by surfactant templating (soft) or dual surfactant/microspheres templating (soft/hard). They all show narrow, bimodal distribution of pores. Soft templating route leads to very thin films showing high specific surface and bimodal porosity with diameters of 10 nm and 54 nm. Dual templating route combines a Pluronic surfactant-based precursor solution with polystyrene (PS) microspheres (diam. 250 nm) in a one-pot simple process. This gives thicker films with a bimodal distribution of pores (8 nm and 165-200 nm). The dye loading of hierarchical films is compared to pure Pluronic-templated TiO_2 films and shows a relative decrease of 29% for Single Templating (ST) and 43% for Dual Templating (DT-250). Finally, a geometrical model is proposed and validated for each system, based on the agreement between calculated specific surfaces and experimental dye loading with N719 dye.

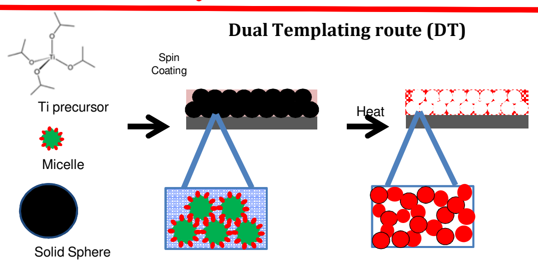
SYNTHESIS & CRYSTALLIZATION

Soft Templating route (ST)



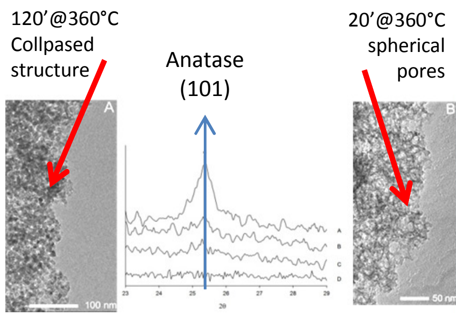
Procedure
$TiCl_4$, n-butanol, water, PPG (Mn = 4000) and F127 (PEO_{106}-PPO_{70}-PEO_{106}, in molar ratio 1 Ti:40 BuOH:10 water:0,00625 PPG: 0.004 F127.
Tetrahydrofuran (29 vol% of the final solution) is added to help the dissolution of PPG. Stirr 3hrs. Dip Coating.
Calcination at 360°C (10-20 min)

Dual Templating route (DT)



Procedure
P123 (PEO_{20}-PPO_{70}-PEO_{20}) and polystyrene (PS) microspheres (dia. 250 nm.)
molar ratio =1 Ti: 0.0124 P123:1.78 HCl: 8.7 n-butanol
Spin coating. Calcination: 30 min at 500°C/under O2

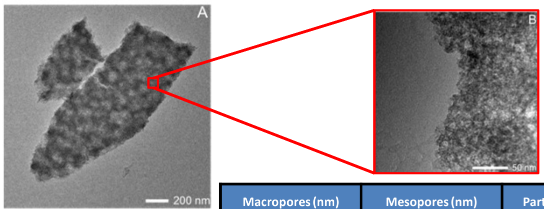
Tuning of calcination for ST route



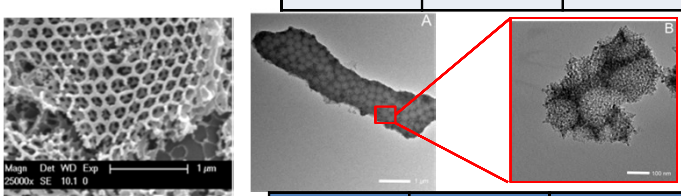
Center: X-ray Diffractograms of ST films calcined at different temperatures (heating ramp 1°C/min): A: 2h@360°C, B: 20min@360°C, C: 10min@360°C, D: 2h@350°C.

POROSITY (TEM&SEM)

TEM shows mesoporosity inside the walls surrounding macropores



Macropores (nm)	Mesopores (nm)	Particle size (nm) (from XRD)
54	10	11,4

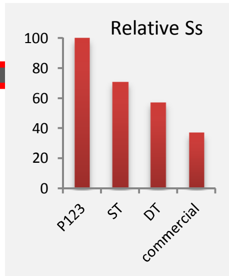


Wall thickness (nm)
42 +/-6

Macropores (nm)	Mesopores (nm)	Particle size (nm)(from XRD)
165-200	8	11,2

GEOMETRICAL MODEL vs. SPECIFIC SURFACE

Single Templating	Dual templating
Random Close Packing (RCP) of spherical particles	Macropores in Hexagonal non Close Packing (HNCP)+ walls made of particles in RCP
$S_S = \frac{3.(\%solid)}{r}$ With r = radius of spherical particles and %solid = 1- % air %air is determined by ellipsometry	$V_{macro} = 0,74\left(\frac{r}{r+\Delta}\right)^3$ $V_{walls} = 1 - V_{macropores}$ $Ss_{macro} = \frac{3.V_{macropores}}{r}$ $Ss_{meso} = V_{walls}.Ss_{pluronic}$ Where r = macropores radius and 2Δ = wall thickness $Ss_{pluronic}$ = 3,63. 10⁸m²/m³ for P123 treated at 500°C
Calculated Ss	
Ss= 3.05 x 10^8 m^2/m^3	Ss_{total} = 2.37 x 10^8 m^2/m^3. (with Ss_{macro} = 1.40 x 10^7 m^2/m^3 and Ss_{meso} = 2.23 x 10^8 m^2/m^3))
Experimental Ss (by Dye Loading with N719) with A_{dye}=2,43.10⁻¹⁸ m² $S_{dye} = dyeloading.N_A.10^{12}.A_{dye}$	
Ss= 3.01 x 10^8 m^2/m^3	Ss_{total}= 2.41 x 10^8 m^2/m^3



CONCLUSIONS

•ST route (F127+PPG): pore sizes10 nm + 54 nm. High specific surface, equivalent to 71% of the corresponding pure-Pluronic template films.
•DT route (PS nanospheres +P123) 8 nm+ 165-200 nm. The specific surface is still 57% of a pure-Pluronic template film.
•The specific surface of hierarchically porous films is still much higher than commercially available porous photoanodes, whose porosity is only 37% compared to a Pluronic-templated film. The one-pot dual templating presented here gives nice pores monodispersity, promising high selectivity in catalysis applications.
•The simple geometrical model presented here can be used to predict the specific surface and percentage of pores in the bimodal porous structures obtained. Furthermore, it can be easily extended to other sol-gel materials and the resulting hierarchical porous structures are therefore of wide interest in porous materials science.