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Surfactant and Polymer Templating

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Design of Transition Metal Oxide and Hybrid Mesoporous Materials

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ABSTRACT

Mesostructured transition metal (Ti, Zr, V, Al and Ce-Zr) oxide-based hybrid thin films, templated by poly(ethylene oxide)-based surfactants or block copolymers, have been prepared reproducibly, displaying 2D-hexagonal (*p6m*) or 2D-centred rectangular (*c2m*) structure. By carefully adjusting the variables involved it is possible to combine both high organisation and excellent optical quality. TiO_2 and ZrO_2-based materials show thermal stability up to 400-550 °C. The elimination of the template can be conducted efficiently and gives rise to high surface area mesoporous films. For the other metal oxide hybrids the inorganic framework is much more fragile, and requires a precise sequence of post-treatments to be stabilised.

In addition, original and homogeneous macrotextures shaped with coral-like, helical or macroporous sieves morphologies have been obtained following a nanotectonic approach based on the template-directed assembly by poly-γ-benzyl-L-glutamate (PBLG) of organically functionalised CeO_2 crystalline nanoparticles.

INTRODUCTION

Hybrid organic-inorganic nanocomposites are extremely versatile in composition, processing, and optical and mechanical properties [1]. One of the most striking examples of those composites are the mesostructured hybrid networks, which are precursors to mesoporous solids [2]. The construction of these networks can be tailored by the adequate use of sol-gel methods, tuning the hydrolysis-condensation of the metallic cations with the self-assembly of the organic counterparts. These materials can be processed as powders, films or fibers, displaying a great mesostructural variety [2, 3]. Indeed, the evaporation-induced self-assembly (EISA) process [4] represents an efficient way for the design of such hybrids. By the adequate set up of the parameters involved one can tune the self assembly of the amphiphilic molecules in supramolecular templates, together with the condensation of the inorganic moieties around them.

Recently, we reported the preparation and characterisation of titania [5], zirconia [6], alumina [7] and vanadia [8] mesoporous films by EISA, using poly(ethylene oxide)-based non-ionic surfactants or block copolymers as structure directing agents. Here, we rationalise the different results obtained for the various systems, focused on the role of the metal cation chemical behaviour in the formation and stabilisation of the mesophases. We also extended this method for the formation of cerium oxide and zirconium-cerium mixed oxide based systems.

The supramolecular template method allows one to texture materials in the mesoscale (dimensions up to 200-300 Å). Macrotexturation requires larger templates, such as latex particles. Here, we present the use of organically modified CeO_2 crystalline nanoparticles to obtain textured oxides [9, 10] using a polypeptide (PBLG) as a template. PBLG presents

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secondary protein-like structures such as α helix or β sheet-like in solvents as THF or DMF [11, 12]. The synthesis approach to integrate both components in a hybrid composite was based on tuning particle-template with template-template and particle-particle interactions through selective functionalisation of the nanoparticles. Hydrophobic interactions between nanoparticles and the phenyl groups of PBLG are attained by modifying the nanoparticle surface with alkyl groups. Phenyl functionalised nanoparticles favour π-π interactions with the phenyl group of the PBLG. Amine functionalised CeO_2 was also used to create hydrogen bonding with the ester group of the PBLG. Finally, a double functionalisation of the nanoparticles was achieved through the simultaneous surface capping by phenyl and amino groups

EXPERIMENTAL DETAILS

Anhydrous metal chlorides ($TiCl_4$, $ZrCl_4$, VCl_4, $AlCl_3$, or $ZrCl_4$-$CeCl_3$) were used as inorganic precursors. Non-ionic poly(ethylene oxide) (PEO)-based surfactants [$C_{16}H_{33}(EO)_nOH$] Brij 56 (n = 10) or Brij 58 (n = 20), or triblock copolymer Pluronic F127 [$OH(EO)_{106}(PO)_{70}(EO)_{106}OH$] (PO = propylene oxide) were applied as structure directing agents. The inorganic precursor was added to a solution of the template in anhydrous ethanol. To this mixture a controlled quantity of water was added. The final dipping solutions contain 1 MCl_x : t template : 40 EtOH : h H_2O (where $t = 0.15$ Brij 56, 0.05 Brij 58 or 5×10^{-3} Pluronic F127; and $h = 0\text{-}20$). Films were prepared by dip-coating glass or silicon substrates at a constant withdrawal rate (1-5 mm s^{-1}) at room temperature (20-25 °C) and controlled relative humidity (RH, 10-80%). The as-prepared films were submitted to a sequence of treatments in order to stabilise the structure and remove the surfactant, which varied according to the system.

A typical preparation of the functionalised nanoparticles can be described as follows [13]: the CeO_2 hydrate (obtained from the hydrate $CeO_2(HNO_3)_{0,5}(H_2O)_4$ delivered by Rhodia) is dissolved in THF leading to a sol of monodisperse particles, which size is of about 3 nm (verified by TEM and XRD). Addition of a functionalised carboxylic acid leads to organic modification of the nanoceria surface. Caprylic acid, 5-phenyl valeric acid or 6-amino caproic acid were used with ratios r = Acid/CeO_2 ranging from 0.2 to 0.6. PBLG was dissolved at 50°C in THF with a total mass ratio ranging from 0.1% to 1%. The sol of organically modified CeO_2 nanoparticles was then slowly added to the PBLG solution under stirring. The molar ratio s = nanoparticles/PBLG was varied from 1 to 100. The obtained solution was then placed in Petri dishes at ambient atmosphere for drying or was used to prepare thin films by dip-coating.

X-ray diffraction (XRD), 2D-XRD [14], simultaneous time resolved SAXS and interferometry [15], TEM, SEM coupled to EDS, and FT-IR spectrophotometry investigations were performed as previously described [5-8].

RESULTS AND DISCUSSION

Formation of transition metal oxide based mesostructured thin films

For the studied systems, upon dip-coating, the evaporation of the solvent is mainly governed by h and RH, the nature of the metallic cation having a small influence; much faster evaporation rates are observed for "dry" systems. In these systems water plays many roles, influencing the evaporation rates, the selective evaporation of EtOH and HCl, the polarity of the medium, and the hydrophilicity and the condensation rate of the inorganic species [16]. Besides, a quite generalised process of film formation was observed by in-situ SAXS measurements for the different metals. The formation path is very similar to that previously reported for PEO-templated SiO_2-based mesostructured films [15]. A disorder-to-order transition, from an isotropic mixture to a very organised 2D-hexagonal coating, takes place after the drying line, with an intermediate state corresponding to a worm-like mesophase [17].

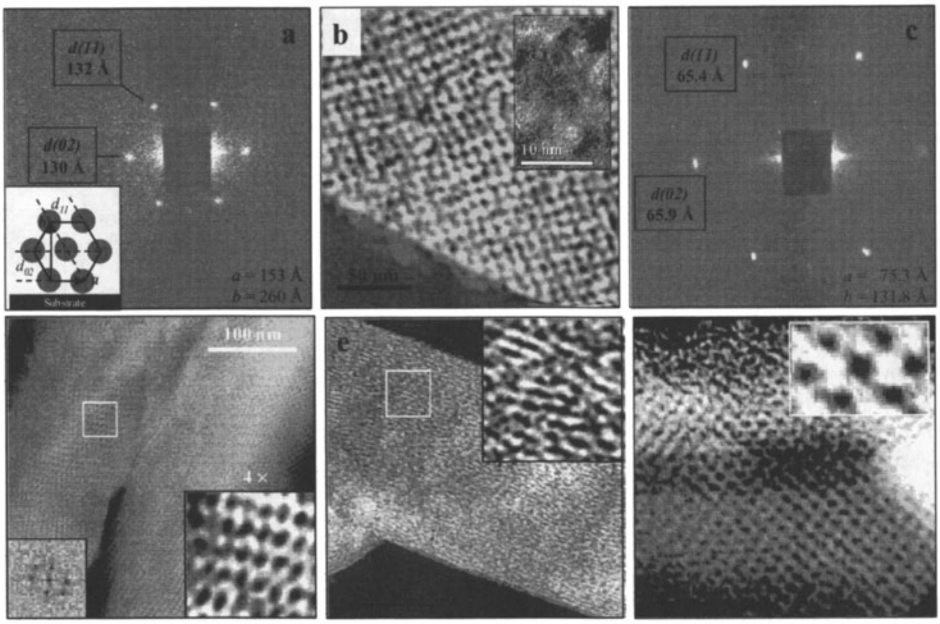

Figure 1. Pluronic F127-templated TiO_2-based films: (a) 2D-SAXS pattern for an as-prepared; and (b) TEM image along the [001] zone axis for a 350 °C treated film. The inset in part (a) is a scheme of the 2D-centred rectangular unit cell (*c2m*), and the inset in part (b) is a HRTEM image showing the presence of anatase nanocrystallites. (c) as-prepared Brij 58-templated VO_x-based hybrid film. TEM images along the [001] zone axis of Brij 58-templated ZrO_2-based mesostructured films treated at (d) 60 °C, and (e) 300 °C. (f) TEM image along the [001] zone axis of a Brij 58-templated Al_2O_3-based film treated at 250 °C.

The organisation of the final mesophase for TiO_2-based systems is mainly dependent on the acidity (the solutions prepared from the metal (Ti, Zr, V) chlorides are very acidic, $pH < 1$) and *h* of the initial solution and RH. Acid plays a double role, acting as a condensation inhibitor and protonating the hydrophilic portion of the template, allowing some electrostatic interactions in the hybrid interface in addition to hydrogen bonding. The low degree of condensation acquired in the first minutes after deposition keeps the structure "fluid" enough to undergo the disorder-to-order transition marked by the organisation of the micelles in a lyotropic liquid crystal mesophase and their alignment within the film-air and film-substrate interfaces. Optimum conditions are found for solutions prepared with only $TiCl_4$, with h = 10-15 and RH = 50% (see Figure 1a).

For ZrO_2-based hybrids, the structure is "frozen" in the worm-like mesophase, probably as a result of the formation of a relatively rigid $[ZrO_{2-x}(OH)_x.nH_2O]^{x+}Cl_x$ framework. In this case, a post-processing is necessary to reach the organised 2D-hexagonal mesophase [6]. Deposition at low humidity followed by a treatment at very high RH (> 80%) for few (10-15) seconds gives rise to very organised 2D-hexagonal mesophases (Figures 1d). The same behaviour is observed for Zr-Ce oxide-based systems with Ce/Zr ratio up to 0.3.

VO_x and Al_2O_3-based hybrid films can only be processed at very low humidity. The coatings quickly absorb water from humid atmosphere, first swelling (with a high increase of the interplanar spacings) and then collapsing after some hours. This feature can be attributed to the presence of molecular aquo complexes in solution, which have low tendency to condense, because of the relatively low acidity of the metal cations. All processing of such films must be conducted at low humidity (< 30 %) and very organised mesophases are obtained (Figure 1c).

TiO_2 and ZrO_2-based hybrids can be directly thermally treated for elimination of the template, displaying stability up to 550 °C, resulting in high surface area (130-200 $m^2\ g^{-1}$) mesoporous oxide coatings [6]. The thermal treatment results in a uniaxial contraction in the direction normal to the substrate [5-8, 14]. As an example, the pores of a Brij 58-templated ZrO_2 film are almost circular with diameter around 35 Å after treatment at 60 °C (see Figure 2d), becoming elliptical with dimensions of about 35×14 Å after treatment at 300 °C (see Figure 2e). The wall thickness also decreases with the thermal treatment, from 35-37 Å at 60 °C to approximately 20 Å after 300 °C. Pluronic F127-templated films display bigger pores and thicker pore walls (Figure 1b) than those templated by Brij surfactants. As a result, F127-templated materials present much higher thermal stability. TiO_2-based coatings are stable up to 350 °C when templated by Brij 58, while the thermal stability increases up to 550 °C for Pluronic F127-templated films. Titania mesoporous films treated at 350 °C or more present semicrystalline walls, as observed by HRTEM (see inset in Figure 1b).

A precise sequence of treatments, described elsewhere [7, 8], is necessary to stabilise Al_2O_3 and VO_x-based hybrids. For Al_2O_3, the template can be removed by a soft chemical treatment (UV/O_3 at room temperature, after a pre-stiffening of the structure at 250 °C), giving rise to mesoporous alumina coatings, as shown in Figure 1f. For vanadium oxide based systems, the stabilisation can be carried out by thermal treatment in N_2 at temperatures ranging from 160 to 250 °C. However, the elimination of the surfactant by UV/O_3 treatment causes the collapse of the mesostructure, as a result of the oxidation of V(IV) to V(V).

Nanotectonic approach of the texturation of CeO_2 based nanomaterials

Alkyl functionalised nanoparticles templated by PBLG lead to coral-like structures for s = 15. Similar morphologies were obtained by Caruso et al. [18] with amorphous TiO_2. In the present case the helical structure of PBLG is clearly altered. The helical morphology is however kept with doubly functionalised (amine and phenyl) particles in DMF for s = 15. Phenyl functionalised nanoparticles lead to different morphologies depending on the ratio s. For $10 < s < 60$, helical morphology was obtained (Figure 2 c). By SEM, we detect helices of 7 µm size composed of smaller ones of 1 µm size. The observation of these helices by TEM reveals anisotropic textures in the 6 nm size. The π-π interactions between nanoparticles and PBLG seem to be effective and allow to obtain original morphology. Homogeneous morphologies are obtained for *r* = 0.2. Above *s* = 60, the solid exhibits macropores with diameters from 500 nm to 1 µm (Figure 2d). Such a regular morphology with very large domains of 500 µm can be reproducibly obtained. Thin films prepared by dip-coating with these solutions also exhibit macropores. Varying the PBLG ratio allows one to control the macropore size [13]. The obtained morphologies are characteristic of phase separation by spinodal decomposition [19, 20]. PBLG can be removed by thermal treatment at low temperature with the aim of obtaining CeO_2 organic free materials, as demonstrated by FTIR and confirmed by EDS [13]. Coral-like structures are kept after calcination at 300°C. The macroporous samples are stable until 500°C. Helical structures remain after elimination of the PBLG at 300°C (SEM picture, Figure 2c).

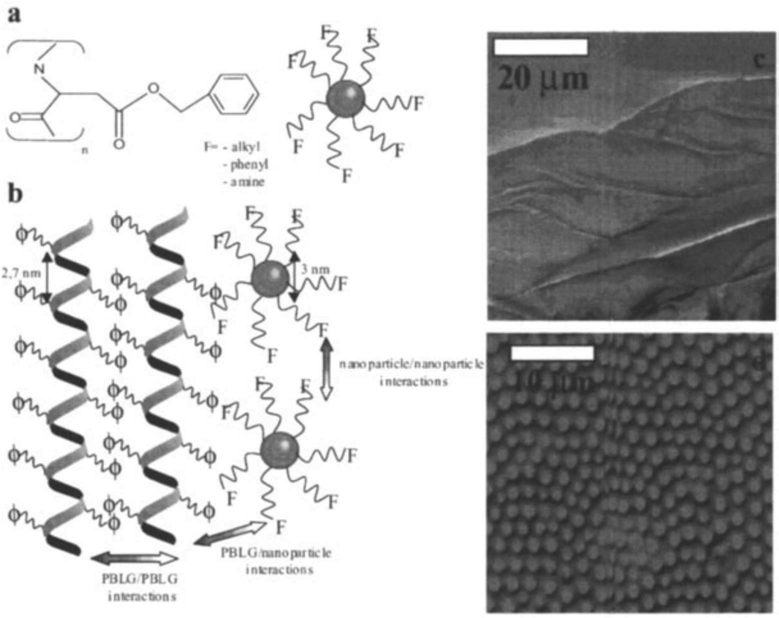

Figure 2. (a) PBLG formula and cartoon of functionalized nanoparticle. (b) Scheme of the possible interactions between the different building blocks (**Φ** = phenyl, F = any function alkyl, phenyl, amine). SEM image of (c) a helical structure of a calcined PBLG sample, and of (d) a hybrid macroporous sample.

An optimum of specific surface area is reached at 300°C, reaching 150 $m^2\ g^{-1}$, when the PBLG is eliminated. At 300°C, the calcined samples exhibit a type I isotherm, which is characteristic of microporous materials [13]. The measured microporosity is due to the voids created upon aggregation of the nanoparticles. This process yields hierarchical porous materials presenting both micro and macro porosity with inorganic walls constituted of nano-crystalline cerium oxide particles as demonstrated by XRD. For higher temperatures, the samples exhibit type III isotherms which are characteristic of macroporous materials. The loss of microporosity is due to the sintering of the ceria nanoparticles.

This original study demonstrates that a single parameter, i. e., *s* ratio, allows a versatile tuning between templating effect and phase separation. The control of the balance between these two processes allows one to tailor diverse morphologies and textures.

CONCLUSIONS

We propose here a generalised method for the preparation of mesoporous transition metal oxide mesoporous thin films, that can be adapted for many different metal cations (Ti, Zr, V, Al, Ce-Zr) by the tuning of the conditions based on the specific chemical behaviour of the inorganic species. A set of post-treatments has been developed to combine high structural organisation and good optical quality, as well as to stabilise the mesophase and remove the template. In particular for TiO_2 and ZrO_2-based systems, the application of such methods resulted in the formation of high organised, crack-free coatings displaying pore diameters in the mesoporous range and high surface area.

Nanotectonic approaches appear to be a biomimetic way to create new materials that keep the properties linked with the crystallinity of the particles. The synthesis method allows for the production of both gels and thin films with pores aligned perpendicularly to the surface. This versatile approach can be extended to other capping groups (functions such as thiol or aldehyde, morphology directors such as block copolymers, dendrimers…) and to a great variety of controlled nanoparticle-based systems (TiO_2, ZrO_2, Al_2O_3,…).

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