Formation and Stabilization of Mesostructured Vanadium-Oxo-Based Hybrid Thin Films

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Mesostructured vanadium-oxo-based hybrid thin films have been prepared by evaporation-induced self-assembly. Anhydrous metal chlorides ($VOCl_3$ or VCl_4) were used as the vanadium source, and the nonionic surfactant Brij 56 or 58 was used as the structure-directing agent in ethanol/water solutions. Mesostructured films were obtained from solutions having V(IV)/V_{total} ratios higher than 0.7, evidencing the role of V(IV) in the formation of a curved inorganic VO_x-based ($2 \le x \le 2.15$) framework. The hybrids obtained are fragile and water-sensitive, so that deposition and all of the processing leading to stabilization of the mesostructure must be performed at low relative humidity. A combination of synchrotron-SAXS and interferometry was applied to evaluate the structural evolution related to the evaporation process during dip-coating. The SAXS data clearly showed a 2D hexagonal structure ($P6m$ space group, $a = 65-80$ Å) that is converted to a 2D centered rectangular ($C2m$ space group) through preferential contraction in the direction normal to the substrate. The structure of the hybrid films is stable up to 250 °C in inert atmosphere.

Introduction

Hybrid organic−inorganic nanocomposites are extremely versatile in terms of composition, processing, and optical and mechanical properties.[1] One of the most striking examples of such nanocomposites are 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.

The synthesis of mesostructured hybrids based on silica[2] and on a variety of metal oxides has been demonstrated.[3−7] Among the studied systems, vanadium oxide-based hybrids are of great interest, because of their potential applications as catalysts, sensors, electrodes, etc. Attempts to prepare VO_x-based hybrids are mainly concerned with the use of alkyltrimethylammonium cationic surfactants or long-chain amines as structure-directing agents, following charge-matching or ligand-assisted mechanisms, respectively.[6−11] A variety of inorganic precursors have been used as vanadium sources, including alkali metal vanadates and vanadium alkoxides. The materials so obtained are usually lamellar and can be converted to hexagonal phases by acidification of the medium or by thermal treatment at moderate temperatures (around 160 °C), even though, frequently, the conversion is only partial and mixed phases are obtained. In all cases, elimination of the template leads to the collapse of the mesostructure. The fragility of these materials can be attributed to the particularities of vanadium chemistry, i.e., the different oxidation states, the coordination, and the existence of V═O bonds that do not contribute to the formation of the inorganic network. Recently, Zhou and Honma[12] reported that vanadate−CTAB hybrids can be

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deposited as thin films. Like the bulk phases, such films undergo phase transformations during heat treatment at 160 °C and are unstable upon elimination of the organic template.

More stable than VO_x-based materials are the vanadium oxo phosphate-based mesostructured hybrids that have been obtained. The tetrahedral phosphate group in such materials helps in the tuning of adequate curvature, and therefore, hybrid materials in a variety of structural arrangements (lamellar, hexagonal, and cubic) can be synthesized.[6,13] However, even for these materials, elimination of the template without collapse of the mesostructure was achieved only for a lamellar phase using an ion-exchange method.[13]

Recently, the process of so-called evaporation-induced self-assembly (EISA) was demonstrated by Brinker and co-workers[14,15] as an alternative approach to the formation of mesostructured hybrids, permitting processing of the macroscopic shape of the material (aerosol, powder, films, fibers, and monoliths[16]). The goal of such a method is to use an organic solvent (usually an alcohol) to dilute the system, thereby reducing the reactivity of the inorganic species toward hydrolysis and condensation. The tuning of the variables involved permits the formation of a liquid-crystalline-like phase surrounded by an inorganic framework upon solvent evaporation.

By this process, mesostructured (and mesoporous) silica-based thin films have been successfully prepared.[17] A great range of structures can be obtained (2D and 3D hexagonal, micellar and bicontinuous cubic, and lamellar), and the basic features of the processes leading to the formation of such mesostructures are beginning to be understood.[17]

In general, mesostructured transition metal (TM)-based hybrids are more difficult to obtain. Their production requires a perfect adjustment of hydrolysis/condensation and self-assembly processes.[7] The EISA approach is especially suitable for the design of such hybrids, as dilution of the system with an organic solvent contributes to a reduction of the reactivity of the TM toward hydrolysis and condensation. In such an environment, water can be added to the system, and the hydrolyzed inorganic moieties become hydrophilic, enhancing their interaction with the polar portion of the template. Fast condensation can be quenched by the addition (or formation in situ) of an acid, such as HCl, which is eliminated from the system during the evaporation process, allowing inorganic polymerization.[18] This approach has been successfully extended to the formation of TM-based mesostructured hybrids, including TiO_2, ZrO_2, SnO_2, WO_3, Nb_2O_5, V_2O_5, and mixed oxides[5,18] (in the case of vanadium oxide-based materials, the hexagonally mesostructured VO_x-based hybrid powders are unstable upon heating[5]).

Recently, we showed that hexagonally mesostructured titania-,[19] zirconia-,[20] and alumina-based[21] hybrid thin films can be grown by an EISA-derived method and converted to mesoporous oxides upon thermal or ozone treatment. Organized films stable up to 400 °C with tailored thicknesses presenting long-range mesostructural order and large (30−60 Å) and narrowly distributed pore sizes can be obtained using nonionic surfactant or block copolymer templates and metal chlorides as inorganic precursors in ethanol/water mixtures upon deposition at controlled humidity in the atmosphere.

Here, we describe, to the best of our knowledge for the first time, the formation of VO_x-based hexagonally mesostructured hybrid thin films by a one-pot synthesis using the EISA approach. The redox reactions taking place in solution and in the hybrid films and their influence on the formation and stability of the mesophase are discussed in terms of UV−vis, FT-IR, and ESR measurements. A combination of time-resolved SAXS and interferometry analyses was applied to evaluate mesophase formation during dip-coating. The results indicate that the as-prepared hybrid coatings are "vanadotropic" (i.e., hybrid liquid-crystalline phases), expanding or contracting through the exchange of water with the atmosphere. These hybrids are fragile and must be readily stabilized before exposure to ambient atmosphere. A condensed and stable mixed-valence VO_x ($2 \leq x \leq 2.15$) framework can be formed around the organic template by thermal treatment (433−523 K) in inert atmosphere. Condensation of the inorganic network leads to preferential contraction in the direction normal to the substrate, resulting in a distortion and a partial degradation (as observed by TEM) of the hexagonal ($P6m$) structure.

Experimental Section

Film Formation. Our approach to the formation of mesostructured VO_x-based hybrid films is based on the EISA process and uses $VOCl_3$ or VCl_4 (Aldrich) as the inorganic precursor in ethanol/water solution, in addition to the nonionic surfactant Brij [$C_{16}H_{33}(OCH_2CH_2)_nOH$] 56 ($n = 10$) or 58 ($n = 20$) (Aldrich) as the structure-directing agent. The dipping solutions were prepared by slowly adding the inorganic precursor into an ethanolic solution of surfactant at 273 K.[22] The final mixture contained 1 V:40 EtOH:x surfactant (where x is 0.10 for Brij 56 or 0.05 for Brij 58). To this mixture, water

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(22) The inorganic precursors are quickly hydrolyzed and must be manipulated in inert, dry atmosphere. Care must be taken during addition of the anhydrous metal chloride into the surfactant alcoholic solution, because the reaction is exothermic and HCl is released.

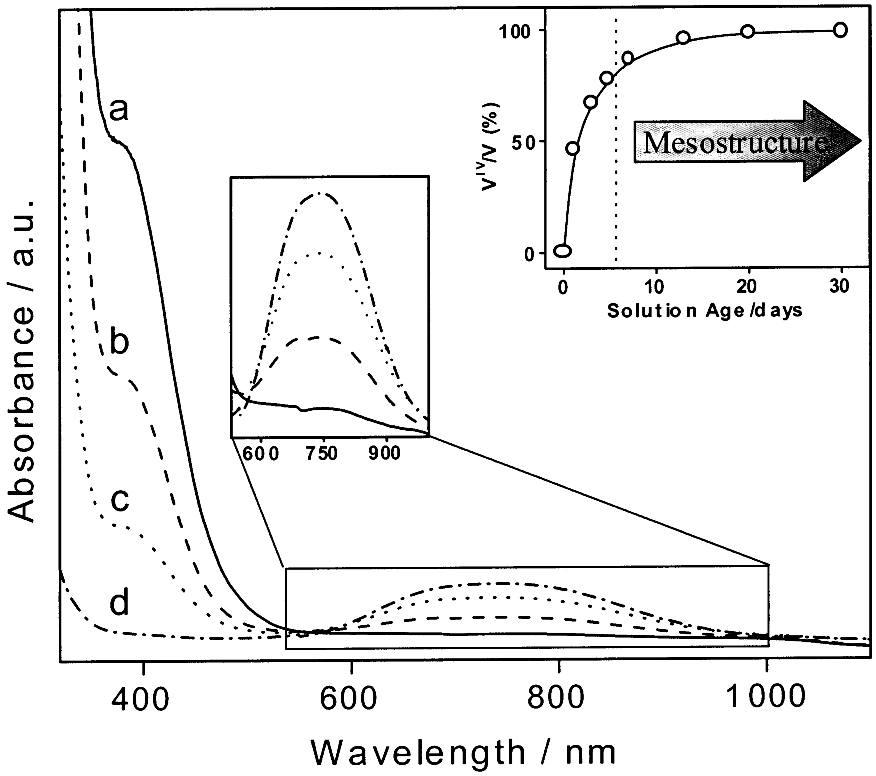

Figure 1. Ultraviolet–visible spectra of a solution containing 1 $VOCl_3$:40 EtOH:0.05 Brij 58:10 H_2O as a function of aging time: (a) fresh, (b) 3 days, (c) 5 days, and (d) 20 days. Inset shows the ratio V(IV)/V_{total} determined from the UV–vis data.

was added to reach a ratio of 3–10 H_2O/V (hydrolysis ratio, *h*), resulting in very acidic solutions (pH < 0) and, thus, quenching condensation. As a result, the dipping solutions are stable for many months. A typical solution was prepared as follows: 0.01 mol of the inorganic precursor (1.928 g for VCl_4 or 1.733 g for $VOCl_3$) was slowly added to a solution containing 0.562 g of Brij 58 (or 0.628 g of Brij 56) and 18.428 g of ethanol. To this final mixture was added 1.8 g of water ($h = 10$).

Films were prepared at room temperature (293–298 K) by dip-coating silicon or glass substrates at constant withdrawal rates between 1 and 3 mm s^{-1}. The relative humidity (RH) inside the dip-coater chamber is a parameter of paramount importance, and thus, it was carefully controlled between 10 and 70%. The best procedure found for stabilizing the formed mesophase involves aging at room temperature at low humidity (<30%) overnight, heating in inert atmosphere at 333 K for 6 h, and thermally treating (ramp of 1 K min^{-1}) in inert atmosphere at 433–523 K for 2 h.

Characterization. When $VOCl_3$ was used as the precursor, the reduction of V(V) to V(IV) took place and was followed by UV–vis spectrophotometry using a Bio-Tek Instruments UVIKON XS spectrophotometer [bands at 379 nm for V(V) and 742 nm for V(IV)].[23] ESR measurements were performed at 77 K for solutions and films using a Bruker ESP 300E apparatus. X-ray diffraction (XRD) patterns were collected in θ–2θ mode using a conventional Philips PW 1820 goniometer (Cu Kα_1 radiation, $\lambda = 1.5406$ Å). TEM images of samples embedded in epoxy resin and ultramicrotomized were collected using a JEOL 100 CX II instrument operating at 120 kV. SEM coupled with EDX investigations (JEOL JSM-5200 scanning microscope operating at 20 kV, coupled with an Oxford Link Pentafet 6880 for surface elemental analysis) were performed to evaluate the morphology and composition of the film surface. FT-IR spectrophotometry was conducted using a Nicolet Magna 500 spectrophotometer, for films scratched from the substrate and dispersed in KBr pellets or directly deposited on thallium bromo-iodide (KRS-5) wafers.

In situ evaluations of the structural evolution of the films during dip-coating were performed in transmission mode using the synchrotron radiation of the SAXS beam-line of ELETTRA (Trieste, Italy) or LURE (Orsay, France). For this experiment, a modified version of a dip-coater was built to fit the SAXS line. The substrate (8-μm-thick silicon wafer) was kept fixed in height at an angle of 3° with respect to the incident X-ray beam; the solution was first moved up, as for the substrate to be immersed in the sol, and then lowered to perform the coating. The diffracted X-rays were collected on a CCD camera every 2 s from the time when the top level of the solution passed the position of the incident X-ray beam. Simultaneously, the progress of the evaporation, and thus the evolution of the thickness, was followed by collecting constructive and destructive interference fringes created by the reflection of a monochromatic visible light beam (440 nm) on the film/substrate system on a second visible-light CCD camera. More details on experiments involving both techniques have been published elsewhere.[15,24]

Results and Discussion

Characterization of the Dipping Solutions. Figure 1 shows selected UV–vis spectra for a yellow dipping solution containing $VOCl_3$ as the inorganic precursor. For fresh solutions, a single band at about 380 nm, characteristic of the V(V) species,[23] was observed. As a function of the aging time, the intensity of this band decreased, while another band at about 730 nm, characteristic of the vanadyl ion (VO^{2+}),[23] could be observed with increasing intensity (the color of the solution changed from yellow to green and finally blue). This result clearly shows the reduction of V(V) to V(IV).

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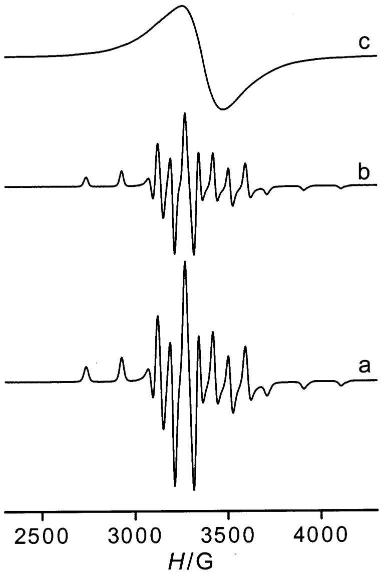

Figure 2. ESR spectra of (a) a solution containing 1 VCl_4:40 EtOH:0.05 Brij 58:10 H_2O, (b) a 2-day-old solution as described in Figure 1, and (c) fresh film deposited from the solution described in part a.

Table 1. Magnetic Parameters Calculated from the Spectra Displayed in Figure 2

sample	g_{iso}	$g_{\parallel}$	$g_{\perp}$	A_{iso}/G	$A_{\parallel}/G$	$A_{\perp}/G$
sol VCl_4[a]	1.980	1.951	1.994	115.1	195.5	74.9
sol $VOCl_3$[a,b]	1.980	1.951	1.994	115.1	195.5	74.9
fresh film[c]	1.977	–	–	110.5	–	–
$[VO(H_2O)_5]^{2+}$ [d]	1.962	1.931	1.978	119.5	205.5	76.5

[a] Solution containing 1 V:40 EtOH:0.05 Brij 58:10 H_2O prepared using VCl_4 or $VOCl_3$ as the vanadium source. [b] 2-day-old solution. [c] Film deposited from a solution containing only VCl_4. [d] Values reported elsewhere.[27]

The reduction of V(V) in acidic alcoholic solution is a well-known process for V_2O_5 gels.[25] However, the reduction rate and extension observed here are much higher than the values previously reported for gels, probably as a consequence of the high acidity of the ethanolic water solutions and the fact that the isolated V(V) species can move freely as it is not trapped inside an inorganic network. By analogy with previously reported data for the reduction of W(VI) to W(V) in WCl_6 alcoholic solutions,[26] one can expect that the mechanism of reaction involves the oxidation of chloride to chlorine by the V(V) species followed by the oxidation of ethanol to acetaldehyde by the produced chlorine.

Selected ESR data acquired for dipping solutions are shown in Figure 2. The low-temperature ESR spectra (77 K) of the dipping solutions exhibit the typical hyperfine structure of localized V^{4+} ($S = {}^1/_2$, $I = {}^7/_2$) in an axially distorted ligand field. The data can be described by the usual spin Hamiltonian[27]

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + AS_z I_z + A_{\perp}(H_x S_x + H_y S_y)$$

where g_i and A_i are the components of the g and A tensors, respectively; H is the magnetic field; and β is the Bohr magneton. The calculated parameters are reported in Table 1. The ESR parameters for the solution prepared using VCl_4 as the vanadium source are characteristic of vanadyl $[VO]^{n+}$ ions. Moreover, when included in a g_{iso} versus A_{iso} diagram for V^{4+} species,[28] the reported values are shifted to relatively high values. The unaveraged tensor components $g_{\parallel}$ and $g_{\perp}$ also show the same trend. This indicates a slight variation of the vanadyl coordination sphere from those reported for the well-known aqueous $[VO(H_2O)_5]^{2+}$ ions. This difference can be related to a slight distortion of the vanadium polyhedron, likely arising from the presence of ligands other than water molecules, probably chloride.[27] Direct interaction with the surfactant polar chain can be excluded in this alcohol/water system.[29] Therefore, isolated species such as $[VO(H_2O)_{5-x}(Cl)_x]^{(2-x)+}$ are likely to be the paramagnetic inorganic moieties present in solution. When the solution was prepared using $VOCl_3$, an identical spectrum was observed, with the only difference being the intensity of the signal, indicating the presence of V(IV) species in solution but in lower concentration. Integration of the intensity for a 2-day-old solution prepared using $VOCl_3$ showed approximately 54% of the intensity acquired for the pure VCl_4 solution, in excellent agreement with UV–vis data. The high values observed for $A_{\parallel}$ and $A_{\perp}$ are related to the effect of the solvent (in the present case, an ethanol/water mixture), which affects the primary solvation sphere, and so the hyperfine coupling to the vanadium, as previously demonstrated for $VOCl_2$ solutions in different solvents.[27] Moreover, this effect can also be attributed to the presence of ligands other than water molecules, such as chloride.[27] The same results where observed for both surfactants (Brij 56 and 58).

Mesostructure Formation. During aging of the $VOCl_3$ solutions, films were successively prepared, and no mesophases were formed for solutions containing less than 70% V(IV) (approximately 5-day-old $VOCl_3$ solutions; see inset in Figure 1). Thereafter, the organization of the mesophases increased with the aging time (using as parameters for organization the intensity and FWHM of the X-ray diffraction peak; see Figure 3). The single peak in the XRD patterns corresponds to the (02) spot observed in the SAXS patterns (see below). The maximum organization was attained after 20 days of aging, and the organization remained constant thereafter, indicating that the ideal dipping solution should contain only V(IV) species.

Vanadium(V) oxide is well know for its tendency to form lamellar structures. The need for V(IV) species to allow curvature of the inorganic framework is a trend widely explored in the preparation of vanadium oxide nanotubes.[30] Recently, Mizuno et al.[13] reported the

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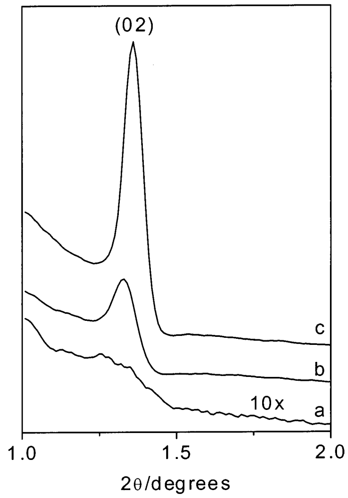

Figure 3. Low-angle XRD patterns for films deposited from a solution containing 1 $VOCl_3$:40 EtOH:0.05 Brij 58:10 H_2O aged for (a) 3, (b) 6, and (c) 20 days.

tunable one-pot synthesis of vanadium oxophosphate–CTAC hybrids in a variety of mesostructural arrangements using as the vanadium source a mixture of V_2O_5 and V metal. The main role of the V metal in this synthesis procedure is the reduction of V_2O_5.

Therefore, VCl_4 was chosen as the vanadium source. Another parameter of paramount importance is the presence of water in the solution. In all cases, water-free solutions led to unorganized coatings. Adjusting *h* to values between 3 and 10 resulted in the formation of very well-ordered mesostructured hybrid films. Water plays many important roles in this system, such as making the inorganic moieties hydrophilic and thereby allowing hydrogen-bond interactions between them and the hydrophilic chains of the surfactant.[29] Moreover, the presence of water influences the evaporation rates of EtOH and HCl through the formation of EtOH/water and HCl/water azeotropes, as well as the polarity of the medium, which is a key factor in the formation of micelles and their organization.[18] The most organized hybrids obtained so far were prepared with $h = 10$ and RH = 10%.

Independently of the surfactant, a very well-ordered 2D hexagonal structure (*P*6*m*) was obtained (Figure 4). Treatment of the films (drying, heating) led to a preferential contraction in the direction normal to the substrate, leading to a distorted hexagonal structure that can be described as 2D centered rectangular (*C*2*m*).[17,19,20] For simplicity, because the 2D hexagonal structure can be described using the parameters of the 2D centered rectangular structure, the latter will be used for indexing of patterns and further discussion. The *d* spacings for as-prepared films (that show a true 2D hexagonal structure) varied in the 50–80 Å range, depending on the RH. The same parameter determined for Brij 58-templated TiO_2 and ZrO_2 mesostructured films was 53 and 65 Å,[19,20] respectively, much less influenced by the humidity, as a consequence of the higher degree of condensation of the inorganic framework. Changing the surfactant (Brij 56 or 58) has a negligible effect, overlapped by the drying or swelling of the structure as a result of the variation in RH. This *d* spacing range corresponds to an interpore distance range from 62.5 to 87.9 Å.

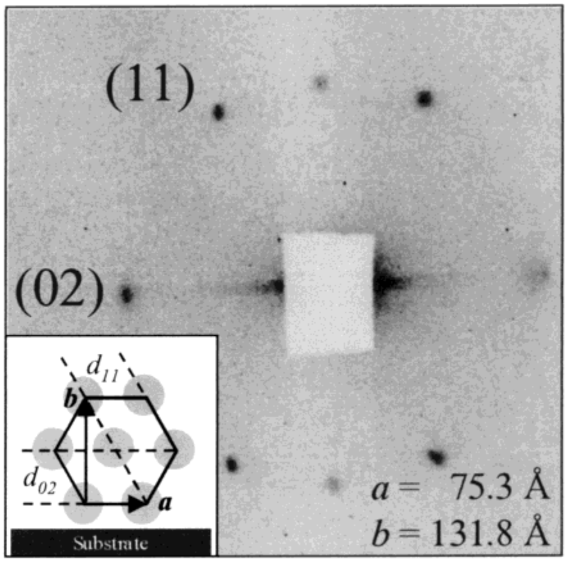

Figure 4. 2D SAXS patterns acquired for as-prepared Brij 58-templated VO_x-based hybrid film deposited from a solution containing only V(IV).

Figure 5 shows the structural evolution of a Brij 56-templated VO_x-based hybrid during dip-coating at RH = 10% [solution containing only V(IV)], and Scheme 1 summarizes the structural and chemical evolution. Two evaporation processes could be distinguished by interferometry, which can be assigned to the evaporation of an ethanol-rich and a water/HCl-rich ethanol/water/HCl ternary mixture (regions 1 and 2, respectively, in Scheme 1).[31] The first evidence for mesostructure formation was observed 30 s after the start of the deposition (10 s after the drying line had reached the analyzed region of the sample), when interferometry showed that the film approximately reached its final thickness (most of the solvent had already evaporated). At this point, only (02) spots were present, indicating that organization was present along only the *c* axis (region 3, Scheme 1).[32] After approximately 1 min, no further changes were observed in the film thickness. In contrast, the peak intensity continued to increase up to 12 min after the start of deposition, probably as a consequence of elimination of small portions of solvent and HCl (region 4). In contrast to the mechanism reported for SiO_2- and TiO_2-based hybrids mesostructure formation during film deposition, here, we did not observed an intermediate wormlike structure.[24a,31] The difference in this case seems to be the lower degree of condensation attained by the VO_x-based network (see below) when compared to the silica-based one, so that a fast transition from a liquidlike (no organization) to a liquid-crystal-like state can occur, also as a consequence of the low humidity

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(31) (a) Crepaldi, E. L.; Soler-Illia, G. J. A. A.; Grosso, D.; Albouy, P.-A.; Amenitsch, H.; Sanchez, C. *Stud. Surf. Sci. Catal.* **2002**, *141*, 235. (b) Grosso, D.; Babonneau, F.; Sanchez, C.; Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Albouy, P.-A.; Amenitsch, H.; Balkenende, A. R.; Brunet-Bruneau, A. *J. Sol-Gel Sci. Technol.* **2002**, in press.

(32) The lack of correlation in the *x* and *y* axes (between micellar rods) is a possible explanation for the presence of only (02) spots. The progressive increase in intensity of the (11) spots (see Figure 5) while the (02) spots remain almost constant in intensity supports an increase in organization along these directions. An alternative explanation is the possible formation of an intermediate lamellar phase, but the absence of harmonics makes the identification of such a phase impossible.

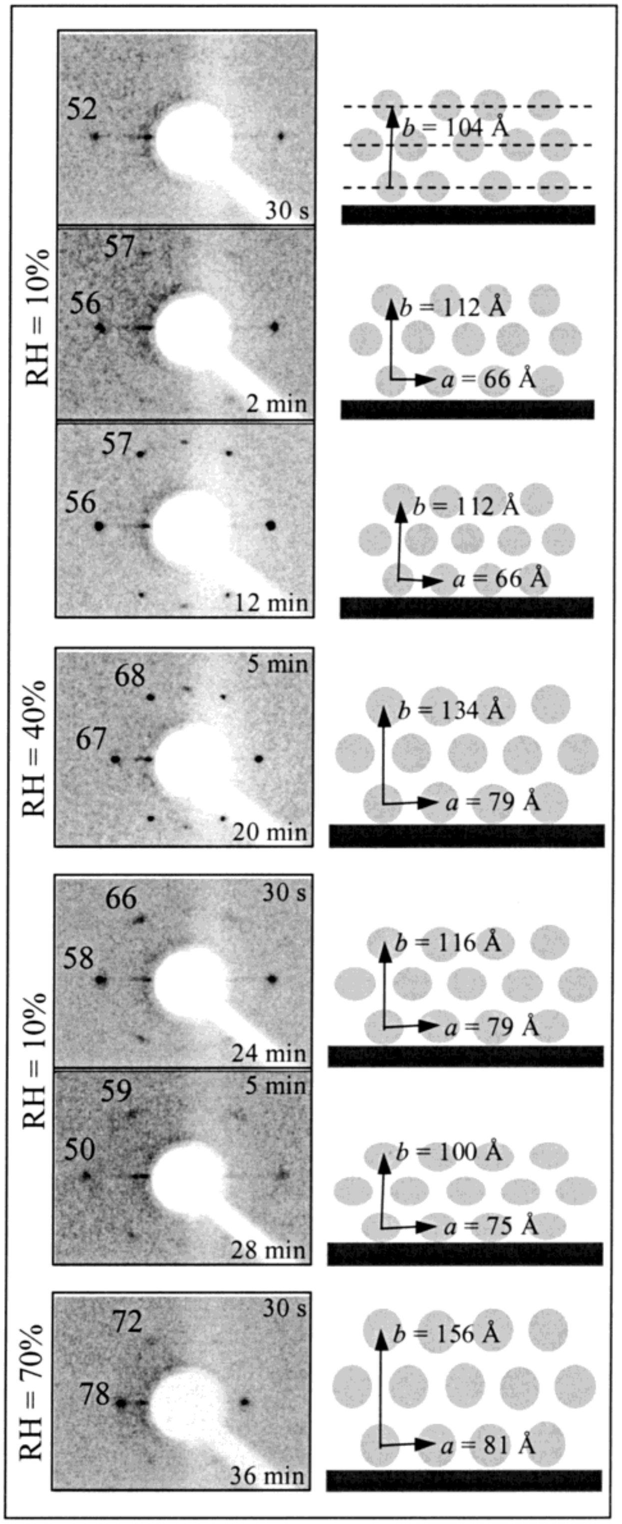

Figure 5. In-situ synchrotron-SAXS analysis of a Brij 56-templated film and representation of the structure. The times in the bottom and top of the figures represent the time from the deposition and the time of exposure to the indicated RH, respectively. The distances are in angstroms.

employed here, which caused rapid evaporation of the solvent.

Exposing a fresh film to higher humidity (40%) resulted in the incorporation of water (swelling) and a total expansion (i.e., in all directions, rather than preferentially in one direction as observed for other metal oxide-based systems[19,20,24a]) of the structure, suggesting that the inorganic species were only fairly condensed and hygroscopic. UV−vis spectra of a film prepared under conditions simulating these (Figure 6a) showed a weak band centered at 760 nm and a very small absorption between 350 and 500 nm, indicating the predominance of V(IV) species (such films present a slight blue color, characteristic of VO^{2+} ions). The FT-IR spectrum of a similar film (Figure 7a) exhibited a well-defined band at 995 cm^{-1} and a clear shoulder located at 950 cm^{-1}, both characteristic of V═O bonds of different lengths. The position of the V═O vibration and the length of the corresponding vanadium−oxygen bond can be estimated through correlations between FT-IR and structural data of well-defined vanadium-oxo compounds.[28] A short vanadyl V═O bond (1.55−1.58 Å, A in Scheme 1), mainly found for V(V)-oxo species, vibrates at 1020 cm^{-1}, whereas the vibration band characteristic of a long V−O bond (2 Å), such as that found in V(IV)-oxo compounds, is located at about 920 cm^{-1}. The IR data obtained for the VO_x hybrids correspond to vanadium-oxo species having V═O bonds of intermediate length, typically 1.65 Å (995 cm^{-1}, B in Scheme 1) and 1.80 Å (950 cm^{-1}, *C* in Scheme 1). This increase in the length is associated with a decrease in the π character of the V═O bond. This feature is generally associated with a closer bonding of the ligand located opposite the vanadyl bond. The IR data suggest the presence of two kinds of vanadium-oxo polyhedra, one corresponding to a VO_{5+1} square-pyramidal environment (strongly axially distorted octahedron) while the other is close to a slightly distorted VO_6 octahedron. Moreover, a weak, broad band centered at 520 cm^{-1}, indicating the presence of some V−O−V bonds, is also observed.[28,33]

The ESR spectra of the fresh hybrid films exhibit a single line without apparent hyperfine structure. This is the typical feature observed for interacting V^{4+} ions. It indicates that the paramagnetic centers are close enough (d < 7 Å) to allow spin−spin interactions. However, mainly dipolar interactions can account for the signal line width of about 224 G. Indeed, the ESR line width is not narrow enough to draw any conclusions about possible spin−spin exchange interactions, which would likely occur though V−O−V bonds.[27]

The relatively high value for g_{iso} calculated from this spectrum (see Table 1) indicates the coordination of some chloride to vanadium. In agreement, EDX analysis of the film surface showed the presence of 0.9 Cl/V. The whole of these results (SAXS, XRD, TEM, FTIR, ESR) indicates that fresh films present a very well-organized structure but a low condensed vanadium oxo chloride inorganic framework. The highly organized mesophases of Brij surfactants surrounded by monomeric or oligomeric inorganic species obtained here in the fresh films are very similar to those recently reported by Çelik and Dag.[34] These authors showed that mixtures of transition metal aqua complex salts and Brij surfactants result in mesophases with liquid-crystal behavior. These phases are not stable, because the low acidic bivalent cations applied in such a work cannot condense. Thus, the main difference between those phases and the VO_x−Brij

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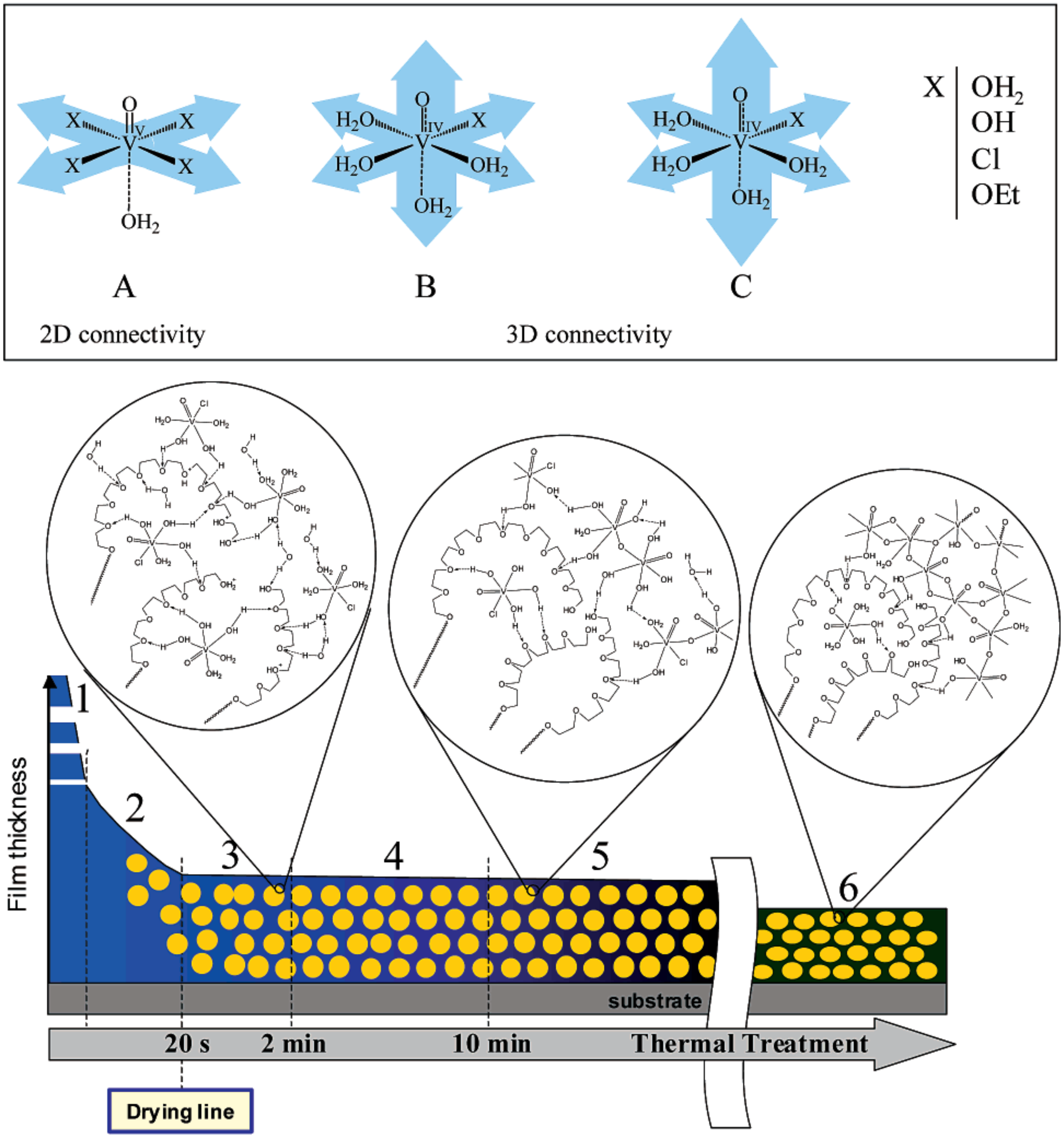
(33) Sanchez, C.; Livage, J.; Lucazeau, G. *J. Raman Spectrosc.* **1982**, *12*, 68.

(34) Çelik, Ö.; Dag, Ö. *Angew. Chem., Int. Ed.* **2001**, *40*, 3800.

Scheme 1. (Top) Representation of the Vanadium Species Present in Solution and in the Films and (Bottom) Representation of the Structural and Chemical Evolution Occurring during Film Formation and Stabilization



hybrids obtained here is that V(IV) species are more acidic than bivalent cations and can condense, reducing the mobility and stabilizing the mesostructure. However, the organization and mobility of the VO_x-based hybrids make such mesophases behave similarly to liquid crystals. Thus, such coatings can be considered "vanadotropic" phases.[18b]

As one can see in Figure 5, a further reduction of RH resulted in a preferential contraction of the structure in the direction normal to the substrate, showing that the coating was adhered to the substrate and that further condensation took place. However, an additional increase in humidity, up to 70%, resulted in a highly preferential (in the direction normal to the substrate) expansion of the structure that was completely lost after a few minutes under these conditions. In fact, the exposure of the as-prepared films to ambient humidity (40−50%) for 10−24 h also resulted in unorganized coatings. This stage in which the film exchanges water with the atmosphere and has a fairly condensed inorganic framework is represented in Scheme 1, region 5. During this process, both the absorption of water and the oxidation of V(IV) to V(V) are important factors. In Figure 6, one can see the effect of the aging of an as-prepared film at RH = 45%. The band at about 760 nm (VO^{2+}) practically disappears, while a band centered at 490 nm [V(V) species], of increasing intensity with time, begins to be observed (a 24-hour-old film displays a pale green color). The intensity of these bands remains constant after approximately 24 h for many weeks. The

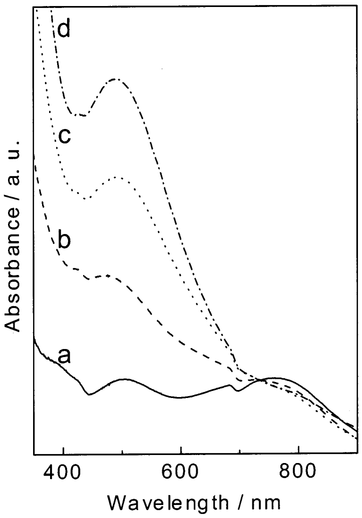


Figure 6. Ultraviolet−visible spectra of a film deposited from a solution containing 1 VCl_4:40 EtOH:0.05 Brij 58:10 H_2O as a function of aging time: (a) 15 min, (b) 90 min, (c) 5 h, and (d) 24 h.

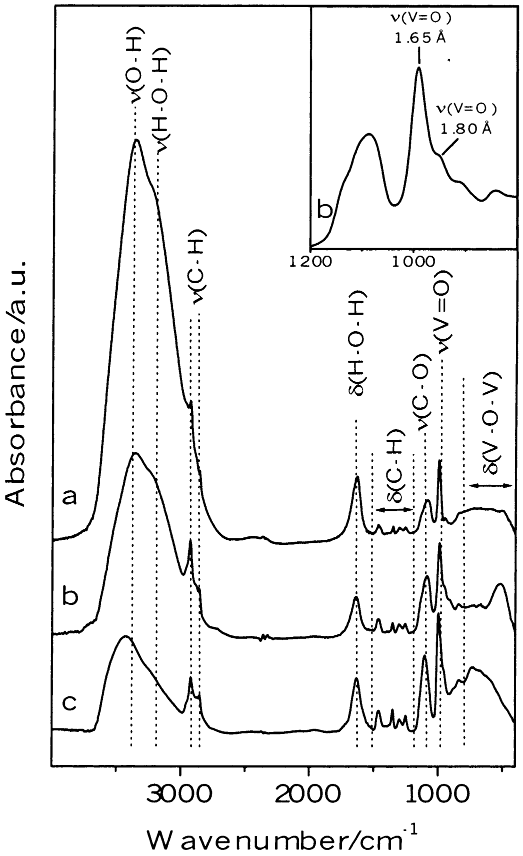


Figure 7. FT-IR spectra of a film deposited from a solution containing 1 VCl_4:40 EtOH:0.05 Brij 58:10 H_2O: (a) fresh, (b) 24-h-old, and (c) 493 K treated under N_2.

high intensity reached by the band at 490 nm is due to the high coefficient of absorption of V(V) when compared to V(IV). ESR measurements for aged films confirm the predominance of V(IV), as only a small reduction in the signal intensity was observed.

Thus, as-prepared VO_x hybrid films are very sensitive to atmospheric humidity and must be kept and treated in "dry" conditions. The aging of the films in low-humidity conditions (10%) results in further condensation, as indicated by FT-IR spectroscopy, which showed an increase in intensity and sharpening of the band at 530 cm^{-1} with time (Figure 7b). This FT-IR spectrum resembles those of amorphous VO_2 or V_3O_7 hydrates.[28] UV−vis spectrophotometry showed a band at 480 nm, of increasing intensity with time, indicating the partial oxidation of V(IV) to V(V) but, in this case, without a significant structural change. After approximately 24 h under these conditions, no additional structural and/or chemical changes were observed. However, exposure to ambient humidity for some hours still resulted in mesostructural collapse.

The reactivity of amorphous V_2O_5 and VO_2 toward air moisture and water is well-known.[25,28] Especially amorphous VO_2, when freshly precipitated, forms many hydrates ($VO_2 \cdot nH_2O$) that are deliquescent.[28] For the system studied here, in which a hydrophilic interface of enormous area between low condensed VO^{2+} moieties and the PEO-based headgroup of the surfactant exists, the low stability is not surprising, and the consolidation of the structure should readily be forced by thermal treatment (see below).

Role of Vanadium(IV) in the Formation of a Curved Interface. The key feature in the synthesis of mesostructured metal-oxo-based materials is to achieve a well-defined segregation of organic and inorganic domains at the nanometric scale. Two aspects are essential to accommodation of the self-assembly process and construction of the inorganic framework: the tuning of reactivity of the inorganic precursors (control of the polymerization rate) and the tuning of the interactions to generate a well-defined hybrid interface. The most relevant thermodynamic factors concerning the construction of inorganic mesostructures via self-assembly processes were first discussed in depth by Huo et al.[3] The free energy of mesostructure formation (ΔG_{ms}) is composed of four main terms, which represent the contributions of the inorganic−organic interface (ΔG_{inter}), the inorganic framework (ΔG_{inorg}), the self-assembly of the organic molecules (ΔG_{org}), and the solution (ΔG_{sol})

$$\Delta G_{ms} = \Delta G_{inter} + \Delta G_{inorg} + \Delta G_{org} + \Delta G_{sol} \qquad (1)$$

In a cooperative assembly route such as the one followed to synthesize these mesostructured VO_x hybrids, the template (Brij) initial concentrations are below those necessary for obtaining liquid-crystalline assemblies. The creation of a well-defined and compatible hybrid interface between the inorganic walls and the organic templates (i.e., ΔG_{inter}) is central to the generation of a well-ordered hybrid structure with adequate curvature.

From the kinetic point of view, the formation of an organized hybrid mesostructure is the result of a delicate balance of two competitive processes: phase separation/organization of the template and inorganic polymerization. This issue, well-known in microscale phase segregation, is essential when working with reactive non-silica-based systems such as vanadia. Under conditions where condensation is slow, the kinetic constants (k_i, related to ΔG_i presented above) of the different processes should be ordered as follows[3]

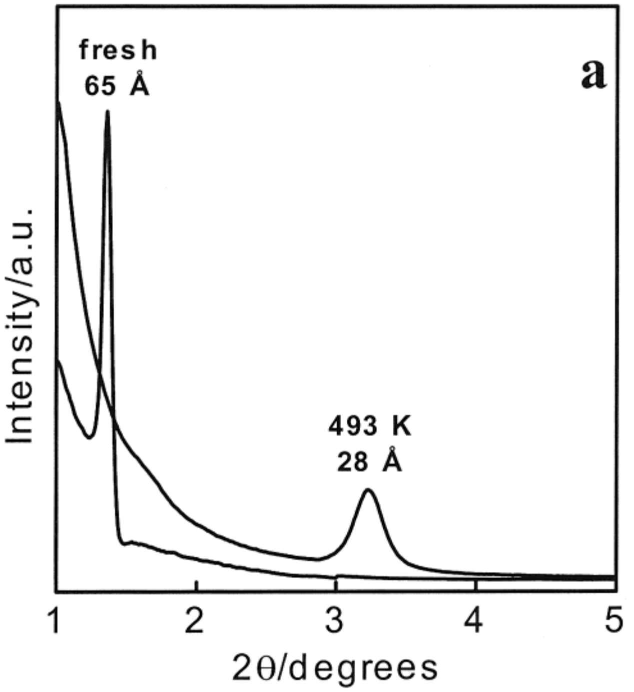
$$k_{inter} > k_{org} > k_{inorg} \qquad (2)$$

Equation 2 is applicable to the present case. Indeed, in highly acidic media, V(IV) species are not able to condense,[35] and therefore, hydrolysis and inorganic condensation are fully separated. The key point will be first to have an efficient hybrid interface and then to segregate the templates in an ordered assembly. The formation of the inorganic phase is subsequently triggered during film deposition and processing i.e., film aging and thermal treatment. The interaction between the polar heads of the template and the $[VO(OH_2)_{5-x}(Cl)_x]^{(2-x)+}$ species (B and C in Scheme 1) likely occurs at the apical position located at the opposite of the V=O bond (Scheme 1a). Depending on the chemical nature of the polar head (PEO in the present case, $-NH_2$ or $-NH_3^+$ in the case of vanadium oxide-based nanotubes[30]), the interaction can occur via complexation or via the solvation of coordinated water molecules. Then, a cooperative process between the hybrid vanadium-oxo−Brij surfactant triggered upon solvent evaporation allows cylindrical micellar structures to form and organize into hexagonal patterns (such a possible path is cartooned in Scheme 1). These species can adjust the needed curvature with more versatility because, during the first step of the deposition, condensation of the inorganic network is completely “turned off”.

Such an interaction will be more efficient if the trans-apical-coordinated position is accessible and if the bond between the sixth ligand and the vanadium is stronger (i.e., a “fuzzy” bond will likely be a less efficient connector). This can be provided by V(IV) species, which have the tendency to adopt less distorted square pyramidal (SP) or even distorted octahedral environments. The increase of the V=O bond lengths observed by FT-IR spectroscopy is highly favorable to this process, because this modification of the π character that occurs during film processing make the water more acidic and the hydroxyl groups bonded to vanadium more nucleophilic. These slight modifications allow some condensation reactions to begin, which, even if not extended, slowly decrease the degree of freedom of the surfactant assembly, helping to “freeze” the organized hybrid mesophase. As shown in the FT-IR spectra, a more extended condensation between oligomeric species likely occurs during the thermal treatment.

A similar self-assembly mechanism might be able to lead to the formation of curved interfaces, thus allowing for the formation of vanadium oxide-based nanotubes. The vanadium oxide sources can be reduced during hydrothermal treatment in the presence of long-chain amines, which play the role of surfactant. The desorption of V(IV) molecular species from the solid to the solution is a favored process, and therefore, an alkylamine- or alkylammonium-templated dissolution/precipitation close to that described for our mesostructured VO_x-hybrids might occur.

Structural Consolidation. Thermal treatment (in inert atmosphere) of films aged at low humidity resulted in preferential contraction in the direction normal to the substrate (represented in region 6 of Scheme 1), as one can see from the XRD results in $\theta-2\theta$ arrangement (Figure 8a). The structure is stable up to 523 K; further heating results in the irreversible deterioration of the ordered coatings. The broad (02) peak indicates the presence of a range of interpore distances. TEM analysis confirms the partial degradation of the structure. In Figure 8b, one can see the existence of channels throughout the structure; however, their organization by hexagonal packing is still present only at short range.



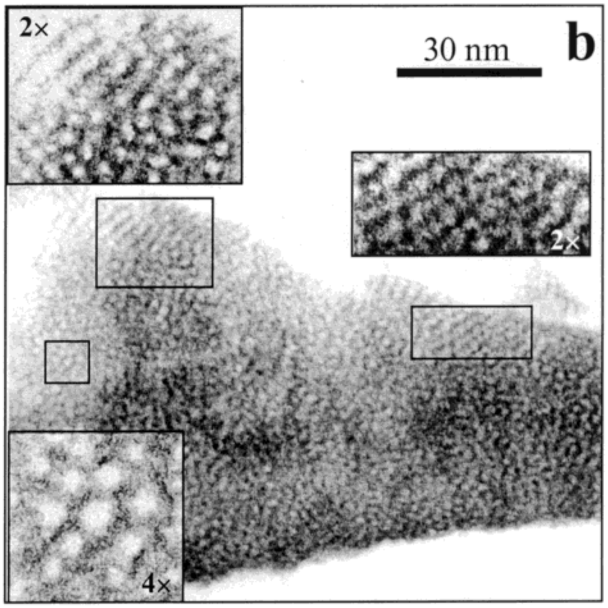


Figure 8. (a) Low-angle XRD patterns ($\theta-2\theta$ mode) for a Brij 58-templated hybrid film. (b) TEM image of the 493 K treated film. The insets are magnifications of the indicated regions.

Films treated at 493 K in N_2 contain only 0.05 Cl/V (as evidenced by EDX analysis). The FT-IR spectrum (Figure 7c) shows an intense, broad band centered at 730 cm^{-1} with shoulders at 670, 625, 578, and 465 cm^{-1} (V−O−V bonds); two bands at 998 and 950 cm^{-1} (short and long V=O bonds); and a drastic reduction in the intensity of the band centered at 3400 cm^{-1} (O−H bonds) when compared to that for the fresh film. This FT-IR spectrum is particularly similar (although less defined) to that reported by Theobald et al.[28] for V_4O_9, especially the intense band at 730 cm^{-1}, which is absent

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[35] Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley & Sons: New York, 1976.

for VO_2 (A) and weak for VO_2 (B). These results indicate that, by this temperature, the inorganic network is composed mainly of condensed mixed-valence (IV and V) vanadium oxide, with a predominance of V(IV). Films so treated display a dark brown color, characteristic of VO_2, and are still transparent and crack-free.

Attempts to eliminate the template, and thus to produce mesoporous mixed-valence vanadium oxide, have been unsuccessful so far. For VO_x-based hybrid films, ozone treatments applied to eliminate the template from TiO_2, ZrO_2, and Al_2O_3 mesostructured hybrid films results in the massive oxidation of V(IV) and the collapse of the structure. The use of solvent (hot ethanol) extraction produces template-free coatings, without the oxidation of V(IV), but also causes structural collapse.

Conclusions

In conclusion, VO_x-based mesostructured hybrid films were reproducibly prepared and found to exhibit a very high degree of organization in a 2D hexagonal (or 2D centered rectangular) structure. As-prepared hybrids contain mainly low condensed V(IV) species. Indeed, the presence of V(IV) seems to be essential to the formation of the mesostructure, probably by the modification of the V coordination sphere when reducing V(V), as demonstrated by spectroscopic data (FTIR, ESR). The decrease of the π character of the V═O axial bond, together with the approach of a trans-apical ligand, favors the development of octahedral (rather than square-pyramidal) metal-oxo environments, which, in turn, leads to a three-dimensional inorganic connectivity (instead of developing planar sheets). This likely permits a better adjustment of the organic−inorganic interface in achieving adequate curvature. Nevertheless, the low acidic V(IV) species are not able to produce extended condensed networks, and the structural organization is governed by the formation of the organic liquid-crystal phase and the interactions at the hybrid interface (the inorganic condensation is turned off during the deposition process). The fresh films thus exhibit a low stability, with a high sensitivity to the incorporation of water from the atmosphere. As a result, all processing should be conducted at low humidity (≤30%). Stabilization of the structure can be achieved by aging the films at low humidity followed by thermal treatment in inert atmosphere, which results in condensed mixed-valence vanadium oxide networks associated with the organic liquid-crystal phase.

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