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Synthesis of ordered mesostructured TiO_x thin films from tetrahydrofuran–water solutions

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ABSTRACT

The co-self-assembly of hybrid mesostructured TiO_x-based films from water-deficient tetrahydrofuran (THF) solutions, including a titania precursor species and ethylene oxide structure-directing agents (SDA), is reported. A variety of TiO_x mesostructures could be obtained, evident from small angle X-ray scattering and electron microscopy measurements, depending on the chemical composition and concentration of the SDA, and the concentration of water in the precursor solution. We find that the TiO_x mesostructured phase evolution with increasing SDA concentration in the THF-based solution follows the cubic → hexagonal → lamellar sequence reported for mesostructured TiO_x films deposited from the conventional aqueous/ethanol evaporation induced self-assembly (EISA) process. However, the unavailability of water molecules and the limited hydrolysis of the titania precursor due to the water-poor conditions in the THF-based solution, effectively reduce the concentration of hydrophilic species in the solution and their interactions with the SDA. As a result, directing a specific TiO_x mesostructure from a THF-based precursor solution requires SDA concentrations lower than that known to direct the same TiO_x mesostructure from the conventional, well studied aqueous/ethanol process. Furthermore, SDAs with very long ethylene oxide hydrophilic segments, which require high overall hydrophilic species concentration to promote self-assembly, are extremely sensitive to the concentration of water and hydrolyzed titania precursor concentrations in the solution, showing sharp mesophase transitions as a function of minute changes in water concentration.

1. Introduction

Hybrid nanostructured materials based on metal oxides, such as titanium dioxide and organic materials are central for various applications in the field of optics, electronics and energy conversion [1–3]. Titanium oxide-based hybrid materials, possessing controlled interfacial structure and high surface area, are conventionally synthesized using the evaporation induced self-assembly (EISA) method, starting from an aqueous/alcohol solution of a metal-oxide precursor and an amphiphilic structure directing agent (SDA) initially below its critical micelle concentration (cmc). Preferential evaporation of the alcohol during dip-coating concentrates the non-volatile SDA and metal-oxide precoursor species leading to two concurent processes: the self-organization of the SDA species into liquid–crystal-like mesophase domains, and the polymerization and cross-linking of the titania precursor [4–8]. The mesophases are fixed by the metal-oxide polymerization forming ordered metal oxide/SDA mesostructured films with symmetry and periodic length determined mainly by the architecture and molecular weight of the SDA species [4,5,9].

In addition to SDA architecture and molecular weight, its concentration in the precursor solution was shown to determine the type of mesophase deposited [8,10]. More specifically, the type of mesostructure to be directed from the multi component precursor solution could be predicted from the water/SDA phase diagram [8]. Importantly, it was shown that in EISA the SDA/water volumetric ratio in the binary phase diagram could be represented by the volumetric ratio between the SDA and *all* hydrophilic non-volatile components in the solution. The hydrophilic non-volatile components include water, hydrochloric acid, and the metal hydroxide species resulting from full hydrolysis of the metal-oxide precursor; provided that the metal hydroxide species selectively swells one component of the SDA and condenses on a time-scale that is slow compared to that of polymer self-organization. The excellent correlation between the experimental results and the prediction corroborates that the hydrolyzed titania precursor in the aqueous/ethanol precursor sol solutions, titanium hydroxide, associates selectively with the SDA hydrophilic segment assisting water molecules in the promotion of SDA self-assembly into micelles and liquid crystalline-like mesophases [8].

Incorporating functional guest species, organic or otherwise, into the mesostructure during film formation requires that the

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guest molecules are compatible with the aqueous/alcoholic sol–gel and SDA components, so that they do not macroscopically phase separate from the precursor solution. However, the aqueous/ethanolic conditions usually used for the synthesis of mesostructured oxides, are incompatible with highly hydrophobic guest molecules and limit the selection of organic functional molecules emendable for co-assembling with the SDA and metal-oxide precursor. Hence, new synthetic conditions are required to permit hydrophobic guest incorporation into the self-assembling mesoscopically ordered hybrid film during processing.

One way to achieve compatibility between the precursor solution and the hydrophobic guest to be incorporated is to replace the polar sol–gel solvents, ethanol and water, with a volatile less polar solvent, tetrahydrofuran (THF) [11]. Despite the chemical differences between THF and ethanol, it was shown that highly ordered silica mesophases can be prepared from THF-based solutions including a metal-oxide precursor species and a SDA species such as Pluronic® block-copolymers [11]. Moreover, solution processing in THF permitted highly hydrophobic, high molecular weight, conjugated polymers to be directly co-assembled within the mesostructured inorganic–organic host matrices during their formation [11–13]. Recently, we have shown that SDA-directed conjugated polymer-incorporated titania mesostructured films, prepared from THF-based precursor solution, are promising for photovoltaic devices [13]. However, the underlying non-aqueous synthesis conditions and mechanisms controlling the type of mesophase obtained and the interfacial structure and interactions have not been analyzed.

Here, the synthesis conditions and film formation mechanism of SDA-directed mesostructured TiO_x-based hybrid materials, processed from water-deficient THF-based precursor solutions, are discussed. We hypothesize that the water-deficient conditions when processing from THF-based solution, result in incomplete hydrolysis of the titania precursor and unavailability of water molecules, effectively reducing the concentration of hydrophilic species in the solution, and their interactions with the SDA necessary to promote its self-assembly. Although early studies reported that water shortage in the precursor solution induces the formation of worm-like mesophases [14], the actual effect of water availability and extent of metal-oxide precursor hydrolysis on the self-organization of SDAs and the ability to direct metal oxide mesostructures under water-deficient conditions has not been studied. Here, we find that ordered SDA-directed TiO_x mesostructures can be processed from water-deficient THF-based precursor solutions using a variety of SDAs. Moreover, we show that the TiO_x mesostructured phase evolution with increasing SDA concentration in the THF-based solution follows the cubic → hexagonal → lamellar sequence, in good correlation with that reported for mesostructured TiO_x-based hybrid films deposited from the conventional aqueous/ethanol EISA process [8,15,16]. However, the higher SDA/hydrophilic weight ratio in the THF-based precursor solution compared to that in aqueous/ethanol precursor solution with the same SDA concentration, directs the deposition of mesophases predicted for TiO_x processed from aqueous/ethanol solutions with lower SDA concentrations. The phase shift compared to that predicted for corresponding water-rich conditions with the same initial SDA concentration, becomes more apparent at high SDA concentrations which require higher overall hydrophilic species concentrations to promote self-assembly. Furthermore, we find that SDAs with very long hydrophilic segments, which also require high overall hydrophilic species concentration to promote self-assembly, are extremely sensitive to the concentration of water and hydrolyzed titania precursor in the solution, showing sharp mesophase transitions as a function of minute changes in water concentration.

2. Experimental

2.1. Materials

Titanium tetraethoxide (TEOT, Aldrich Germany), concentrated 12.1 M hydrochloric acid (HCl) in de-ionized water (Carlo Erba, Italy), and tetrahydrofuran (THF AR, BioLab, Israel) were used as-received. Two structure-directing surfactant triblock poly(ethyleneoxide)-b-poly(propylene-oxide)-b-poly(ethyleneoxide) copolymers were obtained as gifts from BASF, USA, and used as-received: $EO_{20}PO_{70}EO_{20}$ (Pluronic™ P123, Mn = 5750 g/mol), and $EO_{106}PO_{70}EO_{106}$ (Pluronic™ F127, Mn = 12600 g/mol), where 'EO_x' and 'PO_y' represent the lengths of the ethyleneoxide and propyleneoxide blocks, respectively. The Pluronic™ triblock copolymers P123 and F127 are composed of relatively hydrophobic center propyleneoxide blocks (PO) of identical mean lengths (70 PO monomer units), and two hydrophilic ethyleneoxide blocks (EO) on each end that are substantially shorter (20 EO units each) for P123 than for F127 (106 EO units each). Two low-molecular-weight $C_nH2_{n+1}(EO)_m$ surfactants were purchased from Aldrich: Brij 56™ ($n = 16$, $m = 10$, Mw = 683 g/mol) and Brij 58™ ($n = 16$, $m = 20$, Mw = 1125 g/mol). Compared to the Pluronic™ triblock copolymers, the Brij surfactants are diblocks composed of short hydrophilic ethyleneoxide segments (10 and 20 EO monomer units for the Brij 56 and Brij 58, respectively) and $C_{16}H_{33}$ alkyl chains that are significantly more hydrophobic than the propyleneoxide blocks of the Pluronics™.

2.2. Synthesis and film deposition

In a typical process, partial hydrolysis of TEOT was performed by adding 0.35 ml HCl 12 M to 1 ml liquid TEOT and vigorous stirring for about 10 min until the solution was clear. Upon mixing, a slight color change of the solution was observed from colorless to light yellow. Separately, a THF solution of the SDA was prepared, stirred and carefully added to the TEOT solution. The mixture was then stirred for 2 hours prior to film deposition. The molar ratios between all ingredients in the THF-based sol solutions are listed in Table 1. SDA weight percentages in the THF-based solutions, calculated following Alberius et al. [8] are also listed in Table 1 to enable comparison with water/SDA phase diagrams.

Thin films were prepared by dip coating on glass slides, Si and Kapton® polyimide films for TEM, HRSEM and SAXS measurements, respectively. The dip coating was performed at withdrawal speed of 2 mm/s in an environmentally controlled chamber with a relative humidity of 70–80%, unless stated otherwise.

2.3. Film characterization

Small-angle X-ray scattering measurements (SAXS) were performed on polyimide in a "glancing incidence" scattering geometry [12], which shows diffracted intensity exclusively out-of-the-film-plane, using two detectors. The first, is a Bruker Nanostar, KFF CU 2K-90 with Cu Kα radiation with $\lambda = 1.54$ Å ($V = 40$ kV, $I = 20$ mA), a pinhole collimation yielding a beam with 100 μm diameter (FWHM), and a $10 \times 10\ cm^2$ detector positioned 64.3 cm behind

Table 1
SDA wt% and molar ratios between all ingredients in the THF-based sol solutions used to deposit mesostructured TiO_x in this study.

	TEOT	HCl	H_2O	SDA (s)	THF	SDA (wt%)
F127	1	0.9	3	$0 < s < 0.02$	12	$0 < W < 63$
P123	1	0.9	3	$0 < s < 0.02$	12	$0 < W < 45$
Brij 56	1	0.9	3	$0 < s < 0.2$	12	$0 < W < 50$
Brij 58	1	0.9	3	$0 < s < 0.3$	12	$0 < W < 70$