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Synthesis of nanostructured polymer-titanium oxide composites through the assembly of titanium-oxo clusters and amphiphilic block copolymers micelles†

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The titanium oxo-organo clusters [$Ti_{16}O_{16}(OEt)_{32}$] are used as precondensed building blocks for the sol-gel synthesis of titanium oxide nanostructures in the presence of an amphiphilic block copolymer PS-b-PMAA (PS = polystyrene block; PMAA = polymethacrylic acid block) as a structure directing agent. It is shown that clusters—opposite to the more reactive titanium alkoxides—can be organized and hydrolysed under controlled conditions. The resulting polymer-titanium oxide nanocomposites were characterised by TEM, SAXS, ^{17}O MAS NMR spectroscopy.

Introduction

The preparation of nanostructured materials is an important challenge of materials science. This field of chemistry is involved in the synthesis of advanced materials which are made with large assemblies of nanoparticles or metal based clusters. Size reduction of metals and semiconductors to the range of a few nanometers can lead to novel and peculiar properties. As an example, owing to their large active surface, metal nanoparticles can exhibit interesting catalytic properties. Moreover, optical, electric or magnetic properties of a material are strongly dependent on the size and on the shape of the particle as well: optical transitions and spectral characteristics are directly correlated to the particle size of metal colloids (quantum size effects).[1] Therefore the performance of materials in applications requires the control over the size, the morphology and the surface structure, which is based on the appropriate control of the parameters that influence nucleation and growth. Such a control over the growth and morphology of materials can be achieved by the use of organic templates which self-assemble into complex structures, patterning inorganic architectures built from inorganic precursors.

The synthesis of such materials through low temperature chemical routes allows a better control of their microstructure. Among the different processes involving low temperature, sol-gel processes are a way of making highly dispersed materials through the growth of metal oxo-polymers in a solvent.[2–3] These soft chemistry processes are based on hydrolysis-condensation reactions of molecular precursors such as metal alkoxides $M(OR)_4$ (M = Si, Ti...). However, as the transition metal alkoxides are particularly sensitive towards hydrolysis, the resulting oxo-polymers that constitute the sols and gels are generally polydisperse in size and composition.[2,4] An attractive solution for this problem is to use preformed metal-oxo clusters of well defined structure as precursors for making new hybrid organic-inorganic assemblies and new metal oxides. These clusters being already condensed compounds are less reactive towards nucleophilic species compared to metal alkoxides.

The transition metal-oxo clusters are generally synthesised *via* substoichiometric hydrolysis ($H_2O/M < 1$) of metal alkoxides[5] or of metal alkoxides complexed by some ligands like β-diketones or carboxylic acids.[6–7] An alternative strategy using *in situ* generation of water has also be developed in order to synthesize new metal-oxo clusters.[6,8,9,10]

Different works deal with the texturation of titanium oxide with dendrimers or commercial amphiphilic block copolymers (Pluronic® type) as structure directing agents.[11,12] In this paper, we describe an original route for the synthesis of hybrid titanium oxide nanostructures from the complexation driven assembly of titanium oxo clusters [$Ti_{16}O_{16}(OEt)_{32}$] and much less used amphiphilic block copolymers PS-b-PMAA. These polymers consist of one polystyrene block and one polymethacrylic acid block.

Experimental

Syntheses of the block copolymer-titanium oxide nanoparticles composites

The complex [$Ti_{16}O_{16}(OEt)_{32}$] was prepared as described in an earlier publication[13] and the crystals were isotopically enriched by using 20% ^{17}O enriched water for their synthesis.

The PS-b-PMAA block copolymers chosen consist of one polystyrene block (PS) and one polymethacrylic acid block (PMAA) with equal chain lengths (105 monomer units). The synthesis of the PS-b-PMAA polymers which is mainly based on anionic polymerization was performed as described in an earlier publication.[14]

For the hybrid material PS-Ti-I, the block copolymer PS-b-PMAA is first dissolved in toluene at a concentration of 13.5 g L^{-1}. 25 mL of the PS-b-PMAA solution is mixed with 1 mL of a 120 g L^{-1} solution of the complex [$Ti_{16}O_{16}(OEt)_{32}$]

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†Electronic supplementary information (ESI) available: SAXS diffractograms of PS-Ti-I and PS-Ti-II. See http://www.rsc.org/suppdata/jm/b2/b203566a/

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in toluene (3 equivalents of complex $[Ti_{16}O_{16}(OEt)_{32}]$ per PS-b-PMAA). The resulting solution is stirred for 1 hour.

For the hybrid material PS-Ti-II, 25 mL of a 8.4 g L^{-1} PS-b-PMAA solution in toluene is mixed with 1 mL of a 77 g L^{-1} solution of the complex $[Ti_{16}O_{16}(OEt)_{32}]$ in toluene (3 equivalents of complex $[Ti_{16}O_{16}(OEt)_{32}]$ per PS-b-PMAA). After stirring the solution for a few minutes, the flask is evacuated in order to remove the toluene solvent. 25 mL of EtOH is then added to the flask and the resulting mixture is stirred for 1 hour.

After slow evaporation of the solvents, thick coatings were obtained. These xerosols PS-Ti-I and PS-Ti-II were characterised by solid state NMR, X-ray diffraction and transmission electron microscopy.

Characterisation

^{17}O MAS NMR spectroscopy. The ^{17}O Magic Angle Spinning (MAS) NMR spectrum of complex $[Ti_{16}O_{16}(OEt)_{32}]$ was recorded on a Bruker MSL-300 spectrometer operating at 40.40 MHz, using Bruker 4 mm probe. Pulses of 0.7 μs ($\theta = 90°$) width were used for data acquisition with a 1s recycle delay. 2860 FIDs were accumulated.

For the samples PS-Ti-I and PS-Ti-II, ^{17}O MAS NMR spectra were acquired on a Bruker DSX-400 spectrometer operating at 54.25 MHz using a Bruker 4 mm MAS probe. The spectra were recorded using a spin-echo θ-τ-2θ pulse sequence to overcome problems of probe ringing and avoid baseline distorsion ($\theta = 90°$ corresponding to a pulse length of 7.2 μs). The τ delay value was determined by the spinning frequency of the rotor (RO = 15 kHz) and was equivalent to 1/RO. A recycle delay of 1s was employed and 77000 FIDs were accumulated. Chemical shift values were referenced to tap water ($\delta = 0$ ppm).

SAXS and WAXS experiments. The small-angle and the wide angle X-ray scattering patterns were collected on an Enraf Nonius FR590 diffractometer at room temperature.

TEM. TEM images were acquired on a Zeiss EM 912 at an acceleration voltage of 120 kV. One droplet of the suspension was applied to a 400 mesh carbon-coated copper grid and left to dry in air.

Results

Synthetic approach

As the titanium(IV) is particularly sensitive towards hydrolysis, a careful tuning of the hydrolysis-condensation of titanium(IV) and the self-assembly processes is crucial.

The $[Ti_{16}O_{16}(OEt)_{32}]$ cluster was chosen as a precursor as it presents the best compromise with the yield of its synthesis and its stability towards nucleophilic species. Actually, it has been shown that the stability of the titanium-oxo clusters towards nucleophilic species increases with the cluster nuclearity, the number of six-coordinate titanium atoms and the presence of bidentate ligands.[11] In particular, it has been reported that the titanium oxo clusters with a high nuclearity (number of titanium atoms $\geqslant$ 12) are stable in the presence of alcohol or polyol. In the presence of small amounts of water, the titanium-oxo cores can be conserved depending on the solvent used.

Amphiphilic block copolymers (ABCs) consisting of hydrophilic and hydrophobic blocks, can through their incompatibility give rise to their self-assembly into particulate structures such as spherical and cylindrical micelles and also liquid crystalline phases.[15] The general advantage of amphiphilic block copolymers compared to low molecular weight analogues are the increased kinetic stability of the aggregated structures over a wide range of compositions and temperature.[15] This is one of the reasons why the PS-b-PMAA block copolymers were chosen as templates.

Moreover, in contrast to the previously used triblock copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO-PPO-PEO, Pluronic®),[11] the solubility difference between the blocks is more pronounced in the case of PS-b-PMAA. As a consequence, the PS-b-PMAA block copolymer is expected to make the templates more stable against structural changes occurring throughout the reaction. In addition, the carboxylate groups induce a strong chemical binding to the oxo-clusters by ligand exchange.

In this study, two organic solvents that selectively dissolve one of the two blocks are used. In a selective solvent, the diblock copolymers form micelles with a core consisting of the insoluble block and a corona of the soluble block.[15] In the case of symmetric block copolymers, the resulting structures are spherical micelles. In non polar solvents such as toluene, the polystyrene block is pointing outside the micelle core while in polar solvents such as ethanol, the PMAA block is pointing outside the micelle core.[15] Therefore, depending on the polarity of the solvent, different topologies may be formed from the aggregation of the titanium-oxo clusters and the block copolymer micelles.[15]

Block copolymer-titanium oxide nanoparticles composites

Two nanostructured polymer-titanium oxide composites PS-Ti-I and PS-Ti-II have been synthesised from the assembly of the titanium oxo clusters $[Ti_{16}O_{16}(OEt)_{32}]$ and the PS-b-PMAA block copolymers templates. Fig. 1 shows transmission electron microscopy (TEM) micrographs of the samples PS-Ti-I

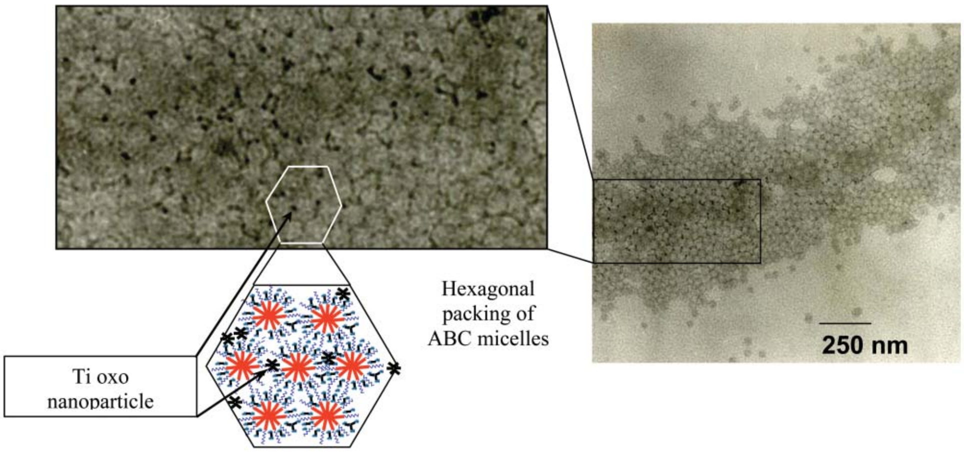

Fig. 1 TEM micrograph of the titanium oxide-block copolymer nanocomposite PS-Ti-I.

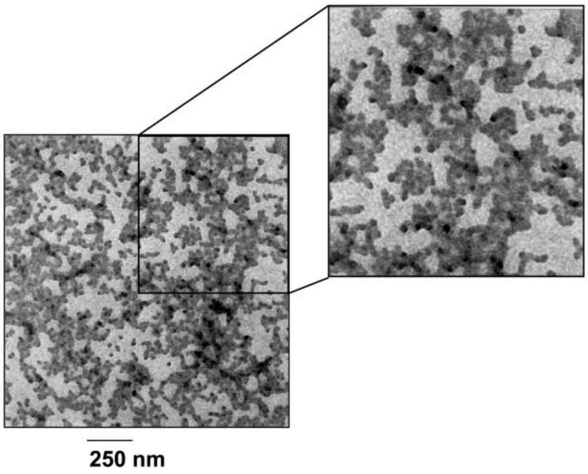

Fig. 2 TEM micrograph of the titanium oxide-block copolymer nanocomposite PS-Ti-II.

prepared by contacting block copolymer and titanium-oxo-clusters in toluene and casting the solution on a carbon-covered microscopy grid. The picture represents hexagonal close packing of spherical diblock copolymers micelles with a diameter of about 30 nm, the white holes representing the polymethacrylic acid cores without any titania inside. Some black dots with a size between 1 and 5 nm are located outside of the micelles cores in the formerly swollen polystyrene matrix. These black regions are likely due to titanium-oxo based nanoparticles made of connected [$Ti_{16}O_{16}$] oxo cores.

Another morphology was observed when ethanol solvent was used instead of toluene. Fig. 2 shows a TEM micrograph recorded on samples PS-Ti-II obtained by casting the ethanol solution. In this case, block copolymer micelles of 30 nm in diameter were formed with a polystyrene core. Titanium-oxo based nanoparticles are located inside or at the surface of the micelles cores, resulting in a strong imaging contrast.

Small angle X-ray scattering (SAXS) experiments were performed on the PS-Ti-I and PS-Ti-II samples, and the patterns exhibit one single peak corresponding to a distance between scattering objects of 24.5 nm. This distance is in agreement with the size of the micelles. No diffraction peaks are observed in the WAXS (wide angle X-ray scattering) patterns indicating that the titanium-oxo based particles are amorphous or too small.

^{17}O MAS NMR spectroscopy

In order to characterise the titanium-oxo based nanoobjects, ^{17}O MAS NMR experiments were performed in solid state with ^{17}O-enriched samples. Indeed amongst the quadrupolar nuclei which can be investigated by solid state NMR, ^{17}O NMR spectroscopy can provide interesting information on oxygen bonding, solvation, crystallographic symmetry and molecular structure. The ^{17}O NMR spectra of the titanium oxide-block copolymer composites PS-Ti-I and PS-Ti-II are identical. Only the spectrum of sample PS-Ti-I is represented in Fig. 3(b). In addition, the spectrum of the parental crystalline [$Ti_{16}O_{16}(OEt)_{32}$] cluster is presented in Fig. 3(a) together with the molecular structure of the cluster (inset in Figure 3). The spectra display three sets of resonances. According to the assignments previously reported for oxo-bridges,[4,16] the signals at 365 ppm, 540 ppm and 750 ppm correspond to the Ti_4-O, Ti_3-O and Ti_2-O oxygens respectively. These signals are quite close to those of the [$Ti_{16}O_{16}(OEt)_{32}$] cluster spectrum (see Fig. 3(a)).

Apparently, the metal-oxo cores of the [$Ti_{16}O_{16}(OEt)_{32}$] clusters are preserved in the titanium-oxo based nanoparticles. Indeed, the ^{17}O NMR resonances are quite close to those of the parental titanium clusters and the line width of the signals ($\Delta v \sim 1600$ Hz) are weak compared to those of usually reported for titanium oxo-polymers ($\Delta v \sim$3000-5000 Hz).[16] Moreover, it has already been demonstrated that the metal-oxo core of the [$Ti_{16}O_{16}(OEt)_{32}$] cluster is quite stable in the presence of a small amount of water (16 equivalents of water per [$Ti_{16}O_{16}(OEt)_{32}$] cluster).[11,17]

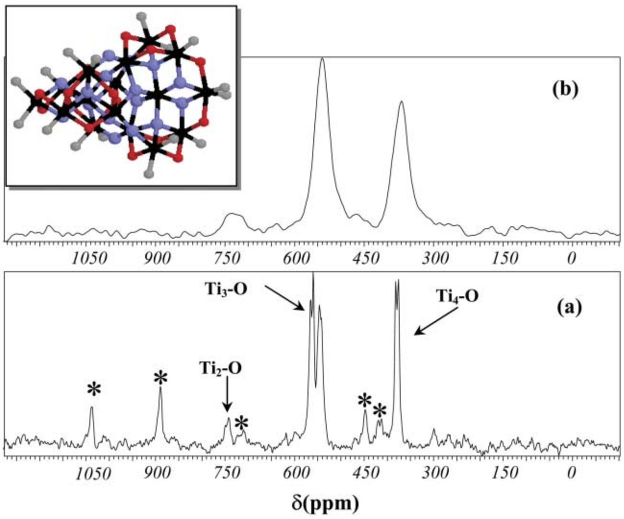

Fig. 3 ^{17}O MAS NMR spectra of (a) [$Ti_{16}O_{16}(OEt)_{32}$] (ν_{rot} (rotation speed) = 6 kHz; ^{17}O (Larmor frequency) = 40.40 MHz; NS (number of scans) = 2860; LB (line broadening) = 25 Hz), (b) the nanocomposite PS-Ti-I (ν_{rot} = 15 kHz; ^{17}O (Larmor frequency) = 54.25 MHz; NS = 77000; LB = 25 Hz). (* = spinning side bands.) Inset: molecular structure of the cluster [$Ti_{16}O_{16}(OEt)_{32}$]. The carbon and the hydrogen atoms are omitted. Ti atoms are represented by black spheres, O atoms of terminal OEt groups by gray spheres, O atoms of bridging OEt groups by red spheres and O atoms of oxo groups by blue spheres.

Discussion

The location of the titanium-oxo based nanoparticles in the polymer matrix and consequently the nature of the interactions with the organic interface is not obvious from the different experiments. However, the [$Ti_{16}O_{16}(OEt)_{32}$] clusters are soluble in non polar solvents as the metal oxo framework is capped by hydrophobic alkoxy groups. As a consequence, it can be expected that at the early stage of the process these clusters will be located in the hydrophobic regions, *i.e.* either in the unpolar solvent or close to the micelle core formed by polystyrene (in polar solvent). On the other hand, it is known that carboxylate ligands are strong complexing ligands. As a consequence, some titanium centres of the [$Ti_{16}O_{16}(OEt)_{32}$] clusters may be covalently bound to the carboxylate ligands of the PMAA blocks, presumably at those which are in direct proximity to the polystyrene regions. Moreover, these complexation reactions are accompanied by esterification reactions between released alcohol and carboxylic acid groups. Indeed infrared spectra recorded on the micellar solution (in toluene or in EtOH) containing the [$Ti_{16}O_{16}(OEt)_{32}$] clusters display a small stretching vibration v(C=O) at 1750 cm^{-1} that is typical of ester species. A small quantity of water released in solution can explain that the titanium-oxo based nanoparticles are built from the connection of [$Ti_{16}O_{16}(OEt)_{32}$] clusters. The formation of the titanium-oxo based nanoparticles proceeds probably through the hydrolysis-condensation of some alkoxy groups thereby forming bridges between [$Ti_{16}O_{16}(OEt)_{32}$] clusters.

On the basis of these experiments and our knowledge on the titanium-oxo clusters reactivity, it is possible to propose a mechanism for the formation of the titanium-oxo based

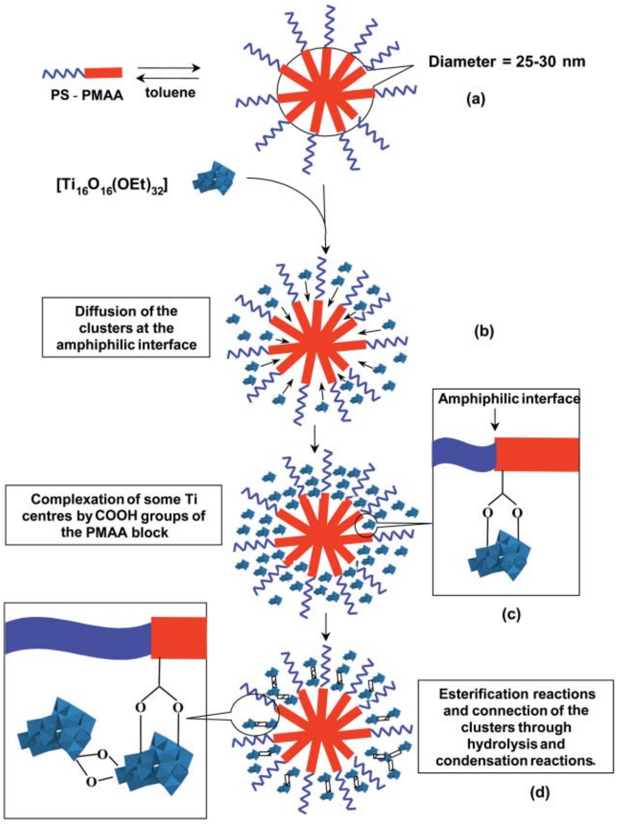

Fig. 4 Proposed mechanism for the formation of the titanium oxide-block copolymer nanocomposite PS-Ti-I.

nanoparticles obtained in toluene (PS-Ti-I). The proposed mechanism is presented in Fig. 4.

In toluene that selectively dissolves the PS block, the amphiphilic block copolymers PS-b-PMAA form spherical micelles with a core consisting of the insoluble block PMAA (Fig. 4 (a)). Once the titanium-oxo clusters are added to the micellar solution, their solubility in hydrophobic solvents leads to their incorporation in the PS corona (Fig. 4 (b)). Some of them can diffuse into the amphiphilic interface between the PMAA block and the PS block and are bound by the carboxylate ligands (Fig. 4 (c)). This interaction between titanium-oxo clusters and the hydrophilic block of the polymer can give rise to a decrease of the amphiphilic character of the polymer as it was previously reported for the texturation of the $[Ti_{16}O_{16}(OEt)_{32}]$ clusters by the triblock copolymer PEO-PPO-PEO.[11] In this latter study, an inadequate self assembly of the template in the stages preceding the formation of the hybrid aggregates is responsible for the lack of any order in the hybrid materials.[11] Obviously, the block copolymer PS-b-PMAA possesses a stronger amphiphilic character than PEO-PPO-PEO. Moreover, as a large excess of the block copolymer is added (Ti/COOH $\approx$ 0.45), only a part of the carboxylate groups of the PMAA blocks are bound to the titanium atoms, and the amphiphilicity of the polymer is preserved.

As a consequence, the addition of the controlled amount of titanium-oxo clusters to the micellar solution does not disrupt the structures of the block copolymer micelles, and a hexagonal mesophase is obtained upon evaporation of the solvent. Moreover, it is to be assumed that the concrete structure of the micelles and those of the hexagonal phase may be assisted by the addition of the titanium-oxo clusters (the pure block copolymer shows a lamellar mesophase in the bulk). The coordination of titanium atoms by carboxylate groups may be followed by some esterification reactions which promote the further hydrolysis and condensation of the titanium-oxo clusters (Figure 4 (d)). The formation of an inorganic framework that is covalently linked to the polymer matrix enhances the stability of the aggregated structures and changes interface curvatures.

For the second hybrid material (PS-Ti-II), as the block copolymer is dissolved in a polar solvent, reverse micelles are formed and the titanium-oxo clusters are located inside the cores of the micelles. Moreover, the solubilization of the PMAA block in the solvent EtOH may favour the esterification reactions and a larger amount of water may be released in the micellar solution. As a consequence, larger titanium oxide aggregates are formed. Therefore, the amphiphilic block copolymers micelles provide some spherical microdomains of suitable size and shape into which the controlled growth of titanium oxide particles is performed. Such an approach has already been performed for the preparation of metal colloids.[18]

Conclusion

Titanium oxide nanoparticle-block copolymer composites with different topologies can be obtained under the structure directing influence of block copolymer micelles. The morphology of the materials is strongly dependent on the polarity of the solvent used to dissolve the block copolymer. In toluene, titanium-oxo based nanoparticles are located in the corona of micelles arranged in an ordered array while in ethanol, titanium-oxo based nanoparticles are incorporated in the micelle cores. Moreover, the titanium-oxo cores are preserved during the assembly, the complexation and the condensation processes. The stability of the titanium-oxo clusters demonstrates the great potential of these complexes as mesoscopic building blocks for the controlled synthesis of titanium oxide mesoporous materials.[19] These materials are accessible by solidification from toluene solutions and calcination under careful temperature programming to split off the ligands and to remove the porogenic polymer. Due to the complexity of these processes and their influence on the structural rearrangement of the titanium coordination spheres, this will be subject of forthcoming work.

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