



## Macromolecular Nanotechnology

## Control on titania nanostructure by combining block copolymer assisted sol–gel synthesis with rapid flux solvent atmosphere treatment



Gianpaolo Chieffi<sup>b</sup>, Rocco Di Girolamo<sup>a</sup>, Antonio Aronne<sup>b</sup>, Pasquale Pernice<sup>b</sup>, Esther Fanelli<sup>b</sup>, Massimo Lazzari<sup>c</sup>, Manuel Gómez<sup>c</sup>, Claudio De Rosa<sup>a</sup>, Finizia Auriemma<sup>a,\*</sup>

<sup>a</sup> Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Complesso Monte Sant'Angelo, via Cintia, 80126 Napoli, Italy

<sup>b</sup> Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy

<sup>c</sup> Centre for Research in Biological Chemistry and Molecular Materials (CIQUS), University of Santiago de Compostela, 15782 Santiago de Compostela, Spain

## ARTICLE INFO

## Article history:

Received 10 April 2014

Received in revised form 28 June 2014

Accepted 27 July 2014

Available online 14 August 2014

## Keywords:

Block copolymers self-assembly

Sol–gel technique

Large area nanopatterning

Titania nanoparticles

Hybrid nanostructured composites

## ABSTRACT

A method is developed for rapid preparation of titania substrates using a sol–gel preparation route in combination with an amphiphilic block copolymer (BCP) template, acting as structure directing agent. The method consists in performing the spin coating of an initial solutions of BCP and titania species in a controlled atmosphere using a flux of solvent vapors (Rapid-Flux-Solvent-Atmosphere, RFSA method). The method is demonstrated in the case of thin films of polystyrene-*b*-poly(oxyethylene) BCP (PS-PEO) with cylindrical morphology of PEO domains in the PS matrix, characterized by the selective inclusion of titanium species inside the PEO cylinders. Upon removal of the organic matrix by heat treatment at 600 °C, titania substrates of different morphology are obtained depending on the concentration of titania precursor and processing conditions. The method allows preventing the negative effect of hydrolysis and condensation reactions of Ti species and titania substrates with morphology reminiscent of that one achieved in the hybrid nanostructured thin films are obtained. The RFSA method is simple, direct, and it is of particular interest for systems that require a short processing time to eliminate the solvent and to obtain regular nanostructured thin-films over large area. Merit figures such as the degree of hexagonal order and the degree of coverage of the surface with titania motifs are identified to characterize the hybrid composites and titania substrates.

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## 1. Introduction

Titanium dioxide nanoparticles have received considerable attention in the last years because of their large specific surface, semiconductive properties, good selectivity toward oxidizing reactions and good photostability in solution [1,2]. These unique properties, coupled with the low cost and safety toward environment and human health

make TiO<sub>2</sub> nanoparticles suitable for a wide range of applications in numerous fields such as hybrid solar cell, electric and photocatalytic systems, and gas sensing [3–7]. However, in order to best exploit these properties in advanced applications, the obtaining of dense arrays of inorganic nano-element with well controlled morphology is required [8–19].

Nanostructured titania substrates with well controlled morphology may be created with different approaches [1,2]. In particular, the methods based on the use of an amphiphilic block copolymer (BCP) coupled with the sol–

\* Corresponding author. Tel.: +39 081 674341; fax: +39 081 674090.

E-mail address: [finizia.auriemma@unina.it](mailto:finizia.auriemma@unina.it) (F. Auriemma).

gel process of a titanium compound as precursor have received large attention [3,20–32].

For instance, exploiting the method of Evaporation Induced Self-Assembly (EISA) [20–25] selective solvents for one of the blocks allow micellar aggregates or inverted micellae to be formed in solution, where titanium species are selectively included inside the hydrophilic regions. The successive evaporation of the solvent allows well-organized arrays of titania nano-dots of uniform size and shape or mesoporous titania templates, respectively, to be obtained. On the other hand, also non-selective solvents may be used to create morphologies characterized by nano-motifs covering the whole area of the support by drop casting or spin coating dilute solutions. In this approach the self-assembly of the BCP associated with the preferential interactions of the titanium species with hydrophilic domains is exploited [3,26–32]. The final morphology is steered by the tendency of the covalently linked distinct macromolecules constituting amphiphilic BCPs to segregate into different domains in order to minimize their mutual repulsions, thus resulting in the spontaneous formation of different types of nanostructures (spheres, cylinders, lamellae) on different supports [33–35]. A key step of the BCP-mesophase separation mediated process is thus the formation of hybrid nanostructures, in which the BCP matrix acts as host for sequestering guest titanium species in specific domains [36] during the sol–gel process [1]. Upon removal of the organic matrix, nanoparticles, worm-like entities, cylinders, nanoclusters or nanoporous matrices of titania nano-motifs may be obtained, reminiscent of the domain-organized nanostructures achieved in the hybrid system [26–32]. Therefore, the final morphology of titania substrates may be finely controlled at nanoscale level by the careful selection of the preparation method of the hybrid nanostructured system and successive processing conditions adopted for removal of the organic component [26–32].

Although the intricate kinetics and thermodynamic phenomena underlying the process of formation of hybrid systems and titania substrates through the latter approach have been, at least in part, understood [1,3,29,32,37,38] and several methods have been devised for tailoring the final morphology over large area [13,26–32], the issue related to the fine control of the structural organization of inorganic nanoparticles at nanometric length over large area for any given combination of BCP, Ti-species, solvent in a fast and low cost process is still a challenge.

In this study, a systematic investigation of different protocols for preparation of titania substrates having controlled morphology over large area is performed, using the self-assembly of an amphiphilic BCP, namely a polystyrene-*block*-poly(ethylene oxide) diblock copolymer (PS-PEO), coupled with a sol–gel process. By dissecting the physicochemical phenomena subtending the whole process, a quick, simple and low cost method for preparing with high reproducibility hybrid nanostructures and highly uniform titania substrates characterized by tailored morphology over large area is rationally devised. The method is based on an innovative spin-coating procedure of initial solutions containing the BCP and a precursor of titanium species under a flux of suitable solvent vapors, so that a

controlled atmosphere is rapidly attained. This method of Rapid-Flux-Solvent-Atmosphere (RFSFA) is of particular interest for systems that require a short processing time to eliminate the solvent and to obtain nanostructured thin-films with a high degree of order over the whole area of the substrate.

## 2. Experimental section

### 2.1. Materials and methods

The PS-PEO block copolymer was purchased from Polymer Source Inc. Toluene, isopropyl alcohol (IPA), titanium tetraisopropoxide (97%, TTIP) were purchased from Aldrich. All reagents were used as received. The number average molecular mass  $M_n$  of the BCP is 136,000 g/mol ( $M_w/M_n$  1.18,  $M_w$  being the mass average molecular mass). The BCP includes a PS amorphous block with  $M_n = 102,000$  g/mol and glass transition temperature of 102 °C and a PEO semi-crystalline block with  $M_n = 34,000$  g/mol and melting temperature of  $\approx 64$  °C. A BCP with volume fraction of PEO blocks equal to 0.23 (calculated considering that the density of PEO and PS are 1.064 g/cm<sup>3</sup> and 0.969 g/cm<sup>3</sup>, respectively [39,40]) was selected in order to have a microphase-separated morphology, in which PEO cylinders are hexagonally arranged in the PS matrix.

Toluene solutions 1 wt% BCP were prepared at room temperature by stirring for at least 1 h up to complete dissolution. Sample solutions of the BCP and relative Ti content ranging from 1 to 80 mol% (mol Ti: mol PEO monomeric units) were obtained according to the following procedure: (1) 0.125 mmol of TTIP and 0.125 mmol H<sub>2</sub>O were dissolved in 5 ml of isopropanol in less than 3 min; (2) 5 ml of toluene was added drop-wise to 5 ml of the homogeneous mixture prepared in the step 1 under stirring for about 1 h, giving a bright light yellow solution 0.0125 M TTIP and 0.0125 M H<sub>2</sub>O. (3) The appropriate amount of the solution prepared at step 2 (20, 50, 200, 400, 800, 1200 and 1600  $\mu$ l) was added to 500  $\mu$ l of the 1 wt% BCP toluene solution, and stirred for 30 min, to obtain BCP solutions containing titanium species (1, 2.5, 10, 20, 40, 60, and 80 mol% Ti, respectively).

All solutions were used immediately after preparation. We checked that during the fast protocol adopted for preparation of hybrid solutions containing Ti species and the BCP (90 min), the solution remained transparent, even without addition of HCl, which is generally added both as a catalyst for the hydrolysis of TTIP and as a retardant for the condensation reactions [29,32,41].

Thin films of neat BCP and PS-PEO/titanium species hybrid system, of thickness 50–100 nm, were obtained at room temperature by spin coating in a closed tank (volume  $\approx 7.3 \times 10^{-3}$  m<sup>3</sup>) at 2500 rpm for 30 s, after deposition of few drops ( $\approx 0.2$  ml) of a solution on a silicon wafer (1 cm  $\times$  1 cm) using a spin coater P6700-Specialty Coating Systems.

The thickness of films was measured with a DEKTAK 3 – Surface Profile Measuring System fabricated by Sloan Technology, by performing at least 10 independent measurements in different regions of the same sample and over different samples. The relative error is less than 10%.

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