RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Advances RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Rapid-Flux-Solvent-Atmosphere method for tailoring the morphology of titania substrates over large area via direct self-assembly of block copolymers

Received 00th XXX 20xx,
Accepted 00th XXX 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gianpaolo Chieffi,[a] Rocco Di Girolamo,[b] Antonio Aronne,[a] Pasquale Pernice,[a] Esther Fanelli,[a] Massimo Lazzari,[c] Claudio De Rosa,[b] Finizia Auriemma*[b]

A fast method to direct self-assembly of block copolymers loaded with metal oxide precursors in specific domains is set up. It consists in performing spin-coating in controlled atmosphere under flux of solvent vapors (Rapid-Flux-Vapor-Atmosphere). Nanostructured thin-films of hybrid composites and regular titania substrates well oriented over large area are rapidly obtained.

In the last decades the development of methods for surfaces decoration with nano-motifs of inorganic materials having regular shape and uniform size, organized at nanometric length scale over large area, has experienced a tremendous progress.[1,2] The interest for such systems derives from the intrinsic properties of nano-sized inorganic particles at fundamental level arising from both isolated entities, and their ensembles.[2,3] In particular, titanium dioxide nanoparticles have received considerable attention because of their electronic and photocatalyst properties, coupled with the low cost and safety toward environment and human health.[4] These properties make TiO_2 nanoparticles suitable for a wide range of applications, in the fields of solar cells (DSSC),[5a-,c] electric and photocatalytic systems,[5d,e] and gas sensing.[5f]

In order to best exploit the intrinsic and ensemble properties of TiO_2 nanocrystals assemblies at nanoscale regime, a large number of methods for preparation of nanostructured titania substrates with well controlled morphology has been developed. One of the most successful approach relies on the combination of the sol-gel techniques and the self-assembly of an amphiphilic block copolymer (BCP) acting as template.[4a,6,7,8] Arrays of titania nanoparticles of well defined morphology covering the whole area of the substrate may be created by drop casting or spin coating solutions of titanium species and BCP in a non selective solvent, exploiting the preferential interactions of the titanium compound with the hydrophilic domains of the BCP.[7,8] The final morphology is dictated by the tendency of the covalently linked chemically 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).[9] In presence of a titanium compound hybrid nanostructures are formed, in which the BCP matrix acts as host for sequestering guest Ti-species[10] in the hydrophilic domains during the sol-gel process.[7,8] Upon removal of the organic matrix, dot-, or worm-like entities, cylinders, nanoclusters, nanoporous networks of titania are obtained, reminiscent of the domain-organized nanostructure achieved in the hybrid system. The final morphology of titania substrates at nanoscale may be finely controlled by selecting the preparation method of the hybrid composite and successive process adopted for removal of the organic component.[7,8]

The problem on how to produce titania nanostructured substrates of well defined morphology has been extensively tackled, and the intricate kinetics and thermodynamic phenomena underlying the whole process partially understood at fundamental level. Although several methods for preparation of titania substrates with controlled morphology have been already set up,[5,8] the issue related to the control of the structural organization of inorganic nanoparticles at nanometric length over large area in a fast process at low cost is still a challenge.

In this Communication, a quick, simple and low-cost method for preparing with high reproducibility hybrid nanostructures and highly uniform titania substrates having tailored morphology over large area is rationally devised. The method is based on the combined use of self-assembly of a block copolymer and sol-gel process of a titania precursor to obtain hybrid nanostructured thin films and relies on the direct self-assembly of the BCP via spin coating of BCP/Ti-species solutions under flux of solvent vapors, so to attain a controlled atmosphere very rapidly. The method, here named of Rapid- Flux-Solvent-Atmosphere (RFSA), is of particular interest for systems that require a short processing time to eliminate the solvent, and allows to keep a tight control on the final morphology of the hybrid system over large area, preventing the hydrolysis and condensation reactions of the titanium species to overwhelm the self assembly of the organic matrix.

The RFSA method is demonstrated in the case of an amphiphilic polystyrene–*block*–poly(ethylene oxide) (PS-PEO) diblock copolymer with number average molecular mass M_n of 136000 g/mol, and volume fraction of PEO blocks of ≈0.20 able to form a microphase-separated morphology, in which PEO cylinders are hexagonally arranged in the PS matrix. The PS-PEO BCP was selected in order to use PEO domains as host for selective inclusion of titanium species to obtain nanostructured hybrid systems via the sol-gel technique. Sample solutions (preparation time ≈90 min) with relative Ti content of 10 and 40 mol % (mol Ti: mol PEO monomeric units) were obtained by mixing a 1wt% PS-PEO toluene solution with a toluene:isopropanol solution (1:1 volume ratio) having the same concentration (0.0125 M) of titanium tetraisopropoxide (TTIP) and water. All solutions were used immediately after preparation, to obtain thin films on a silicon substrate by spin coating using different protocols.

Typical field-emission scanning electron microscopy (FESEM) images of thin films of neat BCP and hybrid systems are shown in Fig. 1. In the case of the neat BCP (Fig. 1A) a pseudo-hexagonal array of PEO cylinders vertically oriented to the film surface appear as dark spots embedded in the bright PS matrix with low lateral order. The vertical orientation of PEO cylindrical domains is controlled by the film thickness (≈70 nm), which is maintained similar to the values of the average distance between the centers of close neighboring domains $d_{c\text{-}c} \approx 69$ nm. The average diameter of cylinders is $D \approx$ 40 nm, even though cylinders having diameters almost doubled are also present, due to coalescence of neighboring cylinders into single domains.

The cylindrical morphology is maintained also in the BCP-TiO$_x$ hybrid systems (Fig. 1B,C). Selective inclusion of titanium species inside PEO domains is indicated by the fact that PEO domains remain dark. Whereas at 10 mol% Ti concentration the cylindrical domains are vertically oriented (Fig. 1B) as in neat BCP, at 40mol% Ti, PEO domains of irregular worm-like shape are also formed beside those with vertical orientation (Fig. 1C).

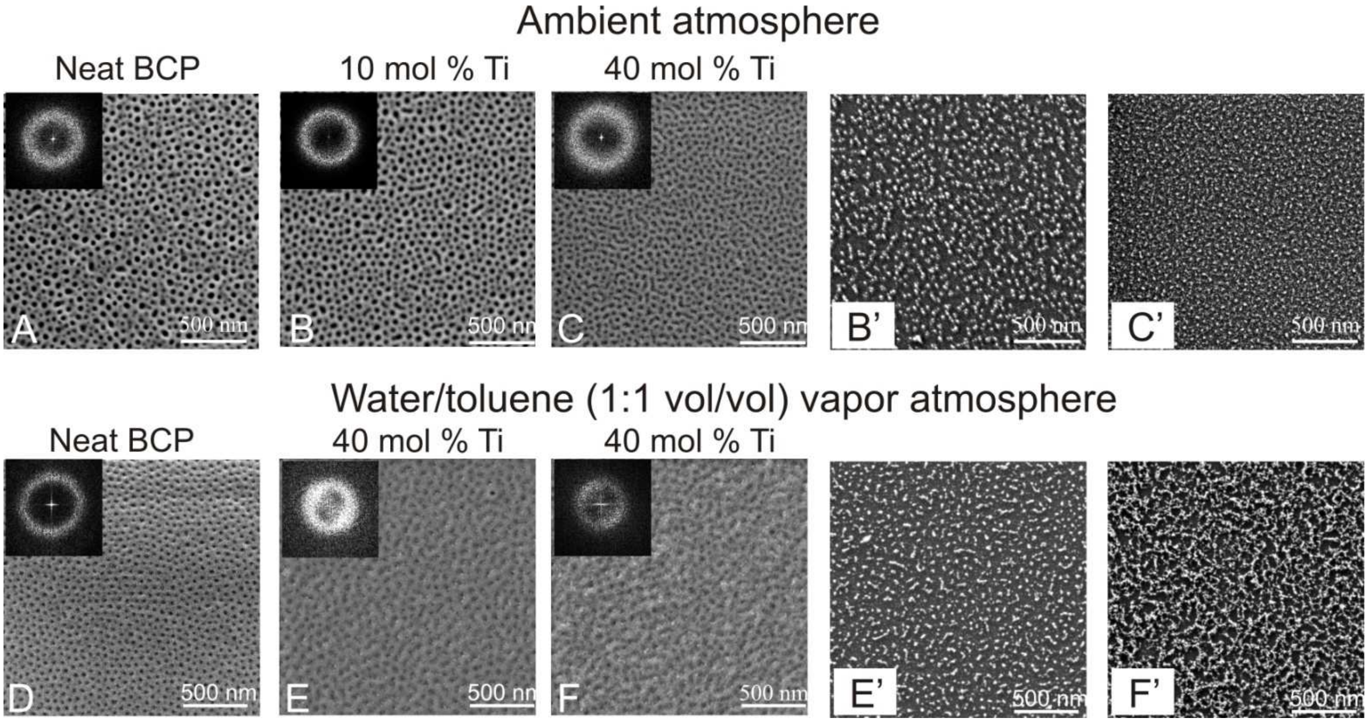

Fig. 1. FESEM images of thin films of neat PS-PEO BCP (A, D), hybrid BCP-TiO$_x$ composites containing 10 (B) and 40 mol% Ti (C, E, F), and corresponding heat treated (600°C at a rate of 2 °C min^{-1} for 4h) titania substrates (B',C',E',F'). Spin coating was performed in ambient atmosphere in A-C and in water/toluene (1:1 volume ratio) vapor atmosphere in D-F after 30 min (D,F, 62 % RH) and 3 min (E, 36 % RH) contact time. The FFT of FESEM images A-C and D-F are shown in the insets.

The average values of the diameter D and the center-to-center distance $d_{c\text{-}c}$ of PEO domains decreases with increasing the Ti concentration ($D \approx 30$ nm, $d_{c\text{-}c} \approx 65$ nm at 10 mol% Ti; $D = 20$ nm and $d_{c\text{-}c} = 60$ nm at 40 mol% Ti). The decrease of D and $d_{c\text{-}c}$ parameters with increase of the concentration of Ti species in the hybrid systems is in agreement with the results of Ref. 7a. Accordingly, based on ref. 11, this decrease has been explained in terms of the effect generated by improvement in the solvent quality toward the hydrophilic PEO chains on the complex micellization behavior of amphiphilic BCPs. In fact, as the titanium concentration increases, also the relative amount of isopropanol increases, resulting in a better solvent for PEO chains. As a consequence, the interfacial tension and the number of BCP chains participating to each cylindrical aggregate decrease and domains of smaller size are formed. However, an additional factor that may influence the size of PEO domains may also consist in the formation of PEO/TiO$_x$ molecular complexes with diverse molar ratios which affect the development of different crystalline forms, as already reported in the case of other PEO complexes strongly stabilized by hydrogen bonding.[12] Such different crystalline organizations, indeed, are likely to induce dimensional changes in the self-assembly of the cylindrical meso-domains.

In all cases, the Fast Fourier Transform (FFT) of FESEM images shows a ring-shaped pattern (inset of Fig. 1A-C). The correlation distance of PEO domains evaluated from the FFT images (Fig. 2A) is close to the center-to-center distance of neighboring PEO domains $d_{c\text{-}c}$ evaluated by direct analysis of FESEM micrographs (see Section S6[†]).

The uniform distribution of Ti species inside the PEO domains is clearly demonstrated by the FESEM images (Fig. 1B',C') relative to the hybrid thin films heat treated at 600 °C. At 460 °C the organic matrix is almost completely degraded (Fig. S1[†]), even if the presence of Ti species slightly increases the thermal stability of the BCP.[8d] Futhermore, at 600 °C amorphous titania is completely transformed into anatase (curve c of Fig. S2[†]). Therefore, the 600 °C treated substrates (Fig. 1B',C') essentially consist of anatase nanoclusters uniformly spreading all over the surface whose morphology is reminiscent of the morphology characterizing the initial hybrid film (Fig. 1B,C). No significant coalescence phenomena are observed during the prolonged annealing at 600°C probably because the domain spacing of the templating BCP matrix in the hybrid systems is large enough to prevent the merging of neighbouring titania nanoclusters into larger clusters. The average size of titania nanoclusters decreases from the value of ≈ 30-35 nm for 10 mol% Ti (Fig. 1B') to ≈ 20-25 nm for 40 mol% Ti (Fig. 1C'). The average distance between neighboring titania nanoclusters of ≈ 60-65 nm, instead, is close to the $d_{c\text{-}c}$ value of neighboring PEO domains in the corresponding hybrid systems (Fig. 1B,C). Simultaneously the degree of coverage of the silicon substrates with titania nanoclusters increases from 18 to 50 %, respectively (Section S4[†]). The three-dimensional Atomic Force Microscopy (AFM) height images of the heat treated samples obtained from the BCP solution with 40mol% Ti (Fig. 2B) show a landscape of TiO_2 nano-pillars of height 4-10 nm standing up from the substrate with low lateral order.

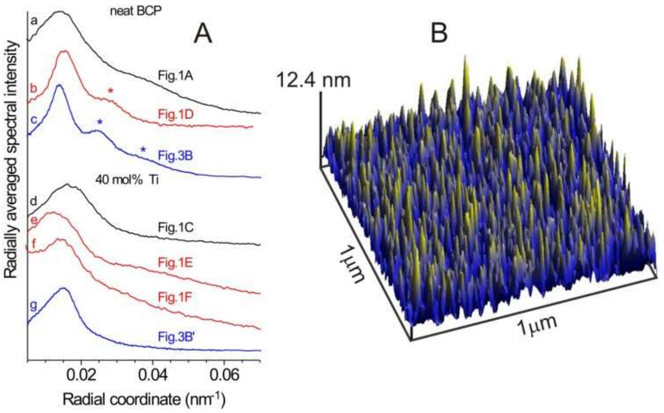

Fig. 2. A: Radially averaged spectral intensity distribution extracted from the Fast Fourier Transforms of FESEM images in the inset of Fig. 1A,C-F and 3B,B'. The second and third order correlation peaks are indicated with an asterisk. B: Three-dimensional AFM height image of the annealed sample obtained from the BCP solution with 40mol% Ti, corresponding to FESEM image of Fig. 1C.

In order to achieve a better orientational control of the titania loaded PEO domains we have used a quite fast and direct self-assembly approach, similar to that one proposed in ref. 13 in the case of the neat BCP. The process consists in performing spin coating under controlled vapor atmosphere in a closed tank, where the atmosphere is regulated by placing a solvent in a Petri dish. Spin coating is initiated only after partial saturation of the environment with the solvent vapor. A water/toluene mixture in 1:1 volume ratio (mol ratio ≈4:1 mol) is used and spin coating is applied after 30 min delay time. Since the vapor pressure of toluene and water at room temperature are nearly identical (≈26 torr),[14] the use of mixed solvents corresponds, according to Rault's law, to a water vapor pressure of about four times higher than toluene, resulting in an atmosphere richer in water vapor. The results are illustrated in Fig. 1D-F.

The FESEM image for the thin film of the neat BCP prepared under water/toluene vapor atmosphere (Fig. 1D, relative humidity RH ≈60%) shows a more uniform and regular morphology than that obtained in ambient atmosphere (Fig. 1A). Vertically oriented PEO cylinders with improved lateral order and uniform diameter develop in these conditions. The result of Fig. 1D may be understood considering that toluene, at room temperature (≈22 °C) is a good solvent for PS and less good for PEO blocks, whereas water is a good solvent only for PEO (Section S3[†]). Therefore with use of vapor solvent environment during the spin coating process it is possible to modify the toluene atmosphere evaporating from the spinning solution, by adding beside of some additional toluene also water vapors in the chamber. Changes in morphology occur because the interfacial energy at air/film interface changes from PS favorable, to an atmosphere favorable also to PEO.[13]

Using the Voronoi construction to count the number of first neighboring domains to each PEO domain (Section S5[†]), a merit figure is associated to the FESEM images of Fig. 1A,D addressing the degree of hexagonal order, given by the ratio between the number of hexa-coordinated PEO domains N_{hexa} to the total number of domains N_{tot}, $R_{hexa} = 100\ N_{hexa} / N_{tot}$. Accordingly, for thin-films of the neat BCP, the degree of hexagonal order R_{hexa} increases from 35 % in the case of spin coating in ambient atmosphere, to 53% in the case of spin coating in a water/toluene (RH ≈ 60%) vapor atmosphere, and 30 min contact time.

However when the same protocol is applied to spin coating of BCP solutions containing titanium species a worm-like disordered morphology is obtained for the hybrid composites, scarcely reminiscent of the cylindrical morphology of the neat BCP thin films prepared in the same conditions. This is illustrated in the FESEM images of Fig. 1E,F) relative to thin films of hybrid composites, prepared by spin coating BCP solutions 40 mol% Ti under water/toluene vapors using 3min (≈36%RH) and 30 min (≈60% RH) contact time. The corresponding annealed samples (Fig. 1E',F') show titania nanoclusters uniformly dispersed on the substrate, with an area coverage of ≈24 and 40%, respectively. Whereas the nanoclusters remain small and well separated entities in the case of Fig. 1E', they form a continuous dendritic network in Fig. 1F'. These data indicate that during the aging time of the solution on the silicon substrates prior of spin coating process and consequent evaporation of the solvent, the sol/gel reactions of hydrolysis and condensation of TTIP occur, up to completely dominate the self-assembly process of the BCP.[8]

In the final steps of the present investigation, the spin coating chamber was modified in order to achieve the desired value of relative humidity in less than one minute, so to "freeze" the confinement of titanium species inside the PEO domains and preserve the cylindrical morphology of the BCP. The dispositive is realized under a flux of a vapor solvent using compressed air as carrier (Fig. 3A).

This method of "Rapid-Flux-Solvent-Atmosphere" (RFSA) allows easily tailoring the solvent vapor atmosphere in the desired amount of time, by simply varying the flux and/or the solvent temperature while recording the values of temperature and RH in the tank every 2s. Spin coating is initiated only after a prefixed contact time (RFSA time) of the solution with the solvent vapor atmosphere of 20 s in Fig. 3. The RH value recorded after 25 s, that is the RH value reached in the tank 5 s after beginning of the spin coating process, is specified.

The FESEM image of neat BCP thin films subjected to 20s RFSA water/toluene (≈50% RH) vapor atmosphere is shown in Fig. 3B. Highly regular and uniform nanostructures on the whole substrate are obtained, consisting of PEO cylinders with perpendicular orientation, diameter D ≈40±5 nm, embedded in the PS matrix at distance $d_{c\text{-}c}$ ≈71±3 nm. The degree of hexagonal order of the resultant nanostructures R_{hexa} equal to 70% is higher than the one achieved with 30 min contact time in the same vapor atmosphere (60%RH, Fig. 1D, R_{hexa}, = 50%). Furthermore the radially averaged spectral intensity distribution extracted from the FFT of the corresponding FESEM image (inset of Fig. 3B) shows a second and third order correlation peak (curve c of Fig. 2A) indicating that the beneficial effect of high levels of water vapors may be enhanced by using a short RFSA time (20 s).

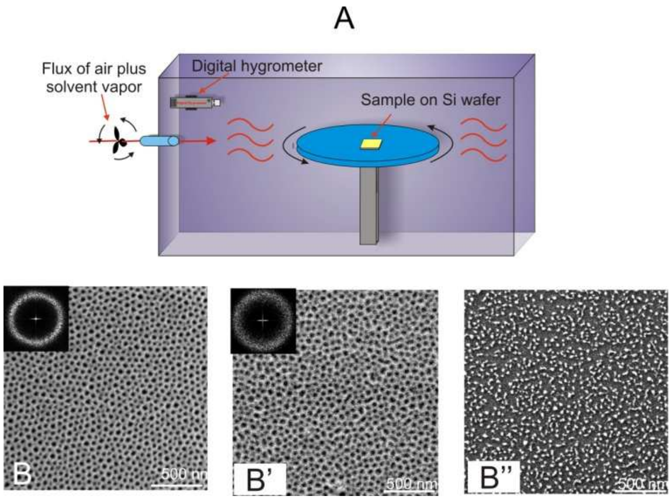

Fig. 3. A: Closed tank for spin coating under flux of solvent vapors equipped with a digital hygrometer automatically recording the values of relative humidity and temperature every 2s. B, B',B'': FESEM images of thin films of neat PS-PEO BCP (B), hybrid composite with 40 mol% Ti (B') and corresponding annealed (600°C at a rate of 2 °C min^{-1} for 4h) titania substrate (B''). In the RFSA protocol, spin coating was applied for 30 s under flux of water/toluene vapors at 1:1 vol ratio after 20 s contact time at ≈52% RH in B, and ≈45% RH in B'. The FFT of FESEM images in B,B'are shown in the inset.

The effect of 20 s RFSA (≈45% RH) protocol with water/toluene atmosphere is beneficial also in the case of the BCP solution 40 mol% Ti as shown by the FESEM image of Fig. 3B'. The RH value is lower than Fig. 3B because the flow rate of compressed air was slightly reduced. A cylindrical morphology of PEO domains in the PS matrix similar to that one of the neat BCP thin films prepared in similar RFSA conditions (Fig. 3B) is obtained, presenting PEO cylinders with average diameter $D \approx 35 \pm 5$ nm at distance $d_{c\text{-}c} \approx 70 \pm 10$ nm. A remarkable increase of the degree of hexagonal order R_{hexa} is reached from the value of 30% in the case of the hybrid nanostructure prepared in ambient atmosphere (Fig. 1D) to 60%.

The FESEM image of the corresponding annealed sample is shown in Fig. 3B''. The annealing of the RFSA-substrate of Fig. 3B' produces a spot-like array of isolated titania nanocluster, uniformly covering the macroscopic substrate, with size $D \approx 30 \pm 8$ nm, center-to-center distance $d_{c\text{-}c} \approx 80 \pm 10$ nm and average height of 10±2 nm (Fig. S5[†]) reminiscent of the morphology shown by the initial hybrid system (Fig. 3B'). It is worth noting that in the case of hybrid films prepared by spin coating the BCP solution with 40 mol% Ti in ambient atmosphere, the annealing produces nanostructures where the shape of titania nanoclusters is irregular and includes both dot-like and worm-like entities (Fig. 1C'), making any evaluation of the degree of hexagonal order difficult, and only the degree of coverage equal to ≈50% can be estimated. In the case of the titania substrates obtained by heat treatment of the RFSA system, instead, a coverage of ≈26% is obtained with the advantage that the shape of titania nanoclusters is more regular (Fig. 3B''). This allows calculating a degree of hexagonal order of ≈40%.

Conclusions

A fast, easy and simple method, addressing the intrinsic difficulty in dealing with sol-gel process coupled with self-assembly of block copolymers is identified, that allows hybrid composites to be prepared in a single step and with high reproducibility. The composites consist of a BCP with selective inclusion of a titania precursor in specific domains. These systems are prepared by spin coating freshly prepared BCP/titanium-species solutions in a closed tank under a controlled atmosphere of solvents vapors able to establish good interactions with the BCP blocks. We demonstrate that a tight control on orientation and degree of lateral order of BCP domains may be achieved in the hybrid systems over large area with use of this protocol, provided that the contact time of the solution with vapors before application of spin coating is very short. In order to use short contact times, a flux of solvents vapors are directed inside the closed tank in the RFSA protocol, so that the desired atmosphere is rapidly reached. Robust titania substrates with a morphology reminiscent of the one achieved in the corresponding hybrid composites are thus obtained, by successive heat treatments. More in general, the RFSA protocol coupled with the selective confinement of a metal oxide species in the hydrophilic blocks of an amphiphilic BCP and successive heating at high temperatures, provides a fast, simple and prompt assembling tool to obtain substrates uniformly covered with metal oxide nanoparticles over large area, potentially suitable for optoelectronic, sensing and catalysis applications, where long range order (periodicity) is not of key issue for achieving high performance.

Acknowledgements

The authors thank the "Ministero dell' Istruzione, dell'Università e della Ricerca" (PRIN2010-2011 and FIRB 2012 Futuro in Ricerca, RBFR122HFZ) from Italy and the Xunta de Galicia (PX2010/168-2) from Spain for financial support.

Notes and references

[a] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale Tecchio 80, 80125 Naples, Italy.

[b] Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Complesso Monte Sant'Angelo, via Cintia, 80126, Napoli, Italy. E-Mail: finizia.auriemma@unina.it; Phone: +39 081 674341; Fax: +39 081 674090.

[c] Centre for Research in Biological Chemistry and Molecular Materials (CIQUS), University of Santiago de Compostela, 15782, Santiago de Compostela, Spain.

† Electronic Supplementary Information (ESI) available: S1. Materials and methods; S2. Heat treated systems; S3. Quality of solvents; S4. Calculation of the degree of coverage of the titania nanoclusters on the silicon surface; S5. Voronoi constructions; S6. Radial profile analysis of FFT-FESEM images. S7. Distribution of the height of TiO_2 nanopillars. See DOI: 10.1039/c000000x/

1 a) C. B. Murray, C. R. Kagan, M. G. Bawendi, *Annu. Rev. Mater. Sci.,* 2000, **30**, 545; b) Z. Quan, H.Y. Fang, *Nano Today*, 2010, **5**, 390; c) M. C. Orilall, U. Wiesner, *Chem. Soc. Rev.*, 2011,**40**, 520

2 a) W. A. Lopes, H. M. Jager *Nature*, 2001, **414**, 735; b) T. P. Bigioni, X.-M. Lin, T. T. Nguyen, E.; Corwin, T. A. Witten, H. M. Jaeger, *Nature Materials*, 2006, **5**, 265.

3 a) J. Cheon, N.-J. Kang, S. M. Lee, J.-H. Yoon, S. Oh, *J. Am. Chem. Soc.*, 2004, **126**, 1950; b) E. Roduner, *Chem. Soc. Rev.*, 2006, **35**, 583.

4 W. Li, Z. Wu, J. Wang, A. A. Elzatahry, D. Zhao, *Chem. Mater.*, 2013, **26**, 287.

5 a) U. Bach, D. Lupo, P. Comte, J. E. Mose, F. Weissörtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature*, 1998, **395**, 583; b) Y. Lee, M. Kang, *Mater. Chem. Phys.*, 2010, **122**, 284; c) Z. Liu, Y. Li, Z. Zhao, Y. Cui, K. Hara, M. Miyauchi, *J. Mater. Chem.*, 2010, **20**, 492; d) A.R. Khataee, M.B. Kasiri *J. Mol. Catal. A-Chem.*, 2010, **328**, 8; e) Q. Zhang, J-B. Joo, Z. Lu, M. Dahl, D. Q. L. Oliveira, M. Ye, Y. Yin, *Nano Res.,* 2011, **4**, 103; f) Y. Wang, G. Du, H. Liu, D. Liu, S. Qin, N. Wang, C. Hu, X. Tao, J. Jiao, J. Wang, Z. L. Wang, *Adv. Funct. Mater.*, 2008, **18**, 1131.

6 a) B. Smarsly, M. Antonietti, *Eur. J. Inorg. Chem.* 2006, 1111; b) D. Grosso, G. J. de A.A. Soler-Illia, E. L. Crepaldi, F. Cagnol, C. Sinturel, A. Bourgeois, A. Brunet-Bruneau, H. Amenitsch, P. A. Albouy, C. Sanchez *Chem. Mater.*, 2003, **15**, 4562; c) P. Yang, D. Zhao, D.I. Margolese, B. F. Chmelka, G.D. Stucky, *Nature*, 1998, **396**, 152; d) G. J. A. A. Soler-Illia, P. C. Angelomé, M. C. Fuertes, D. Grosso, C. Boissiere, *Nanoscale*, 2012, **4**, 2549.

7 a) D. H. Kim, Z. Sun, T. P. Russell, W. Knoll,. J. S Gutmann, *Adv. Funct. Mater.*, 2005, **15**, 1160-1164; b) D. Scalarone, J. Tata, F. Caldera, M. Lazzari, O. Chiantore, *Mater. Chem. Phys.*, 2011, **128**, 166; c) X. Li, K. H. A. Lau, D. H. Kim, W. Knoll, *Langmuir*, 2005, **21**, 5212.

8 a) Y.-J. Cheng, J. S. Gutmann, *J. Am. Chem. Soc.*, 2006, **128**, 4658; b) Y.-J. Cheng, S. Zhou, M. Volkenhauer, G.-G. Bumbu, S. Lenz, M. Memesa, S. Nett, S. Emmerling, W. Steffen, J. S. Gutmann, *Eur. J. Inorg. Chem.,*2013, 1127; c) Y. J. Cheng, P. Muller-Buschbaum, J. S. Gutmann, *Small*, 2007, **3**, 1379-1382; d) J. Gutierrez, A. Tercjak, I. Garcia L. Peponi, I. Mondragon *Nanotechnology* 2008, **19**, 15560.

9 G. H. Fredrickson, F. S. Bates, *Annu. Rev. Phys. Chem.*, 1990, **41**, 525.

10 M. R. Bockstaller, R. A. Mickiewicz, E. L. Thomas, *Adv. Mater.*, 2005, **17**, 1331.

11 U. Jeong, D. Y. Ryu, D. H. Kho, D. H. Lee, J. K. Kim, T. P. Russell, *Macromolecules*, 2003, **36**, 3626; Y. Seo, M. W. Kim, D. H. Ou-Yang, D. G. Peiffer, *Polymer* 2002; **43**, 5629.

12 a) P. Iannelli, P. Damman, M. Dosiere, J.-F. Moulin, *Macromolecules*, 1999, **32**, 2293; b) J. Tata, D. Scalarone, M. Lazzari, O. Chiantore , *Europ. Polym. J.* 2009**, 45**, 2520.

13 S. Kim, R. M. Briber, A. Karim, R. L. Jones, H.-C. Kim, *Macromolecules*, 2007, **40**, 4102.

14 E. B. Munday, J. C. Mullins, D. D. Edie, *J. Chem. Eng. Data* 1980, **25**, 191-194.