

One-step synthesis of titania nanoparticles from PS-P4VP diblock copolymer solution

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Abstract

Polymeric films containing titania nanoparticles have potential as dielectric films for flexible electronic applications. For this purpose, the nanoparticles must be homogeneously distributed. Self-assembly is emerging as a neat, elegant method for fabricating such nanostructured hybrid materials with well-distributed nanoparticles. In this work, we report a micellar solution approach for the assembly of copolymer–titanium precursor nanostructures in which titania nanoparticles were synthesized. The ratio of the amount of titanium precursor, titanium isopropoxide, to the blocks forming the micellar core, poly(4-vinylpyridine), was found to play a key role in controlling film morphology. A sphere-to-ribbon transition was observed when the amount of titanium isopropoxide was increased. The thin film morphology can be tuned using the precursor–copolymer interaction rather than just the polymer–polymer interaction or the polymer–solution interaction. This method provides yet another way to control the morphology of nanostructures.

(Some figures in this article are in colour only in the electronic version)

Monodispersed colloid particles have attracted a great deal of attention because of their potential applications in biosensors [1], photonic crystals [2], colloidal lithography [3], porous membranes [4], nanostamps for soft lithography [5], microlenses [6] and seed particles for core–shell and hollow spheres [7]. Block copolymers are known to assemble into spherical reverse micelles in organic solvents, with the insoluble polar blocks collapsing together to form the core and the soluble non-polar blocks forming the corona, which extends into the solvent environment [8]. The ease and control offered by self-assembly of organic components combined with inorganic components which have electronic, magnetic or photonic properties provides a powerful approach for the synthesis of nanostructured hybrid films. The self-assembled nanofabrication processes using colloidal particles have advantages in that colloidal particles are inexpensive, inherently parallel synthesis and self-assembled process and their production is a high-throughput process [3].

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In recent years, considerable attention has been paid to titanium dioxide (TiO₂) due to its extensive applications as chemical sensors, catalysts and as optical devices [9–11]. Its advantages provide the motivation to find ways of generation and incorporation of TiO₂ nanoparticles into appropriate hosts depending on the nature of the applications [12]. Recently, researchers have developed various routes to synthesize nanostructured TiO₂ using block copolymer templates. Steunou *et al* [13] fabricated polymer titania composites using the sol–gel process. Weng *et al* [14] synthesized needle-like TiO₂ nanostructures using a polystyrene–*block*–poly(4-vinylpyridine) (PS-P4VP) diblock copolymer template. Li *et al* [15] synthesized arrays of titania nanoparticles using monolayer films of diblock copolymer templates. However, using the templating method, the amount of titanium precursor loaded into their micellar film is uncontrollable and the control over template morphology is greatly limited [16].

In this work, we will address the above-mentioned problem by using an *in situ* synthesis method. By making

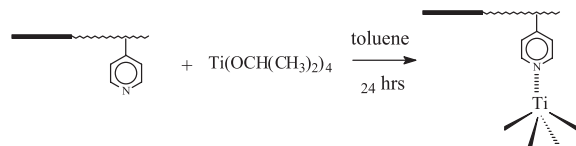


Figure 1. Loading of titanium isopropoxide into the PS-P4VP micelle core.

use of the coordination reaction between titanium isopropoxide and the P4VP in the domains in the micellar solution, titanium dioxide nanoparticles can be synthesized within the copolymer films. Though the morphology of organic block copolymers themselves has been studied extensively, the morphological evolution of the metal-precursor-containing block copolymers has received relatively less attention [17]. The morphology of metal-precursor-containing micellar films can be tuned by changing the amount of titanium isopropoxide. A spherical to ribbon-like transition can be observed at higher titanium isopropoxide to P4VP ratios.

1. Experimental details

1.1. Materials

Polystyrene-*block*-poly(4-vinylpyridine) (PS-P4VP, $M_n^{\text{PS}} = 11\,800 \text{ kg mol}^{-1}$, $M_n^{\text{P4VP}} = 15\,000 \text{ kg mol}^{-1}$, $M_w/M_n = 1.04$) from Polymer Source, Inc. was used as received. Titanium isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) was obtained from Aldrich and used as received.

1.2. Sample preparation

50 mg PS-P4VP was dissolved in toluene in a glass bottle at a 5 mg ml^{-1} concentration, resulting in a slightly cloudy, slightly viscous mixture. Heating the mixture to 120°C using a hotplate yields a clear solution which remains clear when allowed to cool to room temperature. The titania precursor, titanium isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$), was then added to this solution at different titanium isopropoxide/4VP molar ratios of 1/2, 1/1 and 2/1 in a nitrogen environment and magnetically stirred for one day. A mixture of hydrochloric acid (HCl, 37 wt% in water), acetylacetone (AcAcH), $\text{CH}_3\text{COCH}_2\text{COCH}_3$, ethanol and de-ionized water at a fixed molar ratio (ethanol: H_2O :AcAcH:HCl = 10/10/20/0.05) was prepared. HCl was used as catalyst, AcAcH was used as a chelating agent for titanium alkoxide, ethanol was used as a solvent and de-ionized water was used for the hydrolysis reaction. The mixture was added to the polymer-titanium precursor solution under a nitrogen environment and the solution was agitated until a homogeneous solution was obtained. The molar ratio of titanium precursor to AcAcH was 1:4. Each thin film was produced by spin-casting. Before spin-casting, the mica substrate was first coated with a thin layer of carbon to facilitate the peeling of the polymer film from the substrate when immersing in water.

1.3. Dynamic light scattering (DLS)

A Brookhaven BIS200SM laser scattering system equipped with a 522-channel Brookhaven BI9000 digital multiple τ

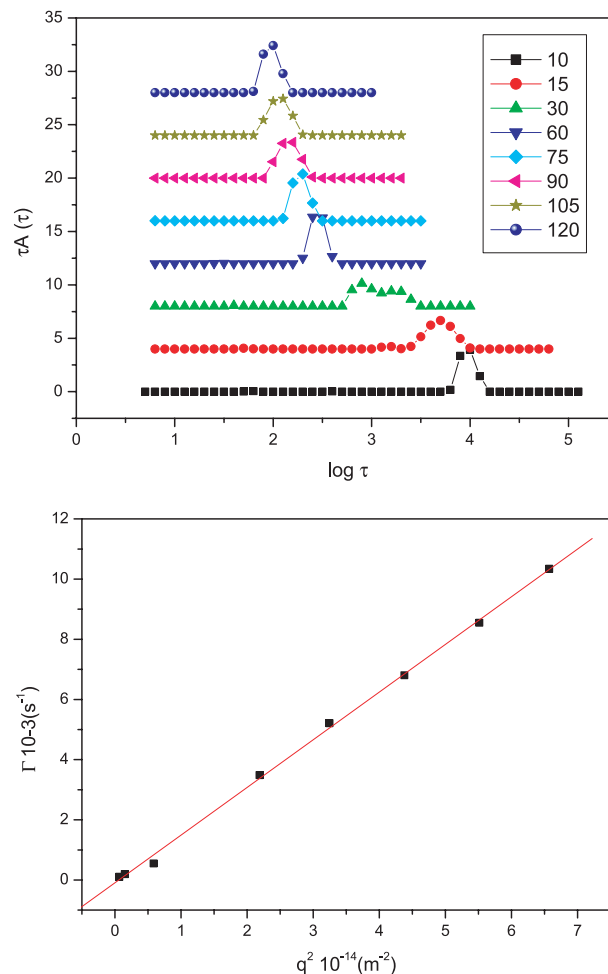


Figure 2. Relationship between relaxation rates Γ and q^2 for 2 mg ml^{-1} PS-P4VP/titanium isopropoxide in toluene with a molar ratio for 4VP/titanium isopropoxide = 1/0.5 at 298 K.

correlator was used to perform both the static and dynamic light scattering experiments. The light source is a power-adjustable vertically polarized 35 mW argon ion laser with a wavelength of 632.8 nm. The time correlation function (TCF) was analysed using REPES [18] inverse Laplace transform supplied with the GENDIST software package, and the probability of rejection was set to 0.5.

1.4. Microscopy

AFM images were taken with a Digital Instrument Dimension 3100 atomic force microscope under ambient conditions. The atomic force microscope was operated in tapping mode with an optical readout using a Si cantilever. The Si tip has a typical tip radius of curvature of less than 10 nm. Transmission electron microscopy (TEM) was performed using a JEOL 2010 operating at an acceleration voltage of 200 kV and with a LaB_6 filament.

2. Results and discussion

Different amounts of $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ were loaded into the micellar core. The reaction scheme is shown in figure 1.

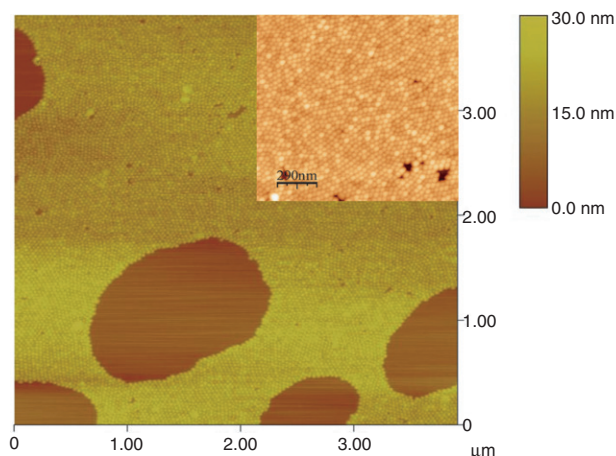


Figure 3. AFM height contrast images of the surface of the PS-P4VP/titanium isopropoxide micellar film with ratio $4VP/Ti = 1/0.5$. The inset is an enlargement of the micellar film.

The titanium isopropoxide has good solubility in the micellar solution as indicated by the solution remaining clear. A strong interaction is expected between the pyridine and $Ti(OCH(CH_3)_2)_4$ due to the coordination occurring between the titanium and the nitrogen in the pyridine ring.

Dynamic light scattering (DLS) measurements were carried out at angles ranging from 10° to 120° . Using the Stokes–Einstein relationship, the hydrodynamic radii, R_h , were calculated. The relationship between relaxation rates (Γ) and the square of the scattering vector (q^2) for PS-P4VP/titanium isopropoxide at a concentration of 2 mg ml^{-1} in toluene at molar ratio $4VP/titanium \text{ isopropoxide} = 1:0.5$ is shown in figure 2. A good linear relationship was observed between Γ and q^2 , and the line passes through the origin, indicating that the peak is due to the translational diffusion. No other small peaks were observed, indicating the complete encapsulation of titanium isopropoxide in the micellar core. R_h was calculated to be 24.6 nm, a little bit larger than for PS-P4VP (22.5 nm [21]). Compared with the PS-P4VP micelles, loading of titanium precursor into the micellar core at a molar ratio of 0.5 has little effect on the size and structure of the PS-P4VP micelle. This can be visualized using AFM measurements as shown in figure 3.

Height contrast images of the surface of the PS-P4VP/titanium isopropoxide micellar film are shown in figure 3. The brighter areas correspond to the P4VP microdomains and the darker areas to the PS matrix. The inset in figure 3 is an enlargement of the micellar film. A well-ordered array of micelles with uniform sizes can be observed. The average diameter of the P4VP domains in the original PS-P4VP film and that after reaction with $Ti(OCH(CH_3)_2)_4$, determined by the Nanoscope particle analysis program, is estimated to be about 28 nm, indicating that there is little change to the P4VP domain size during the reaction. The diameter of the $Ti(OCH(CH_3)_2)_4$ containing micelles is smaller than that measured by light scattering because, in light scattering, the measurement includes the solvent shells surrounding the micelles. From figure 3, we can see there are large holes typically $\sim 1 \mu\text{m}$, across in the film. From the height inside and outside these holes we can determine the

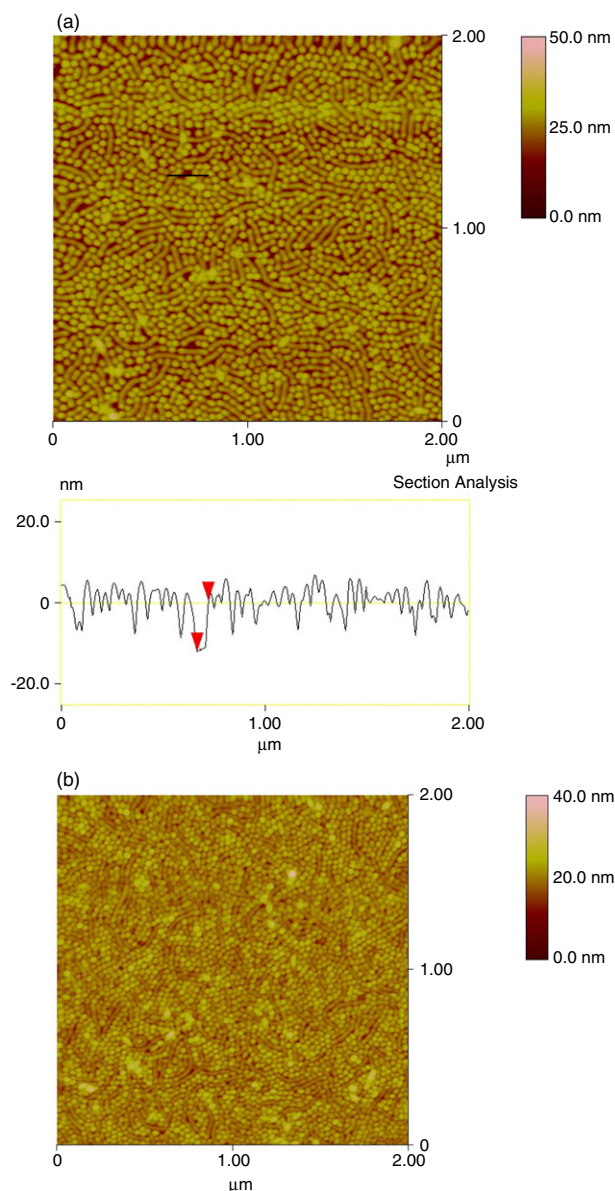


Figure 4. AFM height contrast images of the surface of the PS-P4VP/titanium isopropoxide micellar film with molar ratios (a) $4VP/Ti = 1/1$, (b) $4VP/Ti = 1/2$.

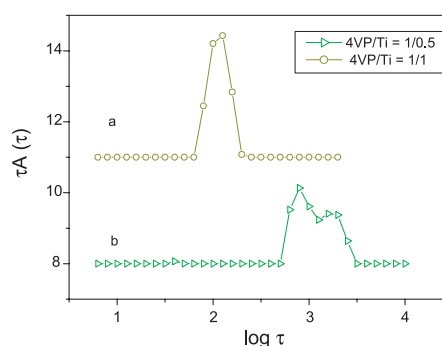


Figure 5. Decay time distribution function at an angle of 90° of 2 mg ml^{-1} PS-P4VP/titanium isopropoxide in toluene for 4VP/titanium isopropoxide molar ratios of (a) $1/0.5$ and (b) $1/1$ at 298 K.

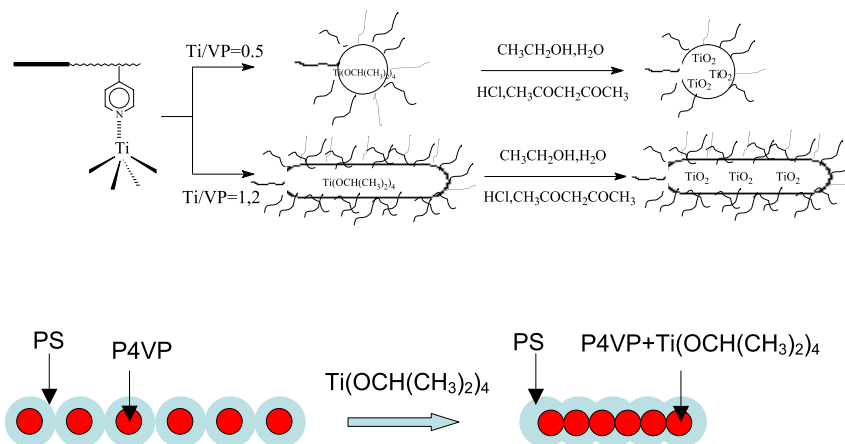


Figure 6. Schematic drawing of the fusion of PS-P4VP micelles due to $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ loading in the P4VP core.

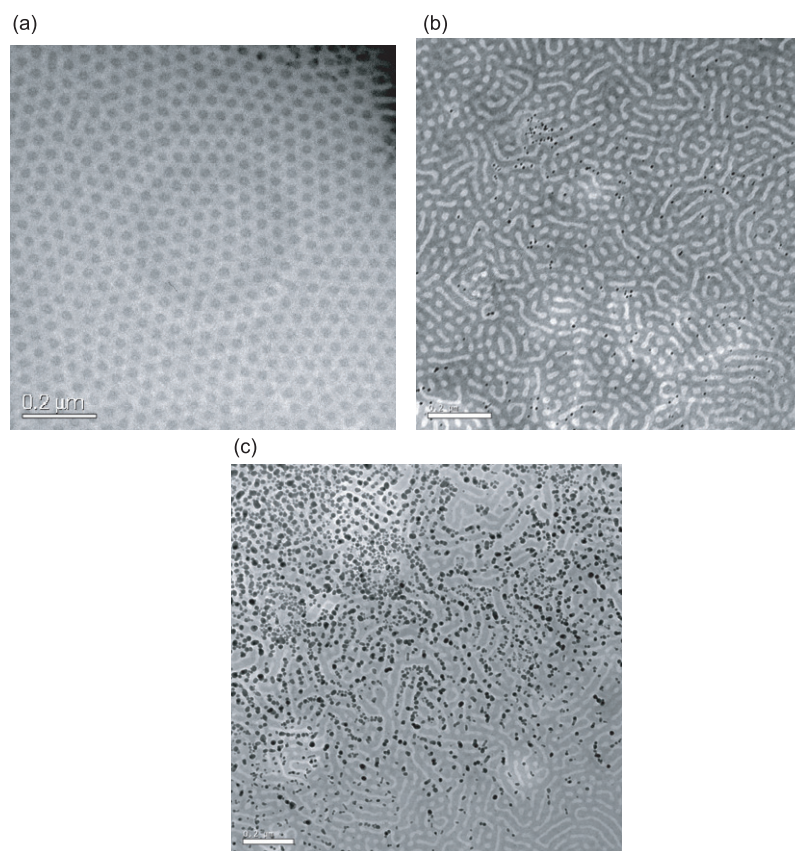
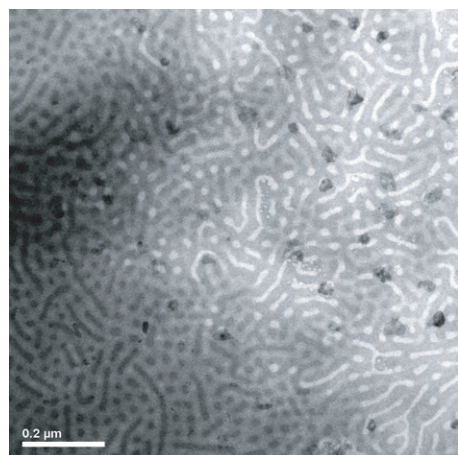


Figure 7. Bright-field TEM images of (a) PS-P4VP, (b) PS-P4VP/ $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (4VP/Ti = 1/1) and (c) PS-P4VP/ TiO_2 . P4VP was stained with iodine and appears dark.

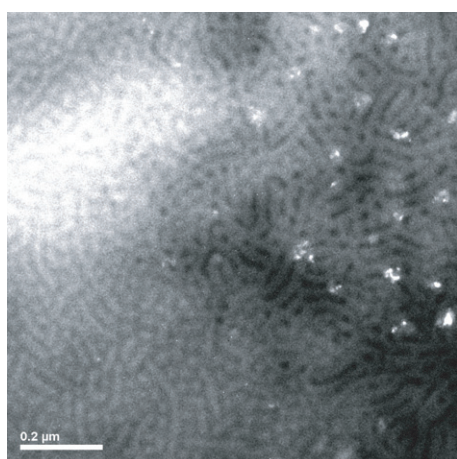
thickness of the film to be about 28 nm, indicating a monolayer of spherical micelles on the substrate.

However, when the molar ratio of 4VP/titanium isopropoxide is increased to 1/1, the unexpected emergence of ribbon-like micelles was observed, as shown in figure 4(a). The cross section in figure 4(a) shows the height of the micelle layer. The spherical micelles remain the same size as for figure 3 (4VP/Ti = 1/0.5), but some of the micelles have fused into ribbons extending to several micrometres in length

with a width of 28 nm. The width of the ribbons is exactly the same as the diameter of the spherical domains formed when the ratio 4VP/Ti = 1/0.5. Figure 4(b) shows that, on decreasing the molar ratio of 4VP/titanium isopropoxide to 1/2, the morphology exhibits little difference to that seen in figure 4(a). The interaction between the AFM tip and the P4VP domains is larger than that between the tip and the PS [19] and the hardness of the P4VP domains increases after incorporation of inorganic moieties [20], especially when the concentration



(a)



(b)

Figure 8. TEM image of PS-P4VP/TiO₂ (4VP/Ti = 1/1): (a) bright field, (b) dark field with the objective aperture on the brightest TiO₂ ring. The bright specks in the dark field imply the presence of crystalline particles.

of Ti is increased from 4VP/Ti = 1/0.5 (figure 3) to 4VP/Ti = 1/1 (figure 4(a)). The range of z in the AFM scan (shown on the right of the figure) is determined by the interaction between the tip and the surface. A higher z range suggests that the surface is harder after the incorporation of Ti. The increase in hardness is also evident when figure 4 is compared to the sample without any titanium isopropoxide [21].

The solution properties corresponding to 4VP/titanium isopropoxide ratios of 1/0.5 and 1/1 were characterized by dynamic light scattering. The decay time distribution functions at an angle of 90° for molar ratios of 4VP/titanium isopropoxide in toluene of 1/0.5 and 1/1 are shown in figure 5. For a molar ratio of 1/0.5, a single peak was observed, indicating monodisperse particles. However, for a molar ratio of 1/1 a broad peak with a small shoulder was observed at a longer relaxation time, indicating the presence of larger particles with larger polydispersity. Taking into account both the DLS and AFM results, it is tempting to speculate that the ribbon-like micelles come from the fusion of several spherical micelles as shown in figure 6, just as we assumed for the

PS-P4VP-sultone system at high molar ratio in our previous paper [22]. In the case where the ratio of 4VP to titanium isopropoxide is large (1/0.5), the PS shell of the micelle is thick enough and the density of the shells is high enough for spherical micelles to be the stable morphology. Contact and the subsequent fusion of the cores does not occur. In cases where the ratio of 4VP to titanium isopropoxide is smaller (1/1), the cores expand, resulting in a relatively low density of shells surrounding the cores if the micelles were to remain spherical. This fluctuation in density may lead to the unfavourable exposure of the core to the solvent. Hence the cores of neighbouring nanospheres merged together.

After hydrolysis, the titania is formed in the self-assembled film and figure 7(a) shows a bright-field TEM image of PS-P4VP micelles containing no titania while figures 7(b) and (c) show PS-P4VP/titania films with a molar ratio of 4VP/titanium isopropoxide of 1/1 before hydrolysis and after hydrolysis, respectively. The films were stained with iodine (I₂) vapour, which binds to P4VP making it dark in bright-field images. A hexagonal array of micelles was observed for PS-P4VP before loading with titanium isopropoxide. After loading titanium isopropoxide with a molar ratio of 4VP/titanium isopropoxide of 1/1, shown in figure 7(b), the ordering disappears and is replaced by ribbon-like micelles. The small amount of tiny dark particles, visible particularly in figure 7(b), may be due to iodine crystals (the staining agent). The images resemble the AFM images in figure 4(a) and show the coexistence of spherical and ribbon-like micelles. After hydrolysis, the TiO₂/I₂ particles were found to mostly concentrate in (but are not strictly confined to) the P4VP domains. Refer to figure 7(c). Looking at the bright field and dark field images in figures 8(a) and (b), respectively, it can be concluded that crystalline nanoparticles, in this case the hydrolyzing agent used here, should lead to formation of TiO₂ crystals in these nanopatterned films according to Que *et al* [23]. The difference in nanoparticle distribution in figures 8(a) and (b) between figure 7(c) may be caused by the uneven distribution of hydrolyzing agent. In some area, the hydrolysis is not completed. This provides an exciting opportunity to prepare hybrid thin films with high dielectric constants for microelectronics applications.

There are two important, competing, issues for the assembly of inorganic materials on organic scaffolds: high density and selectivity [24]. In the case of scaffolds formed by copolymer domains, preferential wetting of one of the copolymer blocks by metals will result in the metal selectively aggregating to the corresponding domain. However, simple coalescence of dense metal nanoparticle aggregates into the overall shape given by the boundaries of the selected copolymer domain has not been achieved so far. This is because of the large surface energies of metals, exceeding those of copolymers by orders of magnitude. Consequently, metal-metal bonds will overwhelm metal-polymer bonds and, except for very small metal concentrations, the final configuration will be a large metal particle that completely ignores the polymer scaffold and mitigates selectivity. Thus, under equilibrium conditions even highly elongated, anisotropic polymer scaffolds may not be able to guide self-assembling metal particles into wire-like nanostructures.

3. Summary

We report our finding of the unexpected transition of spherical micelles to ribbon-like micelles with increasing loading of titanium precursor in polymer micelles. The transition could be due to fusion of the spherical micelles when titanium isopropoxide coordinates to P4VP. Titania nanoparticles were synthesized using an *in situ* reducing method in the PS-P4VP micelles. Aligned particles in the P4VP domains were found. Thus, the morphology can be tuned by simply altering the metal precursor loading.

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