Highly ordered TiO₂ nanostructures by sequential vapour infiltration of block copolymer micellar films in an atomic layer deposition reactor†

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Sequential vapour infiltration operated in an atomic layer deposition (ALD) reactor was used to controllably deliver precursors of TiO₂ into the cores of micellar films of the amphiphilic block copolymer, poly(styrene-block-4-vinylpyridine) (PS-b-P4VP). Vaporized precursors diffused through the PS corona and were exclusively enriched into the P4VP cores. Arrays of hexagonally arranged TiO₂ nanoparticles were produced by burning off the polymeric components after UV-crosslinking the TiO₂-incorporated micellar films. The size of the TiO₂ particles was tunable simply by repeating the cycle numbers, and the interparticle distances were dictated by the distances between neighboring micelles of the original micellar films and could be changed by using block copolymers with different molecular weights. Compared to the extensively used solution impregnation method, the sequential vapour infiltration strategy was distinct in terms of the simplicity accompanying the “dry” process and precise control in particle sizes. More importantly, growth of TiO₂ particles inside micellar cores was not limited by the available pyridyl groups as TiO₂ continued to grow on preformed TiO₂ particles after the pyridyl groups were consumed. Consequently, the particle sizes could be tuned in a much broader range compared to the solution impregnation method in which the particle size was limited by the saturation of impregnated precursors bound to the pyridyl groups. Furthermore, we demonstrated the versatility of this sequential vapour infiltration strategy in producing nanostructures with different morphologies and chemical compositions.

Introduction

Block copolymers (BCPs) are comprised of two or more chemically distinct homopolymer chains covalently linked at one end. BCPs tend to microphase separate under appropriate thermodynamic conditions due to the immiscibility of the constituent blocks, forming a rich variety of well-defined, periodic morphologies with feature sizes typically in the range of 5–50 nm.† Microphase separation also takes place in solutions when BCPs are dissolved in solvents selectively preferential to one block, forming regular micelles or reverse micelles according to the nature of solvents.‡ Amphiphilic diblock copolymers with adequate contrast in polarity between the constituent blocks can be dissolved in nonpolar solvents as reverse micelles with the relatively polar blocks collapsed as micellar cores surrounded by the solvated coronas of the nonpolar blocks. These micelles dispersed in solutions can be transferred to smooth surfaces via spin- or dip-coating, giving rise to monolayers of hexagonally packed arrays of dried micelles upon solvent evaporation. By taking advantage of the monodisperse micelle size and highly ordered arrangement of the micelles deposited on the substrate surface, researchers have fabricated a large number of functional materials for different applications using the micellar arrays as templates, masks, or nanoreactors.§

Moreover, based on the chemical difference between the core-forming blocks and the corona-forming blocks, precursors including organic/metalorganic molecules and metal salts can be specifically incorporated into the micellar cores through hydrogen or covalent bonding, hydrophobic interaction, metal-ligand coordination, etc.∥ § The precursor-incorporated micellar monolayers retain the structural uniformity of the initial micelles and can be used as functional materials with or without removal of the BCPs. Generally, precursors are incorporated in the micellar cores either by premixing them together with the BCP in selective solvents in the preparation of micelles¶ or by immersing the preformed micellar films in the precursor solutions.∥∥ Both incorporation methods are solution-based and limited in terms of solubility and stability of precursors, and frequently involve tedious and time-consuming rinsing and drying steps. Moreover, full exposure to the precursor solution may deteriorate ordering of the BCP micellar
templates and consequently ordering of the final templated products as the solvent may swell the constituent blocks to some extent.

Very recently, Peng and co-workers produced nanoscopic patterned oxides with tunable dimensions by atomic layer deposition (ALD) on BCP templates.\textsuperscript{21–23} In their work, they used phase-separated thin films of polystyrene (PS)/poly(methyl methacrylate) (PMMA) diblock copolymer (PS-\textit{b}-PMMA) with PMMA microdomains embedded in the PS matrix as templates. Precursors diffusing through the PS surroundings were alternatively delivered into the embedded domains in BCP films in the gas state, avoiding the problems associated with solution-based reactions. The driving force for the selective incorporation of precursors into the PMMA domains is the specific metal–ligand interaction between the carbonyl groups in PMMA and the metal precursors. They later on termed this method as sequential infiltration synthesis. In order to enhance the affinity between the PMMA domains and the metal precursors, they exposed PS-\textit{b}-PMMA templates to precursors for longer periods of time at higher temperatures, followed by even longer periods of purging time to minimize the undesired deposition on the PS surface. However, none selective nucleation and growth on the PS surface still occurred at higher ALD cycles, damaging the patterns of the produced materials due to the inadequate contrast in affinity between the precursors to PS and to PMMA.

Based on the significant chemical dissimilarity between the two constituent blocks of amphiphilic BCP micelles (otherwise micelles will not form) and the highly ordered, periodic morphologies of BCP micellar films, it might be applicable to selectively incorporate materials into the micellar cores in BCP micellar films by exposing them to the vapours of the precursor molecules, following the proposed mechanism of sequential infiltration synthesis performed in an ALD reactor. Periodically arranged nanostructures are expected after a routine template removal step. Krishnamoorthy and coworkers prepared TiO\textsubscript{2} nanoparticle arrays by vapor phase incorporation of a volatile titanium precursor into the P4VP core of the PS-\textit{b}-P4VP reverse micelles within an ALD chamber. Their work demonstrates fine tunability in nanoparticle sizes by systematic variation in the number of ALD cycles and shows subsequent use of these nanoparticles as templates for nanolithography.\textsuperscript{24} However, the distinct features of the vapor phase incorporation compared with solution impregnation need to be explored and demonstrated. Moreover, an in-depth understanding of the underlying mechanism, the kinetics of vapour diffusion, and the capability and versatility in structure tuning of the vapor phase process still remain open. In this work, we will demonstrate that the polar micellar cores in BCP micellar films can be alternatively accessed by different precursor vapours and can spatially confine the reactions between the two precursors, producing well-defined, periodic metal oxide nanostructures with tunable sizes, inter-particle spacings, as well as chemical compositions. The vapour-based incorporation strategy is distinguished from the previously employed solution impregnation method in terms of the solvent-free process, high controllability, and accurate, continuous tuning in the feature size. Additionally, the particle sizes can be tuned in a significantly broader range compared to the solution-based incorporation as the growth of particles is not limited to the available active groups in the micellar cores. The particle can continue to grow on the preformed particles in the ALD mode without weakening the lateral ordering of the particles until the enlarged neighboring particles touch.

**Results and discussion**

It has been proved in the solution impregnation of metal salts into BCP micellar cores that poly (\textit{x}-vinyl pyridine) (\textit{x} = 2 or 4; P2VP or P4VP) has a strong complexation ability to bind metal ions.\textsuperscript{17,19} We further made an infrared spectroscopic analysis on PS-\textit{b}-P4VP films before and after exposure to TiCl\textsubscript{4} vapour (Fig. S1, ESI†). A new band centered around 1637 cm\textsuperscript{-1} which should be assigned to the metal-bonded CN stretching appeared in the TiCl\textsubscript{4}-exposed film, indicating the coordination of pyridyl groups in P4VP chains with Ti. However, not all the pyridyl groups were coordinated with Ti as suggested by the presence of free CN stretching (1598 cm\textsuperscript{-1}) in the TiCl\textsubscript{4}-exposed film.\textsuperscript{25} Therefore, we chose diblock copolymers of PS and P4VP (PS-\textit{b}-P4VP) as the amphiphilic BCPs with strong chemical contrast of the two constituent blocks. Scheme 1 shows a schematic illustration of the preparation process of arrays of TiO\textsubscript{2} nanoparticles. PS-\textit{b}-P4VP was first dissolved in 1,4-dioxane, which was a PS-selective solvent,\textsuperscript{26} to form stable reverse micelles with P4VP condensed in the cores and PS extended in the solvent as the coronae. The micelles were then spin-coated on Si substrates, followed by solvent annealing to improve the lateral ordering of the spherical micelles. The micellar film was then alternatively exposed to the vapours of precursors, for example, TiCl\textsubscript{4} and water in the vacuum chamber of atomic layer deposition reactor. These polar precursors penetrated the PS coronae and were selectively enriched in the P4VP cores. Each exposure was followed by nitrogen purging in order to sweep off the unbound precursors or by-products of the reaction between precursors out of the chamber. Reactions between sequentially impregnated precursors took place, forming TiO\textsubscript{2} clusters inside the P4VP microdomains. Such a cycle of exposure–nitrogen–exposure–nitrogen was repeated for different times in order to increase the amount of the impregnated materials. After UV-crosslinking for the

![Scheme 1](image.png)

**Scheme 1** The schematic diagram of the preparation process of arrays of TiO\textsubscript{2} nanoparticles by sequential vapour infiltration on block copolymer micellar templates.
fixation of the polymer component, the BCP films containing TiO2 clusters were burned in air to remove the organic components, leading to the formation of TiO2 nanoparticle arrays patterned on the Si substrates.

Ordering of the BCP micellar films dictates the regularity of the produced TiO2 nanostructures. Because the as-coated BCP micellar films were not well-defined in structure it is necessary to improve the ordering of the BCP micellar films, for example, by solvent annealing.\(^{27-30}\) After annealing in 1,4-dioxane at room temperature for \(~15\) min at which the PS-b-P4VP micellar film took a yellowish color, the BCP film was developed to well-ordered hexagonally spherical micelles (Fig. 1a). The annealed BCP films were withdrawn from the chamber, followed by air drying at room temperature for at least 2 h to evaporate the adsorbed solvent. We then immersed the annealed film in ethanol for 3 h at 50 °C to cavitate the P4VP cores in the film through the selective swelling-induced pore generation mechanism.\(^{31}\) It is much easier to identify the P2VP domains under a scanning electron microscope which are converted to pores after cavitation. The diameter of the swelling-induced pores on the BCP films corresponds to those of the P4VP cores and the surface reconstruction induced by selective swelling does not change the center-to-center distance between the neighboring P4VP cores.\(^{32}\) For the annealed micellar PS-b-P4VP films, the P4VP cores are embedded in the PS matrix with the PS chains exposed to the film surfaces as the PS-selective dioxane energetically favors the immigration of PS chains to the surface. The P4VP block is a type of Brønsted base (proton acceptor) owing to the presence of pyridyl groups (pK\(_a\) = \(~6\)) and can function as a ligand to coordinate with metal species.\(^{33}\) In the vapour impregnation process, TiCl4 was selectively impregnated into the P4VP microdomains because TiCl4 has a much stronger affinity toward the pyridyl groups containing P4VP than the relatively inert PS.\(^{34}\) Consequently, TiO2 clusters grew exclusively in the P4VP microdomains with the following exposure to water vapour whereas the PS regions remain intact and are free of TiO2. Fig. 1b and c exhibit the surface and cross-sectional morphology, respectively, of a PS-b-P4VP micellar film subjected to 150 cycles of TiCl4-water exposure. Densely packed spheres with a diameter of \(~28\) nm appeared on the surface as a monolayer. These spheres were TiO2-incorporated PS-b-P4VP micelles. The incorporation of TiO2 expanded the micelle size but did not change the hexagonal arrangement and the center-to-center distance of the micelles. Therefore, we can conclude that TiO2 was selectively incorporated in each of the P4VP microdomains, confirming the growth of TiO2 exclusively in the P4VP microdomains. In addition, the diameter of the TiO2-incorporated BCP micelles increased with the cycle numbers and higher cycle numbers led to bigger micelles.

The BCP films accommodating the TiO2 particles should be removed without disturbing the ordering of TiO2 particles prior to use. Although plasma etching is frequently employed to etch away the polymeric templates,\(^{4,5,16}\) we explored the possibility to remove the BCP template by a more convenient and efficient burning approach. We found that burning in air at a temperature of 540 °C could completely remove the BCP film.\(^{35}\) However, direct burning in air in deteriorated ordering of the TiO2 arrays due to the displacement of the TiO2 nanoparticles in the melting and decomposing of BCP templates.\(^{36}\) An additional exposure to UV light with a wavelength of 254 nm for 30 min

![Fig. 1](image1.png) The surface SEM image of the annealed PS23k-b-P4VP4.5k film with the morphology of spherical micelles after immersing in ethanol for 3 h at 50 °C to cavitate the P4VP domains (a), the surface (b), and the cross-sectional (c) SEM image of the PS23k-b-P4VP4.5k micellar film subjected to 150 cycles of TiO2 deposition. (a) and (b) have the same magnification and the scale bar in (b) and (c) corresponds to 200 nm.

![Fig. 2](image2.png) Surface SEM images of TiO2 arrays on Si substrates prepared at different cycle numbers after removing the BCP templates: (a) 10 cycles; (b) 20 cycles; (c) 40 cycles; (d) 60 cycles; (e) 80 cycles; (f) 100 cycles; (g) 150 cycles, and the cross-sectional SEM image of the TiO2 arrays prepared at 150 cycles (h). All these images have the same magnification and the scale bar in (h) corresponds to 200 nm.
fixed the BCP film by crosslinking\(^*\) and burning of the UV-crosslinked films led to TiO\(_2\) arrays on the Si substrate with perfectly reserved ordering. Fig. 2a–g show the surface SEM images of the TiO\(_2\) arrays prepared at varying cycles up to 150 cycles after the removal of BCP templates. Near-monodisperse TiO\(_2\) nanoparticles were always hexagonally arranged on the substrate surface with a constant inter-particle spacing and rising particle sizes with the increase of cycles. However, the growth of TiO\(_2\) particle size with cycles was not linear. We correlated TiO\(_2\) particle size with cycles and found that the particles grew very fast at a rate of \(-8\) Å per cycle in the first 20 cycles. In the initial stage, TiO\(_2\) particles were grown mainly through the vapour infiltration mechanism due to the availability of free pyridyl groups in the P4VP microdomains which harvested TiCl\(_4\) rapidly. When the pyridyl groups were consumed by TiCl\(_4\), further exposure to TiCl\(_4\) and water led to the TiO\(_2\) growth on the preformed TiO\(_2\) particles in the ALD mode. Indeed, the TiO\(_2\) particles enlarged their size at a lower rate of \(-1.2\) Å per cycle and this growth rate remained nearly constant for up to 150 cycles (Fig. 3). The particle size on the sample subjected to 20 cycles was \(-16\) nm which was close to the diameter of the P4VP domains. The matching size of the TiO\(_2\) particles and P4VP microdomains implied that TiO\(_2\) growth was confined in the P4VP domains and growth on the PS matrix was suppressed due to the weak adsorption of precursors on the PS surface under a relatively strong purging condition. Higher cycles led to the continuous deposition on the preformed TiO\(_2\) particles and consequently a radial growth of the particle size. For instance, the particle size increased to \(-33\) nm after 150 cycles. Compared to the size of the TiO\(_2\) particles prepared at 150 cycles prior to burning (Fig. 1b and c), the burned TiO\(_2\) particles exhibited a larger diameter (Fig. 2g and h). This should be attributed to the transformation from the sphere-shaped micelles to ellipsoid-shaped TiO\(_2\) particles \(\text{via}\) fusing and merging of the primary TiO\(_2\) nanoparticles embedded in the P4VP domains in the burning treatment, which will be discussed later in line with transmission electron microscopy (TEM) analysis on the produced TiO\(_2\) nanoparticles.

As shown in Fig. 2g and h, the TiO\(_2\) particles kept growing with rising cycles until the contact and merging of neighboring particles, implying that the size of the particles prepared by sequential vapour infiltration can be tuned in a relatively broader range compared to the solution-based precursor impregnation strategy. In the solution impregnation, metal precursors can only bind to the available pyridyl groups, which become saturated when all the pyridyl groups in micellar cores are occupied by metal precursors.\(^{36}\) The metal precursor-saturated micelles lead to nanoparticles with the largest size, which are relatively small because of the limited number of available pyridyl groups. Therefore, the solution impregnation method always produces small particles and the particle size can only be tuned in a narrow window. In clear contrast, in the vapour infiltration approach, precursors can first bind to pyridyl groups in the micellar cores and continue to grow on the preformed TiO\(_2\) particles when the pyridyl groups are used up, leading to even larger particles. In addition, we found it was critical to use highly active TiCl\(_4\) as the Ti precursors for the successful selective deposition in P4VP microdomains. Deposition on the PS-\(b\)-P4VP films using TIP with bulky side groups as the Ti precursor failed under the same deposition conditions due to the weaker complexation capability of TIP with pyridyl groups compared to TiCl\(_4\) and the easy desorption from the polymer surface with the purging of nitrogen gas.

The chemical composition of the TiO\(_2\) nanoparticles was confirmed by X-ray photoelectron spectroscopy (XPS) analysis. As shown in Fig. 4, strong peaks of Ti and O were present in the XPS spectrum of the sample prepared at 150 cycles. The left inset in Fig. 4 displayed two sharp and intense peaks at 464 eV and 548.25 eV originating from Ti (2p\(_{1/2}\)) and Ti (2p\(_{3/2}\)), respectively, indicating the existence of Ti\(^{4+}\) in the sample.\(^{37}\) Furthermore, the high resolution O 1s spectrum (the right inset in Fig. 4) shows two small peaks centered at around 529.45 eV and 532 eV, which can be ascribed to O atoms bound to metals (Ti\(^{3+}\)-O)\(^{38}\) and the possible surface contamination by hydroxyl species,\(^{39}\) respectively. Therefore, we concluded that the periodic nanoparticles on the substrate surface were TiO\(_2\). Signals

![Fig. 3](image-url)  
**Fig. 3** The plot of the TiO\(_2\) particle size with the number of cycles.

![Fig. 4](image-url)  
**Fig. 4** The XPS spectrum of the TiO\(_2\) nanoparticle arrays prepared at 150 cycles after burning off the BCP template in air. Insets are the high resolution spectrum demonstrating the existence of Ti (2p\(_{3/2}\)) and Ti (2p\(_{1/2}\)) species (left inset) and the high resolution O 1s spectrum (right inset).
of Si and C also appeared and they should be attributed to the Si substrate and the contaminants on the sample surface, respectively. TiO\textsubscript{2} nanoparticles were strongly attached on the Si substrate and a harsh ultrasonification on the TiO\textsubscript{2} nanoparticle-deposited Si substrate at a frequency of 21–25 kHz and a power of 200 W for 15 min could not detach the particles from the substrate surface although the Si substrate was broken into pieces. We removed some of the TiO\textsubscript{2} nanoparticles from the sample prepared at 150 cycles by scratching the Si surface with a sharp blade, and then transferred the TiO\textsubscript{2} nanoparticles to a copper grid and probed their fine morphology under TEM. As can be seen from Fig. 5a, most of the particles were in the form of ellipsoids with a long axis of \(\sim 29\) nm and a short axis of \(\sim 19\) nm. Considering that SEM imaging revealed the diameter of the TiO\textsubscript{2} particles was \(\sim 33\) nm which was close to the value of the long axis of the TiO\textsubscript{2} ellipsoid nanoparticles, we concluded that these TiO\textsubscript{2} ellipsoids attached on the Si substrate with their long axis parallel to the substrate surface. The selected area electron diffraction (SAED) analysis on this sample demonstrated the TiO\textsubscript{2} particles were multi-crystalline (inset in Fig. 5a). High resolution TEM confirmed the TiO\textsubscript{2} particles were crystalline and the observed crystalline lattices with a distance of 3.25 Å could be indexed to that of the (110) planes of rutile, suggesting the TiO\textsubscript{2} particles were in the crystalline form of rutile. Note that the burning process at 540 °C played a significant role in the formation of crystalline TiO\textsubscript{2} because the TiO\textsubscript{2} produced by low-temperature was typically weakly crystallized or even amorphous.\(^{40}\)

Because TiO\textsubscript{2} was selectively incorporated into the P4VP microdomains in the PS-b-P4VP films and the distance between neighboring P4VP domains was dictated by the block lengths of the BCP, we could finely tune the center-to-center distances of the TiO\textsubscript{2} nanoparticles by using BCPs with varying molecular weights. Fig. 6 displays arrays of TiO\textsubscript{2} nanoparticles prepared at 40 cycles using PS-b-P4VP with different molecular weights. TiO\textsubscript{2} particles were hexagonally arranged on the substrate surface in both cases. The particle size and interparticle distance of the arrays of TiO\textsubscript{2} nanoparticles templated from different BCPs are listed in Table 1. The center-to-center spacing increased from \(\sim 42\) nm for the sample prepared from PS\textsubscript{23k-b-P4VP}\textsubscript{10k} to \(\sim 57\) nm for the one prepared from PS\textsubscript{124k-b-P4VP}\textsubscript{42k}. In addition, as already shown in Fig. 2d, PS\textsubscript{124k-b-P4VP}\textsubscript{42k} resulted in a center-to-center spacing of \(\sim 34\) nm. Therefore, there was a general trend that higher total molecular weight of the BCP led to a larger distance between P4VP domains, and a correspondingly larger spacing of the produced nanoparticles.\(^{42}\)

However, the size of the TiO\textsubscript{2} particles was not that sensitive to the changing molecular weights as TiO\textsubscript{2} particles prepared from the three BCPs all had an average diameter of around \(21\) nm. This is because BCPs with higher molecular weights do not necessarily give rise to larger micellar cores as the lengths of the soluble PS block and the insoluble P4VP block exhibit an opposite influence to the aggregation number, and consequently the size of the micelles.\(^{41}\) Moreover, the PS corona is a barrier layer for the diffusion of precursors to access the P4VP cores, and the precursor diffusion should be the control step determining the rate of the growth of TiO\textsubscript{2} inside the micelles. Moreover, the diffusion rate varies for micelles of BCPs with different molecular weights as the thickness of their micellar coronae is different. For lower cycle numbers, only a portion of the pyridyl groups in the P4VP cores will be attacked by the precursors. In micelles with bigger cores the number of consumed pyridyl groups may be similar to micelles with smaller cores and more pyridyl groups are left unreacted. In this case, the infiltration of TiO\textsubscript{2} in micelles may not occur in a self-limiting mode. As a result, larger micelles may not lead to larger TiO\textsubscript{2} particle after the same cycles. In addition, as can be seen in Fig. 7b, TiO\textsubscript{2} nanoparticle arrays prepared from PS\textsubscript{124k-b-P4VP}\textsubscript{42k} exhibited a deteriorated ordering and coarsening particle size distribution which should be attributed to the less ordering of the solvent-annealed BCP film due to the limited mobility of the blocks with high molecular weights.

In addition to the hexagonally arranged TiO\textsubscript{2} nanoparticles by sequential vapour infiltration on PS-b-P4VP templates composed of densely packed spherical micelles, we were also able to fabricate parallel TiO\textsubscript{2} nanowires using this strategy on solvent-annealed PS-b-P4VP templates with the morphology of

![Fig. 5](image1.png)  
**Fig. 5** The TEM image (a) and high resolution TEM image (b) of the TiO\textsubscript{2} nanoparticles prepared at 150 cycles scratching from the Si substrate. Inset in (a) shows the electron diffraction pattern of the TiO\textsubscript{2} nanoparticles.

![Fig. 6](image2.png)  
**Fig. 6** SEM images of arrays of TiO\textsubscript{2} nanoparticles prepared from BCPs with different molecular weights: (a) PS\textsubscript{23k-b-P4VP}\textsubscript{10k}, and (b) PS\textsubscript{124k-b-P4VP}\textsubscript{42k}, at 40 cycles. Both images have the same magnification and the scale bar in (b) corresponds to 200 nm.

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<th>(M_n) of P4VP (kg mol(^{-1}))</th>
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parallel cylinders. After burning off the BCP template, TiO2 nanowires appeared on the substrate surface, mimicking the initial morphology of parallel cylinders of the solvent-annealed BCP template (Fig. 7a). Similarly, the width of the TiO2 nanowires could be tuned simply by altering the number of cycles. As shown in Fig. 7, the width of the TiO2 nanowire prepared at 20 cycles was ~9 nm, and increased to ~11 nm, ~13 nm, and ~16 nm when we increased the cycle numbers to 40, 60, and 80, respectively. Although there was a continuous increase in the width of the TiO2 nanowires with rising cycles, resulting in gradually shrinking gaps between neighboring TiO2 nanowires, the center-to-center distance between the neighboring nanowires remained at ~31 nm and was equal to the center-to-center distance between neighboring cylinders in the BCP template. Therefore, the formation of TiO2 nanowires was also through the mechanism of sequential infiltration synthesis exclusively taking place in the P4VP microdomains. We note that the TiO2 nanowires were principally continuous lines although some discontinued points occasionally appeared along the TiO2 nanowires.

Furthermore, this strategy of sequential vapour infiltration on BCP micellar templates can also be used to prepare ordered nanostructures of metal oxides other than TiO2, demonstrating its excellent generality. Hexagonally arranged Al2O3 nanoparticles and Al2O3 nanowires could be fabricated by this strategy on PS-b-P4VP templates in the morphology of spherical micelles and cylinders, respectively, using TMA and water as the precursors. As shown in Fig. 8a and b, the Al2O3 nanoparticles were patterned on the substrate surface with a similar hexagonal arrangement to the case of TiO2 nanoparticles. However, the Al2O3 nanoparticles had a larger diameter than TiO2 nanoparticles prepared at the same cycles. For example, Al2O3 nanoparticles prepared at 20 cycles were ~26 nm in diameter while that of TiO2 nanoparticles prepared at 20 cycles was ~16 nm (Fig. 2b). Larger Al2O3 nanoparticles should be attributed to the higher activity of TMA than TiCl4 which led to a faster growth rate.42,43 Fig. 8c and d show the Al2O3 nanowires prepared from PS-b-P4VP templates of the cylindrical morphology. The Al2O3 nanowires had a morphology resembling the TiO2 nanowires but with a larger wire width. Similarly, the size of Al2O3 nanoparticles and the width of Al2O3 nanowires could also be tuned by changing the cycle numbers. It is necessary to note that small particles were also observed in regions between patterned particles or wires, implying the occurrence of nonselective deposition of Al2O3 on the PS region due to some certain affinity of PS toward TMA and, consequently, physical sorption of TMA molecules on PS.

Conclusions

We used the sequential vapour infiltration operated in the ALD reactor to grow metal oxide nanostructures inside the micellar cores of amphiphilic PS-b-P4VP block copolymer micelles. Highly ordered TiO2 nanostructures including arrays of hexagonally packed nanoparticles and parallel nanowires were obtained by using solvent-annealed block copolymer templates with the morphology of spherical micelles and cylinders, respectively, which were burned off after the infiltration process. The feature size of the TiO2 nanostructures can be easily tuned by altering the cycle numbers. The growth of TiO2 inside the micellar cores was first driven by the strong complexation interaction between the metal precursor and the pyridyl groups in P4VP blocks, and TiO2 continued to grow on the preformed TiO2 particles following the regular ALD mechanism until the contact of neighboring particles. Therefore, the
particle size can be changed in a relatively wider range compared to the solution impregnation method in which complexation saturation significantly limits the size of the produced particles. In addition, the center-to-center distance of the produced nanostructures can be tuned by using BCP templates with different molecular weights because both vapour infiltration and template removal process did not change the ordering of the initial BCP templates. Considering that a large variety of materials can be produced by the ALD strategy and diverse morphologies can be developed by using BCP with different chemical compositions under different thermodynamic conditions, we expect that this sequential vapour infiltration on the BCP template strategy will lead to many well-defined nanostructures of various materials including oxides, metals, and polymers, which may find important applications in a broad spectrum of fields; for instance, optoelectronics, catalysis, sensing, separation, etc.

**Experimental section**

**Materials**

Three BCPs of poly(styrene-block-4-vinylpyridine) (PS-b-P4VP) with various molecular weights were purchased from Polymer Source, Inc. and were used as received. Details of the molecular weights of both blocks and polydispersity index of each BCP are listed in Table 1. All organic solvents including 1,4-dioxane, chloroform, and ethanol were of analytical grade and were commercially acquired and used as received. Trimethylaluminium (TMA) with a purity of >99.99% was obtained from Organometallics Center, Nanjing University, and titanium tetrachloride (TiCl4) with a purity of 99.99% and titanium iso-propylate (TIP) with a purity of 98% were purchased from Aladdin Reagents.

**Preparation of the block copolymer templates**

Si substrates with a lateral area of ~1.2 cm² were cleaned in a "piranha" bath (70/30 v/v solutions of concentrated H₂SO₄ and 30% H₂O₂) at 80 °C for 30 min, and then thoroughly washed with deionized water, and finally dried in a stream of nitrogen gas. The PS-b-P4VP copolymers were dissolved in 1,4-dioxane to obtain solutions with a concentration of 0.5 wt%. The polymer solutions were filtered 3 times through polytetrafluoroethylene (PTFE) filters with a nominal average pore size of 0.22 µm to remove any big aggregates. Block copolymer thin films were fabricated by spin-coating the stock solutions onto pre-cleaned Si substrates at 4000 rpm for 30 s. For the solvent annealing treatment, the films were exposed to saturated solvent vapour in a home-built chamber, which can be coupled with an ellipsometer to in situ monitor the thickness changes of the BCP film during the annealing process. The thickness changes of the film can be reliably determined from the color of the film. The morphology of hexagonally packed spherical micelles and cylinders parallel to the substrate surface were developed by annealing in 1,4-dioxane and chloroform at room temperature, respectively. The samples were removed from the chamber once a characteristic yellowish color appeared followed by an air drying process at room temperature, during which the solvent in film quickly evaporated and the thickness came back to the original value. In order to have a better contrast in SEM examinations, the BCP films were immersed in ethanol at 50 °C for 3 hours to convert the P4VP domains to pores.

**Sequential vapour infiltration of metal oxides in BCP templates**

Vapour infiltration was carried out in a hot-wall ALD reactor (S-100, Cambridge) that was operated at 80 °C under a pressure of 2 Torr using N₂ as the carrier and purging gas. For the TiO₂ preparation, TiCl₄ and deionized water were used as the Ti and O precursors, respectively. We also tried to use TIP as a Ti precursor but it failed to result in TiO₂ nanoparticles in the BCP templates. TMA and deionized water were used as precursors to prepare Al₂O₃. Precursor vapours were alternatively introduced into the ALD chamber in a stream of the carrier gas, being purged after the delivery of each precursor, and exposure mode was applied in this work to insure sufficient precursor adsorption and diffusion. For one growth cycle, the pulse, exposure, and purge time for both precursors were 0.015 s, 20 s, and 50 s, respectively. The pressure in the ALD chamber had an increase of ~0.1 Torr after pulsing TiCl₄. The preparation cycles were repeated for different times. Oxide-incorporated micellar films were stabilized by exposure to the 254 nm UV light generated by a UV lamp operated at 15 W (CL-1000 Ultraviolet Crosslinker, UVP) for 30 min, which were then calcined in air at 540 °C for 3 h to remove the BCP templates.

**Characterizations**

The thickness of the micellar films was measured with a spectroscopic ellipsometer (Complete EASE M-2000U, J. A. Woollam) with a 632.8 nm laser at a 75° incident angle. Fourier transformation infrared spectra (FTIR) of the PS-b-P4VP films before and after TiCl₄ pulsing were obtained from a Nicolet 8700 infrared spectrometer in the attenuated total reflection (ATR) mode. In order to have strong IR signals, we used thicker films and an enhanced infiltration condition. The thick films were obtained by casting the 1 wt% PS-b-P4VP in chloroform solution on clean Si surfaces. After drying, the film was placed in the ALD chamber and subjected to 0.05 s TiCl₄ pulse/20 min exposure/10 min purge two times. No water infiltration was involved for the IR sample. The morphologies of samples were imaged using a field emission scanning electron microscope (SEM, Hitachi S4800) operated at 2 or 5 kV. The morphology of the TiO₂ nanoparticles was also investigated with a transmission electron microscope (TEM, JEM-2100, JEOL) operating at 200 kV after the particles were scratched from the substrate by a shape blade and supported on carbon-coated copper grids. X-ray photoelectron spectroscopy (XPS) analyses were performed with a Thermo ESCALAB 250 system equipped with a monochromatic Al Kα X-ray source (hv = 1486.6 eV). The X-ray anode was run at 150 W, and the pass energy for survey spectra was set at 20 eV with a step size of 0.05 eV. The diameter of the analysis area was approximately 500 µm.
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