Electronic Supplementary Material (ESI) for Nanoscale.

Rapid fabrication of ZnO nanorod arrays with controlled spacing by micelle-templated solvothermal growth

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Supplementary Material

Experimental

Preparation of seeded substrates. Seeded substrates were prepared by thermal annealing of ZnO sol-gel films. The ZnO sol-gel was prepared by hydrolyzing zinc acetate dihydrate (Sigma-Aldrich, >98%) in a 96 wt% 2-methoxyethanol (Sigma-Aldrich, anhydrous, 99.8%) and 4 wt% ethanolamine (Aldrich) solution by stirring at room temperature for 12 hours. All reagents were used as received. The sol was filtered through a 0.2μm Nylon filter and spincast at 4000 rpm onto solvent- and O_2 plasma-cleaned silicon wafers or ITO-glass slides. After casting, the wafers were directly transferred to a hotplate at 200°C for 2 hours to burn off residual organic material.

Preparation of micelle templates. PS-*b*-P4VP diblock copolymer ($M_{n,\ \mathrm{PS}}/M_{n,\ \mathrm{P4VP}}$ = 235kDa/23kDa) and α-MeS-*b*-P4VP diblock copolymer ($M_{n,\ \alpha\text{-MeS}}/M_{n,\ \mathrm{P4VP}}$ = 13kDa/24kDa) from Polymer Source, Inc. (PDI 1.1-1.2) were dissolved in toluene with PS homopolymer (Scientific Polymer Products)(210kDa) and α-MeS homopolymer (Scientific Polymer Products)(11.8kDa), respectively, to 0.5wt% polymer total at mass ratios varying from 100% to 5% BCP. Polymers were used as received. The solutions were stirred for 5-7 hours at room temperature and then left overnight (8-10 hours) in an oven at 80°C to decrease polydispersity in the size and shape of the micelles and encourage uniform blending of the HP and BCP. Solutions were cooled and cast at 2k rpm onto ZnO-seeded substrates to form a monolayer.

Growth of ZnO nanowire forests. The hydrothermal ZnO nanowire growth medium is prepared by dissolving 0.0125M zinc acetate dihydrate (Sigma-Aldrich, >98%) and 0.0250M hexamethylenetetramine (Sigma-Aldrich, >99%) in a solution of deionized (DI) water and acetone, with acetone added to 5 vol% of water. All reagents were used as received. Seeded substrates, prepared as described above, are taped to a glass side using Kapton tape and inserted into a glass vial containing the growth solution such that the substrate is facing downwards while the supporting glass slide is leaning at an angle to the glass wall. This prevents any buildup of precipitate on the sample which may disturb growth. The vial is closed tightly and submerged in a thermostatted water bath held at 70°C. The reaction proceeds for 15-30minutes, depending on desired nanorod length, and are promptly removed from solution and rinsed with DI water and ethanol, and left to dry slowly at room temperature.

Characterization of ZnO nanowire forests. Nanowire forests were imaged by high-resolution scanning electron microscopy in a Hitachi SU-70 scanning electron microscope with a 15kV accelerating voltage. Samples were coated with a thin layer of gold-palladium to enhance conductivity. Quantitative analysis of nanowire dimensions was performed by analysis of a large number of nanowires in representative SEM images of nanowire arrays using Image-J Software. UV-Vis spectra were collected on a Cary 100 UV-Vis spectrophotometer. Atomic Force Microscopy (AFM) was performed using a

Multimode AFM with a Nanoscope IIIa controller (Veeco) under tapping mode. Image analysis was done with an open-source AFM package.[1]

Geometry

The area fraction of spheres of diameter d with **center-to-center** separation l is given below where $\Gamma = (\pi/2\sqrt{3}) = 0.9069$ is the maximum packing fraction for monodisperse hard discs in two dimensions.

$$\phi = \Gamma\left[\frac{d}{l}\right]^2$$

While the above equation is exact for the packing of hard spheres (discs) on a surface, the physical situation for the micelle monolayer is slightly modified by the fact that the monolayer is in fact confluent, and does not feature gaps between the micelles. We therefore replace Γ by Γ_{eff} in what follows, with the understanding that $\Gamma_{\mathrm{eff}} \sim 1$.

Considering the micelle core: the area fraction of the micelle core differs from its volume fraction in the block copolymer. If ϕ_c is the volume fraction of the minority block in the BCP, i.e .the volume fraction of the core relative to the micelle, then the area fraction occupied by the core at a surface is ideally $\phi_c^{2/3}$. In the bulk, $\phi_c=(d_c/d_m)^3$, whereas at the surface the area fraction is $(d_c/d_m)^2= \phi_c^{2/3}$. The reality may diverge from this ideal situation however, due to conformational changes of the block copolymer when in contact with the substrate (differential spreading of the core vs corona chains). d_c is the core diameter, and d_m is the micelle diameter. The presence of homopolymer dilutes the micelles by a factor C_{BCP} Assuming the homopolymer and the BCP micelles have roughly the same dimensions, the concentration in solution is numerically equal to the concentration at the surface, and so the area fraction of micelle cores at the surface is as below, where again Γ_{eff} captures the fact that the actual area fraction can differ (be larger than) from the bounding value of 0.9069 for hard spheres for the case where $\phi_c=1$ and there is no dilution, i.e. $C_{BCP}=1$.

$$\phi = \Gamma_{eff}\phi_c^{\ 2/3}C_{BCP}$$

The separation *l* between micelle cores is then given as below

$$l = \Gamma_{eff}^{1/2}\frac{d_c}{\varphi^{1/2}} = \frac{d_c}{\varphi_c^{1/3}C_{BCP}^{1/2}}$$

Written in terms of the micelle diameter d_m,

$$l = \frac{d_m}{C_{BCP}^{1/2}}$$

Finally, the separation *s* between nanorod surfaces which are centered on the micelle cores is just the difference between the center-center separation of the micelles or micelle-cores, *l*, and the diameter of the nanorods, d_{nr}, i.e. $s=l-d_{nr}$.

Image Analysis

Image analysis was performed by applying appropriate thresholds to the images to highlight the cross-sections of the nanorods relative to their backgrounds using ImageJ software. Rods at the edge of the image were excluded from the analysis to avoid edge-induced artifacts. Rod diameters were identified as the minimum diameter of the circles which completely enclosed the hexagonal cross section of each rod. A circularity criterion of 0.85-1.00 was used to exclude tilted or conjoined nanorods. MATLAB routines ('voronoi') were used thereafter for performing Voronoi tessellation/Delaunay triangulation of the identified rods from which the rod-rod distances were directly produced. To exclude Delaunay Triangulation edges which did not connect nearest neighbor nanorods (thin red lines in Figure 5), especially around the convex image boundary, only those edges whose midpoints intersected two Voronoi polygons were considered. These are the thick lines in pink in Figure 5. The average and standard deviations were calculated for both the diameter and rod-rod distance distributions. The normalized standard deviation in the rod number density is propagated algebraically from the standard deviation in the rod-rod nearest neighbor distance. Since the number density ν is the inverse of the center-center distance squared, $1/l^2$, the normalized standard deviation of the number density is twice that of the rod-rod spacing as shown below.

$$\begin{aligned} \nu &= \left(\frac{1}{l}\right)^2; \quad \sigma_\nu = \left[\left(\frac{\partial \nu}{\partial l}\right)^2 \sigma_l^2\right]^{1/2} \\ \Rightarrow \sigma_\nu &= \left[\frac{4}{l^6}\sigma_l^2\right]^{1/2}; \quad \Rightarrow \frac{\sigma_\nu}{\nu} = 2\frac{\sigma_l}{l} \end{aligned}$$

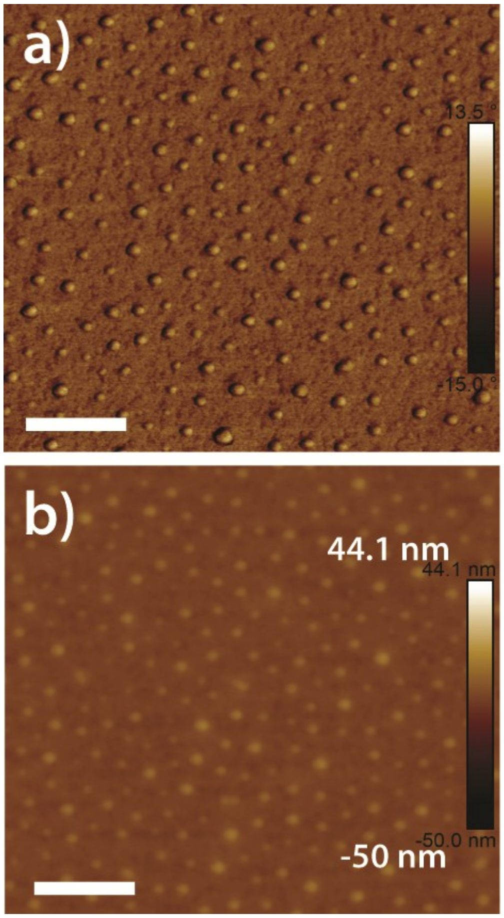

Fig. S1 Phase (a) and height (b) AFM images of 235/23K PS-*b*-P4VP micelle monolayer diluted to 2:1 by mass with PS HP (210K.) Scale bars are 400nm.

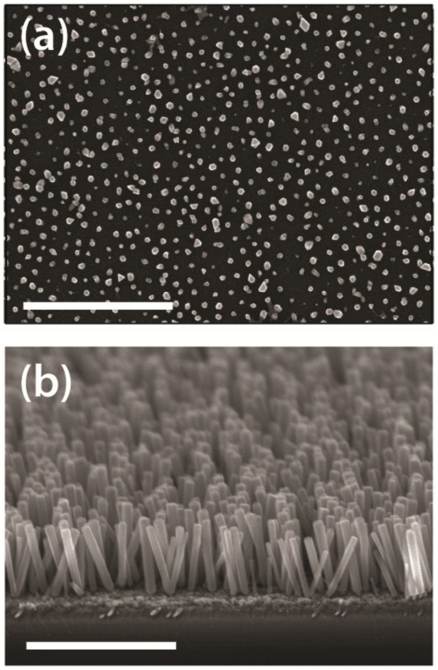

Fig. S2 SEM images of (a) top-down and (b) 70°-angle views of nanorod arrays grown from undiluted 235/23K PS-*b*-P4VP block copolymer micelle templates. Scale bars are 1μm.

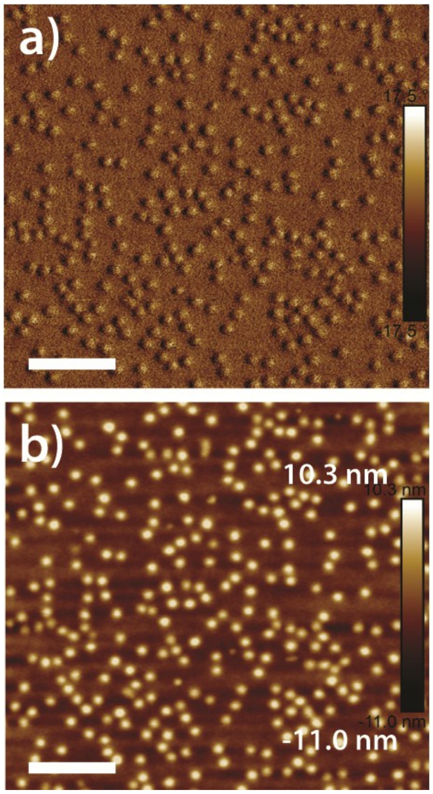

Fig. S3 Phase (a) and height (b) AFM images of 13/24K α-MeS-b-P4VP micelle monolayer diluted to 9:1 by mass with α-MeS HP (11.8K.) Scale bars are 400nm.

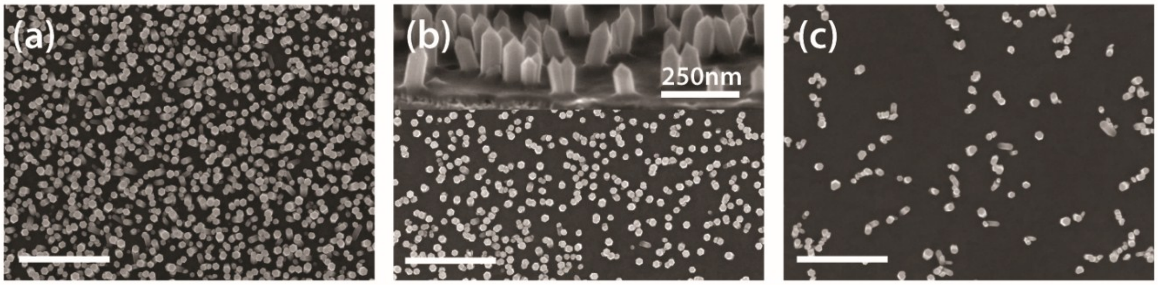

Fig. S4 Scanning electron microscopy images of ZnO nanorod arrays hydrothermally grown through α-MeS-b-P4VP micelle templates diluted with Pα-MeS homopolymer. Top-down images of a) 4:1 HP (11.8K Pα-MeS):BCP (13/24K), b) 9:1 HP (11.8K Pα-MeS):BCP (13/24K), c) 19:1 HP (11.8K Pα-MeS):BCP (13/24K). Inset of b) shows a 70°-tilted view of nanorod array shown in b). Unlabeled scale bars are 1μm. The unusual 'points' observed atop the nanorods in (b) are due to the extremely fast kinetics of post-nucleation ZnO crystal growth proceeding at the elevated temperature of 80°C, where even rapid cooling still requires passing through a viable growth regime.

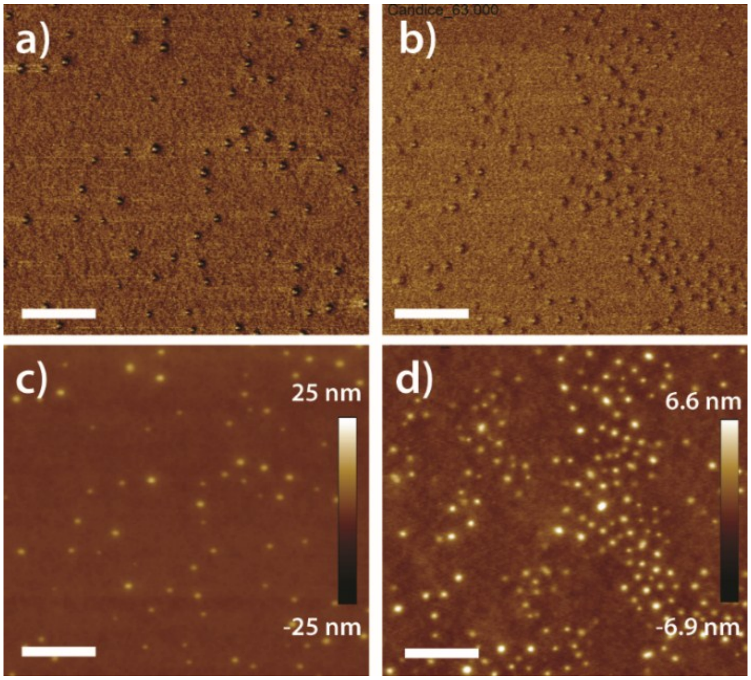

Fig. S5 Micelle aggregation induced by the use of excessively high molecular weight homopolymer. Phase (a,c) and height (b,d) AFM images of 235/23K PS-*b*-P4VP micelle monolayer diluted to 4:1 by mass with PS HP of molecular weight 594K (a,c) and 2,257K (b,d.) Scale bars are 400nm.

References

1. Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J. M.; Colchero, J.; Gomez-Herrero, J.; Baro, A. M., WSXM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology. *Rev. Sci. Instrum.* 2007, 78, 013705.