Supporting Information

Nanoporous Polymer-Infiltrated Nanoparticle Films with Uniform or Graded Porosity *via* Undersaturated Capillary Rise Infiltration

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Water Contact Angle on Films

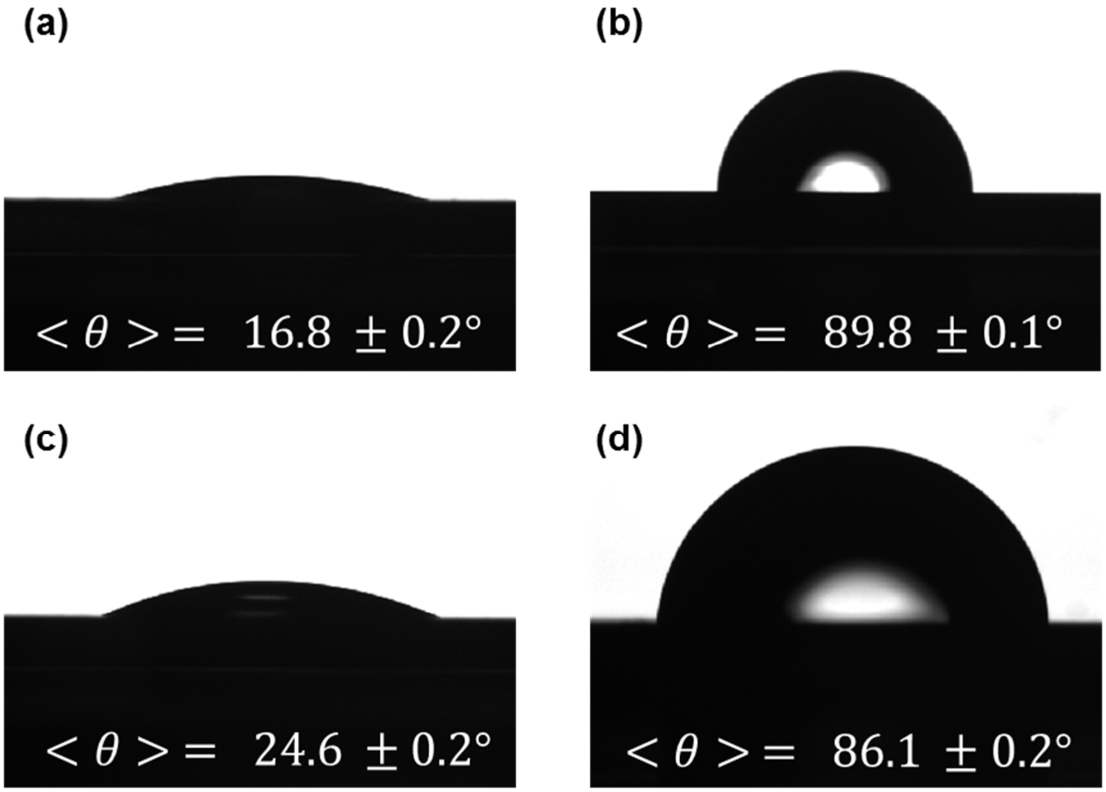

Figure S1. Contact angle measurement of water on (a) pure TiO_2 NPs film, (b) pure PS film, (c) TiO_2/PS bilayer film surface prior to annealing, and (d) a fully saturated TiO_2/PS PINF.

***in situ* Spectroscopic Ellipsometry Raw Data**

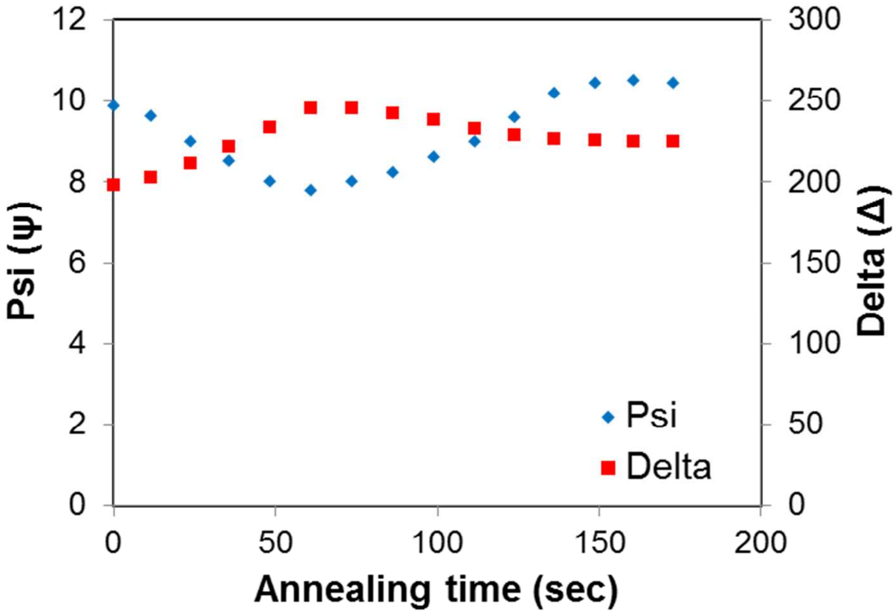

Figure S2. The Δ and Ψ as a function of time at λ =667.9nm obtained from annealing a bilayer film composed of ~190 nm of TiO_2 nanoparticles atop ~45 nm PS film at 150℃.

Spectroscopic Ellipsometry Data Fitting and Modeling

Step 1. The optical constants (A, B, and C) of pure PS film and pure TiO_2 NP film are measured using spectroscopic ellipsometry under ambient conditions. The thickness of the TiO_2/PS bilayer film is determined using a 2-layer Cauchy model, as shown in Figure S3.

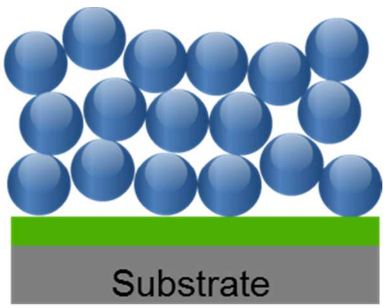

Figure S3. Measurement of thickness of bilayer film consisting of a TiO_2 NPs layer on a PS layer, using a 2-layer Cauchy model.

Step 2. We perform *in situ* spectroscopic ellipsometry to monitor the PS infiltration into the TiO_2 NPs packing. The bilayer sample is placed on the heating stage at ambient condition. The temperature is ramped from room temperature to the setpoint temperature T = 150 ℃ at $30℃\ \mathrm{min}^{-1}$. At the same time the raw data is collected in the form of amplitude ratio ψ and phase difference Δ. When ψ and Δ cease to change, the infiltration process is completed as there is no longer any optical (and structural) changes to the film sample.

Step 3. To analyze the spectroscopic ellipsometry data, we first try fitting with the 3-layer Cauchy model. Since the refractive index of the composite layer is not known beforehand, the optical constants are set as variables, whereas those of the PS and TiO_2 NP layers are fixed. The thicknesses of all 3 layers are also set as variables.

Step 4. For each time step, in order to ensure solution uniqueness, we use the "parameter uniqueness" feature in the CompleteEASE software to determine the most physically feasible solution with the lowest mean squared error (MSE), as shown in Figure S4. Once the solution is updated, we use the "use alternative model" panel, which shows a side-by-side comparison of model fits with gradient and roughness, as shown in Figure S5. We use a gradient model to describe the composite layer if there is a significant improvement in the MSE of the gradient model fit compared to the uniform layer model. Finally, we verify if the solution uniqueness still holds upon updating the model before proceeding to fit the next time step.

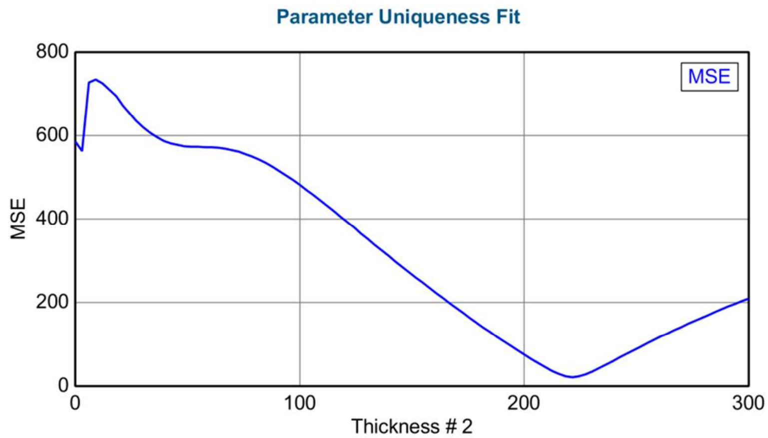

Figure S4. The parameter uniqueness feature maps the MSE of the model as a function of a variable.

Parameter	Ideal	Roughness	Grading	Roughness & Grading
MSE	21.099	19.439	8.595	7.823
Roughness	*N/A*	4.24 ± 0.649 nm	*N/A*	1.86 ± 0.281 nm
A	1.790 ± 0.0048	1.766 ± 0.0056	1.789 ± 0.0019	1.779 ± 0.0023
B	0.01546 ± 0.001755	0.02904 ± 0.002592	0.01758 ± 0.00072026	0.02299 ± 0.001043
C	0.00274 ± 0.00019581	0.00105 ± 0.00031028	0.00253 ± 8.0434E-05	0.00185 ± 0.00012555
% Inhomogeneity	*N/A*	*N/A*	-5.20 ± 0.159	-4.98 ± 0.150
Thickness # 2	221.38 ± 0.458 nm	221.32 ± 0.422 nm	220.96 ± 0.182 nm	221.01 ± 0.166 nm
n of Cauchy @ 632.8 nm	1.84619	1.84490	1.84917	1.84825

Figure S5. The 'try alternative model' panel summarizes the model output of an ideal model, model with roughness, modeling with grading, and model with both roughness and grading. The panel recommends a model which has a significant MSE improvement with the fewest number of variables relative to other models.

Refractive Index Calculation for Graded Cauchy Model

The Cauchy model with simple grading reports the optical gradient across a film with the variable % gradient, and an additional "number of slices" parameter to divide the film into slices of equal thickness with varying refractive index.[1,2] The gradient index describes the gradient in dielectric constant or relative permittivity, ϵ, which is related to the refractive index by:

$$\epsilon = n^2 \qquad \text{(S1)}$$

Note that for Cauchy model is valid for non-absorbing films, where k = 0.[2] If the number of slices is even, then the film refractive index is designated to the middle of the film. Otherwise, the slice at the center would adopt the film refractive index output by the model. A positive value in the % gradient indicates increasing refractive index toward the top surface of the layer, whereas a negative % gradient indicates increasing refractive index toward the bottom surface of the layer.[3] Generally, the number of slices is selected such that the MSE stops improving significantly upon further increase of its value.

Below is a worked example for gradient calculation to illustrate the derivation of refractive indices from a graded Cauchy model:[4]

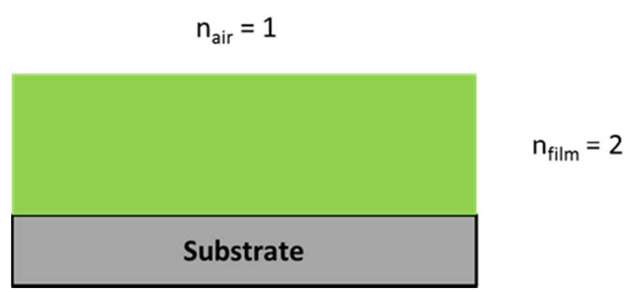

Figure S6. Example system of a film on a substrate, with n = 2 and 1% gradient obtained using a graded Cauchy model.

Figure S6 shows graded Cauchy film with 2 slices, with n_{film} = 2, and 1 % gradient. Since there are only 2 slices, the refractive index value is assumed to be that of the middle of the film. The relative permittivity of the film would be $\epsilon_{film} = 2^2 = 4$. A 1% gradient across the film would translate to 0.005 variation in relative permittivity across the film, relative to that of air, $\epsilon_{air} = 1$. The difference in relative permittivity is then: $\Delta\epsilon = 4 - 1 = 3$. The variation in ϵ of each slice is calculated by:

$$\Delta\epsilon_{\text{slice}} = \frac{\%\ \text{gradient} * \Delta\epsilon}{\text{number of slices}} \qquad \text{(S2)}$$

In this example, $\Delta\epsilon_{slice} = \frac{1\% * 3}{2} = 0.015$. This enables us to assign the refractive indices for the individual slices in the layer, as shown in Figure S7.

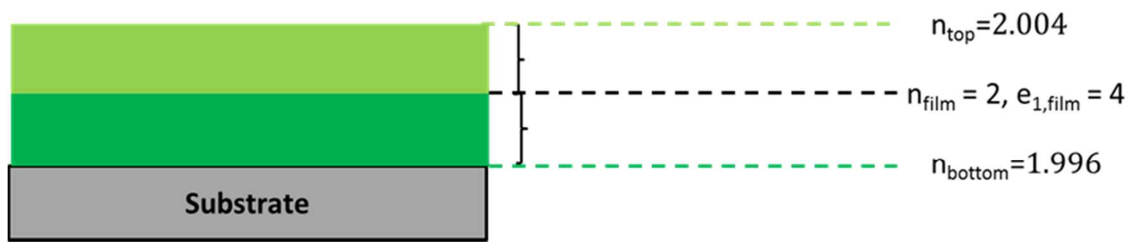

Figure S7. Assignment of refractive indices to individual slices in the graded Cauchy film.

For the top slice, $n_{top} = \sqrt{4 + 0.015} = 2.004$. For the bottom slice, $n_{bottom} = \sqrt{4 - 0.015} = 1.996$.

In our work, the grading is an approximation to understand the structure of the composite qualitatively; the graded Cauchy acknowledges the presence of an optical gradient, but the gradient may be more ambiguous and less well-defined than the model suggests.

References:

(1) Ogieglo, W.; Wormeester, H.; Wessling, M.; Benes, N. E. Spectroscopic Ellipsometry Analysis of a Thin Film Composite Membrane Consisting of Polysulfone on a Porous α-Alumina Support. *ACS Appl. Mater. Interfaces* **2012**, *4*, 935–943.

(2) Ogieglo, W.; Wormeester, H.; Wessling, M., Benes, N. E. Temperature-Induced Transition of the Diffusion Mechanism of N-Hexane in Ultra-Thin Polystyrene Films, Resolved by *In-Situ* Spectroscopic Ellipsometry. *Polymer* **2013**, *54*, 341–348.

(3) J. A. Woollam Co., Inc. CompleteEASE Data Analysis Manual.

(4) Hilfiker, J. Inquiries: CompleteEASE, **2015**.

Volume Fraction-Weighted Mixing Rule for PS/TiO_2 Composite Refractive Index[1-2]

$n_{comp} = \phi_{void} n_{void} + \phi_{PS} n_{PS} + \phi_{TiO_2} n_{TiO_2}$ (S3)

where n_{comp}, n_{void}, n_{PS}, and n_{NP} refer to the refractive indices of the nanoporous composite, void (air), PS, and TiO_2 respectively, whereas ϕ_{void}, ϕ_{PS},and ϕ_{TiO_2} refer to the volume fraction of each component. We perform liquid cell ellipsometry to obtain the porosity p_{NP} and n_{TiO_2}.[3] Then, ϕ_{void} can be calculated by subtracting the ϕ_{PS} from p_{NP}.

(1) Braun, M. M.; Pilon, L. Effective Optical Properties of Non-Absorbing Nanoporous Thin Films. *Thin Solid Films* **2006**, *496*, 505–514.

(2) Zimmermann, L.; Weibel, M.; Caseri, W.; Suter, U. W.; Walther, P. Polymer Nanocomposites with "Ultralow" Refractive Index. *Polym. Adv. Technol.* **1993**, *4*, 1–7.

(3) Lee, D.; Rubner, M. F.; Cohen, R. E. All-Nanoparticle Thin-Film Coatings. *Nano Lett.* **2006**, *6*, 2305–2312.

Molecular Dynamics (MD) Simulation of UCaRI PINFs at low $\phi_{polymer}$

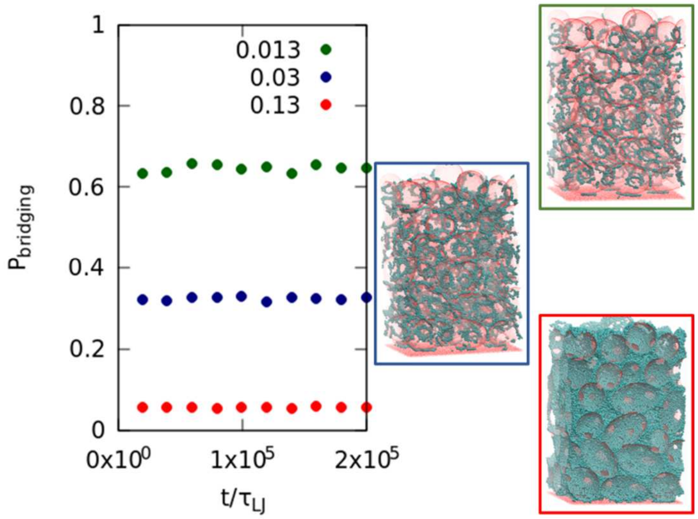

Figure S8. The probability that a polymer chain is in contact with two nanoparticles (P_{bridging}) for three different polymer fractions ($\phi_{polymer}$ = 0.013, 0.03 and 0.13). P_{bridging} increases drastically with lower $\phi_{polymer}$, suggesting the accumulation of polymer chains near particle contacts. Visualizations of each trajectory show that in lower fraction PINFs, the polymers form rings around nanoparticle-nanoparticle contacts.

Uniform Nanoporous PINFs using Various Polymer/Nanoparticle Combinations

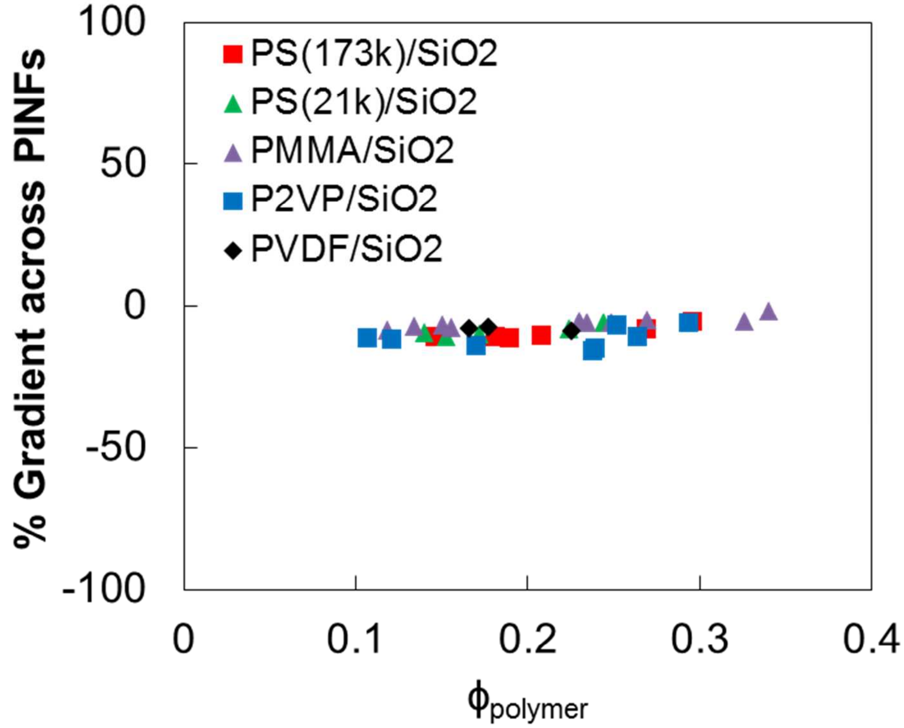

Figure S9: % Gradient of the PINFs for various polymer/nanoparticle systems as a function of polymer composition $\phi_{polymer}$.

Polystyrene (Mn = 21,000 $g\ mol^{-1}$, PDI = 1.04; Mn = 173,000 $g\ mol^{-1}$, PDI = 1.06) and Poly(2-vinylpyrridine) (P2VP) (Mn = 7,800 $g\ mol^{-1}$, PDI = 1.08) are purchased from Polymer Source, Inc. Poly(methylmethacrylate) (PMMA) (approximate Mw = 75,000 g mol^{-1}) is purchased from Scientific Polymer Products Inc. Polyvinylidene fluoride (average Mn = 71,000g mol^{-1}) and silica nanoparticle suspension (Ludox TM-50) are purchased from Sigma Aldrich.