

Electronic Supplementary Information

**Polymer Nanocomposite Films with Extremely High
Nanoparticle Loadings *via* Capillary Rise Infiltration
(CaRI)**

Yun-Ru Huang[†], Yijie Jiang[‡], Jyo Lyn Hor[†], Rohini Gupta[†], Lei Zhang^{†, ⊥}, Kathleen J. Stebe[†],

Kevin T. Turner[‡], Gang Feng[§], Daeyeon Lee^{†, *}

[†] Department of Chemical and Biomolecular Engineering, University of Pennsylvania,
Philadelphia, Pennsylvania 19104, United States

[‡] Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania,
Philadelphia, Pennsylvania 19104, United States

[§] Department of Mechanical Engineering, Villanova University, Villanova, Pennsylvania
19085, United States

[⊥] Department of Mechanical Engineering, University of Alaska Fairbanks, Fairbanks, Alaska
99775, United States

Corresponding author: Daeyeon Lee (daeyeon@seas.upenn.edu)

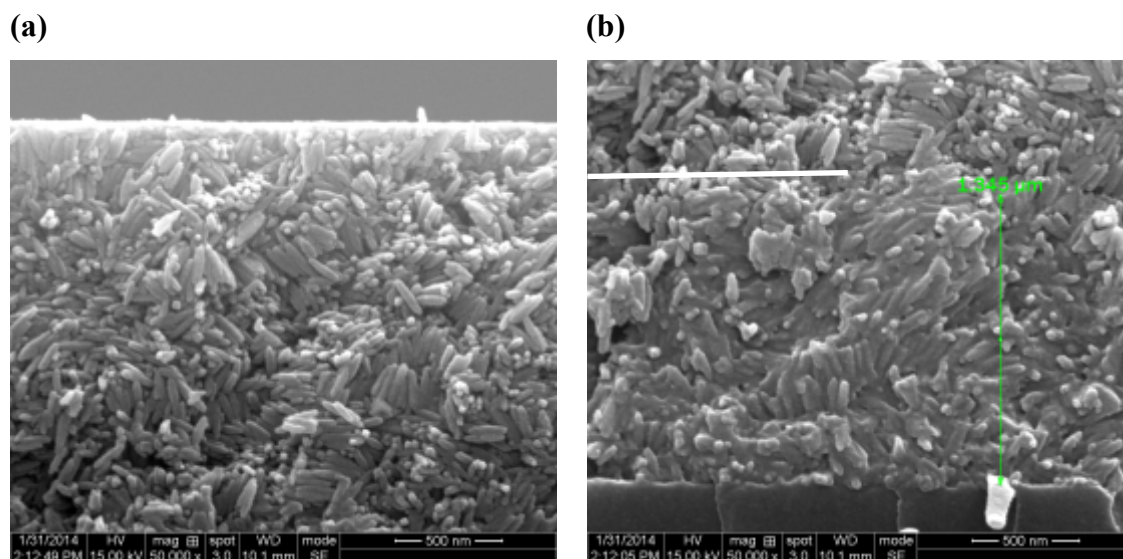


Figure S1. High magnification scanning electron microscopy image of polystyrene front moving into a TiO₂ nanoparticle layer. SEM images close to (a) the top surface of the TiO₂ nanoparticle layer and (b) the interface between the TiO₂/PS interface. Dashed line in (b) shows the location of PS front moving into the TiO₂ nanoparticle layer. A bilayer consisting of PS (Mn = 8,000) and TiO₂ nanoellipsoid layer is annealed at 130° for 2 hr.

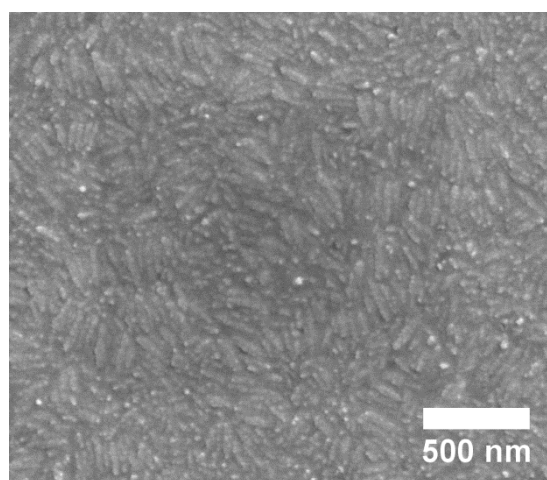


Figure S2. Scanning electron microscope (SEM) image of the top surface of a fully infiltrated AR4 TiO₂ nanoparticle film. The initial thicknesses of AR4 TiO₂ nanoparticle film and PS film are 3.35 and 1.96 μm , respectively.

Determination of the changes in thickness of each layer of PS/TiO₂ PNCF undergoing capillary rise infiltration (CaRI) using *in situ* spectroscopic ellipsometry.

Step 1. The optical constants (A , B and C) of a pure PS film and a pure TiO₂ film are first measured in air at room temperature using a spectroscopic ellipsometer. The thicknesses of PS and TiO₂ layers of a bilayer sample are determined using a two-layer Cauchy model with measured optical constants of the pure PS and TiO₂ films as inputs as shown in Figure S3. Each sample is typically prepared with the thickness of the PS layer being thicker than the amount that would be needed to completely fill the voids in the TiO₂ NP layer.

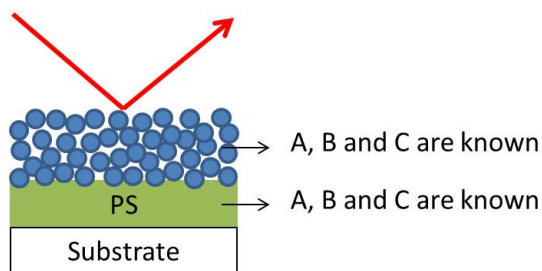


Figure S3. Measurement of thickness of a bilayer film composed using a two-layer Cauchy model.

Step 2. To study the dynamics of PS infiltration into the interstices of the TiO₂ NP layer (Figure S4), we turn on the heating stage at 130°C and monitor the change in amplitude ratio (ψ) and the phase difference (Δ) from the *in situ* spectroscopic ellipsometry. When the ψ and Δ stop changing with time, it indicates that the infiltration process has stopped and in turn all the voids in the TiO₂ NP layer are completely filled with PS. To determine the optical

constants of the PS/TiO₂ PNCF, we use a two-layer Cauchy model with measured optical constants of the pure PS and the thickness of the TiO₂ film fixed.

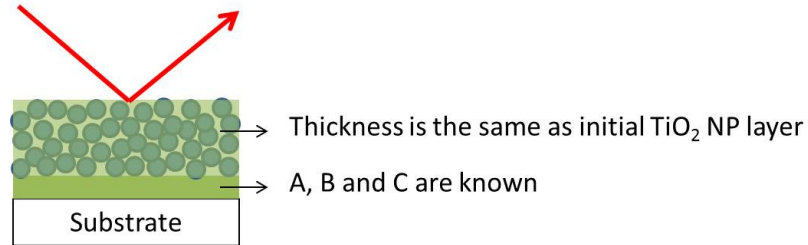


Figure S4. Measurement of the optical constants of PS/TiO₂ PNCF using a two-layer Cauchy model.

Step 3. With the optical constants of pure PS, pure TiO₂ and PS/TiO₂ PNCF as inputs, the *in situ* data can be fitted and the thickness change of each layer in PS/TiO₂ PNCF undergoing CaRI can be determined by using a three-layer Cauchy model (Figure S5).

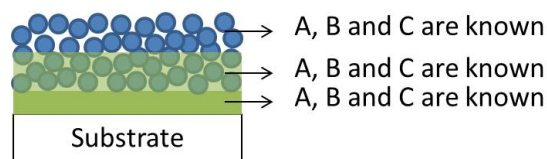


Figure S5. Fitting the thickness of each layer of PS/TiO₂ PNCF undergoing CaRI using a three-layer Cauchy model.

Contact Angle Estimation based on the modified Lucas-Washburn equation

The intercept of the log-log plot of composite thickness vs. time provides a method to estimate the contact angle (θ) of PS on TiO₂ NP surface.

$$\log h = \frac{1}{2} \log \frac{R\sigma \cos \theta}{4\tau^2 \mu} + \frac{1}{2} \log t \quad (S1)$$

We find the values of R , σ , τ and μ based on previous reports as described below:

1. *Estimation of viscosity (μ) of polystyrene in the bulk phase*

Source: Thomas G. Fox Jr., Paul J. Flory. Viscosity-Molecular Weight and Viscosity-Temperature Relationships for Polystyrene and Polyisobutylene. *J. Am. Chem. Soc.*, **1948**, 70, 2384–2395

Closest molecular weight data available for PS 8.8k: $M_w = 7400$.

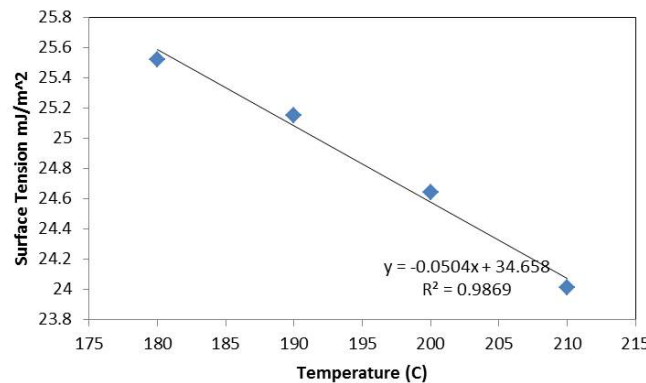
By extrapolating the $\log \frac{\mu_T}{\mu_{217}}$ versus $\frac{1}{T}$ plot in this reference, we obtain $\log \frac{\mu_T}{\mu_{217}} = 3.3$

at $T = 125^\circ\text{C}$. From Table VIII of the reference, we extract $\mu_{217} = 4.1P$ for PS with

an average $M_w = 7200$. Thus, $\log \frac{\mu_T}{\mu_{217}} = 3.3$; $\mu_{217} = 4.1P$; gives $\mu_T = 11.12 \text{ Pa.s}$.

2. *Estimating surface tension (σ) of polystyrene*

Source: D. Y. Kwok; L. K. Cheung; C. B Park; A. W. Neumann, Study on the Surface Tensions of Polymer Melts Using Axisymmetric Drop Shape Analysis, *Polymer Engineering & Science*, **1998**, 38, 757-764.



Plotting surface tension versus temperature for polystyrene and extrapolating the data for $T = 130\text{ }^{\circ}\text{C}$, we obtain $\sigma = 28.1\text{mJ/m}^2$.

3. *Estimation of mean pore size (R) in TiO_2 nanoparticle film*

Source: Antonio Bertei, Benedetta Nucci, Cristiano Nicolella. Effective Transport Properties in Random Packings of Spheres and Agglomerates. *Chemical Engineering Transactions*, **2013**, 32, 1531-1536.

Effective properties for sphere packing evaluated through a Monte-Carlo random walk method allow the calculation of both geometrical parameters and transport properties. Assuming the system investigated by the authors (spherical packings) can sufficiently describe our system, we can refer to the plot of normalized mean pore size as a function of porosity for packings of spheres and agglomerates. The porosity of TiO_2 AR1 NP film is approximately 0.36 (random close packed), giving a normalized

mean pore diameter of $\frac{d_p}{d} = 0.29$. The titania nanoparticles have diameter of approximately 30nm , therefore the pore diameter $d_p \cong 8.7\text{nm}$, giving $R = 4.4\text{ nm}$.

4. *Estimation of tortuosity (τ)*

Source: S. Rémond; J. L. Gallias; A. Mizrahi, Characterization of voids in spherical particle systems by Delaunay empty spheres. *Granular Matter*, **2008**, 10, 329-334.

Assuming TiO_2 NP configuration is random close packing, having a packing density of roughly 63%, $\tau = 1.95$.

5. *Contact angle calculation*

Using all the parameters described above, we estimate the contact angle from the log-log plot intercept. We find that $\theta = 90^{\circ}$ because the intercept divided by the known prefactors always give a very small number, despite considering possibility that the estimated parameters may accommodate errors up to 10^3 orders of magnitude.

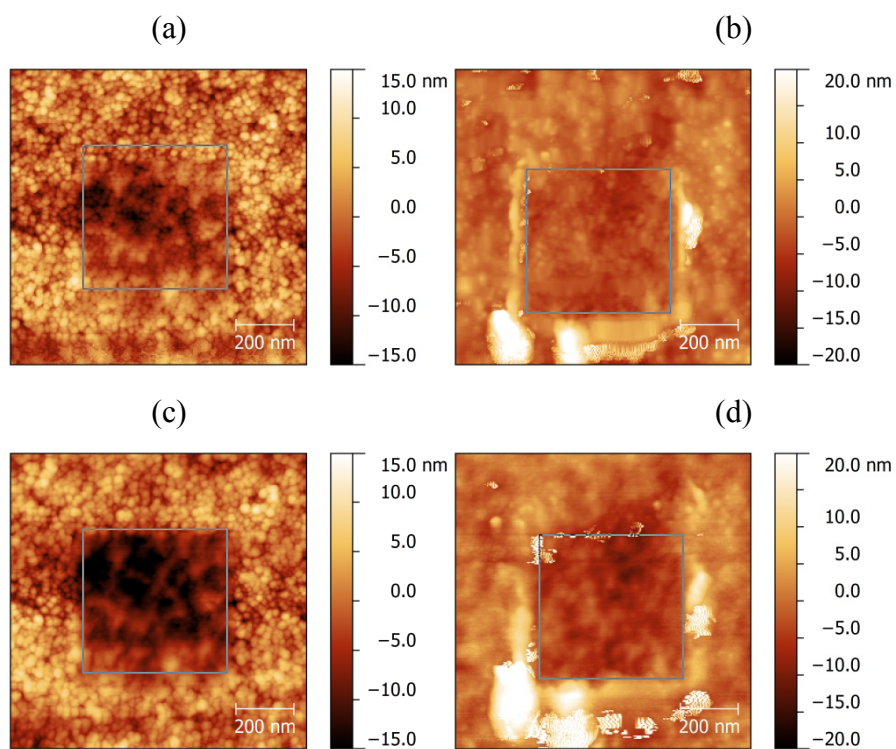


Figure S6. Plan-view images of atomic force microscopy (AFM) images of (a) pure AR1 TiO_2 film and (b) PS/AR1 TiO_2 PNCF after 1 wear scan, and (c) pure AR1 TiO_2 film and (d) PS/AR1 TiO_2 PNCF after 5 wear scans.

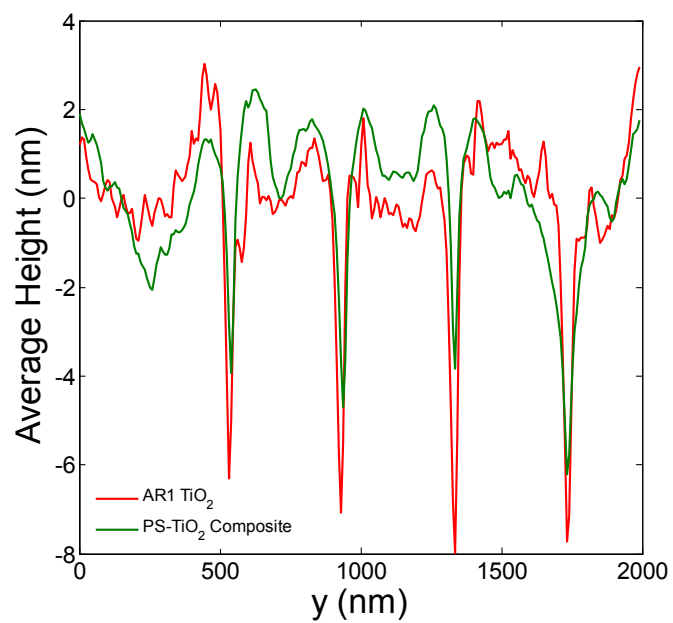


Figure S7. Comparison of the penetration depth relative to the initial surface of PS/AR1 TiO₂ PNCF to pure AR1 TiO₂ film after AFM scratch tests are performed.

Table S1. Average depth of scratch of AR1 TiO₂ film and PS/AR1 TiO₂ PNCF using AFM

Sample	Average scratch depth (nm)
AR1 TiO ₂ film	6.91 ± 0.73
PS/AR1 TiO ₂ PNCF	5.14 ± 1.24