Electronic Supplementary Information

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

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**Figure S1.** High magnification scanning electron microscopy image of polystyrene front moving into a TiO$_2$ nanoparticle layer. SEM images close to (a) the top surface of the TiO$_2$ nanoparticle layer and (b) the interface between the TiO$_2$/PS interface. Dashed line in (b) shows the location of PS front moving into the TiO$_2$ nanoparticle layer. A bilayer consisting of PS (Mn = 8,000) and TiO$_2$ 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 TiO$_2$ nanoparticle film. The initial thicknesses of AR4 TiO$_2$ nanoparticle film and PS film are 3.35 and 1.96 μm, respectively.
Determination of the changes in thickness of each layer of PS/TiO$_2$ 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 TiO$_2$ film are first measured in air at room temperature using a spectroscopic ellipsometer. The thicknesses of PS and TiO$_2$ layers of a bilayer sample are determined using a two-layer Cauchy model with measured optical constants of the pure PS and TiO$_2$ 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 TiO$_2$ NP layer.

![Figure S3](image)

**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 TiO$_2$ NP layer (Figure S4), we turn on the heating stage at 130°C and monitor the change in amplitude ratio ($\psi$) and the phase difference ($\Delta$) from the *in situ* spectroscopic ellipsometry. When the $\psi$ and $\Delta$ stop changing with time, it indicates that the infiltration process has stopped and in turn all the voids in the TiO$_2$ NP layer are completely filled with PS. To determine the optical
constants of the PS/TiO$_2$ PNCF, we use a two-layer Cauchy model with measured optical constants of the pure PS and the thickness of the TiO$_2$ film fixed.

**Figure S4.** Measurement of the optical constants of PS/TiO$_2$ PNCF using a two-layer Cauchy model.

Step 3. With the optical constants of pure PS, pure TiO$_2$ and PS/TiO$_2$ PNCF as inputs, the *in situ* data can be fitted and the thickness change of each layer in PS/TiO$_2$ 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/TiO$_2$ 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 ($\theta$) of PS on TiO$_2$ NP surface.

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

We find the values of $R$, $\sigma$, $\tau$ and $\mu$ based on previous reports as described below:

1. **Estimation of viscosity ($\mu$) of polystyrene in the bulk phase**


   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 $T = 125^\circ C$. From Table VIII of the reference, we extract $\mu_{217} = 4.1P$ for PS with an average Mw = 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 ($\sigma$) of polystyrene**

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

3. *Estimation of mean pore size (R) in TiO$_2$ nanoparticle film*


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

4. *Estimation of tortuosity ($\tau$)*


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 TiO$_2$ PNCF to pure AR1 TiO$_2$ film after AFM scratch tests are performed.
**Table S1.** Average depth of scratch of AR1 TiO$_2$ film and PS/AR1 TiO$_2$ PNCF using AFM

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average scratch depth (nm)</th>
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<tbody>
<tr>
<td>AR1 TiO$_2$ film</td>
<td>6.91 ± 0.73</td>
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<tr>
<td>PS/AR1 TiO$_2$ PNCF</td>
<td>5.14 ± 1.24</td>
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