

## Supplementary Information

### Metal Oxide Arrays from Block Copolymer Thin Film Templates

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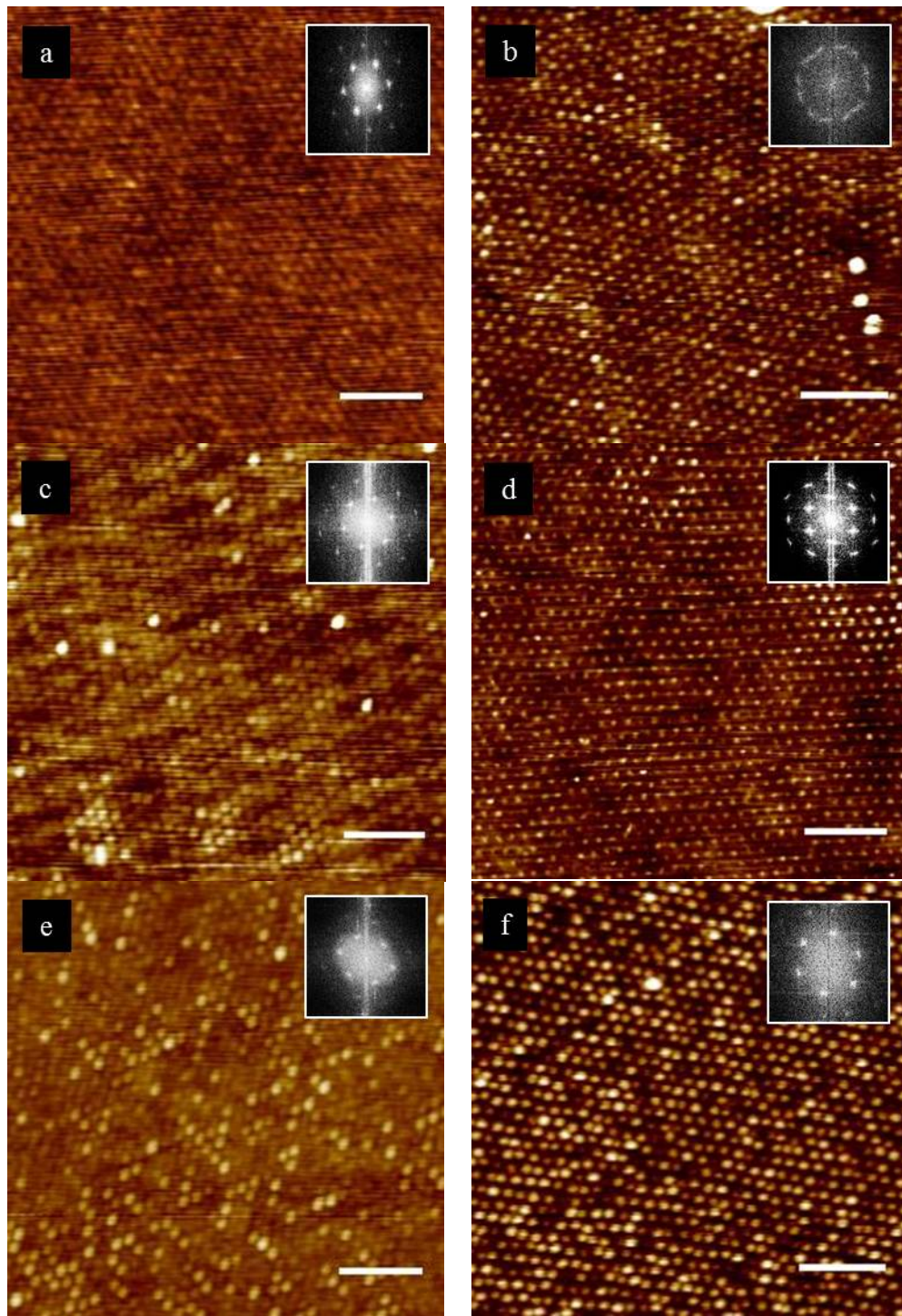
## Methods for Sample Preparation

Table S1. Sample preparation methods prior to immersion and polymer removal.

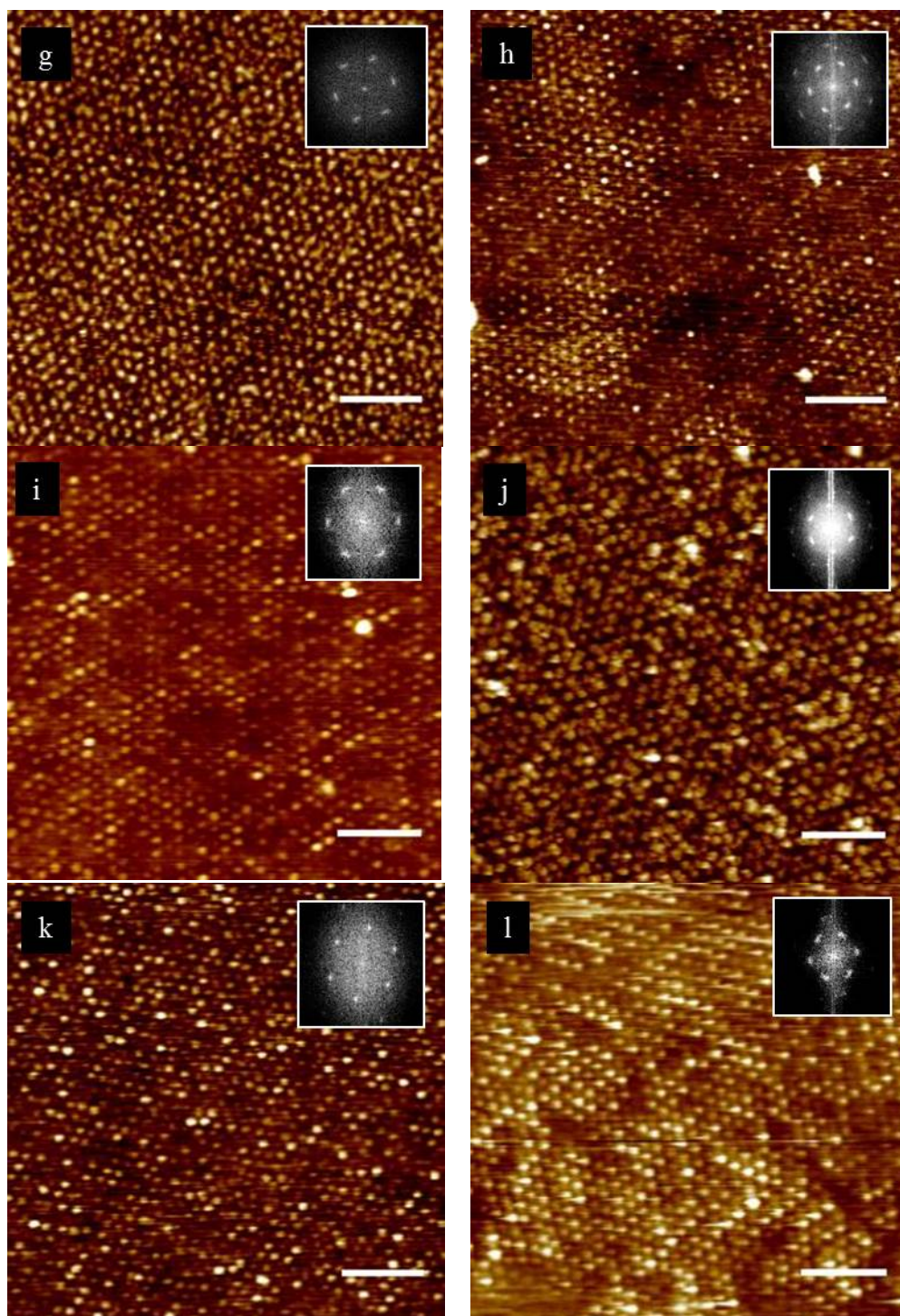
Description	Manuscript reference	Substrate	Annealing procedure	Metal precursor solution
PS- <i>b</i> -PEO	Figure 1a	Si	toluene vapor, 18 h	N/A
PS- <i>b</i> -PEO	Figure 1b	Si	toluene/water vapor (98 % RH), 18 h	N/A
EISA TiO <sub>2</sub>	Figure 1c	SiO <sub>2</sub>	toluene vapor, 2 h	0.7 g titanium tetraisopropoxide, 0.25 g HCl solution (37% in water), 0.5 mL 2-propanol stirred for 30 min
SPICE TiO <sub>2</sub>	Figure 1d	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	0.7 g titanium tetraisopropoxide, 0.25 g HCl solution (37% in water), 0.5 mL 2-propanol
SPICE Au/TiO <sub>2</sub>	Figure 1e	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	0.7 g titanium tetraisopropoxide, 0.25 g HCl solution (37% in water), 0.5 mL 2-propanol stirred for 30 min
PS- <i>b</i> -PEO -Ti	Figure 2a	Transfer from SiO <sub>2</sub> to Cu grid	toluene/water vapor (98 % RH), 2 h	0.7 g titanium tetraisopropoxide, 0.25 g HCl solution (37% in water), 0.5 mL 2-propanol stirred for 30 min
PS- <i>b</i> -PEO -Ti	Figure 2b	Transfer from SiO <sub>2</sub> to Cu grid	toluene vapor, 2 h	0.7 g titanium tetraisopropoxide, 0.25 g HCl solution (37% in water), 0.5 mL 2-propanol stirred for 30 min
SPICE TiO <sub>2</sub>	Figure 2c	Transfer from SiO <sub>2</sub> to SiN grid	toluene/water vapor (98 % RH), 18 h	0.7 g titanium tetraisopropoxide, 0.25 g HCl solution (37% in water), 0.5 mL 2-propanol stirred for 30 min
SPICE MgO	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE Al <sub>2</sub> O <sub>3</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE MnO <sub>2</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min

SPICE Fe <sub>2</sub> O <sub>3</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE Co <sub>3</sub> O <sub>4</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE NiO	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE CuO	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE ZnO	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE ZrO <sub>2</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	0.5 M in 50:50 vol ethanol:water solution stirred for 30 min
SPICE RuO <sub>2</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE SnO <sub>2</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE Ce <sub>2</sub> O <sub>3</sub>	Figure S1	SiO <sub>2</sub>	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min

## Atomic Force Microscopy (AFM) of Metal Oxides







**Figure S1.** AFM height images of metal oxides templated by the SPICE method: (a) MgO, (b) Al<sub>2</sub>O<sub>3</sub>, (c) MnO<sub>2</sub>, (d) Fe<sub>2</sub>O<sub>3</sub>, (e) Co<sub>3</sub>O<sub>4</sub>, (f) NiO, (g) CuO, (h) ZnO, (i) ZrO<sub>2</sub>, (j) SnO<sub>2</sub>, (k) Ce<sub>2</sub>O<sub>3</sub>, and (l) RuO<sub>2</sub>. Insets are FFTs of the entire image. Scale bars represent 200 nm.

The SPICE method was used to template MgO, Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, NiO, CuO, ZnO, ZrO<sub>2</sub>, SnO<sub>2</sub>, Ce<sub>2</sub>O<sub>3</sub>, and RuO<sub>2</sub>. TiO<sub>2</sub> is shown in the main text of the manuscript. Representative AFM height images are shown in Figure S1. FFTs of the image are shown in the insets. The 6-spot pattern is characteristic of hexagonal packing.

### XPS of Metal Oxides

**Table S1.** XPS peak positions and associated full width half maxima (FWHM).

Metal oxide	Position (eV)	FWHM (eV)	Metal oxide	Position (eV)	FWHM (eV)
MgO 2p	50.8	1.7	ZnO 2p <sub>3/2</sub>	1022.7	1.8
RuO <sub>2</sub> 3d <sub>5/2</sub>	280.7	1.8	TiO <sub>2</sub> 2p <sub>3/2</sub> 2p <sub>1/2</sub>	458.9 464.6	1.3 2.3
Al <sub>2</sub> O <sub>3</sub> 2p	74.6	1.8	Fe <sub>2</sub> O <sub>3</sub> 2p <sub>3/2</sub> shake-up 2p <sub>1/2</sub> shake-up	711.2 718.6 724.9 728.2	2.8 5.1 4.0 13.3
CeO <sub>2</sub> 3d <sub>3/2</sub>	916.5	4.4			
MnO <sub>2</sub> 2p <sub>3/2</sub> shake-up 2p <sub>1/2</sub> shake-up	642.2 645.6 654.0 655.3	2.7 5.5 2.5 9.1	NiO 2p <sub>3/2</sub> shake-up 2p <sub>1/2</sub> shake-up	856.7 861.6 874.3 880.0	2.0 7.8 2.6 6.9
Co <sub>3</sub> O <sub>4</sub> 2p <sub>3/2</sub> shake-up 2p <sub>1/2</sub> shake-up	781.7 786.2 797.2 802.9	2.7 8.1 3.5 7.2	Ce <sub>2</sub> O <sub>3</sub> 3d <sub>5/2</sub> 3d <sub>5/2</sub> 3d <sub>3/2</sub> 3d <sub>3/2</sub>	882.0 885.8 900.0 904.2	3.0 3.9 3.5 5.2
CuO 2p <sub>3/2</sub> shake-up 2p <sub>1/2</sub> shake-up	932.9 942.4 952.6 962.4	1.3 5.9 1.8 3.7	ZrO <sub>2</sub> 3d <sub>5/2</sub> 3d <sub>3/2</sub>	182.7 185	1.4 1.5
Cu(OH) <sub>2</sub> 2p <sub>3/2</sub> 2p <sub>1/2</sub>	934.7 954.6	3.7 3.1	SnO <sub>2</sub> 3d <sub>5/2</sub> 3d <sub>3/2</sub>	487.3 495.7	1.4 1.4

XPS data were fit using CasaXPS to determine peak positions and FWHM. Metal oxide signatures were evident in all spectra. No evidence of precursor salts or metals was noted.

### **Titania Loading**

By comparing the PEO cylinder volume ( $V_{PEO}$ ) to the  $TiO_2$  volume ( $V_{TiO_2}$ ), a loading ratio can be calculated. The measured height of titania dots, which has a density ( $\rho_{TiO_2}$ ) and formula weight ( $FW_{TiO_2}$ ), was  $5.4 \pm 1.4$  nm when using PS-*b*-PEO films, which had a PEO density ( $\rho_{PEO}$ ) and monomer formula weight ( $FW_{PEO \text{ unit}}$ ), that were 30 nm thick. PEO cylinders and  $TiO_2$  radii were  $8.7 \pm 0.8$  nm and  $8.5 \pm 1.9$  nm, respectively.

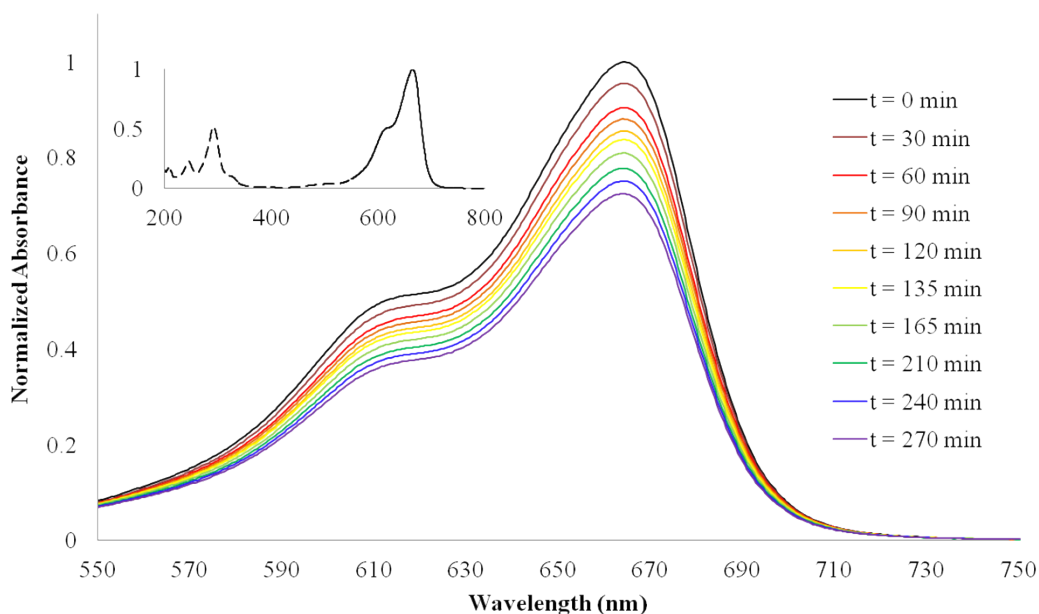
$$\left( \frac{\text{mol}_{Ti}}{\text{mol}_{PEO \text{ unit}}} \right) = \left( \frac{V_{TiO_2} \cdot \rho_{TiO_2}}{FW_{TiO_2}} \right) \left( \frac{FW_{PEO \text{ unit}}}{V_{PEO} \cdot \rho_{PEO}} \right) \quad (S1)$$

$$\left( \frac{\text{mol}_{Ti}}{\text{mol}_{PEO \text{ unit}}} \right) = \left( \frac{1.3 \times 10^{-24} \text{ m}^3 \cdot 4230 \text{ kg} \cdot \text{m}^{-3}}{0.079 \text{ kg} \cdot \text{mol}^{-1}} \right) \cdot \left( \frac{0.044 \text{ kg} \cdot \text{mol}^{-1}}{7.1 \times 10^{-24} \text{ m}^3 \cdot 1130 \text{ kg} \cdot \text{m}^{-3}} \right) \quad (S2)$$

$$\left( \frac{\text{mol}_{Ti}}{\text{mol}_{PEO \text{ unit}}} \right) = 0.38 \quad (S3)$$

The loading ratio ( $\text{mol}_{Ti}:\text{mol}_{PEO \text{ unit}} = 0.38$ ) is less than traditional EISA methods, which can reach up to 2 by employing micelles. However, loading ratios by the SPICE method should be compared to work by Shan *et al.*; they achieved well-ordered arrays by complexing precursors with homopolymers prior to blending with a BCP solution.<sup>1</sup> The reported loading ratios were 0.18-0.30; however, the ratios were calculated based on the homopolymer solution and not the final precursor/homopolymer/BCP solution. In the case of the latter, the loading ratios would have been closer to 0.12-0.20. Therefore, the SPICE method uses relatively large precursor loading ratios and thus minimizes consumed polymer material.

## Methylene Blue Catalysis

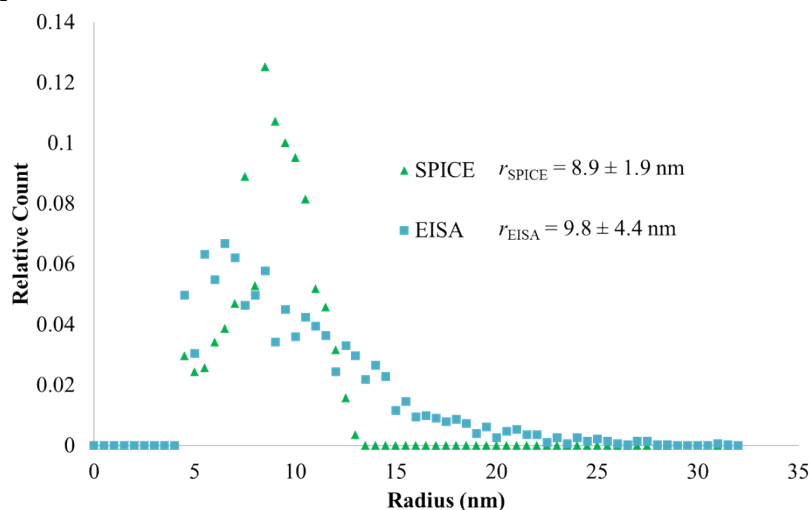


**Figure S2.** Representative time-lapse UV-vis spectra of MB photocatalytically degraded by SPICE TiO<sub>2</sub>. MB solutions were exposed to catalyst and UV irradiation in UV-transparent cuvettes. Inset contains the entire UV-vis spectra of a MB aqueous solution. The peaks between 550-740 nm (solid) were used to evaluate the photocatalytic activity of SPICE TiO<sub>2</sub>, EISA TiO<sub>2</sub>, and Au/SPICE-TiO<sub>2</sub> Au/EISA-TiO<sub>2</sub> surfaces.

MB was used to demonstrate the improved photocatalytic activity of SPICE TiO<sub>2</sub> over traditional EISA TiO<sub>2</sub>. The peaks between 550-750 nm were used to monitor the photocatalytic degradation of MB. Instrument drift was monitored by analyzing a stock MB solution that was not exposed to UV irradiation (Figure S2 inset) prior to each measurement. Time-lapse data clearly exhibit decreases in peak intensity. MB solution concentrations, which were based on integrated peak areas, were fit to first-order kinetics to determine rate constants (Figure 3). By monitoring the UV-vis spectra, it was shown that SPICE TiO<sub>2</sub> was 13% more effective than EISA TiO<sub>2</sub>.



## TiO<sub>2</sub> Dispersion



**Figure S3.** Size distributions of EISA and SPICE TiO<sub>2</sub> were measured according to the AFM images in Figure 1c and Figure 1d, respectively. Radii were calculated using ImageJ and binned in 0.5 nm increments. Counts (y-axis) were normalized for the purposes of comparison. Radii ( $r_x$ ) represent the average and standard deviation of each data set. The data represent over 2700 measurements for each AFM image.

The SPICE method produced a narrower distribution of TiO<sub>2</sub> than the EISA method. The narrower distribution was qualitatively evident by the line scan in Figure 1f, but it is quantified here. The variance ( $\sigma$ ) within the distribution of radii were  $\sigma_{\text{SPICE}} = 3.5$  nm and  $\sigma_{\text{EISA}} = 19.6$  nm.

The index of dispersion ( $D$ ) was calculated by the following expression:

$$D = \frac{\sigma^2}{\mu}, \quad (\text{S4})$$

for which  $\mu$  is the number average of the distribution. The indices of dispersion were  $D_{\text{SPICE}} = 1.5$  nm and  $D_{\text{EISA}} = 39.2$  nm. This narrower size distribution is one of the key benefits of the SPICE method over the traditional EISA method.

1. Shan, L.; Punniyakoti, S.; Van Bael, M. J.; Temst, K.; Van Bael, M. K.; Ke, X.; Bals, S.; Van Tendeloo, G.; D'Olieslaeger, M.; Wagner, P.; Haenen, K.; Boyen, H.-G.; *J. Mater. Chem. C* **2014**, *2*, 701-707.