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-*b*-PEO	Figure 1a	Si	toluene vapor, 18 h	N/A
PS-*b*-PEO	Figure 1b	Si	toluene/water vapor (98 % RH), 18 h	N/A
EISA TiO$_2$	Figure 1c	SiO$_2$	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$_2$	Figure 1d	SiO$_2$	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$_2$	Figure 1e	SiO$_2$	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-*b*-PEO -Ti	Figure 2a	Transfer from SiO$_2$ 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-*b*-PEO -Ti	Figure 2b	Transfer from SiO$_2$ 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$_2$	Figure 2c	Transfer from SiO$_2$ 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$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE Al$_2$O$_3$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE MnO$_2$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min

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SPICE Fe$_2$O$_3$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE Co$_3$O$_4$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE NiO	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE CuO	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE ZnO	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE ZrO$_2$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	0.5 M in 50:50 vol ethanol:water solution stirred for 30 min
SPICE RuO$_2$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE SnO$_2$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min
SPICE Ce$_2$O$_3$	Figure S1	SiO$_2$	toluene/water vapor (98 % RH), 18 h	1 M in ethanol stirred for 30 min

Atomic Force Microscopy (AFM) of Metal Oxides
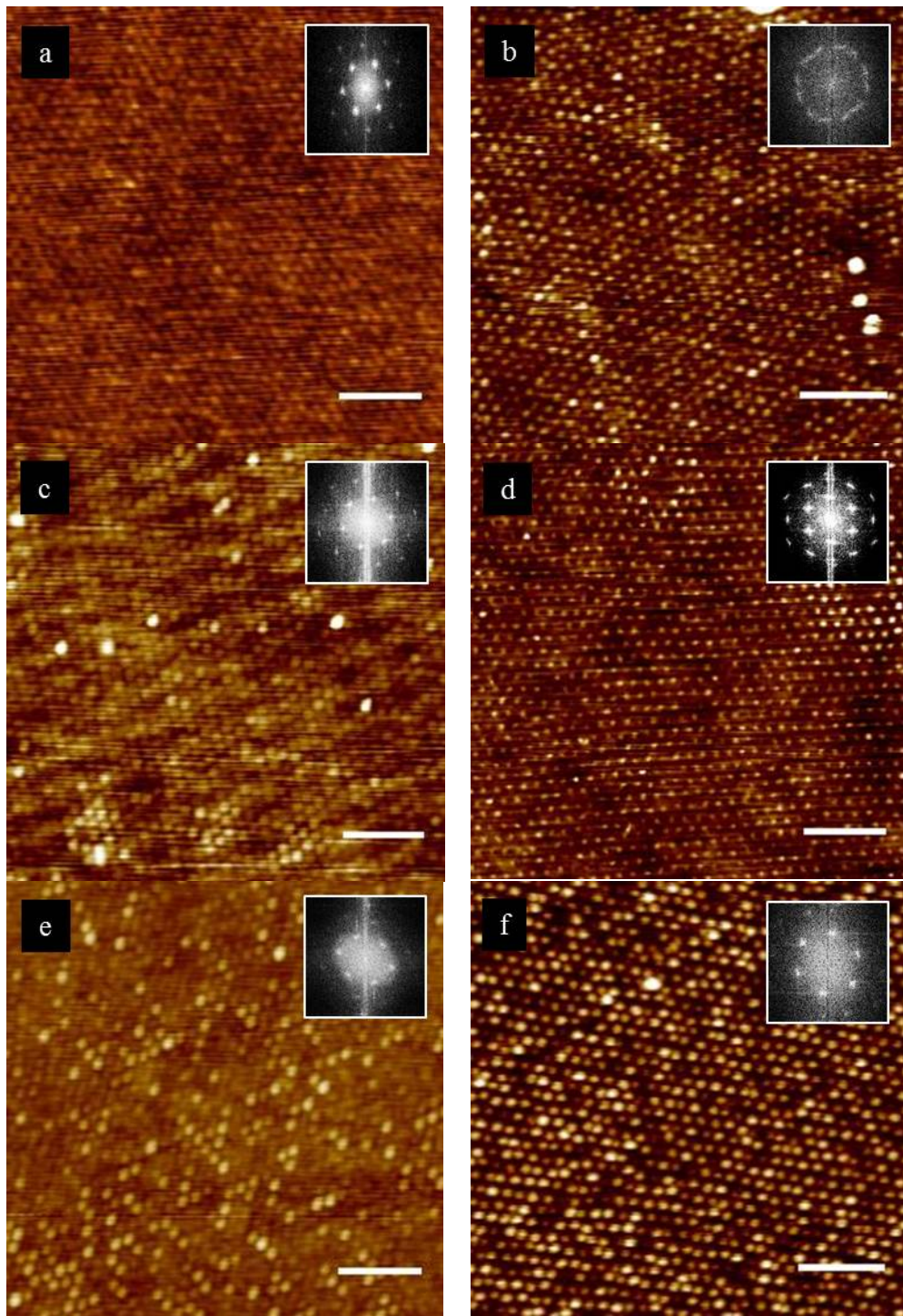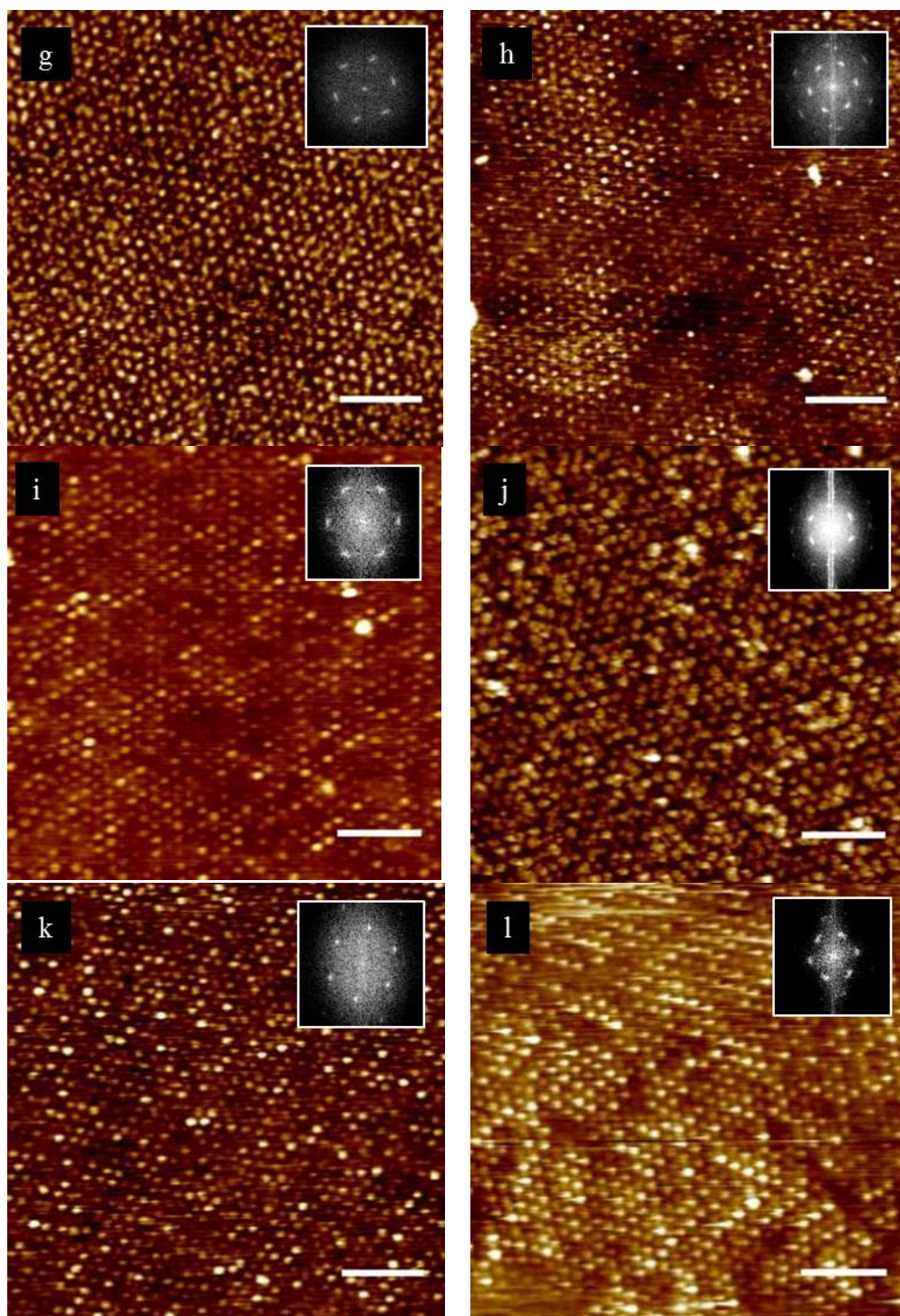
Figure S1. AFM height images of metal oxides templated by the SPICE method: (a) MgO, (b) Al_2O_3, (c) MnO_2, (d) Fe_2O_3, (e) Co_3O_4, (f) NiO, (g) CuO, (h) ZnO, (i) ZrO_2, (j) SnO_2, (k) Ce_2O_3, and (l) RuO_2. Insets are FFTs of the entire image. Scale bars represent 200 nm.

The SPICE method was used to template MgO, Al$_2$O$_3$, MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$, NiO, CuO, ZnO, ZrO$_2$, SnO$_2$, Ce$_2$O$_3$, and RuO$_2$. TiO$_2$ 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			ZnO		
2p	50.8	1.7	2p$_{3/2}$	1022.7	1.8
RuO$_2$			TiO$_2$		
3d$_{5/2}$	280.7	1.8	2p$_{3/2}$	458.9	1.3
			2p$_{1/2}$	464.6	2.3
Al$_2$O$_3$			Fe$_2$O$_3$		
2p	74.6	1.8	2p$_{3/2}$	711.2	2.8
			shake-up	718.6	5.1
CeO$_2$			2p$_{1/2}$	724.9	4.0
3d$_{3/2}$	916.5	4.4	shake-up	728.2	13.3
MnO$_2$			NiO		
2p$_{3/2}$	642.2	2.7	2p$_{3/2}$	856.7	2.0
shake-up	645.6	5.5	shake-up	861.6	7.8
2p$_{1/2}$	654.0	2.5	2p$_{1/2}$	874.3	2.6
shake-up	655.3	9.1	shake-up	880.0	6.9
Co$_3$O$_4$			Ce$_2$O$_3$		
2p$_{3/2}$	781.7	2.7	3d$_{5/2}$	882.0	3.0
shake-up	786.2	8.1	3d$_{5/2}$	885.8	3.9
2p$_{1/2}$	797.2	3.5	3d$_{3/2}$	900.0	3.5
shake-up	802.9	7.2	3d$_{3/2}$	904.2	5.2
CuO			ZrO$_2$		
2p$_{3/2}$	932.9	1.3	3d$_{5/2}$	182.7	1.4
shake-up	942.4	5.9	3d$_{3/2}$	185	1.5
2p$_{1/2}$	952.6	1.8			
shake-up	962.4	3.7			
Cu(OH)$_2$			SnO$_2$		
2p$_{3/2}$	934.7	3.7	3d$_{5/2}$	487.3	1.4
2p$_{1/2}$	954.6	3.1	3d$_{3/2}$	495.7	1.4

XPS data were fit using CasaXPS to determine peak positions and FHWM. 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 (ρ_{TiO_2}) and formula weight (FW_{TiO_2}), was 5.4 ± 1.4 nm when using PS-*b*-PEO films, which had a PEO density (ρ_{PEO}) and monomer formula weight ($FW_{PEO\ unit}$), that were 30 nm thick. PEO cylinders and TiO$_2$ radii were 8.7 ± 0.8 nm and 8.5 ± 1.9 nm, respectively.

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

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

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

The loading ratio (mol$_{Ti}$:mol$_{PEO\ unit}$ = 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.[1] 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.
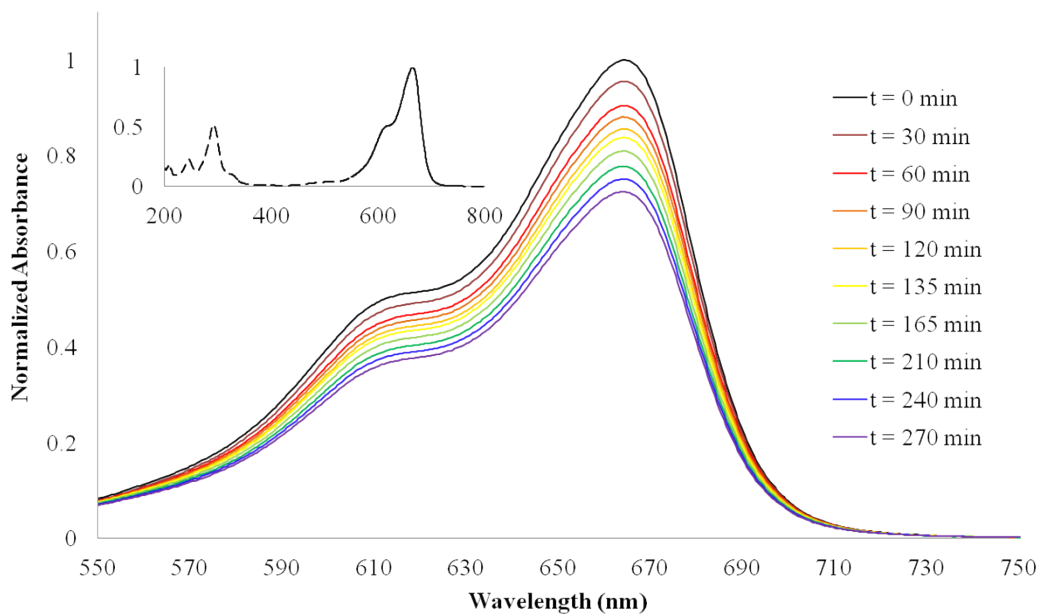
Methylene Blue Catalysis

Figure S2. Representative time-lapse UV-vis spectra of MB photocatalytically degraded by SPICE TiO_2. 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_2, EISA TiO_2, and Au/SPICE-TiO_2 Au/EISA-TiO_2 surfaces.

MB was used to demonstrate the improved photocatalytic activity of SPICE TiO_2 over traditional EISA TiO_2. 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_2 was 13% more effective than EISA TiO_2.
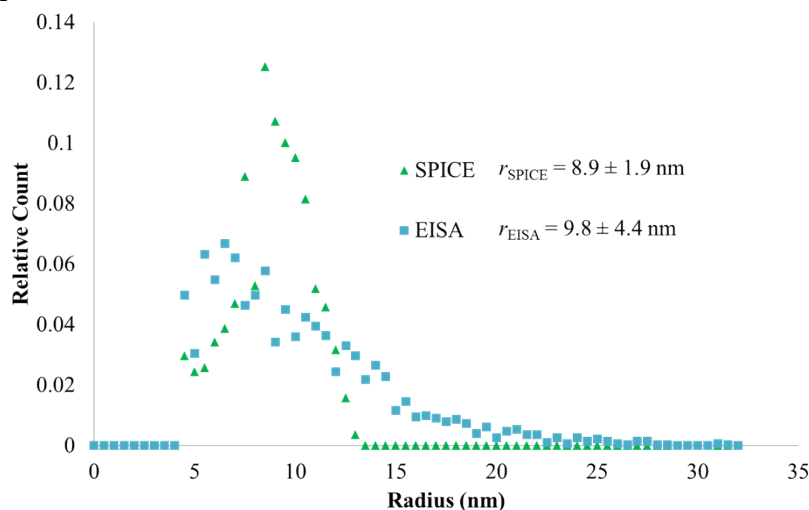
TiO₂ Dispersion

Figure S3. Size distributions of EISA and SPICE TiO$_2$ 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$_2$ than the EISA method. The narrower distribution was qualitatively evident by the line scan in Figure 1f, but it is quantified here. The variance (σ) within the distribution of radii were σ_{SPICE} = 3.5 nm and σ_{EISA} = 19.6 nm. The index of dispersion (D) was calculated by the following expression:

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

for which μ is the number average of the distribution. The indices of dispersion were D_{SPICE} = 1.5 nm and D_{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.