Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information:

Fabrication and optical characterization of polystyrene opal templates for the synthesis of scalable, nanoporous (photo)electrocatalytic materials by electrodeposition

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Table S1: Amount of surfactant added to the PS deposition solution and hotplate temperature during deposition.

	170 nm	200 nm	280 nm	350 nm	390 nm	400 nm	500 nm	510 nm	600 nm
v/v% Concentration	0.1	0.1	0.1	0.05	0.1	1.0	0.4	0.07	0.4
1% TritonX	0	0	0	0	3 drops/ 8 mL	3 drops/ 7.5 mL	1 drop/ 2.5 mL	1 drop/ 2 mL	1 drop/ 3 mL
Hotplate Temp (°C)	65	65	65	65	50	50	50	50	50

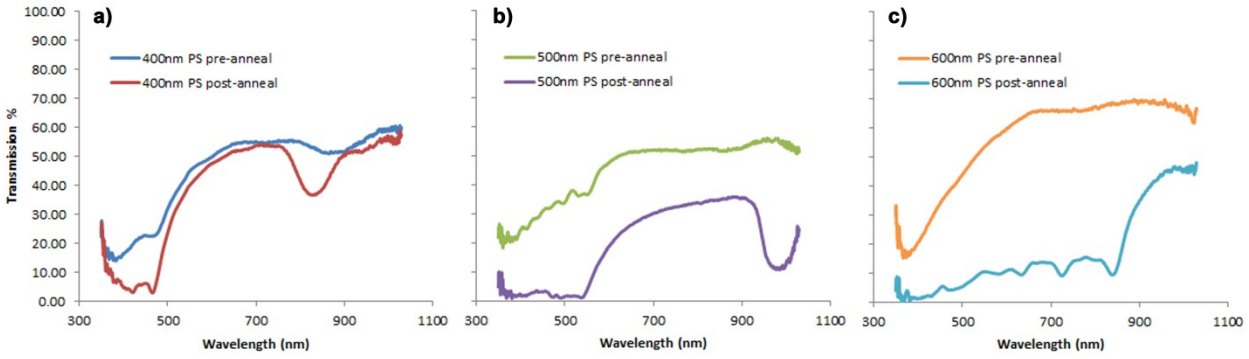

Figure S1: Transmission spectra showing the improvement of the photonic optical properties after a 1 hr ethanol anneal for a) 400 nm, b) 500 nm, c) 600 nm PS bead films.

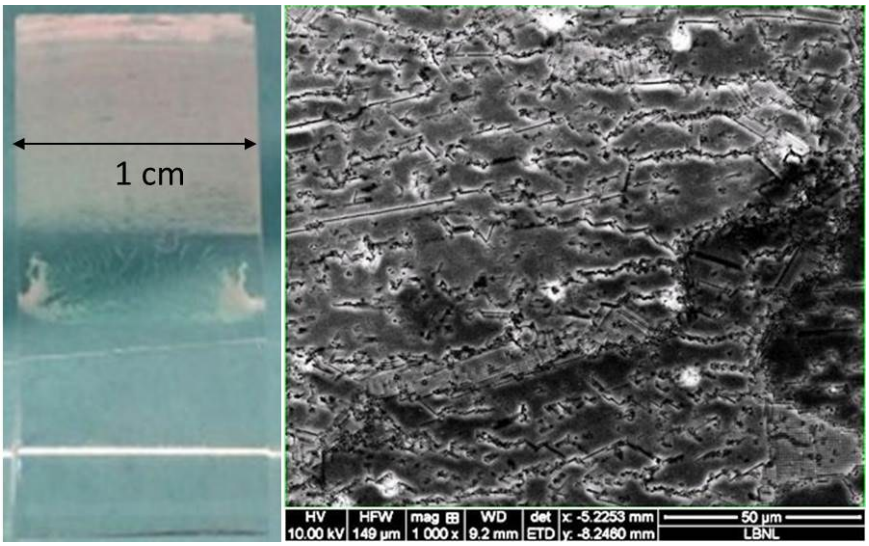

Figure S2: PS bead films deposited using ethanol as the solvent demonstrating homogeneity on the cm scale, but a highly defective PS crystal film on the micron scale.

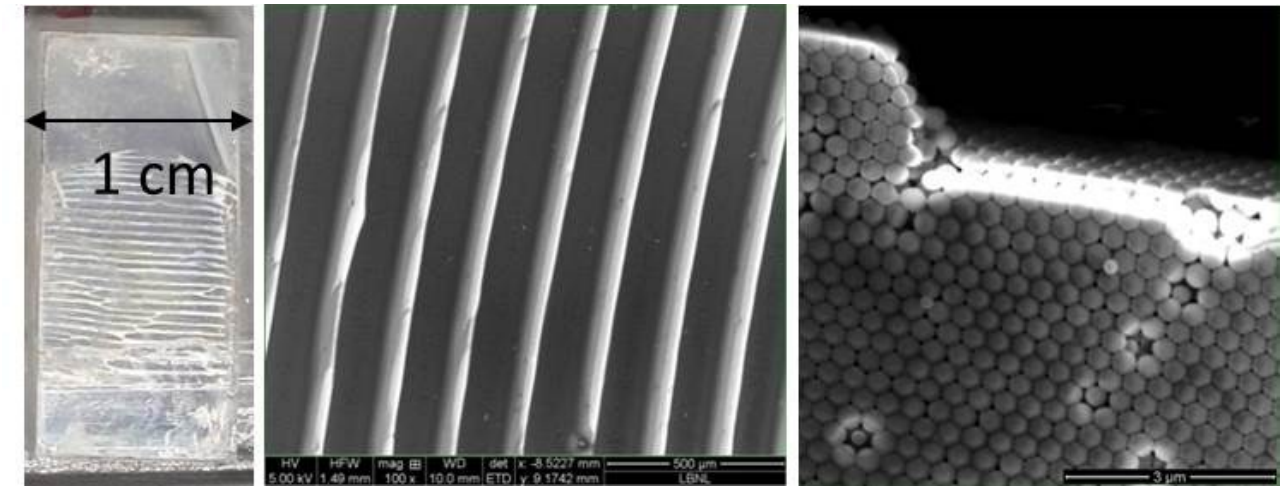

Figure S3: Initial deposition trials using water as the solvent showing order of the beads on the micron scale, but exhibition the coffee ring effect on the cm scale.

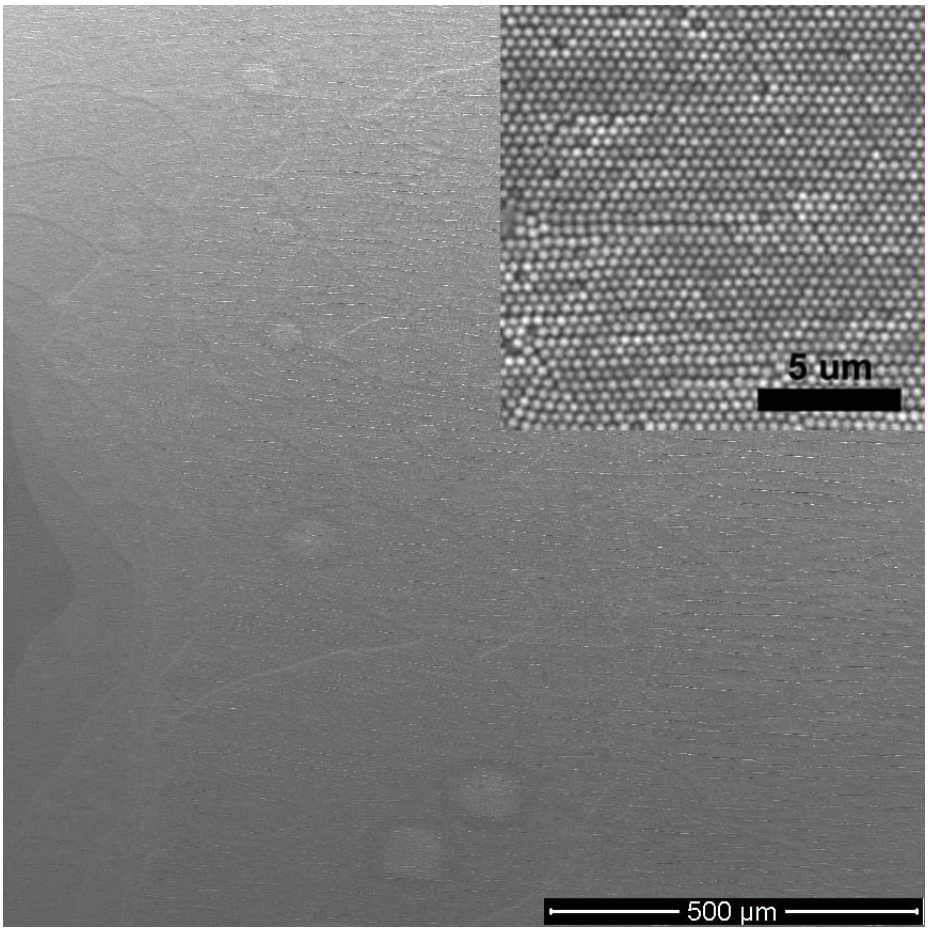

Figure S4: SEM image of a 500 nm PS film showing homogeneity over a > 1mm^2 area. On the left, the drying front can be seen as a stacking of individual layers at the drying front edge.

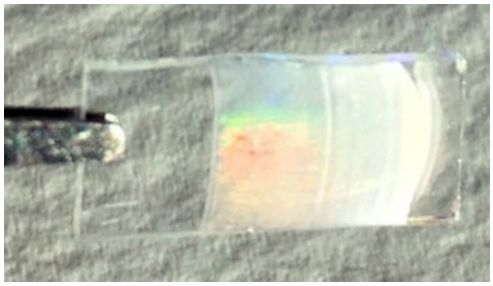

Figure S5: Photo of the 500 nm PS film on quartz.

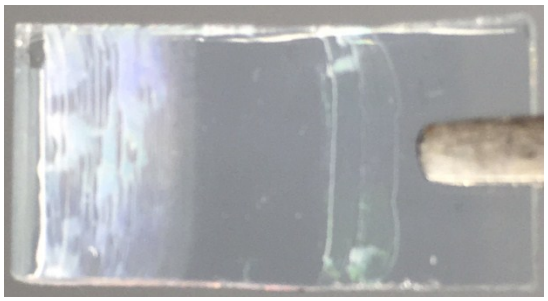

Figure S6: 500 nm PS beads deposited at a lower angle of 45^{o} (from horizontal).

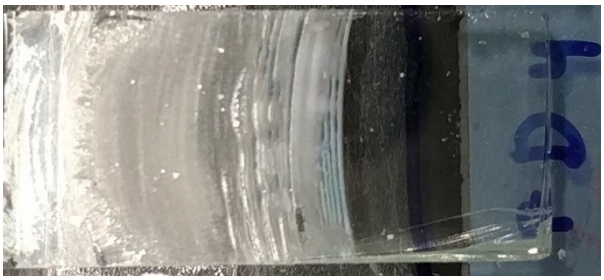

Figure S7: PS beads deposited in a non-saturated (less humid) environment.

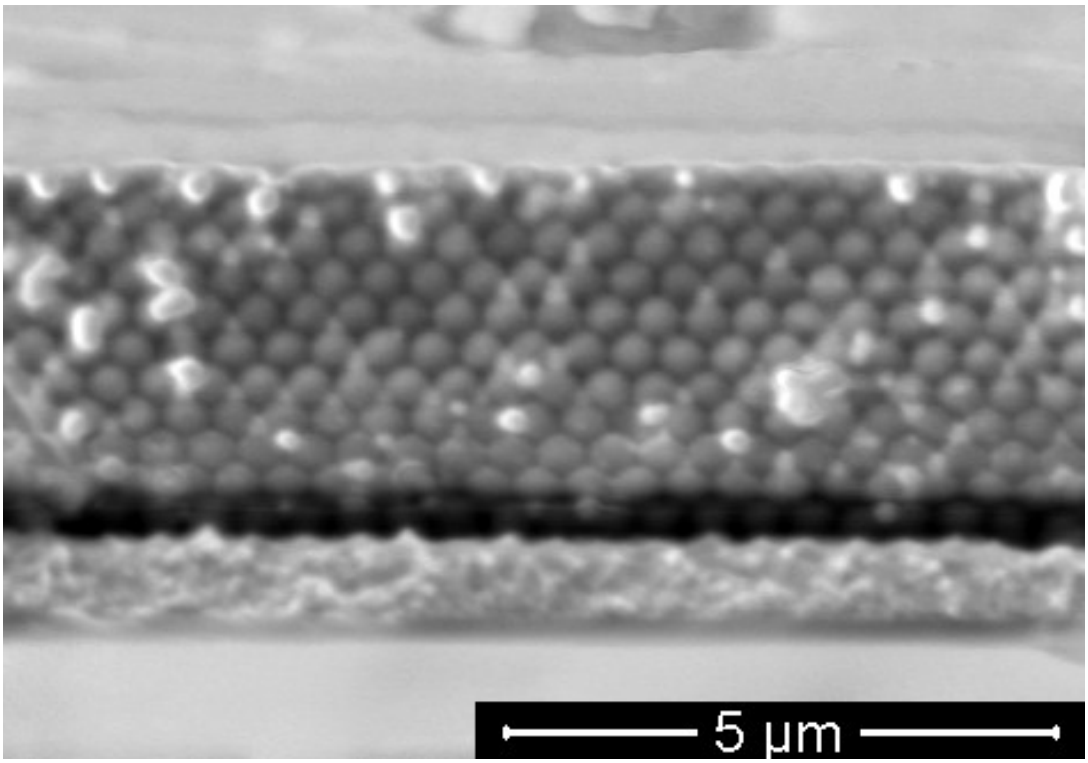

Figure S8: A cross-section of a typical PS bead template made of 500 nm diameter beads. The film is 3.3 µm thick and composed of 10 layers.

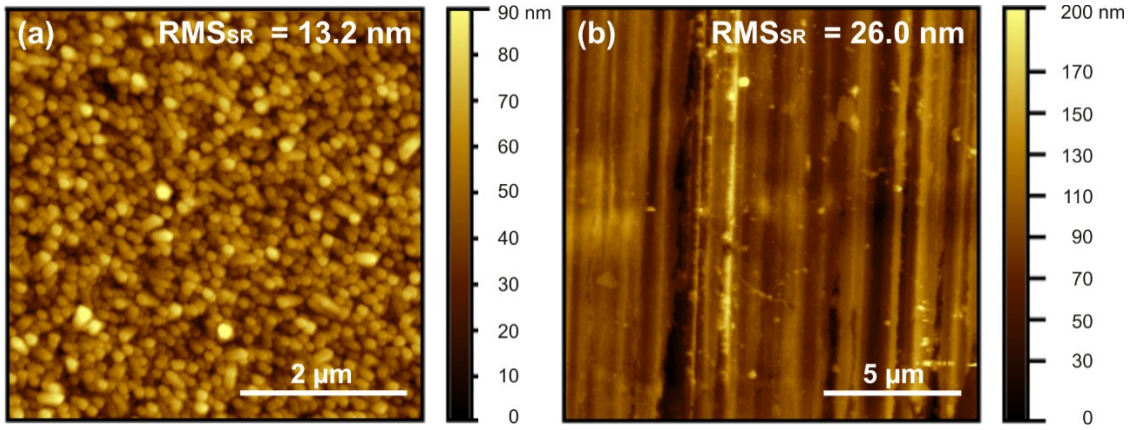

Figure S9: AFM images showing the respective surface roughness as root mean squared (RMS_{SR}) of a) FTO (RMS_{SR} = 13.2 nm) and b) Cu foil (RMS_{SR} = 26.0 nm).

Figure S10: An opal film of 280 nm PS beads on a copper sheet substrate used for the copper electrodeposition.

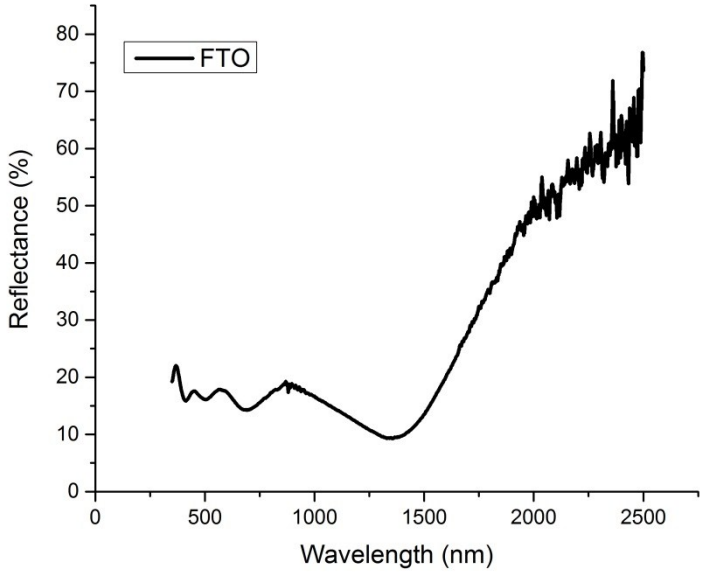

Figure S11: Reflectance of blank FTO substrate, showing an increase of reflectance in the IR.

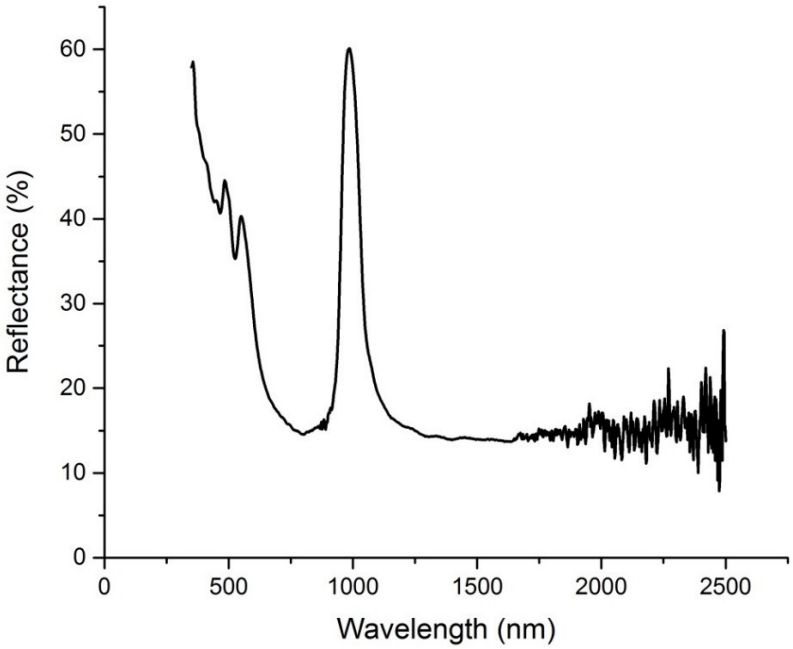

Figure S12: 500 nm PS beads assembled on quartz. The increase in the IR from the FTO is absent.

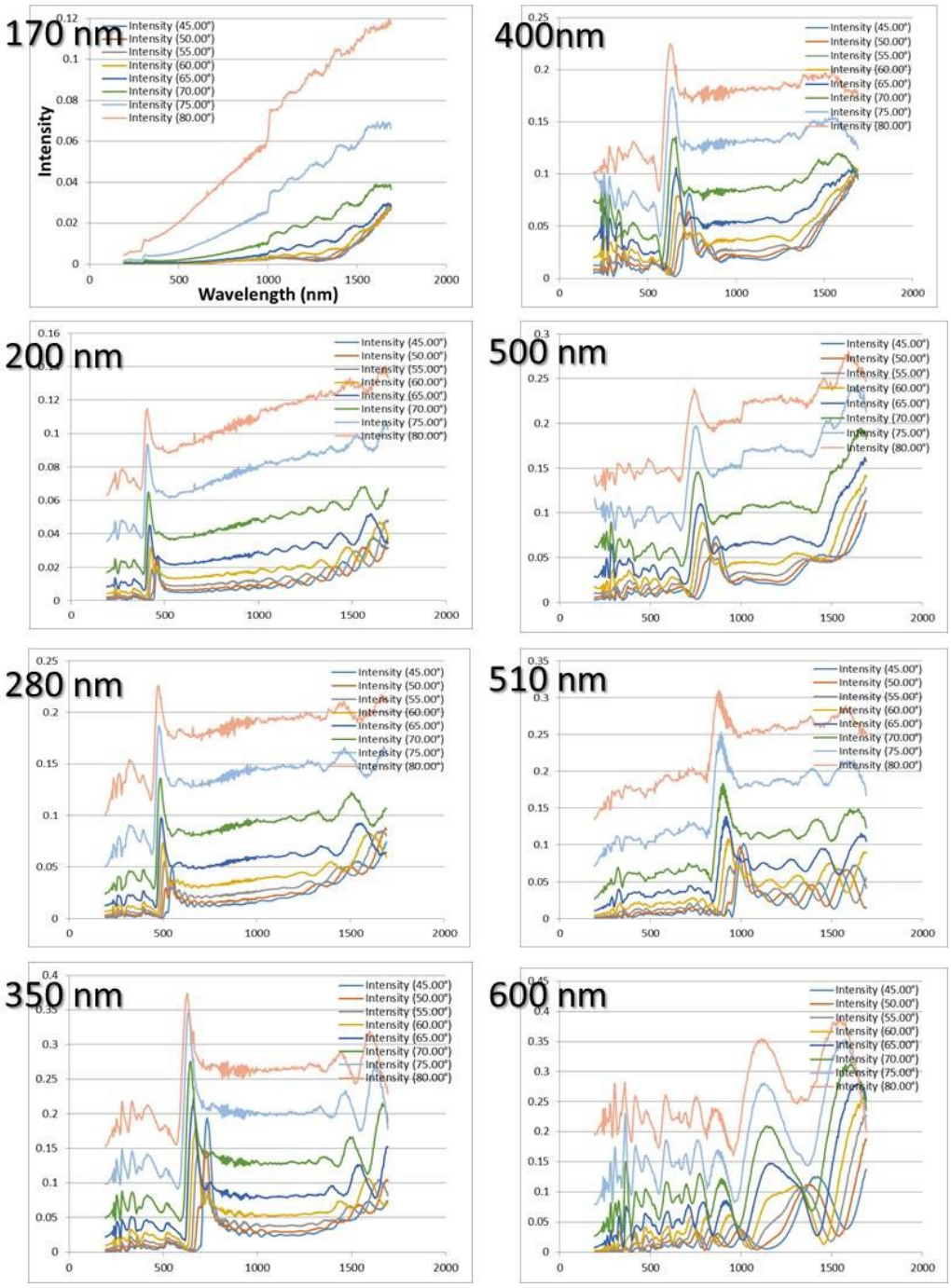

Figure S13: Complete dataset of angle dependent reflectance measurements. The noise in the peaks for the 510 nm data is a result of a detector change.

Table S2: Calculated angle dependence of the PGB reflectance peak in the [111] direction from the Bragg-Snell model.

	170nm	200nm	280nm	350nm	390nm	400nm	500nm	510nm	600nm
Angle	Ref Max (nm)	Ref Max (nm)	Ref Max (nm)	Ref Max (nm)	Ref Max (nm)	Ref Max (nm)	Ref Max (nm)	Ref Max (nm)	Ref Max (nm)
0	398.8	469.2	656.9	821.1	914.9	938.4	1173.0	1196.4	1407.6
45	347.2	408.4	571.8	714.7	796.4	816.8	1021.1	1041.5	1225.3
50	337.4	396.9	555.7	694.6	774.0	793.8	992.3	1012.2	1190.8
55	327.6	385.4	539.6	674.5	751.6	770.9	963.6	982.9	1156.3
60	318.2	374.4	524.1	655.1	730.0	748.7	935.9	954.6	1123.1
65	309.4	364.0	509.7	637.1	709.9	728.1	910.1	928.3	1092.1
70	301.7	354.9	496.9	621.1	692.1	709.8	887.2	905.0	1064.7
75	295.2	347.3	486.2	607.8	677.2	694.6	868.3	885.6	1041.9
80	290.4	341.6	478.2	597.8	666.1	683.2	854.0	871.1	1024.8

Table S3: IO pore diameter compared to original diameter of PS beads. The pore sizes of Cu_2O, $BiVO_4$, and $CuBi_2O_4$ were measured by AFM, whereas the pore size of Cu was measured by SEM due to the extremely rough morphology of the Cu IO substrate.

	PS Bead Diameter of Template in Fig. 6 (nm)	Diameter of Resulting Pore (nm)
Cu_2O	500	450±15
$BiVO_4$	500	450±15
$CuBi_2O_4$	200	212±22
Cu	280	213±9

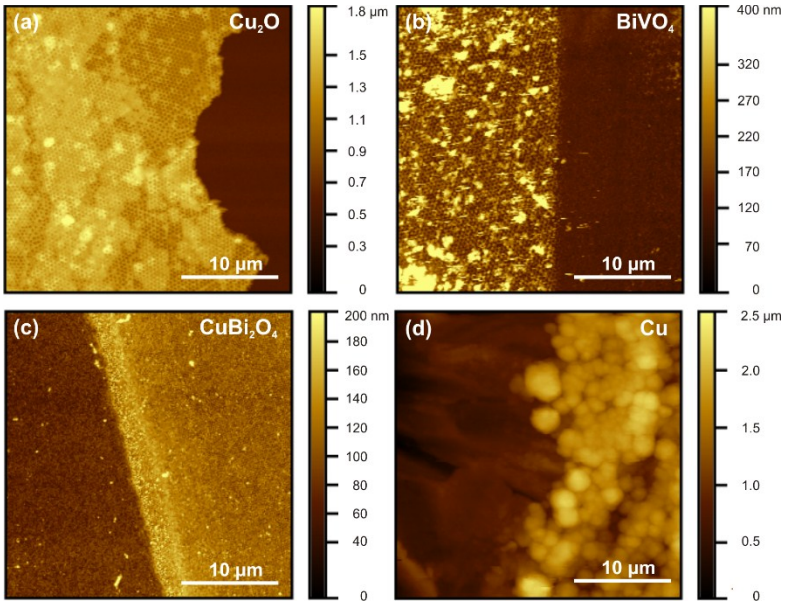

Figure S14: AFM topography images of a) Cu_2O, b) $BiVO_4$, c) $CuBi_2O_4$, and d) Cu. Diameter of the resulting pore size for Cu_2O, $BiVO_4$, and $CuBi_2O_4$, and thickness of the four IO layers were determined from AFM.

Table S4: Height of the IO step edges of Cu_2O, $BiVO_4$, $CuBi_2O_4$, and Cu determined from data in Figure S14.

Material	Height
Cu_2O	~900 nm
$BiVO_4$	~100 nm
$CuBi_2O_4$	~42 nm
Cu	~1.3 µm

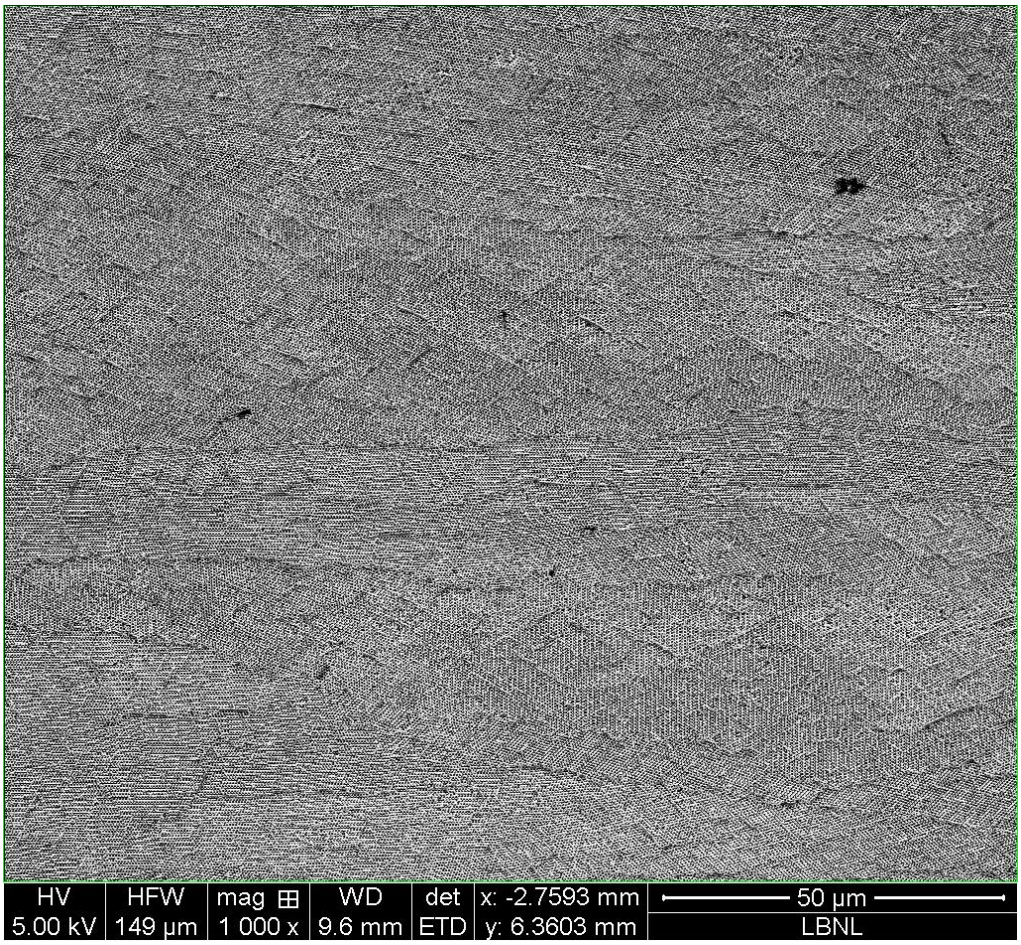

Figure S15: SEM image showing the extent of the inverse opal Cu_2O film deposited through a 500 nm PS template.

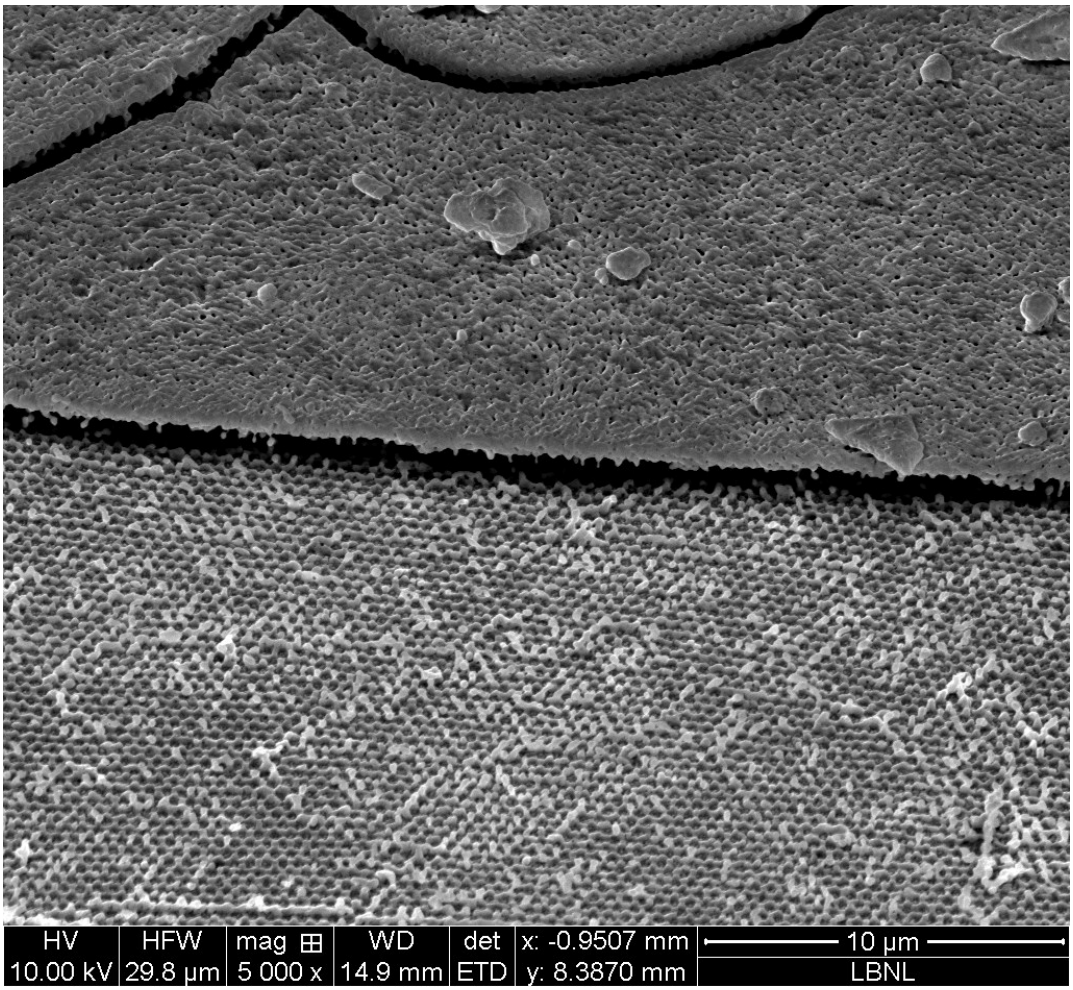

Figure S16: $BiVO_4$ inverse opal film showing the edge where the over-coat layer was peeled off. Taken at a 45^{o} angle.

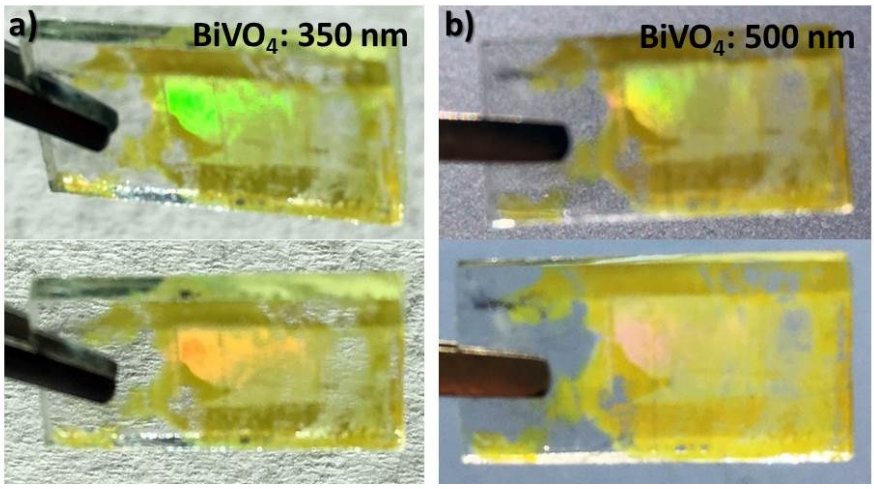

Figure S17: Pictures showing the angle dependent iridescence of inverse opal $BiVO_4$ films electrodeposited from a) 350 nm and b) 500 nm PS bead template.

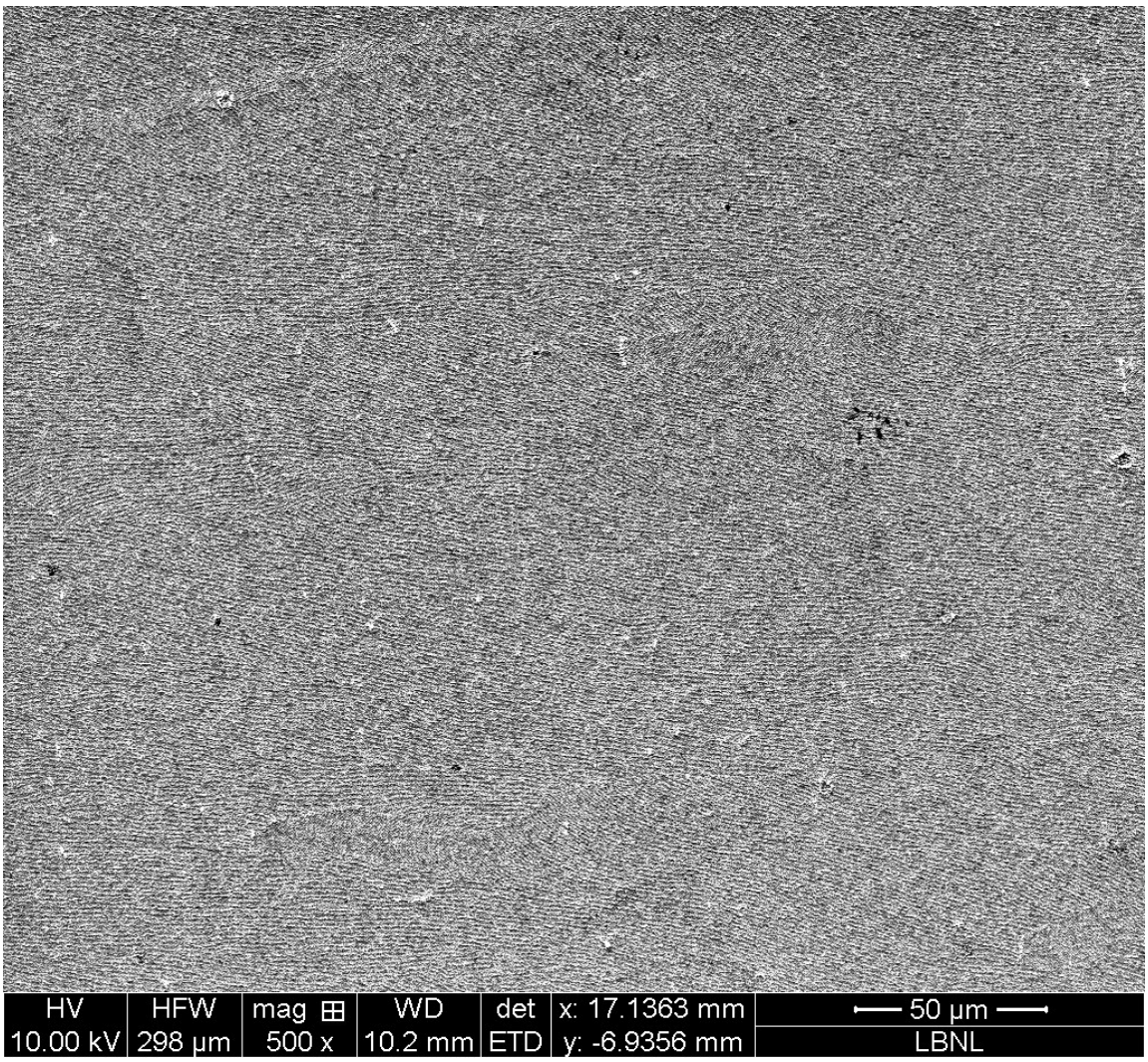

Figure S18: SEM of $BiVO_4$ showing the extent of the patterned area.

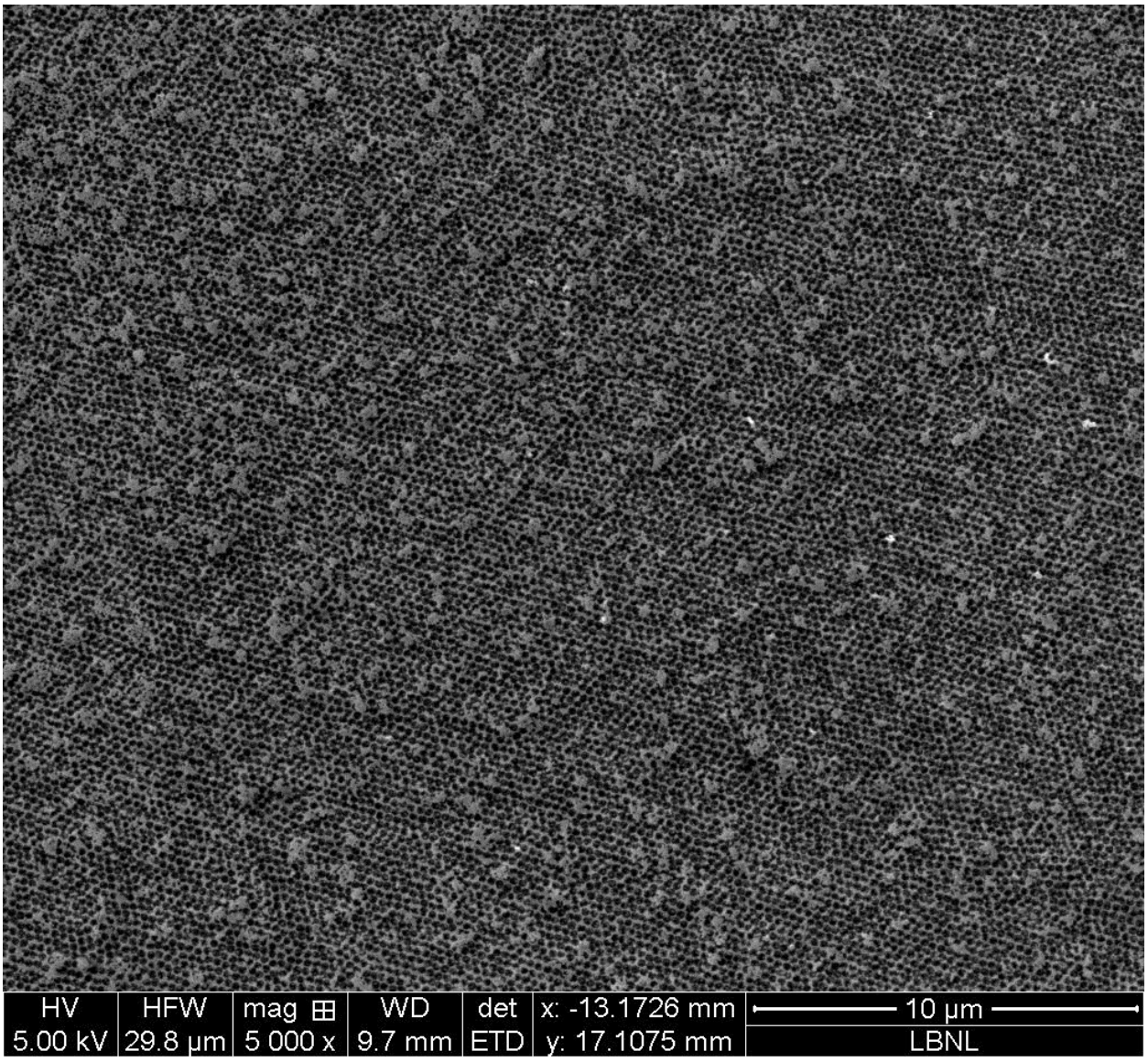

Figure S19: SEM image showing the extent of the inverse opal $CuBi_2O_4$ film deposited through a 200 nm PS template.

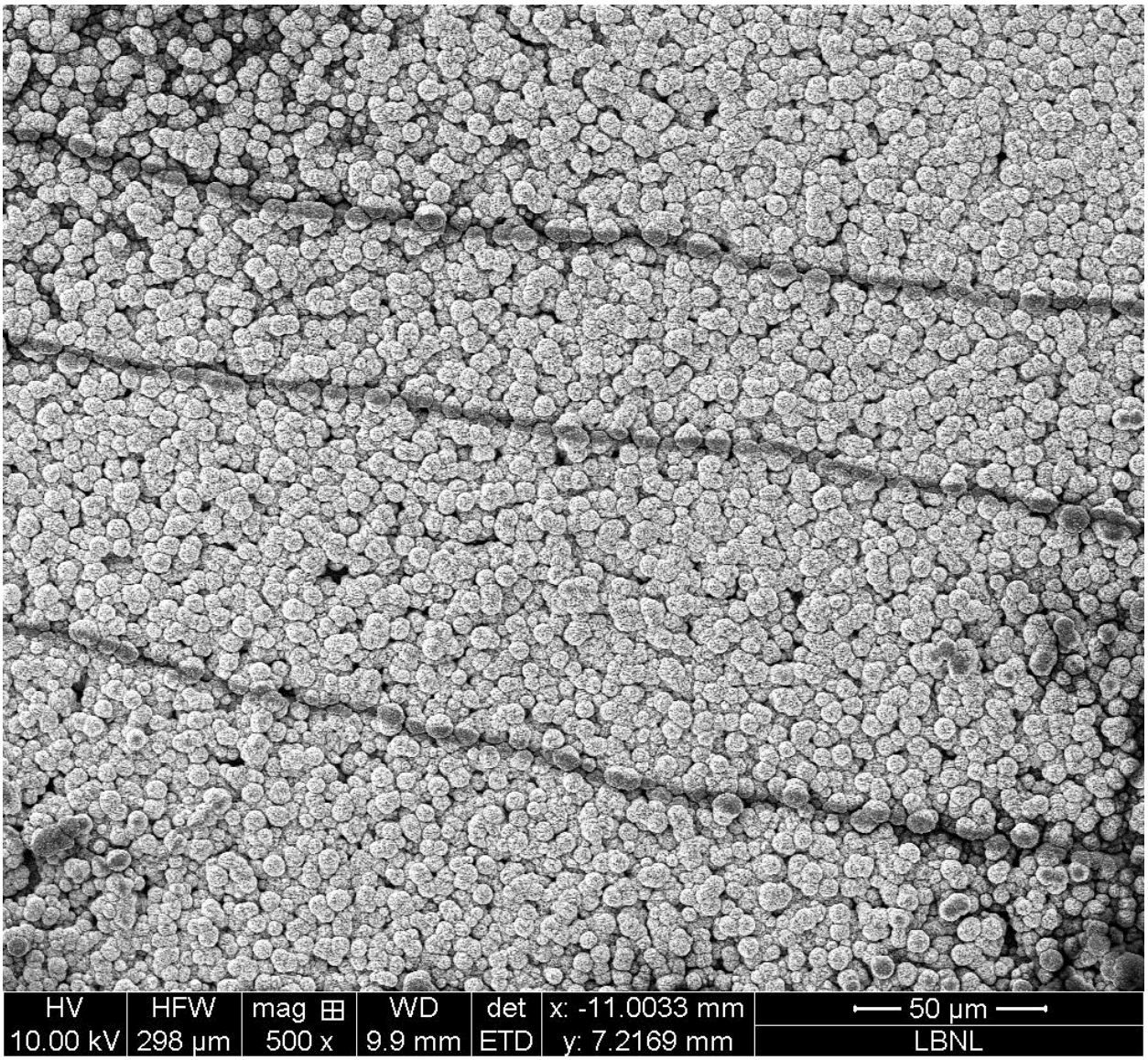

Figure S20: SEM image showing the extent of the inverse opal Cu film deposited through a 280 nm PS template.

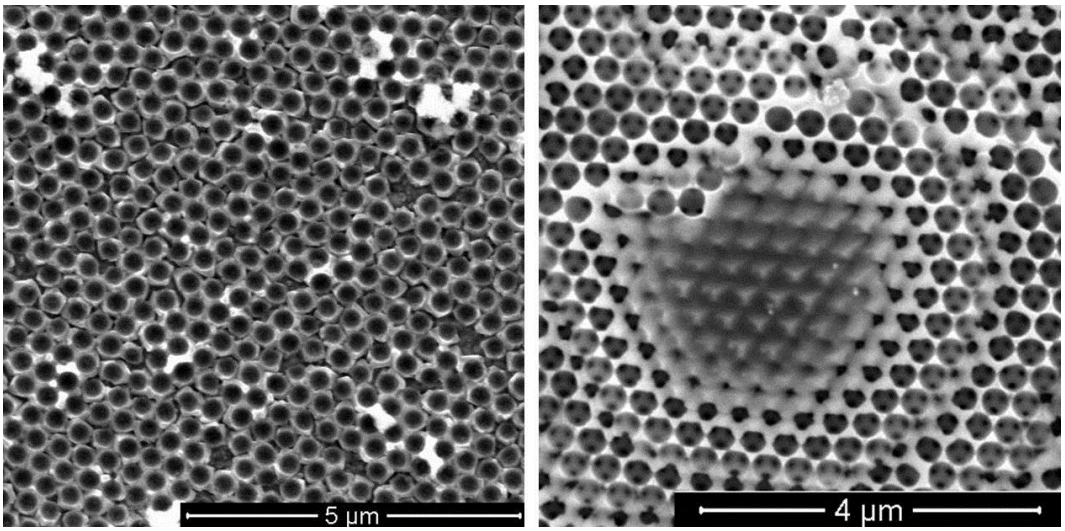

Figure S21: Growth mechanism of Cu_2O through the PS opal template showing nucleation around each individual PS bead (left) for shorter deposition time, and pyramidal peaks growing just above the top layer of PS beads (right) for longer deposition time.

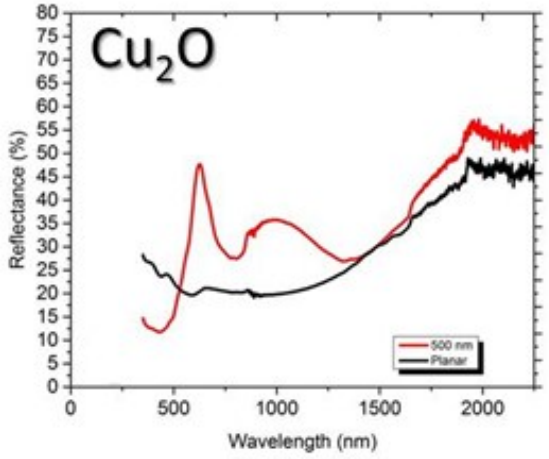

Figure S22: Reflectance spectra of inverse opal Cu_2O film.

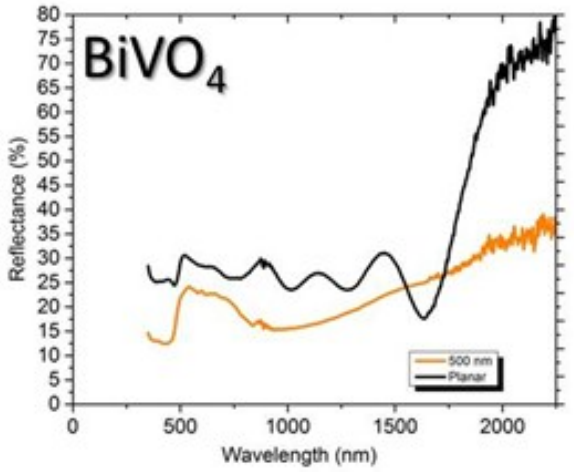

Figure S23: Reflectance spectra of inverse opal $BiVO_4$ (post overcoat removal) film.

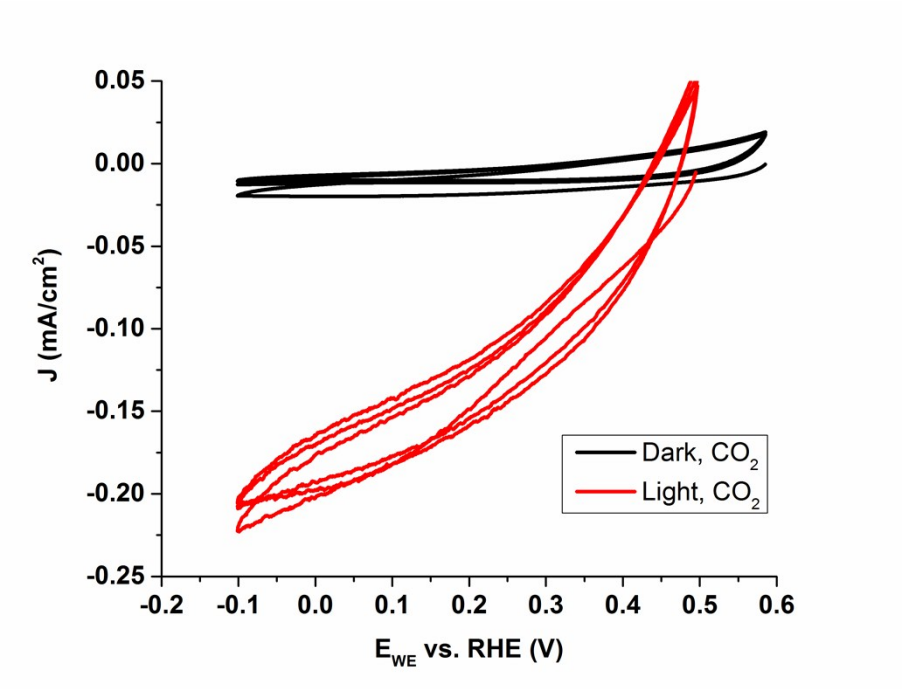

Figure S24: Repeated CV scans of a Cu_2O inverse opal photoelectrode made from a 500 nm PS bead template.

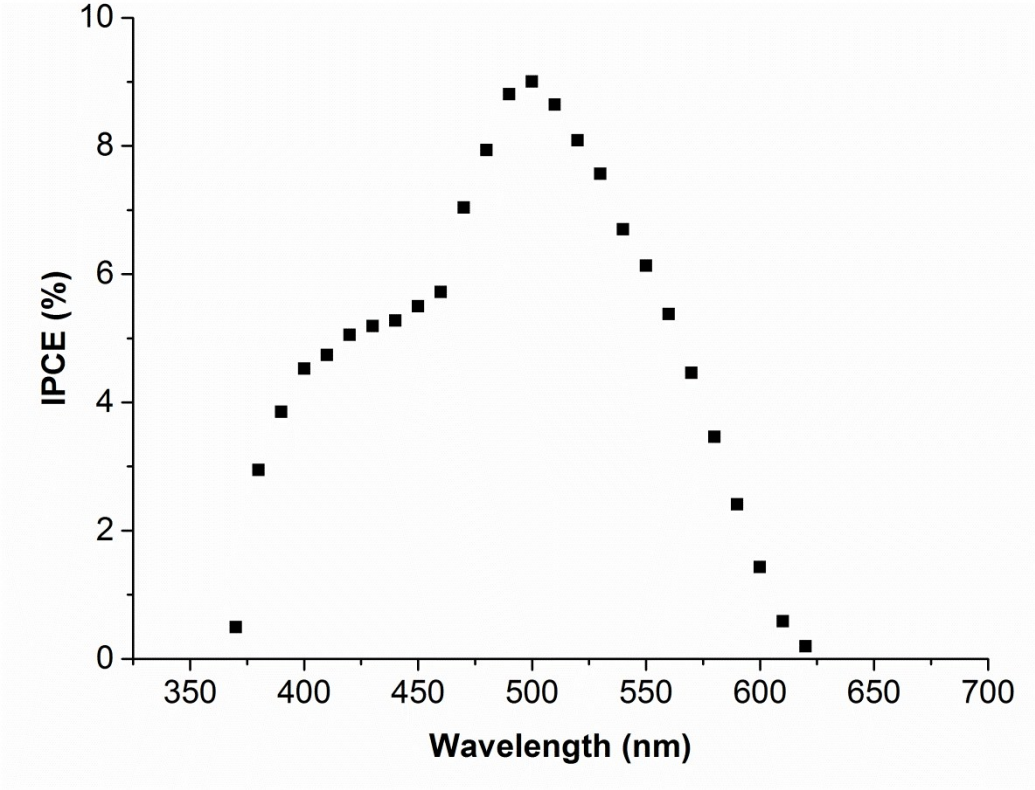

Figure S25: IPCE spectra for a Cu_2O inverse opal photoelectrode made from a 500 nm PS bead template. Measurement was taken in a saturated CO_2 environment at an applied bias of 0.3 V *vs*. RHE.