

Supporting Information for

Suppressing of secondary electron diffusion for high-precision nanofabrication

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Supplementary Text

Materials.

70 wt.-% Zr(OPr)₄/1-propanol solution, hydroquinone (HQ), methyl methacrylate (MAA), ethyl acetate, toluene, isopropanol (IPA), 2-Chlorohydroquinone (Cl-HQ), 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), and propylene glycol monomethyl ether acetate (PGMEA) were purchased from Sigma Aldrich Co. and used without further purification.

Single crystal data.

X-ray crystallographic data for ZrO₂-MAA MOC (CCDC: 2022033) has been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, 3 Cambridge CB21EZ, UK; fax: (+44) 1223-336-033. Data can be obtained free of charge from the Cambridge Crystallographic Data Centre via the Internet at www.ccdc.cam.ac.uk/data_request/cif using the CCDC number given above. The crystalline structure of UiO-66^{1,2} was generated using single crystallographic data from Cambridge Structural Database (CSD entry: SAHYOQ).

Resist films for contrast measurements.

The resist (10 wt.% to solution) with different amounts of HQ (0, 8 wt.%, 32 wt.%) was spin-coated on a Si substrate at 2000 rpm for 60 s. The film thickness measured by the ellipsometry was about 125 nm. A RAITH150 TWO EBL system was used to expose the pad (Dimension: 10 μm×10 μm) with accelerating voltages of 30 kV and an aperture size of 30 μm (corresponding to a beam current of ~303.8 pA). All the samples were developed in IPA for 60 s.

Resist films for EDS analysis.

The 5 wt.% solution was prepared by mixing ZrO₂-MAA MOCs with Cl-HQ (20 wt.% to MOCs) or TEMPO (20 wt.% to MOCs) in PGMEA, respectively. The filtered solution was spin-coated on a Si substrate at 2000 rpm for 60 s and then soft-baked at 100 °C for 60 s. The film thickness measured by the ellipsometry was about 50 nm. The films were observed by a ZEISS field emission SEM and energy dispersive X-ray spectroscopy (EDS).

Since HQ contains three elements of C, H, O (the same organic elements as ZrO₂-MAA MOCs), we selected two other small molecules (Cl-HQ, 2-Chlorohydroquinone and TEMPO, 2,2,6,6-Tetramethyl-1-piperidinyloxy) containing different elements for EDS analysis. The experimental results (**Figure S11**) showed that in the photoresist films, the Cl and N elements could be detected to be evenly distributed in the whole field of vision; suggesting the small

molecule radical quenchers could be relatively evenly dispersed in films after sufficient mixing and there should be no aggregation issue.

Resist films for EBL and cross-section data.

The photoresist test formulation contained ZrO₂-MAA MOCs as a solute (2.5 wt.% to the solution), HQ as a radical quencher (24 wt.% to ZrO₂-MAA MOCs), and PGMEA as a solvent. The filtered photoresist was spin-coated on a Si substrate at 4000 rpm for 60 s. A RAITH150 TWO EBL system was used to expose the pad (Dimension: 10 μm×10 μm) with accelerating voltages of 30 kV and an aperture size of 10 μm (corresponding to a beam current of ~39 pA). The exposure dose was 3100~3500 pC/cm. The designed patterns were 1:1 line-space patterns with a half-pitch of 12 nm and 15 nm and the length was 500 μm. The exposed samples were developed in IPA for 60 s. The obtained samples were cut and the cross-section view of the line-space patterns was evaluated by a field emission SEM (SIGMA-HD, ZEISS).

Supporting Figures

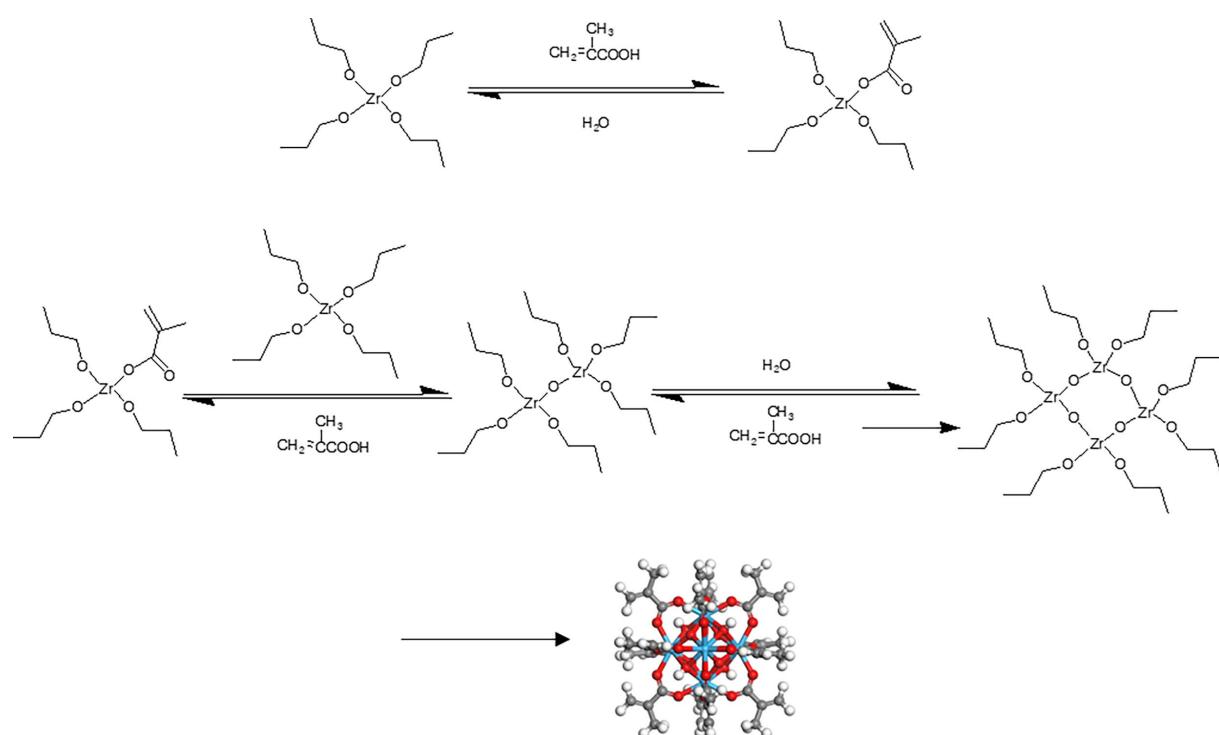


Figure S1. Preparation of ZrO₂-MAA MOC with 12 alkene functionalization under the solvothermal condition of the mono-nuclear Zr-alkoxides $\text{Zr}(\text{OPr})_4$ and methacrylic acid (MAA) by a thermodynamically reversible reaction.

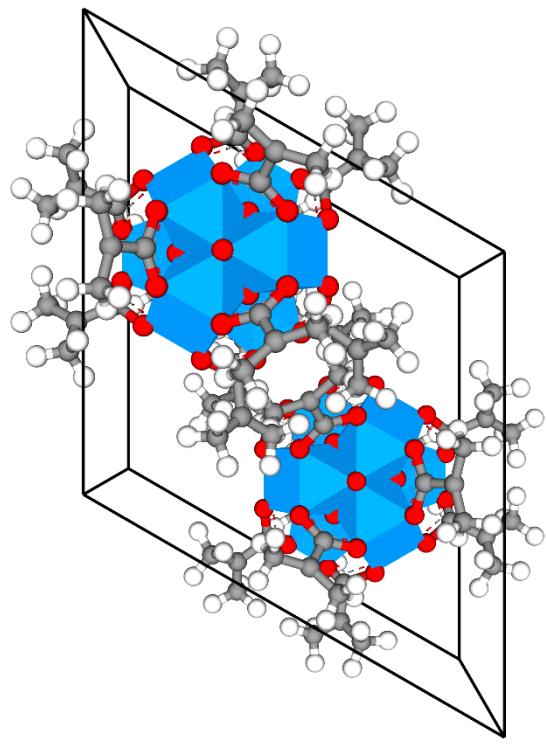


Figure S2. Single-crystal structure of ZrO₂-MAA MOF.

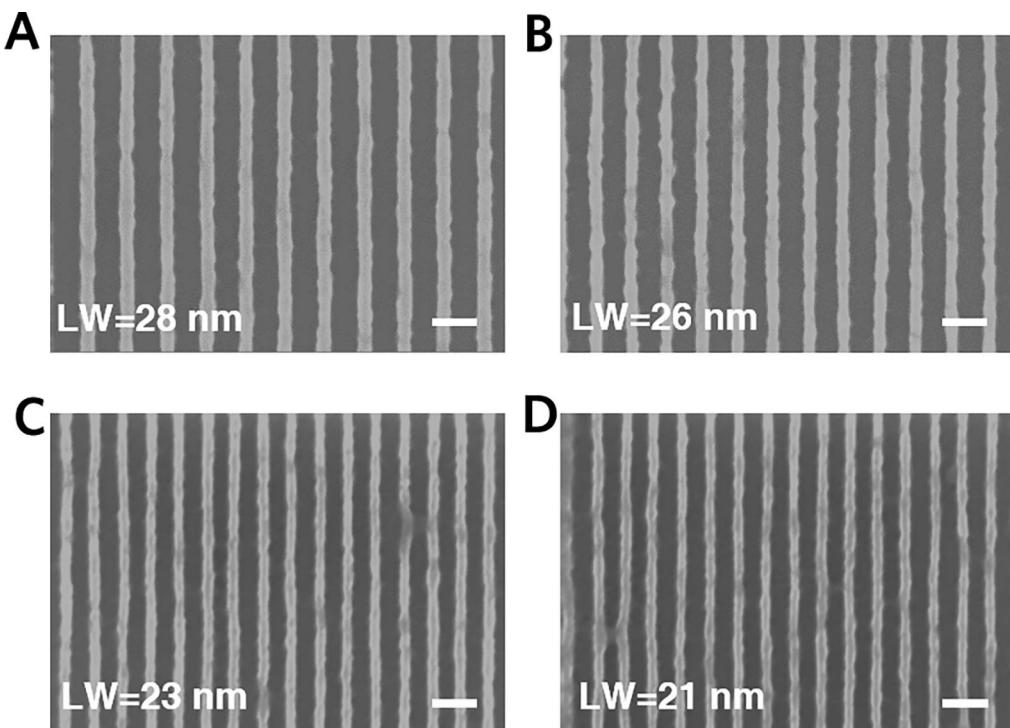


Figure S3. Top-view SEM images of ZrO_2 -MAA MOC single-component photoresist patterns exposed by EBL. **A**, LW=28 nm, 70 $\mu\text{C cm}^{-2}$; **B**, LW=26 nm, 70 $\mu\text{C cm}^{-2}$; **C**, LW=23 nm, 90 $\mu\text{C cm}^{-2}$ and **D**, LW=21 nm, 90 $\mu\text{C cm}^{-2}$. The film thickness was about 50 nm. The samples were developed in toluene for 15 s. The scale bar is 100 nm.

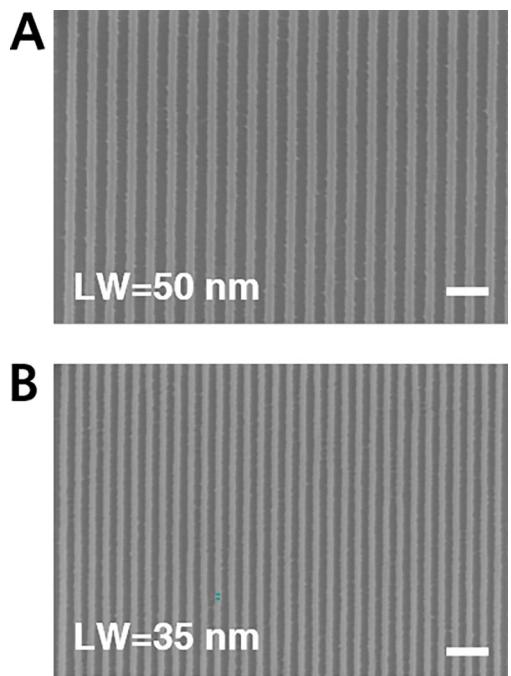


Figure S4. Top-view SEM images of ZrO₂-MAA MOC single-component photoresist patterns exposed by EUV lithography. **A**, LW=50 nm, 27.2 mJ cm⁻²; **B**, LW=35 nm, 27.2 mJ cm⁻². The film thickness was about 50 nm. The samples were developed in toluene for 15 s. The scale bar is 200 nm.

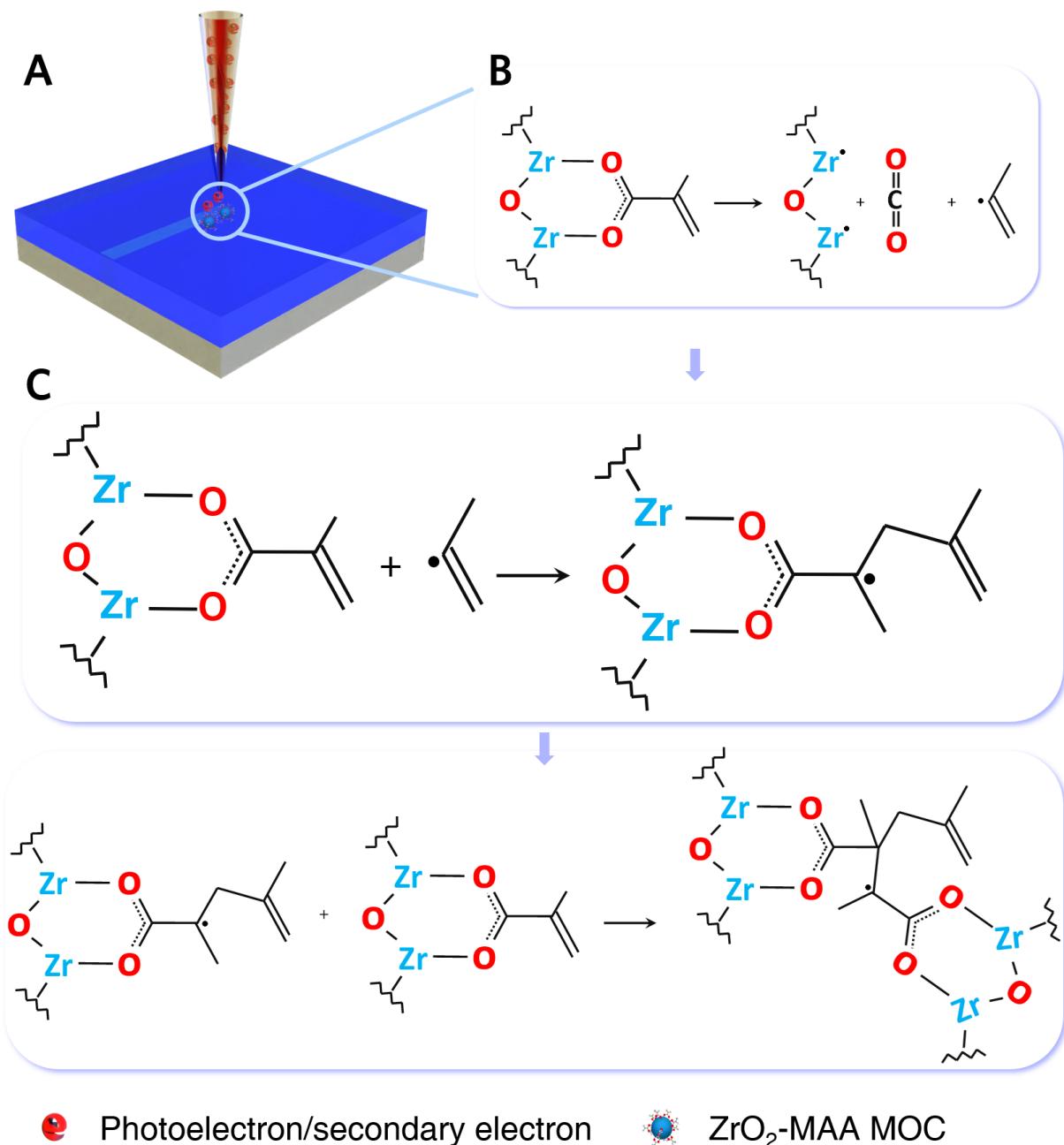


Figure S5. The patterning mechanism for $\text{ZrO}_2\text{-MAA}$ MOC photoresist under EUV and electron beam exposure. **A**, Schematic diagram of radiated photoresist molecules. **B**, Dissociation of one 2-propenyl group and CO_2 from $\text{ZrO}_2\text{-MAA}$ MOC. **C**, The resulting free radical polymerizations.

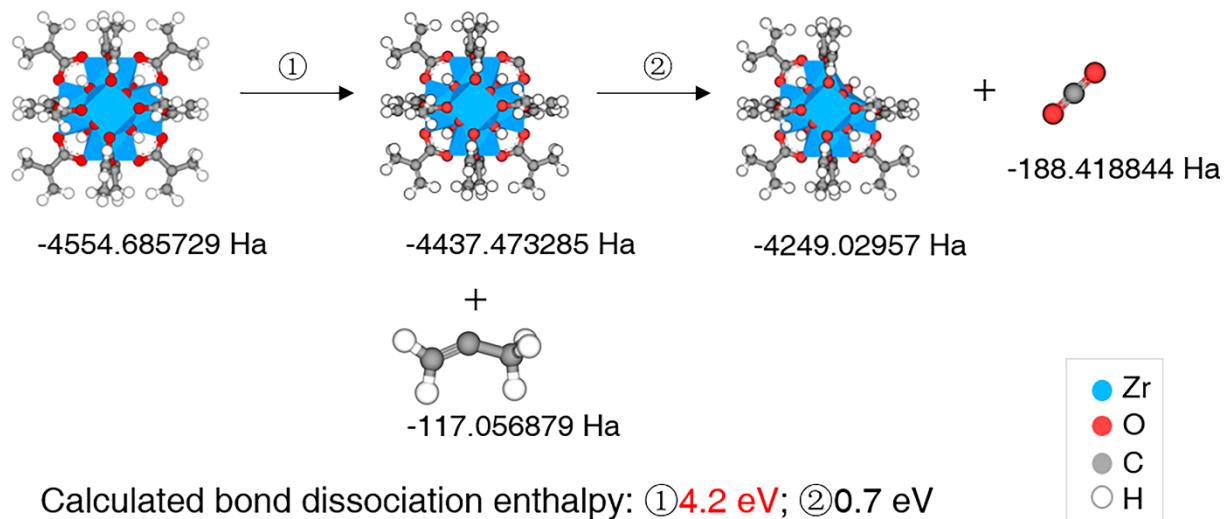


Figure S6. Illustration and bond dissociation enthalpy (BDE) calculation for dissociation of one 2-propenyl group and CO₂ from ZrO₂-MAA MOC.

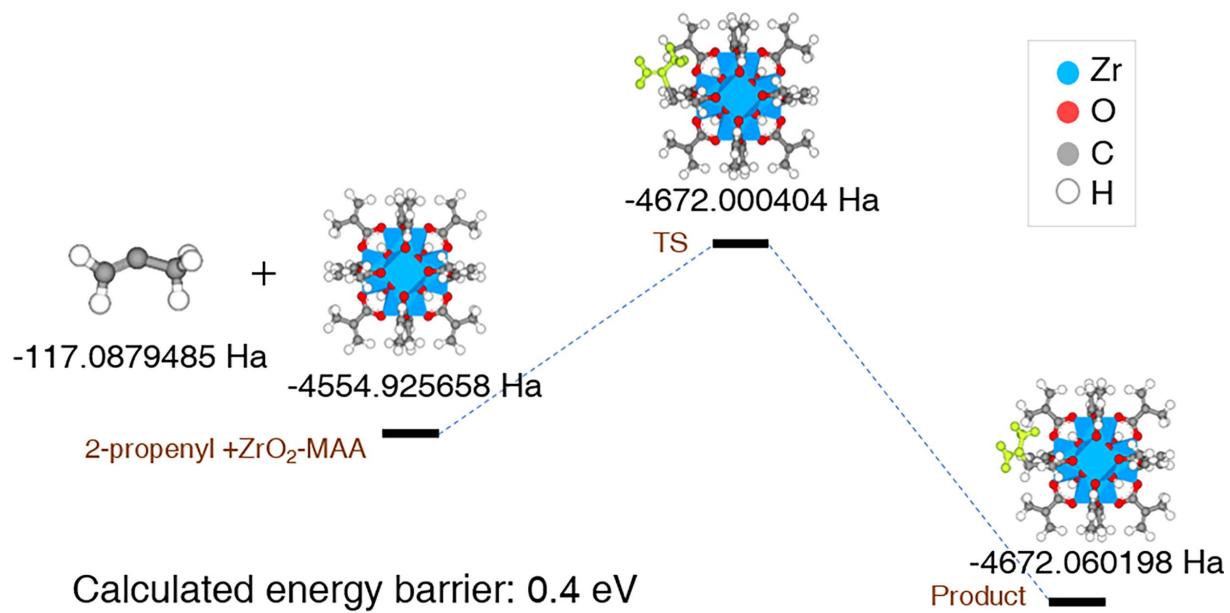


Figure S7. Illustration and density functional theory calculated the energy profile for the addition polymerization process of the 2-propenyl group to a MOC.

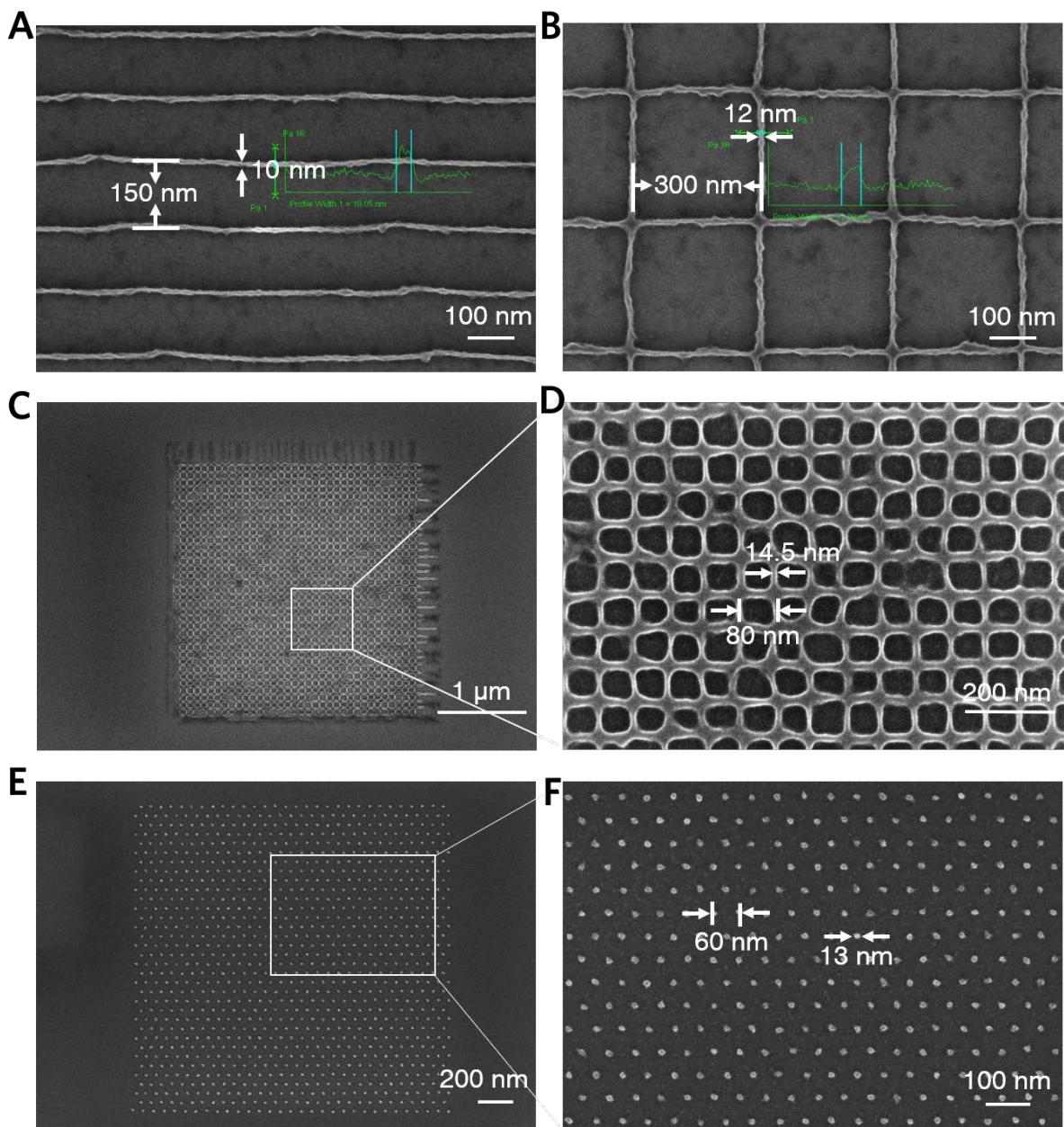


Figure S8. Top-view SEM images of ZrO_2 -MAA MOC single-component photoresist patterns exposed by EBL. **A**, line-space pattern with a feature of 10 nm and period of 150 nm, 1200 pC/cm^2 ; **B**, Grid pattern with a feature of 12 nm and period of 300 nm, 1300 pC/cm^2 ; **C, D**, Grid pattern ($3 \times 3 \mu\text{m}$) with a feature of 14.5 nm and period of 80 nm, 80 $\mu\text{C}/\text{cm}^2$; **E, F**, Dot matrix with a feature of 13 nm and period of 60 nm, 1.2 fC. The exposed films were developed in **A-D**, toluene for 30 s or **E-F**, IPA for 60 s.

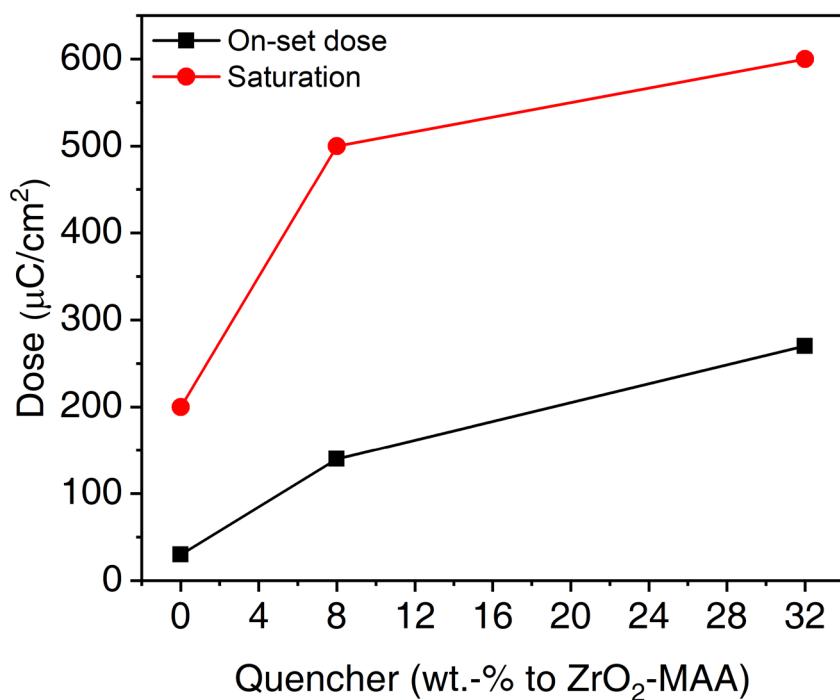


Figure S9. On-set dose and saturation dose of photoresists of ZrO₂-MAA MOCs and different amounts of HQ (wt.% to ZrO₂-MAA MOCs) exposed by EBL.

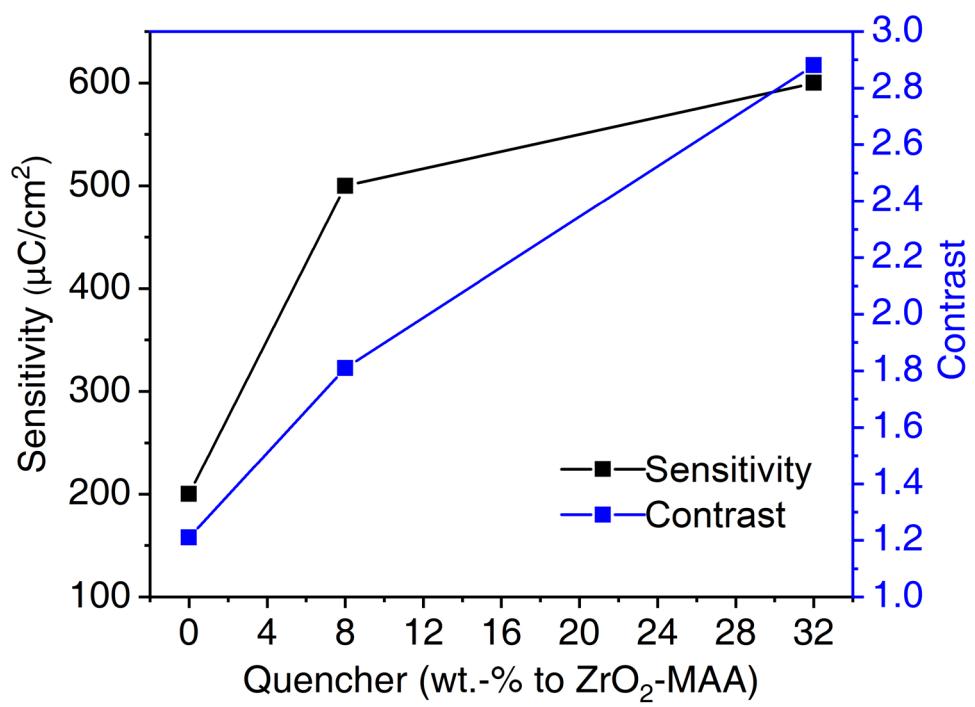


Figure S10. Sensitivity and contrast of photoresists with different amounts of HQ (wt.% to ZrO₂-MAA MOCs).

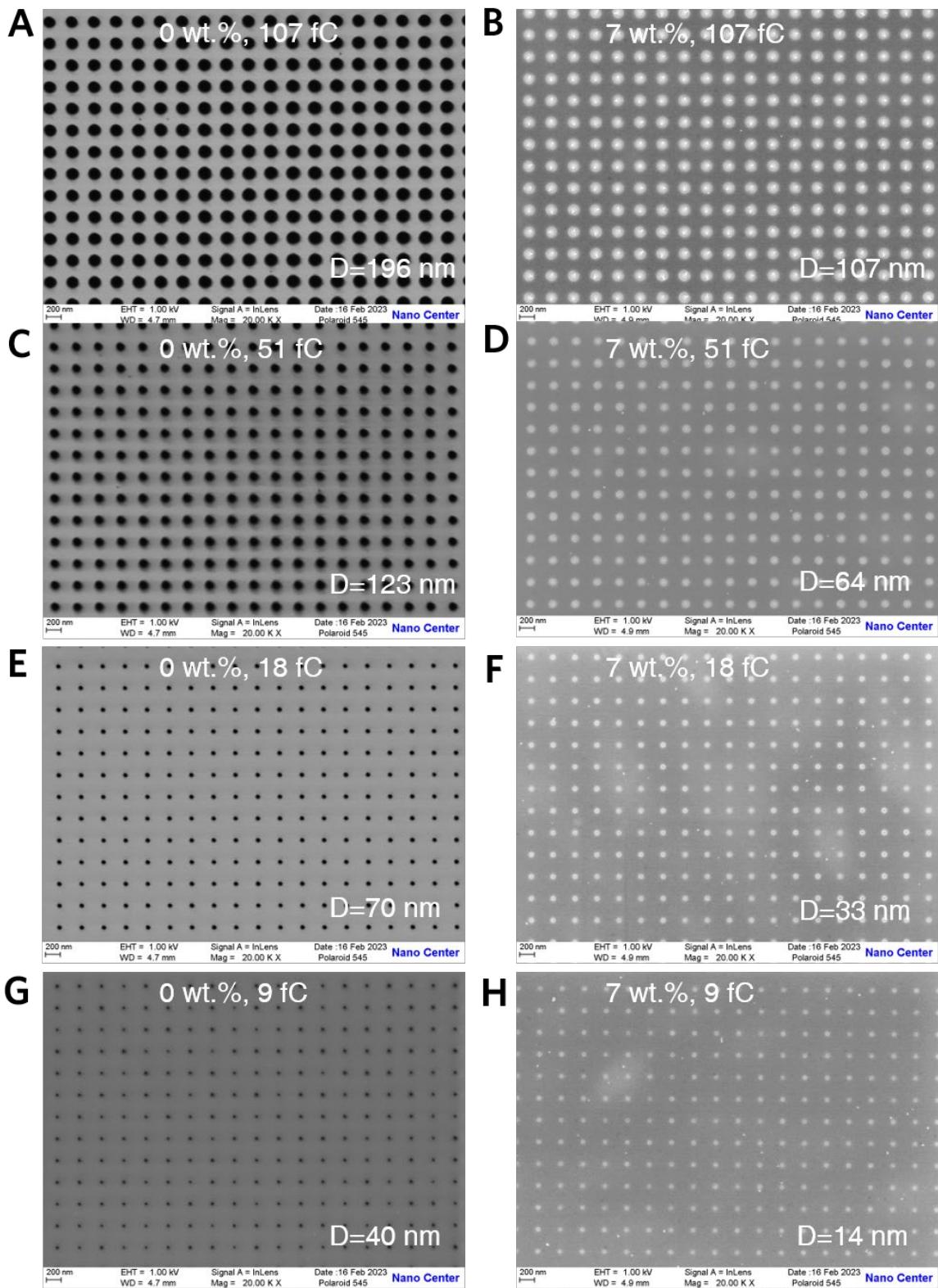


Figure S11. Top-view SEM images of PMMA photoresist patterns without and with (7 wt.% to PMMA) free radical quencher. The electron beam point exposure doses are about **A, B**, 107 fC, **C, D**, 51 fC, **E, F**, 18 fC, and **G, H**, 9 fC, respectively. D represents hole diameter.

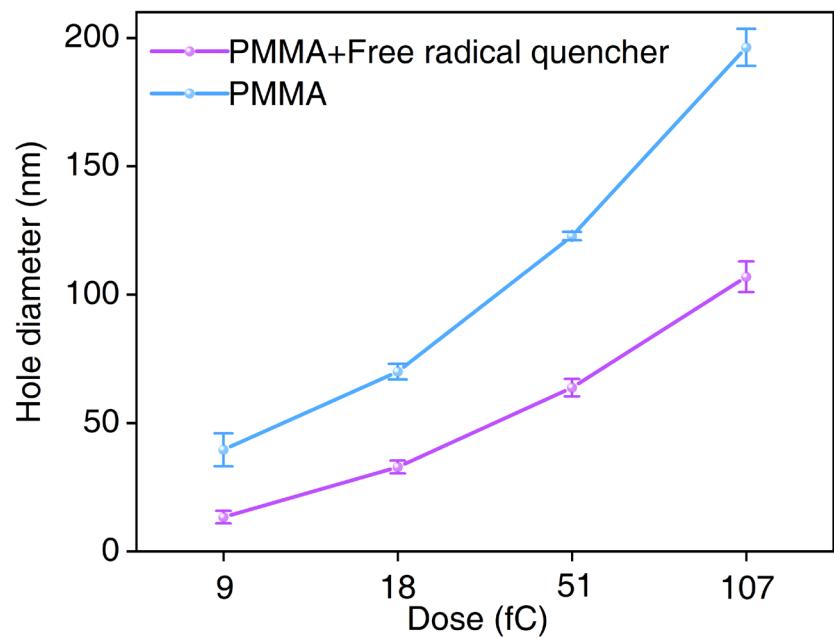


Figure S12. The hole diameter of PMMA photoresist patterns without and with (7 wt.% to PMMA) free radical quencher. The electron beam point exposure dose is 107 fC, 51 fC, 18 fC, and 9 fC, respectively.

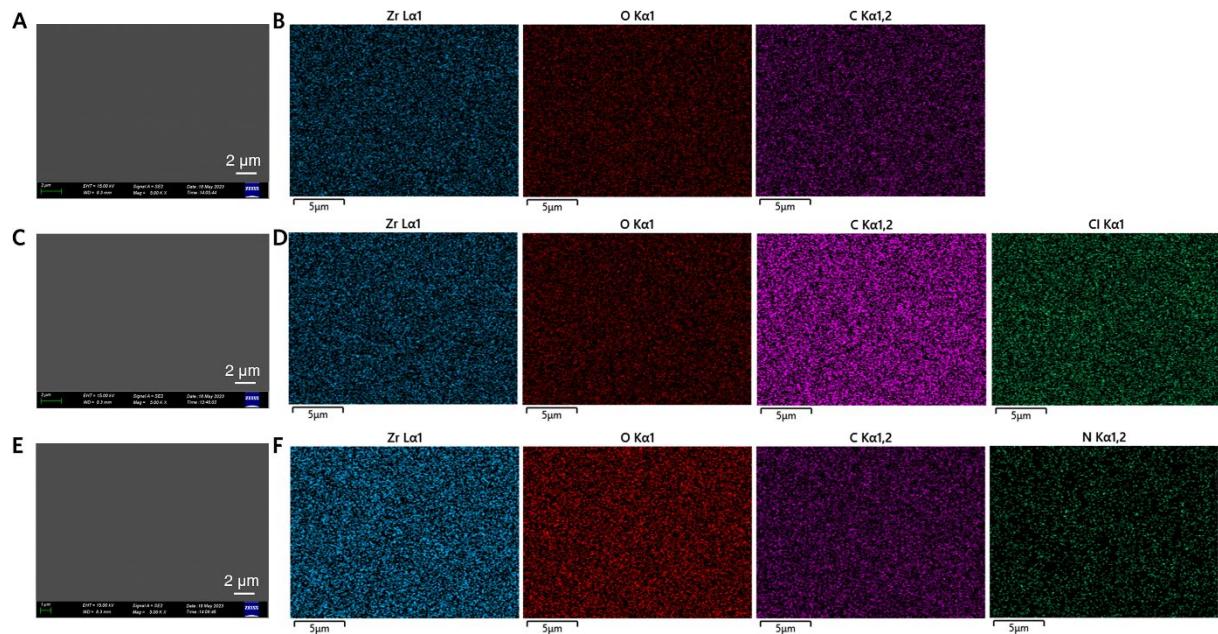


Figure S13. SEM images and corresponding EDS mapping of the photoresist films. **A, B,** Film of photoresist consisting of ZrO₂-MAA MOC and HQ (20 wt.% to ZrO₂-MAA MOC). **C, D,** Film of photoresist consisting of ZrO₂-MAA MOC and CI-HQ (20 wt.% to ZrO₂-MAA MOC). **E, F,** Film of photoresist consisting of ZrO₂-MAA MOC and TEMPO (20 wt.% to ZrO₂-MAA MOC).

Resolution in 1/1 dense pattern

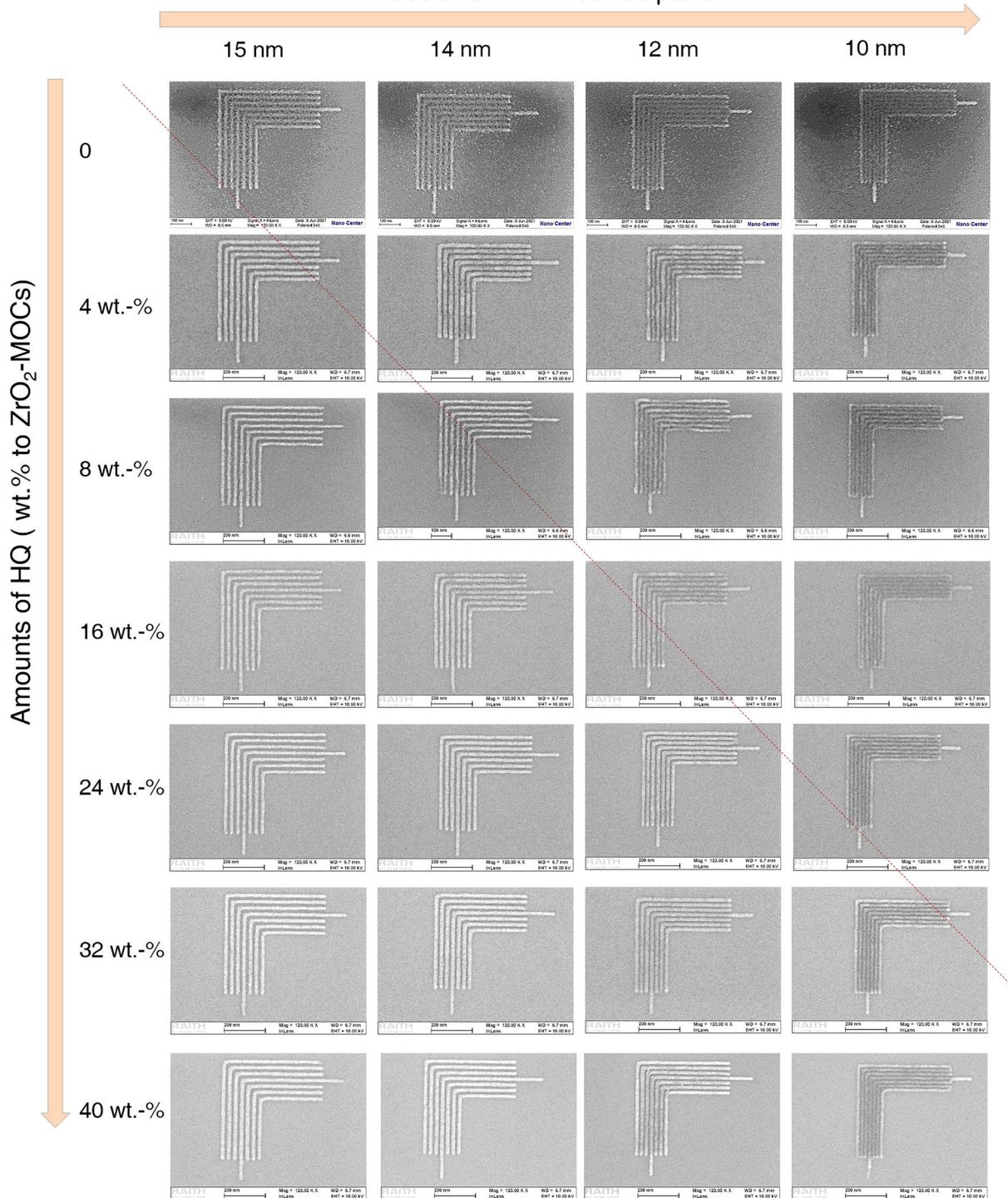


Figure S14. Top-view SEM images of photoresist patterns with different amounts (wt.-% to ZrO₂-MAA MOCs) of HQ exposed by EBL. Nested-“L” line-space patterns with half-pitch of 15-10 nm. The electron beam doses are about 800 pC/cm (0 wt.%), 1200 pC/cm (4 wt.%), 1700 pC/cm (8 wt.%), 2200 pC/cm (16 wt.%), 3000 pC/cm (24 wt.%), 3400 pC/cm (32 wt.%), and 4800 pC/cm (40 wt.%), respectively.

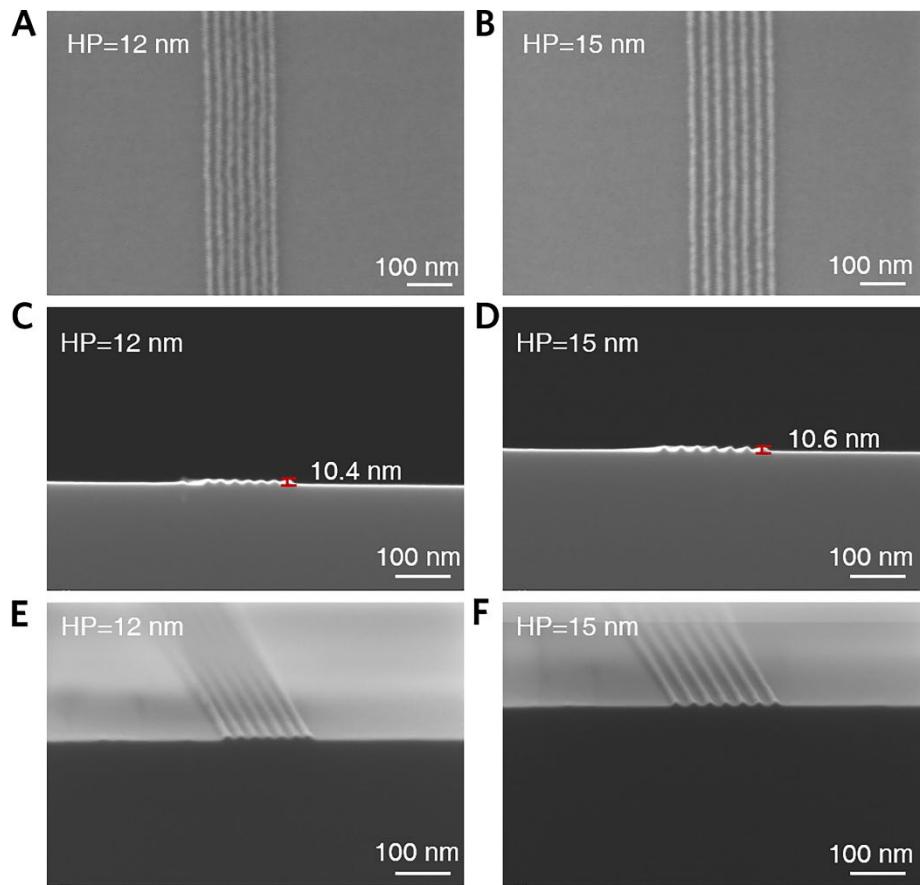


Figure S15. Top-view and cross-sectional SEM images of lines obtained by EBL (Patterning design: line-space, HP is 15 nm and 12 nm). **A, B**, Top-view. **C, D**, Vertical cross-section view. **E, F**, Cross-section view at a tilted angle of 3°. The exposure dose was 3200 pC/cm (**A, C, E**) and 3500 pC/cm (**B, D, F**), respectively.

Supporting Tables

Table S1 Atomistic coordinates for ZrO₂-MAA MOC, optimized using DFT method in Gaussian 16 package with hybrid exchange-correlation functional B3LYP as functional, and Polarized split-valence def2-SVP as basis set.

Atom	x/a	y/b	z/c
O	-3.60073	1.93381	0.02057
C	-5.57243	3.86510	0.27409
H	-3.12359	5.73853	1.26601
O	-3.59230	-1.99366	-0.09706
C	-5.55498	-3.93242	-0.36245
H	-4.60383	-6.39242	-0.58528
H	0.48239	-3.16045	-5.99639
O	-0.05633	-3.58730	-2.00420
C	-0.29973	-5.54584	-3.94993
H	-0.57231	4.54231	6.35950
O	-0.08717	3.54136	1.95802
C	-0.34884	5.49938	3.90188
H	-5.81060	1.22919	3.04270
O	-2.00178	0.00573	3.54267
C	-3.94601	0.24898	5.50273
H	-6.36369	-0.53598	-4.64723
O	-1.97052	-0.05899	-3.60616
C	-3.89806	-0.30727	-5.58226
H	-5.87306	2.81980	0.17458
O	-2.02126	3.53105	0.05767
C	-3.78946	5.63029	0.39432
O	-2.00672	-3.58509	-0.12050
C	-3.76476	-5.69124	-0.46742
O	-3.58976	0.03264	1.95368
C	-5.70135	0.35824	3.70937
O	-3.57142	-0.09258	-2.03032
C	-5.66735	-0.42501	-3.80320
O	-0.07505	-1.99753	-3.59151

C	-0.40115	-3.75136	-5.70460
O	-0.11347	1.95158	3.54521
C	-0.45623	3.70483	5.65612
H	-0.46202	6.28165	4.65829
Zr	-2.53480	-0.02785	-0.03378
O	-1.06945	1.01063	1.01824
O	-1.05629	-1.06055	-1.07301
C	-0.16751	3.15971	3.16527
C	-0.12913	-3.20579	-3.21197
C	-3.18110	-0.14026	-3.23541
C	-3.20955	0.08246	3.16191
C	-3.22722	3.14335	0.10460
C	-3.21373	-3.20190	-0.17686
O	-1.43248	-1.43932	1.37107
O	-1.42569	1.38800	-1.42908
C	-4.27606	4.21358	0.26065
C	-4.25748	-4.27614	-0.33924
C	-0.27981	-4.24733	-4.29005
C	-0.32766	4.20096	4.24226
C	-4.28681	0.23282	4.20435
C	-4.24934	-0.29378	-4.28665
H	-1.98174	1.94683	-1.98616
H	-1.99104	-2.00011	1.92364
O	3.55552	-1.98067	0.03266
C	5.52487	-3.91476	0.28325
H	3.15562	-5.97525	-0.51046
O	3.54815	1.94814	-0.04737
C	5.51239	3.88870	-0.28676
H	3.05604	5.76046	-1.26255
H	-0.47932	3.16999	-5.96932
O	0.02871	3.56123	-1.96948
C	0.28458	5.53756	-3.89579
H	0.48339	-4.64596	6.32013

O	0.02538	-3.60677	1.92452
C	0.27330	-5.58187	3.85315
H	5.95178	-0.47687	-3.16529
O	1.95737	0.04723	-3.58771
C	3.90120	0.30885	-5.54579
H	5.73946	-1.30375	3.08121
O	1.92658	-0.08542	3.55997
C	3.85560	-0.34085	5.53373
O	1.97564	-3.57792	0.04125
C	3.74053	-5.68024	0.37601
H	5.81700	2.84379	-0.19561
O	1.96270	3.53974	-0.06936
C	3.72276	5.64809	-0.39202
O	3.54522	0.06532	-1.99848
C	5.65621	0.40853	-3.75154
H	4.65759	0.42225	-6.32803
O	3.52743	-0.09809	1.98376
C	5.62490	-0.43771	3.75339
H	2.80916	-0.24950	5.83299
O	0.03875	-2.03125	3.52604
C	0.37137	-3.80246	5.62331
H	0.18293	-5.88051	2.80645
O	0.06176	1.98596	-3.57096
C	0.40151	3.75895	-5.66560
Zr	2.49030	-0.01822	-0.01189
Zr	-0.02720	2.48960	-0.01078
Zr	-0.01747	-2.53550	-0.03481
Zr	-0.03308	-0.03491	2.48971
Zr	-0.01124	-0.01083	-2.53534
O	1.01588	-1.06662	1.01738
O	1.02092	1.02469	-1.05385
C	0.09676	-3.23588	3.13566
C	0.11136	3.19078	-3.18005

C	3.16494	0.12361	-3.20632
C	3.13745	-0.15806	3.18842
C	3.17004	3.15694	-0.12094
C	3.18120	-3.19086	0.10224
O	1.37570	1.37980	1.39696
O	1.39349	-1.42030	-1.43022
C	4.22853	-4.26267	0.25746
C	4.21475	4.23225	-0.26953
C	0.26897	4.24212	-4.24760
C	0.25058	-4.28642	4.20455
C	4.24194	0.28401	-4.24752
C	4.20651	-0.31588	4.23819
H	1.92975	1.93562	1.95902
H	1.95405	-1.97415	-1.98776
H	0.38197	-6.37066	4.60342
H	-0.51359	-3.21645	5.92063
H	1.23879	-3.13233	5.73944
H	-6.33900	-4.68676	-0.47719
H	-5.86011	-2.88809	-0.26644
H	-3.17876	-5.99026	0.41698
H	-4.64789	-0.41556	-6.37151
H	-2.85192	-0.20959	-5.88056
H	-5.96936	0.45498	-3.21211
H	-6.35999	4.61644	0.38419
H	-4.63191	6.32825	0.50702
H	-3.19815	5.93267	-0.48541
H	-2.90193	0.15569	5.80955
H	-4.70258	0.35522	6.28581
H	-6.40488	0.46715	4.54769
H	1.27200	3.09182	-5.77575
H	6.29707	4.64379	-0.39175
H	4.56254	6.35004	-0.49983
H	3.13079	5.94152	0.49027

H	-0.25273	5.80706	2.85831
H	0.42720	3.11644	5.95332
H	-1.32412	3.03359	5.76168
H	-1.27029	-3.08254	-5.81528
H	2.85734	0.21557	-5.85334
H	5.76374	1.27464	-3.07831
H	6.35957	0.52512	-4.58896
H	4.60602	-0.45236	6.32198
H	6.32188	-0.55273	4.59635
H	5.92332	0.44815	3.16930
H	3.06822	-5.79528	1.24188
H	0.51555	4.60300	-6.36141
H	0.18573	5.83565	-2.84970
H	0.39578	6.32688	-4.64513
H	-5.77868	-1.29685	-3.13802
H	-5.99523	-0.52330	3.11649
H	-3.09219	-5.79823	-1.33411
H	-0.51065	-4.58906	-6.40876
H	-0.20928	-5.85339	-2.90582
H	-0.40625	-6.32831	-4.70710
H	4.58191	-6.37940	0.48928
H	6.31142	-4.66721	0.39298
H	5.82650	-2.86878	0.19440

Table S2 Crystal data and structure refinement for ZrO₂-MAA MOC.

Bond precision:	C-C = 0.0400 Å	Wavelength=0.71073 Å
Cell:	a=17.3180 (8) Å alpha=90	b=17.3180 (8) Å beta=90 c=18.1144 (6) Å gamma=120
Temperature:		173 K
Volume		4704.9 (5) Å ³
Space group		P 63 m c
Hall group		P 6c -2c
Moiety formula		C48 H60 O32 Zr6 [+solvent]
Sum formula		C48 H60 O32 Zr6 [+solvent]
Mr		1696.28
Dx, g cm ⁻³		1.197
Z		2
Mu (mm ⁻¹)		0.699
F000		1688.0
h, k, l (max)		24, 24, 25
Data completeness=1.84/0.95		Theta (max)=29.633

Table S3 Atomistic coordinates for ZrO₂-MAA MOC.

Space group: P63MC;
 $a = b = 17.3180 \text{ \AA}$, $c = 18.1144 \text{ \AA}$;
 $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.

Atom	x/a	y/b	z/c
O	0.81850	0.33360	0.58440
O	0.59440	0.07730	0.36810
O	0.68580	0.11850	0.46710
O	0.64760	0.16990	0.22790
C	0.63820	0.06700	0.40730
C	0.68330	-0.03970	0.47290
H	0.71860	-0.06100	0.44920
H	0.64540	-0.08230	0.50920
H	0.72180	0.01630	0.49650
C	0.63330	0.14400	0.07000
H	0.68650	0.16300	0.09870
H	0.64580	0.18380	0.02940
H	0.61330	0.08470	0.05150
C	0.62770	-0.02770	0.41720
H	0.67010	-0.01770	0.37740
C	0.95100	0.41500	0.70500
O	0.72080	0.13920	0.45960
O	0.63360	0.09070	0.36160
C	0.68460	0.08460	0.41680
C	0.68400	0.00340	0.42340
H	0.72480	0.01880	0.38170
C	0.61300	-0.07560	0.38230
H	0.57390	-0.05930	0.35790
H	0.57910	-0.12320	0.41640
H	0.64040	-0.09480	0.34630
C	0.74600	-0.00500	0.47240
H	0.80230	0.05000	0.47250
H	0.75540	-0.05230	0.45530

H	0.72270	-0.01800	0.52160
C	0.55400	-0.10400	0.37870
H	0.51080	-0.08800	0.36340
H	0.52680	-0.15410	0.41130
H	0.57710	-0.11870	0.33610
C	0.93700	0.38500	0.67700
Zr	0.73464	0.26536	0.49179
O	0.74200	0.25800	0.36150
Zr	0.59928	0.19855	0.33602
O	0.60985	0.21970	0.44900
C	0.57150	0.14300	0.11130
C	0.58070	0.16140	0.19390
O	0.66667	0.33333	0.30630
O	0.66667	0.33333	0.54820
C	0.84400	0.42200	0.60850
C	0.91600	0.45800	0.65630

Table S4 DFT calculated species and relative energies (Hartree) of the reaction path.

Reactions	Species	Gibbs free energy (Hartree)
①	2-propenyl	-117.0879485
	ZrO ₂ -MAA	-4554.925658
	TS-1	-4672.000404
	P-1	-4672.060198
②	2-propenyl	-117.127299177
	TEMPO	-483.311152523
	P-2	-600.523129185
③	2-propenyl	-117.127299177
	HTEMPO	-558.462682352
	P-3	-675.674771807
④	2-propenyl	-117.127299177
	DPPH	-1416.73726633
	TS-4	-1533.86026858
	P-4	-1533.96729698
⑤	2-propenyl	-117.127299177
	BQ	-381.138158565
	P-5	-498.344129517
⑥	2-propenyl	-117.127296593
	HQ	-382.374353659
	TS-6	-499.499349259
	P-6	-117.801855865

References

1. Valenzano, L., *et al.*, *Chem. Mater.* (2011) **23** (7), 1700.
2. Trickett, C. A., *et al.*, *Angew. Chem. Int. Ed. Engl.* (2015) **54** (38), 11162.