Supporting Information

Development of Nickel-based Negative Tone Metal-Oxide Clusters Resist for sub-10 nm Electron Beam and Helium Ion Beam Lithography

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Powder X-ray Diffraction (PXRD)

The powder X-ray diffraction (PXRD) was performed to analyze the crystal structure of as-synthesized Ni-MOCs resist formulation. The obtained peaks were analyzed with the Match! software-version 3. The restriction of five elements was chosen and found that the peaks were nearly matched with the following chemical structures.

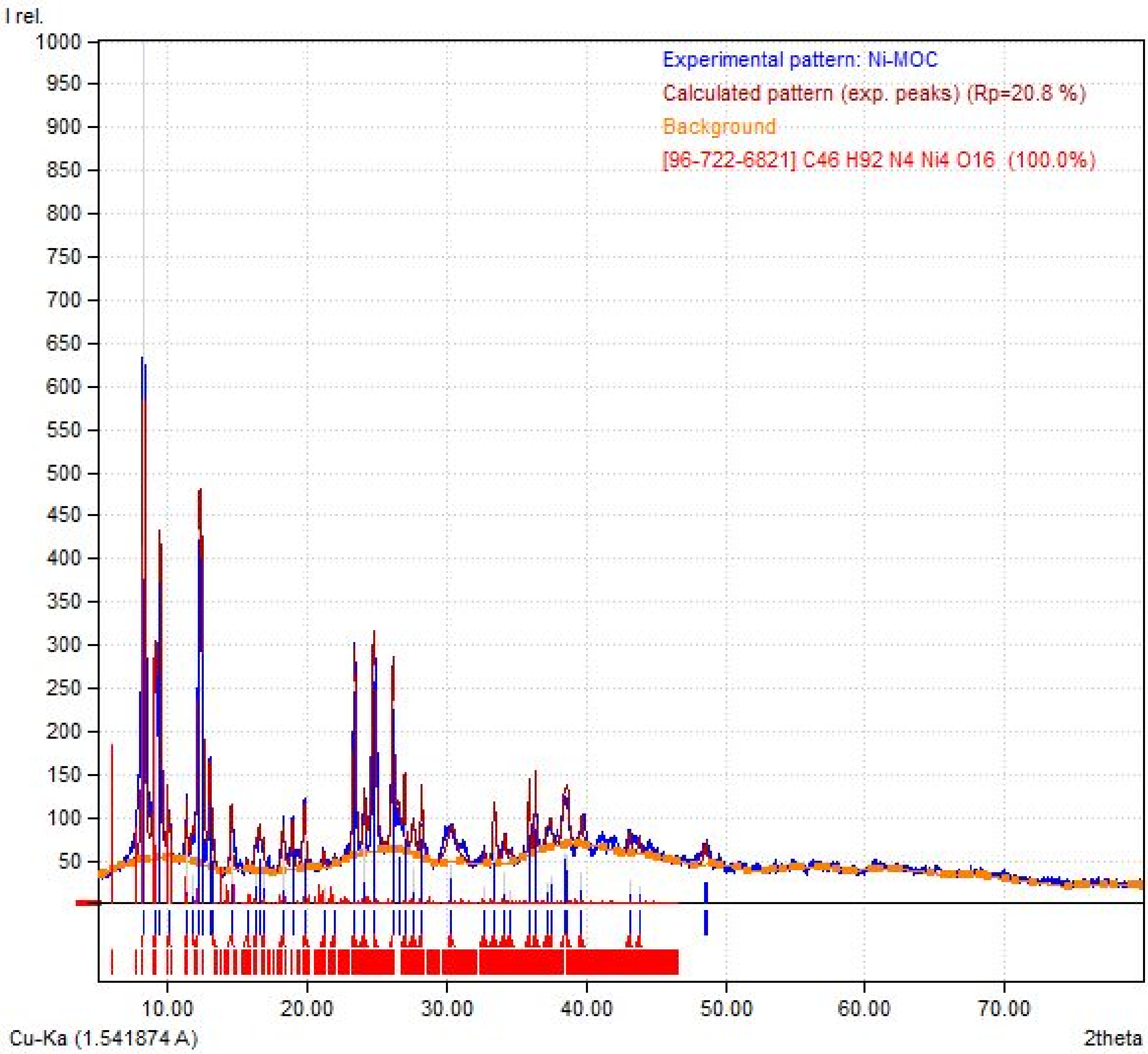

Figure S1: PXRD of Ni-MOCS and matched with reference Ni-based oxo cluster

Input Data: $C_{48}O_{24}H_{108}N_4Ni_4$

Single Unit: $C_{16}O_6H_{27}NNi$

Reference Chemical Formula-

Compound-1[1]

Chemical Formula: $C_{46}H_{92}N_4Ni_4O_{16}$

Crystallographic data

Space group	P 21 21 21 (19)
Crystal system	orthorhombic
Cell parameters	a= 13.09350 Å b= 19.21243 Å c= 22.81600 Å
Cell meas. conditions	T= 120.0 K
Z	4

Compound- 2[2]

Phase Classification
Name: dinickel aspartate-diaqua-oxide tetrahydrate
Formula: $C_4H_{13}NNi_2O_9$
I/Ic: 6.040000
Sample Name: 4112300
Quality: C (calculated)

Crystallographic Data
Space group: I 41/a (88)
Crystal system: tetragonal
Cell parameters: a= 19.13000 Å, c= 11.37900 Å
Cell meas. Conditions: T= 293.0 K
Z: 16

Direct Light scattering spectra of Ni-MOCs resist in Ethyl Lactate solvent

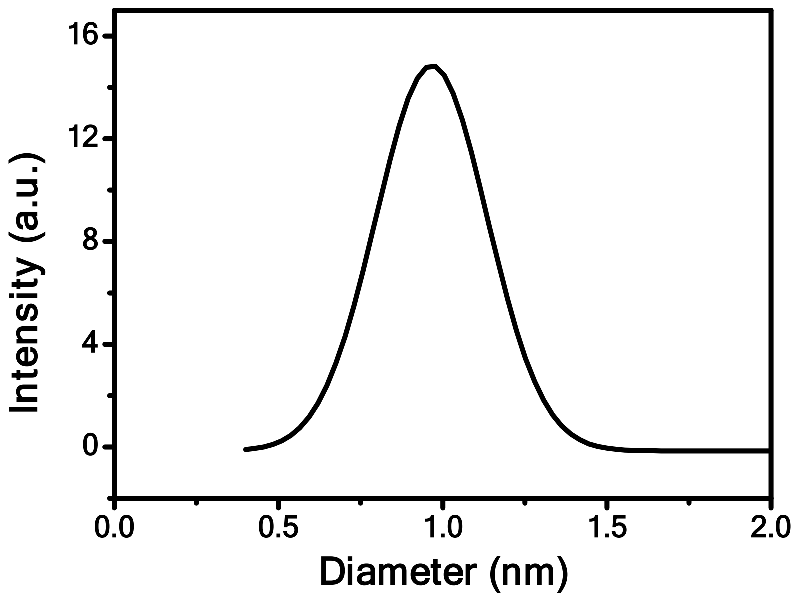

Figure S2: Particle size distribution of Ni-MOCs resist formulation

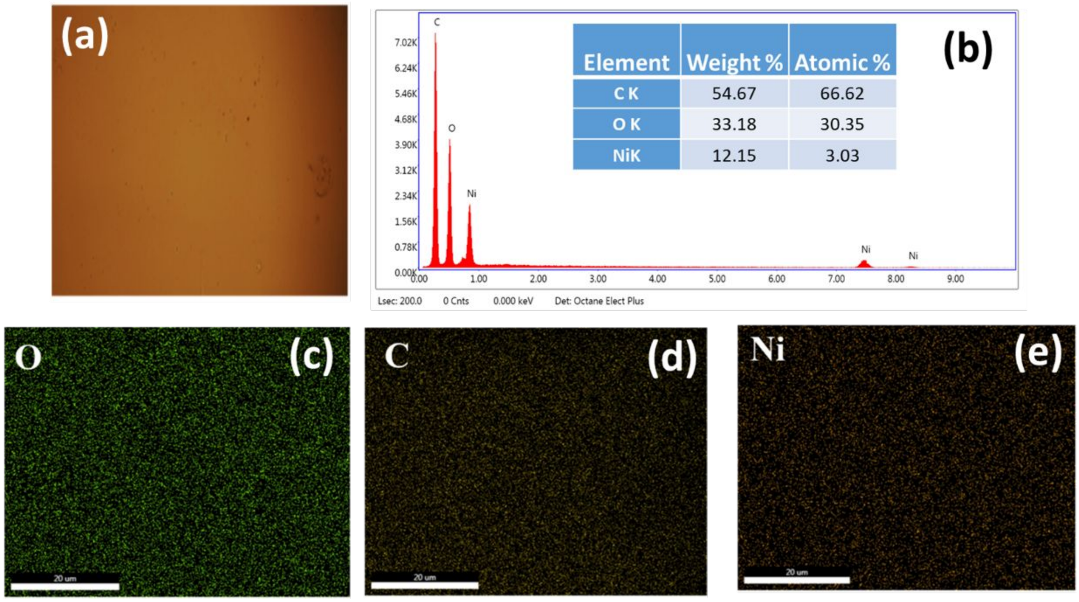

Figure S3: (a) Optical image of spin-coated Ni-MOCs resist thin film (b) EDX and (c,d,e) elemental mapping of Ni-MOCs resist

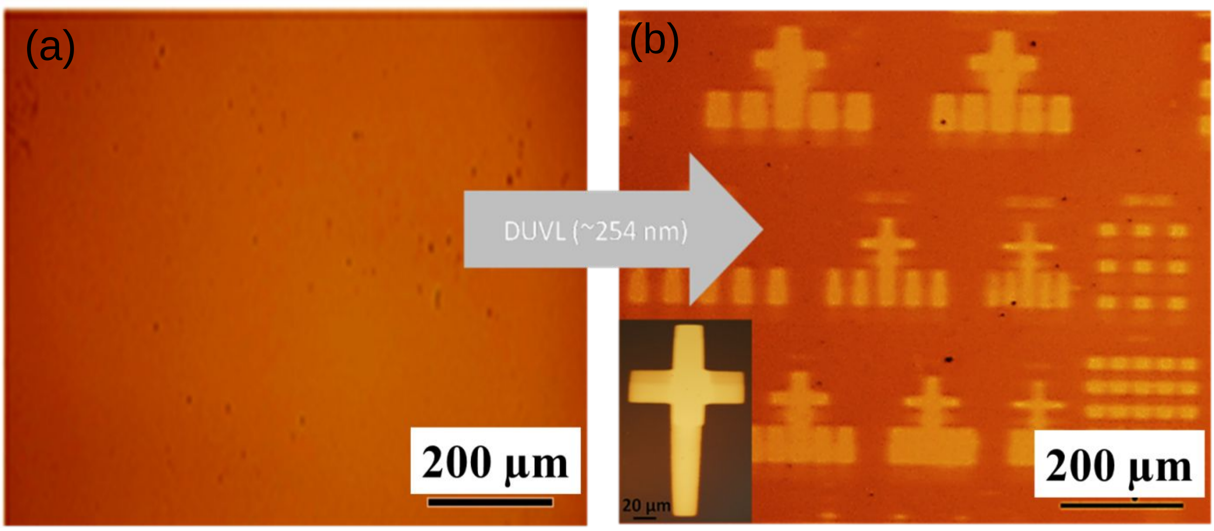

Figure S4: Optical micrographs: (a) thin-film image of spin-coated Ni–MOCs over Si (100) after prebake process; (b) DUV exposure and pattern development of Ni–MOCs resist; inset shows an enlarged view of developed pattern

E-beam exposure for sensitivity analysis

The e-beam exposures were performed with various doses to find the appropriate dose for potential Ni-MOCs resist. The dose increment of $0.1\times E_o$ was applied as shown in Figure S6, where E_o is the base dose. This matrix has adapted to calculate the sensitivity. Also, this exposure matrix is found to be suitable for the analysis of the effect of beam energy.

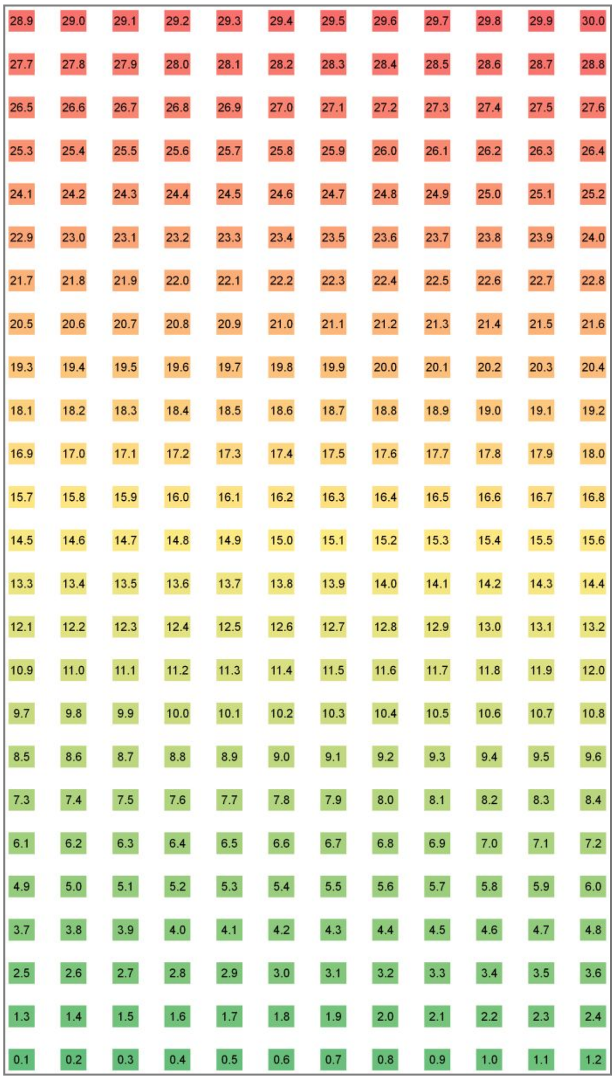

Figure S5: Exposure matrix to calculate the sensitivity. The value of $E_0 = 20$ μC/cm^2 and $\Delta E_0 = 2$ μC/cm^2

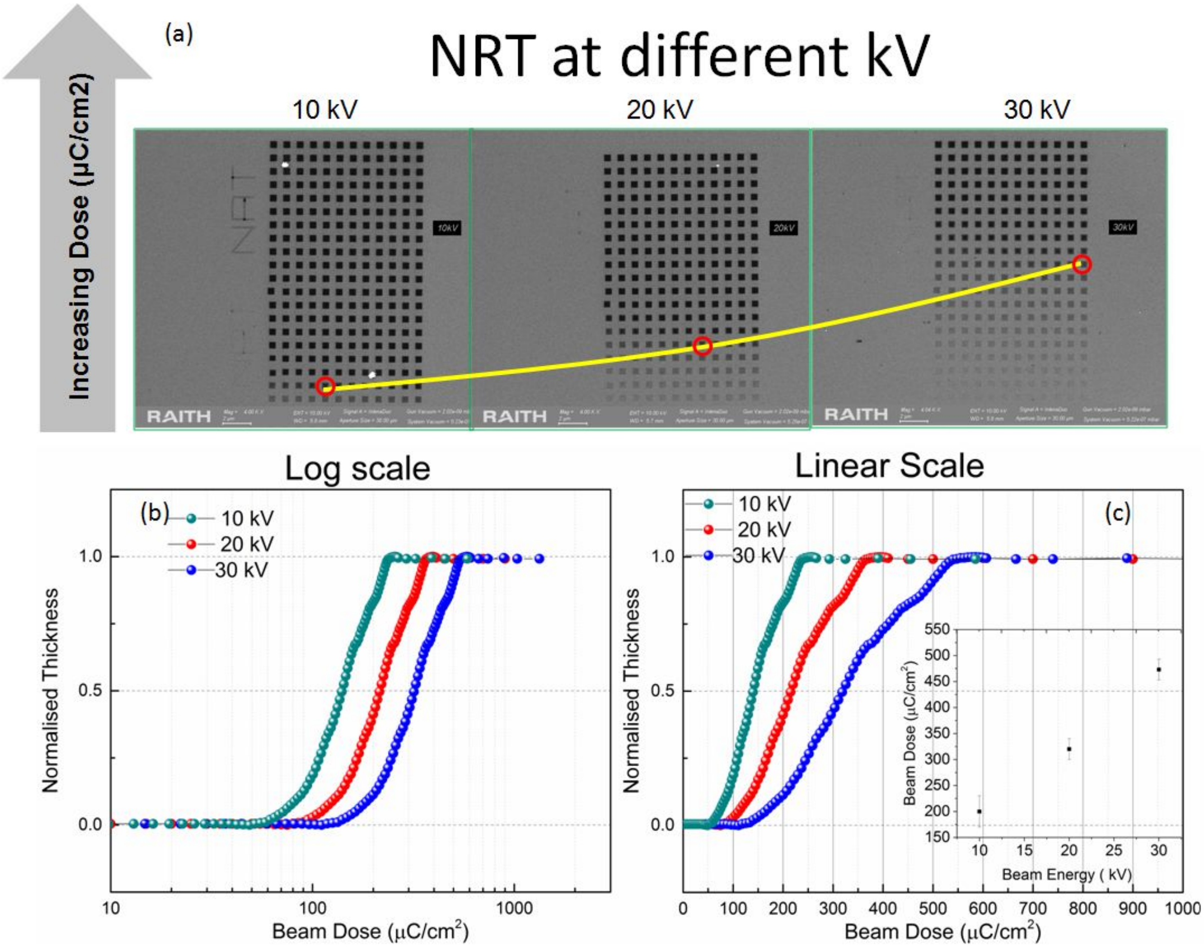

Figure S6: Sensitivity vs. Dose analysis for Ni-MOC (a) SEM micrograph of exposed NRT patterns as mention in Figure S5 at 10 keV, 20 keV and 30 keV. (b) The corresponding NRT for above-exposed patterns in log scale; which shows increased sensitivity with energy, (c) The NRT with linear scale; the linear fit of beam energy vs. dose.

From Figure S6, it is clearly explained that the sensitivity of Ni-MOCs linearly increases while increasing the beam energy from 10 keV to 30 keV. This is happening due to the interaction of beam cross-sectional to the resist film. As the beam energy is higher, the kinetic energy is higher and also higher the beam penetration inside the substrate, thereby lesser interaction to the resist materials. The 30 keV exposures provide less proximity due to the aforementioned reasoning. A similar study has explained by Zheng Cui *et al.*[3]

Table S1. Sensitivity and Contrast of Ni-MOCs at different keV

Beam energy (keV)	Sensitivity (E_D)	Contrast (γ)
10	215	2.38
20	329	2.48
30	473	2.46

References:

1.Schmitz, S.; Monakhov, K. Y.; van Leusen, J.; Izarova, Natalya V.; Heb, V.; Kogerler, P. {Coii/Iii5} Horseshoe and {Niii4} Lacunary Cubane Coordination Clusters: The Isobutyrate/N-Butyldiethanolamine Reaction System. *RSC Adv.* **2016,** *6*, 100664-100669.
2.Anokhina, E. V.; Jacobson, A. J. [Ni_2O(L-Asp)(H_2O)2]·$4H_2O$: A Homochiral 1d Helical Chain Hybrid Compound with Extended Ni-O-Ni Bonding. *J. Am. Chem. Soc.* **2004,** *126*, 3044-3045.
3.Cui, Z., *Nanofabrication: Principles, Capabilities and Limits*. Springer US: **2009**.