Electronic Supplementary Information

Short-range disorder mediated stability of Zn in rock-salt MgO beyond configurational entropy

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Supplementary Figures and Tables

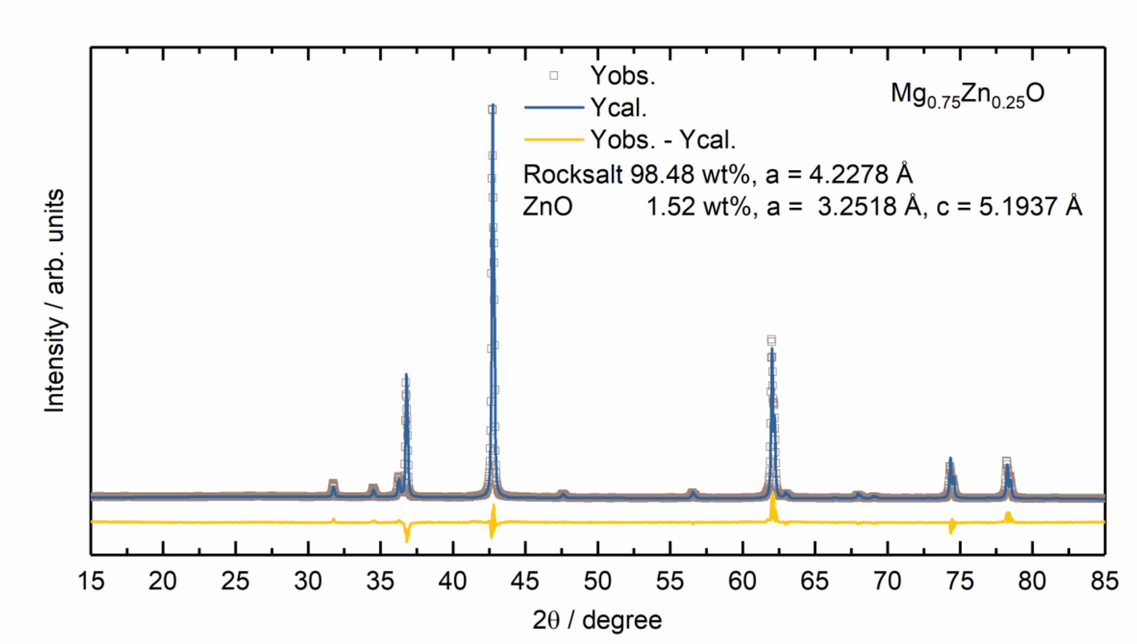

Fig. S1. XRD Rietveld refinement of $Mg_{0.75}Zn_{0.25}O$.

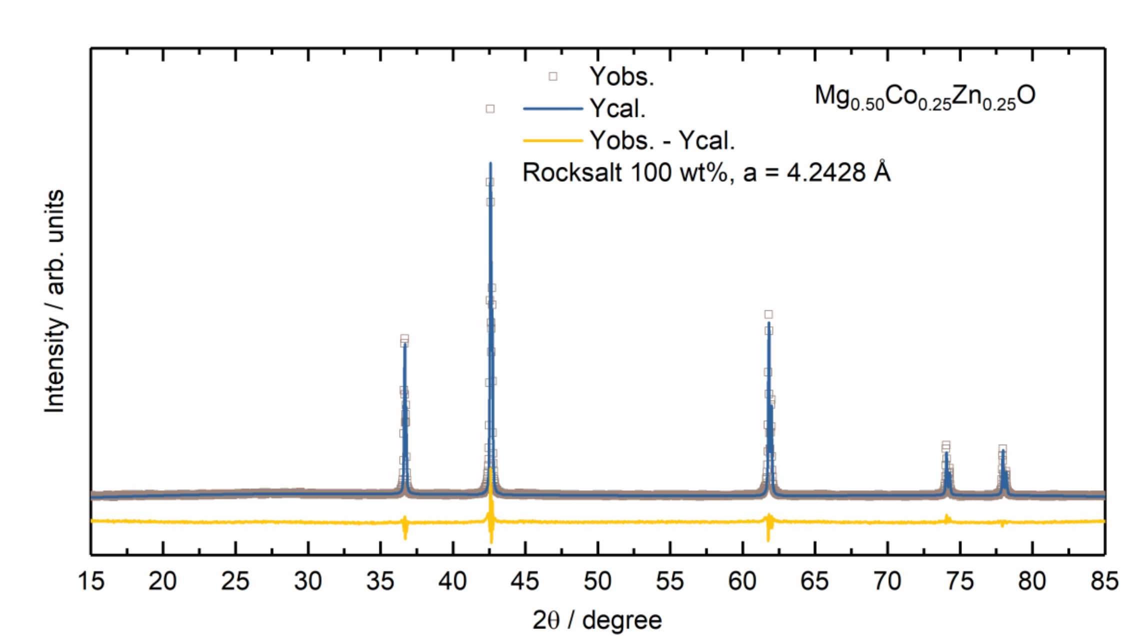

Fig. S2. XRD Rietveld refinement of $Mg_{0.50}Co_{0.25}Zn_{0.25}O$.

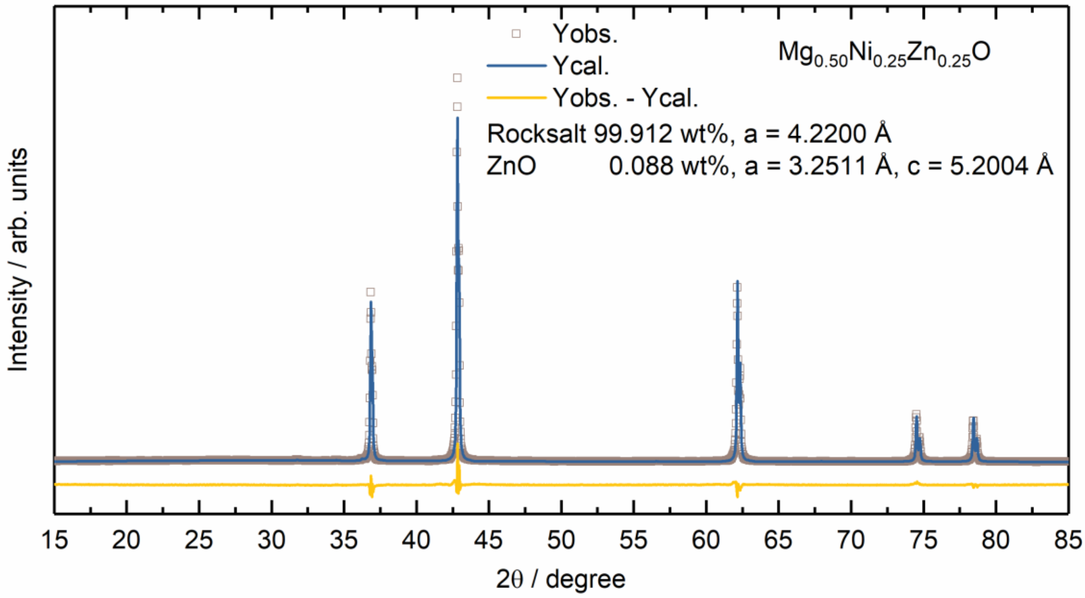

Fig. S3. XRD Rietveld refinement of $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$.

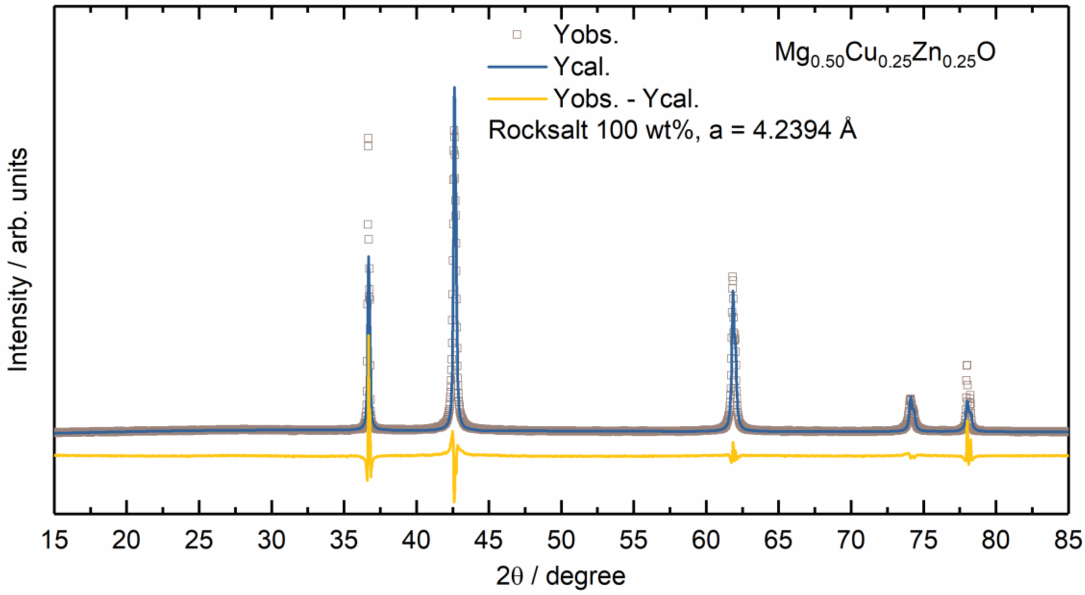

Fig. S4. XRD Rietveld refinement of $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$.

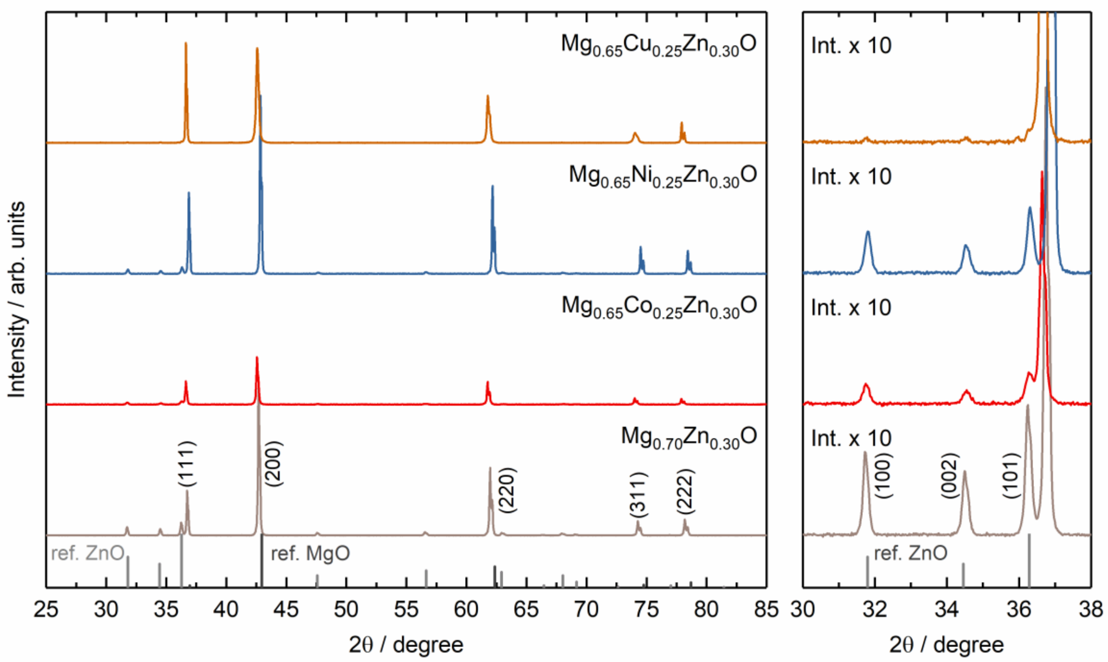

Fig. S5. The XRD patterns of $Mg_{0.70}Zn_{0.30}O$ and $Mg_{0.65}TM_{0.25}Zn_{0.30}O$ (TM = Co, Ni, Cu).

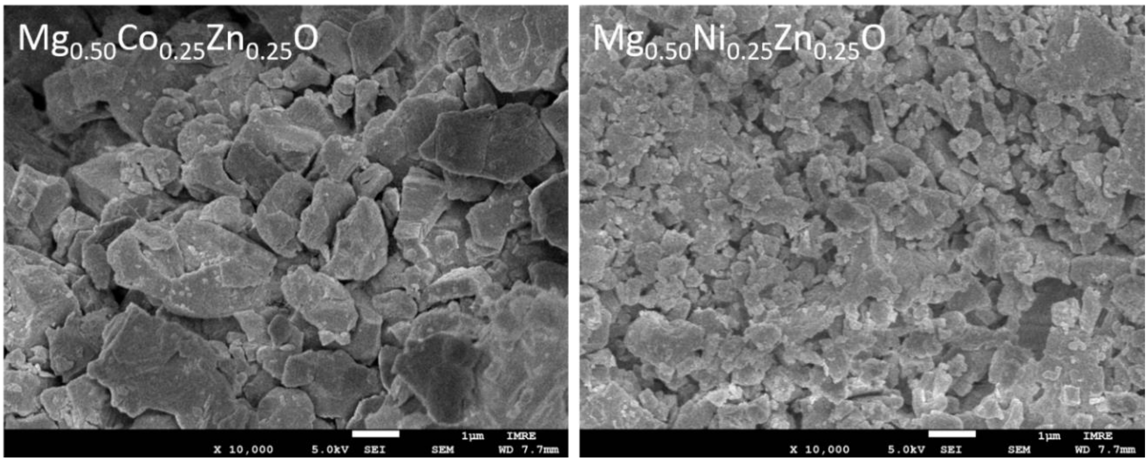

Fig. S6. The SEM images of $Mg_{0.50}Co_{0.25}Zn_{0.25}O$ and $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$.

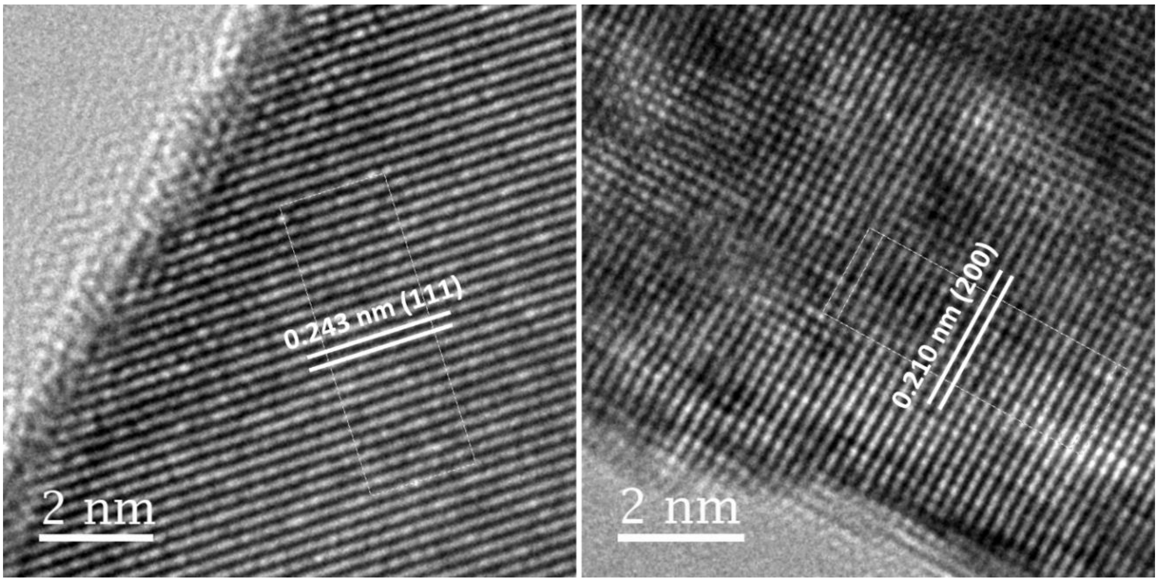

Fig. S7. HRTEM of (111) and (200) lattices in $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$.

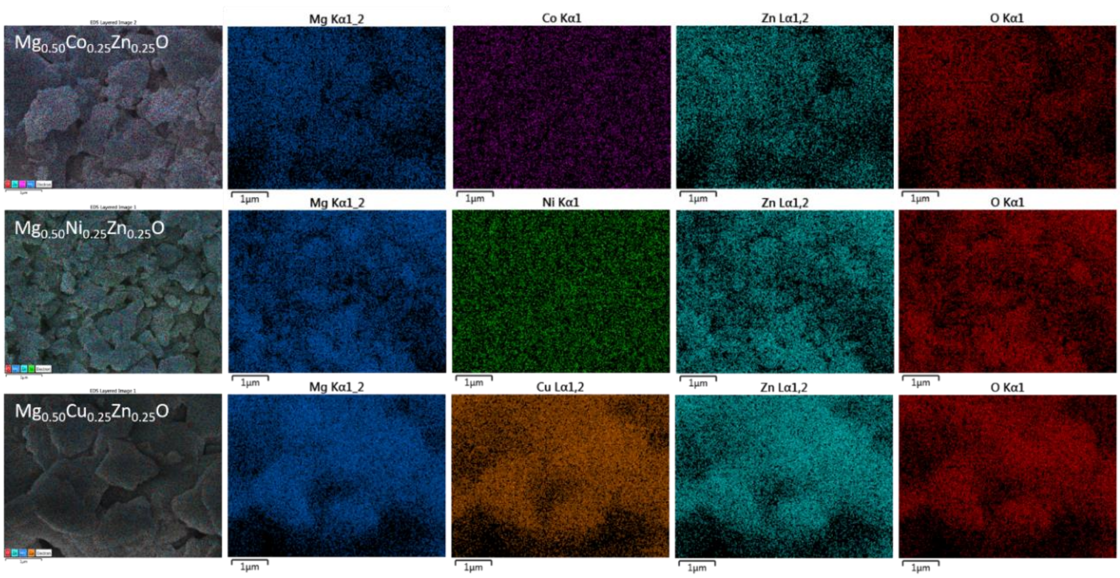

Fig. S8. SEM-EDX mapping of $Mg_{0.50}TM_{0.25}Zn_{0.25}O$ (TM = Co, Ni, Cu).

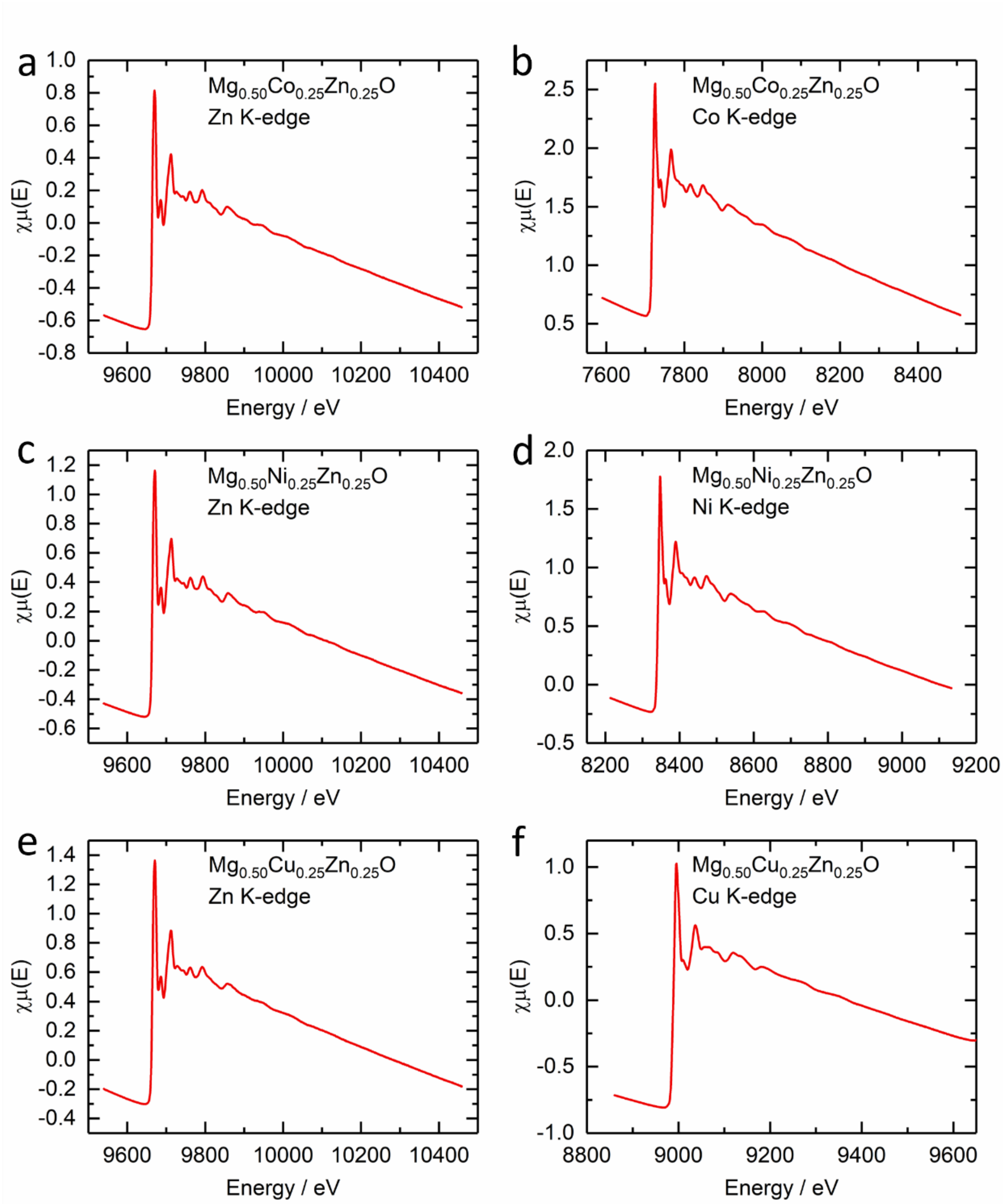

Fig. S9. The EXAFS experimental data of Zn, Co, Ni and Cu K-edges of $Mg_{0.50}Co_{0.25}Zn_{0.25}O$, $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ and $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$.

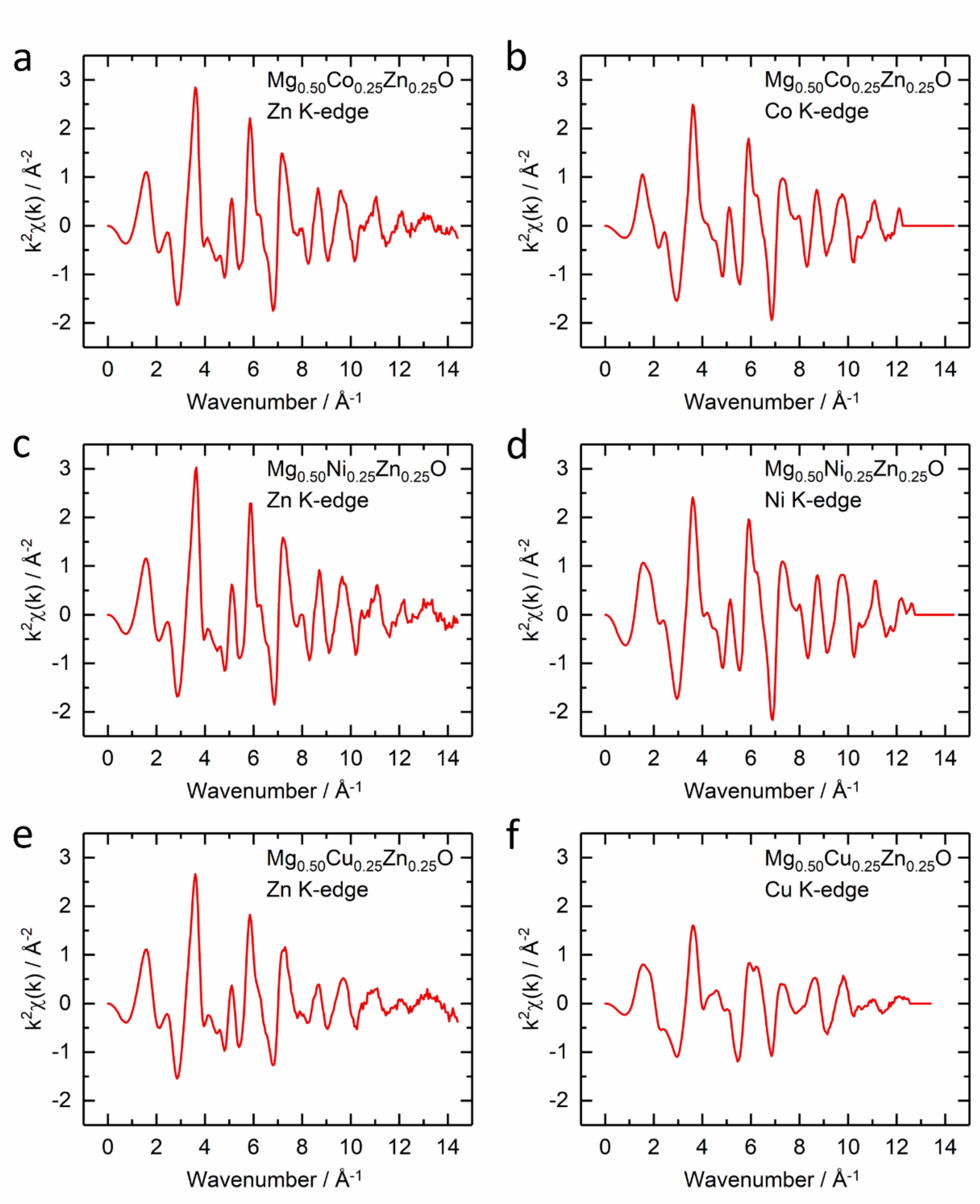

Fig. S10. The EXAFS data in k-space of Zn, Co, Ni and Cu K-edges of $Mg_{0.50}Co_{0.25}Zn_{0.25}O$, $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ and $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$.

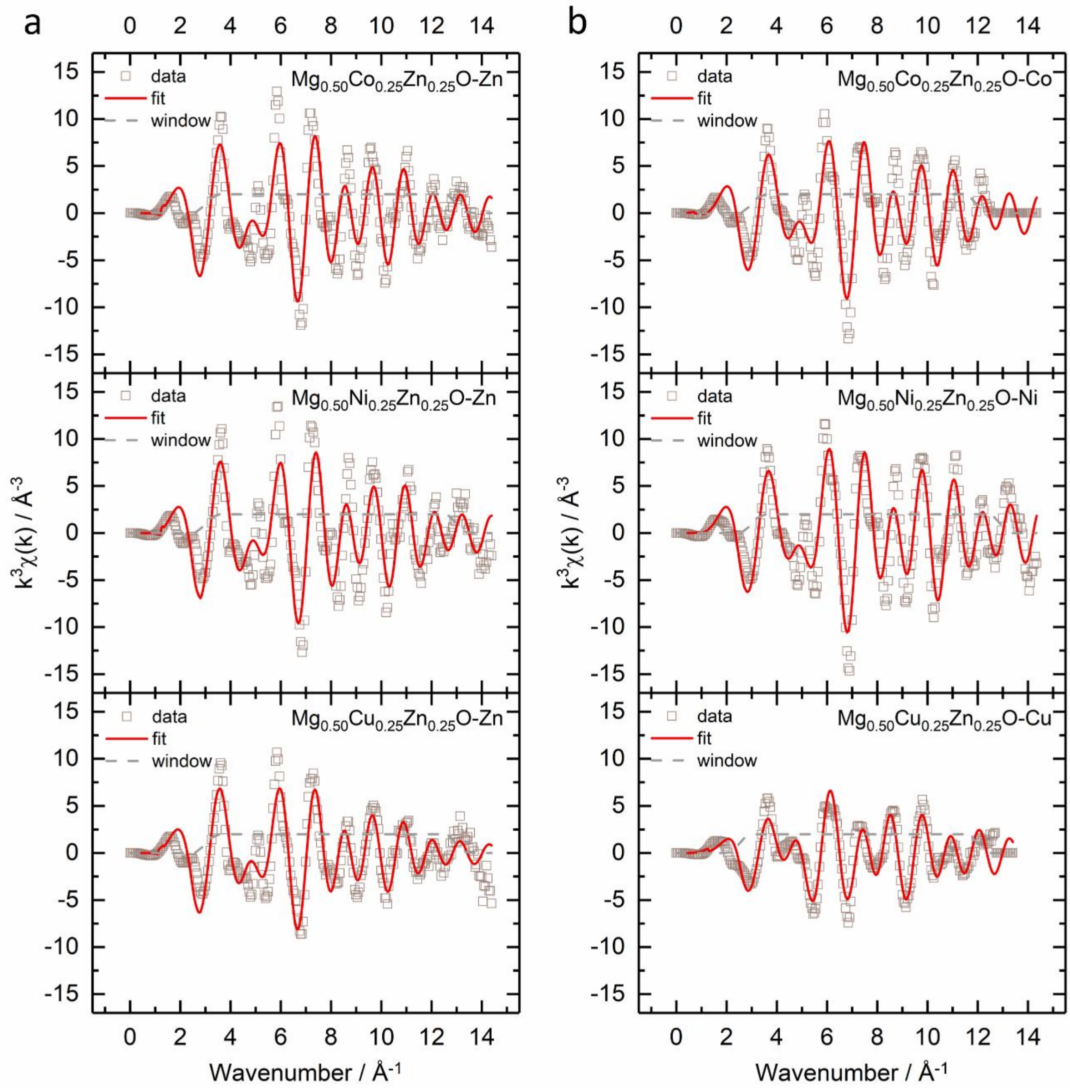

Fig. S11. The fitted EXAFS results of (a) Zn, (b) Co, Ni and Cu K-edges in k-space.

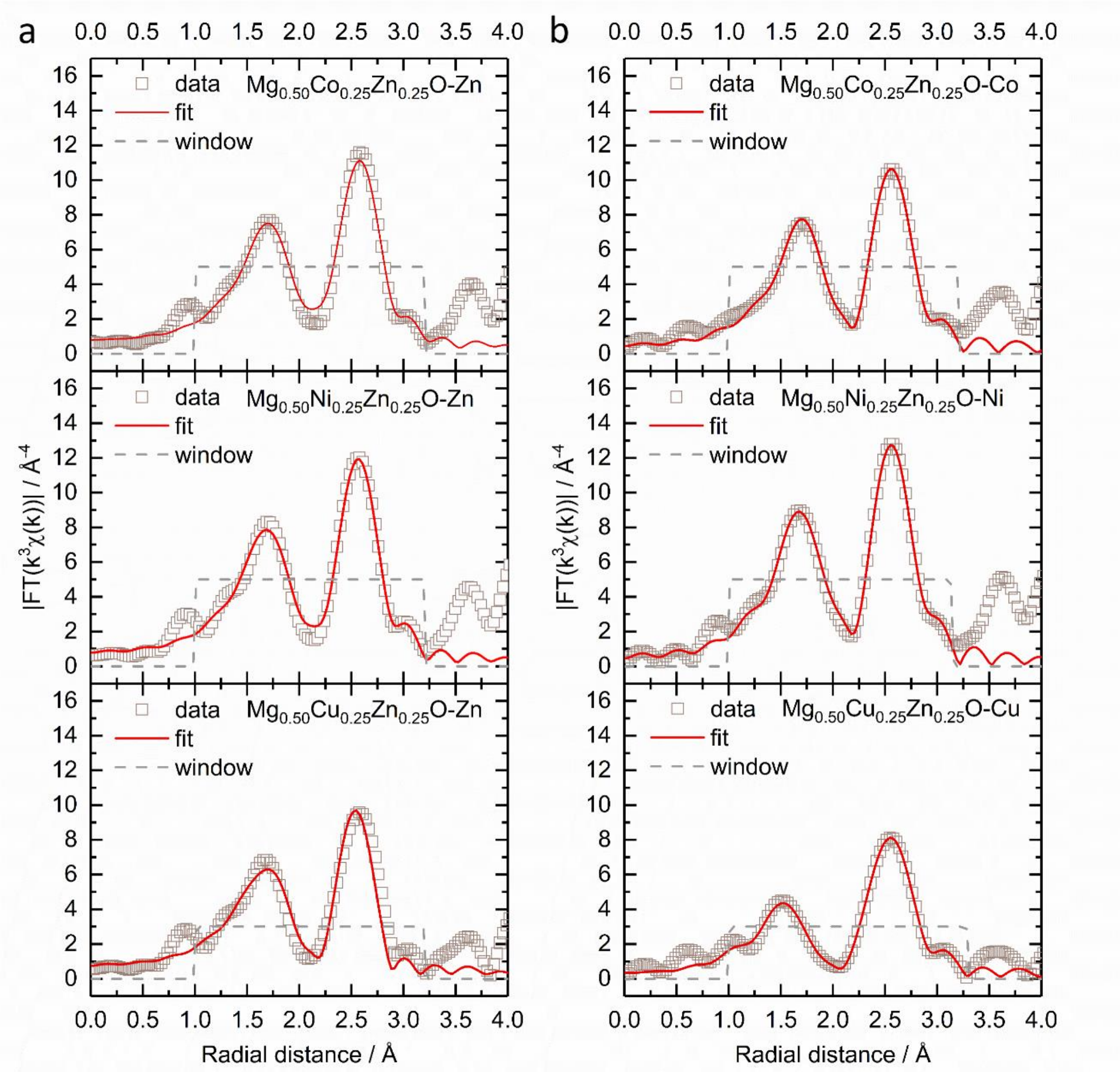

Fig. S12. The k^3-weighting FT-EXAFS and the fitting of (a) Zn K-edge and (b) Co, Ni and Cu K-edges of $Mg_{0.50}TM_{0.25}Zn_{0.25}O$ (TM = Co, Ni, Cu) under a Hanning-shaped window, fixing the coordination number to 6 for the first shell and 12 for the second shell.

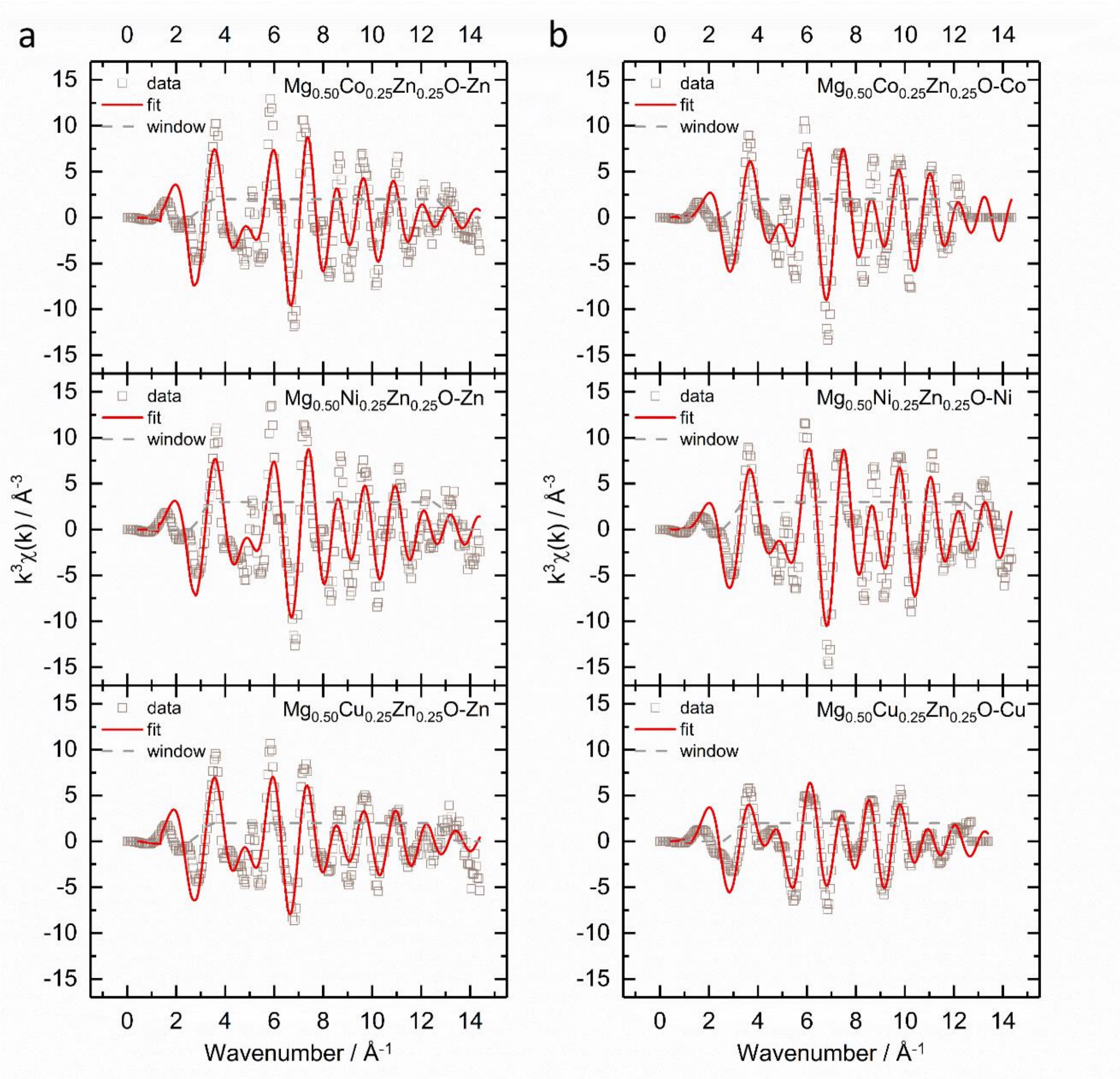

Fig. S13. The fitted EXAFS results of (a) Zn, (b) Co, Ni and Cu K-edges in k-space, fixing the coordination number to 6 for the first shell and 12 for the second shell.

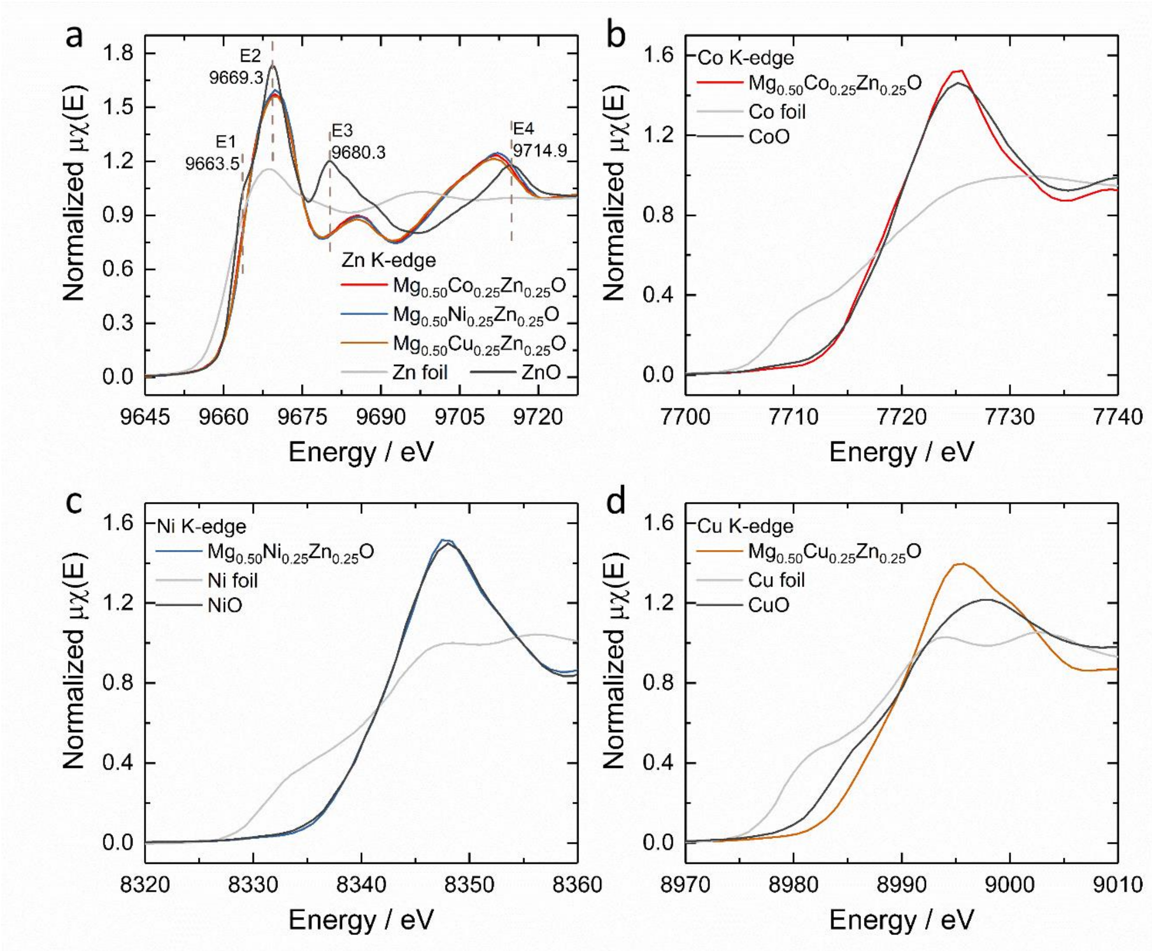

Fig. S14. XANES of (a) Zn, (b) Co, (c) Ni and (d) Cu in $Mg_{0.50}Co_{0.25}Zn_{0.25}O$, $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ and $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ and the reference samples.

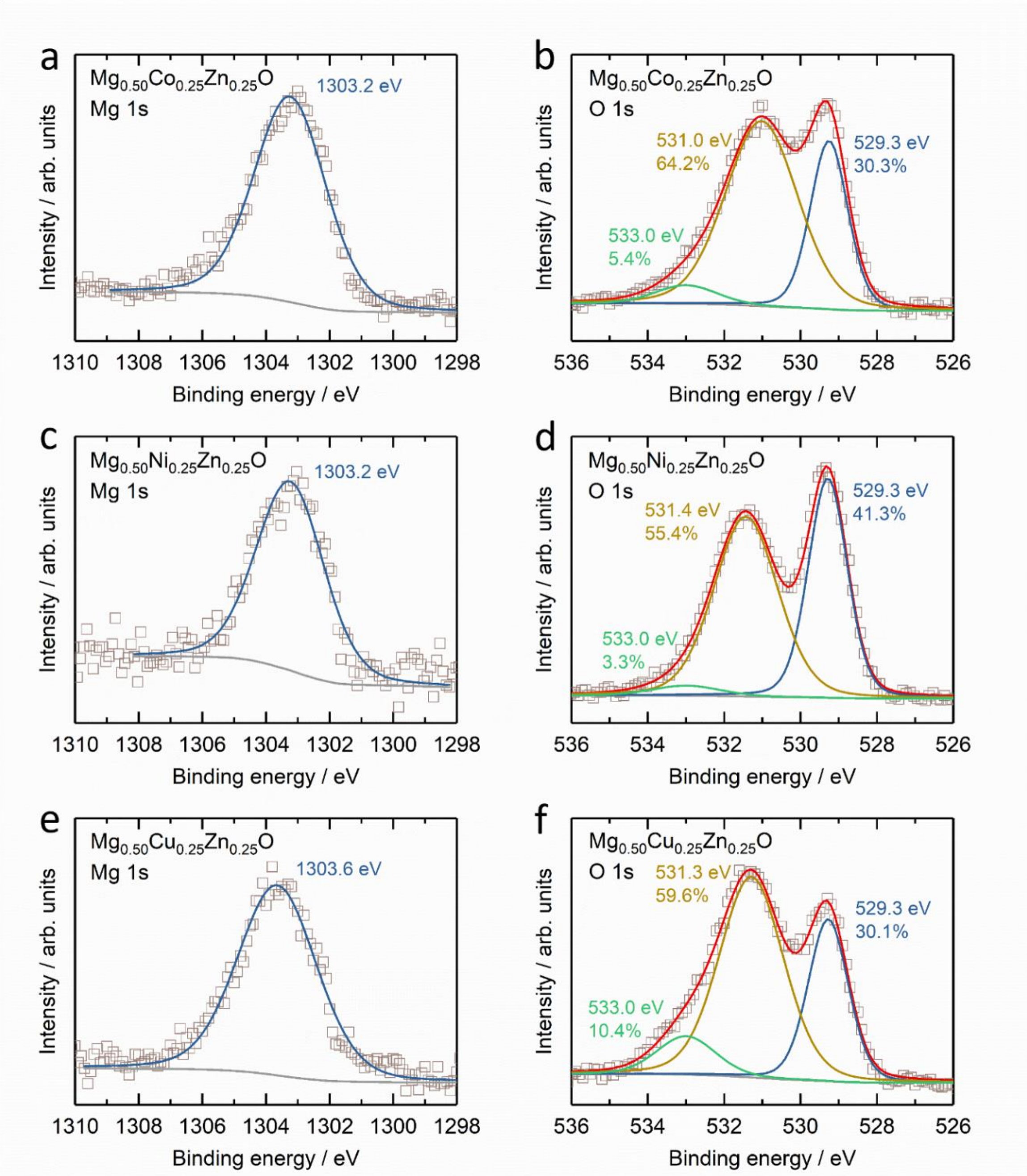

Fig. S15. XPS results of (a, c, e) Mg 1s and (b, d, f) O 1s of (a, b) $Mg_{0.50}Co_{0.25}Zn_{0.25}O$, (c, d) $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ and (e, f) $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$.

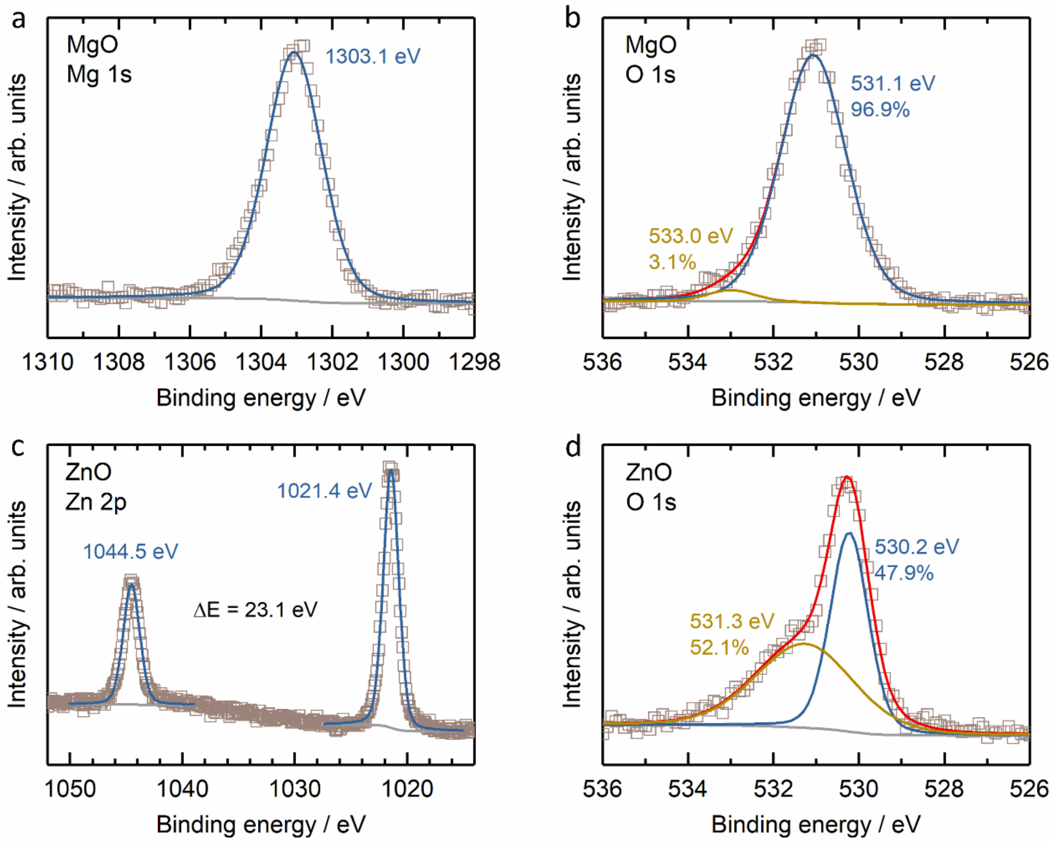

Fig. S16. XPS results of (a) Mg 1s, (c) Zn 2p and (b, d) O 1s of commercial (a, b) MgO and (c, d) ZnO.

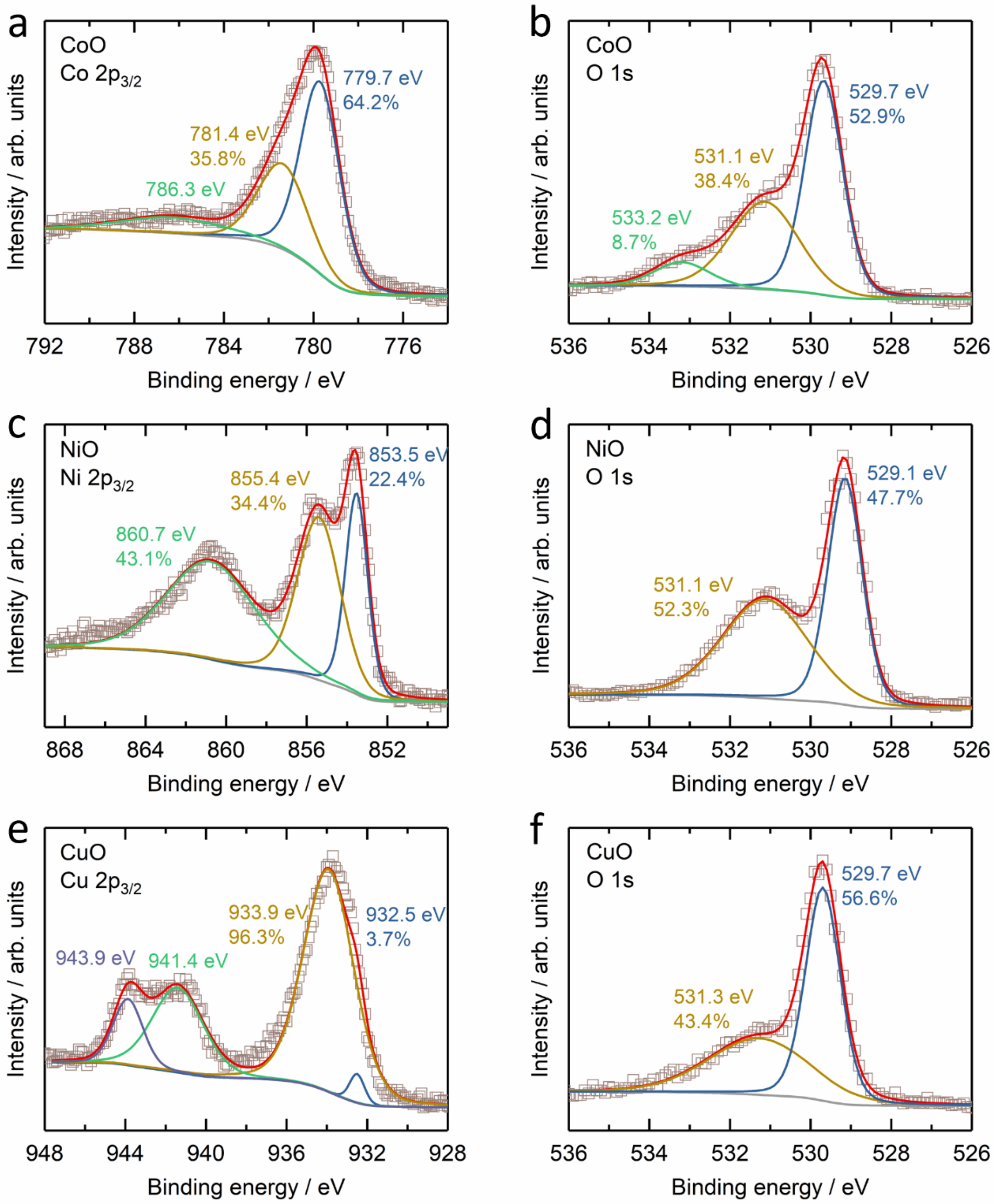

Fig. S17. XPS results of (a) Co $2p_{2/3}$, (c) Ni $2p_{3/2}$, (e) Cu $2p_{3/2}$ and (b, d, f) O 1s of commercial (a, b) CoO, (c, d) NiO and (e, f) CuO.

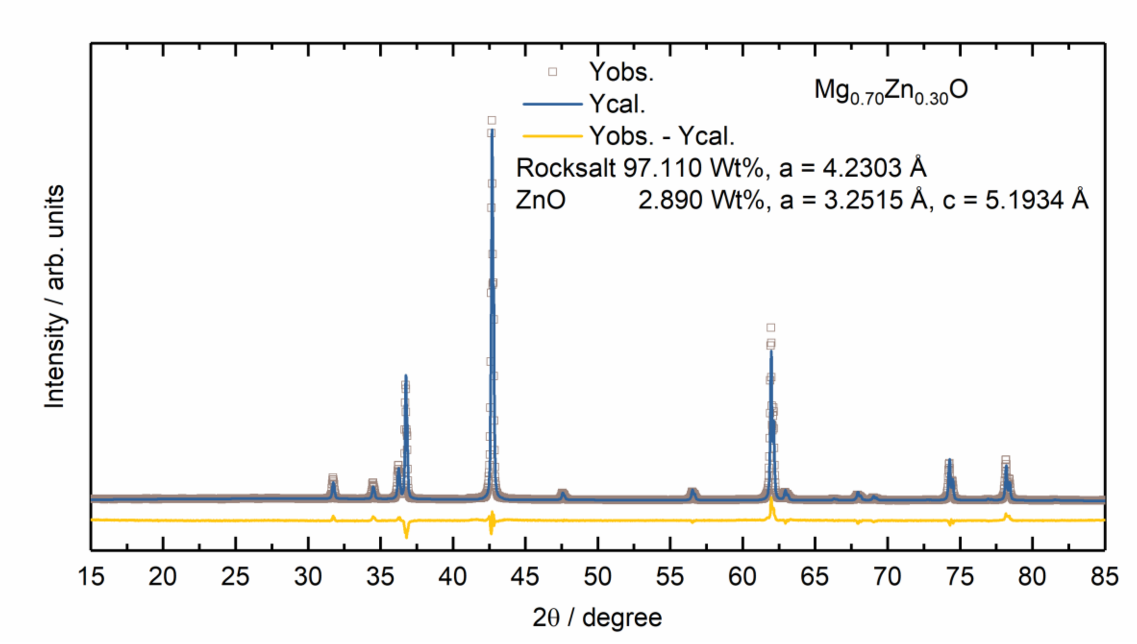

Fig. S18. XRD Rietveld refinement of $Mg_{0.70}Zn_{0.30}O$.

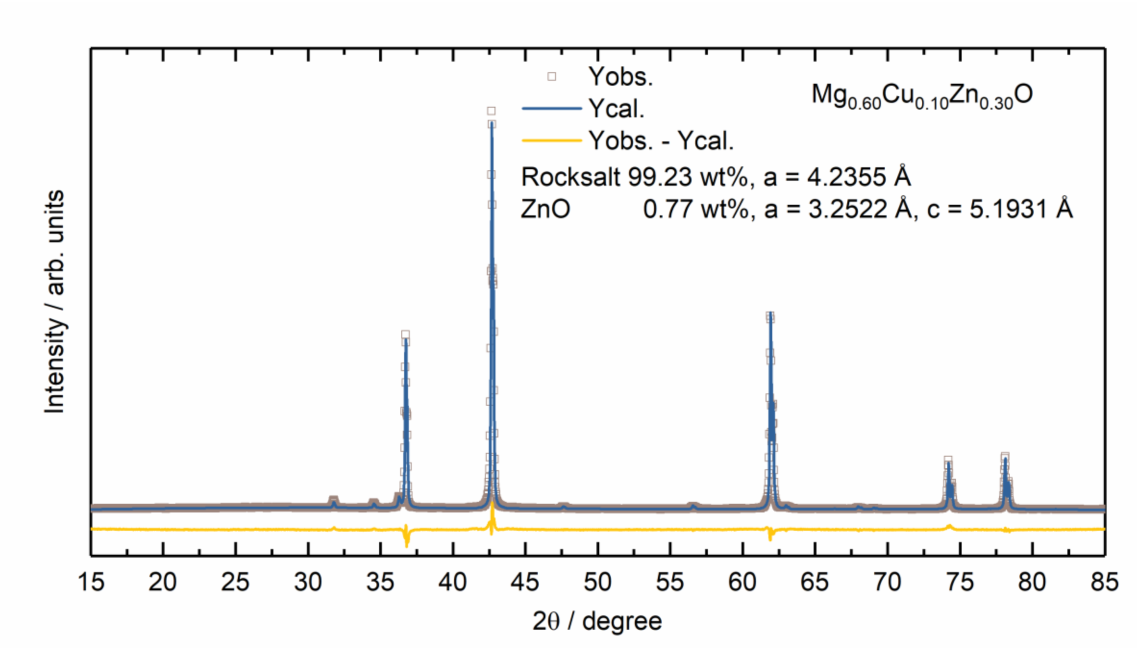

Fig. S19. XRD Rietveld refinement of $Mg_{0.60}Cu_{0.10}Zn_{0.30}O$.

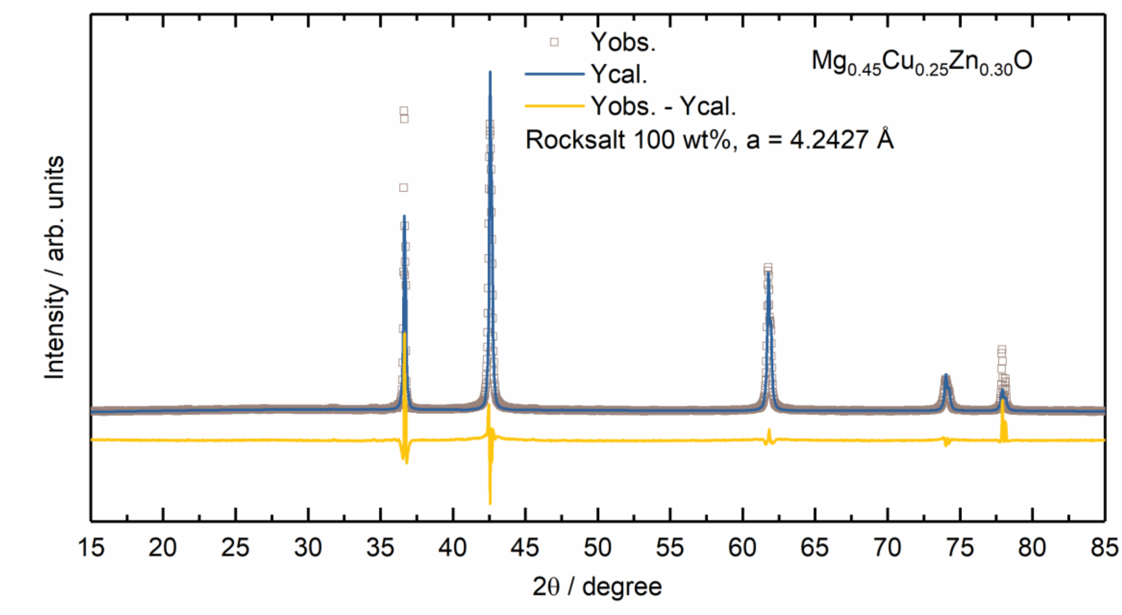

Fig. S20. XRD Rietveld refinement of $Mg_{0.45}Cu_{0.25}Zn_{0.30}O$.

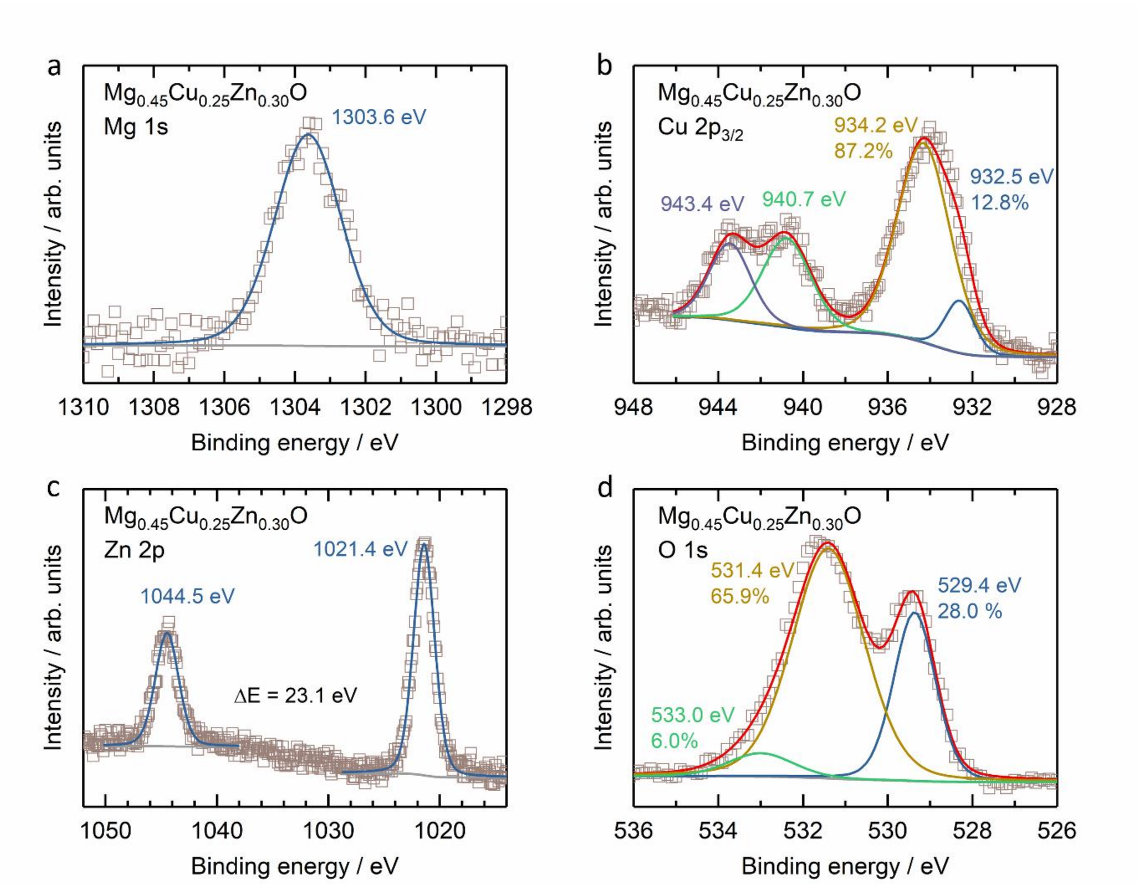

Fig. S21. XPS results of (a) Mg 1s, (b) Cu $2p_{3/2}$, (c) Zn 2p and (d) O 1s of $Mg_{0.45}Cu_{0.25}Zn_{0.30}O$.

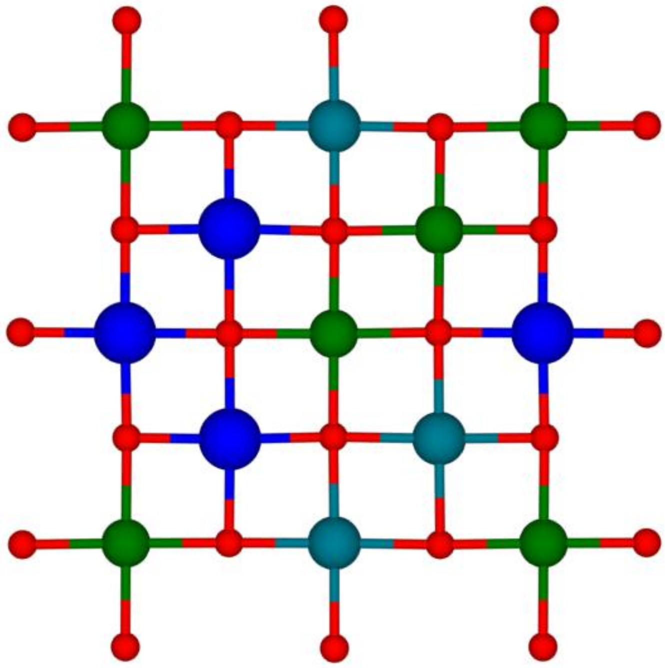

Fig. S22. The slice of $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ viewed from [001] direction.

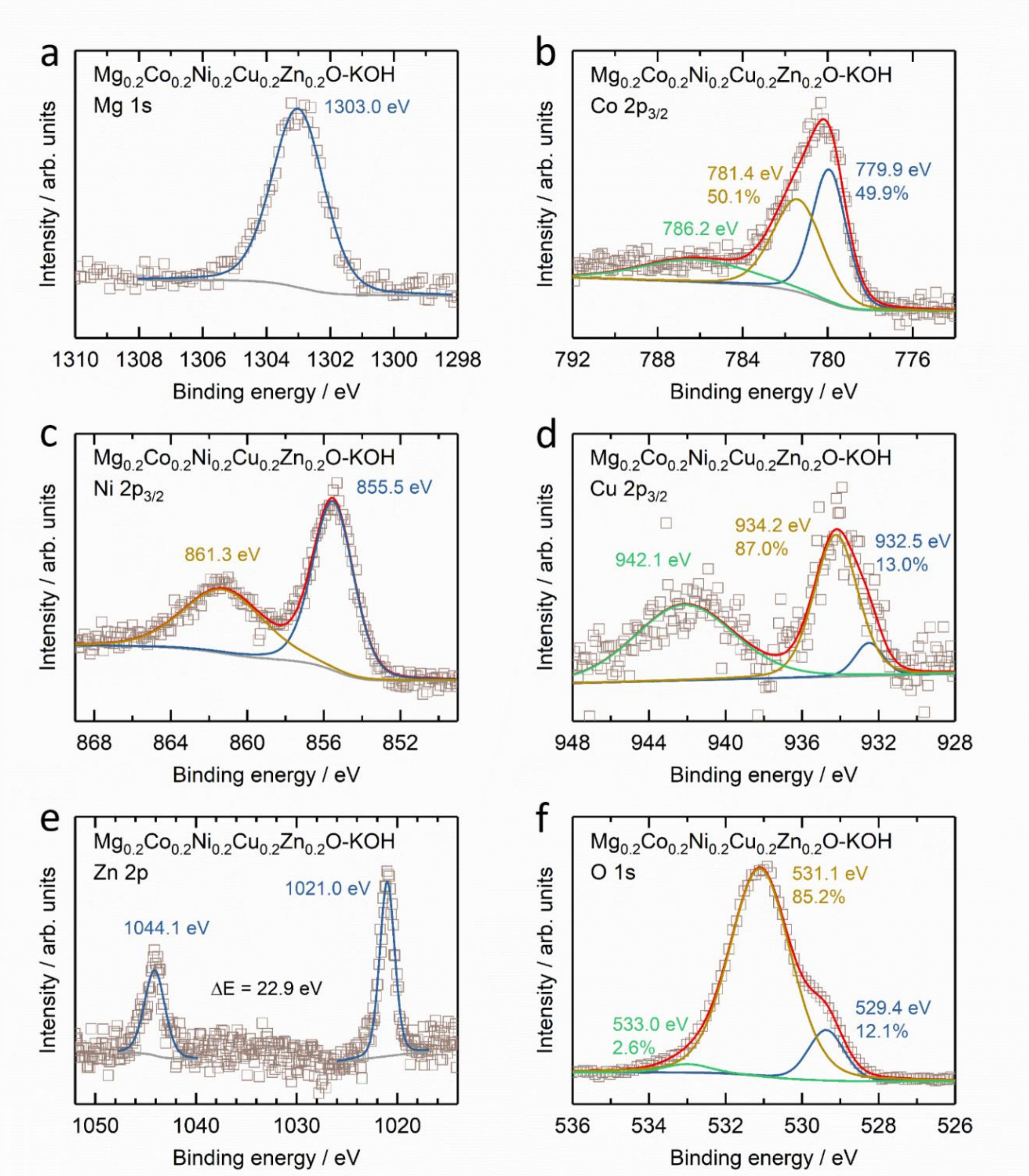

Fig. S23. XPS results of (a) Mg 1s, (b) Co $2p_{3/2}$, (c) Ni $2p_{3/2}$, (d) Cu $2p_{3/2}$, (e) Zn 2p and (f) O 1s of $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ after soaking in 2 M KOH for 4 weeks.

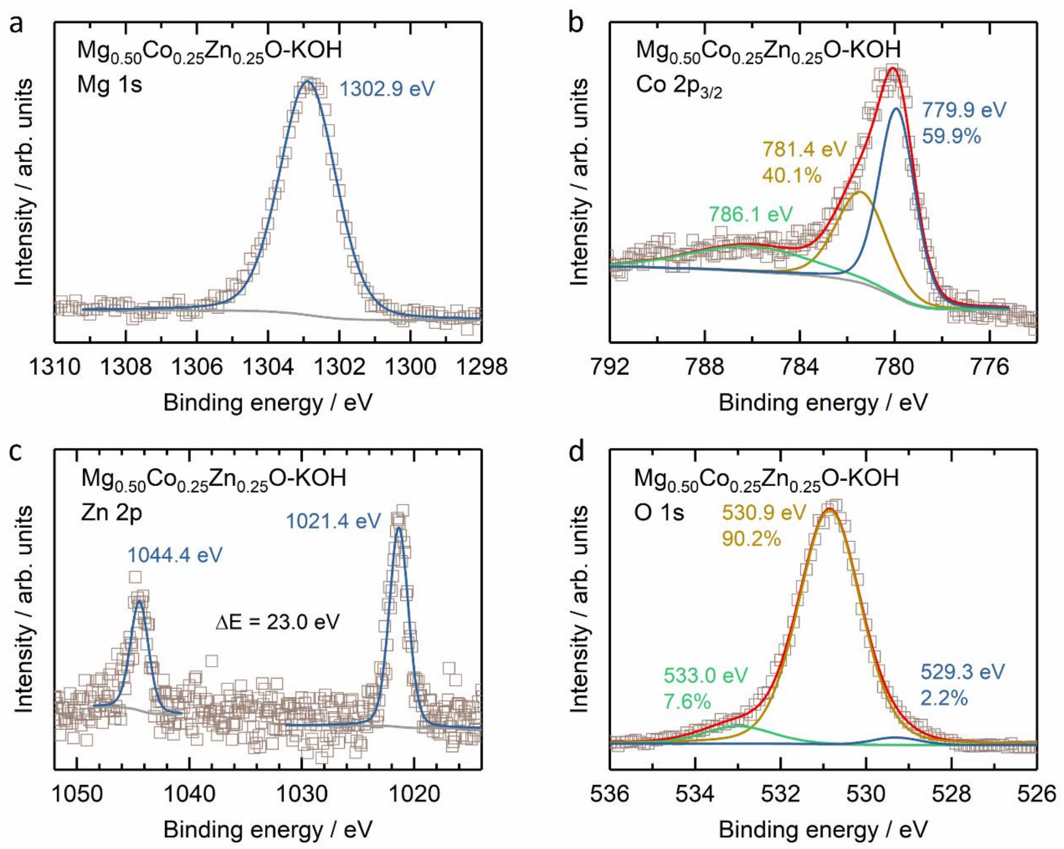

Fig. S24. XPS results of (a) Mg 1s, (b) Co $2p_{3/2}$, (c) Zn 2p and (d) O 1s of $Mg_{0.50}Co_{0.25}Zn_{0.25}O$ after soaking in 2 M KOH for 4 weeks.

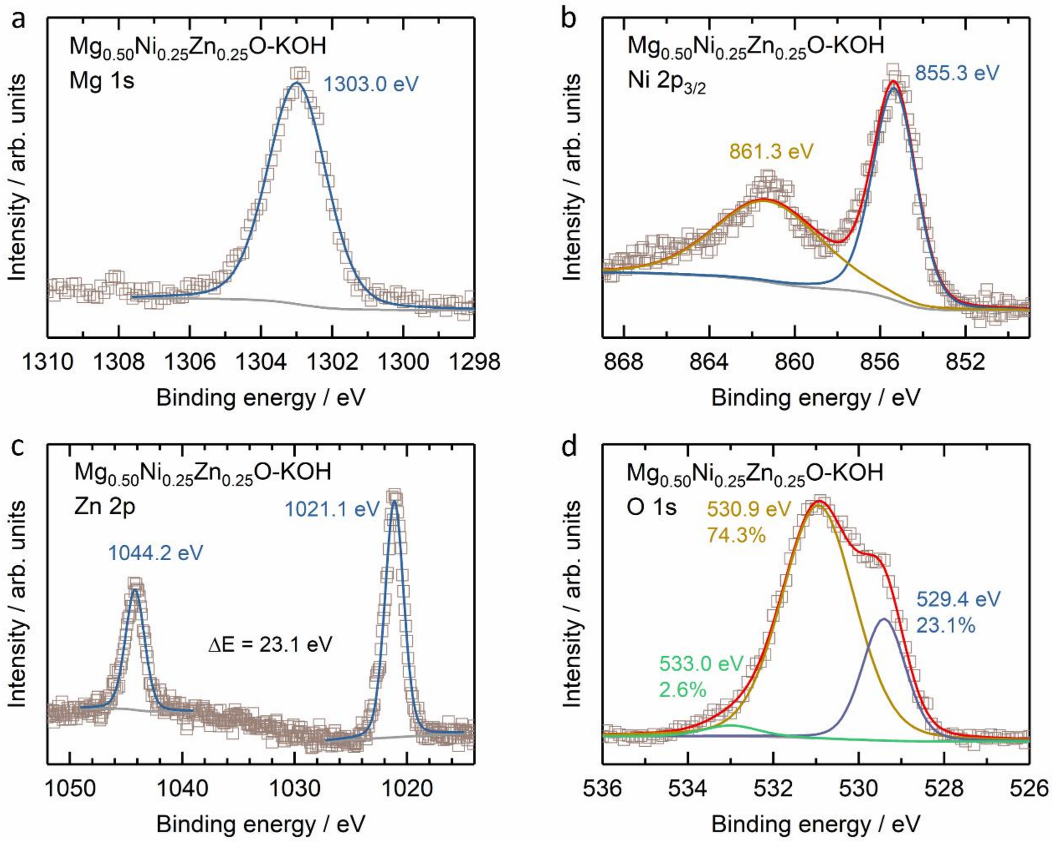

Fig. S25. XPS results of (a) Mg 1s, (b) Ni $2p_{3/2}$, (c) Zn 2p and (d) O 1s of $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ after soaking in 2 M KOH for 4 weeks.

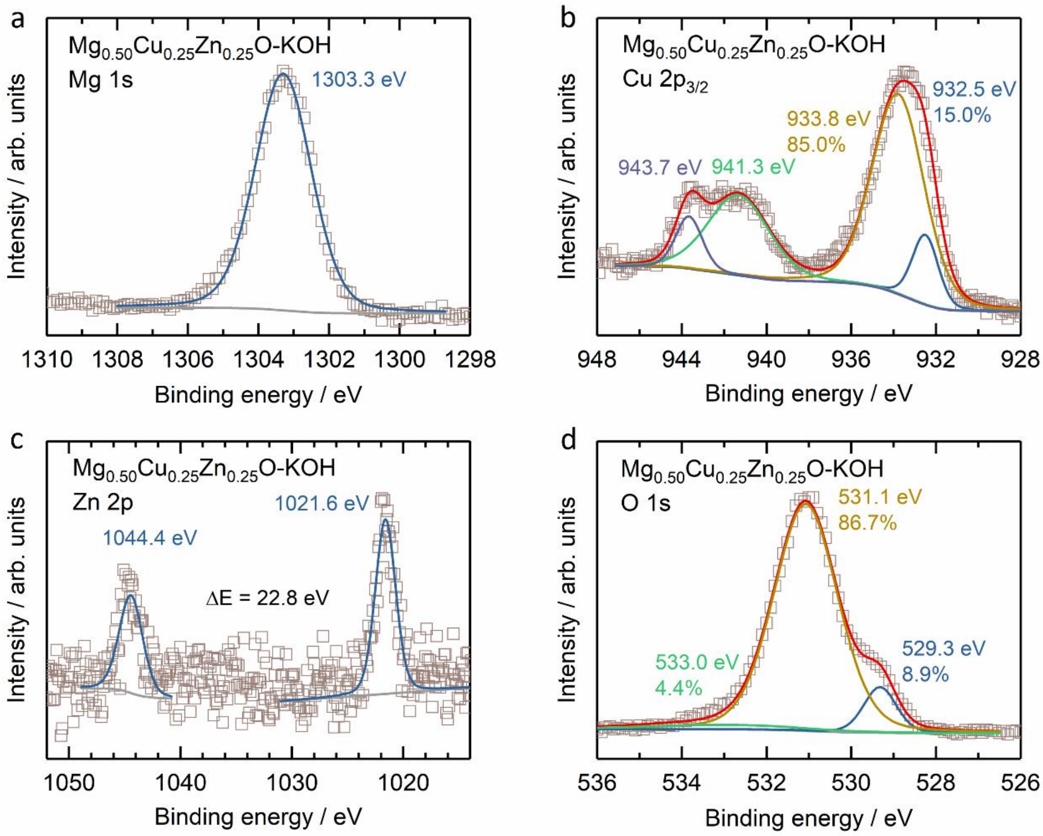

Fig. S26. XPS results of (a) Mg 1s, (b) Cu $2p_{3/2}$, (c) Zn 2p and (d) O 1s of $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ after soaking in 2 M KOH for 4 weeks.

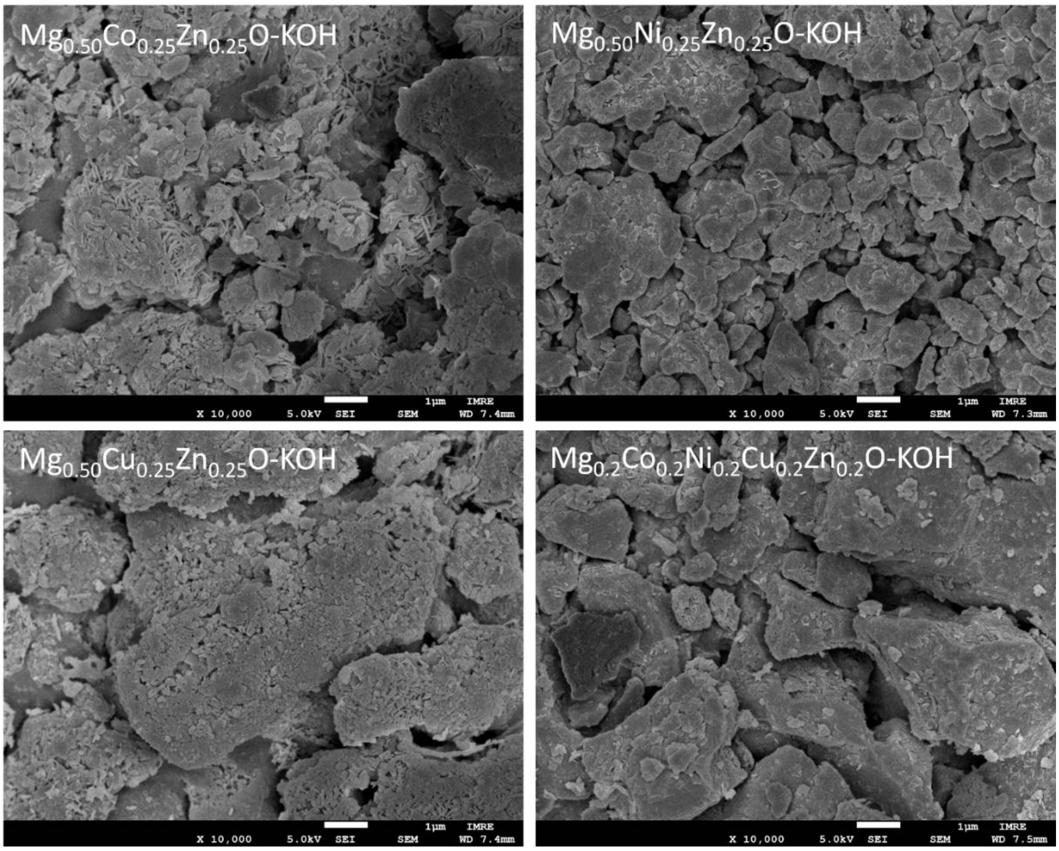

Fig. S27. SEM images of $Mg_{0.50}TM_{0.25}Zn_{0.25}O$ (TM = Co, Ni, Cu) and $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ after soaking in 2 M KOH for 4 weeks.

Fig. S28. The optical photographs of $Mg_{0.50}Co_{0.25}Zn_{0.25}O$, $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$, $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ and $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ before and after soaking in 2 M KOH for 4 weeks at room temperature under constant stirring. The oxide-raw stands for the raw oxides and the oxide-KOH for the oxide soaked in 2 M KOH for 4 weeks.

Table S1 EXAFS fitting parameters of $Mg_{0.50}TM_{0.25}Zn_{0.25}O$ (TM = Co, Ni, Cu)

Edge	Path	CN	σ^2 / Å^2	ΔE_0 / eV	R / Å	R-factor
$Mg_{0.50}Co_{0.25}Zn_{0.25}O$ Zn K-edge	Zn-O	5.6(0.4)	0.0081(0.0011)	5.63(0.78)	2.13(0.01)	0.003
	Zn-Mg	8.1(0.9)	0.0050(0.0013)	7.37(1.19)	2.99(0.02)	
	Zn-Co/Zn	0.2(0.1)	0.0050(0.0013)	7.37(1.19)	2.99(0.01)	
$Mg_{0.50}Co_{0.25}Zn_{0.25}O$ Co K-edge	Co-O	6.4(0.3)	0.0063(0.0007)	2.33(0.62)	2.12(0.01)	0.0004
	Co-Mg	9.6(0.6)	0.0044(0.0006)	4.15(0.69)	2.98(0.01)	
	Co-Co/Zn	2.8(0.6)	0.0044(0.0006)	4.15(0.69)	2.98(0.01)	
$Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ Zn K-edge	Zn-O	5.7(0.5)	0.0078(0.0012)	5.59(0.88)	2.12(0.01)	0.003
	Zn-Mg	7.9(0.9)	0.0054(0.0013)	6.81(1.31)	2.96(0.02)	
	Zn-Ni/Zn	2.0(1.0)	0.0054(0.0013)	6.81(1.31)	2.98(0.01)	
$Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ Ni K-edge	Ni-O	6.2(0.4)	0.0060(0.0007)	0.44(0.67)	2.10(0.01)	0.001
	Ni-Mg	8.1(0.8)	0.0043(0.0008)	3.21(1.09)	2.96(0.02)	
	Ni-Ni/Zn	2.3(0.9)	0.0043(0.0008)	3.21(1.09)	2.97(0.01)	
$Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ Zn K-edge	Zn-O	5.7(0.5)	0.0099(0.0015)	4.92(0.95)	2.12(0.01)	0.003
	Zn-Mg	7.9(1.4)	0.0073(0.0015)	6.89(1.39)	2.98(0.02)	
	Zn-Cu/Zn	2.1(1.1)	0.0073(0.0015)	6.89(1.39)	3.00(0.01)	
$Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ Cu K-edge	Cu-O	3.1(0.6)	0.0067(0.0025)	0.00(2.44)	2.00(0.02)	0.012
	Cu-Mg	6.1(1.3)	0.0054(0.0026)	6.43(2.12)	2.97(0.02)	
	Cu-Cu/Zn	1.2(0.5)	0.0054(0.0026)	6.43(2.12)	2.99(0.02)	

Note: CN, coordination number; σ^2, Debye-Waller factor to account for both thermal and structure disorder; ΔE_0, inner potential correction; R, distance between absorber and backscatter atoms; R-factor indicates the goodness to the fit. The amplitude reduction factor S_0^2 was fixed to 0.98 for Zn, 0.76 for Co, 0.89 for Ni and 0.89 for Cu. Fitting range: Zn K-edge $3.0 \leq k$ (/Å) ≤ 13 and $1.0 \leq R$ (Å) ≤ 3.2; Co K-edge $3.0 \leq k$ (/Å) ≤ 11.939 and $1.0 \leq R$ (Å) ≤ 3.2; Ni K-edge $3.0 \leq k$ (/Å) ≤ 12.896 and $1.0 \leq R$ (Å) ≤ 3.15; Cu K-edge $2.5 \leq k$ (/Å) ≤ 12 and $1.0 \leq R$ (Å) ≤ 3.3.

Table S2 EXAFS fitting parameters of $Mg_{0.50}TM_{0.25}Zn_{0.25}O$ (TM = Co, Ni, Cu), fixing the coordination number to 6 for the first shell and 12 for the second shell.

Edge	Path	CN	σ^2 / Å^2	ΔE_0 / eV	R / Å	R-factor
$Mg_{0.50}Co_{0.25}Zn_{0.25}O$ Zn K-edge	Zn-O	6	0.0088(0.0008)	7.40(0.88)	2.14(0.010)	0.008
	Zn-Mg	11.5(0.1)	0.0076(0.0012)	8.10(1.16)	3.02(0.019)	
	Zn-Co/Zn	0.5(0.1)	0.0076(0.0012)	8.10(1.16)	3.01(0.012)	
$Mg_{0.50}Co_{0.25}Zn_{0.25}O$ Co K-edge	Co-O	6	0.0056(0.0004)	2.10(0.66)	2.12(0.006)	0.002
	Co-Mg	9.4(0.2)	0.0040(0.0013)	4.62(0.80)	2.98(0.011)	
	Co-Co/Zn	2.6(0.2)	0.0040(0.0013)	4.62(0.80)	2.98(0.011)	
$Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ Zn K-edge	Zn-O	6	0.0085(0.0005)	6.19(0.68)	2.13(0.007)	0.002
	Zn-Mg	9.0(0.3)	0.0068(0.0008)	6.87(0.81)	2.97(0.008)	
	Zn-Ni/Zn	3.0(0.3)	0.0068(0.0008)	6.87(0.81)	2.97(0.005)	
$Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ Ni K-edge	Ni-O	6	0.0056(0.0003)	0.88(0.50)	2.10(0.004)	0.002
	Ni-Mg	8.9(0.2)	0.0045(0.0006)	4.14(0.59)	2.97(0.008)	
	Ni-Ni/Zn	3.1(0.2)	0.0045(0.0006)	4.14(0.59)	2.97(0.005)	
$Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ Zn K-edge	Zn-O	6	0.0102(0.0011)	7.40(1.32)	2.14(0.015)	0.02
	Zn-Mg	9.7(0.4)	0.0073(0.0020)	1.34(1.16)	2.88(0.016)	
	Zn-Cu/Zn	2.3(0.4)	0.0073(0.0020)	1.34(1.16)	2.75(0.021)	
$Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ Cu K-edge	Cu-O1	4	0.0079(0.0007)	6.31(1.24)	2.02(0.010)	0.003
	Cu-O2	2	0.0173(0.0030)	6.31(1.24)	2.28(0.019)	
	Cu-Mg	8.7(0.3)	0.0086(0.0008)	3.97(1.06)	2.97(0.012)	
	Cu-Cu/Zn	3.3(0.3)	0.0086(0.0008)	3.97(1.06)	2.99(0.008)	

Note: CN, coordination number; σ^2, Debye-Waller factor to account for both thermal and structure disorder; ΔE_0, inner potential correction; R, distance between absorber and backscatter atoms; R-factor indicates the goodness to the fit. The amplitude reduction factor S_0^2 was fixed to 0.98 for Zn, 0.76 for Co, 0.89 for Ni and 0.89 for Cu. Fitting range: Zn K-edge $3.0 \le k$ (/Å) ≤ 13 and $1.0 \le R$ (Å) ≤ 3.2; Co K-edge $3.0 \le k$ (/Å) ≤ 11.939 and $1.0 \le R$ (Å) ≤ 3.2; Ni K-edge $3.0 \le k$ (/Å) ≤ 12.896 and $1.0 \le R$ (Å) ≤ 3.15; Cu K-edge $3.0 \le k$ (/Å) ≤ 12 and $1.0 \le R$ (Å) ≤ 3.3.

Table S3 SEM-EDX results of the metal element ratios in $Mg_{0.50}Co_{0.25}Zn_{0.25}O$.

	Mg	Co	Zn
1	54.1	22.7	23.2
2	49	24.9	26.1
3	44.9	27.4	27.7
Average	49.3	25.0	25.7
SD	3.76	1.92	1.86

Note: SD stands for standard deviation. It also applicable to Table S3-S9.

Table S4 SEM-EDX results of the metal element ratios in $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$.

	Mg	Ni	Zn
1	46.6	26.6	26.8
2	50.1	25	24.9
3	49.9	24.9	25.2
Average	48.9	25.5	25.6
SD	1.60	0.78	0.83

Table S5 SEM-EDX results of the metal element ratios in $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$.

	Mg	Cu	Zn
1	56.4	20.9	22.7
2	52.3	24.3	23.4
3	49.9	25.2	25.0
Average	52.9	23.5	23.7
SD	2.68	1.85	0.96

Table S6 SEM-EDX results of the metal element ratios in $Mg_{0.20}Co_{0.20}Ni_{0.20}Cu_{0.20}Zn_{0.20}O$.

	Mg	Co	Ni	Cu	Zn
1	18.7	18.9	17.9	22.3	22.3
2	16.4	22.6	21.2	20.3	19.6
3	18.2	18.7	19	22.1	22
4	17	21.1	20.6	20.4	21
5	19.7	18	17.3	22.5	22.4
6	16.1	22.4	21.5	20.6	19.4
7	18.2	17.9	17.2	23.8	22.9
8	21.6	16.3	16.3	22.6	23.2
9	18.1	20.7	20.2	20.9	20.2
Average	18.22	19.62	19.02	21.72	21.44
SD	1.60	2.05	1.82	1.15	1.35

Table S7 SEM-EDX results of the metal element ratios in $Mg_{0.50}Co_{0.25}Zn_{0.25}O$ soaking in 2 M KOH for 4 weeks.

	Mg	Co	Zn	K
1	52.6	39	8.3	0.1
2	58	35.2	5.8	0
3	58.2	33.6	8.1	0.1
4	59.8	31.4	8.8	0
5	58.1	34.2	7.7	0
6	61.5	31	7.5	0.1
7	62.2	29.1	8.7	0
8	61.9	30.9	7.1	0.1
9	59.3	33.8	6.9	0
10	63.7	30.2	6.1	0
Average	59.53	32.84	7.5	0.04
SD	2.97	2.78	0.98	0.05

Table S8 SEM-EDX results of the metal element ratios in $Mg_{0.50}Ni_{0.25}Zn_{0.25}O$ soaking in 2 M KOH for 4 weeks.

	Mg	Ni	Zn	K
1	50.8	25.2	24.1	0
2	51.2	26	22.8	0.1
3	50.1	26.9	23	0
4	49.5	27.4	23	0
5	49.4	27	23.5	0.1
6	49.9	26.3	23.8	0
7	49.8	26.6	23.3	0.2
8	49.1	27.3	23.5	0.1
Average	49.98	26.59	23.38	0.06
SD	0.67	0.69	0.41	0.07

Table S9 SEM-EDX results of the metal element ratios in $Mg_{0.50}Cu_{0.25}Zn_{0.25}O$ soaking in 2 M KOH for 4 weeks.

	Mg	Cu	Zn	K
1	63.6	29.5	6.9	0
2	63.9	28.5	7.6	0
3	68.3	20.8	10.8	0.1
4	75.2	17.2	7	0
5	75.2	13.1	11.7	0
6	73	16.9	10	0.1
7	74.6	15.5	10	0
8	65.6	25.2	9.3	0
9	74.5	13.9	11.6	0
10	72.9	15.8	11.3	0
Average	70.68	19.64	9.62	0.02
SD	4.57	5.74	1.77	0.04

Table S10 SEM-EDX results of the metal element ratios in $Mg_{0.20}Co_{0.20}Ni_{0.20}Cu_{0.20}Zn_{0.20}O$ soaking in 2 M KOH for 4 weeks.

	Mg	Co	Ni	Cu	Zn	K
1	20.8	19.6	19.5	19.4	20.5	0.1
2	21.3	18.9	19	20.3	20.6	0
3	17	22	21.6	19.9	19.5	0
4	19.5	20.3	20	19.7	20.3	0
5	18.2	21.7	21.6	19.4	19.1	0
6	21.2	21.9	20.3	17.3	19.3	0
7	19.9	19.2	19.1	20.2	21.7	0
8	18.6	20.9	20.1	19.6	20.5	0.3
9	18.6	20.9	19.9	20.1	20.4	0
10	19	19.6	20	19.9	21.5	0
average	19.41	20.5	20.11	19.58	20.34	0.04
SD	1.33	1.09	0.85	0.82	0.82	0.09