Supplementary Information

for

Tuning Electronic Structure for Enhanced Photocatalytic Efficiency: Theoretical and Experimental Investigation of $CuM_{1-x}M'_xO_2$ (M, M′=B, Al, Ga, In) Solid Solutions

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Thermodynamic stability

To schematize the thermodynamic solubility limit of $CuM_{1-x}M'_xO_2$, we compared their enthalpy of mixing (ΔH_{mix}) and the configurational entropy (ΔS_{mix}), ΔH_{mix} is defined as:

$\Delta H_{mix}[CuM_{1-x}M'_xO_2] = E(CuM_{1-x}M'_xO_2)-xE(CuM'O_2)-(1-x)E(CuMO_2)$

where $E(CuM_{1-x}M'_xO_2)$ is the total energy of $CuM_{1-x}M'_xO_2$ and $E(CuM'O_2)$ and $E(CuMO_2)$ are the total energies of ground states of $CuM'O_2$ and $CuMO_2$.

ΔH_{mix} of $CuAl_{1-x}Ga_xO_2$ solid solutions can be reliably represented by a regular solution model, which has a symmetry of x=0.5. To capture the asymmetry of ΔH_{mix} with respect to composition of $CuAl_{1-x}B_xO_2$ ($0 \le x \le 0.417$), $CuGa_{1-x}B_xO_2$ ($0 \le x \le 0.167$), $CuIn_{1-x}B_xO_2$ ($0 \le x \le 0.167$), $CuAl_{1-x}In_xO_2$ and $CuGa_{1-x}In_xO_2$, a sub-regular solution model was used. The regular solution model and sub-regular solution model can be represented mathematically by the following equation:

$\Delta H_{mix} = x(1-x)*\Omega(x)$

$\Delta H_{mix} = x(1-x)*[\Omega_1(1-x)+ \Omega_2 x]$

where x is the molar concentration, Ω is the interaction parameter.

$\Omega(x,0.0\ K) = \Delta H_{mix}(x,0.0\ K)/[x(1-x)]$

The entropy of a solid solution is a sum of the configurational entropy (ΔS_{mix}) and the vibrations entropy. The vibrational entropy is negligible compared to ΔS_{mix}, ΔS_{mix} has a simple functional form.

$\Delta S_{mix} = -k_B[x\ln x+(1-x)\ln(1-x)]$, k_B is a Boltzmann constant.

The stability of solid solution is determined by the Gibbs-free energy of mixing (ΔG_{mix}), which includes not only ΔH_{mix} but also the contribution of ΔS_{mix} and temperature, which is given by:

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = (1-x)x* \Omega + k_B T[(1-x)\ln(1-x) + x\ln x]$

where, ΔS_{mix} is positive and $-T\Delta S_{mix}$ is negative, indicating $-T\Delta S_{mix}$ has stabilizing effect. Moreover, from ΔG_{mix}, one obtains the solubility limits for binodal and spinodal decomposition, and the critical temperature as shown in **Figure 2b**.

The calculation of lattice mismatch

The lattice mismatch, $\triangle a/a$, and $\triangle c/c$ between $CuMO_2$ and CuM'_xO_2, can be calculated by the following equation:

$$\frac{\triangle a}{a} = \frac{|a_{CuMO_2} - a_{CuM'O_2}|}{a_{CuMO_2}}$$

$$\frac{\triangle c}{c} = \frac{|c_{CuMO_2} - c_{CuM'O_2}|}{c_{CuMO_2}}$$

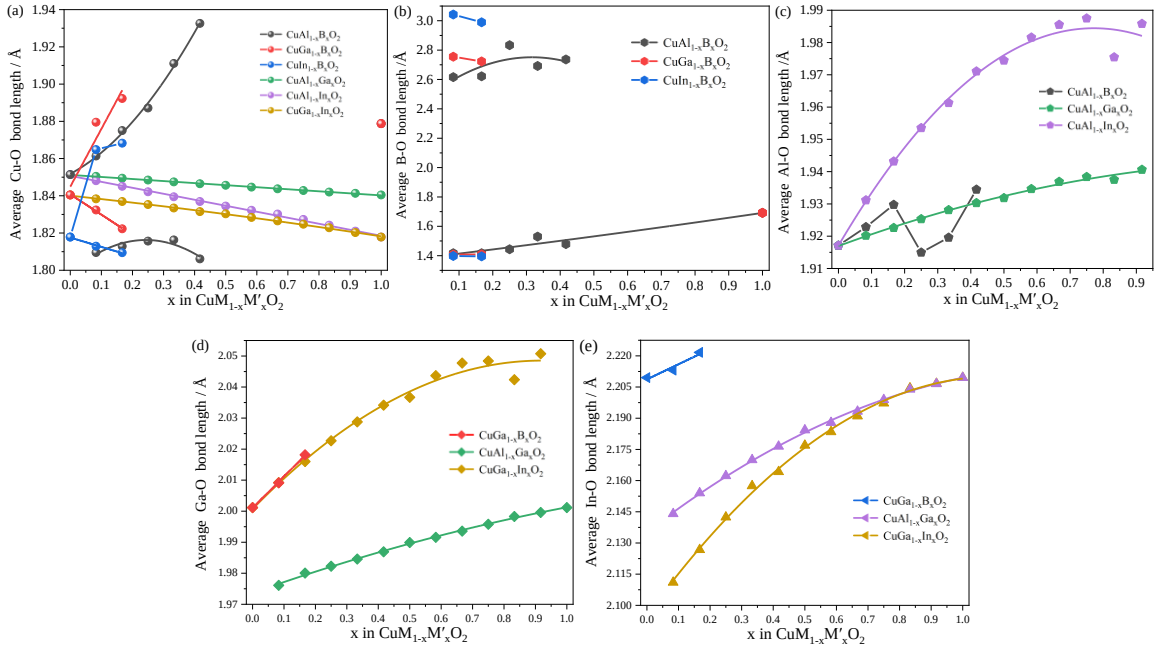

Figure S1. Average (a) Cu-O, (b) Al-O, (c) B-O, (d) Ga-O and (e) In-O bond lengths of $CuM_{1-x}M'_xO_2$ solid solutions as a function of content x.

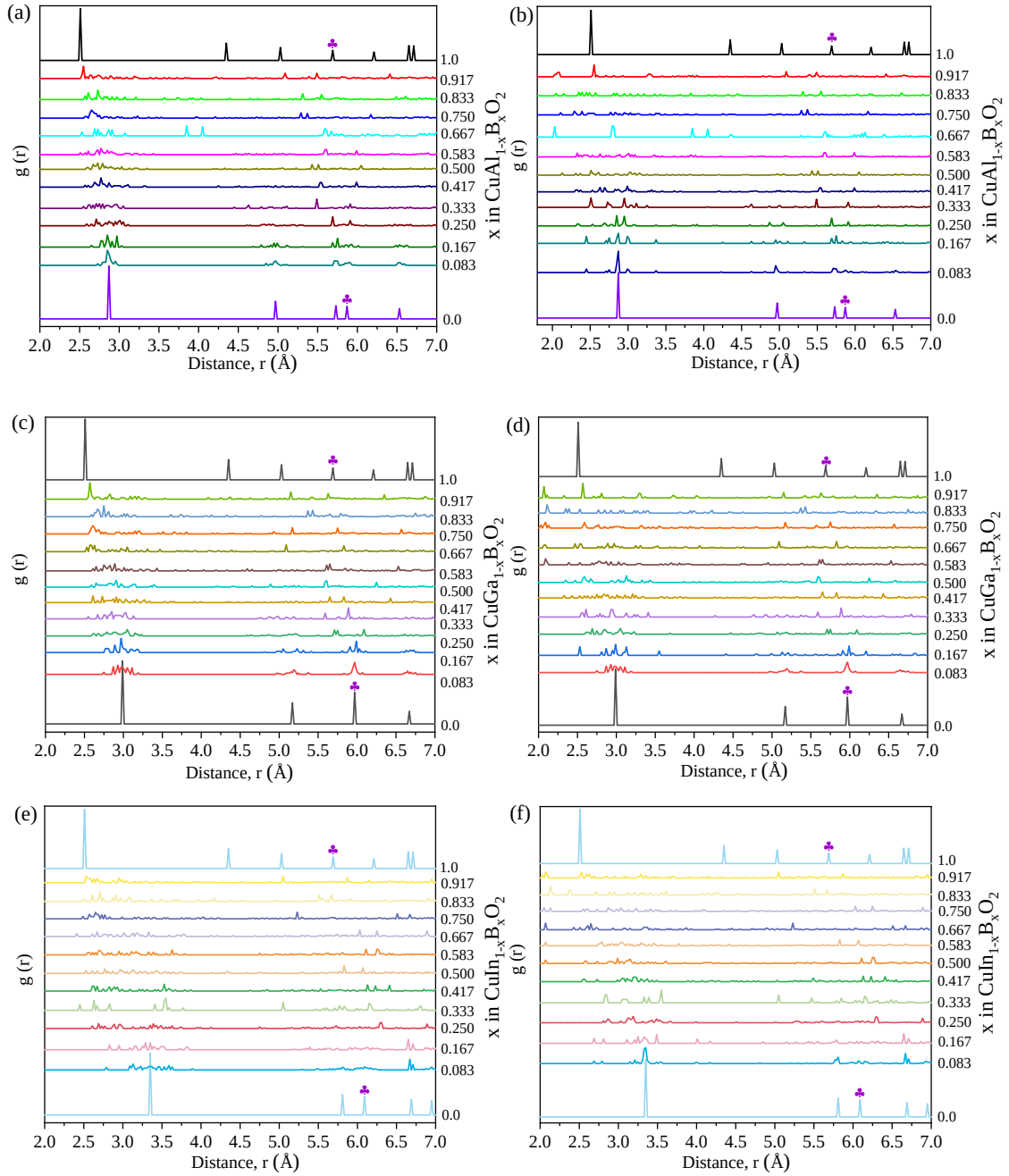

Figure S2. The partial radial distribution functions (a, c, e) Cu-Cu and (b, d, f) M-M average nearest neighbor occurrence vs distance for $CuM_{1-x}B_xO_2$ compounds, the corresponding RDF peaks of Cu-Cu and M-M in the nearest interlayer are marked with clubs.

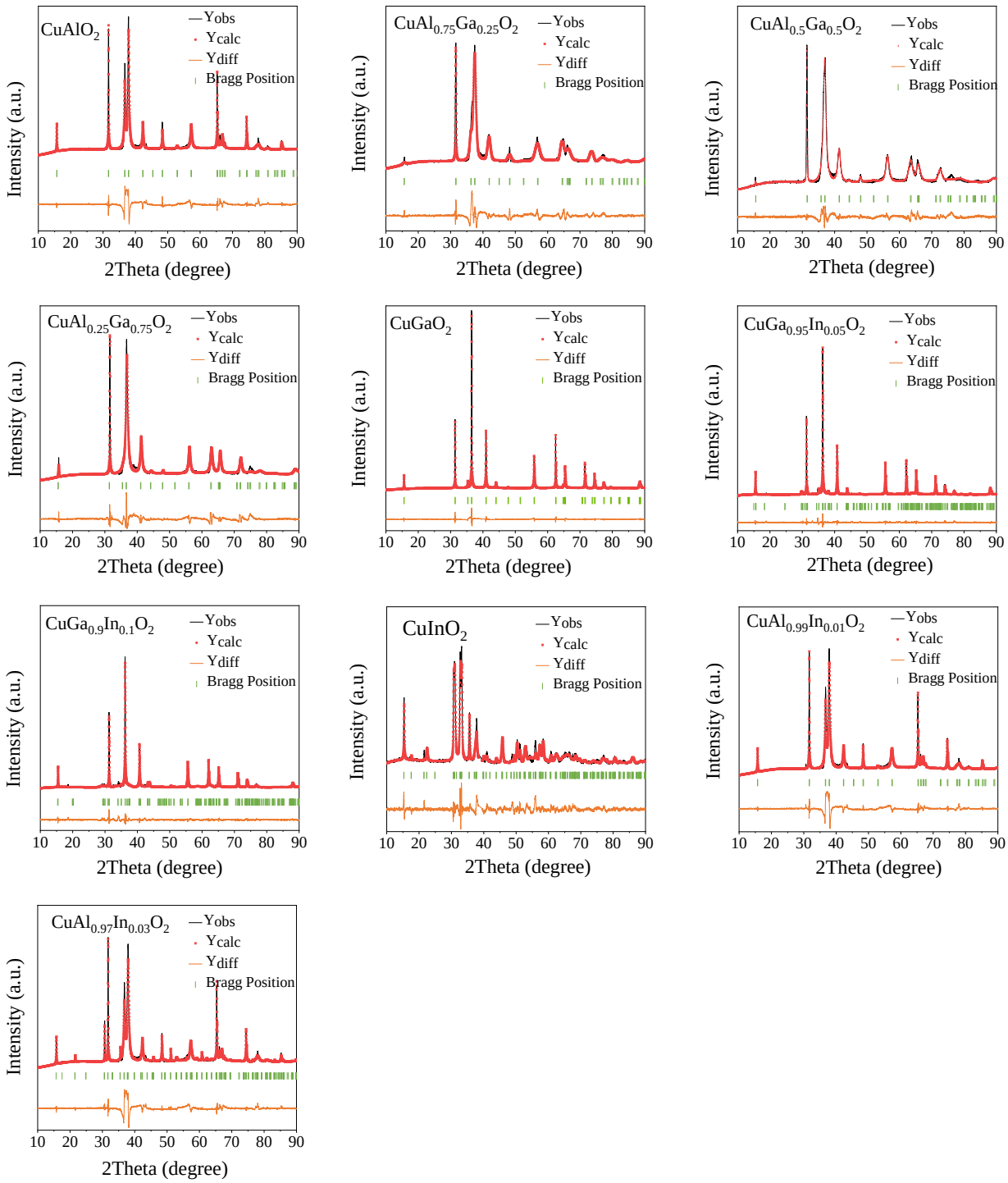

Figure S3. Powder X-ray diffraction and Rietveld plots of $CuAl_{1-x}Ga_xO_2$, $CuGa_{1-x}In_xO_2$ and $CuAl_{1-x}In_xO_2$ samples.

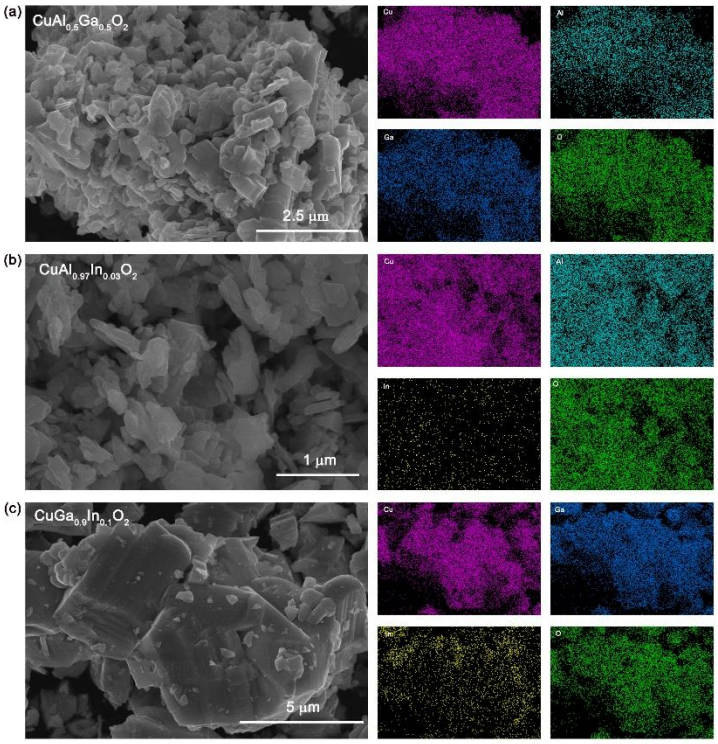

Figure S4. The SEM images and EDS element mappings of (a) $CuAl_{0.5}Ga_{0.5}O_2$, (b) $CuAl_{0.97}In_{0.03}O_2$, (c) $CuGa_{0.9}In_{0.1}O_2$ samples.

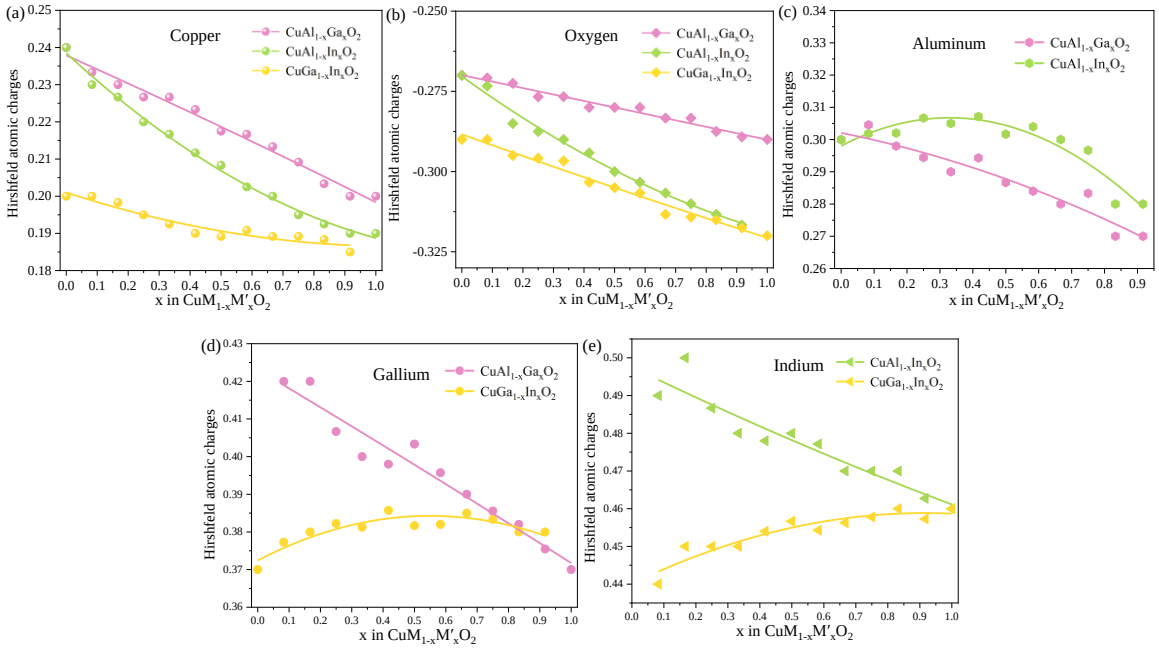

Figure S5. Average Hirshfeld charge Cu, O, Al, Ga and In atoms in $CuM_{1-x}M'_xO_2$ solid solutions.

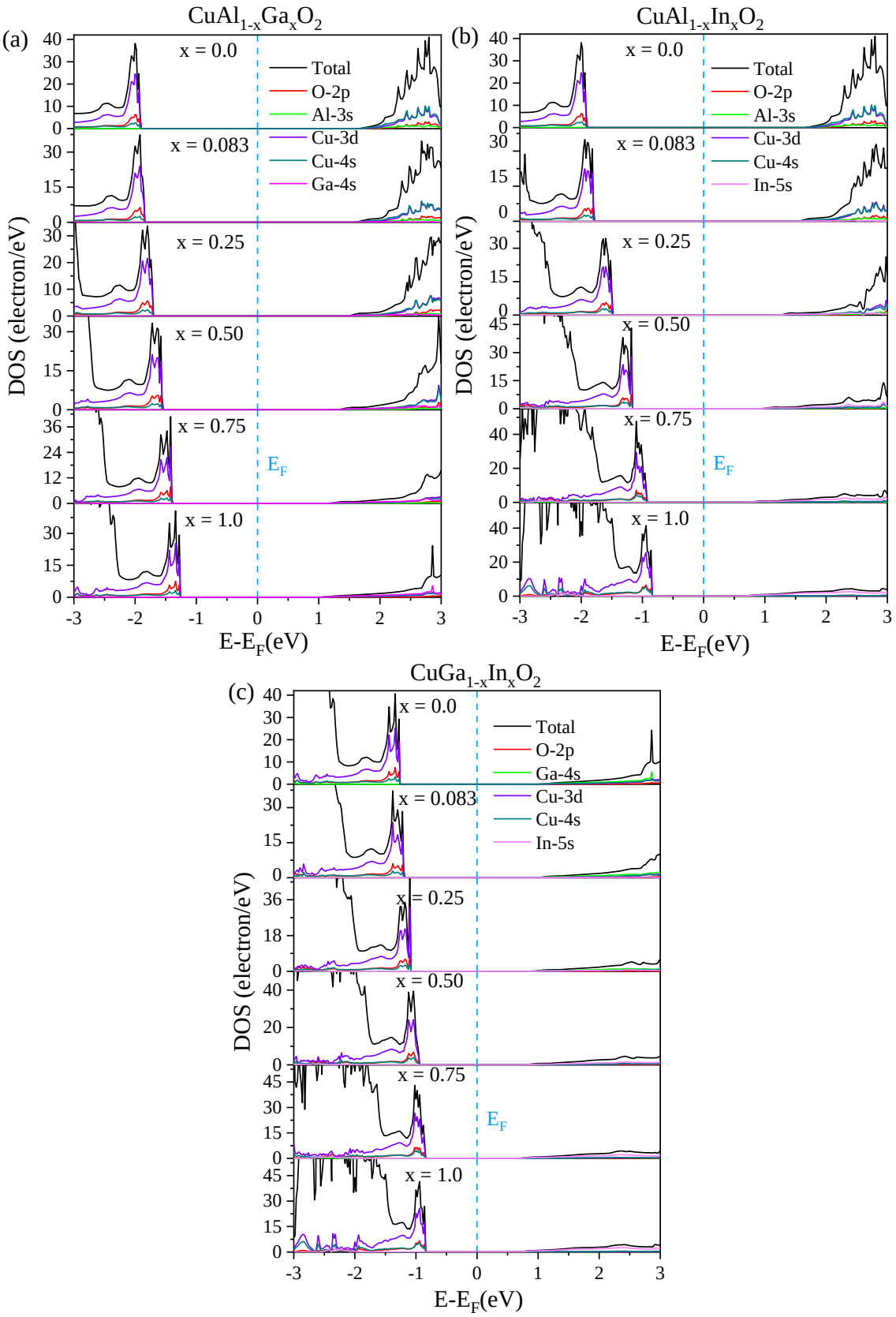

Figure S6. Projected density of states of $CuAl_{1-x}Ga_xO_2$, $CuGa_{1-x}In_xO_2$ and $CuAl_{1-x}In_xO_2$ solid solutions as a function of content x.

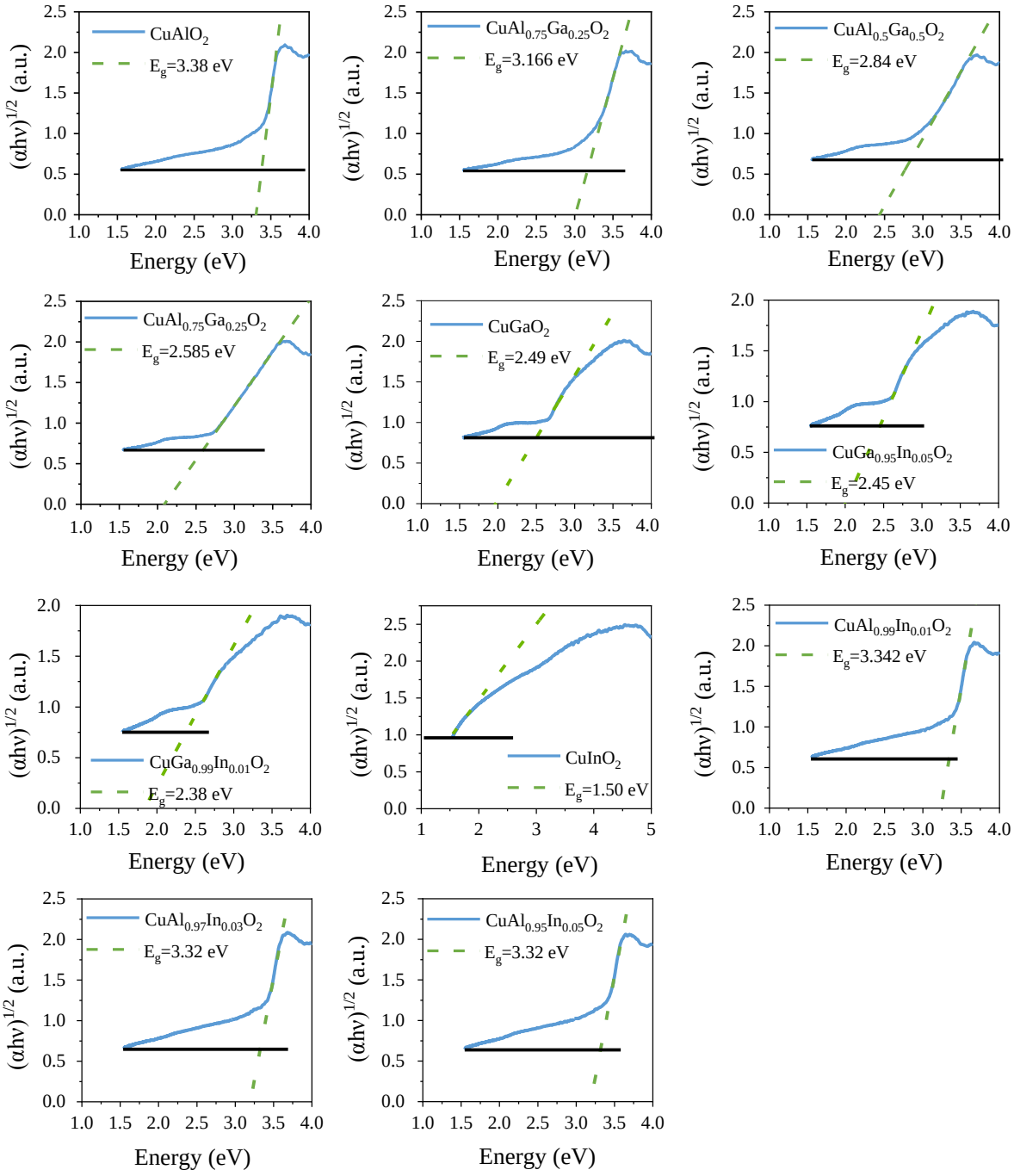

Figure S7. Optical band gaps of $CuAl_{1-x}Ga_xO_2$, $CuGa_{1-x}In_xO_2$ and $CuAl_{1-x}In_xO_2$ samples were estimated by the Tauc plot method.

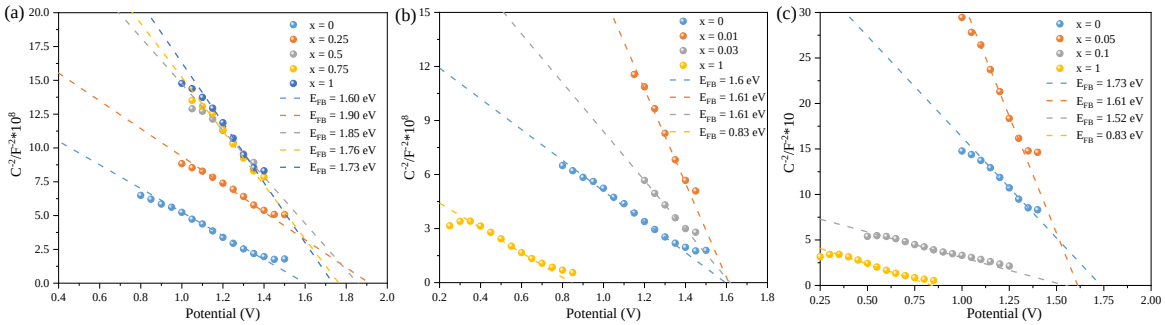

Figure S8. Mott–Schottky plots of $CuAl_{1-x}Ga_xO_2$ (x=0, 0.25, 0.5, 0.75, 1), $CuAl_{1-x}In_xO_2$ (x=0, 0.01, 0.03, 1) and $CuGa_{1-x}In_xO_2$ (x=0, 0.05, 0.1, 1) in aqueous Na_2SO_4 solution.

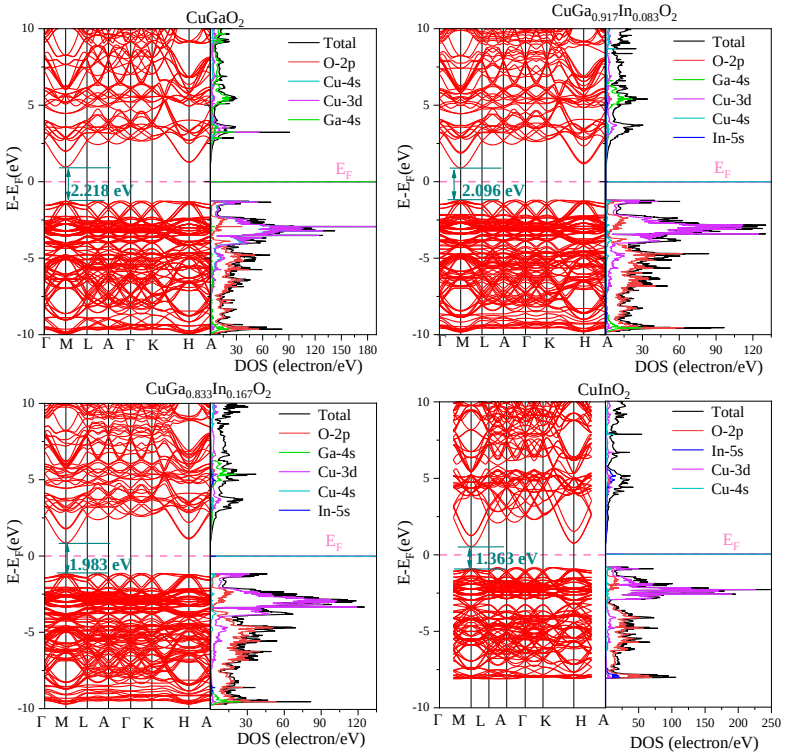

Figure S9. Band structure and the corresponding density of states of $CuGa_{1-x}In_xO_2$ solid solutions.

Table S1 The calculated lattice constants of $CuBO_2$, $CuAlO_2$, $CuGaO_2$ and $CuInO_2$.

	This work	Computational reference value		Experimental value/Å
	Lattice constants /Å	Lattice constants /Å	Computational method	
$CuBO_2$	a=b=2.5117, c=16.5031	a=b=2.512, c=16.504[29] a=b=2.6, c=16.6[30]	GGA- PBEsol PBE-GGA	a=b=2.53, c=16.58 (Pulsed laser deposition technique[35])
$CuAlO_2$	a=b=2.8659, c=16.9179	a=b=2.861, c=16.978[31] a=b=2.89, c=17.0[30]	WIEN97 PBE-GGA	a=b=2.8617, c=16.9407 (Hydrothermal method[36]) a=b=2.8730, c=16.9460 (Solid-state reaction[40])
$CuGaO_2$	a=b=2.9864, c=17.1373	a=b=2.9770, c=17.1710[32] a=b=2.963, c=17.172[33]	TB-LMTO LAPW	a=b=2.9748, c=17.155 (Hydrothermal method [37]) a=b=2.986, c=17.229 (Hydrothermal method)[49] a=b=2.976, c=17.160 (Solid-state reaction[38])
$CuInO_2$	a=b=3.3488, c=17.3237	a=b=3.34, c=17.5[30] a=b=3.359, c=17.529[34] a=b=3.2920, c=17.3880[33]	PBE-GGA GGA-PBE TB-LMTO	a=b=3.2922, c=17.388 (Cation exchange reaction)[39]

Table S2. Rietveld refinement results of XRD pattern for all compositions of $CuAl_{1-x}Ga_xO_2$, $CuGa_{1-x}In_xO_2$ and $CuAl_{1-x}In_xO_2$ samples.

Material	**Lattice parameter**				
	a, b (Å)	c (Å)	α, β (°)	γ (°)	V (Å^3)
$CuAlO_2$	2.8578	16.9288	90.0	120.0	119.8725
$CuAl_{0.75}Ga_{0.25}O_2$	2.8883	16.9688	90.0	120.0	122.5952
$CuAl_{0.5}Ga_{0.5}O_2$	2.9305	17.0566	90.0	120.0	126.8562
$CuAl_{0.25}Ga_{0.75}O_2$	2.9616	17.1356	90.0	120.0	130.1631
$CuGaO_2$	2.9766	17.1632	90.0	120.0	131.6990
$CuAl_{0.99}In_{0.01}O_2$	2.8665	16.9384	90.0	120.0	119.6908
$CuAl_{0.97}In_{0.03}O_2$	2.8783	16.9482	90.0	120.0	119.9165
$CuInO_2$	3.3215	17.4000	90.0	120.0	166.2350
$CuGa_{0.95}In_{0.05}O_2$	2.9894	17.1701	90.0	120.0	132.9590
$CuGa_{0.9}In_{0.1}O_2$	2.9923	17.1724	90.0	120.0	133.1642
$CuGa_{0.85}In_{0.15}O_2$	2.9919	17.1767	90.0	120.0	133.1579

Table S3. The atomic percentage of different cations extracted from SEM-EDS for $CuAl_{0.5}Ga_{0.5}O_2$, $CuAl_{0.97}In_{0.03}O_2$ and $CuGa_{0.9}In_{0.1}O_2$ samples.

Material	Atomic concentration from XPS				
	Cu (%)	Al (%)	Ga (%)	In (%)	O (%)
$CuAl_{0.5}Ga_{0.5}O_2$	26.1	13.2	13.8	0.0	47.3
$CuAl_{0.97}In_{0.03}O_2$	25.7	24.3	0.0	1.1	48.5
$CuGa_{0.9}In_{0.1}O_2$	21.7	0.0	25.8	2.4	50.1