SUPPORTING INFORMATION TO

Ab initio study of Cu-based delafossites as alternative to nickel oxide in photocathodes: effects of Mg-doping and surface electronic features.

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Mg - M substitution energies

Table S1. Mg defect formation energies (ΔH_D in eV) at different thermodynamic stability condition

$CuM_{0.92}M_{0.08}O_2$	O-rich	Cu-rich	M-rich
M = Al	0.403	1.409	1.409
M = Ga	0.287	1.288	1.288
M = Cr	1.442	1.294	1.591

Calculation of workfunction values

In order to evaluate the absolute potentials of valence and conduction bands (VB and CB, respectively), we applied a similar approach as in the recent work by M. Toroker and E. A. Carter [20]. In particular we used the delafossite (011) orthorhombic surface slab model to compute the vacuum energy by evaluating the electrostatic potential along the direction normal to the surface plane. The workfunction is set as the difference between this vacuum energy and the Fermi energy associated with the slab model. The band gap center is defined by adding to the negative of the workfunction (the VB maximum edge) half of the band gap, computed on the system bulk. Figure S1 depicts the calculations of the electrostatic potential of vacuum for our materials and the relative workfunction values taken as the difference from the Fermi level and E_{vacuum}. All the data needed for the calculation of the valence band edge are listed in Table S2. Note that in the calculation of V_{oc} these values have been converted from eV to Volt for the normal hydrogen electrode.

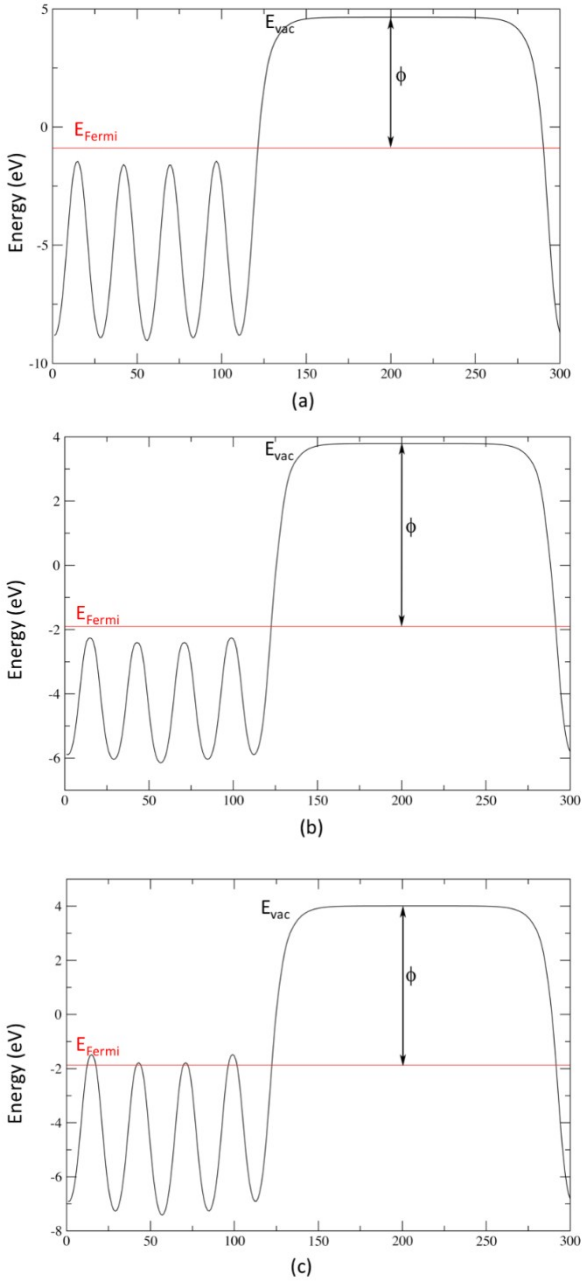

Figure S1. Workfunction calculations for (a) $CuAlO_2$; (b), $CuGaO_2$ (b) and $CuCrO_2$ (c). The red line indicates the position of the Fermi level, the black arrow indicates the workfunction (i.e. the energy needed to remove an electron from the surface).

Table S2. Energy levels used in the calculation of the valence band edge. Valence band maximum and conduction band minimum are taken from the calculation on the surface (PBE+U), while the band gap is computed from the bulk structure with the HSE06 hybrid density functional.

(eV)	E_{vac}	VB_{max}	CB_{min}	**BGC**	E_{gap} **(HSE)**	VB_{edge}
CuAlO2	5.152	-0.106	1.852	0.873	3.352	-5.955
CuGaO2	4.176	-1.210	-0.119	-0.664	2.100	-5.890
CuCrO2	4.372	-0.735	0.507	-0.114	2.83	-5.903