SUPPORTING INFORMATION

Electronic Structure and Photocatalytic Activity of Wurtzite Cu−Ga−S Nanocrystals and their Zn substitution

Tarek A. Kandiel[a b], Dalaver H. Anjum[c], Philippe Sautet,[d] Tangui Le Bahers,[d] and Kazuhiro Takanabe[a*]

[a] Division of Physical Sciences and Engineering, KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), 4700 KAUST, Thuwal 23955-6900, Saudi Arabia.
E-mail: kazuhiro.takanabe@kaust.edu.sa
[b] Department of Chemistry, Faculty of Science, Sohag University, Sohag 82524, Egypt.
[c] Imaging and Characterization Lab, Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.
[d] Université de Lyon, Université Claude Bernard Lyon1, ENS Lyon, CentreNationale de Recherche Scientifique, 46 allée d'Italie,
69007 Lyon Cedex 07, France.

Experimental details

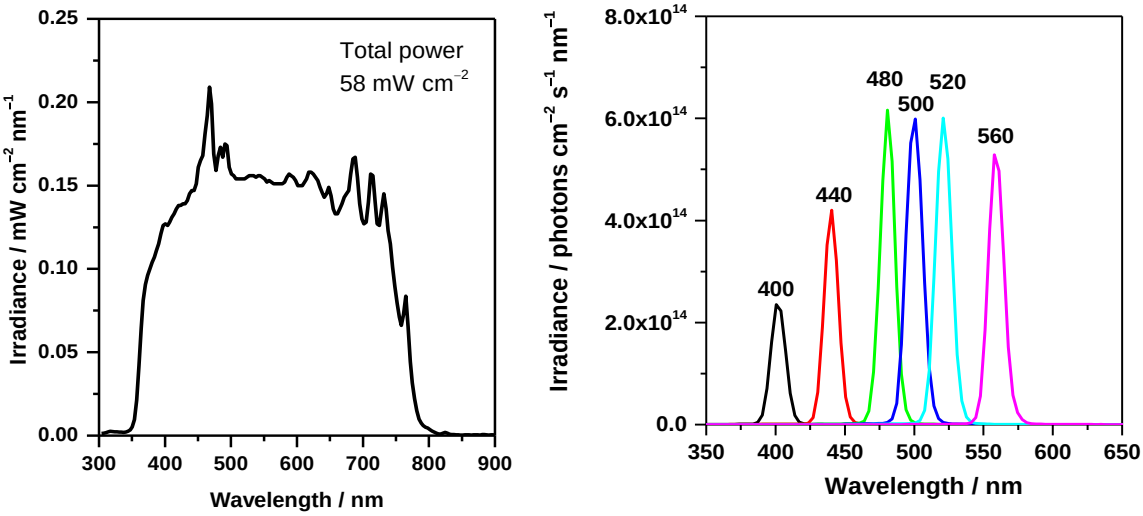

Figure S1. Photon distribution of the 300 W Xe lamp (left) full arc and (right) adapted with band-pass filters used for the apparent quantum efficiency calculations.

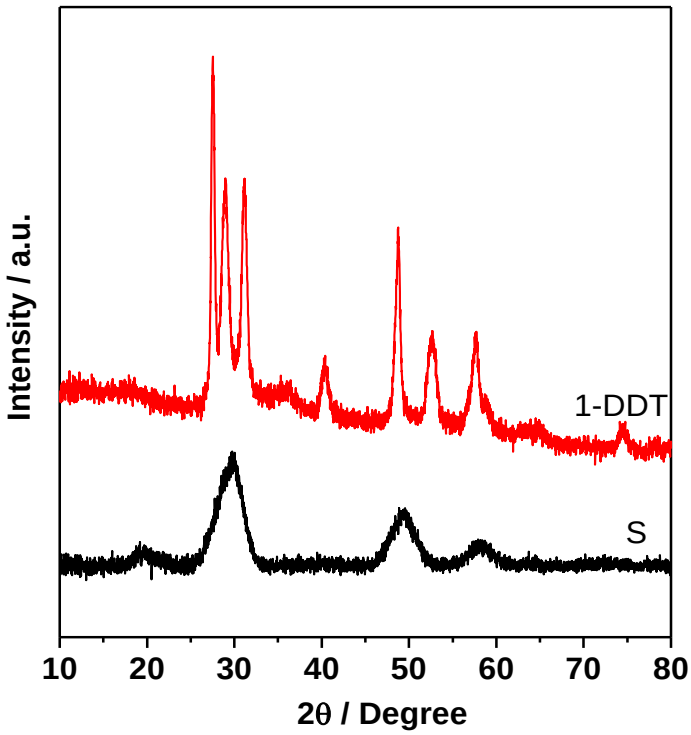

Figure S2. X-ray diffraction patterns of $CuGa_5S_8$ ternary nanocrystals prepared using 1-dodecanethiol (1-DDT) and sulfur metal (S) as a sulfur source.

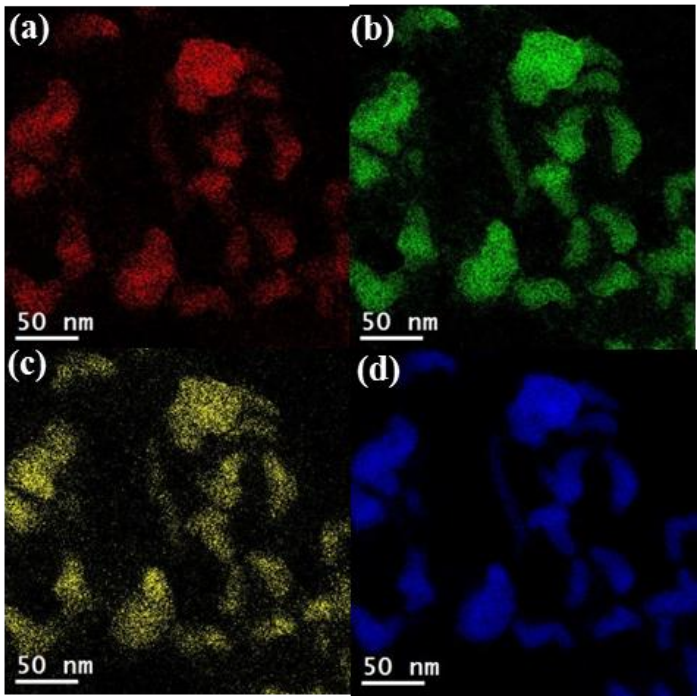

Figure S3. EFTEM elemental mapping of (a) Cu, (b) Ga, (c) Zn and (d) S in $Zn_{0.6}$-$CuGa_5S_8$ nanocrystals.

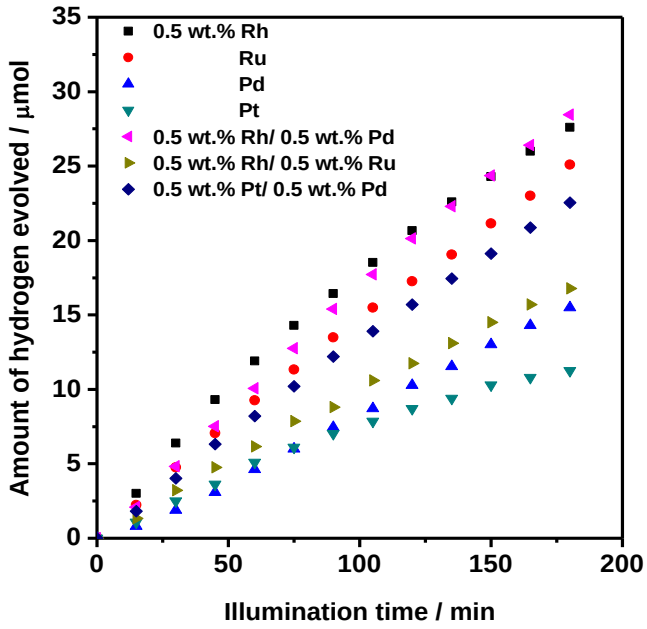

Figure S4. Time courses of photocatalytic H_2 evolution using $Zn_{0.6}$-$CuGa_5S_8$ loaded with various cocatalyst from an aqueous Na_2S (0.05 mol L^{-1})/Na_2SO_3 (0.3 mol L^{-1}) solution under visible-light illumination (λ 385-740 nm).

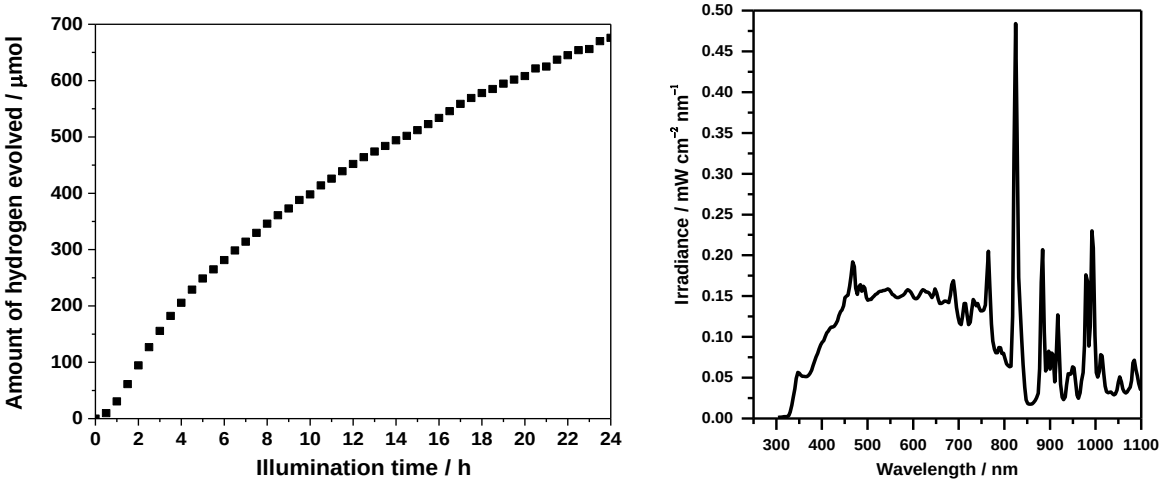

Figure S5. Time course of photocatalytic H_2 evolution using $Zn_{0.6}$-$CuGa_5S_8$ loaded with 0.5 wt% Rh from an aqueous Na_2S (0.05 mol L^{-1})/Na_2SO_3 (0.3 mol L^{-1}) 150 mL solution under solar light illumination (right).

Theoretical details

Geometry

The chalcopyrite structure of $CuGaS_2$ is a body-centered tetragonal cell that has the space group **I-*42d***. The cell parameters and Wyckoff positions are presented in Table S1. In this structure, the Cu and Ga atoms are located in tetrahedron made of sulfur atoms. The sulfur atoms are located in tetrahedron made by 2 Cu and 2 Ga atoms. The computed and experimental lattice parameters are in the Table S1. The average error on the lattice parameter is around 0.6% that is in the standard error range for PBE0 functional.[1]

Table S1. Crystal structure parameters of the chalcopyrite structure of $CuGaS_2$.

Cell Parameters		Wyckoff positions
Exp[2]	**Computed**	
$\boldsymbol{a}$ = 5.347 Å $\boldsymbol{c}$ = 10.474 Å	$\boldsymbol{a}$ = 5.389 Å $\boldsymbol{c}$ = 10.523 Å	S: ***8d*** $\left(x, \frac{1}{4}, \frac{1}{8}\right)$ Cu: ***4a*** $(0, 0, 0)$ Ga: ***4b*** $\left(0, 0, \frac{1}{2}\right)$

For the wurtzite $CuGaS_2$, the wurtzite structure of ZnO was selected as starting point. The unit cell of the wurtzite structure contains two Zn atoms and two O atoms. Starting from a 2x2x1 supercell of wurtzite, all the oxygen atoms were substituted by sulfur atoms. Half of the Zn atoms were substituted by Cu atoms and the other half by Ga atoms. All possibilities of relative positions of Cu and Ga in the cation sublattice were built with the solid solution tool implemented in CRYSTAL14 using the CONFCNT keyword. Among the 20 configurations generated, one of them lead to the structure presented in the Figure S6. The two advantages of this structure are that, the surrounding of sulfur, copper and gallium atoms is the same than in the chalcopyrite structure and the Cu and Ga atoms are mixed in the sublattice of the cations in agreement in the experimental observation.

(a)

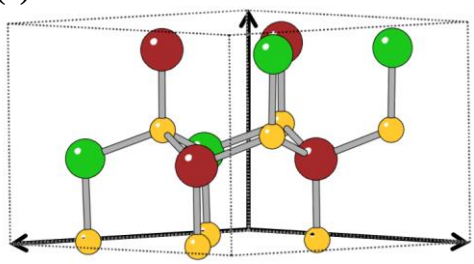

Figure S6. Unit cell of the selected wurtzite structure of $CuGaS_2$.

The newly created structure is no longer in a hexagonal group, but in a monoclinic one. Nevertheless, by fully relaxing the cell parameter of the new structure, it is found that they stay almost in the hexagonal restrictions that are $\boldsymbol{a} = \boldsymbol{b} \neq \boldsymbol{c}$ and $\boldsymbol{\alpha} = \boldsymbol{\beta} = 90°$ and $\boldsymbol{\gamma} = 120°$, with $\boldsymbol{a}$ = 7.43 Å, $\boldsymbol{b}$ = 7.60 Å, $\boldsymbol{c}$ = 6.07 Å, $\boldsymbol{\alpha} = \boldsymbol{\beta} = 90°$, $\boldsymbol{\gamma}$ = 119.3°. All the fractional coordinates of the atoms are gathered in Table S2.

Table S2. Fractional coordinates of the optimized wurtzite structure of $CuGaS_2$.

Atom	x	y	z
S	-0.3307	-0.1614	0.0169
S	0.1693	-0.1614	0.0169
S	-0.3323	0.3354	0.0052
S	0.1677	0.3354	0.0052
S	-0.1677	-0.3354	-0.4948
S	-0.1693	0.1614	-0.4831
S	0.3307	0.1614	-0.4831
S	0.3323	-0.3354	-0.4948
Cu	-0.3353	0.3294	0.3810
Cu	0.1647	0.3295	0.3810
Cu	-0.1647	-0.3294	-0.1190
Cu	0.3353	-0.3295	-0.1190
Ga	-0.1697	0.1607	-0.1116
Ga	0.3304	0.1607	-0.1116
Ga	-0.3303	-0.1607	0.3884
Ga	0.1696	-0.1607	0.3884

Starting from this wurtzite structure, the gallium rich compound $CuGa_5S_8$ was created from the 1x1x4 supercell of the wurtzite by substitution of 4 Cu atoms by 4 Ga atoms, and removing 8 Cu atoms, leading to the formula $Cu_4Ga_{20}S_{32}$. The $CuZn_{0.5}Ga_2S_4$ compound was created from the unit cell of the wurtzite structure by substitution of 1 Cu atom by 1 Zn atom, and by removing 1 Cu atom leading to the formula $Cu_2ZnGa_4S_8$. Finally, the $CuZn_{0.43}Ga_{2.43}S_{4.57}$ was created from the $CuGa_5S_8$ structure by substitutions of 3 Ga atoms by 3 Zn atoms and by adding 3 Cu atoms giving the formula $Cu_7Zn_3Ga_{17}S_{32}$.
The schemes of all the computed structures are presented in Figure S7. Because the unit cell of $CuGaS_2$ and $CuZn_{0.5}Ga_2S_4$ is four times smaller than the two other wurtzite structures, they were multiplied by 4 along the ***c*** direction to facilitate the comparison.

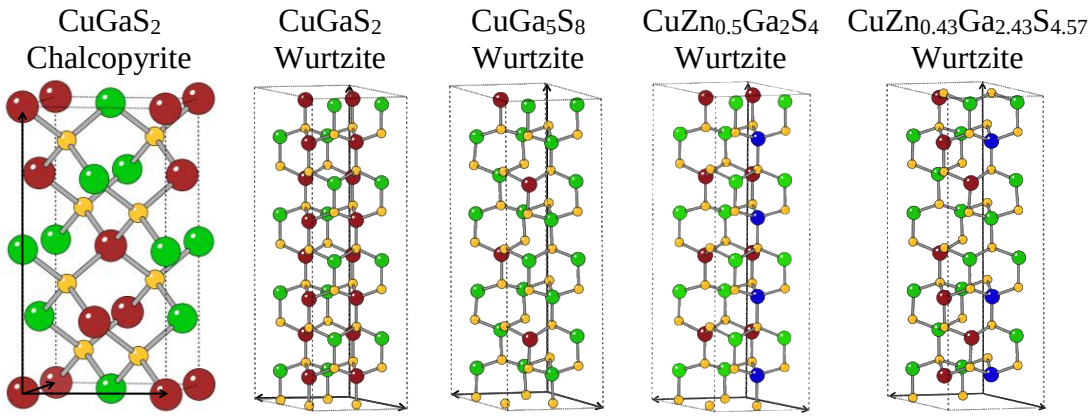

Figure S7. Structures of the different compounds. The yellow, green, red and blue colors correspond to S, Ga, Cu and Zn atoms respectively.

Electronic structure

The densities of states of all the compounds are presented in Figure S8.

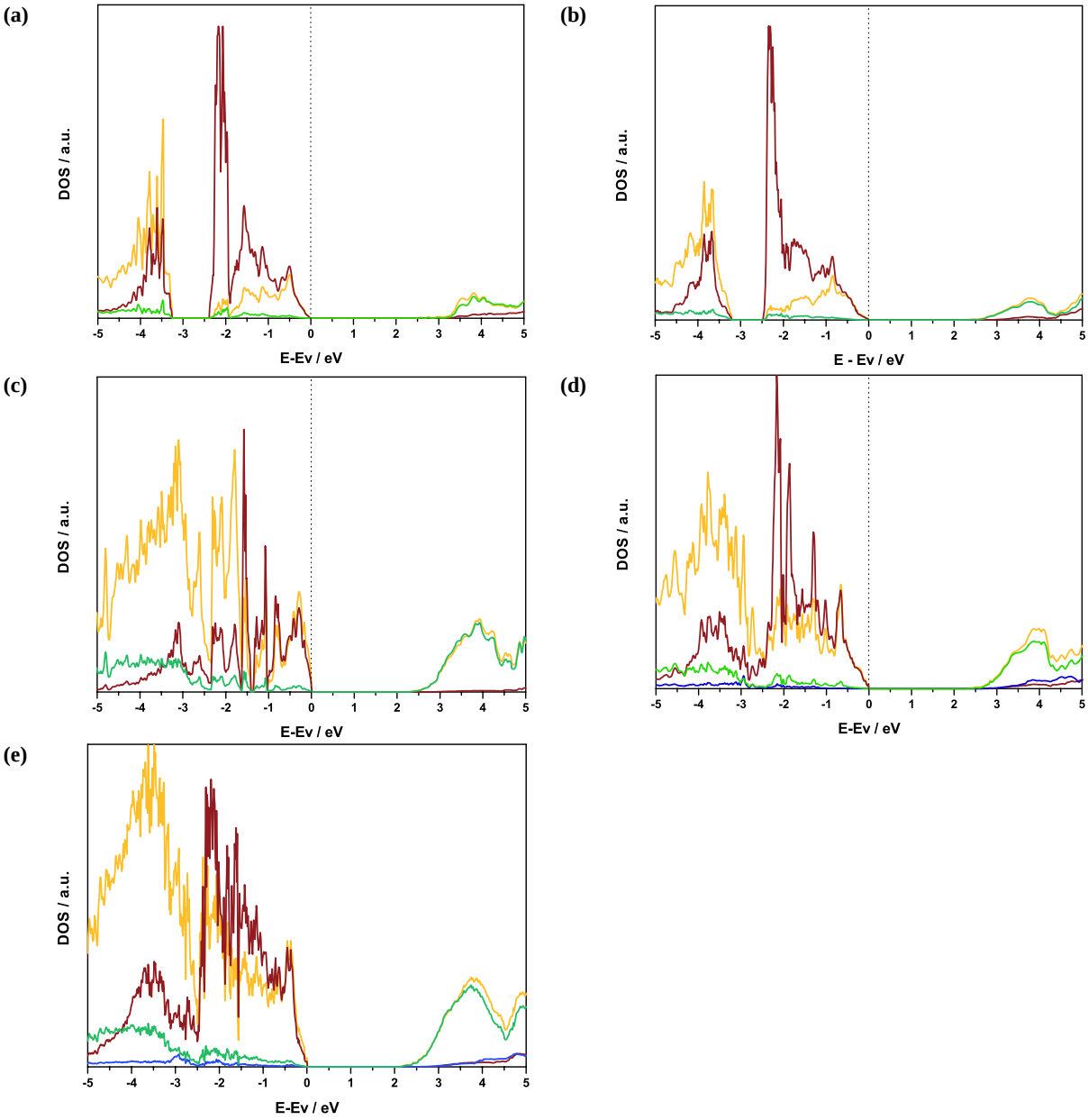

Figure S8. Projected density of states of (a) chalcopyrite $CuGaS_2$, (b) wurtzite $CuGaS_2$, (c) wurtzite $CuGa_5S_8$, (d) wurtzite $CuZn_{0.5}Ga_2S_4$ and (e) wurtzite $CuZn_{0.43}Ga_{2.43}S_{4.57}$. The yellow, red, green and blue lines correspond to projections on S, Cu, Ga and Zn atoms respectively.

The band structures of wurtzite and chalcopyrite $CuGaS_2$ are presented in Figure S9. They both preset a direct bandgap at the Γ-point. For all the other compounds, a direct bandgap is also computed.

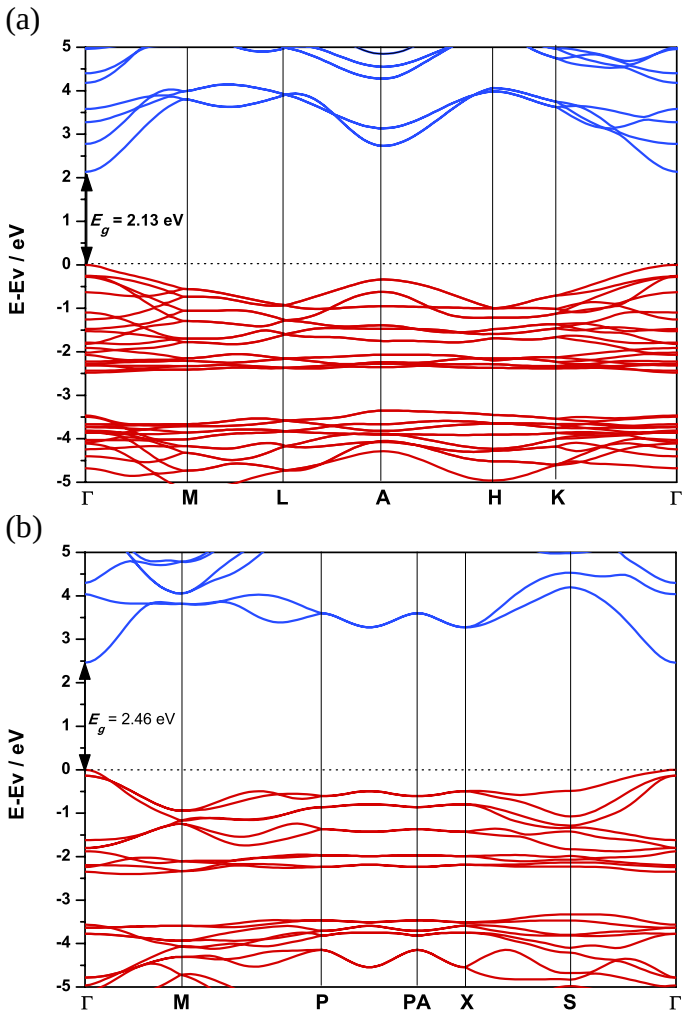

Figure S9. Band structures of $CuGaS_2$ calculated with HSE06 for (a) wurtzite and (b) chalcopyrite.

References.

1. T. Le Bahers, M. Rérat, and P. Sautet, *J. Phys. Chem. C*, 2014, **118**, 5997–6008.
2. S. C. Abrahams and J. L. Bernstein, *J. Chem. Phys.*, 1973, **59**, 5415.
3. J. Jaffe and A. Zunger, *Phys. Rev. B*, 1983, **28**, 5822–5847.