Electronic Supplementary information†

Observation of enhanced photocurrent response in M-$CuInS_2$ (M = Au, Ag) heteronanostructures: phase selective synthesis and application

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Table S1 Crystallographic data for $In(acda)_3$ (**1**) and $Cu(PPh_3)_2(acda)$ (**2**).

	$In(acda)_3$(**1**)	$Cu(PPh_3)_2(acda)$(**2**)
Empirical formula	$C_{18}H_{24}InN_3S_6$	$C_{42}H_{38}CuNP_2S_2$
Formula weight	589.58	746.33
T, K	120(2)	120(2)
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
a /Å	11.906(5)	10.610(7)
b /Å	13.462(5)	12.954(8)
c /Å	15.476(5)	14.539(9)
α / deg	69.790(5)	84.106(2)
β / deg	83.070(5)	72.903(2)
γ / deg	89.517(5)	72.028(2)
V / Å^3	2309.3(15)	1816.5(2)
Z	4	2
μ, mm^{-1}	1.577	0.836
λ, Å	0.71073	0.71073
F(000)	1192	776
Crystal size, mm^3	0.27 × 0.16 × 0.08	0.20× 0.18 × 0.16
D_{calc} / g cm^{-3}	1.696	1.365
No. of data/ restraints /params	32181/ 133 / 490	6386/ 1/ 441
No. of reflns [$I > 2\sigma(I)$]	10325	6386
GOF on F^2	1.031	1.023
Final R indices[$I > 2\sigma(I)$]	$R1^a$ = 0.0358, $wR2^b$ = 0.0768	$R1^a$ = 0.0452, $wR2^b$ = 0.1171
R indices (all data)	$R1^a$ = 0.0515, $wR2^b$ = 0.0827	$R1^a$ = 0.0702, $wR2^b$ = 0.1403

Table S2 Selected Interatomic Distances (Å) for the complex In(acda)$_3$ (**1**) and Cu(PPh$_3$)$_2$(acda) (**2**).

In(acda)$_3$ (**1**)		Cu(PPh$_3$)$_2$(acda) (**2**)	
In(1)–S(2)	2.572(2)	Cu–P(1)	2.271(1)
In(1)–S(3)	2.575(1)	Cu–P(2)	2.260(1)
In(1)–S(6)	2.619(1)	Cu–S(1)	2.449(1)
In(1)–S(7)	2.574(1)	Cu–S(2)	2.382(2)
In(1)–S(8)	2.570(2)		
In(1)–S(9)	2.673(1)		
In(2)–S(11)	2.588(2)		
In(2)–S(12)	2.592(2)		
In(2)–S(14)	2.623(2)		
In(2)–S(15)	2.589(1)		
In(2)–S(17)	2.588(1)		
In(2)–S(18)	2.623(1)		

Table S3 Selected Bond Angles (deg) for the complex In(acda)$_3$ (**1**) and Cu(PPh$_3$)$_2$(acda) (**2**).

In(acda)$_3$ (**1**)		Cu(PPh$_3$)$_2$(acda) (**2**)	
S(2)–In(1)–S(3)	70.11(3)	P(1)–Cu–P(2)	123.67(4)
S(2)–In(1)–S(6)	101.78(3)	P(1)–Cu–S(1)	106.76(4)
S(2)–In(1)–S(7)	109.56(3)	P(1)–Cu–S(2)	111.58(4)
S(2)–In(1)–S(8)	152.68(3)	P(2)–Cu–S(1)	108.89(4)
S(2)–In(1)–S(9)	89.32(3)	P(2)–Cu–S(2)	119.32(4)
S(3)–In(1)–S(6)	165.71(3)	S(1)–Cu–S(2)	73.95(4)
S(3)–In(1)–S(7)	101.86(3)		
S(3)–In(1)–S(8)	95.81(3)		
S(3)–In(1)–S(9)	96.27(3)		
S(6)–In(1)–S(7)	69.15(3)		
S(6)–In(1)–S(8)	96.17(3)		
S(6)–In(1)–S(9)	95.34(3)		
S(7)–In(1)–S(8)	95.96(3)		
S(7)–In(1)–S(9)	157.31(3)		
S(8)–In(1)–S(9)	68.49(3)		
S(11)–In(2)–S(12)	69.11(3)		
S(11)–In(2)–S(14)	87.24(4)		
S(11)–In(2)–S(15)	100.71(3)		
S(11)–In(2)–S(17)	99.21(3)		
S(11)–In(2)–S(18)	165.06(3)		
S(12)–In(2)–S(14)	149.42(3)		
S(12)–In(2)–S(15)	96.07(3)		
S(12)–In(2)–S(17)	110.41(3)		
S(12)–In(2)–S(18)	105.67(3)		
S(14)–In(2)–S(15)	68.73(3)		
S(14)–In(2)–S(17)	91.77(3)		
S(14)–In(2)–S(18)	101.79(3)		
S(15)–In(2)–S(17)	151.20(3)		
S(15)–In(2)–S(18)	93.70(3)		
S(17)–In(2)–S(18)	68.94(3)		

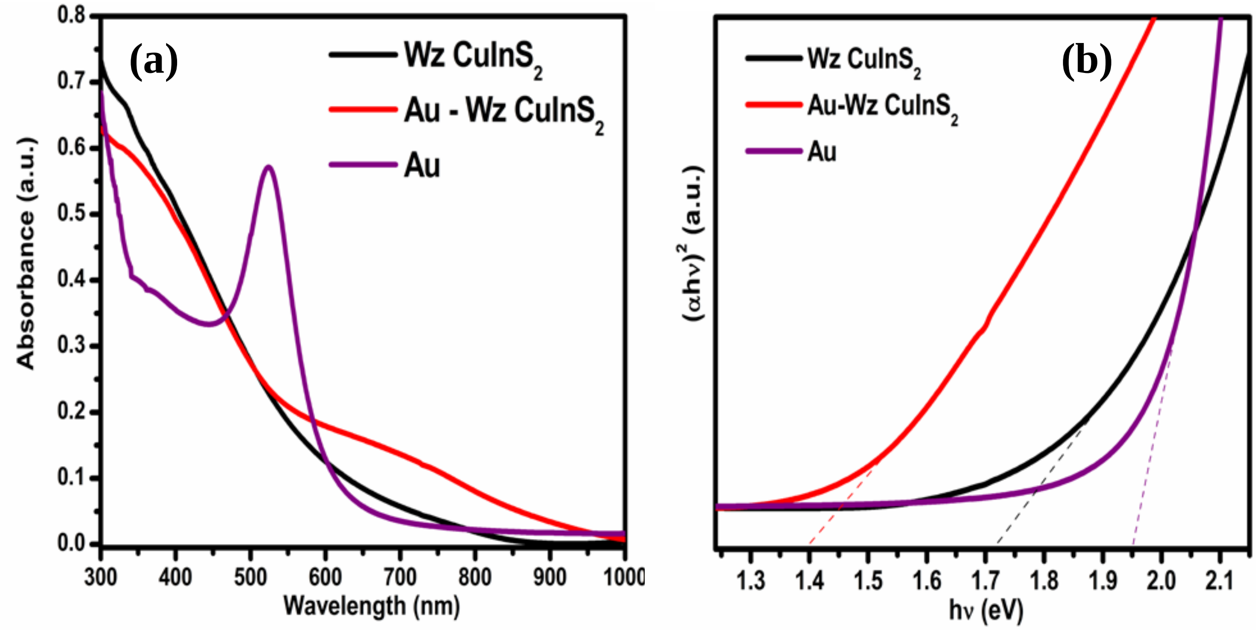


Fig. S1 (a) Absorption spectra of pure Au nanoparticle, pure Wz $CuInS_2$ and Au-Wz $CuInS_2$ heterostructure. (b) Corresponding Tauc's plot.

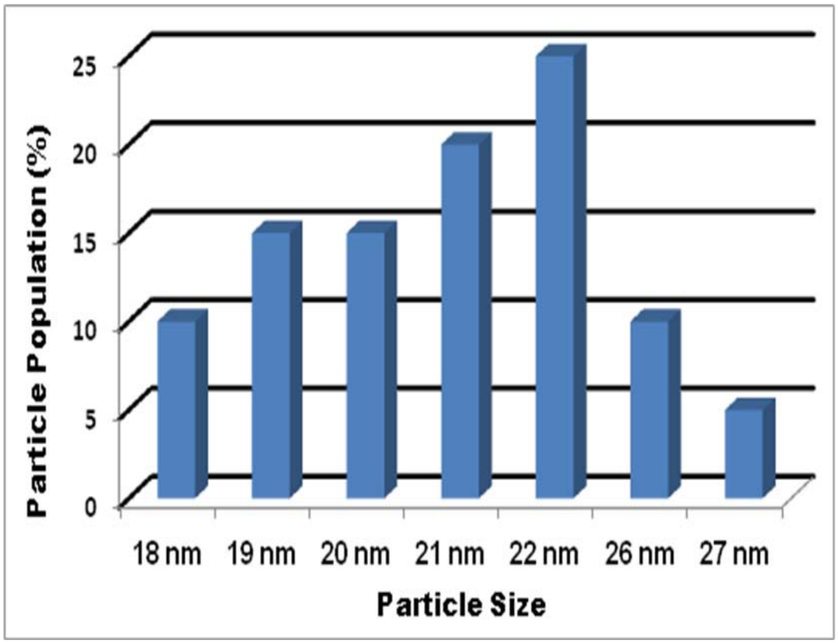


Fig. S2 Particle size distribution plot for Wz $CuInS_2$ nanoparticles. Size varies in the range of 18-27 nm.

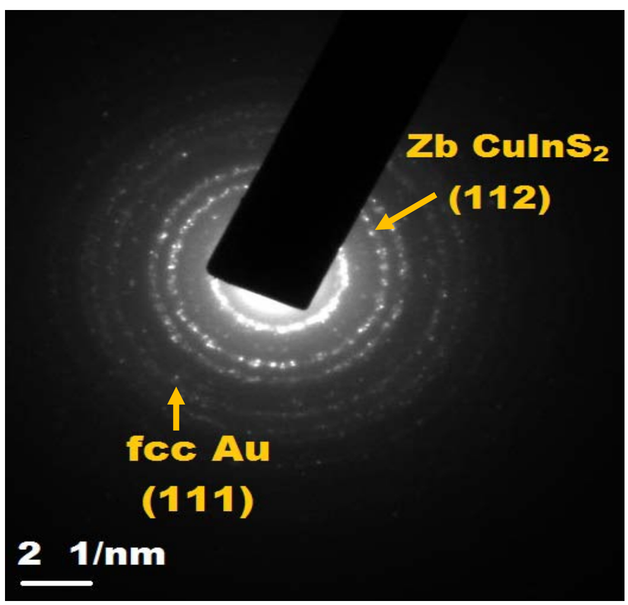


Fig. S3 SAED pattern of Au-$CuInS_2$ (Zb). (112) plane of Zb $CuInS_2$ and (111) plane of fcc Au coexists.

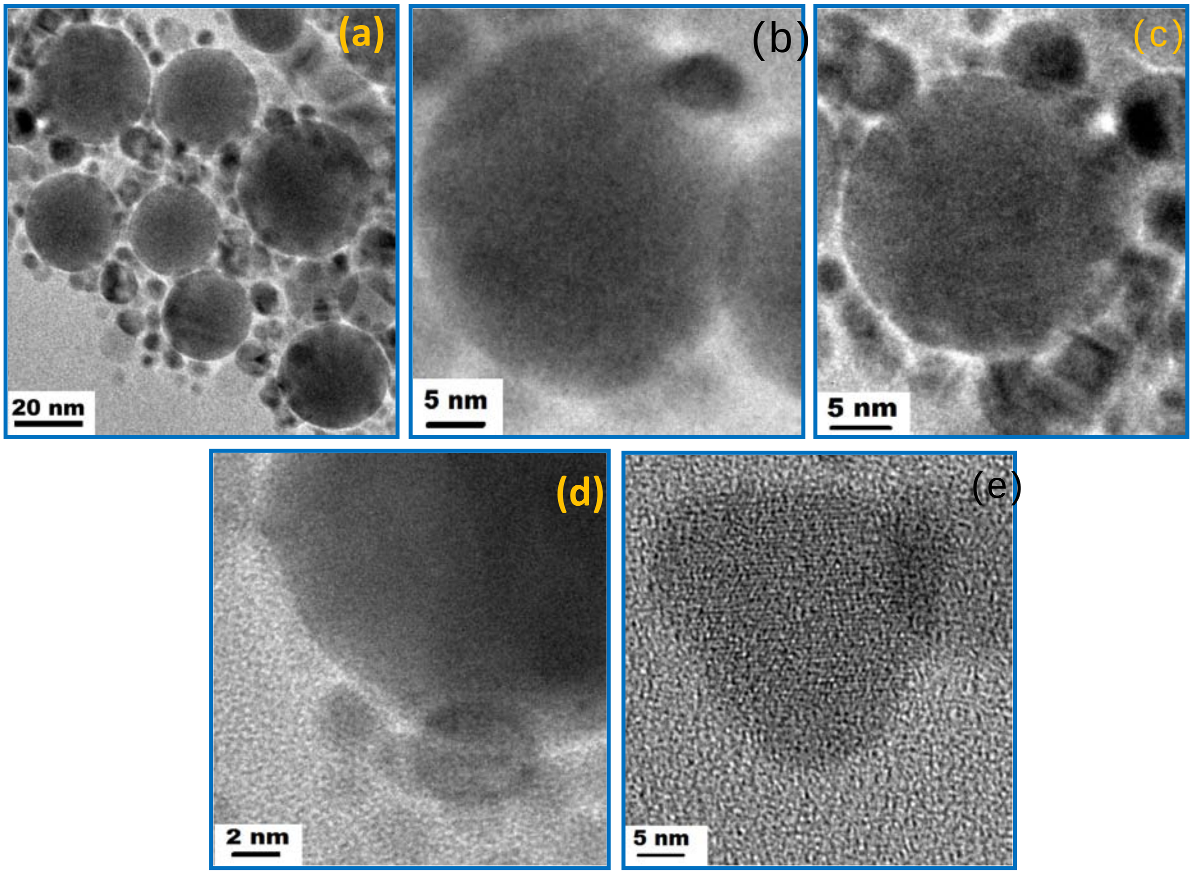
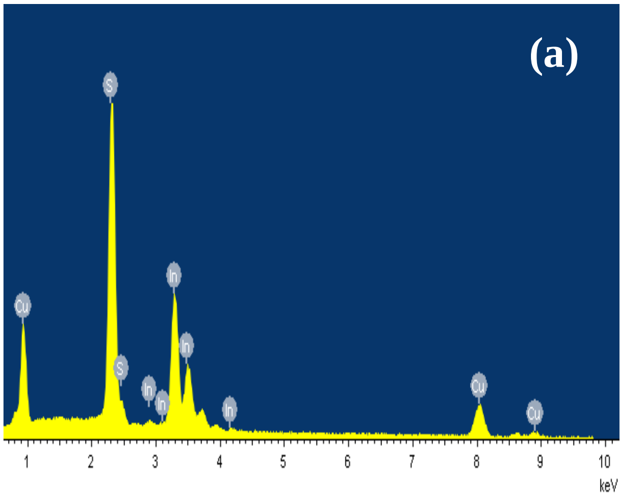
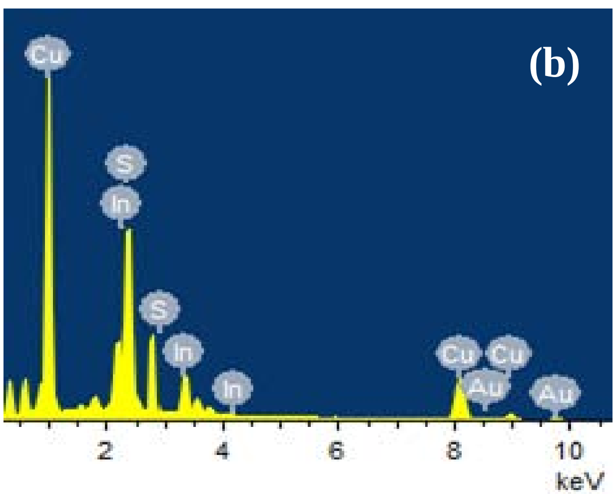


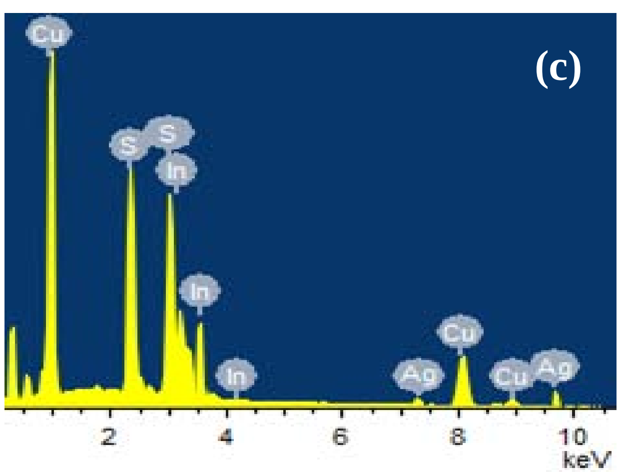
Fig. S4 (a) TEM image of Ag-Wz $CuInS_2$ heterostructure. (b) TEM image of a single Ag-Wz $CuInS_2$. heterostructure. (c) TEM image of a single Ag-Wz $CuInS_2$ heterostructure indicating haphazard decoration of silver. (d) HRTEM image of Ag-Wz $CuInS_2$. (e) HRTEM image of a single Ag-Zb $CuInS_2$.



Element	Weight%	Atomic%
S	25.35	48.88
Cu	25.28	24.63
In	49.37	26.49
Totals	100.00	



Element	Weight%	Atomic%
S	20.98	45.31
Cu	23.30	25.34
In	38.99	23.50
Au	16.73	5.85
Totals	100.00	



Element	Weight%	Atomic%
S	24.07	47.16
Cu	24.12	24.06
In	43.61	23.87
Ag	8.20	4.91
Totals	100.00	

Fig. S5 EDX spectra of (a) $CuInS_2$, (b) Au-Wz $CuInS_2$, (c) Ag-Wz $CuInS_2$ (left panel) and corresponding atomic percentage in tabular form (right panel).

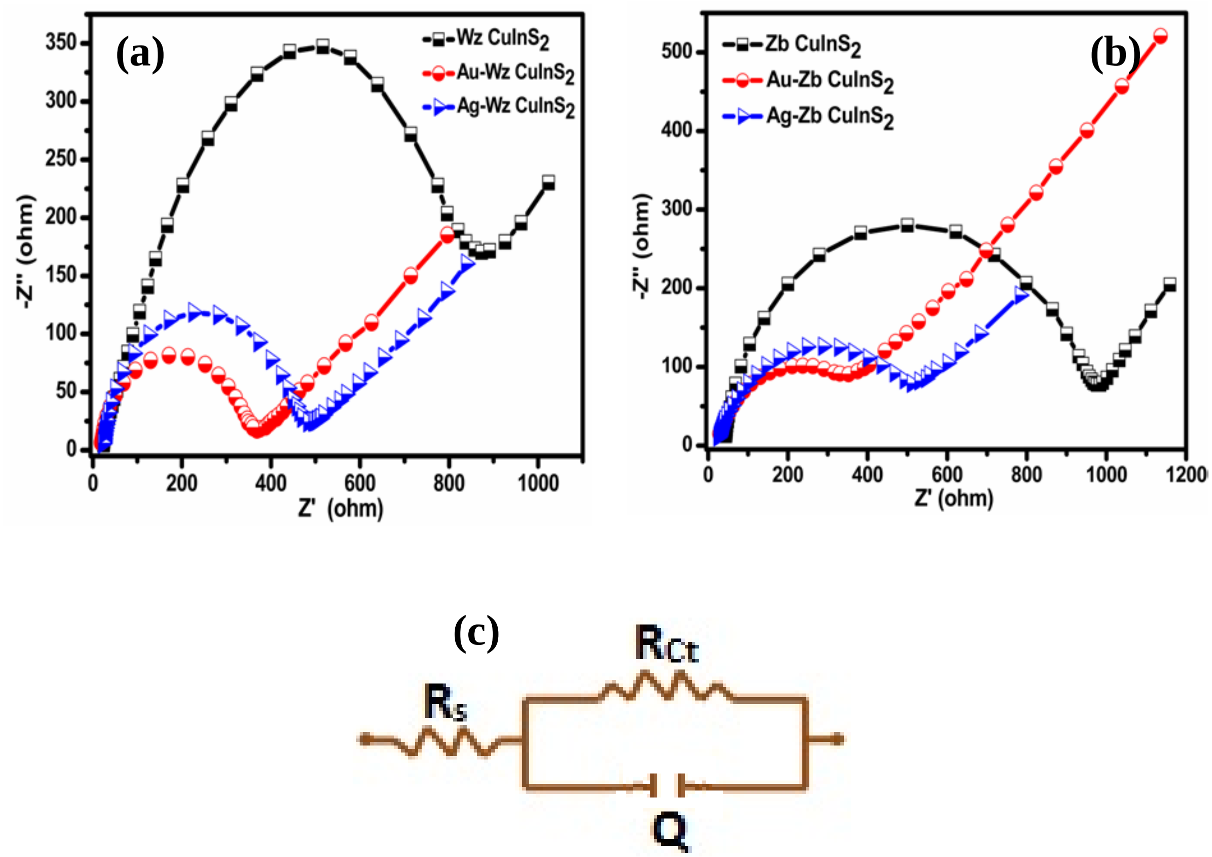


Fig. S6 Nyquist plot of $CuInS_2$, Au-$CuInS_2$ and Ag-$CuInS_2$ in (a) Wurtzite and (b) Zinc blende phases. (c) Corresponding equivalent circuit diagram to calculate different impedance parameters.

Table S4 Variation of impedance parameters of $CuInS_2$, Au- $CuInS_2$ and Ag- $CuInS_2$ in Wz and Zb phases obtained from the equivalent circuit fitting

Sample	R_s (ohm)	R_{Ct} (ohm)
Wz-$CuInS_2$	**23.0**	**904**
Au-Wz-$CuInS_2$	**12.8**	**357**
Ag-Wz-$CuInS_2$	**18.6**	**470**
Zb-$CuInS_2$	**40.4**	**987**
Au-Zb-$CuInS_2$	**14.4**	**466**
Ag-Zb-$CuInS_2$	**19.6**	**576**

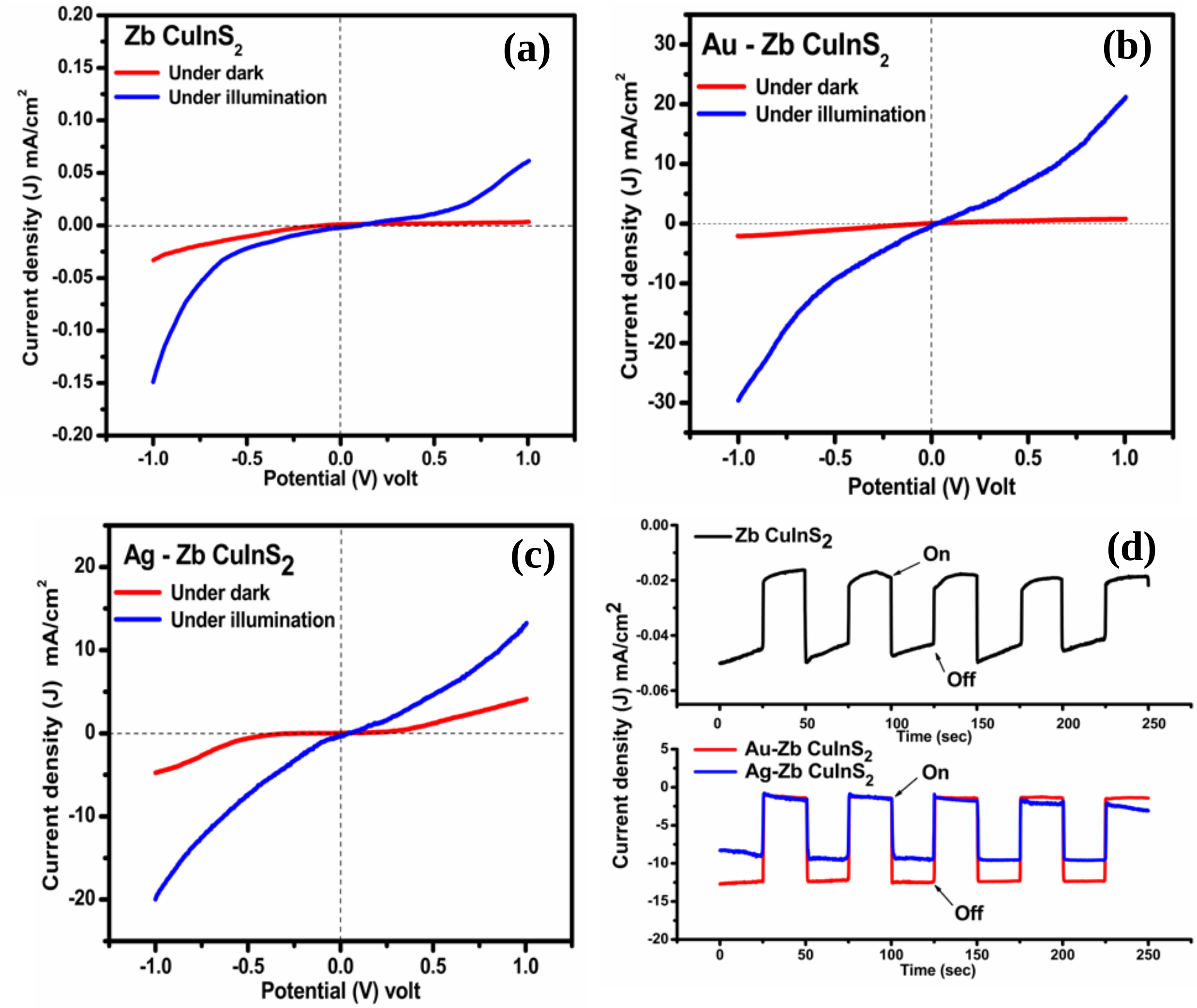


Fig. S7 Current density versus voltage plots for (a) Zb $CuInS_2$, (b) Au- Zb $CuInS_2$ and (c) Ag-Zb $CuInS_2$ (Zb) under dark and under illuminations. (d) Current density versus time plots during successive on and off cycles of light for Zb $CuInS_2$, Au- Zb $CuInS_2$ and Ag- Zb $CuInS_2$ at -0.61 V vs Ag/AgCl.

Table S5 Summary of photocurrent data of pure and heterostructured $CuInS_2$

Sample	Current density under illumination at 0 V vs RHE (mA/cm^2)	I_{light}/I_{dark}
Wz-$CuInS_2$	-0.063	3.4
Au-Wz-$CuInS_2$	-13.38	10.1
Ag-Wz-$CuInS_2$	-10.51	8.4
Zb-$CuInS_2$	-0.031	3.1
Au-Zb-$CuInS_2$	-12.24	9.4
Ag-Zb-$CuInS_2$	-9.68	7.2

Table S6 Comparison of the photocurrent data between the $CuInS_2$ based heterostructures available in literature and the data obtained in present report

Sample	Current density under illumination at 0 V vs RHE (mA/cm^2)	Reference
$Pt/CdS/CuInS_2$	-6.0	1
$Pt/CdS/Cu(In,Ga)S_2$	-6.8	2
$CuInS_2/CdS/ZnS$	-0.04	3
$Pt/TiO_2/CdS/CuInS_2$	-13.0	4
Au-Wz-$CuInS_2$	-13.38	Our Study

References

(1) S Ikeda,. T. Nakamura,. S. M. Lee, T. Yagi, T. Harada, T. Minegishi, M. Matsumura, *ChemSusChem*., 2011, **4**, 262-268.

(2) W.Septina,; Gunawan; S. Ikeda, T. Harada, M. Higashi, R. Abe, M. Matsumura, *J. Phys. Chem. C*., 2015, **119**, 8576-8583.

(3) W. Yang, Y. Oh, J. Kim, H. Shin.; J. Moon, *ACS. Appl. Mater. Interfaces*., 2016, **8**, 425-431.

(4) J. Zhao, T. Minegishi, L. Zhang, M. Zhong, Gunawan, M. Nakabayashi, G. Ma, T. Hisatomi, M. Katayama, S. Ikeda, N. Shibata, T. Yamada, K. Domen, *Angew. Chem.*, *Int. Ed*., 2014, **53**, 11808-11812.