Supporting Information

Black phosphorus quantum dots facilitate carrier separation for enhancing hydrogen production over hierarchical $Cu_7S_4/ZnIn_2S_4$ composites

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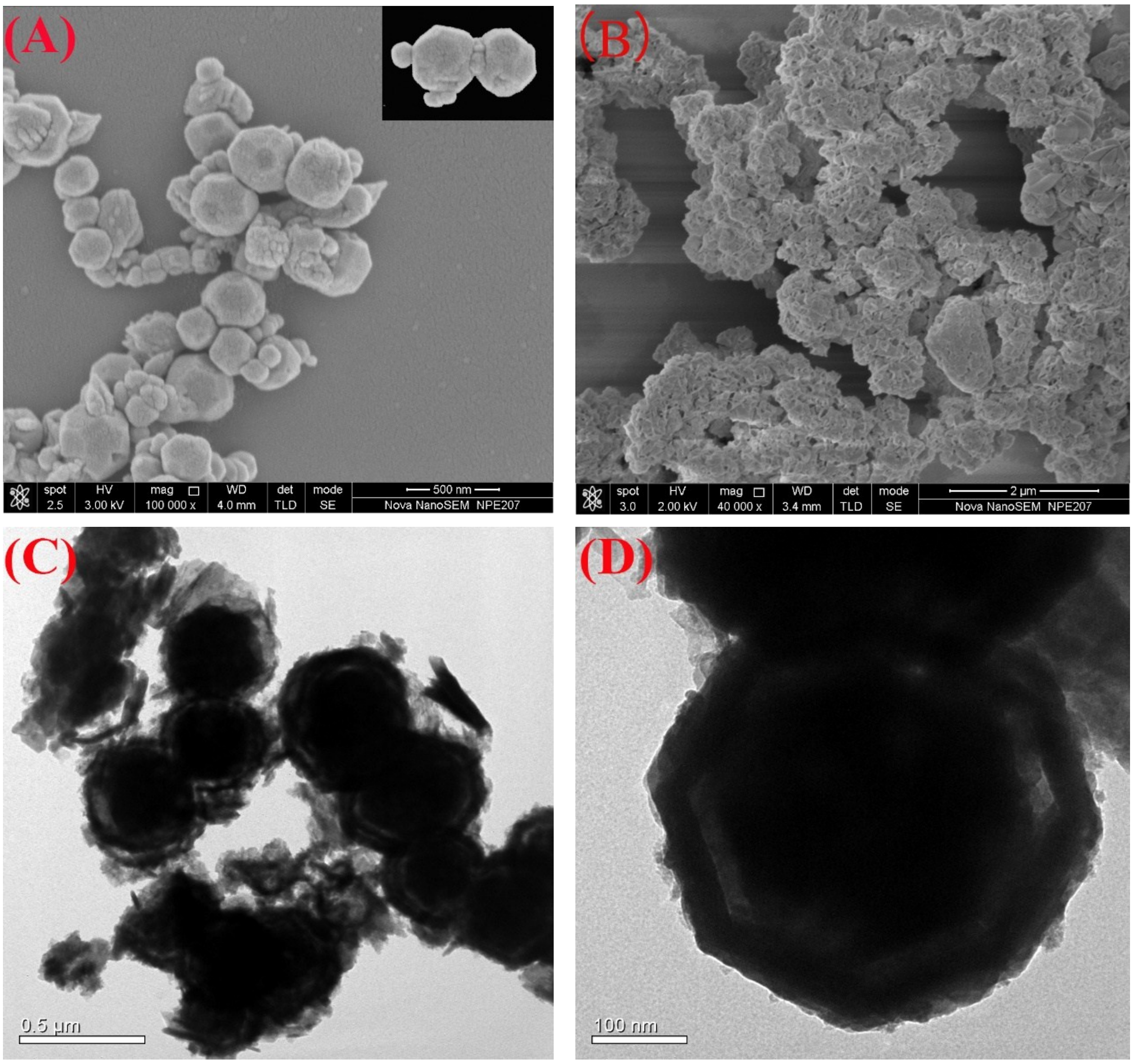


Fig. S1. FESEM images of (A) Cu_2O, (B) $ZnIn_2S_4$ and TEM images of (C) Cu_7S_4, (D) enlarged Cu_7S_4 samples.

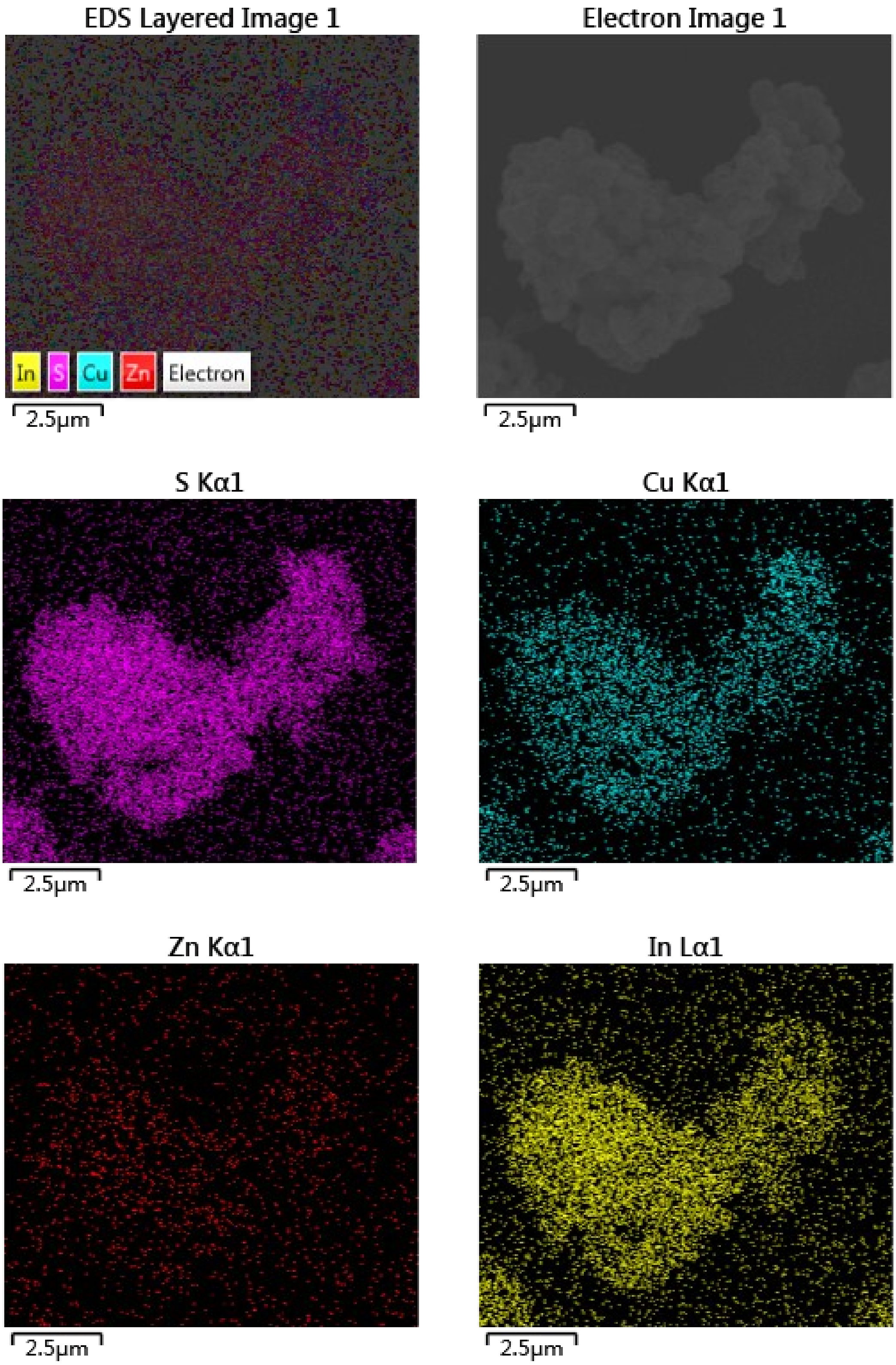


Fig. S2. EDS mapping profiles of 20%Cu_7S_4/$ZnIn_2S_4$ samples.

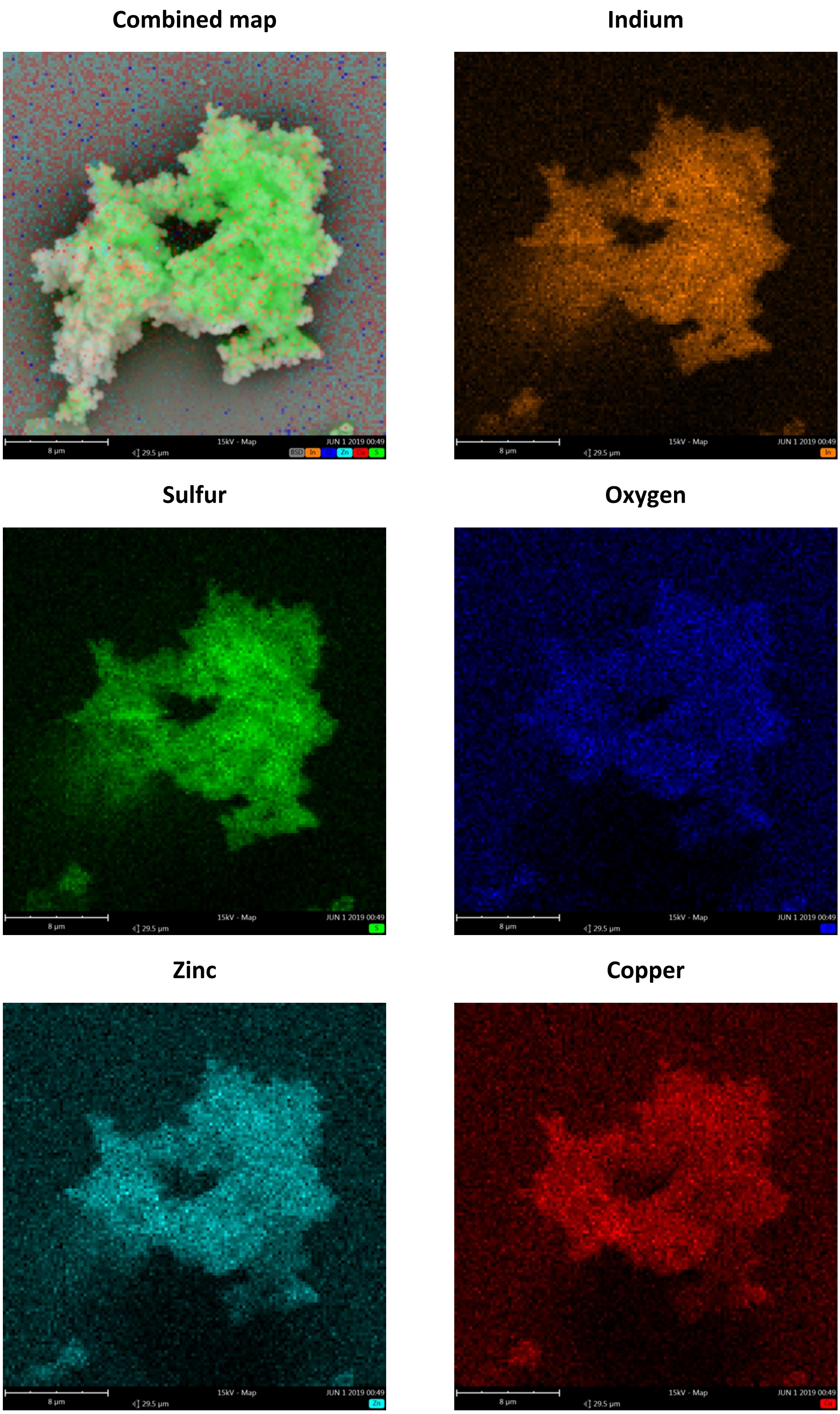


Fig. S3. EDS mapping profiles of 30%Cu_7S_4/$ZnIn_2S_4$ samples.

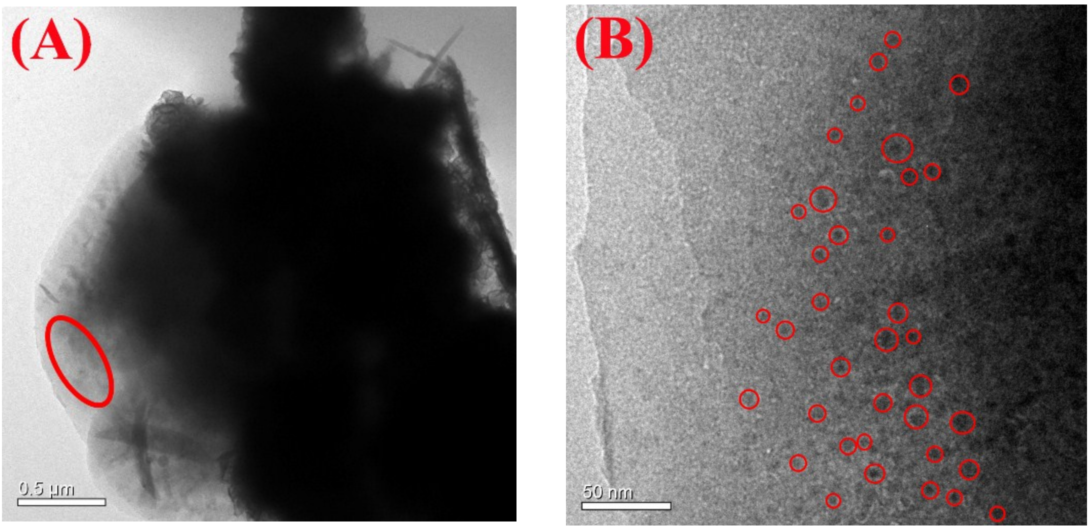
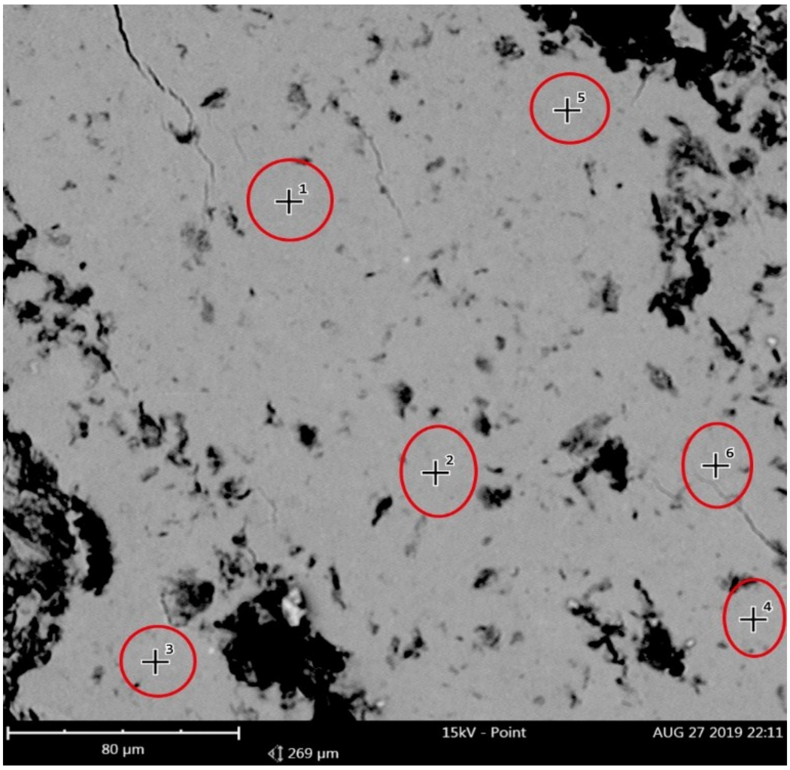
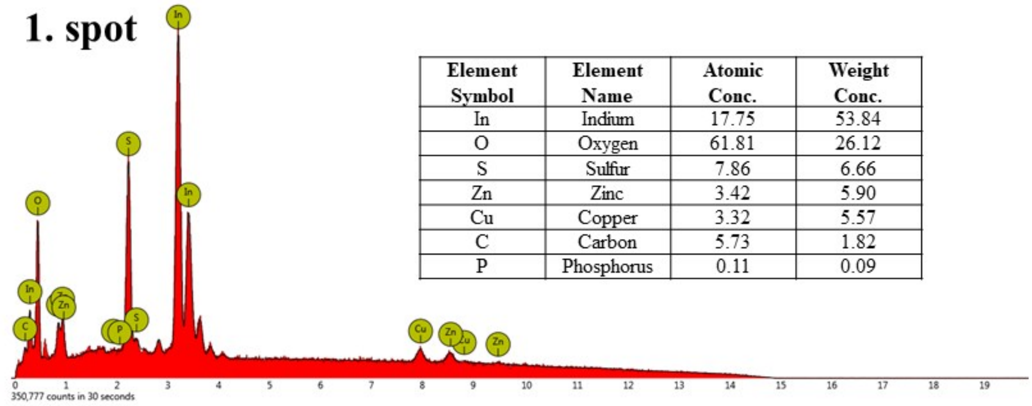


Fig. S4. TEM images of the deposition of BPQDs on the surface of $ZnIn_2S_4$.



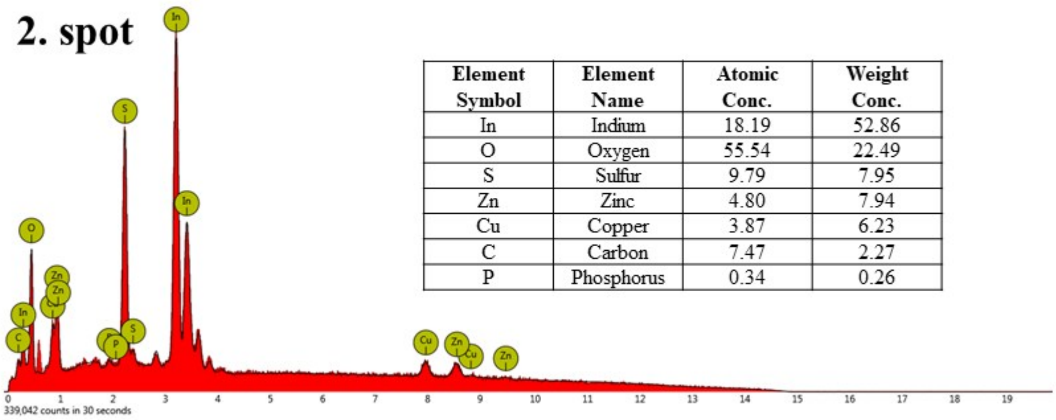
FOV: 269 µm, Mode: 15kV - Point, Detector: BSD Full, Time: AUG 27 2019 22:11

1. spot

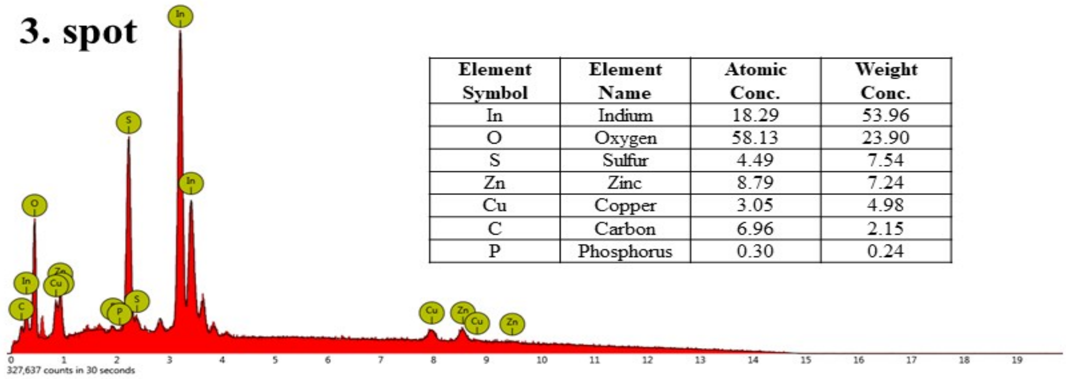


Element Symbol	Element Name	Atomic Conc.	Weight Conc.
In	Indium	17.75	53.84
O	Oxygen	61.81	26.12
S	Sulfur	7.86	6.66
Zn	Zinc	3.42	5.90
Cu	Copper	3.32	5.57
C	Carbon	5.73	1.82
P	Phosphorus	0.11	0.09

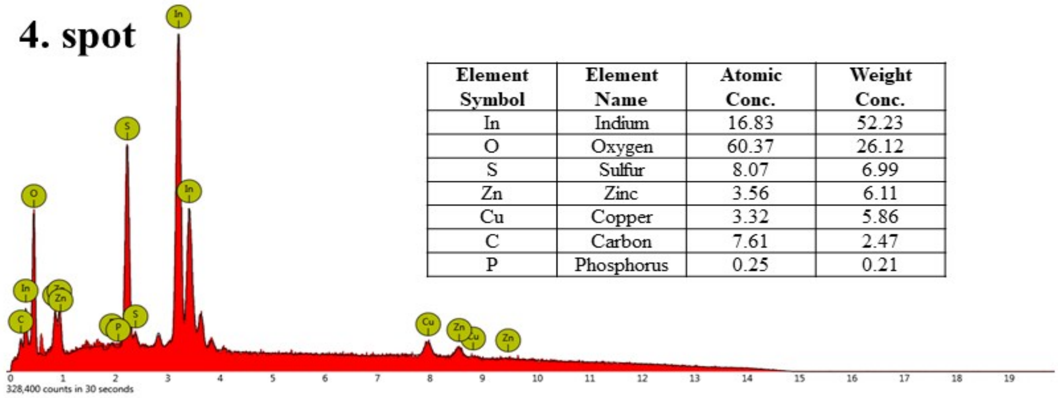
2. spot



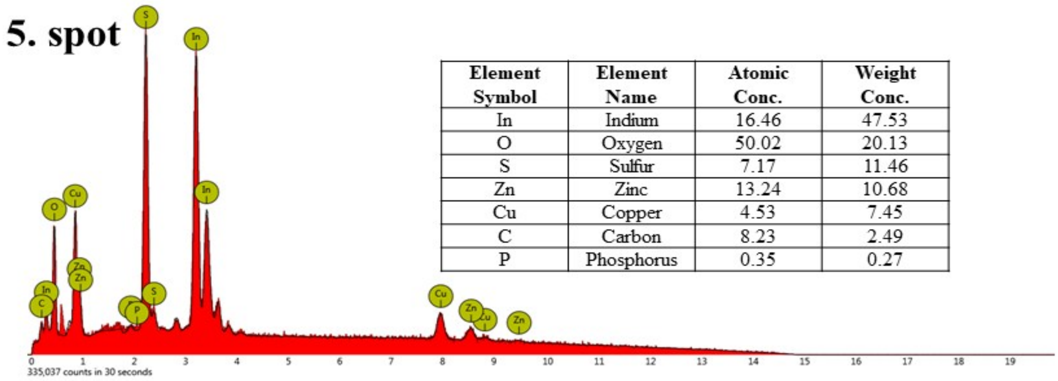
Element Symbol	Element Name	Atomic Conc.	Weight Conc.
In	Indium	18.19	52.86
O	Oxygen	55.54	22.49
S	Sulfur	9.79	7.95
Zn	Zinc	4.80	7.94
Cu	Copper	3.87	6.23
C	Carbon	7.47	2.27
P	Phosphorus	0.34	0.26



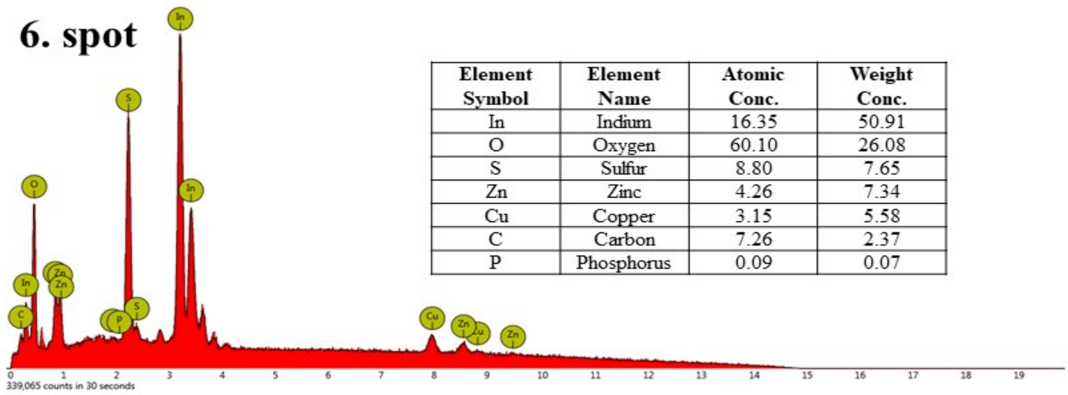
Element Symbol	Element Name	Atomic Conc.	Weight Conc.
In	Indium	18.29	53.96
O	Oxygen	58.13	23.90
S	Sulfur	4.49	7.54
Zn	Zinc	8.79	7.24
Cu	Copper	3.05	4.98
C	Carbon	6.96	2.15
P	Phosphorus	0.30	0.24



Element Symbol	Element Name	Atomic Conc.	Weight Conc.
In	Indium	16.83	52.23
O	Oxygen	60.37	26.12
S	Sulfur	8.07	6.99
Zn	Zinc	3.56	6.11
Cu	Copper	3.32	5.86
C	Carbon	7.61	2.47
P	Phosphorus	0.25	0.21



Element Symbol	Element Name	Atomic Conc.	Weight Conc.
In	Indium	16.46	47.53
O	Oxygen	50.02	20.13
S	Sulfur	7.17	11.46
Zn	Zinc	13.24	10.68
Cu	Copper	4.53	7.45
C	Carbon	8.23	2.49
P	Phosphorus	0.35	0.27



Element Symbol	Element Name	Atomic Conc.	Weight Conc.
In	Indium	16.35	50.91
O	Oxygen	60.10	26.08
S	Sulfur	8.80	7.65
Zn	Zinc	4.26	7.34
Cu	Copper	3.15	5.58
C	Carbon	7.26	2.37
P	Phosphorus	0.09	0.07

Fig. S5. Quantitative results of BPQDs@Cu_7S_4/$ZnIn_2S_4$ through random selection of 6 points by tableting method.

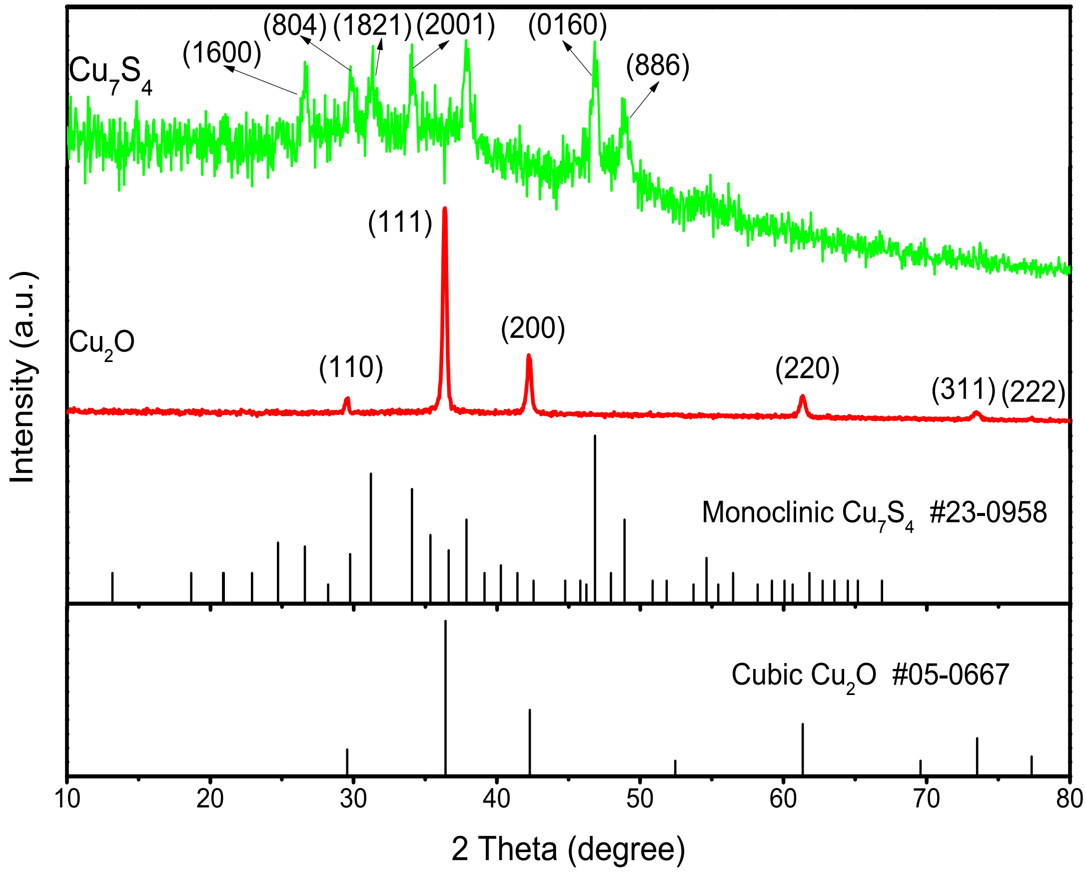


Fig. S6. XRD patterns of Cu_2O, Cu_7S_4 samples.

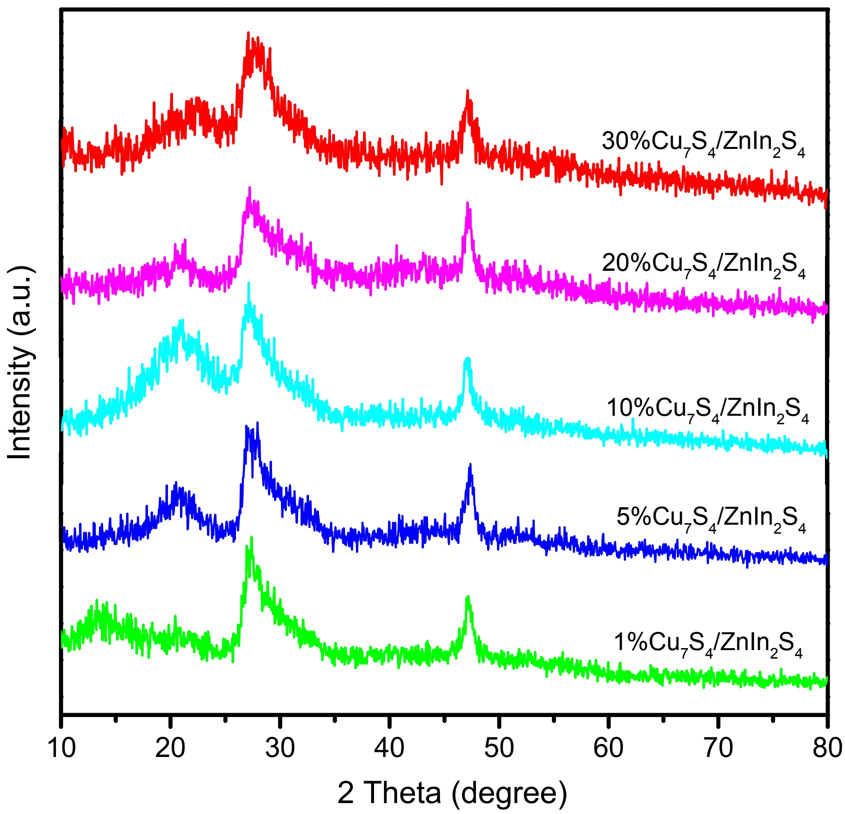


Fig. S7. XRD patterns of different contents of $Cu_7S_4/ZnIn_2S_4$ samples.

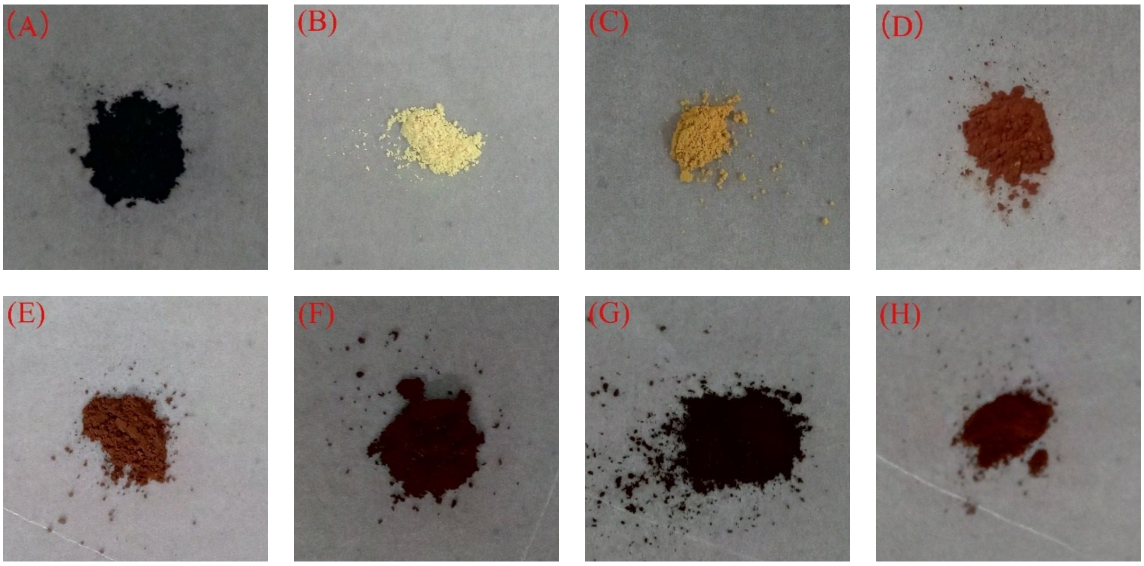


Fig. S8. Appearance color contrast of (A) Cu_7S_4, (B) $ZnIn_2S_4$, (C) 1%Cu_7S_4/ $ZnIn_2S_4$, (D) 5%Cu_7S_4/ $ZnIn_2S_4$, (E) 10%Cu_7S_4/ $ZnIn_2S_4$, (F) 20%Cu_7S_4/ $ZnIn_2S_4$, (G) 30%Cu_7S_4/ $ZnIn_2S_4$ and (H) BPQDs@10%Cu_7S_4/ $ZnIn_2S_4$ composites.

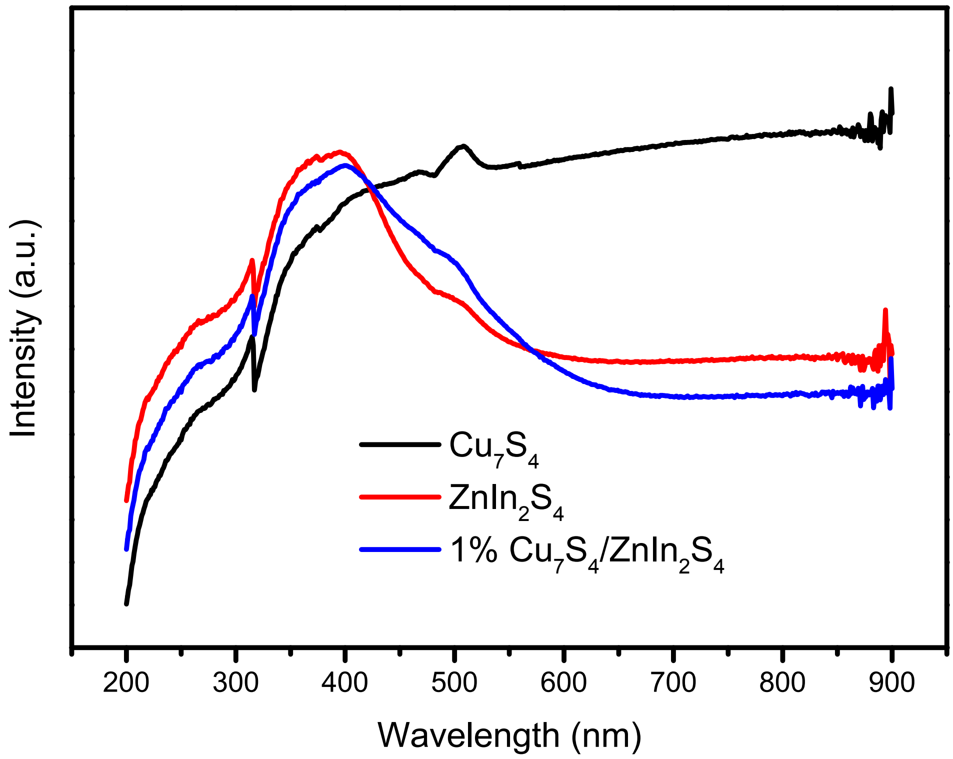
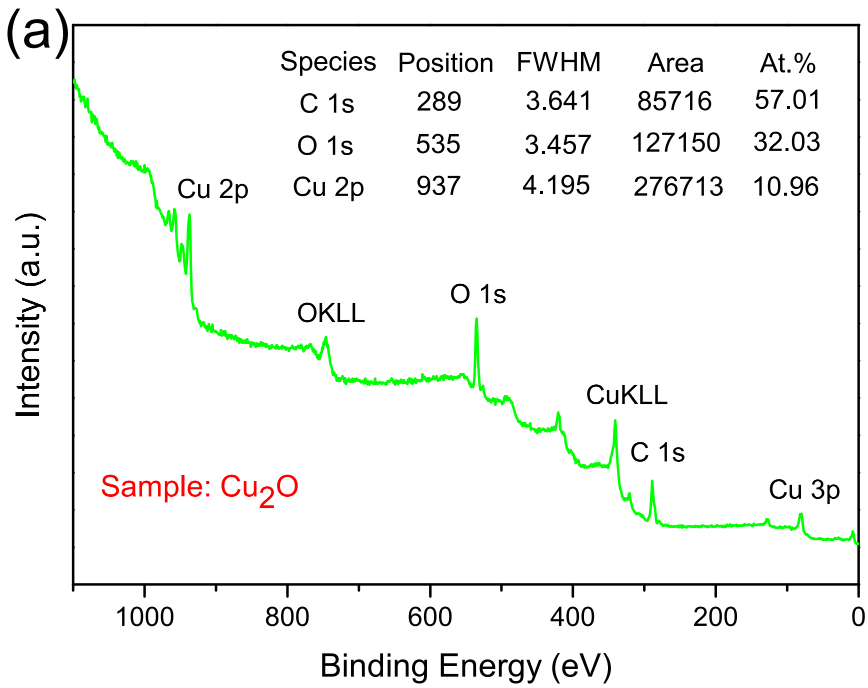
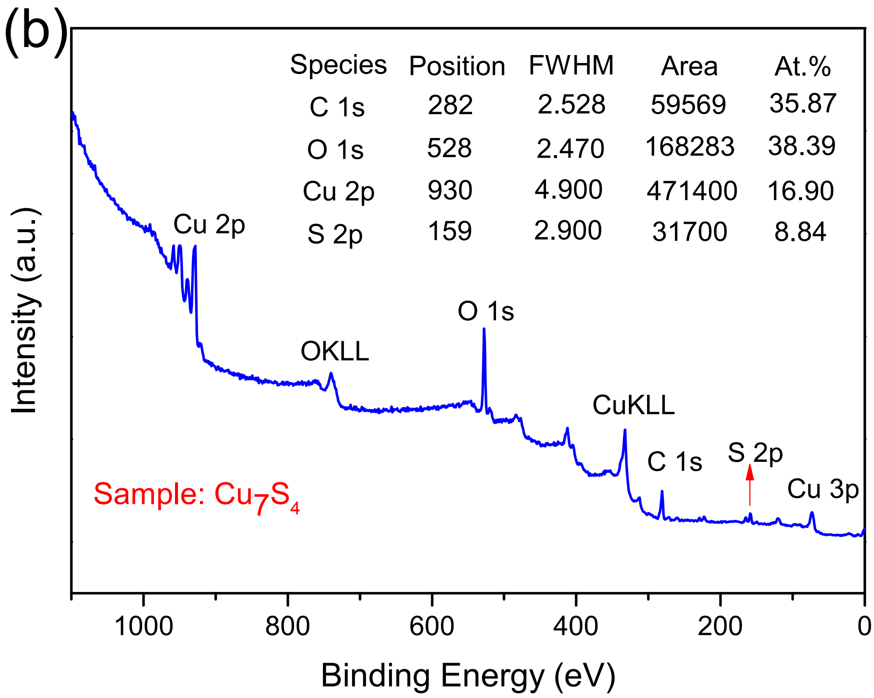


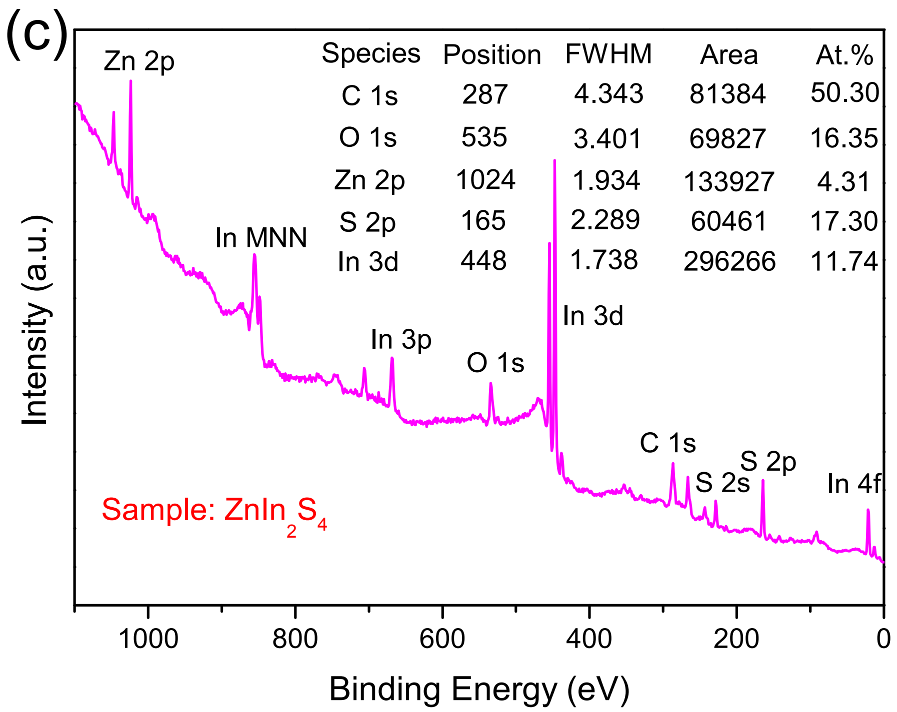
Fig. S9. UV-vis/DRS spectra of Cu_7S_4, $ZnIn_2S_4$ and 1%Cu_7S_4/$ZnIn_2S_4$.

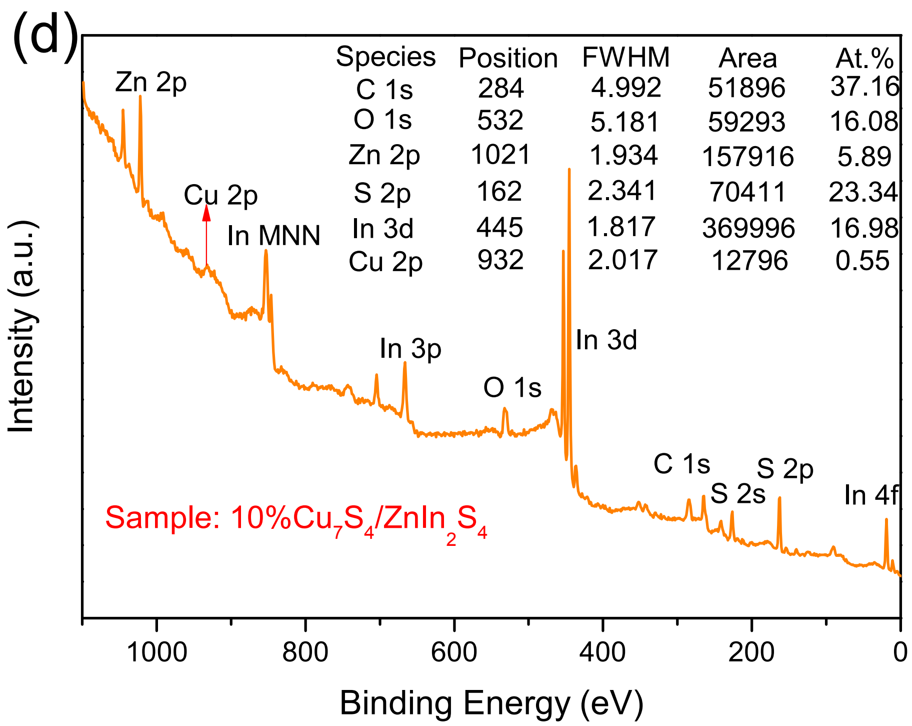


(a)
Species Position FWHM Area At.%
C 1s 289 3.641 85716 57.01
O 1s 535 3.457 127150 32.03
Cu 2p 937 4.195 276713 10.96
Cu 2p
OKLL
O 1s
CuKLL
C 1s
Cu 3p
Sample: Cu2O
Intensity (a.u.)
1000
800
600
400
200
0
Binding Energy (eV)



(b)
Species Position FWHM Area At.%
C 1s 282 2.528 59569 35.87
O 1s 528 2.470 168283 38.39
Cu 2p 930 4.900 471400 16.90
S 2p 159 2.900 31700 8.84
Cu 2p
OKLL
O 1s
CuKLL
C 1s
S 2p
Cu 3p
Sample: Cu7S4
Intensity (a.u.)
1000
800
600
400
200
0
Binding Energy (eV)


(c)
Zn 2p
Species Position FWHM Area At.%
C 1s 287 4.343 81384 50.30
O 1s 535 3.401 69827 16.35
Zn 2p 1024 1.934 133927 4.31
S 2p 165 2.289 60461 17.30
In 3d 448 1.738 296266 11.74
In MNN
In 3p
O 1s
In 3d
C 1s
S 2s
S 2p
In 4f
Sample: $ZnIn_2S_4$
Intensity (a.u.)
1000
800
600
400
200
0
Binding Energy (eV)


(d)
Zn 2p
Species Position FWHM Area At.%
C 1s 284 4.992 51896 37.16
O 1s 532 5.181 59293 16.08
Zn 2p 1021 1.934 157916 5.89
S 2p 162 2.341 70411 23.34
In 3d 445 1.817 369996 16.98
Cu 2p 932 2.017 12796 0.55
Cu 2p
In MNN
In 3p
O 1s
In 3d
C 1s
S 2s
S 2p
In 4f
Sample: $10\%Cu_7S_4/ZnIn_2S_4$
Intensity (a.u.)
1000
800
600
400
200
0
Binding Energy (eV)

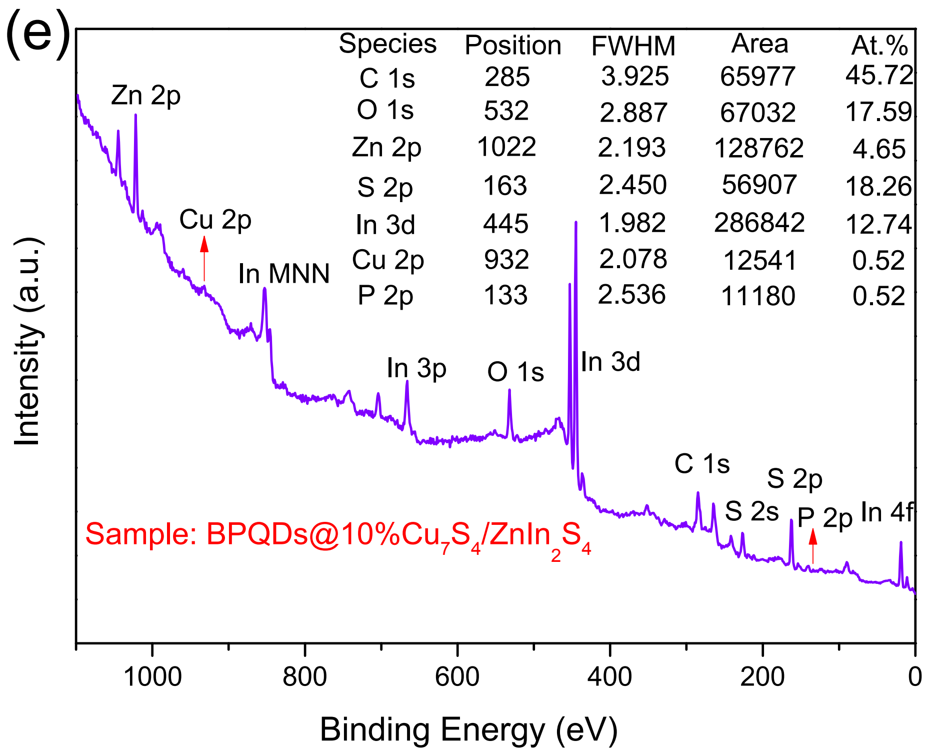


Fig. S10. Full-spectrum XPS scan of Cu_2O, Cu_7S_4, $ZnIn_2S_4$, 10%Cu_7S_4/$ZnIn_2S_4$ and BPQDs@10%Cu_7S_4/$ZnIn_2S_4$ samples.

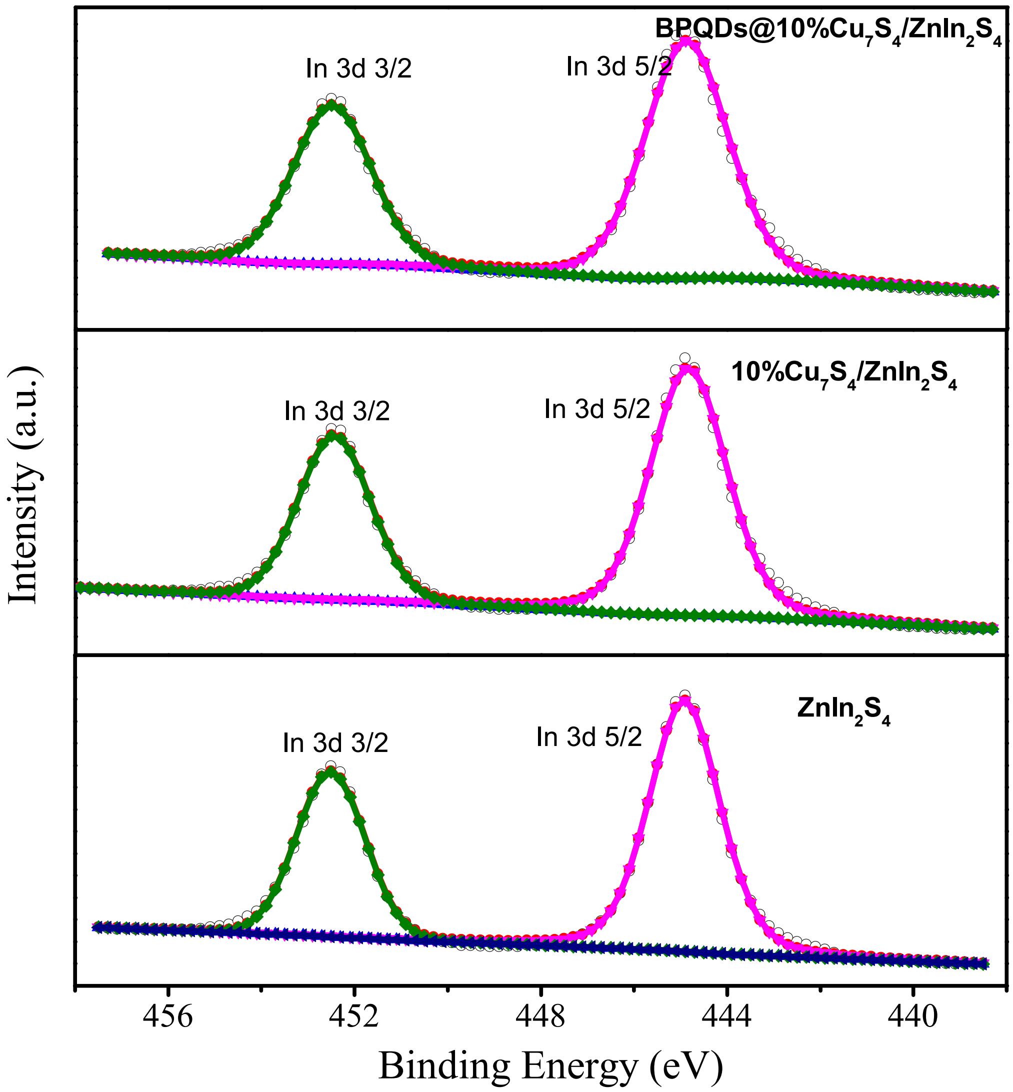


Fig. S11. In high-resolution XPS spectra of $ZnIn_2S_4$, $10\%Cu_7S_4/ZnIn_2S_4$ and $BPQDs@10\%Cu_7S_4/ZnIn_2S_4$ samples.

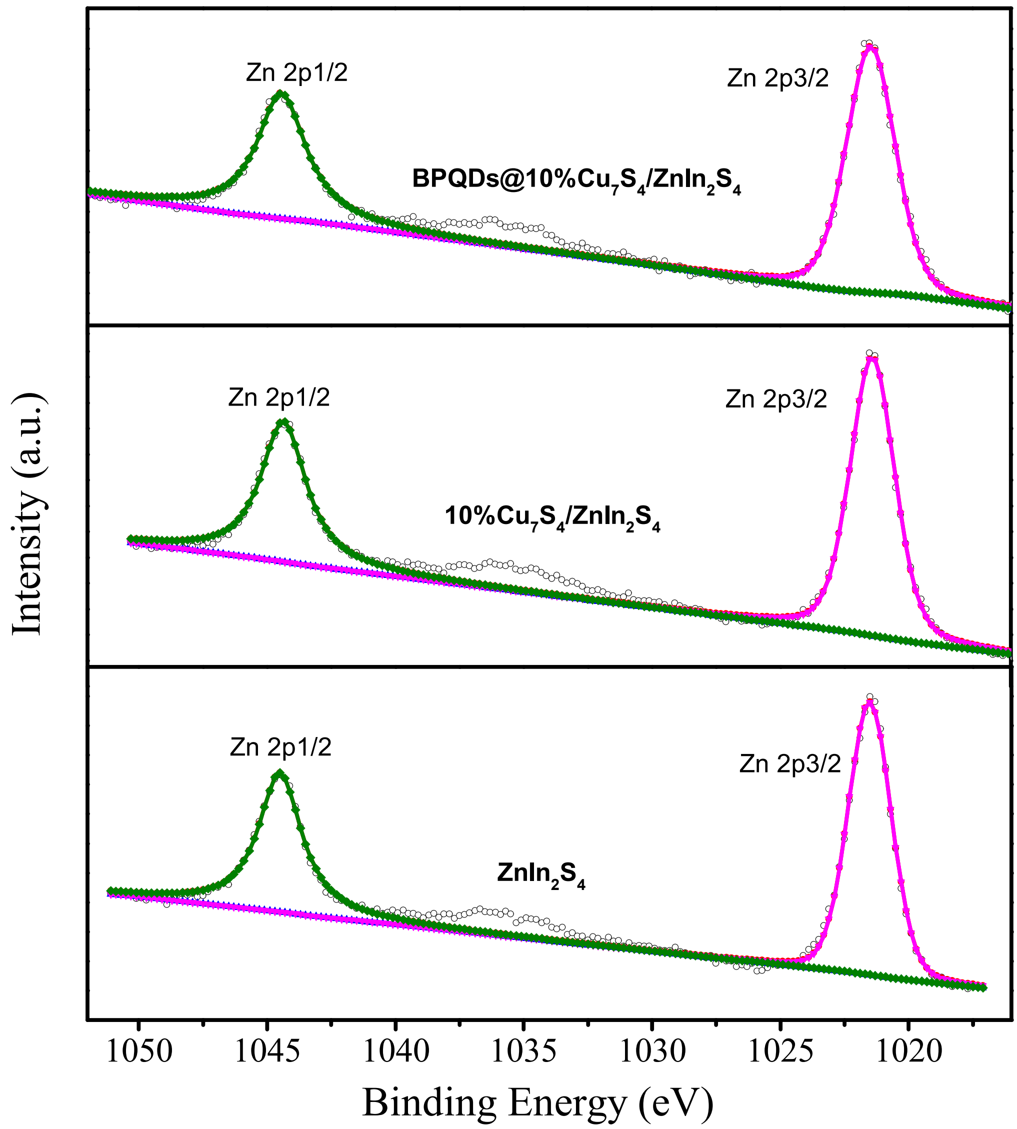


Fig. S12. Zn high-resolution XPS spectra of $ZnIn_2S_4$, 10%Cu_7S_4/$ZnIn_2S_4$ and BPQDs@10%Cu_7S_4/$ZnIn_2S_4$ samples.

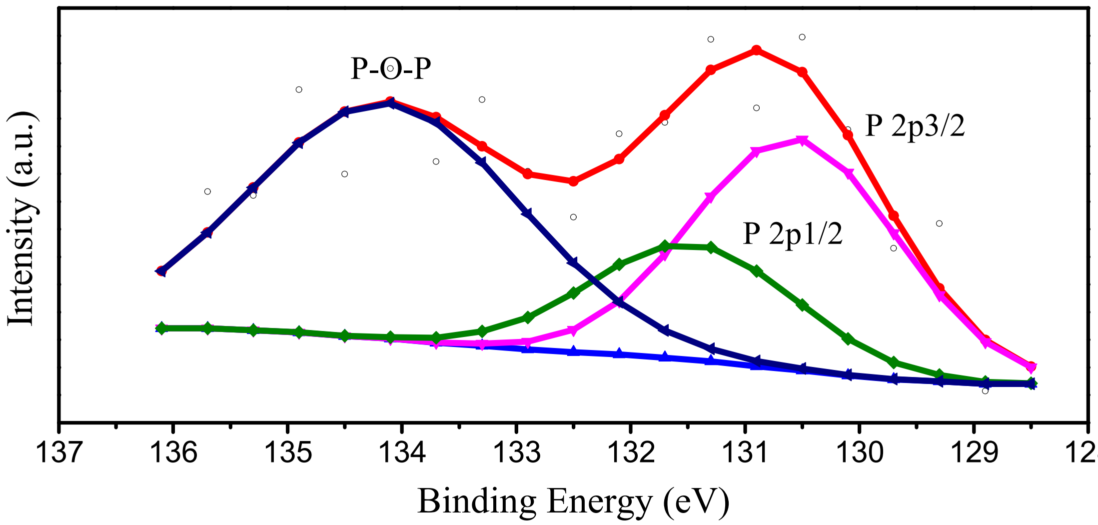


Fig. S13. P 2p high-resolution XPS spectra of BPQDs@10%Cu_7S_4/$ZnIn_2S_4$ samples.

Table S1 High-resolution XPS data of Cu 2p.

Elemental orbit	Samples	Position (eV)	Species	Contents (%)
Cu 2p	Cu_2O	931.6	Cu^+ 2p3/2	42.5
	Cu_7S_4	931.6	Cu^+ 2p3/2	24.1
	10% $Cu_7S_4/ZnIn_2S_4$	931.6	Cu^+ 2p3/2	/
	BPQDs@10% $Cu_7S_4/ZnIn_2S_4$	932.0	Cu^+ 2p3/2	/

Table S2 High-resolution XPS data of S 2p.

Elemental orbit	Samples	Position (eV)	Species	Contents (%)
S 2p	Cu_7S_4	161.6	S 2p3/2	39.6
	$ZnIn_2S_4$	162.0	S 2p3/2	66.2
	10% $Cu_7S_4/ZnIn_2S_4$	162.0	S 2p3/2	85.3
	BPQDs@10% $Cu_7S_4/ZnIn_2S_4$	161.8	S 2p3/2	59.0

Table S3 High-resolution XPS data of In 3d.

Elemental orbit	Samples	Position (eV)	Species
In 3d	$ZnIn_2S_4$	444.9	In 3d5/2
		452.5	In 3d3/2
	10% $Cu_7S_4/ZnIn_2S_4$	444.8	In 3d5/2
		452.4	In 3d3/2
	BPQDs@10% $Cu_7S_4/ZnIn_2S_4$	444.9	In 3d5/2
		452.5	In 3d3/2

Table S4 High-resolution XPS data of Zn 2p.

Elemental orbit	Samples	Position (eV)	Species
Zn 2p	$ZnIn_2S_4$	1021.5	Zn 2p3/2
		1044.5	Zn 2p1/2
	10% $Cu_7S_4/ZnIn_2S_4$	1021.4	Zn 2p3/2
		1044.4	Zn 2p1/2
	BPQDs@10% $Cu_7S_4/ZnIn_2S_4$	1021.4	Zn 2p3/2
		1044.4	Zn 2p1/2

Table S5 High-resolution XPS data of P 2p.

Elemental orbit	Samples	Position (eV)	Species	Contents (%)
P 2p	BPQDs@10% $Cu_7S_4/ZnIn_2S_4$	130.6	P 2p3/2	35.5
		131.5	P 2p1/2	17.7
		134.1	P-O-P	46.8

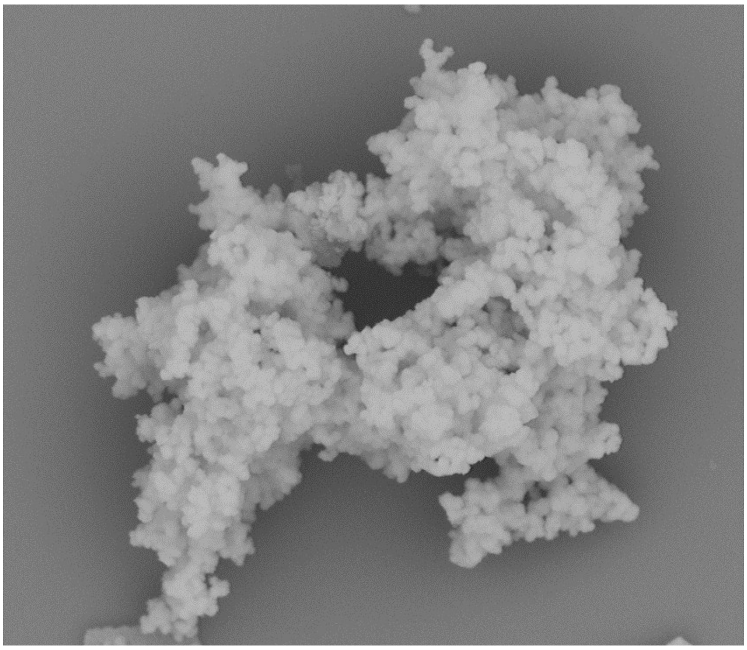


Fig. S14. Agglomerated phenomenon of 30% $Cu_7S_4/ZnIn_2S_4$ samples.

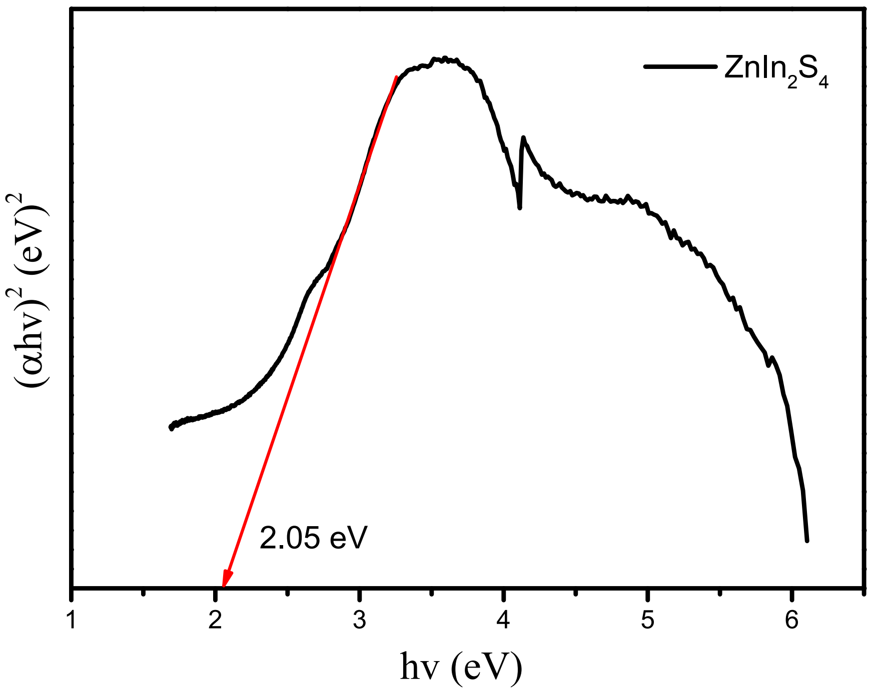


Fig. S15. Optical band gaps of pristine $ZnIn_2S_4$ determined by Kubelka-Munk plot.

Table S6 Comparison of photocatalytic H_2 generation performance with reported literatures.

Catalyst	Sacrificial agent Cocatalyst	H_2 evolution rate (umol/g/h)	Ref.
BPQDs@Cu_7S_4/$ZnIn_2S_4$	Na_2S, Na_2SO_3	885	This work
MoS_2/$ZnIn_2S_4$	Na_2S, Na_2SO_3	120	[1]
Co/CQDs/$ZnIn_2S_4$	TEOA	1760	[2]
RGO/$ZnIn_2S_4$	lactic acid	817	[3]
MoS_2/$ZnIn_2S_4$	Na_2S, Na_2SO_3	3060	[4]
Graphene/$ZnIn_2S_4$	Na_2S, Na_2SO_3	40.9	[5]
MoS_2/CQDs/$ZnIn_2S_4$	TEOA	3000	[6]
WS_2/$ZnIn_2S_4$	Na_2S, Na_2SO_3	199	[7]
NiS/CQDs/$ZnIn_2S_4$	TEOA	568	[8]
$AgIn_5S_8$/$ZnIn_2S_4$	Na_2S, Na_2SO_3 2% Pt	949.9	[9]
$In(OH)_3$/$ZnIn_2S_4$	TEOA 0.5% Pt	1470	[10]

Notes and references

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