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A Promising Visible-Light Driven Hydrogen Production from Water on Highly Efficient $CuCo_2S_4$ Nanosheets Photocatalyst

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Calculations:

1. **Donor concentration (N_A): Slope from Mott-Schottky plot (Fig. 3c for $CuCo_2S_4$)**

$$slope = \frac{2}{\varepsilon_o \varepsilon_r q N_A}$$

ε_0 = permittivity of vacuum,

ε_r = relative permittivity/*dielectric constant*

E = electron charge

N_A = donor concentration for $CuCo_2S_4$ NSs.

N_A =2/3.75 x 8.85 x10^{-10} x 1.602 x 10^{-19} x 0.5209 x 10^9

= **$7.22*10^{18}$ cm^3**

Donor concentration for $Cu_{0.5}Co_{2.5}S_4$

N_A =2/3.75*8.85x10^{-10}*1.602x10^{-19}*1.632x10^9

=$6.1339*10^{17}$ cm^3

Donor concentration for Co_3S_4

N_A =2/3.75*8.85x10^{-10}*1.602x10^{-19}*2.339x10^9

=$4.279*10^{17}$ cm^3

2. Number of H_2 molecule produced:[1,2]

Volume of gas liberated in reaction in 1 h = 38 ml = 0.038L

Form std. gas equation **PV= nRT**

n = 0.038L x 1 atm / 0.082 L.atm mol^{-1} K^{-1} x 298 K

The corresponding amount of hydrogen in moles = 0.00155 mole h^{-1}

1 mole gas = 6.023 x 10^{23} molecules

0.00155 moles will have = 6.023x 10^{23} x 0.00155

H_2 molecule (*per* cm^2 *per s*) = 6.023 x 10^{23} x 0.00155 / (31.4 x 60 min x 60 s)

= **8.2855 x 10^{15}**

3. Apparent quantum yield (AQY %):[3]

$$AQY = \frac{2\ x\ nH_2}{Number\ of\ incident\ photons} = \frac{2.nH_2}{(IA\lambda)/(hc)}\ x\ 100\ (\%)$$

where nH_2 is the number of H_2 molecule produced per second, *I* is the incident solar irradiance (W/cm^2) over the irradiated area *A* (cm^2), λ is the wavelength of the present study (420–555 nm), *h* Planck's and *c* is the speed of light. In order to get accurate value of efficiency study, we have measured AQY at all the wavelength from the cut-off 420 nm to band gap wavelength 555 nm at an interval of 5 nm as shown below.

nH_2 = 8.2855 x 10^{15} per second

I = 52500 lux = 0.00768 W/cm^2

A = 31.41 cm^2

Thus,

$$AQY = \frac{2\ x\ 8.2855\ x\ 10^{15}}{(0.00768\ x\ 31.41\ x\ \boldsymbol{\lambda}\ x\ 10^{-9})/(6.626\ x\ 10^{-34}\ x\ 3\ x\ 10^{8})}\left(\frac{s^{-1}}{(\frac{W}{cm2}.cm2.m)/(J.s.m.s^{-1})}\right)x\ 100\%$$

Apparent quantum yield at all wavelengths (5 nm interval):

Sl. N.	Wavelength (λ value in above equation)	AQY (%)
1	420	3.25
2	425	3.21
3	430	3.18

4	435	3.14
5	440	3.10
6	445	3.06
7	450	3.03
8	455	3.00
9	460	2.97
10	465	2.93
11	470	2.90
12	475	2.88
13	480	2.85
14	485	2.82
15	490	2.80
16	495	2.76
17	500	2.73
18	505	2.71
19	510	2.68
20	515	2.65
21	520	2.63
22	525	2.60
23	530	2.58
24	535	2.55
25	540	2.53
26	545	2.51
27	550	2.90
28	555	2.48

Average AQY = 2.84 %

4. **Turn over frequency (TOF)** = $\frac{Amount\ of\ product\ (mol)}{Amount\ of\ catalytic\ active\ site\ x\ time\ (s)}$

Where, amount of H_2 product = 0.00155 mol

BET Surface area = 62.9 $m^2.g^{-1}$ = 629 $cm^2.mg^{-1}$

Catalyst loading = 60 mg

Volume = 128.33 $mL.mol^{-1}$

Average number of atoms on surface (/cm^2)

$$= \left[\frac{3\ x\ 6.023\ x\ 10^{23}}{128.33}\right]^{2/3} \text{ atom.cm}^{-2}$$

$= 4.150 \text{ x } 10^{14}$ atom.cm^{-2}

Atoms on Surface (or catalytic active site)

$= 60$ mg x 629 cm^2.mg^{-1} x 4.15 x 10^{14} atom.cm^{-2}

$= 1.56 \text{ x } 10^{19}$ atom

Therefore,

$$\textbf{TOF} = \frac{0.00155\ mol\ x\ 6.023\ x\ 10^{23}\ mol^{-1}}{1.56 \text{ x } 10^{19} \text{ atom x } 3600 \text{ s}}$$

$= \mathbf{0.017\ s^{-1}.atom^{-1}}$

5. Rate of H_2 production

0.00155 mole h^{-1} = 1.55 mmol h^{-1} = 1550 μmol h^{-1} = $\frac{1550}{0.060}$ μmol h^{-1}g^{-1} = 25833 μmol h^{-1}g^{-1} = ~25900 μmol h^{-1}g^{-1}

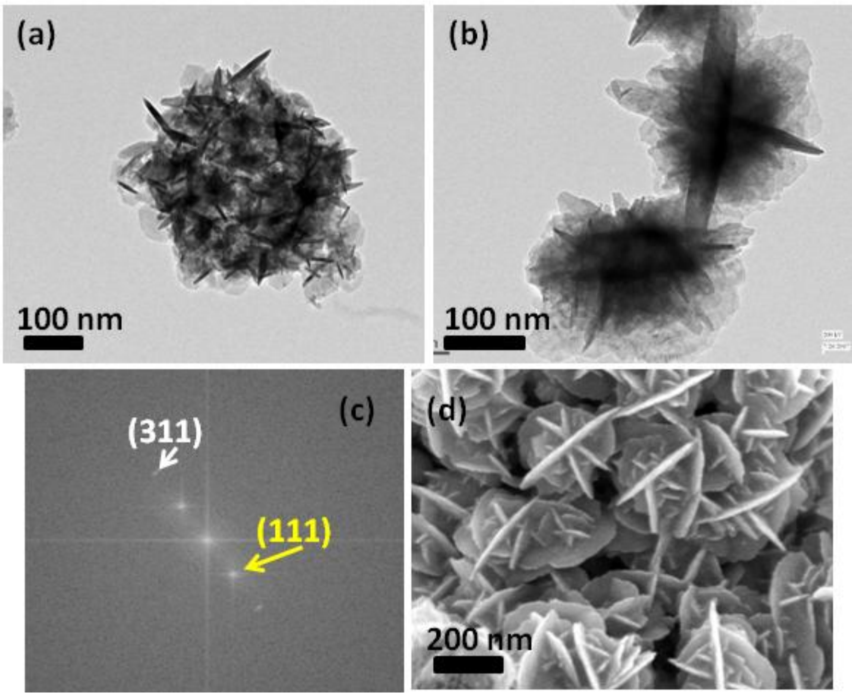


Fig. S1. (a,b) Additional TEM images showing the formation of agglomerated flower like structure by 2D $CuCo_2S_4$ NSs. (c) Calculated FFT image. (d) FESEM image of $CuCo_2S_4$ NSs forming open hierarchical 3D structure.

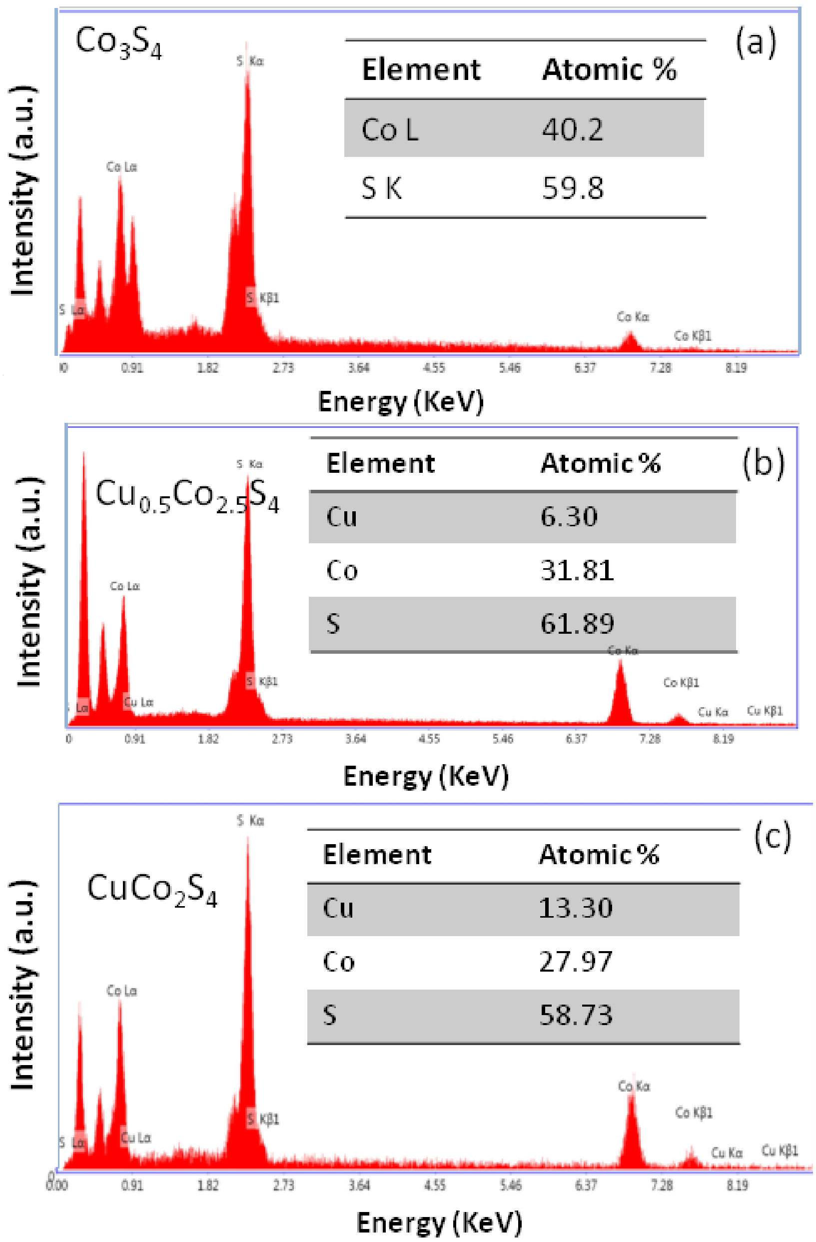


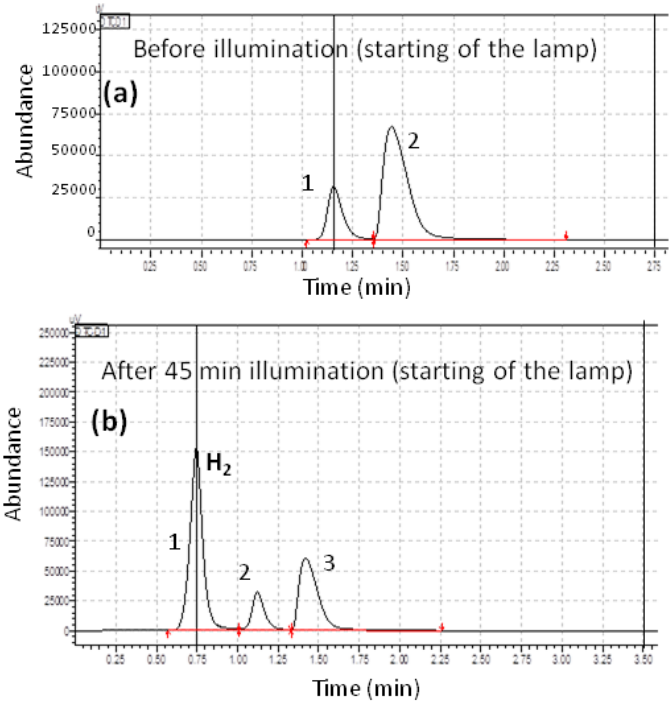
Fig. S2. FE-SEM-energy dispersive spectroscopy spectra and obtained elemental ratios for (a) Co_3S_4, (b) $Cu_{0.5}Co_{2.5}S_4$ and (c) $CuCo_2S_4$ nanostructures.

Table S1. Quantitative stoichiometric elemental amount obtained from AAS analysis.

Sl. No.	Sample	Cu (ppm)	Co (ppm)
1	Co_3S_4	0	3.90
2	$Cu_{0.5}Co_{2.5}S_4$	0.63	3.10
3	$CuCo_2S_4$	1.50	2.88

Table S2. Types of different sacrificial reagents and the corresponding measured pH values.

Sl. No.	**Sacrificial reagent**	**Measured pH**
1	Water	7.00
2	MeOH (10%)	9.07
3	Lactic Acid (10%)	1.87
4	Na_2S	12.45
5	Na_2SO_3	11.12
6	Na_2S/ Na_2SO_3 (1:1)	12.46



Peak Unit	Ret. Time	Area	Height	unit
1	1.156	167940	31452	22.652
2	1.443	573456	66953	77.348
Total		741396	98404	100

Peak Unit	Ret. Time	Area	Height	unit
1	0.746	845558	153199	55.582
2	1.121	179876	32190	11.824
3	1.418	495857	60596	32.594
Total		1521292	245985	100.000

Fig. S3. GC data. (a) Sample collected before starting the photocatalytic reaction and (b) sample collected after 45 min of photocatalytic reaction.

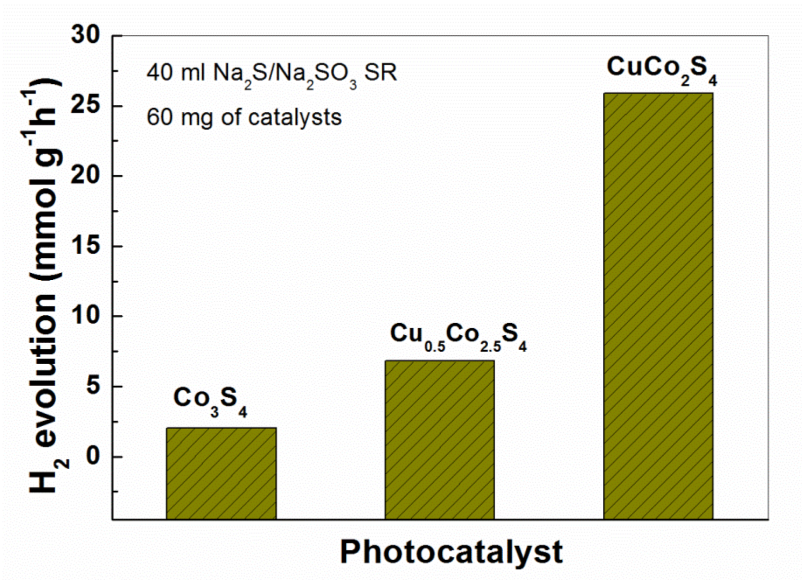


Fig. S4. Amount of H_2 evolved per hour per gram of different studied thiospinel NSs photocatalysts.

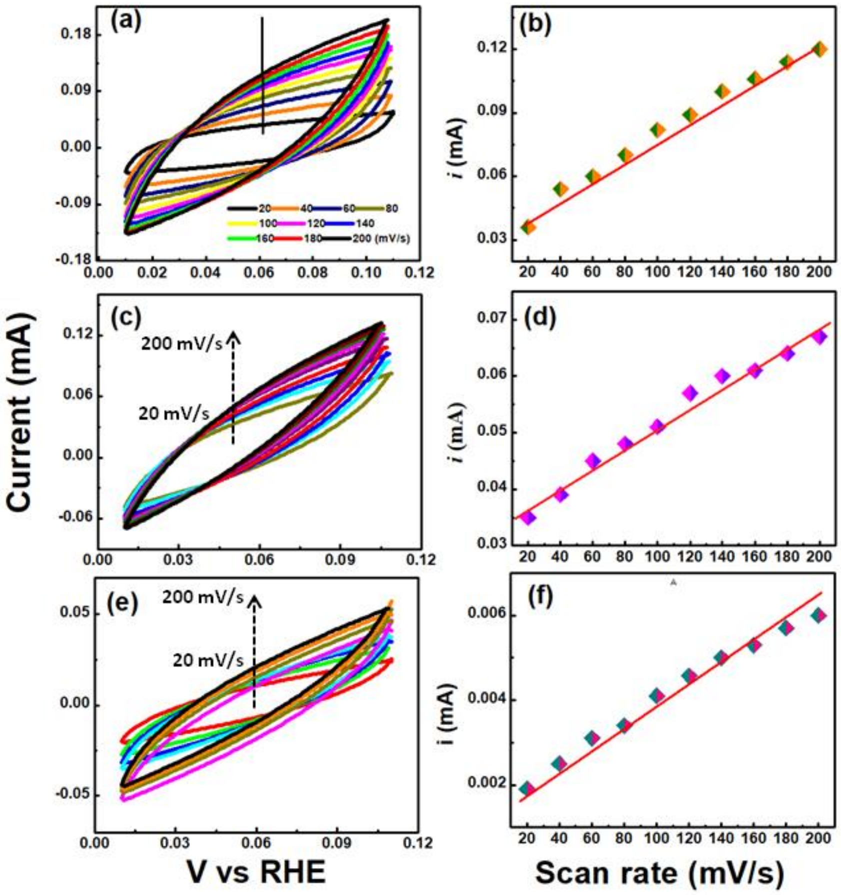


Fig. S5. (a,c,e) Current vs. Voltage (RHE) cyclic voltammograms at different scan rates and (b,d,f) current vs. scan rate measured on $CuCo_2S_4$, $Cu_{0.5}Co_{2.5}S_4$ and Co_3S_4 based electrodes, respectively to calculate double layer capacitance (C_{dl}).

Calculations of ECSA for $CuCo_2S_4$

Double layer charging (C_{dl}) or capacitance was estimated via slope between Δi at different scan rates (υ) of 20 to 200 mV s^{-1} in a non-Faradaic region.

$\Delta i = C_{dl} \times \upsilon$

C_{dl} = 1.75 mF

C_s = 0.040 mF cm^{-2} at 1 M KOH.[4,5]

Where Δi is change in current at different scan rate, υ is scan rate, C_s is specific capacitance

$$ECSA = \frac{C_{dl}}{C_s} = \frac{1.75}{0.040}$$

= 43.75 cm^2

Table S3. Calculated C_{dl} and ECSA values for all three samples as noted from Fig. S5.

Sl. No.	**Sample**	**C_{dl} (mF)**	**ECSA (cm^2)**
1	$CuCo_2S_4$	1.75	43.75
2	$Cu_{0.5}Co_{2.5}S_4$	1.53	38.25
3	Co_3S_4	0.529	13.22

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