

Supporting Information

Synthesis of graphitic carbon nitride (g-C₃N₄)

Urea and thiourea were used as precursors for the synthesis g-C₃N₄ via solid-state thermal polymerization process. A 1:1 mixture of urea and thiourea was thoroughly mixed in a covered silica crucible and heated at 550° C for one hour in a muffle furnace. Pale yellow graphitic carbon nitride samples were collected and milled into fine powder after cooling to room temperature [24].

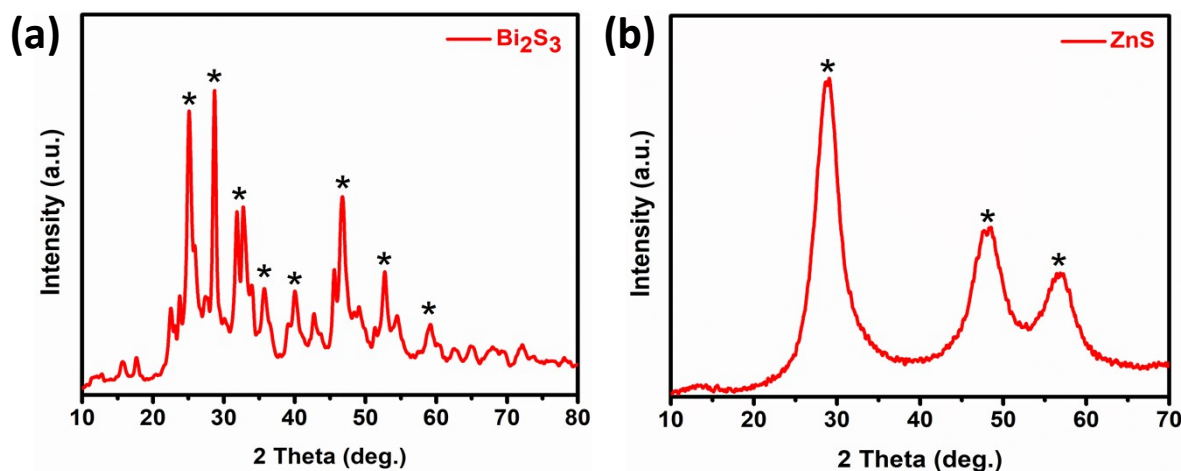


Fig S1. XRD diffraction pattern of Bi₂S₃ and ZnS

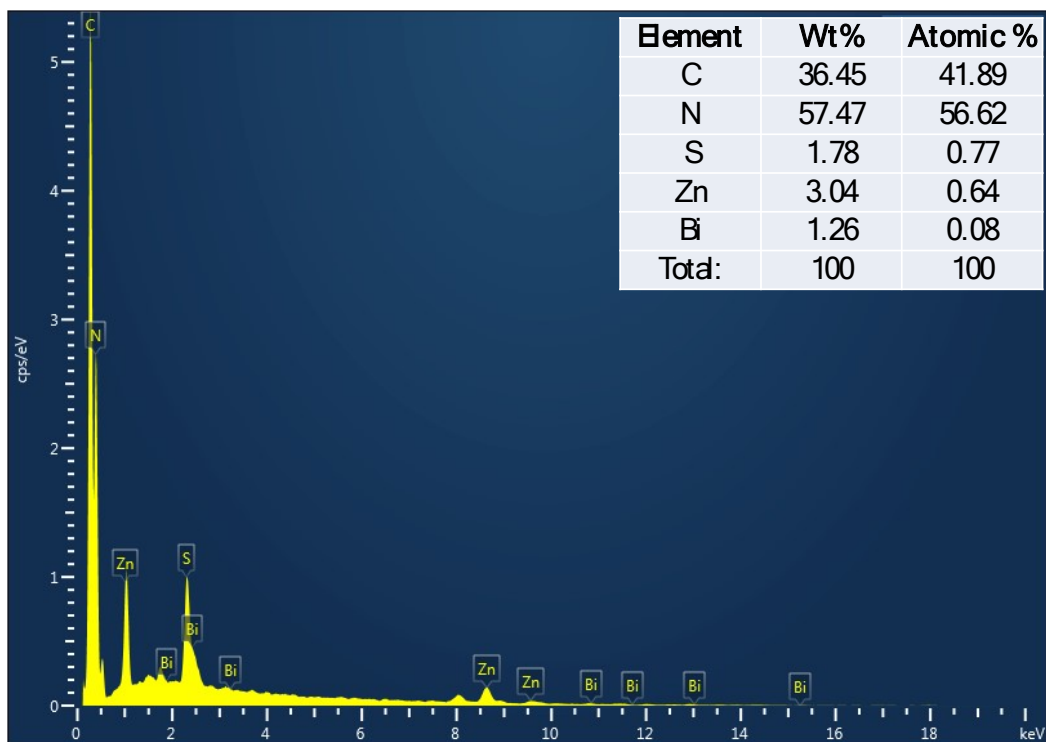


Fig S2. EDS spectra of g-C₃N₄/Bi₂S₃/ZnS composite

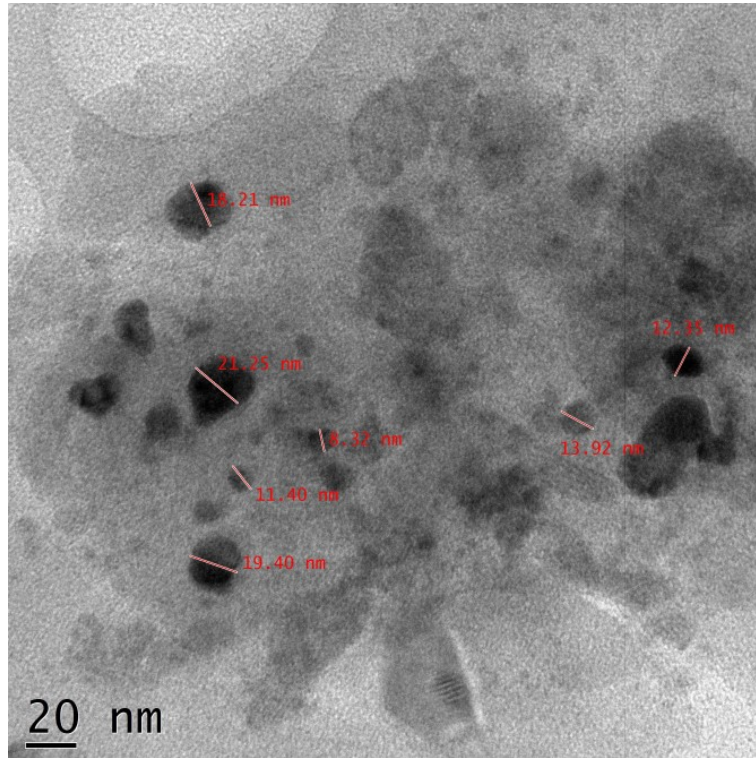


Fig S3. TEM image of g-C₃N₄/Bi₂S₃/ZnS

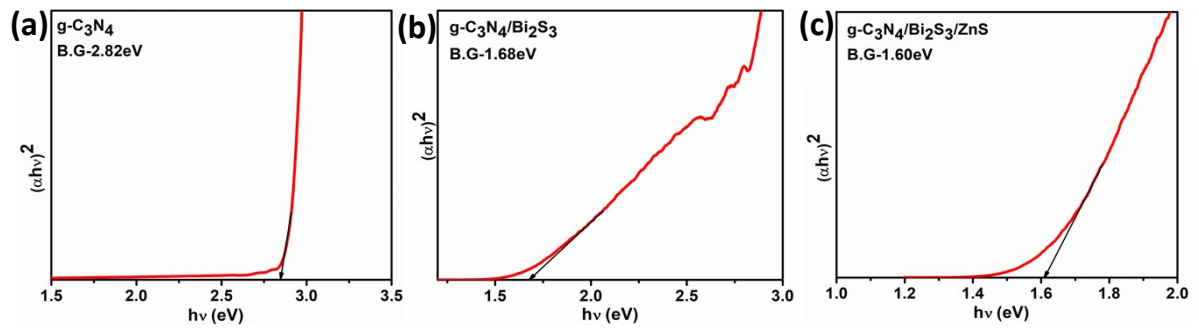


Fig. S4. Tauc plot of (a) g-C₃N₄ (b) g-C₃N₄/Bi₂S₃ and (c) g-C₃N₄/Bi₂S₃/ZnS

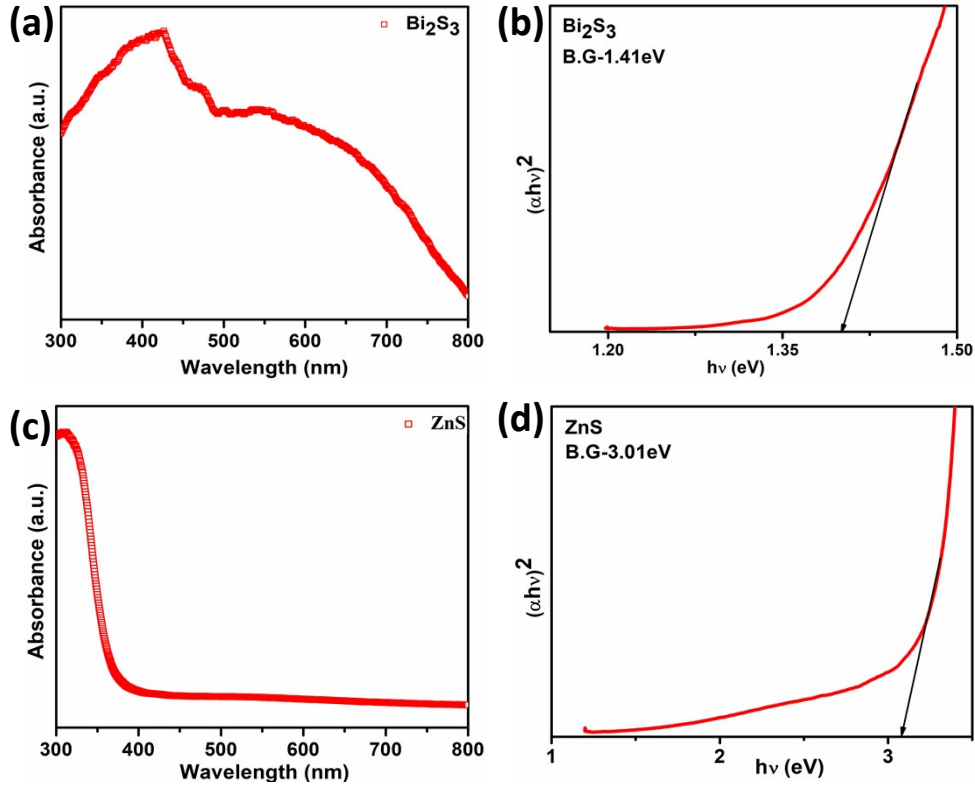


Fig. S5: (a) UV-DRS plot of Bi_2S_3 (b) Tauc plot of Bi_2S_3 (c) UV-DRS plot of ZnS (d) Tauc plot of ZnS

Using the Nernst equation, the measured applied potential vs Ag/AgCl was transformed into a reversible hydrogen electrode (RHE):

$$E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + E^{\circ}_{\text{Ag}/\text{AgCl}} + 0.059 \text{ pH} \quad (1)$$

$E^{\circ}_{\text{Ag}/\text{AgCl}}$ - standard electrode potential of Ag/AgCl (0.197 V)

The following equation was used to determine the photoelectrodes' solar to hydrogen conversion efficiency (η) for the PEC hydrogen evolution reaction:

$$\eta = J (1.23 - V) / P_{\text{light}} \quad (2)$$

where, P_{light} , J and V are the illumination intensity (100 mW cm^{-2}), photocurrent density at the measured bias and applied potential versus RHE, respectively.

Table S1: Comparison with previously reported literature

System	Photocurrent Density (mA.cm ²)	Potential	Electrolyte	Ref
Ag/g-C ₃ N ₄ (1 : 10)	0.00640	V _{SCE}	0.05 M Na ₂ SO ₄	1
WO ₃ / g-C ₃ N ₄	0.82	1.23 V _{RHE}	0.5 M Na ₂ SO ₄	2
g-C ₃ N ₄ -S/BiOI	0.70	V _{Ag/AgCl}	0.1 M Na ₂ SO ₄	3
0.5 g-C ₃ N ₄ /Ti-Fe ₂ O ₃	2.55	V _{Ag/AgCl}	1 M NaOH	4
g-C ₃ N ₄ /BiVO ₄	0.42	V _{RHE}	0.5 M Na ₂ SO ₄	5
TiO ₂ @Co-C ₃ N ₄	1.79	1.23 V _{RHE}	0.1 M Na ₂ SO ₄	6
Pd@g-C ₃ N ₄	0.0788	1.23 V _{RHE}	0.1 M Na ₂ SO ₄	7
g-C ₃ N ₄ /Bi ₂ S ₃ /ZnS	0.99	1.23 V _{RHE}	0.1 M Na ₂ SO ₄	This work

Table S2: Parameters of Nyquist Plots

Sample	R _s (Ω)	R _{CT} (kΩ)	CPE (μΩ ⁻¹)
g-C ₃ N ₄	93.1	187	0.998
g-C ₃ N ₄ /Bi ₂ S ₃	71.8	52.6	0.999
g-C ₃ N ₄ /Bi ₂ S ₃ /ZnS	48.6	50	0.998

In order to quantify the Faradaic efficiency, the volume of gas collected per area of electrode was recorded every 30 min.

$$\text{Faradaic Efficiency (\%)} = \frac{n H_2 (Exp)}{n H_2 (Act)} \times 100 \quad (1)$$

$$n H_2 (Th) = \frac{Q}{2 F}$$

$$Q = I \times t$$

$$I = J \times A$$

where $n H_2$ is the amount of hydrogen generated, Q is the total amount of charge passed through the cell (C), F is the Faraday constant (96485 C mol^{-1}), J is the photocurrent density (A m^{-2}), I is the photocurrent (A), t is the time (s) and A is the area of the electrode (m^2) [8].

The number of moles of hydrogen directly measured from photocurrent density (I-t curve) $n H_{2 (Exp)}$ and the number of moles of hydrogen calculated from the GC responses $n H_{2 (Act)}$ and the Faradaic efficiencies are depicted in **Table S3** and **Table S4**.

Table S3: Faradaic efficiencies of the g-C₃N₄/Bi₂S₃

Time (min)	$n H_{2 (Exp)}$ (mol)	$n H_{2 (Act)}$ (mol)	Faradaic Efficiency (%)
30	0.042×10^{-3}	6.915×10^{-5}	61.5
60	0.035×10^{-3}	5.652×10^{-5}	62.3

Table S4: Faradaic efficiencies of the g-C₃N₄/Bi₂S₃/ZnS

Time (min)	$n H_{2 (Exp)}$ (mol)	$n H_{2 (Act)}$ (mol)	Faradaic Efficiency (%)
30	0.118×10^{-3}	1.257×10^{-4}	94.2
60	0.119×10^{-3}	1.257×10^{-4}	95.0

Cyclic voltammograms (CV):

Figure S1 depicts the CV of g-C₃N₄, Bi₂S₃ and ZnS. Pt and Ag/AgCl/KCl served as the counter electrode and reference electrode, respectively, g-C₃N₄, Bi₂S₃ and ZnS films (as working electrodes) were recorded in an aqueous KCl solution.

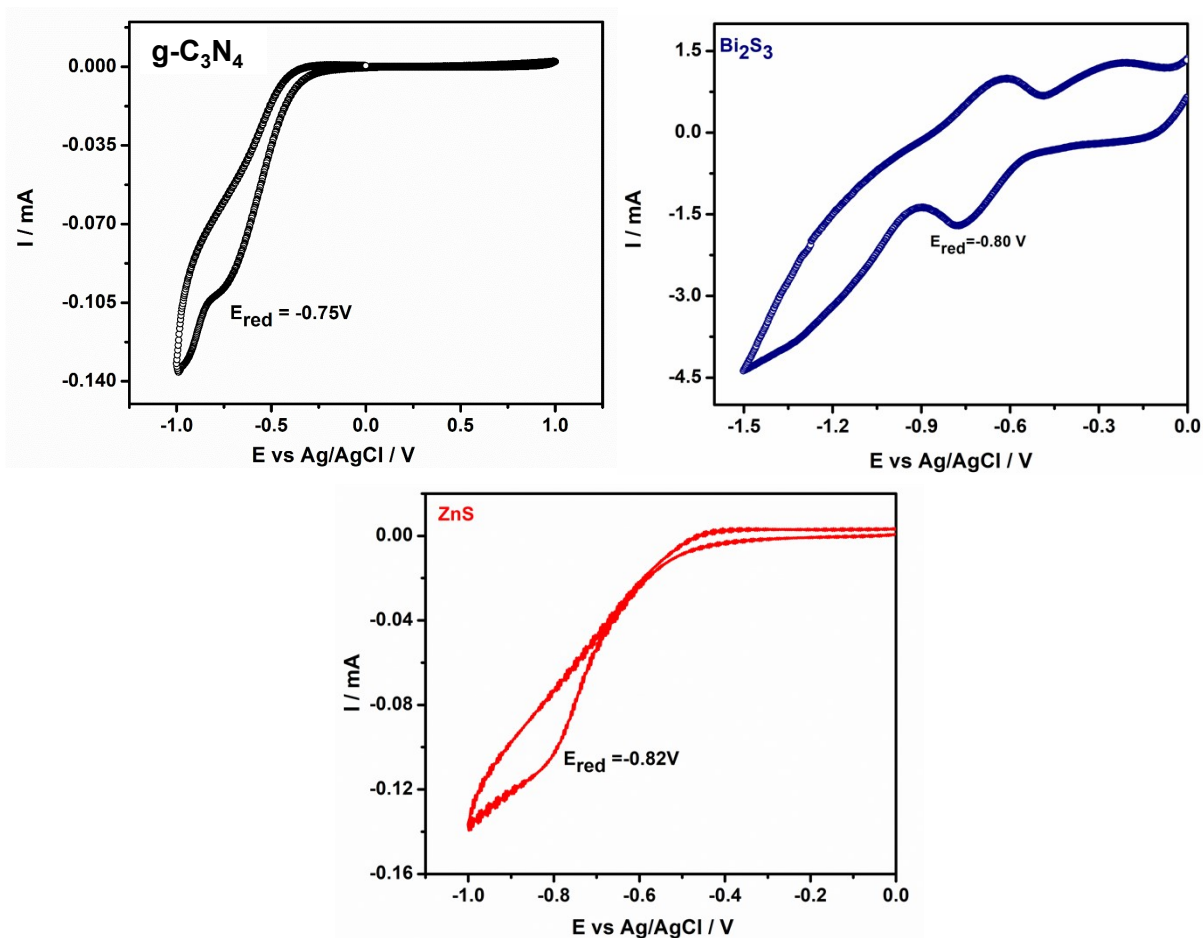


Fig S6. CV plots of g-C₃N₄, Bi₂S₃ and ZnS

The following approach was used to compute the locations of the valence band (VB) and conduction band (CB) for g-C₃N₄

$$E_{\text{red}} = -0.75 \text{ V versus Ag/AgCl/KCl}$$

$$\text{Electrode potential of reference electrode} = +0.197 \text{ V}$$

$$E_{\text{red}} \text{ versus NHE (normal hydrogen electrode)}$$

$$E_{\text{red}} = -0.75 \text{ V} + 0.197 \text{ V} = -0.55 \text{ V (NHE)}$$

We converted V (volts) into eV (electron volts),

$$\text{Therefore } E_{\text{red}} = -4.5 \text{ eV (0 V vs NHE)} - (-0.55 \text{ V}) = -3.95 \text{ eV (CB)}$$

The optical bandgap energy value was then added to the CB energy to determine the VB location of g-C₃N₄.

$$E_{\text{red}} = -3.95 \text{ eV} + (-2.82 \text{ eV}) = -6.77 \text{ eV (VB)}$$

For Bi₂S₃:

$$E_{\text{red}} = -0.80 \text{ V} + 0.197 \text{ V} = -0.60 \text{ V (NHE)}$$

$$E_{\text{red}} = -4.5 \text{ eV (0 V vs NHE)} - (-0.60 \text{ V}) = -3.90 \text{ eV (CB)}$$

$$E_{\text{red}} = -3.90 \text{ eV} + (-1.41 \text{ eV}) = -5.31 \text{ eV (VB)}$$

For ZnS:

$$E_{\text{red}} = -0.82 \text{ V} + 0.197 \text{ V} = -0.62 \text{ V (NHE)}$$

$$E_{\text{red}} = -4.5 \text{ eV (0 V vs NHE)} - (-0.62 \text{ V}) = -3.88 \text{ eV (CB)}$$

$$E_{\text{red}} = -3.88 \text{ eV} + (-3.07 \text{ eV}) = -6.95 \text{ eV (VB)}$$

References

1. F. Qi, Y. Li, Y. Wang, Y. Wang, S. Liu and X. Zhao, *RSC Adv.*, 2016, **6**, 81378–81385.
2. C.-H. Wang, D.-D. Qin, D.-L. Shan, J. Gu, Y. Yan, J. Chen, Q.-H. Wang, C.-H. He, Y. Li, J.-J. Quan and X.-Q. Lu, *Phys. Chem. Chem. Phys.*, 2017, **19**, 4507–4515.
3. K. M. Alam, P. Kumar, P. Kar, U. K. Thakur, S. Zeng, K. Cui and K. Shankar, *Nanoscale Adv.*, 2019, **1**, 1460–1471.
4. Y. Liu, F.-Y. Su, Y.-X. Yu and W.-D. Zhang, *International Journal of Hydrogen Energy*, 2016, **41**, 7270–7279.
5. Y. Li, M. Yang, Z. Tian, N. Luo, Y. Li, H. Zhang, A. Zhou and S. Xiong, *Front. Chem.*, 2019, **7**, 334.
6. J. Safaei, H. Ullah, N. A. Mohamed, M. F. Mohamad Noh, M. F. Soh, A. A. Tahir, N. Ahmad Ludin, M. A. Ibrahim, W. N. R. Wan Isahak and M. A. Mat Teridi, *Applied Catalysis B: Environmental*, 2018, **234**, 296–310.
7. M. Karimi-Nazarabad, E. K. Goharshadi and S. J. Mahdizadeh, *J. Phys. Chem. C*, 2019, **123**, 26106–26115.
8. H. Qi, J. Wolfe, D. Fichou and Z. Chen, *Sci Rep*, 2016, **6**, 30882.