Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Understanding the Charge Transfer Dynamics of Cu_2WS_4-CNT-FeOOH Ternary Composite for Photo-electrochemical Studies

Preeti Dagar[a], Nandan Ghorai[a], Manisha Bungla[b], Hirendra N. Ghosh[a, c,d] and Ashok K. Gangulb[b,e,f*]*

[a] *Institute of Nano Science and Technology, Sector-81, Knowledge City, SAS Nagar, Punjab-140306, India*

[b] *Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India*

[c] *Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*

[d] *Department of Chemical Sciences, National Institute of Science Education and Research Bhubaneswar, Jatni, Khurda 752050, Odisha, India*

[e] *Department of Materials Science and Engineering, Indian Institute of Technology Delhi, New Delhi-110016, India*

[f] *Department of Chemical Sciences, Indian Institute of Science Education & Research, Berhampur, Laudigam, Odisha 760003, India*

* Authors for correspondence

E-mail: ashok@chemistry.iitd.ac.in, hnghosh@barc.gov.in, hnghosh2004@gmail.com

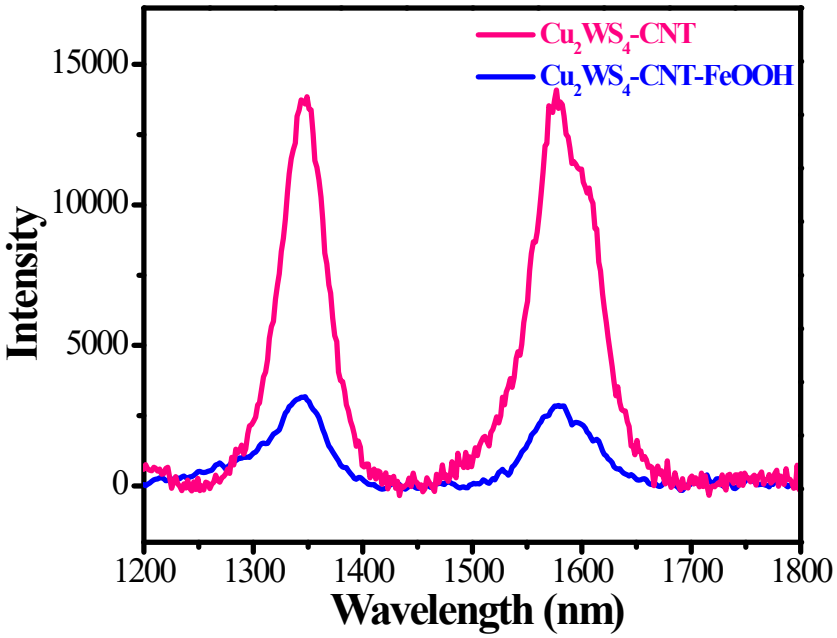

Fig. S1 Raman spectra for Cu_2WS_4-CNT and Cu_2WS_4-CNT-FeOOH.

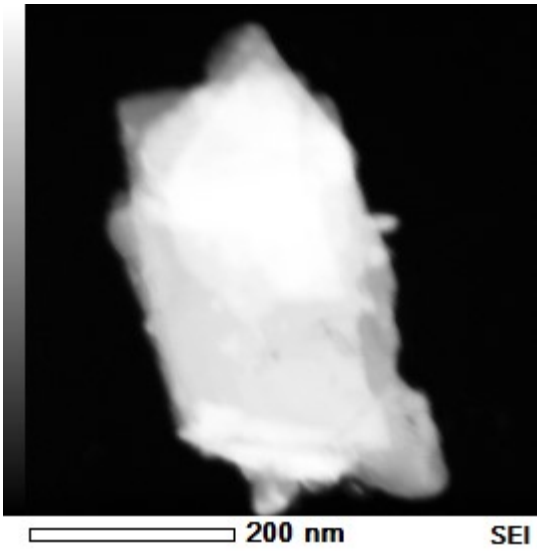

Fig. S2 Area selected for transmission electron microscopy elemental mapping of Cu_2WS_4-CNT-FeOOH.

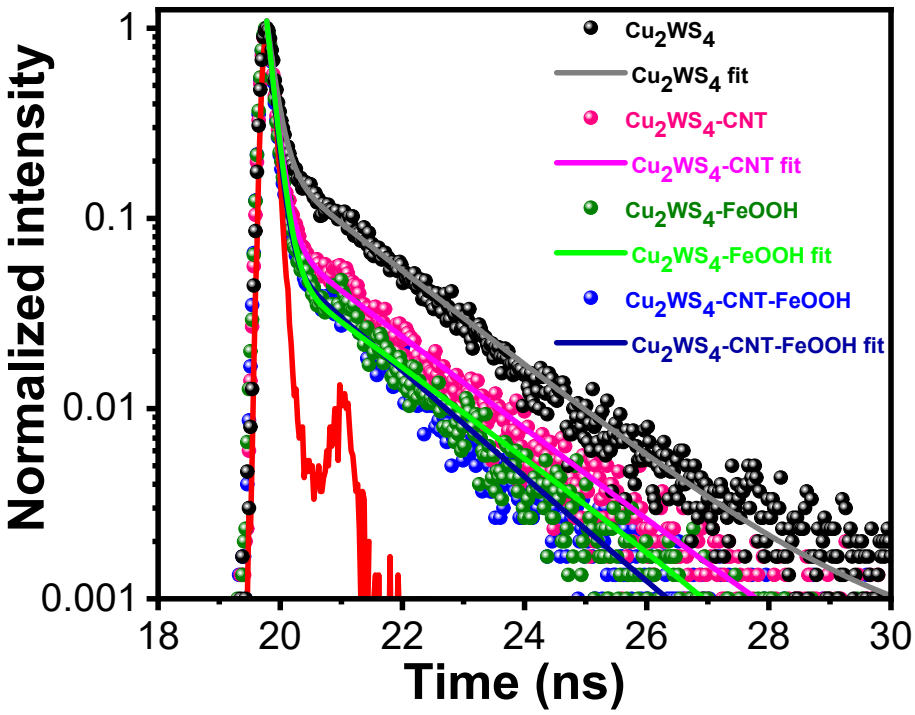

Fig. S3 Time resolved photoluminescence (TRPL) decay curve at 350 nm excitation wavelength.

The TRPL data has been fit using the following equation

$$y = y_0 + A_1 * exp\left(\frac{-(x - x_0)}{\tau_1}\right) + A_2 * exp\left(\frac{-(x - x_0)}{\tau_2}\right)$$

Here, y_0, x_0, A to the y-offset of the exponential fit, x-offset, scaling factor and τ is the decay time constant. The summary of TRPL fittting parameters of all samples is given in Table S1.

Table S1. Summary of TRPL fitting parameters of Cu_2WS_4 and composite samples.

Sample	$\mathbf{a_1}$	τ_1	$\mathbf{a_2}$	τ_2	τ_{avg} **(ns)**
Cu_2WS_4	1.03	0.15	0.07	6.62	0.56
Cu_2WS_4- FeOOH	1.12	0.15	0.08	5.51	0.49
Cu_2WS_4-CNT	1.02	0.13	0.08	2.43	0.31
Cu_2WS_4-CNT-FeOOH	1.35	0.13	0.06	2.58	0.23

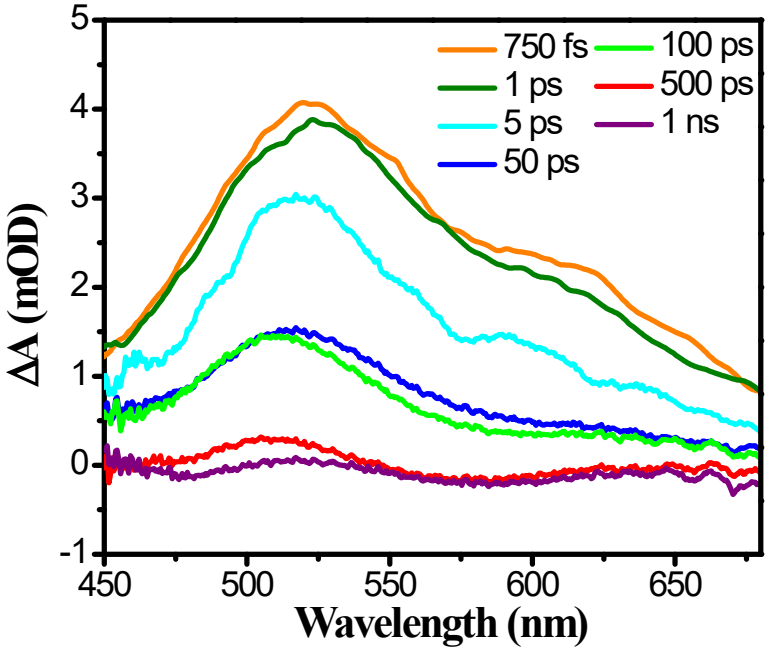

Fig. S4 Transient absorption spectra of pristine FeOOH sample dispersed in ethanol solvent at different time delays after the 350 nm laser pump excitation.

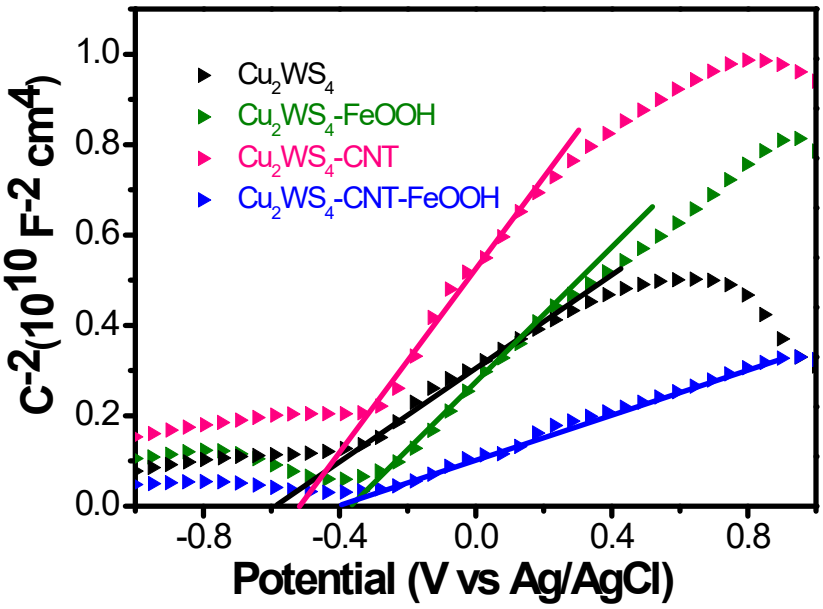

Fig. S5 Mott-Schottky plot for Cu_2WS_4 and composites.

Table S2. Comparison of current density values obtained @ 1.23 V and 1.8 V vs RHE in both dark and illuminated conditions.

Sample	Current density (μA/cm^2) @1.23 V		Current density (μA/cm^2) @1.8 V	
	Dark	Light	Dark	Light
Cu_2WS_4	0.06912	2.7715	0.2995	11.5842
Cu_2WS_4-CNT	1.6227	9.3094	5.7958	35.0290
Cu_2WS_4-FeOOH	0.7704	22.6016	2.3421	63.7840
Cu_2WS_4-CNT-FeOOH	0.5899	32.3281	4.7575	92.5006

Table S3. Comparison of Photocurrent densities obtained by (J_{light}-J_{dark}) at 1.23 V and 1.8 V vs. RHE where J_{light} and J_{dark} are the current densities under light and dark conditions.

Sample	Photocurrent density (μA/cm^2) @1.23 V	Photocurrent density (μA/cm^2) @1.8 V
Cu_2WS_4	2.7023	11.2847
Cu_2WS_4-CNT	7.6867	29.2332
Cu_2WS_4-FeOOH	21.8312	61.4419
Cu_2WS_4-CNT-FeOOH	31.7382	87.7431

Table S4. ABPE values calculated at 1.0 V vs. RHE from the LSV curves.

Sample	ABPE (%)
Cu_2WS_4	0.0004
Cu_2WS_4-CNT	0.0012
Cu_2WS_4-FeOOH	0.0039
Cu_2WS_4-CNT-FeOOH	0.0062