Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Highly efficient charge transfer through double Z-scheme mechanism by Cu promoted MoO_3/g-C_3N_4 hybrid nanocomposite with superior electrochemical and photo catalytic performance

Sulagna Patnaik[a], Gayatri Swain[a], K. M. Parida[a]*

[a]Centre for Nano Science and Nanotechnology, Siksha O Anusandhan (Deemed to be University), Bhubanswar-751030, Odisha, India

Corresponding Author:

***E-mail:** kulamaniparida@soauniversity.ac.in

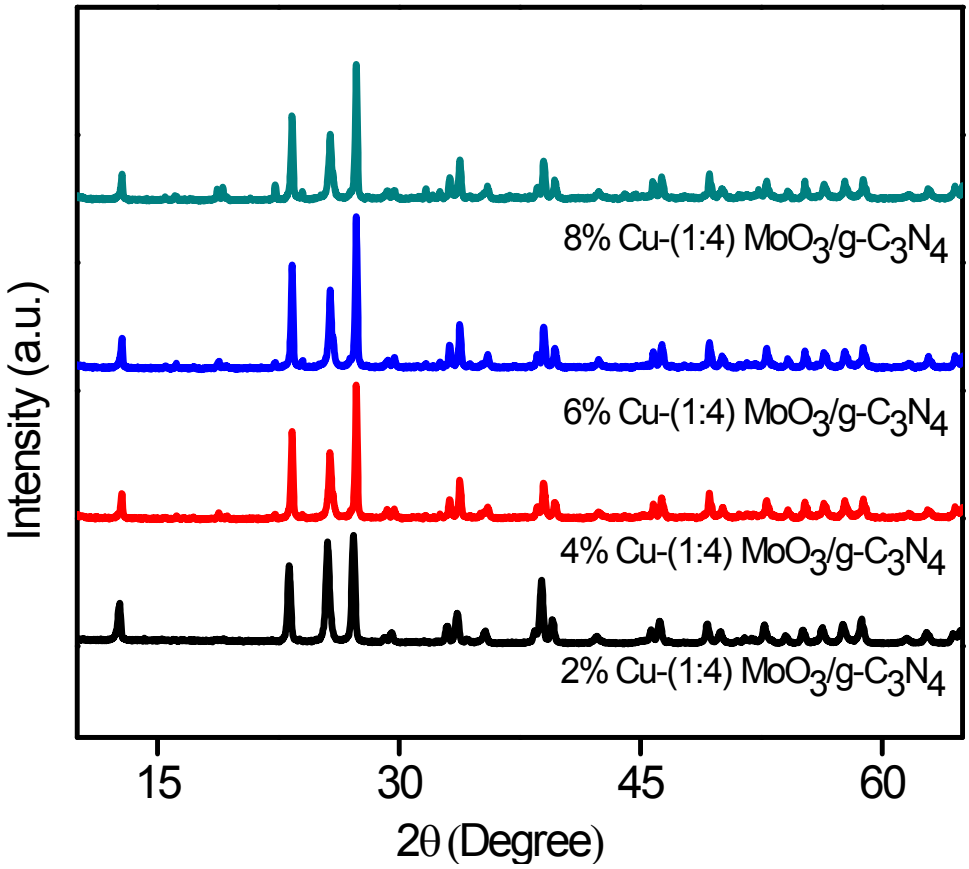

Figure S1. XRD spectra of MoO_3/g-C_3N_4 composite containing different content of Cu

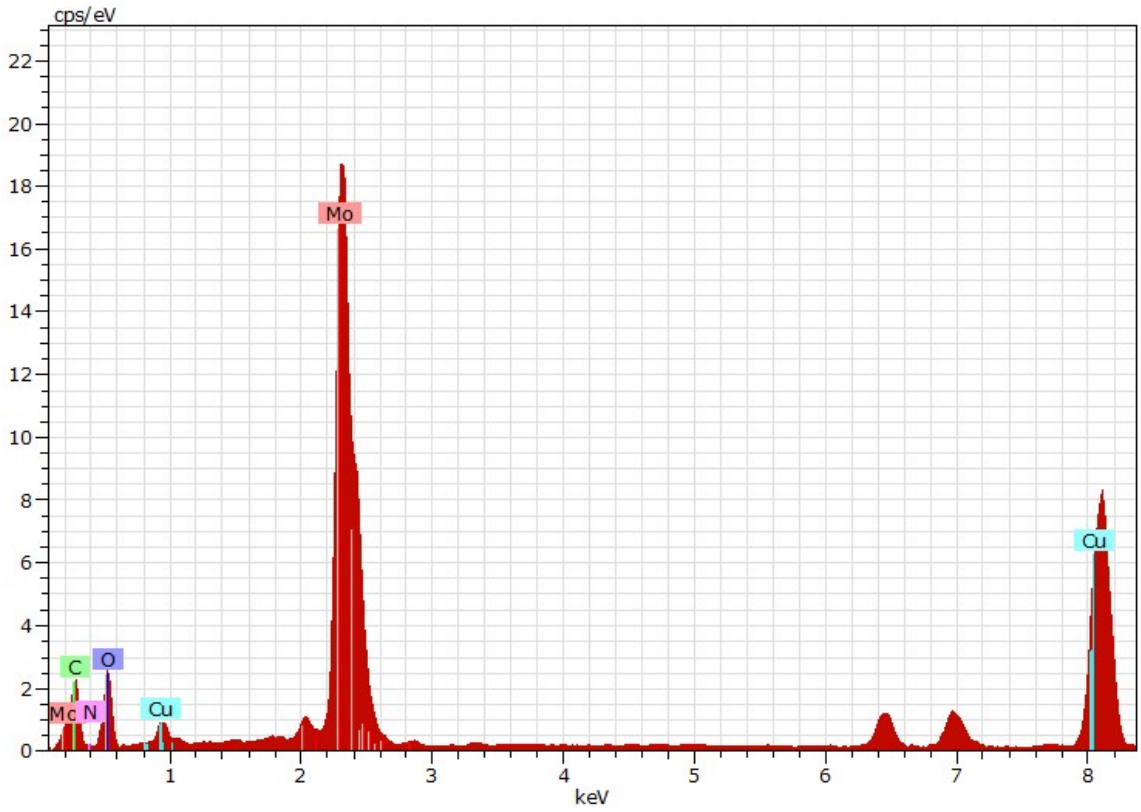

Figure S2. EDS of diiferent elements present in the Cu-MoO_3/g-C_3N_4

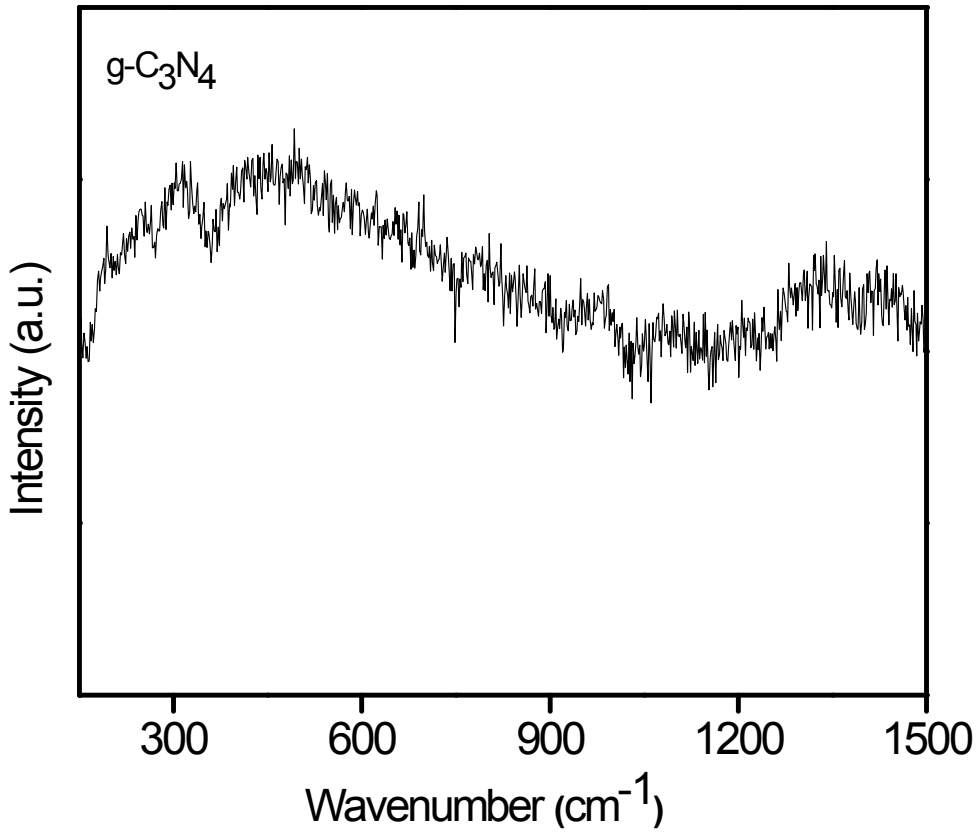

Figure S3. Raman spectra of neat g-C_3N_4

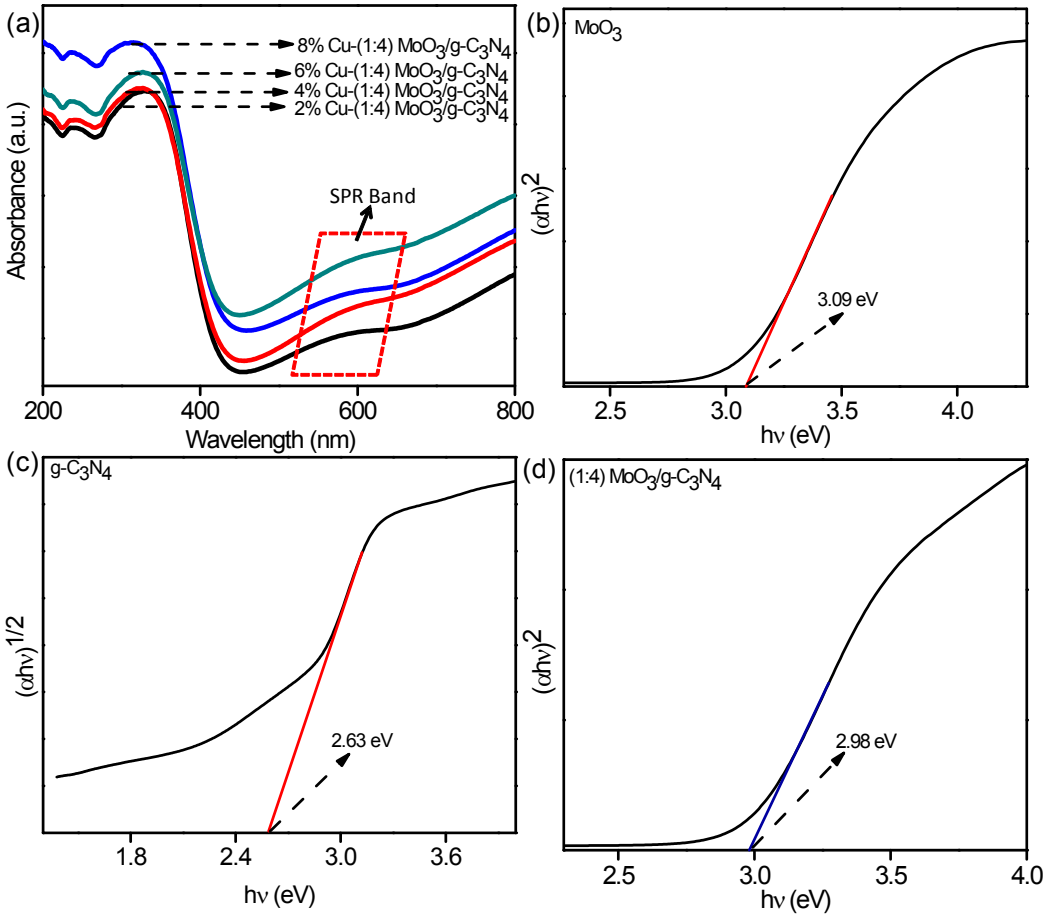

Figure S4. (a) UV-Vis absorption spectra of various percentage of Cu loading MoO_3/g-C_3N_4 composite and Band gap potential of (b) MoO_3, (c) g-C_3N_4 and (d) (1:4) MoO_3/ g-C_3N_4

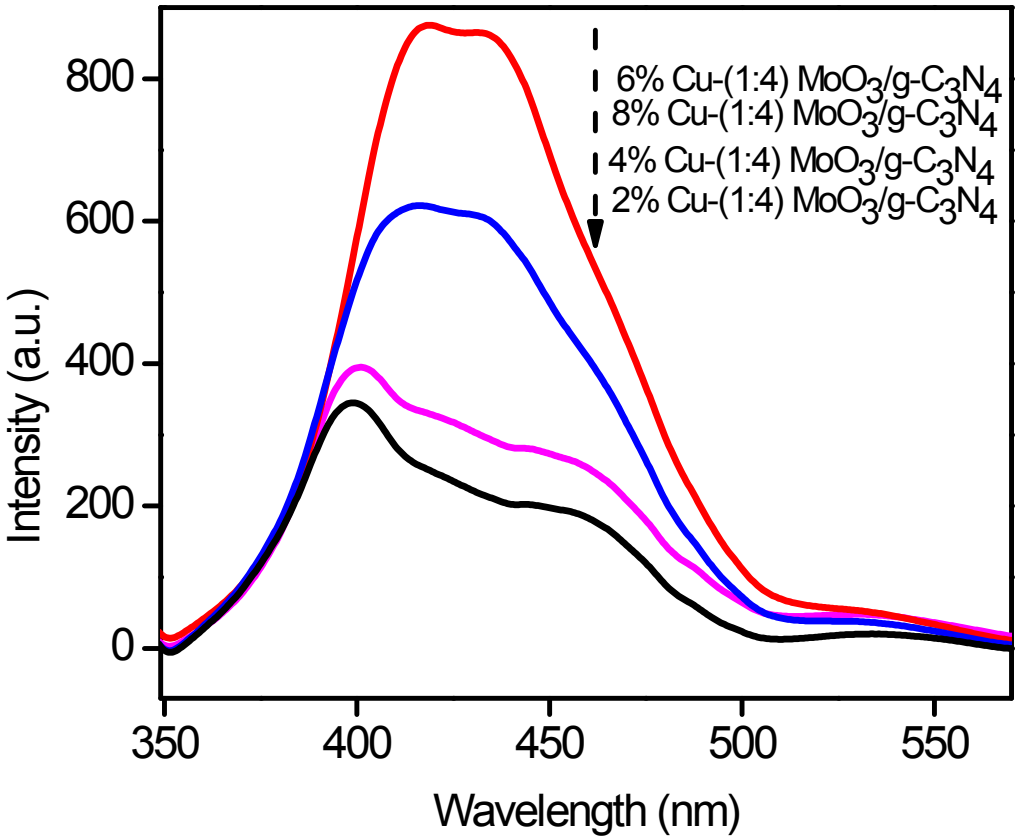

Figure S5. PL spectra of MoO_3/g-C_3N_4 composite with different amount of Cu

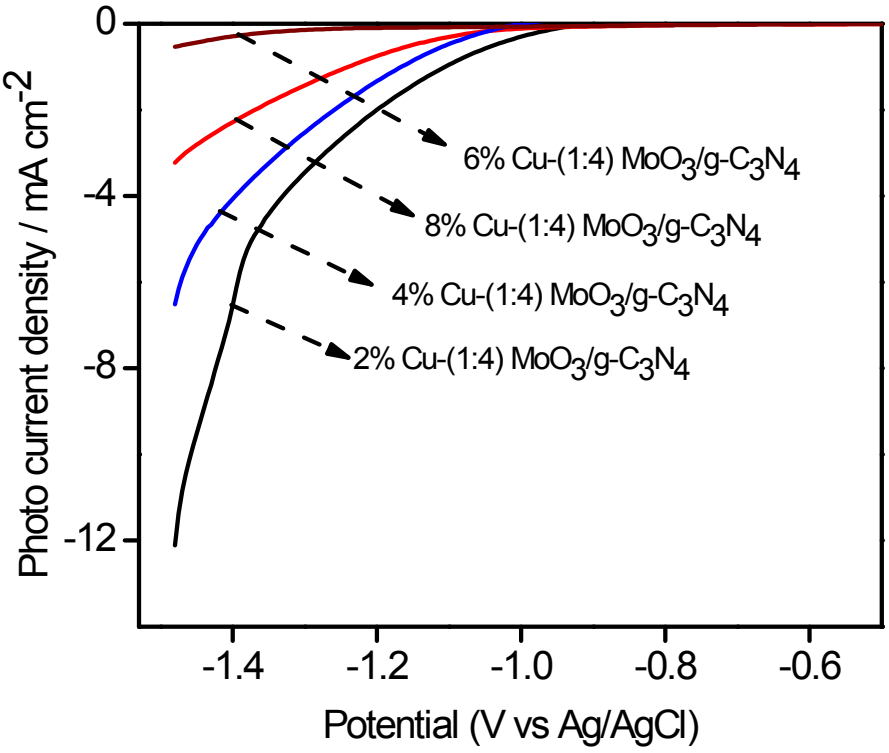

Figure S6. LSV plot of various weight % of Cu loading MoO_3/g-C_3N_4

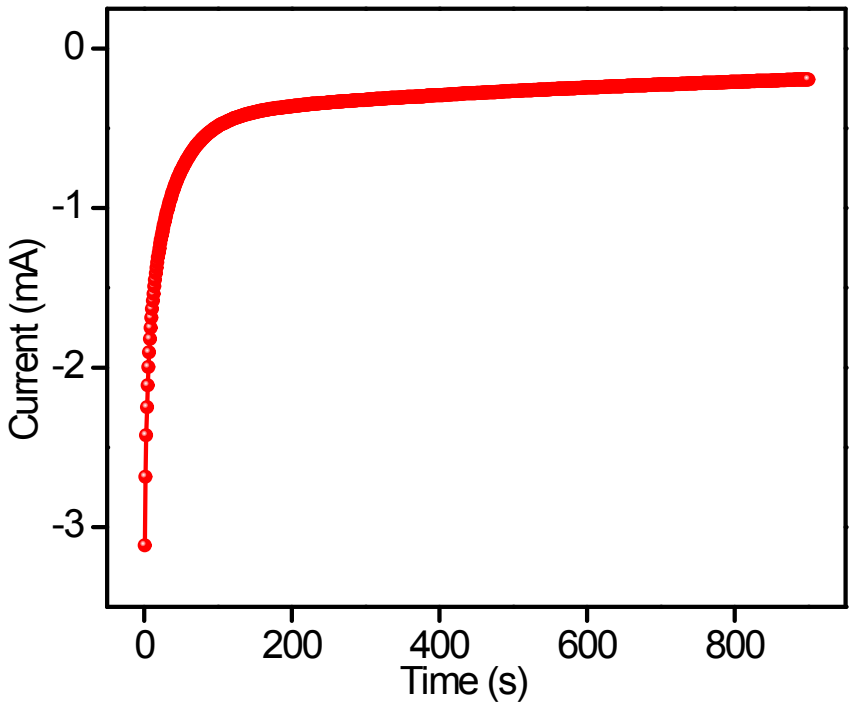

Figure S7. Chronoampeometry test for 2%Cu-(1:4)MoO_3/g-C_3N_4 at -1.30 applied potential

Electrochemical stability

In order to investigate the stability of the electrocatalytic activity chronoamperometry was carried for 900s. Figure S7 shows the corresponding chronomperometric response of time dependence cathodic photocurrent of Cu-MoO_3/g-C_3N_4 electrodes in 0.5 M Na_2SO_4 solution (pH = 6.3) at -1.30 V applied potential Vs. Ag/AgCl. When the photocatalyst was irradiated with light, the cathodic photocurrent rapidly increased at the initial stage and then became relatively stable with time. The current density exhibits a very slow attenuation and a high relative current of 65% still persists even after 900s [1].

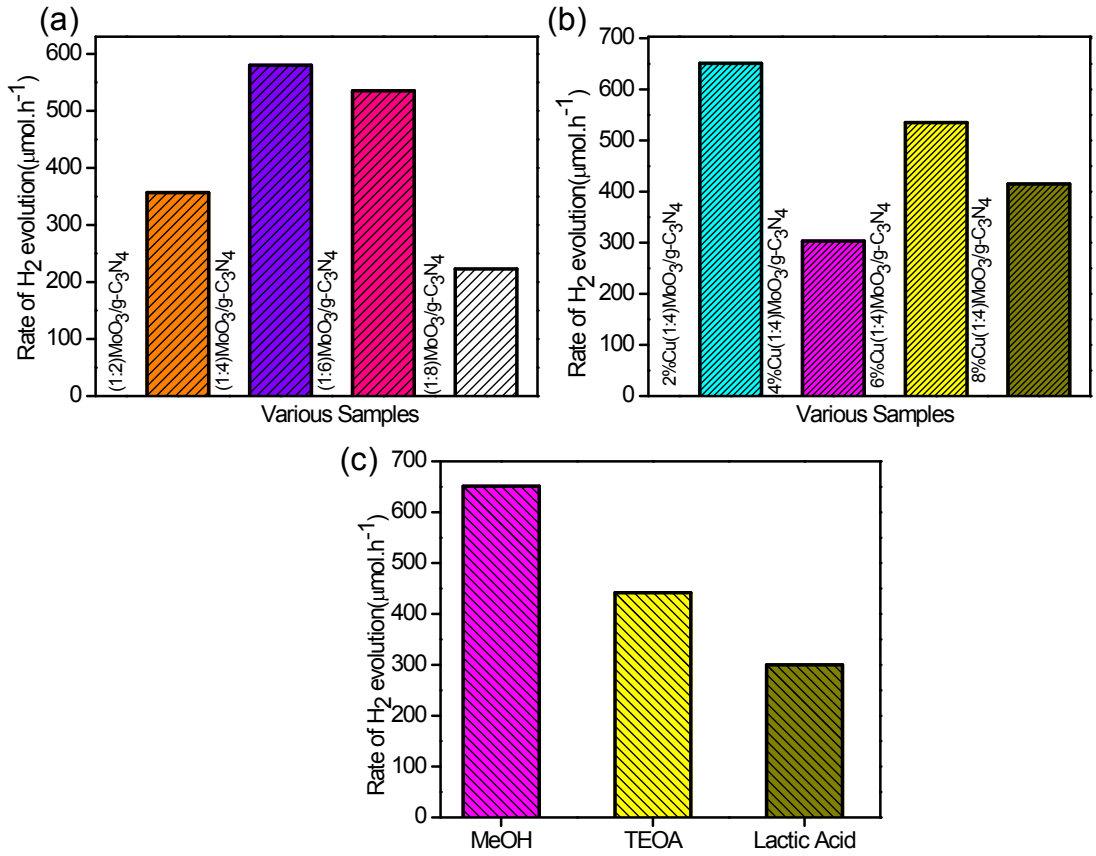

Figure S8. Hydrogen evolution study of (a) various weight percentages of MoO_3/g-C_3N_4 and (b) Cu loaded MoO_3/g-C_3N_4 (c) H_2 evolution study of 2% Cu-(1:4) MoO_3/ g-C_3N_4 composite using various scavenger component

Actually sacrificial agents play a decisive role in H_2 evolution because they act as electron donors and consume the photogenerated holes during photo catalytic reaction. To compare the effect of various sacrificial agents oxidation potentials are important. However, along with oxidation potential, permittivity and chain length in case of organic sacrificial agents also affect the rate of H_2 evolution [2]. In the present study, all the three factors are responsible for enhanced H_2 evolution rate of Cu-MoO_3/g-C_3N_4 composite in presence of methanol. It should be noted that, in the case of using 20% methanol solution as the electron donor, H_2 is also produced from water as a result of methanol conversion according to the following equation [3]

$$CH_3OH + H_2O = CO_2 + 3H_2$$

Moreover, the presence of oxygen vacancy defects of MoO_3 strongly enhances interactions, because of electron back-donation from surface Mo^{3+} into the π* orbital of molecular CO and methanol get oxidized to CO_2 easily [4].

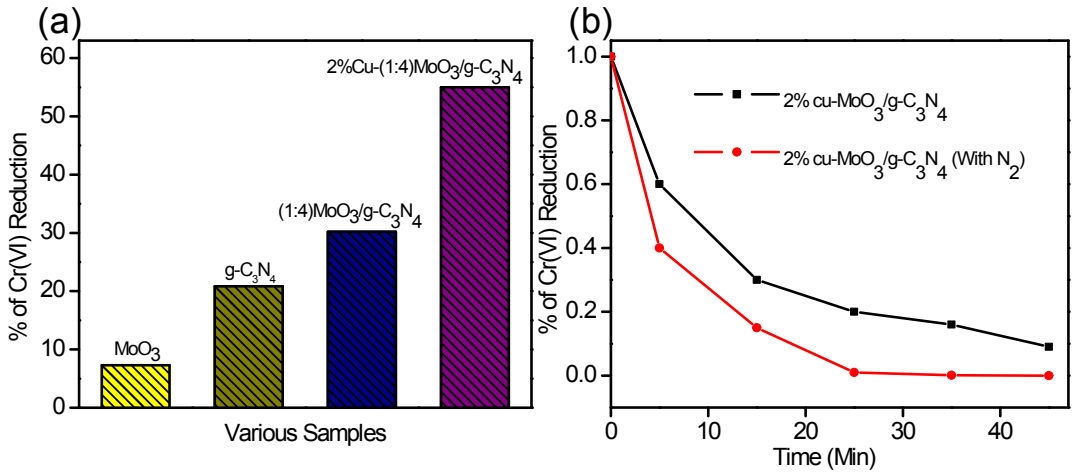

Figure S9. (a) Reduction of Cr(VI) by neat and composite sample (b) Photoreduction of Cr (VI) in the presence of N_2 gas

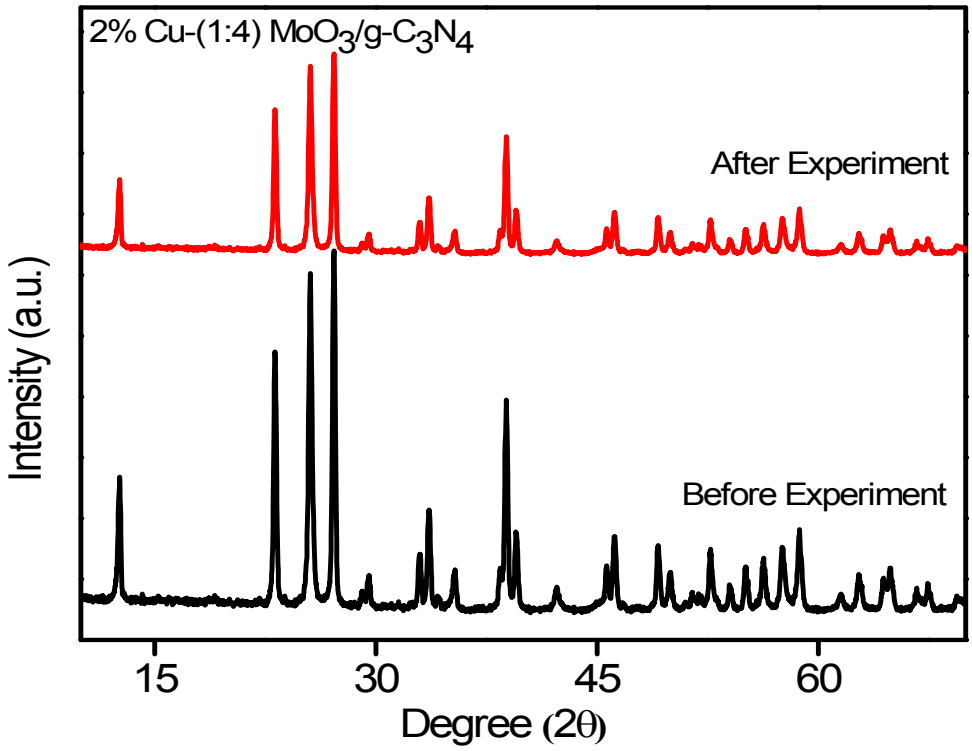

Figure S10. XRD plot of 2% Cu-(1:4) MoO_3/ g-C_3N_4 photocatalyst before and after H_2 evolution experiment

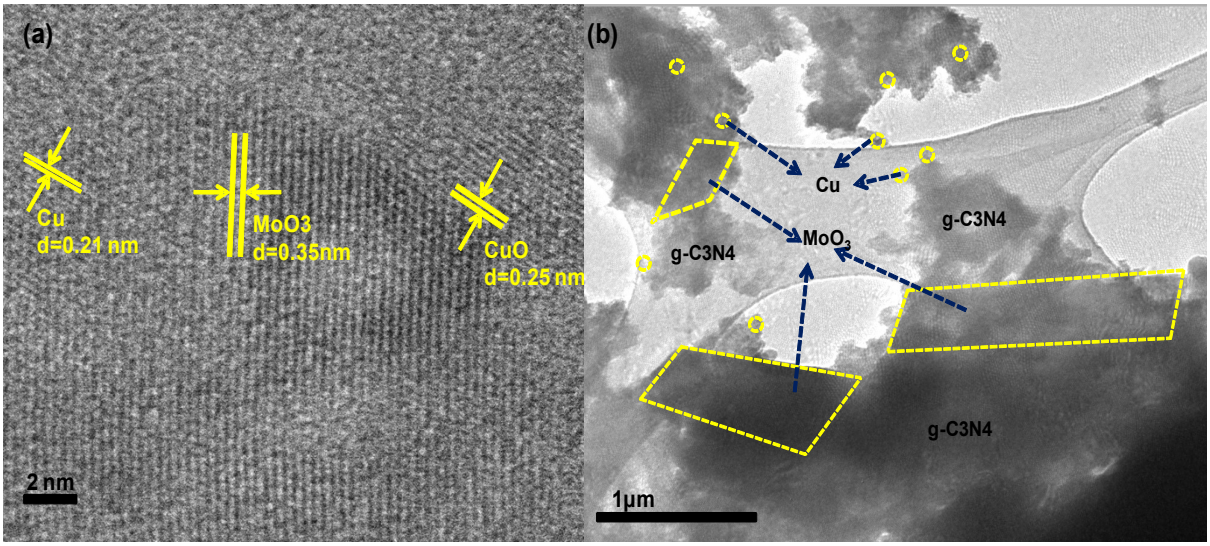

Figure S11. (a) HRTEM and (b) TEM images of 2% Cu-(1:4) MoO_3/g-C_3N_4 photocatalyst after H_2 evolution experiment

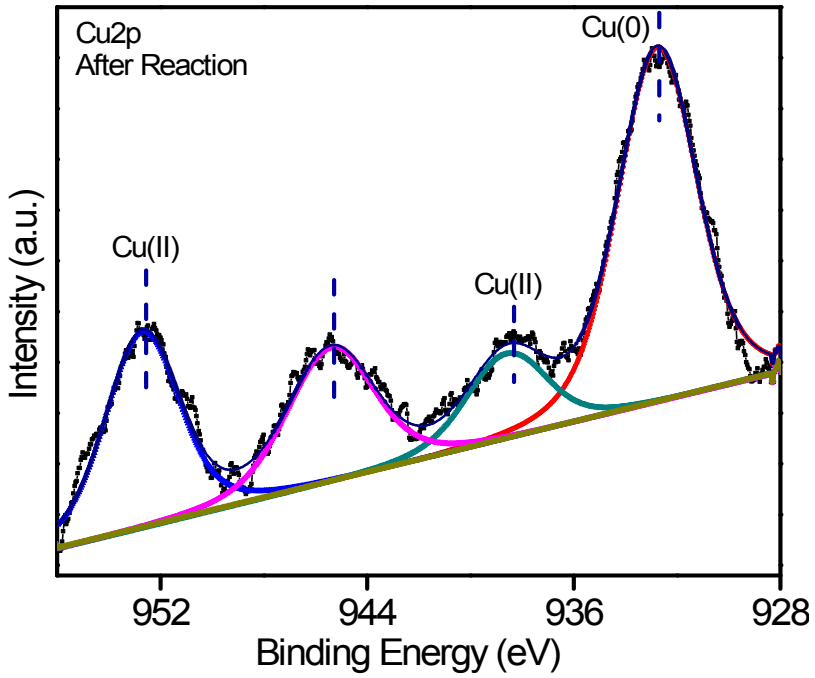

Figure S12. XPS images of 2% Cu-(1:4) MoO_3/ g-C_3N_4 photocatalyst after H_2 evolution experiment

As the enhanced photo activity of the catalyst involves both SPR effect of Cu NPs and shifting of Fermi level of CuO under visible light irradiation both the reactions, $Cu^0 \leftrightarrow Cu^{2+}$ takes place simultaneously. Cu^{2+} ions has tendency to get partially reduced by consuming photo generated electrons and as the photo generated electrons get transferred on to the surface of Cu^0 after equilibration, they also get oxidised to Cu^{2+}. The TEM, HRTEM (Figure S11) and XPS image (Figure S12) of Cu in case of used photo catalyst further confirms the presence of both Cu^0 and Cu^{2+}.

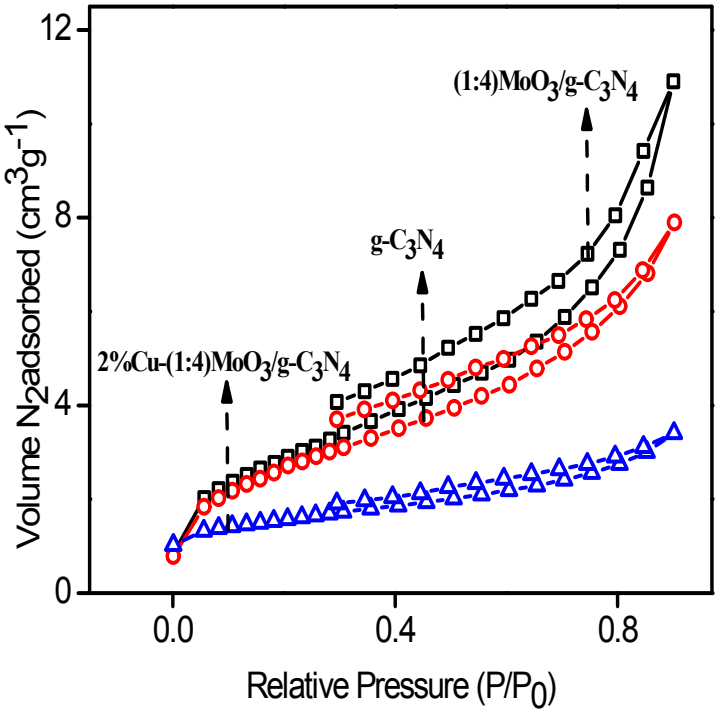

Figure S13. N_2 adsorption and desorption isotherms of g-C_3N_4, (1:4) MoO_3/g-C_3N_4 and Cu-MoO_3/g-C_3N_4 nanocomposite

The details of BET surface areas and pore diameter of g-C_3N_4, (1:4) MoO_3/g-C_3N_4 and Cu-MoO_3/g-C_3N_4 nanocomposites are shown in Table S1 and the isotherms were shown in figure S13. Pure g-C_3N_4 exhibits a lower surface area. However, in situ formation of MoO_3/g-C_3N_4 composite by calcinations method led to the increase in the BET value of photocatalyst, which might be due to the evolution of a number of gases and introduction of porosity. But upon Cu loading the surface area decreases due to pore blockage. Although the surface area decreases, the photo catalytic activity shows an increasing trend owing to increase in the number of active sites and efficient charge separation [7].

Name of the sample	Surface area(m^2g^1)	Pore volume (cm^3g^{-1})	Pore size (nm)
g-C_3N_4	9.65	0.0122	5.065
(1:4)MoO_3/g-C_3N_4	10.7	0.0169	6.311
2%Cu-(1:4) MoO_3/g-C_3N_4	2.72	0.0039	5.876

Table S1. Details of surface area and pore volume of g-C_3N_4, (1:4) MoO_3/g-C_3N_4 and Cu-MoO_3/g-C_3N_4

Photocatalyst	Incident light (λ)	Reaction solution	H_2 Evolution	Conversion Efficiency	Ref
ZnO/ZnS/g-C_3N_4	300 W visible light	0.25 M Na_2S/ 0.25 M Na_2SO_3 aq sol^n	1205 µmol/g/4h	NA	6
WO_3/g-C_3N_4/Ni(OH)*x*	300 W Xe lamp, UV cut-off filter (λ > 400 nm)	15 vol%TEOA	576 µmol/(g-1 h-1)	NA	7
CdS/Au/ g-C_3N_4	λ > 420 nm	0.1M Na2SO4/0.5 wt. % Pt	19.02 µmol g-1 h-1	NA	8
g-C_3N_4/Au/C-TiO_2	λ > 420 nm	TEOA	129.0 µmol g-1 h-1	NA	9
g-C_3N_4/Au/CdZnS	λ > 420 nm	0.25 M Na_2S and 0.35 M Na_2SO_3	6.3 mmol/g in 4h	NA	10
$CoTiO_3$/ g-C_3N_4	λ > 420 nm	10 vol.% ethanol 3 wt.% Pt	858 µmol·h-1·g-1	38.4% at 365 nm 3.23% at 420 ± 20 nm	11
Ag_3PO_4/Ag/ g-C_3N_4	λ > 420 nm	TEOA	4.1 lmol/gh	NA	12
WO_3/ g-C_3N_4	λ > 420 nm	TEOA, 1 wt.% Pt	400 µmol h-1 gcat-1	NA	13
g-C_3N_4/WO_3	λ > 420 nm	TEOA, 1 wt.% Pt	2.84 µmol h-1	0.9% at 420 nm	14
Cu-MoO_3/g-C_3N_4	λ > 420 nm	10 vol.% Methanol	652 µmol/h	Present work	

Table S2 State-of-the-art advancement in the field of Z-scheme photocatalysis for H_2 evolution, NA (Not available)

References

1. N. Sagara, S. Kamimura, T. Tsubota, T. Ohno, *Appl Catal B: Env.*,2016, **192,** 193–198.

2. M. Wang, S. Shen, L. Li, Z. Tang, and J. Yang, *J. Mater. Sci*., 2017, **52**, 5155–5164

3. M. R. Gholipour, C. T. Dinh, F. Béland and T. O. Do, *Nanoscale*, 2015, **7**, 8187

4. A. Galin ´ ska and J. Walendziewski, *Energy & Fuels,* 2005, **19***,* 1143-1147

5. S. Sakthivel, M.V. Shankar, M. Palanichamy, B. Arabindoo, D.W. Bahnemanna and V. Murugesanb, *Water Res.* 2004, **38**, 3001–3008.

6. Z. Dong, Y. Wu, N. Thirugnanam and G. Li, *Applied Sur. Sc.,* 2018, **430**, 293-300

7. M. You, J. Pan, C. Chi, B.Wang, W. Zhao, C. Song, Y. Zheng, and C. Li, *J. Mat. Sci.* 2018, **53**, 1978–1986

8. X. Ding, Y. Li, J. Zhao, Y. Zhu, Y. Li, W. Deng, and C. Wang, *APL MATERIALS* , 2015, **3**, 104410-1

9. Y. Zou, J. W. Shi, D. Ma, Z. Fan, C. Niua and L. Wang, *ChemCatChem*, 2017, **9**, 3752-3761

10. X. Ma, Q. Jiang, W. Guo, M. Zheng, W. Xu, F. Ma, B. Hou, *RSC Adv.*, 2016,**6**, 28263-28269

11. R. Ye, H. B. Fang, Y. Z. Zheng, N. Li, Y. Wang, and X. Tao, *ACS Appl. Mater. Interfaces*, 2016, **8**, 13879–13889

12. M. You, J. Pan, C. Chi, B. Wang, W. Zhao, C. Song, Y. Zheng, and C. Li*, J. Mat. Sci.*, 2018, **53**, 1978-1986

13. C. Cheng, J. Shi, Y. Hu and L. Guo, *Nanotechnology*, 2017, **28**, 164002

14. G. Zhao, X. Huang, F. Fina, G. Zhang and J. T. S. Irvine, *Catal. Sci. Technol*., 2015, **5**, 3416