

Electronic Supporting Information (ESI)

Development of hierarchical copper sulfide-carbon nanotube (CuS-CNT) composites and utilization of its superior carrier mobility in efficient charge transport towards photodegradation of Rhodamine B under visible light

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1. Device Fabrication method

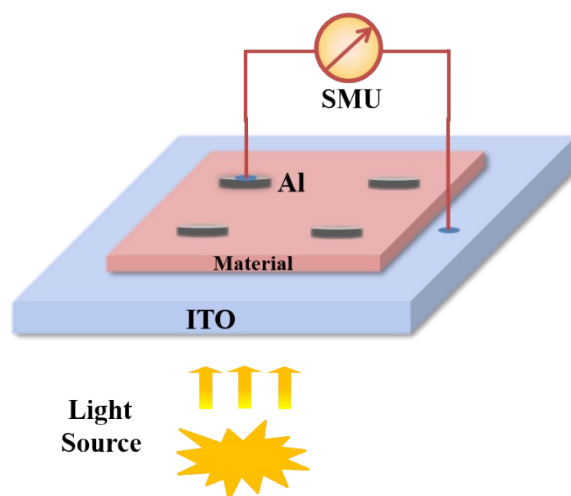


Figure S1. Schematic diagram of the fabricated Schottky diode.

To fabricate our Schottky diode, an ITO coated glass substrate was first cleaned using 2 propanol, acetone and distilled water. In parallel, we have made a stable dispersed medium of the synthesized materials (CuS and CNT-CuS) in Dimethyl formamide (DMF) solvent by ultra-sonication. After drying the glass substrate, the well-dispersed medium was coated onto the glass substrate using the spin coating unit (SCU 2700) at the rate of 1200 rpm for 3 mins. The as-prepared films are then dried in a vacuum oven for 1 hour. Finally, the aluminium (Al) electrode as metal contact was deposited onto the coated film using the Vacuum Coating Unit (12A4D, HINDHIVAC) to achieve Al/CuS/ITO and Al/T-CuS/ITO configuration under pressure 10^{-6} Torr. A typical quad punch-hole shadow mask was used to control the effective area of the Schottky contact as $7.065 \times 10^{-6} \text{ m}^2$. The thickness of the deposited film was measured as $1 \text{ }\mu\text{m}$ by a surface profiler.

2. Calculation of optical bandgap

To measure the gap between the conduction and valence band, we have used Tauc's equation in the fundamental absorption edge (530-565 nm). According to Tauc's equation ¹,

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (\text{S1})$$

where α is the absorption coefficient, E_g is the bandgap, h is Planck's constant, ν is frequency, A is a constant, and $n=2$ and $\frac{1}{2}$ is corresponding to the allowed indirect and direct optical transition respectively.

3. Calculation of dielectric constant

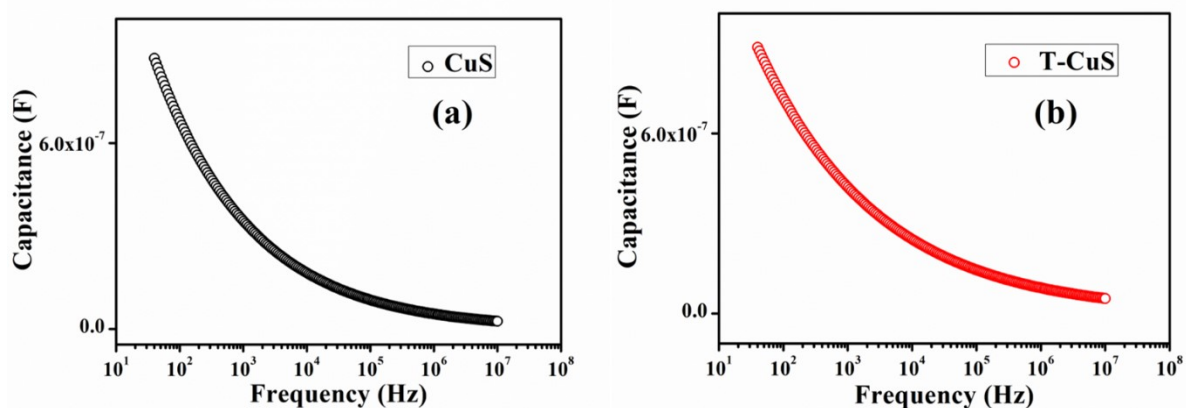


Figure S2. Capacitance vs. frequency plot for the CuS and CNT-CuS thin film.

The dielectric constant (ϵ_r) of our synthesized materials was estimated from the capacitance (C) vs. frequency (f) plot (Figure S2). with the help of Eq. (S2);

$$\epsilon_r = \frac{C_0 d}{\epsilon_0 A_{eff}} \quad (S2)$$

where ϵ_0 is the permittivity of free space, C_0 is the saturated capacitance, d is the thickness of the deposited film and A_{eff} is the effective diode area ².

4a. Weight (%) test of CNT

Here we have tested the CNT (wt.%) content with the help of EDX analysis in three different spots and take an average value and also, we have performed EDX Mapping of the composite. Here from the different spot, we get an average Wt. % of CNT in the composite is around 2.80% which is close to 3%.

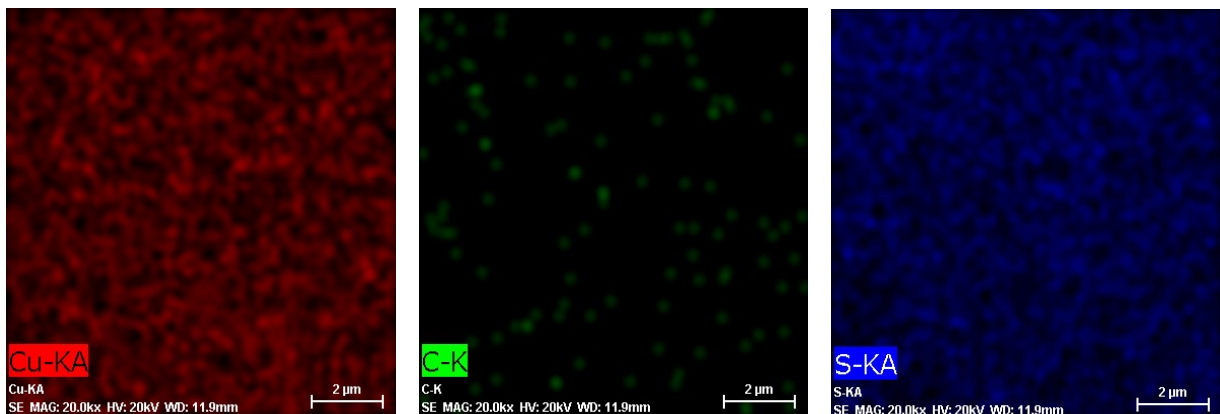


Figure S3. EDX Mapping of the sample T-CuS (3%)

4b. EDX Spectrum data of T-CuS (3%)

Spot No	Cu (Wt.%)	C (Wt.%)	S (Wt.%)
Spot 1	51.31	2.72	45.97
Spot 2	51.78	2.87	45.35
Spot 3	51.96	2.81	45.23
Average	51.68	2.80	45.52

5. Charge Transfer Characteristics of CNT

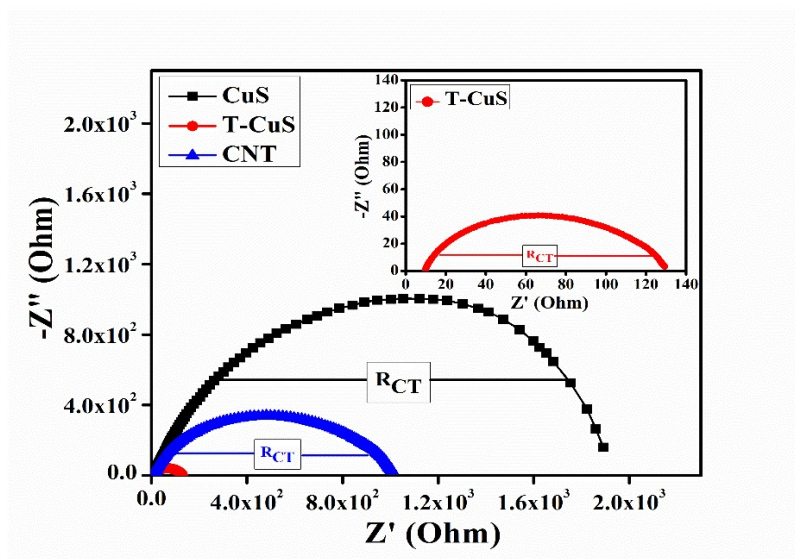


Figure S4. Nyquist Plot for CuS, CNT and T-CuS Composite.

The EIS Nyquist plot is an effective tool to investigate the conductance and charge transfer characteristics of the materials. Figure S4 revealed that the diameter of the semi-circular arc for the T-CuS composite was significantly smaller than for the bare CuS and the diameter of the semi-circular arc for pure CNT is lies between bare CuS and the T-CuS composite. So, it can be concluded that the charge transfer for CNT is higher than bare CuS but lower than T-CuS composite.

6. Adsorption of RhB by the catalysts

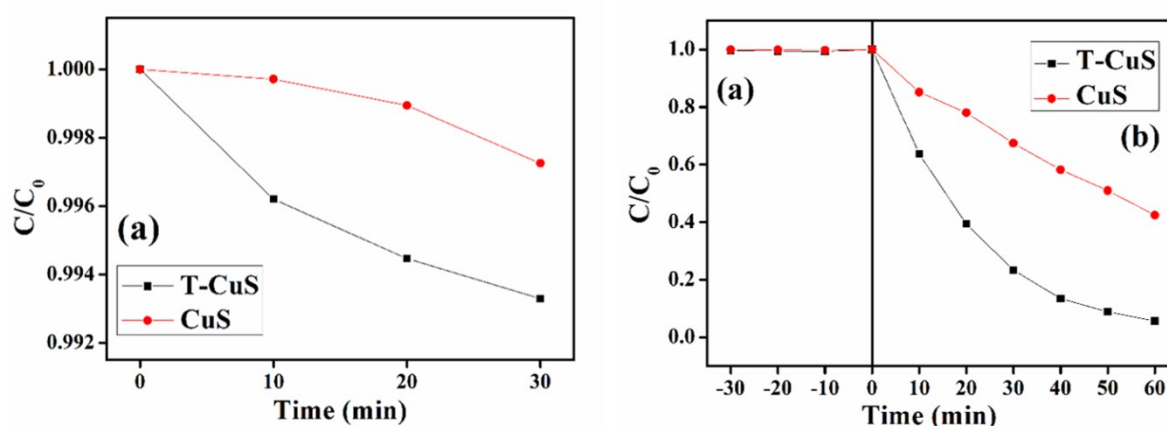


Figure S5. The adsorption profiles of aqueous RhB solution on bare CuS and the T-CuS composite, as a function of time in the dark.

The adsorption of RhB on the photocatalysts were measured since the pre-adsorption of the dyes aids the migration of the charge carriers. The adsorption experiments

were performed by continuous stirring 100 mL of aqueous RhB solution with 30 mg of each catalyst (CuS and T-CuS) for 30 min in the dark condition.

Figure S5 displays the adsorption profiles of aqueous RhB solution as a function of time in the dark on the bare CuS and the T-CuS composite, respectively. The bare CuS demonstrated no adsorption in the dark, as the concentration of the RhB solution remained almost unchanged. In addition, the T-CuS composite also showed negligible adsorption behaviour to RhB, which was less than 1% for 30 min of stirring. These results indicate that the adsorption experiments did not show a significant effect on RhB removal and for these reasons, the pre-adsorption was not displayed in the degradation plots in the main manuscript.

7. Photodegradation process

The photocatalytic performance of the as-prepared samples was evaluated by photocatalytic degradation of Rh B under UV light irradiation. In the experiment, 30 mg of the samples and 1 mL H₂O₂ were dispersed in 100 mL of Rh B aqueous solution (100 ppm). The mixed suspensions were magnetically stirred for 30 mins in the dark to attain an adsorption-desorption equilibrium. Under ambient conditions and stirring, the mixed suspensions were exposed to visible light produced by a solar simulator (Abet Technologies, Model 10500). At regular time intervals, 3 ml of the examined suspensions were extracted and centrifuged to remove the suspended impurities. The absorption of Rh B in the filtrate centred at 553.5 nm was then examined using a UV-Vis spectrometer and the degradation process was analysed.

For the recyclability test, the catalyst was extracted after the degradation cycle by centrifugation and washed with isopropyl alcohol followed by Millipore water and reused in the next cycle. In this study, all the experiments have been repeated three times and displayed almost similar activity.

8. Function of H₂O₂ in the degradation process

The catalytic process without adding H₂O₂, was observed to be very slow at ambient temperature. When a small amount (1 ml) of H₂O₂, is added to the aqueous solutions, it absorbs light under illumination and undergoes O–O bond cleavage from its electronically excited state, leading to sufficient production of hydroxyl radicals (OH⁻). These OH⁻ are very

effective in degrading organic pollutants and that is why the activation of H_2O_2 is necessary to accelerate the process³.

9. Optimization of the composite material with different CNT content

To determine the optimum composite photocatalyst for achieving the highest photocatalytic activity, the T-CuS composites with different CNT content were prepared and they were labelled as “T (x%)-CuS”, where x stands for the weight % of the CNT (0%, 2%, 3% and 4%). Figure S6 shows the variation of RhB concentration (C/C_0) with time in the presence of different catalysts under visible-light irradiation for 60 min irradiation. It was seen that no considerable change in the RhB concentration was observed for catalyst-free suspensions. After adding the pristine CuS catalyst, the RhB solution was found to be bleached up to 58% of its initial concentration. On the other hand, the RhB solution was degraded up to 82%, 94% and 89% with the T (2%)-CuS, T (3%)-CuS, T (4%)-CuS, respectively. The result demonstrates that the photocatalytic activity of T-CuS composites was first enhanced and then diminished with the increasing amount of CNT. Among the prepared samples, the composite with 3% CNT content showed the highest photocatalytic activity (94%).

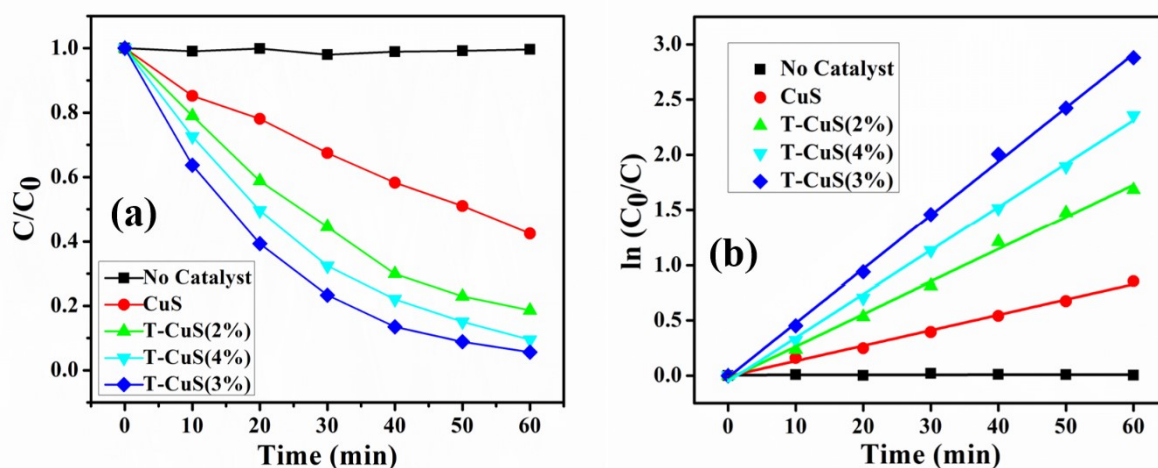


Figure S6. (a) Changes in concentration vs. time and (b) $\ln(C_0/C)$ vs. time plot in the presence of different catalysts under visible-light irradiation.

10. Identifications of reactive species

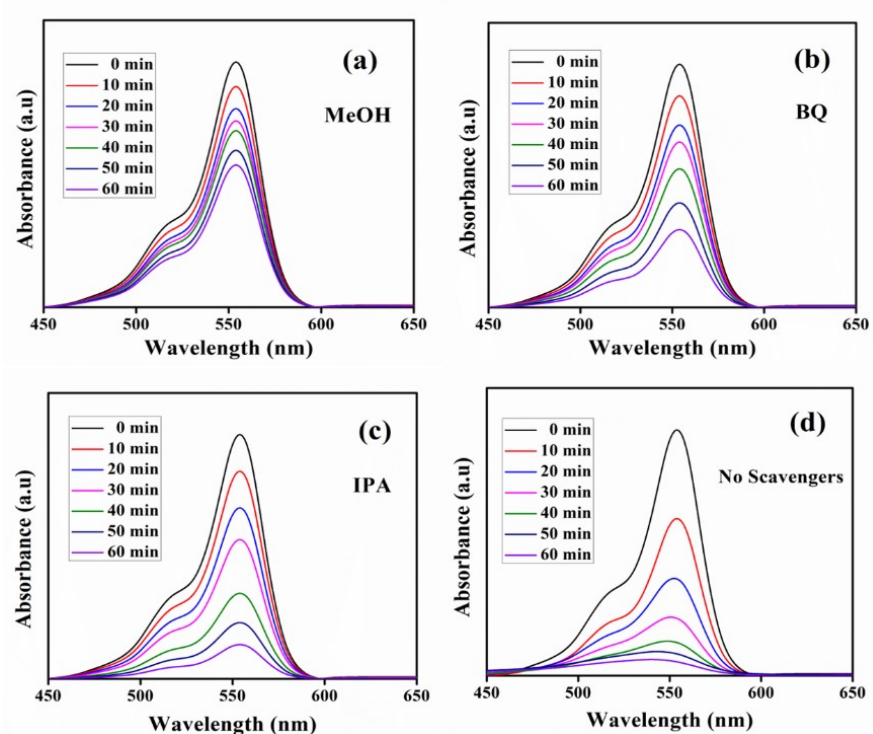


Figure S7. Absorbance spectra of degraded RhB aqueous solution by T-CuS in presence of (a) methyl alcohol (b) benzoquinone (c) iso-propyl alcohol and (d) No scavengers.

11. Recycling test

Recycling test have been done to decompose Rh B solution for three cycle and the efficiency of CuS and T-CuS catalyst did not change significantly.

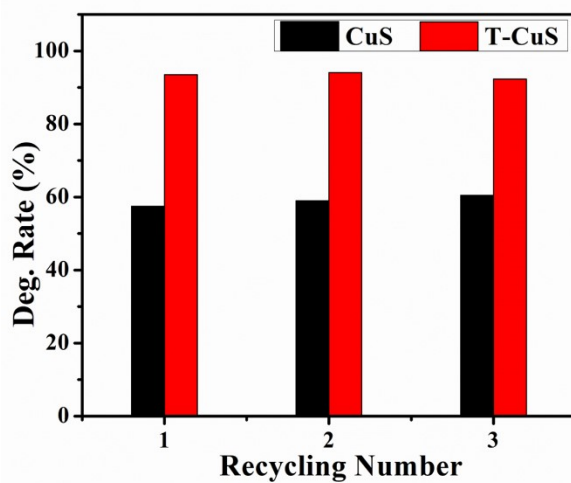


Figure S8. Recycle performance of CuS and T-CuS catalyst for Rh. B decomposition.

12. Photocatalytic activity of a non-azo dye

Here, we conducted the catalytic experiment with the bare CuS and CuS-CNT (3%) to degrade the Brilliant Green (BG) dye, which belongs to the non-azo groups, and we observed the almost similar results as we obtained in the case of Rh B. It was found that the addition of bare CuS catalyst bleached the BG solution to 47% from its initial concentration. Furthermore, the T-CuS nanocomposites enhanced the degradation by up to 93%.

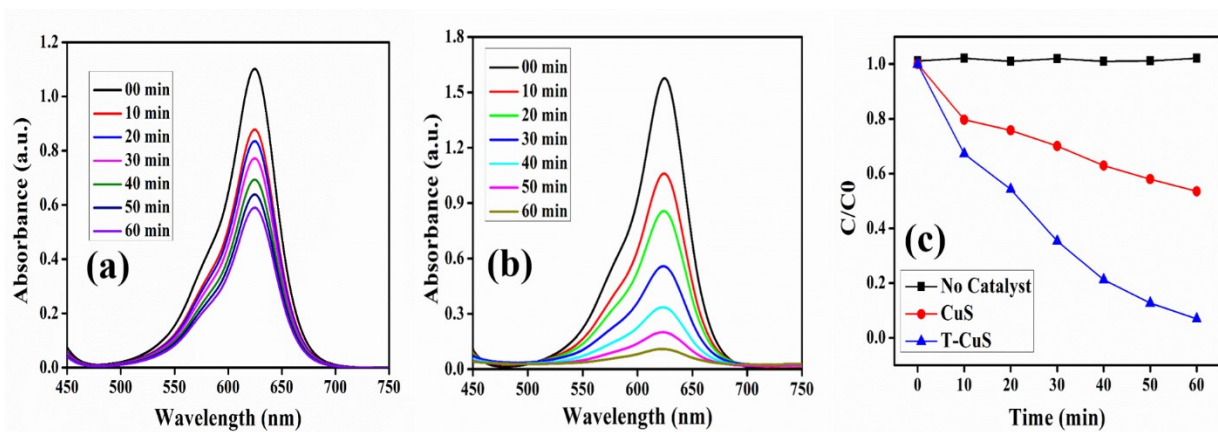


Figure S9. Absorbance spectra of aqueous brilliant green solution at different intervals of time in the presence of (a) CuS and (b) T-CuS nanocomposite under solar irradiations. (c) Photocatalytic degradation behaviour of brilliant green solution.

References

1. J. Tauc, *Amorphous and liquid semiconductors*, Springer Science & Business Media, 2012.
2. K. C. Kao, *Dielectric phenomena in solids*, Elsevier, 2004.
3. M. Roy, S. Sengupta, S. Bala, S. Bhattacharya and R. Mondal, *Cryst Growth Des*, 2016, **16**, 3170–3179.