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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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In this work, the synthesis of visible light sensitive copper sulfide (CuS) nanoparticles and their composites with carbon nanotubes (T-CuS) via a solvothermal technique has been reported. The synthesized nanoparticles (NPs) and its composite were significantly characterized by powder x-ray diffraction (PXRD), scanning electron microscope, transmission electron microscope, X-ray photoelectron spectroscopy, UV-vis spectroscopy, Photoluminescence (PL) spectroscopy and Thermo-Gravimetric Analysis (TGA). The effect of carbon nanotubes (CNTs) in the crystallinity, microstructures, photo-absorption, photo-excitation, thermal stability and surface area of CuS as was investigated. Current-voltage (I vs. V) characteristics of both CuS as well as T-CuS inherited Schottky diodes have been measured to determine the charge transport parameters like photosensitivity, conductivity, mobility of charge carrier, and transit time. The photocatalytic performance of bare CuS and T-CuS in the decomposition of Rhodamine B dye was studied by a solar simulator. The T-CuS composite showed higher photocatalytic activity (94%) compared to bare CuS (58%). The significance of charge carrier mobility to transfer photo-induced charges (holes and electrons) through complex networks of composites and facilitating the photodegradation process is explained. Finally, the reactive species responsible for the Rhodamine B degradation were also interpreted.

Introduction

Organic dye and pigments discharged into water sources, largely by the paint and textile industries, are causing serious environmental issues and harming the ecosystem in other ways 1. Over the last few decades, various biological and physicochemical experiments based on physical as well as chemical adsorption approaches have been made to decompose these industrial pollutants. However, these processes often produce secondary pollutants and are not cost-effective from the economical viewpoint 2. The photocatalytic approach based on semiconductor materials has demonstrated significant efficiency in wastewater purification among all advanced oxidation techniques known to exist 3. There are some well-known semiconducting photocatalysts namely, TiO2 and ZnO which have been widely used to decompose organic pollutants,

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3 Electronic Supplementary Information (ESI) available: Device fabrication method, Calculation of bandgap and dielectric constant, Weight (%) test of CNT, Charge Transfer Characteristics of CNT, Adsorption of RhB by the catalysts, Photodegradation process, Function of H2O2 in the degradation process, Optimization of the composite material with different CNT content, Identifications of reactive species, Recycling test, Photocatalytic activity of a non-azo dye. Figure S1, S2, S3, S4, S5, S6, S7, S8, S9. Equation S1, S2. See DOI: 10.1039/x0000000x
but their use are hindered due to their wide range bandgaps, which are 3.2 eV and 3.37 eV for TiO₂ and ZnO, respectively, limiting their light absorption mainly in the ultraviolet (UV) region of solar spectrum 4,5. This reduces the redox reactions with the impurities and significantly affects the rate of degradation 6.

On the other hand, copper (II) sulfide (CuS) has a narrow direct bandgap of 2.29 eV, for which it can efficiently capture visible light from the solar spectrum and make it practically functional to use as a 'visible-light-driven photocatalyst'. It also has excellent optical and electronic properties which show great potential in many fields like solar cells 7, energy storage 8, gas sensors 9, biosensors 10 and photocatalysis 11. Copper sulfide has some excellent features, such as environmentally friendly, non-toxicity, low cost, biocompatibility, higher physical and chemical stability and ease of recyclability which enhances its effectiveness for being a prospective photocatalyst. On the contrary, CuS nanomaterials also have an intrinsic drawback of having poor photocatalytic performance, especially when exposed to visible light, due to the quick electron (e⁻)-hole (h⁺) recombination. There have been several attempts to enhance the electron transfer during the photocatalytic process by reducing the electron-hole recombination in these materials. Carbon nanomaterials are eco-friendly, cost-effective and good electron acceptors; so, they could suppress electron-hole recombination effectively 12. Among them, Carbon nanotubes (CNT) are unique in terms of their morphological, structural, and electrical characteristics, such as their organised structure with a high surface to volume ratio, lightweight, and high electrical conductivity. CNT increases the emigration rate of photo-generated electrons, thereby pushing electrons and holes away which prohibits electron(e⁻)-hole(h⁺) recombination. Absorption of light also induces electrons into the CNTs and enhances the participation of electrons in the photocatalytic reaction 13,14. For higher photocatalytic performances, the electrons are expected to swiftly transfer and their subsequent recombination should be as slower as possible 15. Further, the fast electron transfer depends on the mobility of the carriers. To enhance the mobility and the associated charge carrier transport properties, CNT is incorporated with bare CuS in this work. This enhanced mobility of the charge carriers in T-CuS composite reflects in better photocatalytic performances than bare CuS. This report describes the synthesis of the carbon nanotubes-copper sulfide (T-CuS) composite and demonstrates its capability in the decomposition of the organic dye (Rhodamine B) in the presence of visible light.

Experimental

Materials

The chemicals used in this study were Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), ethylene glycol (HOCH₂CH₂OH), deionized (DI) water, absolute ethanol (C₂H₅OH) and hydrogen peroxide (H₂O₂). All of them were purchased from Merck (Merck specialties private limited). In addition, Sodium sulphide (Na₂S·9H₂O) and multi-walled carbon nanotubes (CNT) were purchased from RANKEM Laboratory Reagent and from Sigma Aldrich, respectively. All the chemicals in the synthesis were used without any additional purification.

Synthesis of CuS nanoparticles

Here, a solvothermal method was used to synthesise the CuS nanoparticles (NPs). At first, 0.9964 g of Cu(NO₃)₂·3H₂O was mixed in 30 mL ethylene glycol and placed on a magnetic stirrer for 30 min to prepare a homogeneous solution (solution 1). Then, 0.9604 g of Na₂S·9H₂O was mixed with 20 mL ethylene glycol and another homogeneous solution was prepared using magnetic stirring for 30 min (solution 2). Thereafter, solution 2 was put into solution 1 drop by drop and the collected mixture was stirred for 1 hr. Next, the obtained solution was kept in a Teflon-lined solvothermal autoclave and kept inside an oven at the temperature of 160 °C for 16 hrs. After that, the precipitate was rinsed with DI water (four times), ethanol (four times) and finally, collected by centrifugation techniques. At the end, the final product, CuS nanoparticles collected and were dried at 60 °C for 16 hrs.

Synthesis of CNT-CuS composite

Here, a similar solvothermal method was used to synthesise the CuS-CNT composites (T-CuS). In this process, a certain amount (3%) of carbon nanotubes (CNTs) were dispersed in Cu(NO₃)₂ precursor solution and then stirred for 30 min. After that, Na₂S solution was dropwise added into the previous mixer. This final prepared solution was kept under a magnetic stirring for 6 hrs. Then, the final solution was kept in a Teflon-lined autoclave. After that, the autoclave was placed in a hot air oven at temperature of 160 °C for 16 hrs. Finally, the collected samples were washed multiple times with DI water and absolute ethanol and then kept on the hot plate at 60 °C for 12 hrs. The synthesis process of the CNT-CuS composite is collectively shown in Fig. 1.

Fig. 1 Schematic diagram of the synthesis process of CNT-CuS nanocomposite.

Material characterization techniques

The crystallographic structure and phase purity of synthesized materials (CuS and T-CuS) were analysed by powder X-ray diffractometer (Bruker D8 Advance) having Cu-Kα (λ = 1.5418 Å) radiation, operated at the scan rate of 0.02/°sec. The surface morphology was studied with the help of a scanning electron microscope (FEI Inspect F50) and the elemental combination was determined by EDX (energy dispersive x-ray) analyser. Information regarding the microstructure of the synthesised materials was analysed with the help of a transmission electron microscope (JEOL JEM 2100 F). XPS (X-ray Photoelectron
Spectroscopy; Omicron Nanotechnology) with Al-Kα radiation (E= 1486.7 eV), was utilized to examine the electronic states of the elements present on the surface of the samples. The absorption spectra and their photocatalytic behaviour of synthesized materials were recorded by a UV-Vis (Perkin Elmer, Lambda 365) spectrophotometer and a solar simulator [Model 10500, Abet Technologies] subsequently. The Photoluminescence (PL) spectra were collected by a spectrofluorimeter (Cary Eclipse Fluorescence spectrometer, Agilent Technologies). The thermal stability of both of the materials were investigated by a thermogravimetric analyser (DTG-60H, Shimadzu) within the temperature range from 30 °C to 800 °C in the N2 atmosphere. The estimation of the Brunauer-Emmett-Teller (BET) surface area of synthesised materials by N2 adsorption-desorption was done by using (Autosorb iQ2, Quantachrome, USA) at 77 K. The measurements of current-voltage (I-V) characteristics were performed with a source measurement unit (Keithley 2635B).

Results and discussion

Structural properties

XRD analysis

Fig. 2 displays the PXRD pattern of CuS and T-CuS nanocomposites. The diffraction peaks of prepared CuS were observed at 2θ ≈ 27.12°, 27.68°, 29.28°, 31.78°, 32.85°, 38.83°, 47.94°, 52.71°, 59.34°, 73.99° and 79.07° were assigned to (100), (101), (102), (103), (006), (105), (110), (108), (116), (208) and (213) crystallographic planes of the hexagonal copper sulfide structure (JCPDS Card No. 06-00464, a= 6.792 Å and c=16.34 Å). The narrow, sharp peaks indicate the crystallinity of the bare CuS. The peaks at 25.89° and 43.56° were assigned to (002) and (101) planes of the CNTs respectively. This XRD pattern showed that the major diffraction peaks of the T-CuS composite were similar to those of bare CuS, which explains that the attachment of CNT did not affect the preferred orientations of CuS and result in to grow a new crystallographic phase. Also, very small diffraction peaks of CNT were observed in the composite. It might have occurred due to the less amount of loading and relatively weak diffraction peaks of CNT.

FESEM analysis

The FESEM images of synthesized CuS and T-CuS nanocomposite were displayed in Fig. 3. The microstructural and morphological information from SEM images suggests that the CuS and T-CuS composite consists of nearly hexagonal-shaped nanostructures, which contains some agglomeration in the pattern. It is clear in Fig. 3(b) that CuS nanocomposites were properly attached to the CNT during the hydrothermal synthesis. From the EDAX spectra (Fig. 3c), the appearance of constituting elements (C, O, Cu and S) in the composite was precisely noted. Further, the quantitative interpretation of the EDAX exhibited that in the synthesized material, the molar ratio of Cu to S was close to one, indicating the stoichiometric formation of CuS NPs.

Fig. 2 XRD pattern of synthesized CuS and T-CuS nanocomposite.

Fig. 3 (a) FE-SEM image of CuS and (b) T-CuS and (c) EDAX spectra of the T-CuS nanocomposite.

Fig. 4 (a) TEM image of CuS and (b) T-CuS composite. (c) HRTEM and (d) The SAED pattern of CuS NPs attached with CNT.
TEM analysis
The TEM images (Fig. 4a and 4b) further revealed that the hexagonal-like CuS NPs were uniformly attached to the carbon nanotubes, suggesting the formation of a strong interface with nominal aggregation of particles. The finier attachment between the CuS NPs and CNT (Fig. 4b) by this familiar bonding could assist the transfer of charge carriers; and thus, suppress e⁻h⁺ recombination-which is advantageous for better photocatalytic response that will be discussed in the following paragraph. Fig. 4d shows the SAED pattern of T-CuS NPs with various concentric diffraction rings, suggesting the polycrystalline nature of the materials.

XPS study
X-ray Photoelectron Spectroscopy (XPS) of T-CuS nanostructures was measured to examine the elemental composition and identify the chemical bond type as well as the oxidation states. The existence of the C, Cu, S, and O in the T-CuS composite was verified by the XPS survey spectrum scan (0-1200 eV) (Fig. 5a) confirming the presence of elemental Cu and S in the nanocomposite. The core level XPS spectrum of C-1s, Cu-2p and S-2p are shown in Fig. 5(b-d) subsequently. XPS peak for C-1s of the composite was deconvoluted into four distinct peaks centred at the corresponding binding energies (B.E.) of 284.40, 285.10, 287.60 and 290 eV, that could be ascribed to C=O, C-C, C-O and π-π* shake-up features respectively (Fig. 5b).

This suggests the probable existence of graphitic layers which prefer fast electron transfer and the O-containing group could easily transfer from the excited CuS to the carbon network and the sp² hybridization of carbon atoms show high mobility of photo-induced holes and electrons. The electrons could easily transfer from the excited CuS to the carbon nanotube through the π-conjugated carbon network and the ‘quenching’ of fluorescence occurs. The CNT composites are efficient to suppress the recombination rate of electrons and holes by fast electron transfer. This kind of extended separation of photo-induced charge carriers and their immediate processes is advantageous for catalytic degradation, which will be discussed in the following.

The higher resolution XPS spectrum of S-2p (Fig. 5d) represents the existence of two peaks at B.E. values of 161.9 eV and 163.3 eV, which could suggest to S 2p₁/₂ and S 2p₃/₂ states, sequentially. S²⁻ species are responsible for the detection of these two peaks.

Optical properties
UV-vis absorbance study
UV-vis absorbance spectra of the synthesized CuS and T-CuS nano-composite were recorded in the 300-750 nm wavelength range (Fig. 6a) to study their optical properties. The optical band gaps (Eg) of the catalysts were deduced followed by Tauc’s equation S1. The estimated value of the bandgaps of the synthesized CuS and T-CuS from Tauc’s plot (Fig. 6b) was 2.29 eV and 2.19 eV, respectively, close to the previously reported value. The broadness of the absorption band and the reduced bandgap of theCNT-attached material compared to bare NPs suggests the improvement in photon absorption and more e⁻h⁺ pair generation for the photocatalytic experiment. The more generated e⁻h⁺ pairs participating in the degradation process should enhance the deterioration rate for T-CuS than bare CuS.

Photoluminescence (PL) study
PL was used to study the interaction among the holes and electrons, originating from the excitation of photons in synthesized catalysts. Fig. 7 represents the PL spectra of CuS and T-CuS composite at 370 nm excitation. The bare CuS exhibit an eminent emission centred at 425 nm, which was sufficiently weakened after loading CNT. This is because, there exists an effective interfacial linkage in the composite materials, so that, electrons and holes acquire a dedicated pathway to interact between CuS and CNT layers. The high electrical conductivity and sp² hybridization of carbon atoms show high mobility of photo-induced holes and electrons. The electrons could easily transfer from the excited CuS to the carbon nanotube through the π-conjugated carbon network and the ‘quenching’ of fluorescence occurs. The CNT composites are efficient to suppress the recombination rate of electrons and holes by fast electron transfer. This kind of extended separation of photo-induced charge carriers and their immediate processes is advantageous for catalytic degradation, which will be discussed in the following.

Fig. 5 XPS Analysis (a) full scan spectrum of T-CuS (b) spectrum C 1s for T-CuS composite. narrow scan of (c) Cu-2p and (d) S-2p states.
Thermal stability analysis

Thermal stability of the as-synthesized CuS and T-CuS composite was examined by the thermo-gravimetric analysis (TGA), executed with a gradual increase in temperature (10 °C /min) ranging from 25 °C to 800 °C in N₂ atmosphere. Fig. 8 represents the TGA graph of the T-CuS composite, showing two definite stages of weight loss where 78% of weight remained up to 800 °C temperature. The initial weight loss (7.35%) for bare CuS was observed between 100-300 °C which indicates the solvent desorption and moisture absorption. Additionally, the bare CuS undertook a rapid weight loss (38.28%) due to the decomposition of CuS into Cu₂S and phase transition of sulfur elements, leaving 67 % residue. The first weight loss (11.35%) of T-CuS around 100-300 °C is observed due to removal of solvent and the residual organic molecular absorbed on the samples. In the second stage (300-450 °C), the weight loss (13.65%) for T-CuS was observed due to the oxidation of CNT and phase conversion of CuS. This result indicates that the CNT composite (T-CuS) is thermally more stable than bare CuS.

Electrical properties

To understand electronic charge, transfer characteristics of the above-discussed materials, current-voltage (I – V) measurements of the Schottky diodes fabricated as-(Al/CuS/ITO) & (Al/T-CuS/ITO) & (Al/T-CuS/ITO) structure (E.S.I.), were investigated using a bias voltage range of ±1 Volt in dark and light (~ 1000 W/m²) conditions at 300K temperature. The measurement of charge flow, known as dc conductivity (σ), was evaluated from the ohmic (linear) region of the characteristic curves (Fig. 10a) of both devices under dark and illumination/light conditions (Table 1). A notable increment in current in illumination conditions reflects the photosensitivity of the synthesized materials. The definition of photosensitivity (S) (Equation 1), like, , (here denotes the current in dark conditions) was derived for two different devices. The CNT-based device with greater absorption capacity has better sensitivity than bare CuS (Table 1). In addition, the higher conductivity of the composite material means efficient charge transport with excellent mobility. For any semiconductor material, carrier mobility determines how fast a carrier, i.e., e⁻ or h⁺, can move through its complex network and reach active sites before recombination. Since CNT provides higher electronic mobility (~ 10⁵ cm²/V s at 300 K), it is expected the enhancement of electron transport and e⁻-h⁺ pair separation through its high-quality complex network.
To observe the overall effect of CNT in the photo-degradation process and to better understand the charge transfer mechanism, the current-voltage (I-V) mechanism was further analyzed by introducing the transit time ($\tau$) and carrier mobility ($\mu_{eff}$). For this purpose, log I vs. log V graphs are plotted for the positive voltages as shown in Fig. 10b, which represents two distinct linear regions, suggesting different conduction mechanisms. Interfacial trap states at the metal-semiconductor junction modify the conduction mechanism of charge carriers which revised the I-V characteristics. In small bias (Region-I), current shows ohmic ($I \alpha V$) behaviour with the slope value approximately to one. At this region, the current is guided by the intrinsic charge carriers of the material. The carriers injected from the junction spread over the space at the intermediate potential difference (Region II) and create a spatially distributed field of charge. This field dominates the charge carriers and their “mobility” becomes a key factor for the quadratic current ($I \alpha V^2$). Furthermore, Space charge limitation current (SCLC) theory was used in this region to determine the effective carrier mobility ($\mu_{eff}$) and carrier transit time ($\tau$).

The electron mobility was evaluated from the slope of the I-V$^2$ plot (Fig.11a and 11b), followed by the equation of Mott-Gurney,

$$I = \frac{9\mu_{eff}E_0 A_{eff}}{8d} \left( \frac{V^2}{d^2} \right)$$

here $A_{eff}$, $E_0$, $\varepsilon_r$, and $d$ represents the effective area of the diode, the permittivity of free space, dielectric constant of the materials (Fig. S2, equation S2 in the E.S.I) and the thickness of the diode, respectively. The carrier transit time or transition time ($\tau$) was also extracted using the following equations

$$\tau = \frac{9\varepsilon_r E_0 A_{eff}}{8d} \left( \frac{V}{I} \right)$$

The calculated values of $\mu_{eff}$ and $\tau$ are given below in Table-1. Our results reflected higher mobility for the carbon nanotube and its effective contribution to the transfer of charge carriers smoothly. The CNT-based composite showed greater mobility & transit time than the bare CuS NPs. The result shows compatibility with previously reported data of a carbon-based (rGO) composite. Both in dark and in the illumination, the mobility of carriers increased remarkably up to 4-5 times. The enrichment of mobility & transition time can increase the efficiency of charge transfer and thus the photocatalytic activity.

Transient photo-response spectra and electrochemical impedance spectroscopy (EIS) were performed to investigate the photo-electrochemical characteristics of the as-prepared catalysts, and are shown in Figures 12a and 12b respectively. The photocurrent intensity of the T-CuS composite was found to be significantly higher (Fig. 12a) than that of the bare CuS, as expected. This result suggests that incorporating CNT into the CuS nanoparticles could facilitate the separation of photo-generated electrons and holes and their swift transfer through the complex network. Furthermore, the EIS Nyquist spectra, which is an effective tool for investigating the conductance and charge transfer facility, revealed that the diameter of the semicircular arc for the T-CuS composite was significantly smaller than for the bare CuS (Fig. 12b). This finding affirms that the addition of CNT significantly reduced the charge transfer resistance in the composite material, allowing electrons and holes to migrate to active sites during the degradation process, as discussed further below.

### Table 1: Charge transport parameters

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<tr>
<th>Material</th>
<th>$\mu_{eff}$ (cm$^2$/V·s)</th>
<th>$\tau$ (ns)</th>
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<tr>
<td>CuS</td>
<td></td>
<td></td>
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<tr>
<td>T-CuS</td>
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Photocatalytic activity

Photocatalytic decomposition of RhB under solar simulator is used to investigate the photocatalytic behaviour of bare CuS and T-CuS nanocomposites. The degradation procedure was recorded by monitoring the major absorption peaks of aqueous RhB solution centred at 553.5 nm using a UV-Vis spectrometer (Fig. 13a and 13b) and the decomposition process was determined by the following Eq.

\[
\text{Degradation(\%)} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) and \(C_t\) represent the RhB concentration at the time \(t=0\) & \(t\) time after its initial condition, respectively. The linear behaviour of \(\ln(C_0/C)\) vs. exposure time (min) graph of both bare CuS and T-CuS composites (Fig. 13d) indicates the presence of pseudo-first-order decomposition kinetics. No significant change in RhB concentration was observed in the catalyst-free suspension after exposed to solar-simulated light for 60 minutes. It was found that the addition of bare CuS catalyst bleached the RhB solution to 58% from its initial concentration. Furthermore, the T-CuS nanocomposites enhanced the degradation by up to 94% due to the synergistic effect of CuS-NPs and CNTs (Fig. 13c). Recycling test in Fig. S8 (E.S.I.) demonstrated that the decomposition efficiency of T-CuS catalyst did not change significantly after repeated use of three cycles.

The reactive species trapping experiments were carried out to determine the active species in the 3% T-CuS photocatalytic system. First, 0.1 mmol of methyl alcohol (MeOH), a scavenger of photogenerated \(h^+\), 0.1 mmol of iso-propyl alcohol (IPA), a scavenger of hydroxyl •OH and 0.1 mmol of benzoquinone (BQ), a scavenger of superoxide •O2− were separately added in the photodegradation system. Further, the photodegradation experiment was performed under the same procedure without adding scavengers. The absorption plots of degraded RhB by T-CuS in presence of different scavengers are shown in Figure S7 (Supporting Information). Fig. 14 shows the effect of the scavengers on the degradation percentage of RhB with 60 min irradiation time.

As seen in Fig. 14, the RhB solution degraded up to 86% of its initial concentration which demonstrates that the decomposition of RhB was slightly suppressed in the presence of IPA, as compared to 94% in the absence of scavengers. This finding indicates that •OH has a minor impact on degradation of RhB using T-CuS catalyst. In case of MeOH, the value of \((C/C_0)\) was not reduced below 42%, indicating that holes \((h^+)\) play a significant role in RhB degradation. However, when BQ was present during the reaction, the concentration of \((C/C_0)\) was somewhat reduced by up to 68%. This suggests that •O2− radical is also markedly responsible for photocatalytic degradation of RhB.
RhB. Here, RhB degradation was observed to be obviously inhibited on the addition of BQ and MeOH; in contrast, IPA had a very small effect on the dye degradation. This implies that the photogenerated holes (h\(^+\)) and \(\bullet \text{O}_2^-\) radicals play the main role in removal process of the dye, whereas \(\bullet \text{OH}\) plays a minor role in the dye degradation.

To explain the synergetic effect of CNTs and CuS in the composite, we analysed the photocatalytic degradation process. In presence of visible light illumination, excitons of interfaces are generated on the surface of CuS NPs and segregated into free holes in the valence band (VB) & free electrons in the conduction band (CB). Though, this photogenerated h\(^+\) and e\(^-\) tending recombination before the appearance of the active site resulting in a poor photocatalytic response. When the CuS NPs bind with CNTs, the photo-induced e\(^-\) in the conduction band of CuS can be separated effectively at the carbon nanotube interfaces, leaving h\(^+\) in the valence band of CuS due to its favourable energy level (Fig. 15) \(^{40,41}\). CNT is photoexcited to produce electrons in its lowest unoccupied molecular orbital (LUMO) and holes in its highest occupied molecular orbital (HOMO). It is well known that CNT is an excellent electron acceptor, which will trap the CB electrons of CuS. Simultaneously, the photoexcited CNT is a good electron donor, readily leading to the migration of the photoexcited electrons in the LUMO of CNT to the CB of CuS. The interesting electron transfer process can efficiently prevent the recombination of the CB electrons with the VB holes in CuS. This is the dominant mechanism resulting in the enhanced photodegradation performance of the T-CuS composites compared to bare CuS \(^{42}\). Therefore, photo-generated electrons in CuS can reach effortlessly to the active site through the CNT network and reduce the dissolved \(\text{O}_2\) present in the aqueous medium, into the hugely reactive superoxide anion (\(\text{O}_2^-\)) and react further with \(\text{H}_2\text{O}\) to form hydroxyl (OH\(^-\)) radicals \(^{43}\). Furthermore, photo-induced h\(^+\) can react also with \(\text{H}_2\text{O}\) or \(\text{OH}^-\) to oxidize them to \(\text{OH}^+\) \(^{44}\). The \(\text{O}_2^-\), \(\text{OH}^-\) and the photo-generated h\(^+\) are jointly involved in the decomposition process of RhB solutions \(^{45,46}\). Fig. 15 shows a pictorial view of the photocatalytic activity of the T-CuS photo-catalyst.

![Fig. 15 Pictorial representation of photocatalytic degradation of RhB in the presence of T-CuS nanocatalyst under solar simulator.](image-url)

**Conclusion**

The CuS NPs were synthesized successfully and the CNT incorporation with CuS was assisted by PXRD, FESEM, FEG-TEM, XPS, UV-Vis and PL data. The importance of charge transport kinetics and higher charge carrier mobility of the photocatalysts for RhB decomposition was reported. It was seen that in presence of visible light, the T-CuS exhibited higher photocatalytic activity than the bare CuS. The higher mobility of the composites helped the photo-induced charges to quickly transfer between the active site and the target molecules at the time of the degradation process. Strong interfacial contacts, higher absorption of visible light and reduced recombination of e\(^-\)-h\(^+\) pairs are the additional crucial key factors for enhancing the photocatalytic performance of the composites. Overall, addressing the challenge of visible light-induced photocatalysis, the superiority of CNT composites over as-synthesized bare CuS catalysts was demonstrated in this study. Finally, our results shed light on design of carbon-based semiconductor (T-CuS) composites and established them as promising photo-catalysts for various potential applications in wastewater treatment.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

The author would like to special thanks to the University Grants Commission (UGC) for providing the NET-SRF fellowship programme.

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