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NOVEL SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF POLYMER DOPED G-C₃N₄ COMPOSITE PHOTOCATALYST

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ABSTRACT

Polyaniline doped G-C₃N₄ (CNPANI) composite sample was synthesized by standard impregnation method. The effect of CNPANI composite on structure, particle size and morphology of composite sample was investigated. The prepared sample was characterized by XRD, FT-IR and SEM – EDS techniques. The photocatalytic activity of the novel photo catalyst was evaluated using Rhodamine B(Rh-B) ASA target pollutant. The CNPANI composite sample exhibit enhanced photocatalytic performance under visible light irradiation than pure G-C₃N₄.

KEYWORDS

Polyaniline, Carbonnitride, Composite photocatalyst and Rhodamine B.

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INTRODUCTION

During the past 30 years, various inorganic semiconductors and molecular assemblies have been developed as catalysts for hydrogen production from water and as an environmental purification under visible light¹. For photocatalysis, precious metal species must be used in most cases as extra co-catalysts to promote the transfer of photo induced charge carriers from bulk to the surface at which organic dyes are converted into CO₂ and H₂O. Synthetic polymer semiconductors have also been used for dye degradation; however, they are active only in the UV region and have moderate performance. Here another polymer like semiconductor made of only carbon and nitrogen

can function as metal free photocatalyst under visible light. Carbon nitride can exist in several allotropes with diverse properties but the graphitic phase is regarded as the most suitable under ambient conditions. The novel photocatalytic activity for the removal of organic pollutants under visible light irradiation², the metal-free g-C₃N₄ photocatalyst possess an interesting electronic property as well as high thermal and chemical stability, therefore making them valuable materials for photocatalysis applications. However, to date the photocatalytic efficiency of bare pure g-C₃N₄ is still limited due to higher recombination rate of photogenerated electron-hole pairs. Many methods have been used to extend the photocatalytic performance such as doping with metal or non-metal elements³. These methods are effective because the high surface area and small particle size it enhances e⁻ - h⁺ pairs separation⁴.

In this work, for the first time Polyaniline/g-C₃N₄ composite was synthesized by impregnation method. The composite should increase the visible light harvesting efficiency by increasing the surface area and to evaluate the photodegradation of Rh-B under visible light irradiation.

MATERIAL AND METHODS

Melamine (99%), monomer aniline (99.5%) and Ammonium persulphate (NH₄)₂S₂O₈ (APS), Rhodamine-B (Rh-B) were purchased from Sigma-Aldrich. HPLC grade Methanol, Ethanol, Hydrochloric acid, Sodium hydroxide and Diethyl ether, were obtained from S.D fine Chemicals. For all the experiments deionized water was used. All other reagents were of analytical grade and were used as received without further purification.

Synthesis of Photocatalysts

Synthesis of pure G-C₃N₄ Composite Photocatalyst (CN)

The metal free pure g-C₃N₄ composite sample was synthesized by thermal treatment of precursor melamine it was placed in a crucible with a cover under ambient pressure in air. After dried at 80°C for 24 hr, the precursor was put in a Muffle furnace and heated to 550°C for 3 hr with a heating rate of 10°C min⁻¹. The resultant yellow product was

collected and ground into a powder for further use⁵. Figure No.1 shows the composite sample pure g-C₃N₄.

Synthesis of PANI-g-C₃N₄ Composite photocatalyst (CNPANI)

The pure g-C₃N₄ composite was prepared according to the procedure⁵. PANI-g-C₃N₄ composite photocatalyst was synthesized by oxidative polymerization of aniline monomer. A fixed amount of CN, ammonium persulphate (APS) and 1M HCl solution were added into 60ml of deionized water in a beaker. The mixed solution was magnetically stirred for 1 hr in an ice water bath. After that, aniline monomer was injected drop wise to the above cooled mixture. The resultant mixture was allowed to react in the ice bath for 8 hr. The precipitated emerald green CNPANI composite powder was filtered and washed with ethanol and deionized water until the filtering solution became colourless. Finally, the product was dried in a vacuum environment⁶. The sample CNPANI is as shown in Figure No.2.

RESULTS AND DISCUSSION

Characterization of metal free composite photocatalyst

XRD Analysis

The crystalline and phase structure of the pure G-C₃N₄ is determined by X-ray diffraction (XRD) as shown in Figure No.3. The X-Ray diffraction patterns of pure CN exposed an intense broad peak at 2θ value of 27.57°, indexed to (002) planes which is a characteristic pointer of layered stacking with a distance of 0.326nm in the conjugated aromatic system and the inplanar repeating tri-s-triazine unit with a distance of 0.675nm can be observed from the diffraction peak at 2θ = 13.12°, indexed with (100) plane [119]. It is evident that melamine is converted into g-C₃N₄ composite by means of pyrolysis which is proven by the presence of both the characteristic diffraction peaks of pure CN, which is also reliable with the reported results on g-C₃N₄.

Figure No.3 illustrates the XRD pattern of CNPANI composite sample. The pure G-C₃N₄ has two diffraction peaks at 27.5° and 13.1°, which can be

indexed as graphitic materials at the peaks (002) and (100). These two peaks are in good agreement with the G-C₃N₄ reported in the literature⁷. Particularly, no obvious diffraction peaks of PANI polymer is observed in CNPANI composite sample. This is due to the weak crystallinity and small doping content of PANI. However, the presence of PANI in the composite can be confirmed by FT-IR (Figure No.4) and EDAX analysis.

SEM with EDAX Analysis

The morphology of pure CN and CNC composite samples are investigated by SEM. Figure No.5 and Figure No.6 show the SEM images of pure CN and CNPANI. Both the samples display aggregated morphologies. The pure CN sample appears to have aggregated particles which contain smaller crystal with the crystallite size of 16.81nm. However, under high resolution, formation of a composite structure is observed the size distribution varies in the range 5-30 μ m where two distinct morphologies are seen. One of the morphological regions exhibits low pixel intensity (dark contrast) in the SEM images. These regions of low pixel intensity are attributed to regions composed of polymer PANI. The alternate aggregated morphological region has very high pixel intensity (light contrast) which attributed to the presence of CNPANI composite sample⁸.

The elemental composition of g-C₃N₄ and polymer doped G-C₃N₄ composite sample is determined by EDAX measurements. The following Figure No.7 show the EDAX spectra of CN and CNPANI. The results listed in Table No.1 and Table No.2 show that the g-C₃N₄ network is not affected by polymerization. The only difference is the amount of carbon, nitrogen and oxygen in the composite sample CNPANI vary, when compared to pure g-C₃N₄.

Photocatalytic Activity

Effect of Oxidative Degradation

The rates and efficiencies of photoassisted degradation of organic dyes are improved in the presence of oxygen. The effect of degradation of Rh-B dye in the presence of pure CN and molecular oxygen is as shown in the Figure No.9. From the graph it is observed that 45% of dye degradation is

achieved in the presence of oxygen bubbling at pH 8 within 120 minutes irradiation, whereas in the absence of molecular oxygen the degradation is about only 40%. For CN and 57 % for CNPANI.

Degradation Kinetics

Figure No.10 display the pseudo first order plots for the photodegradation of Rh-B over pure CN and CNPANI composite photocatalyst. The pseudo-first order rate constant k is evaluated through the linear regression of $\ln C_0/C$ versus t . The corresponding values of the pseudo-first order rate constant k as well as the determination coefficient R^2 are calculated. The CNPANI sample exhibits the photodegradation rate (k) is calculated to be 0.006698 min^{-1} , which is 1.5 times higher than that of pure CN. The correlation constant for the fitted line is calculated to be $R^2 = 0.964$. The obtained value of the determination coefficient R^2 indicates that pseudo-first order rate is suitable for describing the photodegradation process of Rh-B with CNPANI composite photocatalyst⁹.

Renewable Catalytic Activity

Renewable catalytic activity is another important factor for a photocatalyst. To demonstrate the stability of composite catalysts, the catalytic activity of the pure CN and CNPANI is performed four times under the same experimental condition (2g/l at pH 7.6). After each cycle, dried and reused for other cycles. Figure No.11 and Figure No.12 (a and b) illustrate the cyclic runs of Rh-B degradation using CN and CNPANI photocatalysts.

Degradation of Dye during the Course of Reaction

Figure No.13 depict the degradation spectra of Rh-B dye using CN and CNPANI. From the figure it is explained that as the reaction time increases, the primary absorption peak of Rh-B in the photocatalytic system CN shift from 553 to 500nm within 120 minutes irradiation. It is indicated that the N, N-de-ethylated rhodamine becomes the major constituent in this system. The cleavage degree of Rh-B is estimated to be 40 % in the presence of pure CN composite photocatalyst but in CNPANI composite photocatalyst the absorption peaks shift from 553nm to 480nm. It indicates that only partial N-de-ethylation of Rh-B is obtained. It

shows that only 57% degradation of Rh-B using this photocatalyst. It has been assumed that the Friedel-Crafts acylation of benzene like PANI dramatically affect the efficiency of the photocatalyst. Compared with traditional semiconductor photocatalysts, the CB of g-C₃N₄ is located at a more negative potential. Such a feature enables the photo-induced e⁻ in the CB of G-C₃N₄ has minimum reduction capability.

Mechanism

Based on the results and the analysis above, the photocatalytic mechanisms to explain the enhanced activities of polymer doped g-C₃N₄ composites are proposed and illustrated.

In the CNPANI system as shown in Figure No.14, the g-C₃N₄ can be excited and generate the electron-hole pairs under the visible light irradiation and PANI also absorb photon to occur π-π* transition.

While g-C₃N₄ catalyst is supposed to originate electron donation from melom units to the aromatic substrate present in the PANI, substrate having lower lying molecular orbitals interact stronger with the g-C₃N₄ surface. On the other hand, it has to be considered that substitutions on the aromatic ring alter the symmetry of the molecular orbitals, resulting in an inferior overlap with the HOMO of localized melom units. These two effects, donar acceptor interaction and change of symmetry, together with steric effect make the photocatalytic property rather difficult when compared to other polymers.

Table No.1: Atomic and weight percentage of CN composite sample

| S.No | El AN | Series | Unn. C [wt.%] | Norm. C [wt.%] | Atom. C [at. %] |
|------|-------|----------|---------------|----------------|-----------------|
| 1 | N 7 | K-series | 58.15 | 58.15 | 54.53 |
| 2 | C 6 | K-series | 40.73 | 40.73 | 44.55 |
| 3 | | Total | 100.00 | 100.00 | 100.00 |

Table No.2: Atomic and weight percentage of CNPANI composite sample

| S.No | El AN | Series | Unn. C [wt.%] | Norm. C [wt.%] | Atom. C [at. %] |
|------|-------|----------|---------------|----------------|-----------------|
| 1 | N 7 | K-series | 54.95 | 54.95 | 51.13 |
| 2 | C 6 | K-series | 45.05 | 45.05 | 48.87 |
| 3 | | Total | 100.00 | 100.00 | 100.00 |



Figure No.1: Pure g-C₃N₄ composite sample (CN)



Figure No.2: PANI-g-C₃N₄ composite sample (CNPANI)

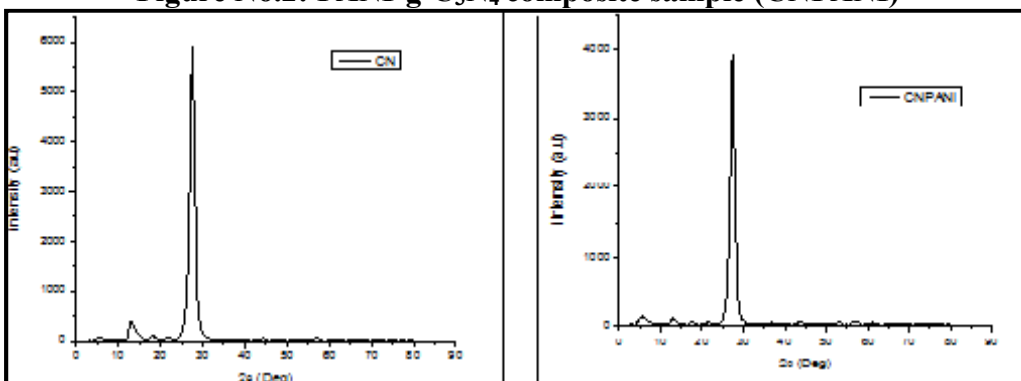


Figure No.3: XRD Patterns of CN and CNPANI Composite Sample

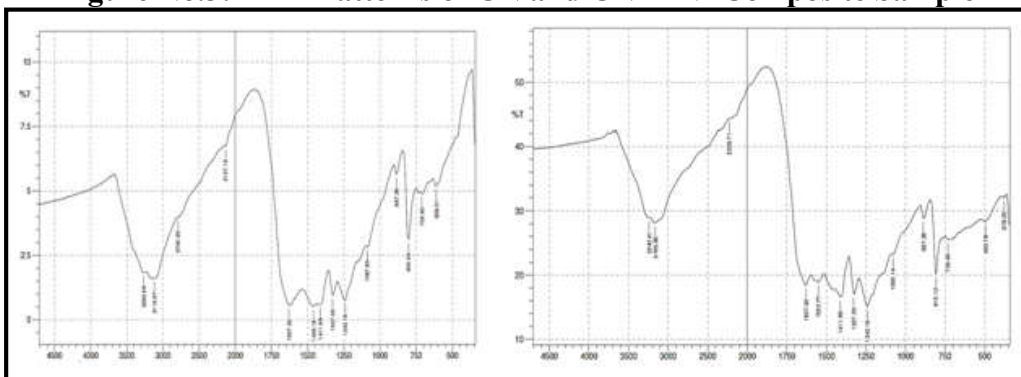


Figure No.4: FT-IR spectrum of CN and CNPANI composite sample

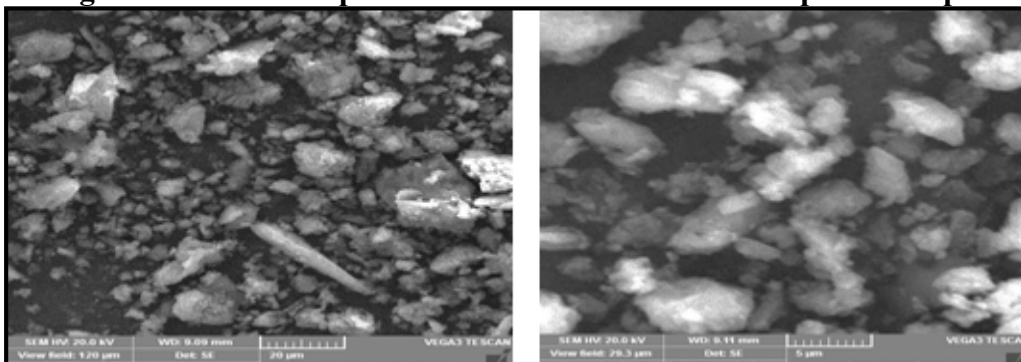


Figure No.5: SEM micrographs of CN composite sample

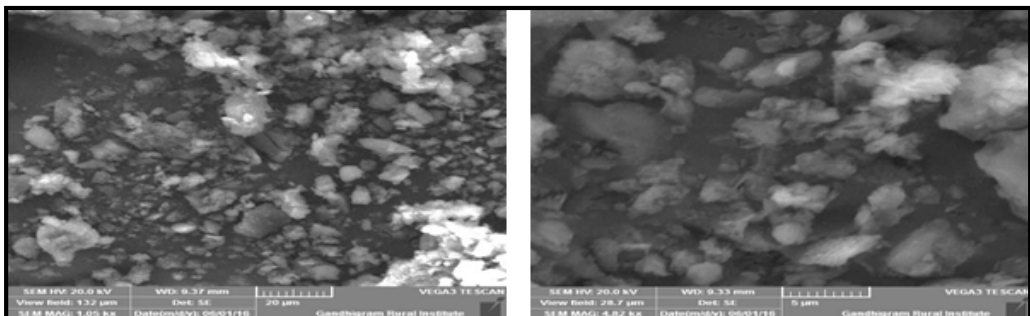


Figure No.6: SEM micrographs of CNPANI composite sample

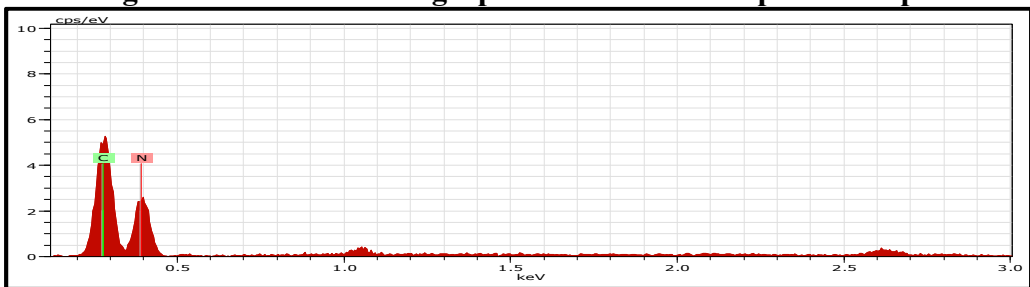


Figure No.7: EDAX spectrum of CN composite sample

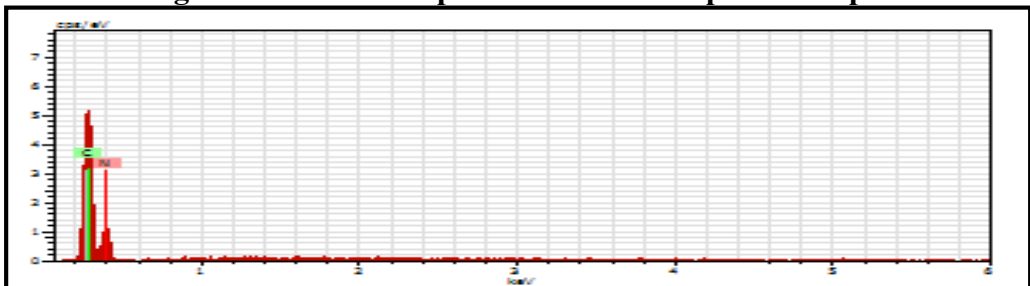


Figure No.8: EDAX spectrum of CNPANI composite sample

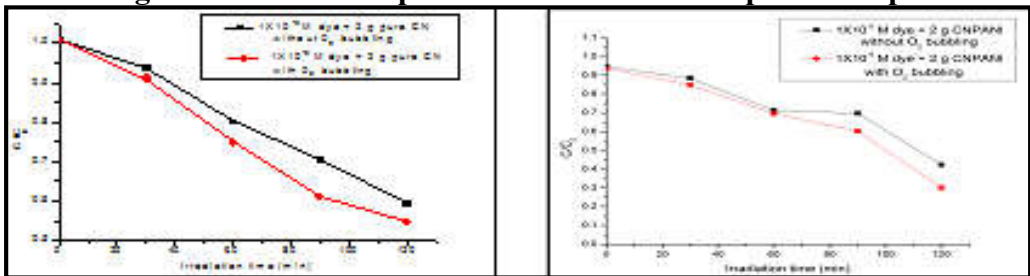


Figure No.9: Effect of O₂ bubbling on photodegradation of Rh-B Over CN and CNPANI composite photocatalyst

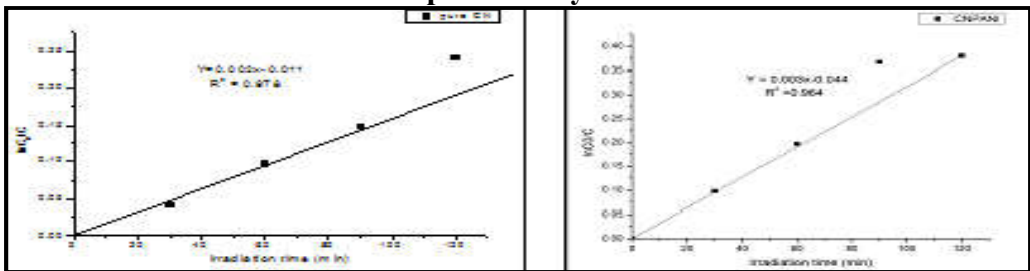


Figure No.10: First-order plots for the photodegradation of Rh-B using CN and CNPANI composite photocatalyst

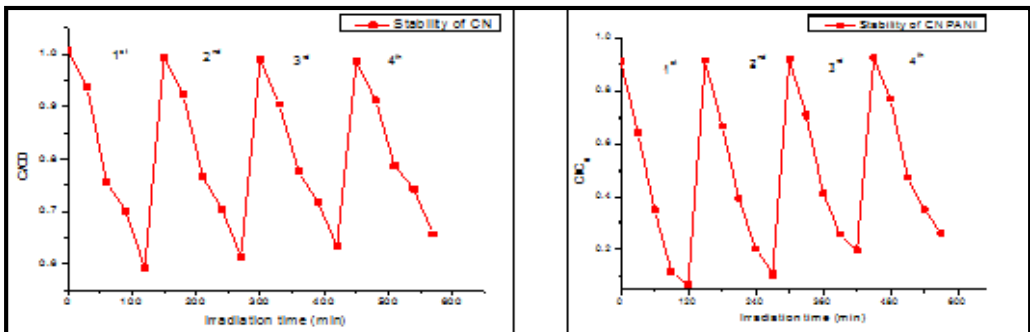


Figure No.11: Recycling runs in the photodegradation of Rh-B using CN and CNPANI composite photocatalyst

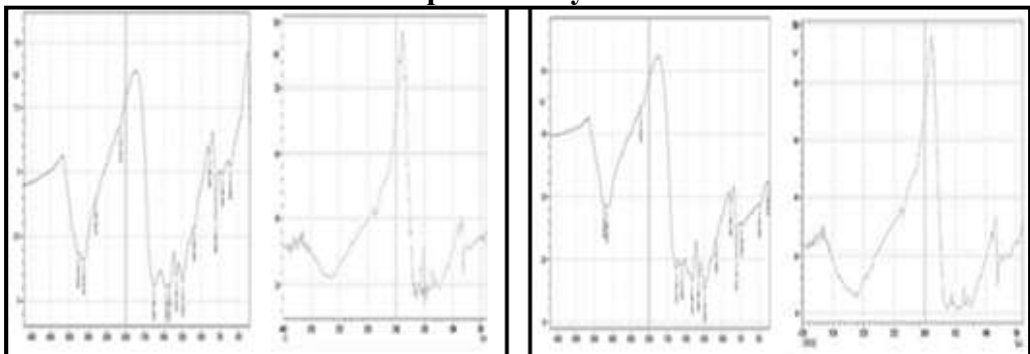


Figure No.12(a): FT-IR spectrum of CN before and after the reaction (b) FT-IR spectrum of CNPANI before and after the reaction

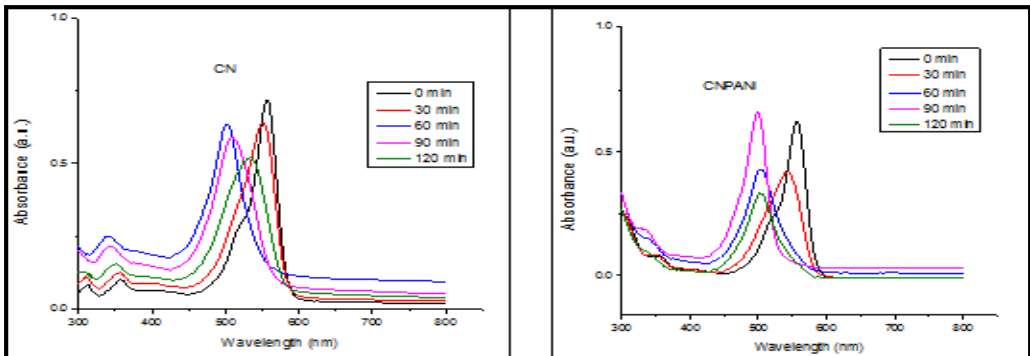


Figure No.13: UV-visible absorption spectral changes for the Rh-B by CN and CNPANI composite photocatalyst

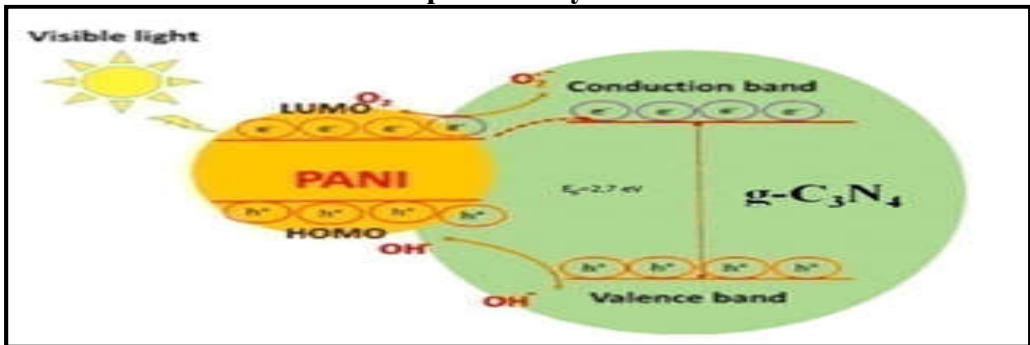


Figure No.14: Schematic diagram of the separation and transfer of photogenerated charge carriers in CNPANI system under visible light

CONCLUSION

Novel PANI-g-C₃N₄ polymer composite sample is successfully synthesized and characterized using XRD, FT-IR, SEM, EDAX and UV-Visible spectroscopy. The absorbance intensity is found to be stronger than that of pure g-C₃N₄. The photodegradation rate of CNPANI (0.006698 min⁻¹) is 1.5 times higher than that of pure g-C₃N₄. In this study the photodegradation and photomineralization of the pollutants in the presence of sunlight and oxygen are tested but CNPANI composite shows only 57% efficiency. The results indicate that the degradation rate could be influenced not only by the different parameters but also by the type of photocatalyst and the model pollutant. Here, the very low efficiency of photocatalyst is due to the repulsive interaction between the positively charged PANI back bone and the cationic part of the Rh-B dye.

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CONFLICT OF INTEREST

We declare that we have no conflict of Interest.

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