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Graphitic Carbon Nitride Composited with Conjugated Polymers as a Promising Photocatalyst.

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ABSTRACT

As a promising two-dimensional conjugated polymer, graphitic carbon nitride (g-C_3N_4) has been utilized as a low-cost, robust, metal free and visible-light-active photocatalyst in the field of water splitting, CO_2 reduction, artificial photosynthesis, pollutant degradation, and toxic metal removal. However, pure g-C_3N_4 based photocatalyst seriously restricts its practical use owing to low specific surface area, narrow absorb window ca. 450 nm, low charge carrier mobility and therefore high electron-hole recombination rate. To address these challenges, particularly decreasing the electron-hole recombination rate, various strategies were used like metal/non-metal doping, copolymerization and construction of various semiconductor-semiconductor composite or heterojunction. Herein, we present an overview on construction of g-C_3N_4 – conjugated polymer based semiconductor heterojunction with an aim to highlight the efficiency of the composite photocatalyst towards pollutant degradation and hydrogen evolution. We mainly highlight the advancement with carbon based conjugated polymers like graphene oxide, carbon nanotubes, carbon dots, and polyaniline.

Keywords: ***Photocatalyst, Heterojunction, Carbon nitride, Conducting polymers, Graphene oxide***

I INTRODUCTION

Increase in global energy crisis together with environmental issues are becoming serious threats to the long-term development of human society. Researchers are trying to find green technologies as sustainable ways to address such challenges. Semiconductor-based photocatalysis has emerged as a potential solution being economic, renewable, clean and safe requires only the inexhaustible solar light as a driving force, and a suitable semiconductor as a photocatalyst.[1,2] Although a good number of semiconductor photocatalysts were developed in this field, their photocatalytic activity under visible-light illumination is still limited mainly due to their narrow absorption window in visible region of solar spectrum along with fast photo corrosion. To overcome this, nanostructured polymeric g-C_3N_4 which is a novel metal free visible light induced semiconductor photocatalyst with a suitable band gap energy of 2.7 eV has been recently developed.[3-5] g-C_3N_4 is the most stable allotrope of carbon nitride with unusually high thermal and chemical stability. Varieties of low-cost nitrogen-rich precursors such as, cyanamide, dicyandiamide, melamine, ammonium thiocyanate, urea, thiourea, and guanidine have been used to prepare g-C_3N_4. It was Berzelius and Liebig in the 1830s who laid the foundation of embryonic form of g-C_3N_4 called as melon.[6] Melon is a linear polymer consisting of interconnected tri-s-triazines via secondary nitrogen, while g-C_3N_4 is in the form of 2D sheets consisting of tri-s-triazines interconnected via tertiary amines. Thus the framework topology of g-C_3N_4 is constructed by repeated tri-s-triazine (heptazine) units with abundant surface terminated NH_2 groups. It is a promisingly high performance material due to hardness, lightweight, non-toxicity, abundance, preparation from easily available starting material and excellent stability at an ambient condition.[7]

Although g-C_3N_4 have been explored as a material with promising potential in the field of photocatalysis however, the photocatalytic efficiency of pristine g-C_3N_4 is still low, due to the high electron–hole recombination rate, the absorbance of only blue light of the solar spectrum (450 nm) , low surface area of g-C_3N_4 (~10 m^2/g) without forming textured pores and grain boundaries which eventually disrupt the delocalization of electrons. To improve the quantum efficiency and to promote the photocatalytic activity, strategies such as non -metal doping, transitional metal incorporation, copolymerization, conjugated polymer modification, coupling with other semiconductors, introduction of carbon-dopants have been developed.[8,9] Coupling with various carbon rich materials not only compensate the disadvantages of individual semiconductor materials but also induce synergetic effects like visible light harnessing abilities, enhanced electron hole separation ability and improved photo stability.

Herein, we present an overview on construction of g-C_3N_4 – conjugated polymer based semiconductor heterojunction with an aim to highlight the efficiency of the composite photocatalyst towards pollutant degradation and hydrogen evolution. We paid our special concern to carbon based conjugated polymers like graphene oxide, carbon nanotubes and carbon dots.

II Synthesis of graphitic carbon nitride (g-C_3N_4)

Pristine g-C_3N_4 can be simply prepared by the thermal condensation of several low-cost nitrogen-rich precursors such as cyanamide, dicyandiamide, melamine, thiourea, urea, ammonium thiocyanate and guanidine. In a typical synthesis involving melamine as precursor, weighed amount of melamine were placed in a crucible with a cover and then heated at 550 ^{0}C for 3 h. After being cooled down to room temperature, the yellow product was collected and ground to fine powders. Inspite of the large specific surface area of monolayer g-C_3N_4, the bulk counterparts display a low specific surface area of <10 m^2g^{-1} attributed to the stacking of g-C_3N_4 layers. Several reports emphasize the importance of delaminating/exfoliating g-C_3N_4 into a few layers giving rise to intriguing optoelectronic properties towards advanced photocatalytic activity. Ultrasonication assisted liquid exfoliation in acidic pH or even in ionic liquids is the most frequent used method. The obtained g-C_3N_4 powder was then mixed with 50 mL of ultrapure H_2O under sonication overnight to produce well-dispersed thin-layer light yellow colored g-C_3N_4.[10]

III Construction of g-C_3N_4 – conjugated polymer based semiconductor heterojunction

Construction of a semiconductor–semiconductor heterojunction is an effective way to enhance the photocatalytic performance of semiconductor photocatalysts by promoting the separation of photo induced electrons and holes. As mentioned above, the structure of g-C_3N_4 is flexible due to its polymeric nature, which favors the formation of heterojunction with close interconnection between g-C_3N_4 and various semiconductors. A large number of semiconductors have been coupled with g-C_3N_4 to form semiconductor–semiconductor heterojunction, including metal oxides(TiO_2, ZnO, NiO, Cu_2O, Fe_2O_3 etc), metal oxynitrides (e.g., TaON, and ZnGaNO), metal chalcogenides (e.g., CdS, $CuInS_2$ and CuGaSe), bismuth-based compounds (e.g., $BiPO_4$, $BiVO_4$, BiOCl, Bi_2WO_6, BiOBr, and BiOI), silver-based compounds (e.g., Ag_2O, Ag_3PO_4, Ag_3VO_4, Ag_2S, AgCl) and organic semiconductors (e.g., poly3-hexylthiophene, polypyrrole, graphitized polyacrylonitrile, Polyaniline), carbon nanotubes and carbon dots. All the aforementioned composites exhibit enhanced photocatalytic activity. Now, we shall begin by highlighting the photocatalytic performance of g-C_3N_4-conjugated polymer heterostructure under two sub categories *viz*, (1) Heterojunction with carbonaceous materials such as graphene, CNT, fullerene and carbon dots (2) Heterojunction with organic conjugated polymers.

3.1 g-C_3N_4 heterojunction with carbonaceous materials.

Carbon nanostructured materials are very important candidates for solar energy harvesting with high quantum yield achieved by accelerating the transfer of electron from the surface of a photocatalyst to the interface. Moreover these materials offer good chemical stability, conductivity and high surface area. Integration of g-C_3N_4 with different conjugated carbon species having unpaired electrons in the lattice significantly enhance the delocalization of charges and hence delayed charge recombination with better photocatalytic activity.

Ordered mesoporous carbon, has a tubular structure with large pore size (mesopore), fast charge mobility and increased surface area suitable for semiconductor based photocatalysis. Ordered mesoporous carbon (OMC)/ g-C_3N_4 composites were synthesized by a simple low temperature thermal condensation method. Shi et al. [11] synthesized OMC by using SBA-15 as surfactant template, sucrose as carbon source and H_2SO_4(98%) as dehydrating agent.[11] The OMC/ g-C_3N_4 composites were synthesized by mixing the specified amounts of OMC with melamine and subjected to calcinations. In the OMC/ g-C_3N_4 a clear interface was formed between the carbon particles and g-C_3N_4 , which favors the transfer of photogenerated electron from the surface of g-C_3N_4 to OMC(Fig.1a).Delayed electron–hole recombination was further confirmed by photoluminescence (PL) wherein, intensity of the spectra decreases appreciably with increase in the content of OMC. Based on these observations, OMC/ g-C_3N_4 composite were tested successfully towards visible light photo degradation of rhodamine B (RhB) and 2,4-dichlorophenol (2,4-DCP). In comparison to pristine g-C_3N_4 the photocatalytic efficiencies were found to be 10 and 3.68 times towards degradation of RhB and 2,4-DCP respectively.[11] Similarly in another report H. Zhang et al.[5] fabricated g-C_3N_4 decorated with carbon dots (CDs) synthesized via a facile impregnation- thermal method as a promising photocatalyst towards phenol degradation. CDs are predominantly composed of graphitic carbon (sp^2carbon) with a size less than 10 nm and unique optical and electronic properties. CDs were synthesized by the pyrolysis of citric acid and branched poly(ethylenimine). Under visible light irradiation, low CDs content of 0.5 wt% in the composite resulted in a 3.7 times faster reaction rate for phenol photo degradation than pristine g-C_3N_4.To increase the specific surface area of CD based composite, Y. Peng et al.[12] synthesized CD-SBA-15- g-C_3N_4 composite photocatalyst with high surface area and big pore channels for phenol degradation. The composite exhibit 4 times higher degradation rate than pristine g-C_3N_4. Another carbon species multi-walled carbon nanotubes (MWNT) are also good candidates for the improvement of photocatalysis. [13,14] In general multi-walled carbon nanotubes were used as electron sinks to improve the photogenerated charge carrier separation and delay their recombination (Fig 1b).

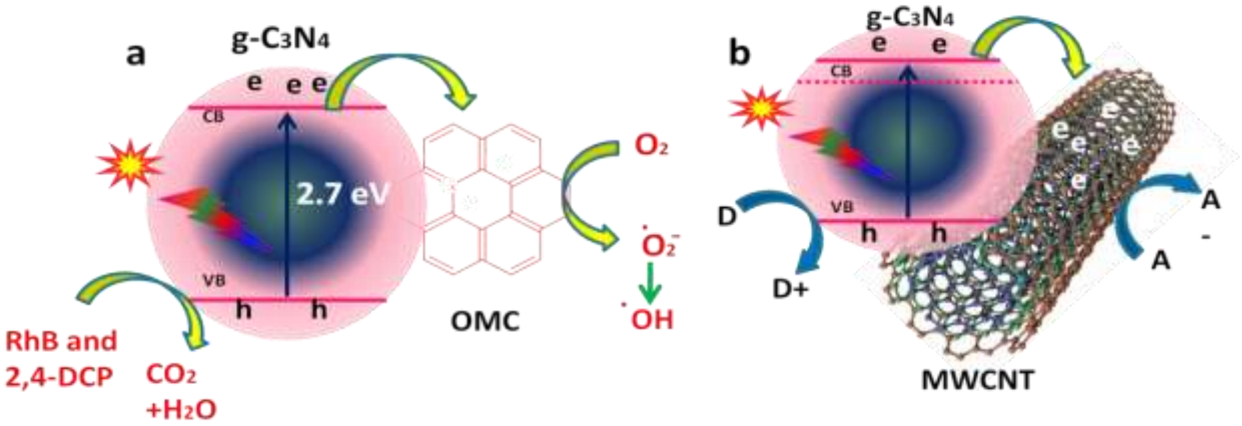

Figure 1. Pictorial representation of charge transfer in (a) OMC- g-C_3N_4 composite.(b) MWCNT- g-C_3N_4 composite.

Suryawansi et al.[13] synthesized a metal-free photocatalyst of g-C_3N_4 functionalized with multiwall carbon nanotubes (MWCNTs) to maximize its photocatalytic H_2 evolution ca. 42 mmol/g under visible light irradiation . There is a 100% improvement of its activity at an optimum loading of 0.5 weight% of MWCNT. The pi-conjugated networks of the composite delays the process of recombination of photogenerated electron–hole pairs. Xu *et al.* [15] reported the photocatalytic activity of the CNT/g-C_3N_4 catalysts towards the degradation of methylene blue dye. The results showed that the degradation rate of the CNT/white g-C_3N_4 composite was nearly 8.1 times more than that of pristine g-C_3N_4 . Ma et al. [14]reported synthesis of self assembled 3 dimensional graphitic carbon nitride nanosheets and carbon nanotubes driven by π– π stacking and electrostatic interactions as highly porous and active metal free photocatalyst .The photocatalyst exhibits remarkably catalytic oxygen evolution activity and stronger durability.

Graphene, a 2D macromolecular sheet of carbon atoms with a honeycomb like structure, has attracted much attention due to its outstanding mechanical, thermal, and optoelectronic properties.[16-18] Especially, its high thermal conductivity (~5000 W m^1K^{-1}), excellent mobility of charge carriers (200 000 $cm^2V^{-1}s^{-1}$), and extremely high specific surface area up to ca. ~2600 m^2/g motivated researchers to explore its photocatalysis. Graphene can be easily obtained through chemical oxidation dispersion reduction procedure. Graphene oxide (GO) obtained from graphene possesses an abundant assortment of oxygen-containing group. By considering the exceptional properties of graphene and g-C_3N_4 nanosheets as well as the geometric advantages of 2D/2D face-to-face interaction, fabrication of graphene/ g-C_3N_4 nano heterostructure from past two years in the field of energy conversion and environmental decontamination is a hot area of research.[19,20] In the composite highly conducting GO layers acts as an efficient electron trap **(Fig.2)** and it was found that by increasing graphene loadings, the HOMO-LUMO band gap of the rGO/ g-C_3N_4 was reduced thus modifying the band structures of the nanohybrids.

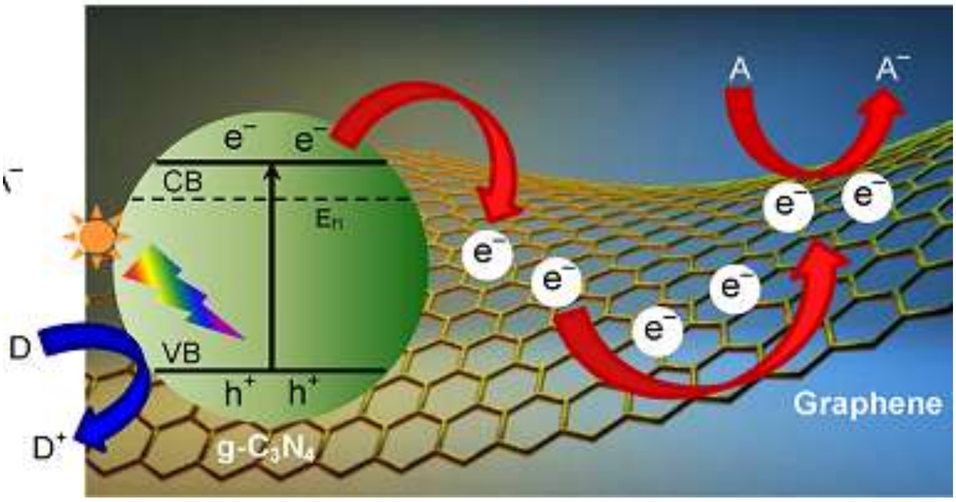

Figure 2. Graphene as an conducting electron trap.

Ong *et al* [21]. employed a facile wet impregnation strategy followed by calcination in an inert atmosphere to fabricate g-C_3N_4/graphene composite with urea as a starting material as shown in Fig 3a .Same group of workers reported a 2D/2D hybrid heterojunction photocatalyst with effective interfacial contact by incorporating reduced graphene oxide (rGO) and protonated g-C_3N_4 (pCN) synthesized by a novel combined ultrasonic dispersion and electrostatic self-assembly strategy followed by a $NaBH_4$-reduction process.[22] Compared with pure g-C_3N_4 and rGO/ g-C_3N_4 , the rGO/ pCN photocatalysts demonstrated a remarkable enhancement on the CO_2 reduction in the presence of H_2O vapor. PL data confirm enhanced charge separation in the composite.[22] The photocatalytic activity of porous g-C_3N_4 /graphene composite was evaluated by Yu et al. for the degradation of MB. By visible light irradiation for 51 min, 58% of MB is degraded by using neat- g-C_3N_4 as photocatalyst; where as 87% of MB is degraded by using the porous g-C_3N_4 /graphene hybrid photocatalyst. Likewise Q. Xiang *et al.* [19] prepared a series of graphene/g-C_3N_4composite with varying graphene content as a photocatalyst with high visible-light photocatalytic H_2-production activity. Typically the heterostructure were fabricated by the impregnation chemical reduction strategy wherein, polymerization of melamine were carried out in the presence of graphene oxide as precursors followed by calcination at 550 ^{0}C under a flowing nitrogen atmosphere and reduction by hydrazine hydrate. In the resulting layered composite, graphene sheets act as conductive channels to efficiently separate the photogenerated electron and hole to enhance the visible-light photocatalytic H_2-production activity .The optimal graphene content was found to be 1.0 wt %, and the corresponding H_2-production rate was 451 μ mol $h^{-1}g^{-1}$, which exceeded that of pure g-C_3N_4 by more than 3.07 times[19]. Attenuated PL intensity in composite material in comparison to pristine g-C_3N_4 confirm better charge recombination wherein, graphene sheets act as a good acceptor of the photogenerated electrons as shown in Fig. 3b.

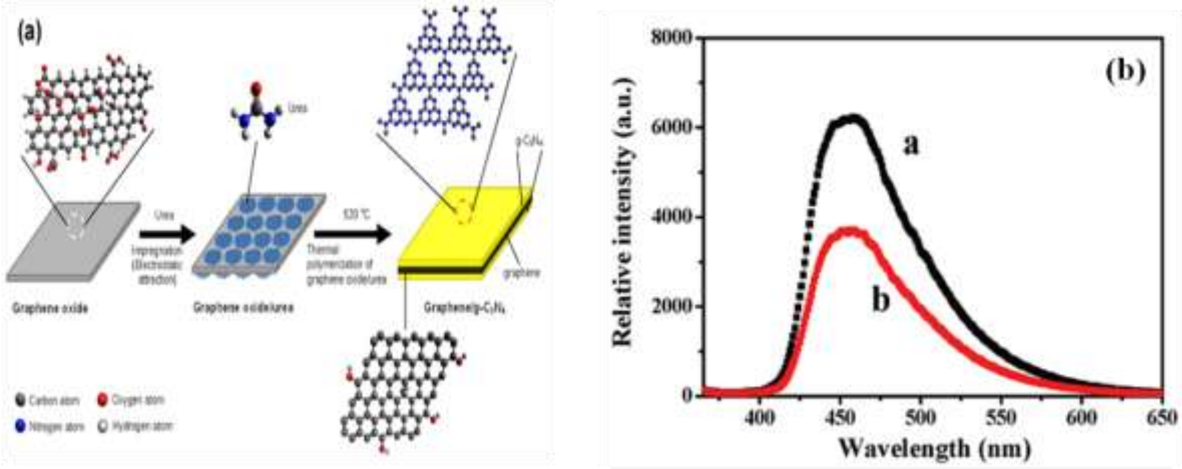

Figure3. Fabrication of g-C_3N_4 /graphene from urea precursor (a) and PL spectra of g-C_3N_4 /graphene composite ;(a) for g-C_3N_4 and (b) for g-C_3N_4 /graphene composite; images adopted from references 21 and 19 respectively with proper permission from *American Chemical Society* (2011 and 2016).

In a similar report A. Du *et al.*[23] reported the same optoelectronic results in Graphene/ g-C_3N_4 composite by using Density Functional theory (DFT). Results indicate that the charge transfer at the graphene/ g-C_3N_4 interface enhances the electron conductivity of g-C_3N_4 , potentially facilitating photocatalytic performance of the composite.[23] Through the innovative nanostructure design of a 3D porous framework, Tong and co-workers[24] have just reported a 3D porous g-C_3N_4 /GO aerogel through a hydrothermal treatment by employing GO and g-C_3N_4 nanosheets as building blocks followed by freeze-drying. In this case, g-C_3N_4 served as a photocatalyst, while GO promoted the 3D network as well as accelerated the electron conductivity.

3.2 g-C_3N_4 heterojunction with organic conducting polymers.

Conducting polymer is regarded as one of the main organic semiconductors with visible-light absorption and π-conjugated electronic systems. By taking the advantage of the aromatic based conjugated system and π electronic structures of the g-C_3N_4 polymer, it facilitates the hybridization of g-C_3N_4 with conducting polymers to form organic−organic or polymer− polymer surface heterojunction. So far, the widely studied conducting polymers include polyaniline (PANI)[25], Polypyrrole (PPy)[26], graphitized polyacrylonitrile (g-PAN), poly3-hexylthiophene (P3HT)[27], and poly 3,4-ethylenedioxythiophene (PEDOT).[28] Among all the conducting polymers, PANI and PPy are the most extensively reported conducting polymers, which possesses all the necessary requirements suitable for efficient solar energy harvesting like nontoxicity, high chemical stability, high visible light absorption coefficient ~5 $\times 10^4$,exceptional electron and hole conducting properties, corrosion resistant and cost-effective synthesis. Importantly, PANI acts as both an electron donor and a remarkable hole acceptor upon the light illumination. Inspired by the aforementioned unique properties Ge et al.[25] synthesized the PANI/ g-C_3N_4 composite photocatalysts by an in situ deposition oxidative polymerization of an aniline monomer together with g-C_3N_4 at low temp~ 5 ^{0}C.The composite belong to heterojunction of the type "II" wherein the synergistic effect between PANI and g-C_3N_4 result in efficient charge separation and hence better photocatalytic performance(Fig 4a). Briefly upon visible light irradiation $\pi-\pi^*$transition occur, migrating the excited electron to the π^*-orbital. Upon close and careful examination of band edges/energy levels of g-C_3N_4 (VB and CB) and PANI (π-orbital and π^*-orbital), it was established that the edge potentials Of π-orbital and π^*-orbital were more negative than VB and CB edge potentials of g-C_3N_4 (Fig.4b). Owing to this the excited electrons from PANI could be easily injected into the CB of g-C_3N_4 , while the holes on the VB of g-C_3N_4 transferred to the π-orbital of PANI, leading to effective charge separation. The composite has been successfully tested for the photo catalytic degradation of methylene blue(MB) dye from aqueous medium (Fig.4b).In another work by Zhang et al.[29] hierarchical nanocomposites of PANI nanorods arrays were deposited on the g-C_3N_4 nanosheets synthesized by a dilute polymerization at -20^{0}C.

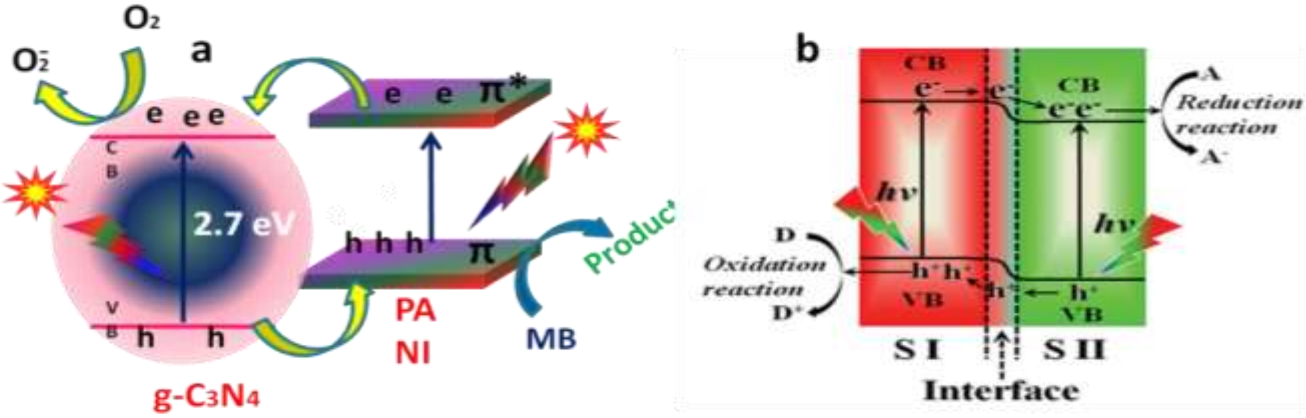

Figure 4. **Heterojunction-II formation by PANI- g-C_3N_4 composite with PANI as electron source (a) and interfacial activity in case of heterojunction-II (b).**

Looking for an efficient photocatalyst for H_2 evolution reaction especially in absence of sacrificial agents like Na_2S /Na_2SO_3,methanol, and triethanolamine (TEOA) Y. Sui et al. synthesized PPy/ g-C_3N_4 composite by in situ radical assisted polymerization of pyrrole using sodium persulfate as oxidizing agent. At optimized 1.5 wt% of polypyrrole (PPy) photocatalytic H_2 evolution from pure water was found to be maximum as is evident from decreased PL intensity. The H_2 evolution rate increases 10 up to 50 times for PPy/ g-C_3N_4 visible active catalyst in comparison of either native PPy or g-C_3N_4 . Research with the conducting polymer composites offer new inroads into the exploration and utilization of heterostructure and heterojunction materials for environmental and photochemical application.

IV CONCLUSION

In this review, we have summarized the use of carbon nitride and its modifications using carbonaceous materials to achieve the excellent photocatalytic performance of the heterojunction. It was summarized that by compositing g-C_3N_4 with various conducting carbonaceous semiconducting polymers, photocatalytic efficiency towards H_2 evolution and pollutant degradation from aqueous medium were evaluated.

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