

Recent Developments of Dye Degradation Using g- C_3N_4 Composites

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Abstract:

Nowadays the presence of toxic dyes in surface water has drawn much attention owing to the deleterious effects on human-beings, aquatic animals and non-biodegradability of the dyes. Much work has been done for the removal of colored dyes from polluted water by various methods namely adsorption and photo-degradation. Lately, a non- metallic, bio-compatible semiconducting material graphitic carbon nitride (g-C3N4) has taken prominence but the rate of electron-hole pair recombination is very high and insignificant visible light activity has limited its application. Thus the g-C3N4 with other nano-material composites have taken prominence in degrading dyes. The tunable band-gap of g- C3N4 provides enough scope for modification forming composites with metals and non-metallic with increasing catalytic activity.

Keywords: g-C3N4, semiconducting nano-composite, photo-catalyst, organic dyes, advanced oxidation process, photo-degradation.

and its pollution due to anthropogenic activities like rapid industrialization has become a serious concern in the present world. The rapid growth of textile, leather and food industries produce large amount of colored dyes in effluents that are found in surface water[1]. The different treatment methods adopted for removal of dyes such as adsorption, coagulation, membrane separation and filtration require greater maintenance and are cumbersome[2, 3]. A more efficient and timesaving process is photo-catalytic degradation by advanced oxidation process (AOP) using composite of $g-C_3N_4$ semiconductors [4, 5]. The generation of highly reactive hydroxyl radicals (OH) by O_3/UV and $O_3/UV/H_2O_2$ conventionally and Fenton-reagent ($Fe^{2+}/H_2O_2/UV$) nonconventionally can effectively degrade the obstinate dyes. However, the production of iron sludge and extreme low pH working conditions of AOP is compensated by heterogeneous Fenton like processes using semiconductor composites under solar light[6]. The low-cost, chemical endurance, bio-compatibility and tunable band gap of $g-C_3N_4$ and its hybrid materials have proven to be more promising for heterogeneous photo-catalysts in AOP for dye degradation[7]. The photo-degradation of MB dye was 99% with 40 wt% g-C₃N₄/I-TiO₂ in 80 min, g-C₃N₄/Fe₃O₄/Ag₃PO₄/AgCl (30%) nano-composite was 98% for RhB dye under visible light[8, 9].

2. Materials and Methods

g-C₃N₄ mainly consist of graphitic layers having system and conjugation of aromatic are constructed from units of tri-s- triazine attached by planner amine groups. Recently, interesting developments has been observed in the modification of g-C₃N₄ based photo-catalysts including the structural/morphological features and their photo- catalytic activity. Vrious synthesis procedures such as template method, solvo-thermal method, thermal polymerisation method, chemical functionalization method, ultrasonication method, Sol-gel method etc. are used for the fabrication of $g-C_3N_4$ and its composites.

Sol-gel Method:

It is one of the most easiest process for the fabrication of $g-C_3N_4$ and its composites having low cost, ambient processing temperature etc. $g-C_3N_4$ -TiO₂ nanocomposite was prepared by Cheng et al. by taking tetra-n-butyl titanate as precursor [10].

1. Introduction Water scarcity and i

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Ultrasonication Method:

In ultrasonication method the multilayered g- C_3N_4 can be separated in to few layered 2D sheets reported by Zhang et al.[11]. By using this process and 10M HCl Ma et al. fabricated 2D g- C_3N_4 taking dicyandiamide as the precursor[12].

Chemical precipitation Method:

Liet al. synthesized $Ag_2CO_3/g-C_3N_4$ nanocomposite by in situ addition of Ag_2CO_3 and NaHCO₃ using chemical precipitation method[13]. Zn/ln-LDH/ g-C₃N₄ photocatalyst was synthesized by Lang et al. by taking Zn(NO₃)₂.6H₂O and ln(NO₃)₂.6H₂O,NaHCO₃ and Na₂CO₃ for Zn-ln layered double hydroxide with Zn-ln molar ratio 3.0 and melamine as precursor for g-C₃N₄[14].

Template-assisted Method:

Porous g-C₃N₄ photo-catalysts were synthesized by taking various template such as organic and inorganic molecules. Mainly silica materials are used as templating agent. Porous g-C₃N₄ were synthesized by Groenewolt et al. and Wang et al. using poly-condensation and thermal condensation taking silica template[8,9]. Twisted hexagonal rod like g- C₃N₄ was synthesized by Zheng et al. with SiO_2 as templating agent[10]. B.F modified mesoporous $g-C_3N_4$ was synthesized by Wang et al. using 1-butyl-3methylimidazolium tetra-fluoroborate as a soft template[15].

composite	dye Synthetic Process	
CoFe ₂ O ₄ /g-C ₃ N ₄ [17]	RhB	calcination
g- <u>C₃N₄/NH₂-MIL-88B(</u> Fe) [18]	MB	hydrothermal
g-C ₃ N ₄ /ZnFe ₂ O ₄ [19]	RhB orange	7 Coprecipitation
g-C31V4/CIN1/Bl2Fe4O0 [20]		nydrothermai

Table 1. g-C3N4 composites used for photo-
degradation of dyes

3. Result and Discussion

The photo-degradation of various dyes was studied under Xe lamp by $ZnO/Fe_3O_4/g-C_3N_4$ composite prepared by ultra sonication and solid state thermal process. The activity of ZnO/Fe $_{3}O_4/g-C_3N_4$ markedly enhanced than prestine g- C_3N_4 and ZnO. Due to the existence of the hetero-junction among the interfaces of g- C_3N_4 and ZnO, photo-catalytic activities of the ZnO/Fe₃O₄/g-C₃N₄ nanocomposites will be enhanced because of the reaction towards visible light will be higher and electronhole recombination will be diminished.In case of $ZnO/Fe_3O_4/g-C_3N_4-50\%$ the repeatability studies shows that even after 5 recycles it shows a quite higher photocatalytic activity. ZnO/Fe₃O₄/g-C₃N₄-50% degrade Methyl orange(MO), Alizarin yellow R (AYR), and Orange G (OG) were 97.87%, 98.05%, and 83.35%, respectively, because of the adsorption of the dye molecules on the surface of photocatalyst and the structural aspects of dye molecule [21]. The CdS/g-C₃N₄/MOF composite with a significant surface area of 238.43 m^2/g exhibited an extraordinary photo-catalytic activity towards Rhodamine B under the visible light radiation. The degradation of RhB after 90min was 90.2%. The activity was superior to that of bare CdS, MOF, g-C₃N₄ having alike circumstances. The improved separation of the electron-hole pairs visible-light activity made CdS/g-C₃N₄/MOF composite more superior. The rate constant of the reaction kinetics for $CdS/g-C_3N_4/MOF$ (k = 0.0414 min⁻¹) is more compared to the rate constants of the pure CdS $(k = 0.0055 \text{ min}^{-1})$, MOF (k = 0.0025 min^{-1}) and g-C₃N₄ (k = 0.0048 \min^{-1}) [22]. The ternary composite g- $C_3N_4@Ag/AgVO_3(10\%)$ exhibited high photocatalytic performance with RhB and complete degradation occured in 12 min. The reaction obeys a pseudo-first-order kinetics. The g- $C_3N_4@Ag/AgVO_3(10\%)$ was having much faster activity with a rate constant, $k = 0.400 \text{ min}^{-1}$, that was 2.5 times that of neat $g-C_3N_4$ (k = 0.158 min⁻ ¹) and 22.2 times as high as and $Ag/AgVO_3$ composite (k = 0.018 min^{-1}) [23]. In the g-C₃N₄/Cu₂O complex the micrographs revealed the porous structure that retained the cubic shape of Cu₂O. The EDS spectra supported the occurance of g- C_3N_4 within the cubic morphology. The $g-C_3N_4/Cu_2O$ composite with 10% of $g-C_3N_4$, exhibited the best visible light photo-catalyst for methylene blue (MB) and Rhodamine-B (RhB) degradation. The UV-DRS analysis and Tauc plot showed a reduced band gap of 2.05 eV for the material. The composite, g-C₃N₄/Cu₂O with 5% Cu₂O, degraded 81% of MB and 85.3% of RhB in 120 min. Even after three repeated cycles the decrease in the catalyst performance was less than 5% for both MB and RhB dyes. The enhanced photo-catalytic show of the composite was recognised to the highly



porous morphology and the tunable band gap active in visible region [24]. As reported, the ntype transition metal oxide Nb₂O₅ with a wide band gap of ~ 3.4 eV restricts its application only in the UV region. The $g-C_3N_4$ and $m-Nb_2O_5$ (g- C_3N_4 -mNb₂O₅) composites exhibited higher photo-catalytic performance because of the synergistic effect involving g-C₃N₄and m Nb₂O₅. The 4% g-C₃N₄-m Nb₂O₅ composites showed the highest efficiency and good recyclability for degradation of both RhB[25]. In the reported study of SrTiO₃/g-C₃N₄ (CNSTO) composites prepared by sonication mixing, exhibited high degradation of organic dyes for optimum % age of $g-C_3N_4$. The materials were synthesized with varying the g-C₃N₄ ratios 10, 20, 30, 40 and 50%. The photo-catalysts generated

radicals OH in the trend, 20CNSTO 50CNSTO 30CNSTO > > 10CNSTO > 40CNSTO. The photocatalyst presented stable photo-catalytic activity among the repeated cycles and about 95% of the initial dye degradation was maintained [26]. Wang et al. prepared a light weight, non-toxic, neutral pH $g-C_3N_4/MgO$ composite responsive by calcination method to show the photocatalytic degradation of methyl orange(MO) using hydrogen peroxide (H_2O_2) .

A comparative study between g-C₃N₄/MgO and $g-C_3N_4/TiO_2$ showed that the catalytic property of $g-C_3N_4/MgO$ is higher with and without irradiation of light. The g-C₃N₄/TiO₂ composite is unable to degrade MO without the presence of light. When the pH of the MO solution was higher than 4 there was total degradation of MO. The reusability and stability of the material was found to be intact after 3 cycles [27]. K. Prakash et al. synthesized the lily flower like $SrO_2/g-C_3N_4$ composite by dry synthesis method for the degradation of RhB dye. The complete degradation of RhB with in 60 min. With varying photo-catalytic dose, initial concentration the prestine $g-C_3N_4$ degraded only 65% of RhB. However after composition of SrO₂ on g-C₃N₄ the degradation efficiency increased due to diminished electron-hole pair recombination. The dose variation from 10-75mg showed that at 50mg of $SrO_2/g-C_3N_4$, the degradation of RhB was maximum. The catalyst generated more of hydroxyl radical('OH) enhancing the degradation efficiency[28]. The proposed mechanism for the dye degradation was as follows,

 $SrO_2/g - C_3N_4 \xrightarrow{hv} SrO_2(e^- + h^+)/g - C_3N_4(e^- + h^+)$ (1)

$$\operatorname{SrO}_2(e^- + h^+)/g - \operatorname{C}_3\operatorname{N}_4(e^- + h^+) \xrightarrow{\text{hu}} \operatorname{SrO}_2(e^-)/g - \operatorname{C}_3\operatorname{N}_4(h^+)$$
 (2)

$$e^- + O_2 \to O_2^-$$
 (3)

$$O_2^- + H_2 O \rightarrow OH \tag{4}$$

 $e^- + H^+ + O_2 \to H_2 O_2$ (5)

$$H_2 O_2 + O_2^- \to OH^- + OH^- + O_2$$
 (6)

 O_2^- "OH +dye \rightarrow degraded products (7)

Synthesis of of $g-C_3N_4$ by incorporation of another semiconducting material CeVO₄ that exhibited better performance than the prestine g-C₃N₄. The performance was further increased by doping Ag nano-particles, that inhibited the electron-hole recombination owing to surface plasmon resonance (SPR). As reported the inclusion of 7% of Ag into CeVO₄/ g-C₃N₄ completely degraded MB dye in 120 min compared to other ternary composites. The photocatalytic degradation followed a pseudofirst order mechanism [30].

4. Conclusion

More recently semiconducting 2D material graphitic carbon $nitride(g-C_3N_4)$ has been extensively used as a base material for water purification specifically for organic dve degradation. The tuning of bandgap, possible variation in recombination of electron-hole pair and increasing its surface area could be achieved by hybridising $g-C_3N_4$, with metal and non-metal nano-composites from sensors to pervoskites and spinels. The increased photodegradation is mainly contributed to the hetero-conjugation, increase in formation of hydroxy radical('OH) and more active towards visible radiation. The prospective of $g-C_3N_4$ composites could be vastly exploited for environmental aspects and energy.

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Figures with captions



Fig 1. Composites and methods for $g-C_3N_4$ modification [16]



Fig. 2. (a) s-Triazine and tri-s-train as tectons of g-C₃N₄ (b) Schematic presentation of charge transfer in g-C₃N₄[29].





Fig 3. Photo-degradation of MB dye by a ternary $Ag/CeVO_4/g-C_3N_4$ composite (a) 7% $Ag/CeVO_4/g-C_3N_4$ showed highest percentage of degradation (b) the reaction kinetics was pseudo-first order for all composites (c) schematic diagram of charge carrier separation in $Ag/CeVO_4/g-C_3N_4$ [30].