Fe(III)-grafted K-doped g-C₃N₄/rGO composite photocatalyst with efficient activity towards the degradation of organic pollutants[§]

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Abstract. The quick recombination of charge carriers and the low oxidizing ability of VB holes of g-C₃N₄ limits its practical application. Herein, we have synthesized a visible-light sensitive Fe(III)-grafted K-doped g-C₃N₄/rGO heterostructure photocatalyst to tackle the above problem so as to achieve enhanced photocatalytic activity. The prepared samples were characterized by standard analytical techniques such as XRD, FT-IR, EPR, SEM, TEM, DRS and PL spectroscopy. EPR analysis reveals that the grafted iron exists in +3 oxidation state in the composite material. As compared to pristine g-C₃N₄, surface grafted nanocomposite photocatalyst exhibits excellent photocatalytic performance for the degradation of Rhodamine B (RhB), Methylene Blue (MB) and Methyl Orange (MO) under visible light irradiation. The enhanced activity could be attributed to the creation of defect levels in the band gap, shift of absorption band towards the visible region and intimate interfacial interactions between graphene and g-C₃N₄, effectively promoting separation of photoinduced charge carriers. The idea to tune the bandgap of graphitic carbon nitride by introducing alkali metal along with its composite formation with graphene could present a new concept to effectively steer the photocatalytic activity.

Keywords. Fe(III)-grafted K-g-C₃N₄/rGO; visible light induced photocatalyst; dye degradation.

1. Introduction

The water pollution caused by dye industries poses a serious threat to the environment and human life.¹ Heterogeneous photocatalysis using semiconducting material is regarded as a potential tool to mitigate the environmental problem as it could utilize solar light which is easily accessible and freely available on earth.^{2,3} Many wide bandgap semiconductors such as TiO₂, ZnO and SrTiO₃ have been employed for the degradation of organic pollutants.⁴⁻⁶ Among them, TiO₂ is the most widely researched photocatalyst due to its fascinating properties like strong oxidation ability, stability and non-toxicity.⁷ However, the major drawback associated with TiO₂ is its wide bandgap energy and quick recombination of charge carriers, which limit its applicability. To utilize solar energy in an efficient way, the design and development of a cost-effective and efficient photocatalyst operating

under visible light is high in demand. Recently, 2D polymeric graphitic carbon nitride (g-C₃N₄) having bandgap energy in the visible range has attracted considerable attention for its promising application in the decomposition of organic pollutants.⁸ The excellent photocatalytic activity towards the degradation of organic pollutants was achieved by g-C₃N₄ nanosheets. However, substantial charge recombination led to lower photocatalytic activity and therefore not applicable for practical application.⁹ To address the above issues, Shao research group reported the doping of K into g-C₃N₄ to tune the bandgap energy of g-C₃N₄.¹⁰ They also emphasized that the incorporation of K increases the visible light absorption and enhances the oxidizing ability of valence band holes of g-C₃N₄. The results of photocatalytic activity demonstrated that the efficiency of g-C₃N₄ could be enhanced by incorporating alkali metals into g-C₃N₄, which separates the charge carriers more efficiently. It is well-documented in the literature that the photocatalytic performance of any modified semiconductor could be further enhanced by constructing heterostructure with carbonaceous species.^{4,8} Among various carbonaceous species, graphene is a

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[§] Dedicated to Professor M V George on the occasion of his 90th Birth Anniversary.

rising star and has attracted special attention due to its large specific surface area and high electron mobility which make it special among the family of carbonaceous species.¹¹

In recent years, the surface modification of semiconductors with Fe(III) ions has become a research hotspot in the field of photocatalysis since it can increase the lifetime of photogenerated charge carriers through interfacial charge transfer (IFCT) mechanism.^{12–14} The reaction mechanism of surface modified photocatalysts is different than that of other metals deposited mechanism as it follows the interfacial electron transfer from VB of the semiconductor to the surface grafted species, which acts as electron trapping sites promoting the rapid separation of charge carriers and thereby enhancing the photocatalytic activity.¹³ Liu *et al.*, reported the synthesis of Fe(III)-grafted $g\text{-C}_3\text{N}_4$ photocatalyst for efficient removal of an aqueous solution of organic pollutants under visible light irradiation.¹⁵ They found that grafted Fe(III) favors in extending light absorption ability and separating the charge carriers through the interfacial charge transfer mechanism. However, to the best of our knowledge, there is no report on the synthesis of Fe(III)-grafted K-doped $g\text{-C}_3\text{N}_4/\text{rGO}$ composite photocatalyst and its activity towards the degradation of organic pollutants under visible light source.

In the current work, we have employed different strategies such as doping of K metal into $g\text{-C}_3\text{N}_4$, constructing heterostructure with graphene and grafting with Fe(III) ions to achieve efficient visible light active photocatalyst; i.e., Fe(III)-grafted K doped $g\text{-C}_3\text{N}_4/\text{rGO}$ composite using photoreduction followed by impregnation technique. The photocatalytic performance of prepared samples was investigated by degrading different organic pollutants under visible light irradiation. Moreover, the stability of synthesized photocatalyst was also investigated by performing four successive runs. The mechanism of Fe(III)-grafted K doped $g\text{-C}_3\text{N}_4/\text{rGO}$ composite involving the role of interfacial charge transfer in the degradation of organic pollutants has also been discussed.

2. Experimental

2.1 Preparation of $g\text{-C}_3\text{N}_4$ and K-doped $g\text{-C}_3\text{N}_4$

The chemicals used in this study were obtained from Sigma-Aldrich and used as such without any further purification. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) and K-doped $g\text{-C}_3\text{N}_4$ were prepared by the reported procedure.¹⁰ In a typical experiment, dicyandiamide (2 g) was dispersed into 10 mL of

Scheme 1. Schematic illustration for the preparation of Fe(III)-grafted K-CN/rGO.

double distilled water and then an aqueous KOH solution (0.09 M, 10 mL) was added slowly dropwise with stirring. The suspension was heated at 100 °C to remove the water and the obtained solid product was dried at 80 °C in an oven followed by milling and annealing at 520 °C for 2 h. The obtained material was named as K doped $g\text{-C}_3\text{N}_4$. The graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is prepared by similar procedure without the addition of KOH, the prepared materials were abbreviated as CN ($g\text{-C}_3\text{N}_4$), K-CN (K-doped $g\text{-C}_3\text{N}_4$), respectively.

2.2 Preparation of Fe(III)-grafted K-doped $g\text{-C}_3\text{N}_4/\text{rGO}$

Graphene oxide was synthesized according to modified Hummer's method¹⁶ whereas K-doped $g\text{-C}_3\text{N}_4/\text{reduced}$ graphene oxide (rGO) was prepared according to the procedure reported in the literature.¹⁰ A certain amount $g\text{-C}_3\text{N}_4$ nanosheet was mixed with 20 mg of graphene oxide in water and then the suspension was allowed to ultra-sonication for 30 min. Afterwards, the mixture was illuminated to visible light under oxygen to reduce graphene oxide to deoxygenated graphene oxide.¹⁷ The product was filtered and washed with water several times and dried at 80 °C for 12 h. The prepared catalyst was labelled as K-CN/rGO. A schematic diagram showing the preparation of Fe(III)-grafted K- $g\text{-C}_3\text{N}_4/\text{rGO}$ is given Scheme 1. For the preparation of Fe(III)-grafted K-doped $g\text{-C}_3\text{N}_4$ composite, required amount of already prepared K-doped $g\text{-C}_3\text{N}_4/\text{rGO}$ was dispersed in 30 mL water containing the desired amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.1 wt%) and stirred for 1 h to get a homogeneous suspension. The suspension was heated at 90 °C for 1 h and subsequently washed several times with water and ethanol to remove the unwanted materials. The resulting material was allowed to dry at 110 °C for 24 h to obtain the final product. Fe(III)-grafted K- $g\text{-C}_3\text{N}_4$ was prepared using a similar procedure without the addition of reduced graphene oxide and the catalyst is abbreviated as K-CN/rGO, K-CN/rGO/Fe(III), respectively.

Figure 1. XRD patterns of different photocatalysts.

2.3 Characterization

The crystal structure and phase of the prepared samples were examined using Shimadzu XRD (model 6100) with [Cu K α radiation (1.54065 Å)] operated at a voltage of 30 kV with a current of 15 mA. The surface morphology was examined with a JSM-6510 microscope (JEOL) scanning electron microscopy. Transmission electron microscope was used to get more insight about the morphology of prepared samples. TEM images of the samples were recorded on a JEOL-JEM 2100 instrument operating at 120 keV. The optical properties of the prepared samples were examined by UV-Vis diffuse reflectance spectrum (DRS) using Perkin Elmer Lambda 35. BaSO₄ was used as a reflectance standard. The EPR spectra were recorded at 100 K using JEOL-JES-FA200 ESR spectrometer. Photoluminescence (PL) spectra of the samples were recorded at room temperature using Hitachi (F-2500) in reflection mode at an excitation wavelength of 380 nm.

Figure 3. EPR spectrum of K-CN/rGO/Fe(III) composite.

2.4 Photocatalytic activity and hydroxyl radical determination

The photocatalytic performance of prepared samples was examined by studying the degradation of RhB, MB and MO under visible light source using a 500 W xenon lamp in an immersion well photochemical reactor as shown in our previous literature.¹⁹ The temperature of the reaction was maintained at 25 °C by circulating cold water throughout the experiments. In a typical procedure, the required amount of prepared photocatalyst was dispersed in 200 mL aqueous solution of organic pollutants (10 ppm) and stirred in the dark for 30 min to ensure the adsorption–desorption equilibrium. The suspension was then irradiated and samples were collected at different time intervals, centrifuged and analyzed. The photodegradation of the pollutants was monitored by measuring the change in absorbance at their λ_{max} (Rhodamine B, 553 nm), (Methylene Blue, 663 nm) and (Methyl Orange, 464 nm) using a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. The photodegradation efficiency of the catalyst was calculated using the following formula as given in Eq. 1:

Figure 2. UV-Vis DRS spectra (a) and their corresponding Tauc plots of $(ah\nu)^{1/2}$ Vs. E_g of different samples (b).

Figure 4. SEM image of K-CN/rGO (a), TEM images of K-CN/rGO, (b, c), TEM image of K-CN/rGO at high magnification (d) and TEM image of K-CN/rGO/Fe(III) (e).

$$\text{Degradation efficiency (\%)} = (C_0/C_t)/C \times 100 \quad (1)$$

Where C_0 is initial concentration of the pollutant at the adsorption-desorption equilibrium and C_t is the final concentration of the pollutant at irradiation time (t). The amount of hydroxyl radical was quantitatively estimated by the terephthalic acid photoluminescence (TA-PL) probe method.¹⁹ In this experiment, the desired amount of Fe(III)-grafted K-CN/rGO was suspended in an aqueous solution of TA (5×10^{-4} M in 2×10^{-3} M NaOH solution) and then the solution was stirred in the dark for 30 min to maintain the adsorption-desorption equilibrium. The PL intensity of 2-hydroxyterephthalic acid was found to increase with increasing irradiation time and the emission was monitored

at 425 nm at an excitation wavelength of 340 nm.²⁰ In this reaction, the generated hydroxyl radicals react with terephthalic acid to give fluorescent adduct, i.e., 2-hydroxyterephthalic acid which is estimated by photoluminescence spectroscopy.

3. Results and Discussion

The phase structure of pure CN and various photocatalysts such as K-CN, K-CN/Fe(III) and K-CN/rGO/Fe(III) was investigated using powder XRD measurement and the XRD patterns of different samples are shown in Figure 1. It could be seen from the

Figure 5. FTIR spectra of CN, K-CN, K-CN/Fe(III) and K-CN/rGO/Fe(III).

figure that the XRD patterns of all the samples exhibit two distinct diffraction peaks at 13.1° and 27.3° , corresponding to (100) and (002) crystal planes of graphitic carbon nitride (JCPDS 87-1526).¹⁰ The intensity of all the modified samples is comparatively lower than that of the pure graphitic carbon nitride. The results suggest that the crystal growth of graphitic carbon nitride is hindered by the incorporation of potassium. This could be due to the insertion of K ions into interstitial sites of

in-planar $g\text{-C}_3\text{N}_4$ that help to enlarge the interlayer spacing and hinder the crystal growth.¹⁰

The optical properties of the prepared samples were investigated by UV–Vis diffuse reflectance spectroscopy and the results are shown in Figure 2a, b. It could be seen from the figure that pure $g\text{-C}_3\text{N}_4$ showed an absorption onset at 450 nm which infers to the band to band transition. Compared to pure $g\text{-C}_3\text{N}_4$, all modified catalysts show a redshift which may arise due to modification by different strategies. In the case of Fe(III)-grafted K-doped $g\text{-C}_3\text{N}_4$ there is a clear shift of optical response towards the higher wavelength, which could be due to the interfacial charge transfer (IFCT) from the valence band of $g\text{-C}_3\text{N}_4$ to surface grafted-Fe(III). The bandgap energies of the prepared samples were calculated from the Tauc plot shown in Figure 2b. The optical band gap energies of the prepared samples were calculated using the classical Tauc relation shown below in Eq. (2).

$$(ah\nu) = A(h\nu - E_g)^{n/2} \quad (2)$$

Where ‘a’ is absorption coefficient, A is a constant and $n = 1$ or 4 which depends upon direct and indirect allowed transition. The value of n for $g\text{-C}_3\text{N}_4$ would be taken as 4.^{8,21} Considering n as 4, a graph of $(ah\nu)^{1/2}$ vs photon energy ($h\nu$) has been plotted which is shown in Figure 2b.

Figure 6. Change in absorbance of RhB, MB and MO in presence of K-CN/rGO/Fe(III) at different time intervals (a–c) and change in concentration of RhB, MB and MO in the absence and presence of different catalysts (d–f).

The presence of Fe(III) in the Fe(III)-grafted K-g-C₃N₄/rGO was confirmed by EPR measurement and the result is shown in Figure 3. A clear signal at low magnetic field of 154 mT ($g = 4.23$) was observed, indicating that iron ions are present in +3 oxidation state.²²

The morphology of K-CN/rGO and Fe(III)-grafted K-CN/rGO was examined by SEM and TEM analyses and the results are depicted in Figure 4a–e. The SEM image of K-CN/rGO Fe(III) shown in Figure 4a indicates that the sheets of graphene and graphitic carbon nitride are clearly seen in the figure. Figure 4b, c shows the TEM images of K-CN/rGO which also indicate that the graphene and graphitic carbon nitride are intimately bound together, giving a sign of composite formation. The TEM image of K-CN/rGO is also given at high magnification value as shown in Figure 4d. TEM image of Fe(III)-grafted K-CN/rGO is illustrated in Figure 4e, where clusters of Fe(III) ions are clearly visible onto the surface of graphitic carbon nitride.

FTIR analysis was carried out to elucidate the chemical bonding among different photocatalysts and results are shown in Figure 5. The spectrum of g-C₃N₄ shows a broad peak at 3242 cm⁻¹ could be ascribed to N-H stretching vibration of g-C₃N₄. In addition, several strong absorption peaks are observed in the range of 1200–1400 cm⁻¹ which could be assigned to stretching of aromatic C–N.²¹ The sharp and intense peak at 809 cm⁻¹ corresponds to the C–N out-of-plane bending modes of C–N heterocyclic.¹⁰ On the other hand, in composite materials, the intensity of these characteristic absorptions are decreased due to the introduction of a potassium atom, graphene oxide and Fe(III) ions. Similar peaks were observed in the case of modified catalysts and no peaks corresponding to K or Fe(III)-related species were observed. The peaks related to graphene were also not observed in the composite and the reason for the absence of peaks related to graphene is the overlapping of graphene peaks with peaks of graphitic carbon nitride.

The photocatalytic activity of the synthesized material was investigated by studying the degradation of three pollutants such as RhB, MB and MO under visible light source in aqueous suspension with continuous bubbling of air. The degradation was monitored by measuring the change in absorption intensity at their ($\lambda_{\text{max}} = 553 \text{ nm}$, 663 nm and 464 nm for RhB, MB and MO, respectively). The change in absorption intensity at different time intervals for irradiation of an aqueous solution of RhB, MB and MO is shown in Figure 6a–c. The absorption intensity of all pollutants decreases with increasing the irradiation time as observed by the decrease in characteristics absorption maximum of all

pollutants. The change in the concentration of RhB, MB and MO as a function of irradiation time in the absence and presence of different catalysts such as

Figure 7. Degradation efficiency of Fe(III)-grafted K-CN/rGO composite photocatalyst for degradation of RhB under visible-light source at 100 min for four cyclic runs.

Figure 8. PL spectra of different catalysts at excitation wavelength 380 nm.

Scheme 2. Schematic representation of the photocatalytic mechanism of Fe(III)-grafted K-CN/rGO composite under visible light.

carbon nitride (CN), K-doped CN, K-doped-Fe-grafted CN and Fe(III)-grafted-K-doped CN/rGO is shown in Figure 6d–f. The results clearly indicate that efficient degradation was observed with Fe(III)-grafted K-CN/rGO as compared to other photocatalysts showing around 100% degradation of all dyes within 100 min of irradiation time under visible light source.

The photostability and recyclability of a photocatalyst is important from an application point of view.⁸ To evaluate the stability of K-CN/rGO/Fe(III) photocatalyst, four successive runs were performed by adding recovered photocatalyst to a fresh solution of RhB under analogous conditions. Figure 7 displays the results of stability towards the degradation of RhB in the presence of K-CN/rGO/Fe(III) after four repeated cycles. It could be seen from the figure that the degradation efficiency of K-CN/rGO/Fe(III) is maintained after four runs and only a slight decrease was observed in the degradation. The results indicate that modified graphitic carbon nitride is stable enough and its triazine ring is not degraded during the photocatalytic reaction. The reason for the excellent stability of graphitic carbon nitride is the interaction of K ions, Fe(III) ions and graphene with graphitic carbon nitride. The K and Fe(III) ions are tightly bound with graphitic carbon

nitride to increase its stability against self-degradation of triazine rings. Therefore, the modified graphitic carbon nitride can be used as a stable photocatalyst with improved photocatalytic activity for practical applications in environmental remediation.

The Photoluminescence (PL) study was conducted to determine the charge carrier recombination phenomena in the prepared samples. Figure 8 illustrates the PL spectra of different photocatalysts such as CN, K-CN, K-CN/Fe(III) and K-CN/rGO/Fe(III). Among them, the PL spectrum of Fe(III)-grafted K-CN/rGO showed the lowest intensity around 475 nm, indicating maximum electron–hole pair separation in the composite materials. The low intense PL signal of K-CN/rGO/Fe(III) is due to the presence of K, Fe(III) ions and graphene sheet present in the material which help to minimize the back electron transfer and may, in turn, increase the lifetime of generated charge carriers.

A schematic representation showing the mechanism of Fe(III)-grafted K-CN/rGO for degradation of organic pollutants is shown in Scheme 2. The role of graphene is demonstrated to store and shuttle electrons to surface adsorbed species. The reason for K doping into $g\text{-C}_3\text{N}_4$ is to extend the VB edge of graphitic carbon nitride towards the positive potential so as to enhance

Figure 9. Increase in emission intensity of TA-OH on irradiation of a basic solution of terephthalic acid in the presence of CN (a), K-CN (b), K-CN/Fe(III) (c) and K-CN/rGO/Fe(III) (d)

the oxidizing ability of VB holes. Under visible light irradiation, electrons are either transferred to CB of g-C₃N₄ or surface grafted Fe(III) ions through interfacial charge transfer mechanism. These processes separate electron-hole pair in a more effective way. The electron in the CB of graphitic carbon nitride would transfer to the graphene followed by grafted Fe(III) ions which in turn transfer to the oxygen molecules to get hydroxyl radicals *via* multi-electron reduction reaction.¹⁵ It is well-known that Fe(III) ions can convert into Fe(II) ions after getting an electron from the semiconductor, but the converted Fe(II) is unstable and quickly converts into stable Fe(III) ions through multi-electron reduction reaction during photocatalysis.¹⁵ During multi-electron reduction, hydroxyl radicals are dominantly generated due to the more positive potential of Fe³⁺/Fe²⁺ (0.771 V, vs SHE) than that of one-electron reduction of O₂ (O₂ + H⁺ + e⁻ → HO₂[•], -0.046 V vs SHE).¹³ So, it is possible that the species generated during the multi-electron reduction reaction would be the hydroxyl radical. Meanwhile, the separated holes would react with water molecules to give hydroxyl radicals. The generated hydroxyl radicals through the above processes could degrade the organic pollutants. The hydroxyl radical formation capacity of all samples was investigated by photoluminescence probe method and their results are shown in Figure 9. From these results, we could conclude that K-CN/rGO/Fe(III) generates more hydroxyl radicals than other samples which could be explained due to the presence of graphene and Fe(III) ions. A good correlation was found in the generation of hydroxyl radical and photocatalytic performance by K-CN/rGO/Fe(III) composite photocatalyst.

4. Conclusions

In summary, a novel visible light-active Fe(III)-grafted K-CN/rGO photocatalyst was synthesized by photoreduction followed by impregnation technique. The modified composite photocatalyst showed excellent photocatalytic activity for the degradation of RhB, MB and MO under visible-light in aqueous suspension. The enhanced photocatalytic activity could be attributed to the efficient separation of charge carrier by interfacial charge transfer and largely promoted light absorption effect. Moreover, the catalyst showed excellent stability after four successive runs, indicating that the triazine ring of graphitic carbon nitride was not degraded during the photocatalytic reaction. The present work provides new insight to combine K ions, Fe(III) ions and graphene to modify pure graphitic carbon nitride to develop efficient photocatalyst for practical applications.

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