Hydrothermal synthesis of nitrogen doped graphene supported cobalt ferrite (NG@CoFe$_2$O$_4$) as photocatalyst for the methylene blue dye degradation

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ABSTRACT

A magnetic NG@CoFe$_2$O$_4$ photocatalyst was developed via a facile hydrothermal method, and subsequently characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and vibrating sample magnetometry (VSM) techniques. The CoFe$_2$O$_4$ nanoparticles were found to have a size between 100-150 nm and were uniformly dispersed on the nitrogen doped graphene. Magnetic studies showed that the NG@CoFe$_2$O$_4$ photocatalyst can be easily separated from the solution by a simple bar magnet. The photocatalytic degradation of methylene blue dye (MB) was studied under visible irradiation. The photocatalytic performance of NG@CoFe$_2$O$_4$ photocatalyst exhibited improved photodegradation performance when compared with pure CoFe$_2$O$_4$. The synthesized NG@CoFe$_2$O$_4$ can be a potential candidate as a visible-light active magnetically separable photocatalyst, so could be used as a potent separation tool in waste water treatment.

INTRODUCTION

About 10000 types of dyes and pigments are synthesized annually worldwide. Approximately 20-30% of the dyes drained from the textiles industry directly into the sea water. Due to the presence of non-biodegradable moieties in the structure and their toxic nature, most of these wastes are harmful for the human health and causes a lot of environmental hazards. So a number of traditional methods like ion exchange, precipitation, coagulation and flocculation, membrane filtration, electrochemical and biological methods have been suggested [1, 2]. To overcome the limitations of standard procedures, oxidative process are applied as an upcoming method for the decomposition of organic wastes. To overcome the limitations of traditional methods, advanced oxidation processes are employed as an upcoming waste management technology for decomposition of organic dyes in polluted water [3–5]. Therefore, the photo-Fenton method is a proficient and economical procedure for handling of wastewater [6–9]. This approach is effective for the generation of extremely reactive, potent oxidant and non-selective reagent hydroxyl radicals (OH) produced due to the photodecomposition of water [1, 5, 8]. The high oxidation potential (2.80) of hydroxyl radicals promote the degradation of non-biodegradable organic pollutants, unsaturated compounds in aqueous medium releasing carbon dioxide, water and other biproducts. [1, 2, 4, 10, 11].

Nowadays material chemists are facing a lot...
of challenges in synthesis of new substances with excellent physicochemical features and various synthetic procedures involved in this technology. Spinel ferrite (MFe₂O₄) magnetic nanocomposites have attracted lots of attention due to their ability to act as the magnetic materials with the excellent chemical stability [12–13]. Applying recycled and external magnetic material facilitate the removal of spinel ferrites magnetic nanocomposites from the treated waste. [14–16]. Cobalt ferrite (CoFe₂O₄) magnetic nanocomposites are very potent metal oxides compared to other spinel ferrites, because they have various applications in diverse fields like sensors [17,18], semiconductor photocatalysts [19, 20], biomedical [21], cancer treatment [22], magnetic optical behaviour [23], electrical [24] and antibacterial [25]. It is an extremely stable n-type semiconductor, with a narrow optical band gap (2.0 eV) making it effective even under visible light treatment [26, 13]. So cobalt ferrite magnetic nanocomposite with controlled morphology with desirable physical and chemical properties is considerably significant. Graphene composed of a two-dimensional (2D) sheet of covalently bonded sp² carbon atoms, is a structural unit of 3D graphite and 1D carbon nanotubes. The intrinsic strength of this material is predicted to be unmatchable to any other found material [27]. Due to excellent physico-mechanical properties, such as high mobility, optical transparency, quantum Hall effect, mechanical stiffness, etc. graphene and graphene based composite materials are used not only in the micro-, nano-, and opto-electronic industries but also in biotechnological industries [28, 29]. Considering the close relation and controlled interplay of parameters in tuning the performance characteristics of the ferrite materials as photocatalysts, it is thought of investigating CoFe₂O₄ particles anchored and dispersed on a heteroatom doped graphene surface. Out of all heteroatom doped graphene arrangements, nitrogen doped graphene (NG) is in the spotlight owing to its intrinsically high electrical conductivity [30, 31]. At the same time, nitrogen doping is observed to be slightly buckling the graphene layers, and this morphological modification can be helpful in anchoring nanoparticles on its surface [32, 33]. Compared to previous studies on Fe₂O₃/graphene and CoFe₂O₄/graphene, this material is benefited from much lower amount and much wider bandwidth that turn NG@CoFe₂O₄ to a properly designed catalyst. Considering its simple synthetic method and controllable ratio in the final composites, these kinds of synthesized materials would be highly valuable in commercial use [34, 35]. In this paper, we have synthesized cobalt ferrite anchored on nitrogen doped graphene magnetic nanocomposite via hydrothermal route. This newly synthesized nanocomposite is then and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) and UV–visible (UV–vis) spectroscopy. We have also studied the photocatalytic activity of cobalt ferrite magnetic nanoparticles for degradation of MB under visible light irradiation.

EXPERIMENTAL

Materials

Iron acetate, cobalt acetate, potassium permanganate (KMnO₄), potassium hydroxide (KOH) and Vulcan carbon (Vulcan XC-72) were procured from Sigma-Aldrich. Phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄) and ethanol (EtOH) were purchased from Thomas Baker and were used without any further purification.

Synthesis of reduced graphene Oxide (RGO) and nitrogen doped graphene (NG)

Reduced graphene oxide (RGO) was prepared from the graphite powder flakes by modified Hummer’s method [36]. Nitrogen-doped graphene (NG) was prepared using RGO. A 60 mL solution (0.5 mg mL⁻¹) of RGO was taken in a round bottom flask and ultrasonicated for 30 min. The solution was then transferred into Teflon-lined autoclave and maintained at 180 °C for 24 h. The NG was collected by filtration, washed with alcohol and distilled water, followed by drying at 80 °C for 12 h.

Synthesis of cobalt ferrite supported nitrogen Doped graphene oxide (NG@CoFe₂O₄)

In a typical procedure 50 mg of NG was dispersed in 15 mL of distilled water. The resulting solution was admixed with 50 mg of iron acetate (Fe(C₆H₁₂O₆)) and cobalt acetate (Co(C₆H₁₂O₆)) in the 2:1 molar ratio. Thereafter the solution was raised to 35 mL by adding absolute ethanol. The resulting solution mixture was stirred at room temperature for 24 h so that Co³⁺ and Fe²⁺ ions are attached to the nitrogen and oxy functional groups...
on the graphene framework. The reaction mixture shifted into a 50 mL Teflon lined stainless steel autoclave and maintained at 120°C for 12 h. The resulting solution was filtered followed by washing several times and finally dried at 60 °C. The product obtained is designated as NG@CoFe₂O₄. CoFe₂O₄ is prepared by the similar procedure for the comparison.

The schematic representation of the synthetic procedure is given in Fig. 1.

**Photocatalytic test**

For exploring photocatalytic activity, 2.5 mg methylene blue (MB) was dissolved in 100 mL of distilled water to form a clear solution. Absorption spectrum of 5 mL of MB dye solution was measured using UV–visible spectrophotometer for recording λ<sub>max</sub>. As synthesized NG@CoFe₂O₄ nanocomposite (1 mg) was mixed with 5 ml MB solution and vigorously stirred in dark for 1 h in order to achieve the adsorption–desorption equilibrium between methylene blue and the as synthesized photocatalyst. Thereafter the mixture was illuminated under the visible light. After exposing the solution solar radiation for 20 min., a 5 mL aliquot was taken from the mixture at different time intervals and absorbance was recorded at λ<sub>max</sub> = 663 nm. For comparison, the photocatalytic experiment was also conducted in the presence of pure CoFe₂O₄.

**Spectroscopic and microscopic measurements**

The phase purity, crystalline nature and size of the as-synthesized samples were determined from powder X-ray diffraction (PXRD) using D8 X-ray diffractometer (Bruker) at the scanning rate of 12° min⁻¹, with Cu Kα radiation (λ = 0.15405 nm). Transmission electron microscopy (TEM) images were recorded on Tecnai G2 S-Twin transmission electron microscope with field emission gun operating at 200 kV. Samples for TEM measurements were prepared by evaporating a drop of the colloid onto carbon-coated copper grid. The energy spectra were obtained by energy-dispersive X-ray spectrum equipped on a transmission electron microscope. Scanning electron microscopy (SEM) images of the samples were recorded on FEI Nova Nano SEM 450. The infrared spectra were recorded on a Shimadzu Fourier transform infra-red spectrometer (FT-IR) over the range of wave number 4000–400 cm⁻¹, and the standard KBr pellet technique was employed. The magnetic moment as a function of applied field was recorded using vibrating sample magnetometer (VSM), Lakeshore 7410. Thermogravimetric analysis was carried out using a Perkin Elmer SGA 6000 thermal analyzer with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere from room temperature to 900 °C. Light irradiation in photodegradation experiment was carried out using a UV–Visible spectrophotometer (PG...
instrumentations, US T-90). All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Crystalline structure and morphology

The structures of the as prepared samples RGO, NG, CoFe₂O₄ and NG@CoFe₂O₄ were confirmed by PXRD technique. The PXRD results are depicted in Figs. 2 and 3. The X-ray diffraction pattern of RGO shows one characteristic peak (2θ°) at 24.9° (002). The PXRD pattern of NG has a characteristic peak (2θ°) at 24.3° (002). The results obtained for NG are in agreement to literature (JCPDS Card No. 75-1621) [37]. Fig. 3a-b depicts almost all diffraction peaks of the cobalt ferrite nanorods and its nanocomposite with nitrogen doped graphene; CoFe₂O₄@NG is indexed to cubic spinel cobalt ferrite (JCPDS No. 00-022-1086). The crystal growth of cobalt ferrite nanorods between the interlayer of NG destroyed the regular layer stacking, leading to weakening the (0 0 2) diffraction peak [38]. The strong and sharp diffraction peaks show highly crystalline nature of CoFe₂O₄ and CoFe₂O₄@NG nanocomposites.

The average crystallite size of these nanoparticles was calculated using the Scherrer's formula shown in Eq. 1.

$$\beta = \frac{k\lambda}{L\cos\theta}$$ (1)

where, L (nm) is the crystallite size, λ (nm) is
the wavelength of Cu Ka radiant, $\lambda = 0.15405$ nm, $\beta$ (°) is the full-width at half-maximum (FWHM) of the diffraction peak, $\theta$ is the diffraction angle and $K$ is the Scherrer constant equal to 0.89. The prominent peaks were used to calculate the average crystallite size of the CoFe$_2$O$_4$ and CoFe$_2$O$_4$@NG nanoparticles. The calculated average crystallite sizes of nanoparticles are in the range of 25-40 nm.

**Fourier-transform infrared (FT-IR) Characterization**

Fig. 4 shows FTIR spectra of the GO, graphene and cobalt ferrite nanorods/graphene composites. The peaks of GO located at 3353, 1730, 1621, 1386, 1239, 1082 and 1032 cm$^{-1}$ are due to the vibration and deformation bands of O-H, C=O stretching vibrations of carbonyl groups, C=C stretching vibrations of aromatic zone, C-OH stretching vibrations, C-O vibrations from epoxy groups and C-O vibrations from alkoxy groups, respectively [37]. All these band appeared due to the oxygen containing functional groups are not visible in the FTIR spectrum of nitrogen doped graphene (Fig. 4b) possibly due to nitrogen doping and hydrothermal process. The absorption band appeared at 1568 and 1212 cm$^{-1}$ are assigned to skeletal vibration frequencies of the graphene sheets [40-42]. In Fig. 4c there is a slight red shift of the skeletal vibration of graphene sheets for the NG@CoFe$_2$O$_4$ nanocomposites, which can be explained due to the introduction of CoFe$_2$O$_4$ into the nitrogen doped graphene framework. Additional band at 589 cm$^{-1}$ in Fig. 4c could be assigned to lattice absorption of Fe-O, confirming the existence of CoFe$_2$O$_4$ [43].

**SEM and TEM analyses**

The morphological features of the as synthesized samples were investigated by SEM analysis. Fig. 5a-b depicts the typical SEM images of GO prepared by the modified Hummer’s method. The SEM image (Fig. 5a) shows GO sheets have layered structures with uniform surface and wrinkled
from edges. After hydrothermal reduction and doping with the nitrogen an appreciable change in surface morphology takes place as shown in the Fig. 5b. The NG sheets are thinner than GO and the highly wrinkled. The NG sheets are exfoliated and not restacked, that is in accordance to the PXRD results. Fig. 5c shows formation of nano rods of cobalt ferrite structure. In Fig. 5d the distribution of the cobalt ferrite nano rods on the nitrogen doped graphene sheets is clearly visible. Fig. 6a-d show the typical TEM images of GO, NG, CoFe₂O₄ and NG@CoFe₂O₄ respectively. Fig. 6a-b reveal the lamellar structure of GO and NG. Fig. 6c-d shows CoFe₂O₄ nanotubes and uniformly decorated CoFe₂O₄ on the nitrogen doped graphene layers with high density. Notably, the layered structure of NG may support the anchoring of CoFe₂O₄ nanotubes on it. The anchoring of CoFe₂O₄ also hinders the agglomeration of NG sheets.

**Thermal analysis**

Fig. 7 shows the TGA graph of NG and NG@CoFe₂O₄ from room temperature to 950 °C at the heating rate of 10 °C min⁻¹. The TGA graphs of nanocomposites NG@CoFe₂O₄ (Fig. 7b) displays the hybrid character in its thermal stability as it is
more stable than NG (Fig. 7a). The weight loss in case of NG@CoFe₂O₄ is less as compared to the NG. The initial rapid weight loss of the composite is possibly due to the portion of nitrogen doped graphene content in the NG@CoFe₂O₄ nanocomposite. These measurements show notable quantity of nitrogen doped graphene in nanocomposites.

**Magnetic characterisation**

Magnetic hysteresis loops of the samples shown in Fig. 8, indicate the strong magnetic nature to a diverging magnetic field. The saturation magnetization of the bare CoFe₂O₄ nanorods and NG@CoFe₂O₄ composites are 64.2 and 41.5 emu/g, respectively (Fig. 8a-b). The coercivity values are 1062.6 and 493.2 Oe, respectively. The reason for weaker saturation magnetization value of NG@CoFe₂O₄ composites is essentially due to the presence of non-magnetic NG in NG@CoFe₂O₄. The alteration of the magnetic behaviour due to the presence of NG in CoFe₂O₄ indicates that magnetic properties of the hybrid materials could be tuned by adjusting the ratio of ferrite material to NG [44].

**Photodegradation of methylene blue (MB)**

Methylene blue (C₁₆H₁₈N₃SCl) is an important dye used in the textile industries. It is also called as methylthionium chloride. It shows λ_max at 662 nm with molar absorption coefficient (ε) 19 M⁻¹cm⁻¹ [45]. The photodegradation of MB has been reported in the literature with various metal oxides and metal ferrites such as ZnO [45],

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Fig. 8: Magnetic hysteresis loop of (a) CoFe₂O₄ and (b) NG@CoFe₂O₄

Fig. 9: Absorption spectra of the MB solution taken at different photocatalytic degradation times using NG@CoFe₂O₄ as photocatalyst
MgFe₂O₄ and MFe₂O₄ (M= Mn, Co) [46, 47]. In order to demonstrate the potential application of the prepared nanocomposite, NG@CoFe₂O₄, the photocatalytic experiments were performed on the prepared photocatalyst against MB dye. In the photocatalytic process, the decrease in the value of absorbance for the characteristic absorption peaks (662 nm) as a function of degradation time was monitored. Fig. 9 depicts the UV-Vis absorption spectrum of 5mL of aqueous solution of MB (20 mgL⁻¹) with 5 mg of NG@CoFe₂O₄ at an interval of every 20 min. indicating that there is almost a complete degradation of the dye after 140 min. The photodegradation efficiency of NG@CoFe₂O₄ was found to be higher than that of bare CoFe₂O₄.

Fig. 10 depicts the percentage degradation of MB versus exposure time (minutes) in the presence of CoFe₂O₄ (curve b) and NG@CoFe₂O₄ (curve c). Curve c clearly indicates that the NG@CoFe₂O₄ nanocomposite has the excellent photocatalytic activity compared to bare CoFe₂O₄ (curve b). In Fig. 10, Curve a shows the percentage degradation of MB versus time in the absence of photocatalyst.

Recyclability and reusability of the Catalyst (NG@CoFe₂O₄)

The reuse and recycling capabilities of the adsorbents are essential for their functional applications. For a greener and eco-friendly strategy, the reusability of a catalyst is desired. Through which the process becomes free of waste and also reduces the operational expense of the method. The recycling performance and reusability of as-prepared catalyst (NG@CoFe₂O₄) was examined by recycling the catalyst for photodegradation of MB organic azo-dye. The results are depicted in Fig. 11. Such outcome confirm that NG@CoFe₂O₄ nanocomposite can be recoverable by magnetic

![Fig. 10: Kinetics of photodegradation of methylene blue (a) no catalyst (b) CoFe₂O₄ and (c) NG@CoFe₂O₄ nanocomposites](image)

![Fig. 11: Removal efficiency of MB on NG@CoFe₂O₄ in different catalytic cycles](image)
Mechanism of MB photodegradation

The notable enhancement of MB dye degradation capability for the NG@CoFe$_2$O$_4$ nanocomposites was given to the introduction of the NG into the photocatalyst arrangement. The diagrammatic representation of the dye degradation pathway is depicted in Fig. 12. In a typical process, the electrons (e$^-$) migrate from conduction band (CB) to valence band (VB) by the visible light irradiation. Accordingly the holes (h$^+$) created in the valence band react with hydroxyl (OH$^-$) coming from water to form •OH radicals [48]. As formed •OH radicals force to start oxidation degradation of MB. It can be clearly seen in the figure that there is no external charge carrier so in that case the delocalized electrons in the bare CoFe$_2$O$_4$ could possibly rapidly recombine with the holes produced in the conduction band prior to being captured by OH$^-$ [49, 50], prohibiting the further dye degradation. On the other hand, NG@CoFe$_2$O$_4$ nanocomposites act as a charge carrier due to the presence of a large number of aromatic structures in nitrogen doped graphene that could effectively confine the delocalized electrons and consequently prevent the recombination of electrons and holes [51]. On the basis of above mentioned factors, the holes in the CB have greater possibility to react with OH$^-$ to produce OH• radicals. A much higher dye degradation performance was observed for the NG@CoFe$_2$O$_4$ nanocomposites. The role of nitrogen doped graphene is given as

a. The adsorption of MB is aided on the surface of NG@CoFe$_2$O$_4$ due to π–π interaction between aromatic domain of the dye MB and NG sheets.

b. It prevents the electron hole recombination in CoFe$_2$O$_4$, as it acts as photoelectron acceptor so promoting an effective photocatalytic degradation of MB molecules.

CONCLUSION

In conclusion, we have summarized the structural and magnetic photocatalytic behaviour of CoFe$_2$O$_4$ and NG@CoFe$_2$O$_4$ nanocomposites fabricated via hydrothermal method. PXRD results validate the formation of NG@CoFe$_2$O$_4$ nanocomposites. SEM and TEM micrographs reveal the morphological and topological traits of CoFe$_2$O$_4$ and NG@CoFe$_2$O$_4$ nanocomposites. The average crystallite size of amalgamated nanocomposites, calculated
from TEM analysis was found to be in the range of 100-150 nm. The photocatalytic results show that NG@CoFe$_2$O$_4$ is excellent photocatalyst for photodegradation of MB compared to bare CoFe$_2$O$_4$. The magnetic nature of this photocatalyst (NG@CoFe$_2$O$_4$) is also helpful in its easy separation with the help of simple bar magnet.

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**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

**REFERENCES**


