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Excellent stability, recyclable nature and high photo-catalytic performance of graphite oxide/Fe_3O_4 nanocomposites

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ABSTRACT

In this paper, we report excellent stability and enhanced photo-catalytic activity of graphite oxide (rGO)/Fe_3O_4 nanocomposites (NCs) for the decomposition of organic dyes compared with pure Fe_3O_4 nanoparticles (NPs) and bulk Fe_3O_4 particles. The rGO/Fe_3O_4-NCs were prepared by the ultrasonic method at low temperature. Fe_3O_4 nanoparticles (~10 nm) are well supported by rGO sheets as confirmed by electron microscopic studies. Powder X-ray diffraction, FTIR and X-ray photoelectron spectroscopic studies confirm the formation of rGO/Fe_3O_4-NCs. BET surface area of rGO/Fe_3O_4-NCs was found to be ~160 m^2/g, which is approximately three times higher than that of pure Fe_3O_4-NPs. The rGO/Fe_3O_4-NCs as photo-catalysts show excellent performance in the degradation of organic dye (~94% in 80 min). This is also noteworthy that the rGO/Fe_3O_4-NCs show excellent stability and recyclable nature for further studies.

Keywords: Nanocomposites; Oxides; Pollutants; Photo-catalysis

1. Introduction

The wastewater containing organic contaminants from the industries is released into the natural environment. The contaminated natural environment can cause serious risk to human health. Water pollution is a very serious issue for our society among all these contaminated natural environments. Therefore, employing an economical way to decompose organic contaminants from wastewater is one of the current interests of the researchers for water purification. Several methods have been employed for the removal of organic dyes from water [1–4]. Fe_3O_4 is a promising catalyst which can be used to decompose the organic pollutants into inorganic constituents [5]. The magnetic nature of Fe_3O_4 nanoparticles causes the aggregation of nanoparticles, which can trigger the reduction of decomposition rate of organic dyes. Therefore, in order to diminish the above-mentioned cause, Fe_3O_4 nanoparticles could be functionalized by carbon support such as graphite oxide. It not only avoids the agglomeration of particles but also promotes to enhance the catalytic efficiency due to high electrical conductivity and specific surface area.

The rGO/Fe_3O_4 nanocomposites are magnetic in nature and also show good optical properties [6]. The magnetic rGO/Fe_3O_4 nanocomposites were used as an adsorbent in the removal of antibiotic contaminants from water by a magnetically guided process [6]. The band gaps of Fe_3O_4 nanoparticles for direct and indirect transitions were reported of ~2.8 and 1.9 eV, respectively [7]. The rGO/Fe_3O_4 nanocomposites have also been reported as the potential catalysts in numerous

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applications including biosensors [8], electrochemical sensors [9], photo-catalysis [10,11], environmental remediation [12,13]. Molten salts have been used in the synthesis of Fe_3O_4 nanoparticles at high temperature (600°C–800°C) for microwave absorption applications and electro-chemical performances [14,15]. Graphene-based zinc oxides (rGO/ZnO) [16–18] and titanium oxide (rGO/TiO_2) [19–23] nanocomposites were reported as good photo-catalysts for the degradation of organic dyes. But these photo-catalysts are not convenient for recycling due to their excellent dispersive nature. Therefore, it is difficult to separate and recover the photo-catalysts after photo-degradation reactions. Thus, the magnetic photo-catalysts with graphitic oxide sheets are more appropriate to separate the photo-catalysts by applying an external magnetic field for further use.

Previously, we have reported the synthesis of Fe_3O_4 nanoparticles (~8 nm) as bifunctional electro-catalysts in water splitting [24]. Also, we have developed a variety of photo-catalysts for the mineralization of organic pollutants [25–27]. In this paper, we focus on the synthesis of rGO/Fe_3O_4 nanocomposites using the ultrasonic process at room temperature. The structural and morphological studies were investigated in detail. The rGO/Fe_3O_4 nanocomposites are used as the effective photo-catalysts in rapid degradation of organic pollutants under the solar light irradiation. Retention capacities with stability of the photo-catalysts were also investigated.

2. Experimental

Fe_3O_4-NPs have been synthesized using a very simple, ecofriendly and economic co-precipitation procedure as reported elsewhere [9]. The resulted dark brown powder of Fe_3O_4-NPs were taken with rGO sheets in 10:1 weight ratio (Fe_3O_4-NPs:rGO sheets) with ethylene glycol (EG, 2 mL) and de-ionized water (DI-H_2O, 15 mL) for the synthesis of rGO/Fe_3O_4 nanocomposites. This mixture was placed under ultrasonic process for 30 min at room temperature followed by the centrifugation process. The resulting product after centrifuge was washed by DI-H_2O for three to four times. The final product was dried at 50°C for 6 h. The final product (i.e., rGO/Fe_3O_4-NCs) was analyzed by powder X-ray diffraction (XRD, Rigaku MiniFlex, USA) for phase identification. Electron microscopic (JEOL (USA), JSM-7600F for FESEM and JSM-2100F for TEM) studies were conducted to observe the surface morphology of rGO/Fe_3O_4-NCs and Fe_3O_4-NPs. FTIR data of the powder samples were recorded in the range from 400 to 4,000 cm^{-1} on Bruker TENSOR-27 Spectrometer (USA). BET surface area measurements of rGO/Fe_3O_4-NCs and Fe_3O_4-NPs were carried out by surface area analyzer at 77 K (Micromeritics ASAP-2020, China). The photo-catalytic performances of rGO/Fe_3O_4-NCs and Fe_3O_4-NPs were studied against the decomposition of organic dyes (i.e., methylene blue) under sunlight irradiation. The photo-degradation of dye was observed at λmax of 664 nm of methylene blue. The data were recorded on UV–Vis spectrophotometer (Shimadzu, UV-1650, Germany). The photo-catalyst (1.0 mg) was taken with 50 mL of methylene blue (10 mg/L) and then put on magnetic stirring (in dark) for half an hour to get the suspension with the equilibrium of adsorption/desorption. Note that the pH of the solution was adjusted to 8. The suspension was placed under direct sunlight. The sample was taken from the suspension and centrifuged to separate the catalysts. The transparent solution was taken as sample in a cuvette to collect the absorption spectra. The experiments were repeated three times to check the reproducibility of the results.

3. Results and discussion

XRD, FTIR and Raman studies were carried out for structural information of the synthesized nanostructured materials. XRD studies of rGO, Fe_3O_4-NPs and rGO/Fe_3O_4-NCs are shown in Fig. 1a. The appeared peak at 2θ of 25.25° corresponds to (002) reflection of standard graphite oxide. The diffraction peaks at 2θ of 30.4°, 35.8°, 43.4°, 53.8°, 57.3° and 62.9° match with (220), (311), (400), (422), (511) and (440) reflections of Fe_3O_4 in the nanocomposites. XRD pattern of

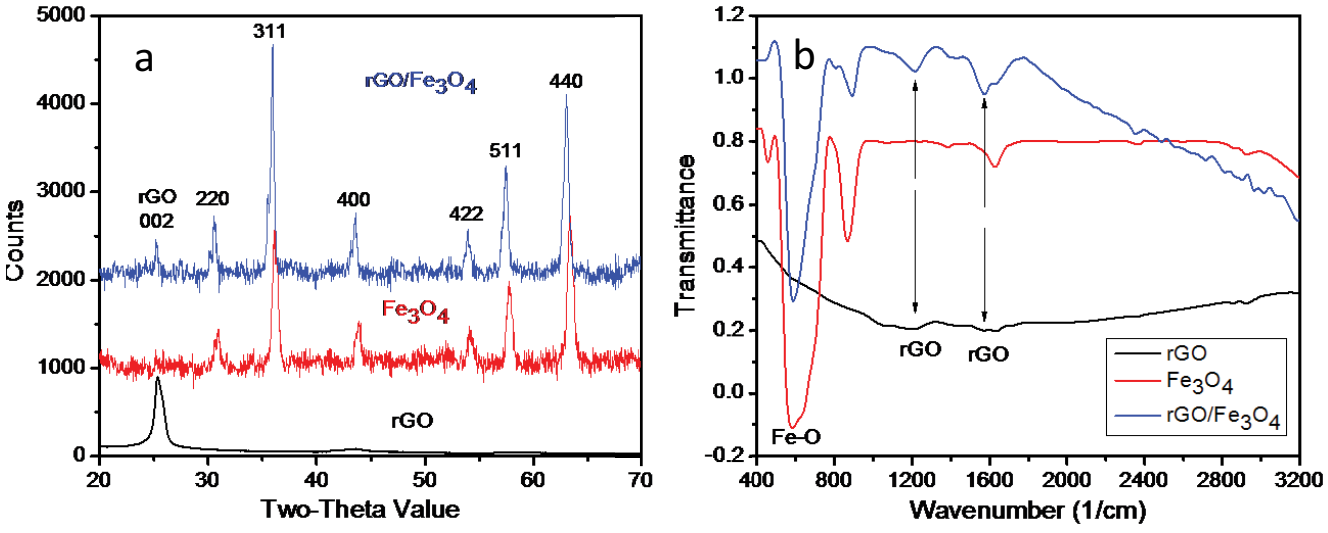

Fig. 1. (a) XRD, and (b) FTIR spectra of rGO, Fe_3O_4-NPs and rGO/Fe_3O_4-NCs.

pure Fe_3O_4-NPs shows no peak of graphite oxide. All the reflections can be analyzed with cubic unit cell structure of Fe_3O_4 (JCPDS#74-2402). FTIR spectra of rGO, Fe_3O_4-NPs and rGO/Fe_3O_4-NCs were shown in Fig. 1b. A strong band was detected at ~590 cm^{-1}, which resembles Fe–O vibration of Fe_3O_4 [28]. FTIR bands of rGO at ~1,215 and ~1,580 cm^{-1} resemble C=O and C–H vibrations, which are clearly visible in rGO/Fe_3O_4-NCs as also reported elsewhere [29,30]. Raman spectroscopic technique is a strong tool to investigate the nature of carbonaceous materials. Figs. 2a and b show Raman spectra of rGO/Fe_3O_4-NCs and Fe_3O_4-NPs, respectively, which clearly differentiate the formation of rGO/Fe_3O_4-NCs and Fe_3O_4-NPs. The D and G bands of rGO were appeared at ~1,370 and ~1,575 cm^{-1}, respectively (Fig. 2a). The D and G bands could be related to sp^3 defects and sp^2 carbon atoms in the hexagonal lattice rGO. Higher intensity of the D band than the G band also confirms the presence of sp^3-defects as also reported elsewhere [12]. A strong Raman band was also observed at ~688 cm^{-1}, which confirmed the presence of Fe_3O_4. Our results are also in good agreement with previous reports [12,31]. Therefore, XRD, FTIR and Raman confirm the formation of rGO/Fe_3O_4 nanocomposites.

The electron microscopic studies were carried out for the morphological characterization of the prepared nanostructured materials. Fig. 3a shows FESEM image of rGO/Fe_3O_4-NCs. TEM study of rGO/Fe_3O_4-NCs confirms the formation of rGO/Fe_3O_4-NCs. This is clearly shown that spherical-shaped nanoparticles of Fe_3O_4 are supported by rGO sheet as shown in Fig. 3b. HRTEM study of rGO/Fe_3O_4-NCs shows the formation of lattice fringes. The d-spacing value was found to be ~2.49 Å from the lattice fringes, which corresponds to (311) basal plane of Fe_3O_4-NPs (Fig. 3c). TEM image of pure Fe_3O_4-NPs also shows the formation of spherical-shaped nanoparticles with an average diameter of ~10 nm (Fig. 3d). The aggregation of Fe_3O_4-NPs was also observed in small extent, which could be due to the magnetic interaction of the particles. HRTEM study of Fe_3O_4-NPs gives d-spacing of ~2.48 Å, which is consistent with (311) reflection (Fig. 3e). TEM study of commercial rGO sheets is given as Fig. 3f. A small difference was observed in d-spacing value of rGO/Fe_3O_4-NCs from pure Fe_3O_4-NPs, which could be due to the presence of rGO in nanocomposites.

N_2 adsorption–desorption measurements were carried out to obtain the specific surface area of the nanostructured materials. Fig. 4 shows the N_2 adsorption–desorption isotherms for BET surface area of Fe_3O_4-NPs and rGO/Fe_3O_4-NCs. The nanostructured materials (Fe_3O_4-NPs and rGO/Fe_3O_4-NCs) were degassed at 120°C/12 h before to collect the data. The related pressure (P/P_0) range was kept from 0.0 to 1.0. The specific surface area of rGO/Fe_3O_4-NCs was found to be ~160 m^2/g, which is calculated from the multipoint BET method. BET surface area of pure Fe_3O_4-NPs was found to be ~55 m^2/g, which is lower than that of rGO/Fe_3O_4-NCs as expected. The photoluminescence (PL) spectra of Fe_3O_4-NPs and rGO/Fe_3O_4-NCs are shown in Fig. 5. PL spectra of Fe_3O_4-NPs and rGO/Fe_3O_4-NCs show the peaks at ~695 and ~697.5 nm, respectively [32]. We have clearly observed that the appeared peak in rGO/Fe_3O_4-NCs is shifted to the right side. The migration of the peak to high wavelength side is due to the presence of rGO in rGO/Fe_3O_4-NCs. PL spectra governs the movement of electrons, charge separation and

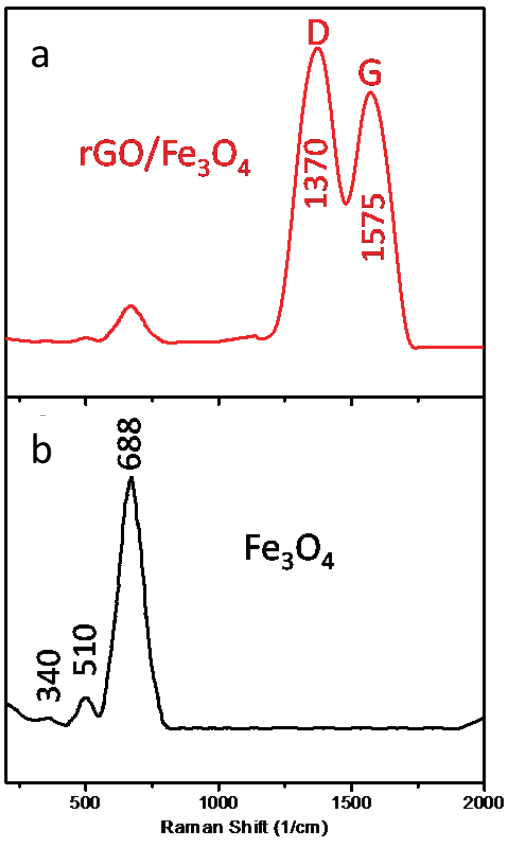

Fig. 2. Raman spectra of (a) rGO/Fe_3O_4-NCs and (b) Fe_3O_4-NPs.

electron–hole pair recombination rate. The rGO/Fe_3O_4-NCs show lower PL intensity than Fe_3O_4-NPs, which could be due to the sp^2-hybridized carbon atoms of rGO, having high electrical conductivity and high mobility of electrons.

Photo-catalytic activities of Fe_3O_4-NPs and rGO/Fe_3O_4-NCs were investigated to degrade the methylene blue dye (MBD) under sunlight irradiation. Figs. 6a and b illustrate the photo-catalytic efficiencies of Fe_3O_4-NPs and rGO/Fe_3O_4-NCs with time. A cumulative trend of photo-degradations of MBD has been observed in both slots as clearly shown with the change of absorption spectral lines with irradiation time. The photo-degradation process of MBD has been completed of ~94% after 80 min of using the rGO/Fe_3O_4-NCs photo-catalysts. The nanocrystalline Fe_3O_4 and bulk Fe_3O_4 photo-catalysts degrade the MBD of ~70% and ~40%, respectively, in 80 min (Fig. 6c). The results are summarized with experimental conditions in Table 1. This is noticeable that rGO/Fe_3O_4-NCs show excellent photo-catalytic efficiency compared with Fe_3O_4-NPs and bulk Fe_3O_4 particle. The kinetic linear plots of photo-degradation reactions using rGO/Fe_3O_4-NCs and Fe_3O_4-NPs show pseudo-first order reaction (Fig. 6d). Fe_3O_4 nanoparticles were reported as poor photo-catalysts and degraded ~57% of methylene blue in 5 h, while rGO/Fe_3O_4 nanocomposites showed >95% degradation of methylene blue in 120 min under sunlight irradiation [12]. rGO/TiO_2 nanocomposites were reported as the photo-catalysts, which degraded ~90% of methylene blue in 180 min [23]. Liu et al. [18] have reported the photo-degradation of

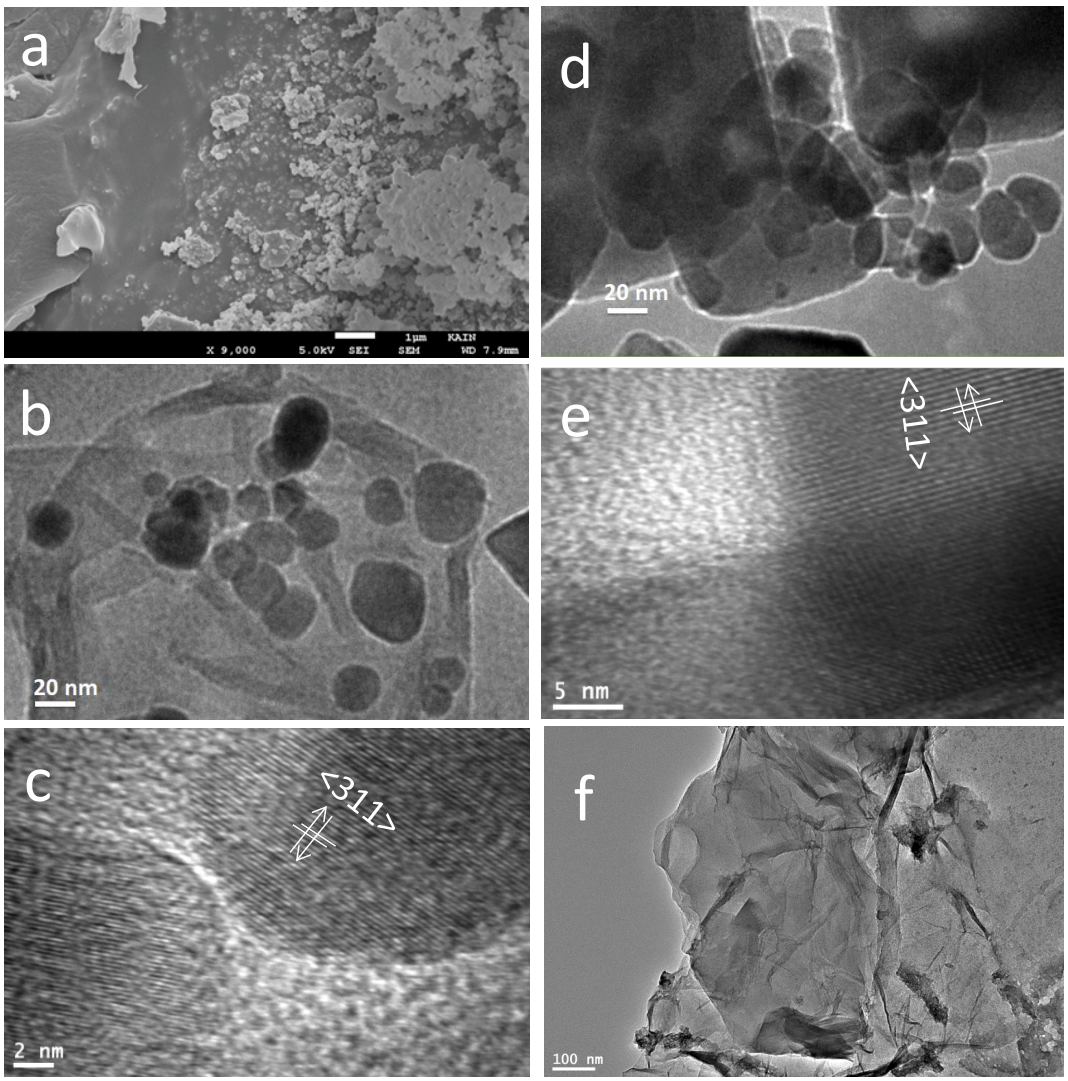

Fig. 3. (a) FESEM images of rGO/Fe_3O_4-NCs. (b,c) TEM and HRTEM micrographs of rGO/Fe_3O_4-NCs. (d,e) TEM and HERTEM image of Fe_3O_4-NPs. (f) TEM image of rGO sheets.

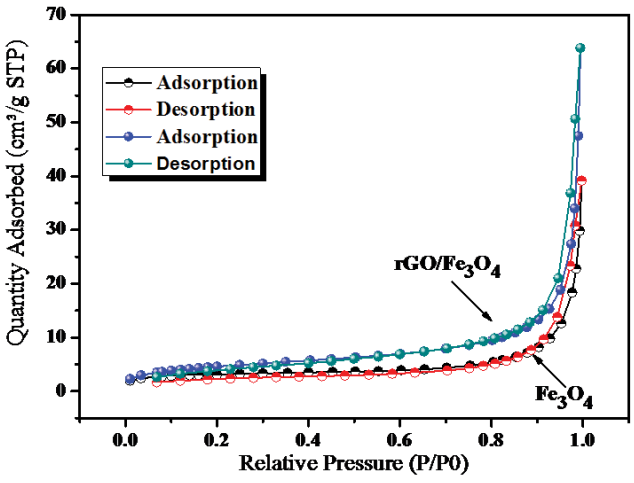

Fig. 4. BET surface area plots of Fe_3O_4-NPs and rGO/Fe_3O_4-NCs.

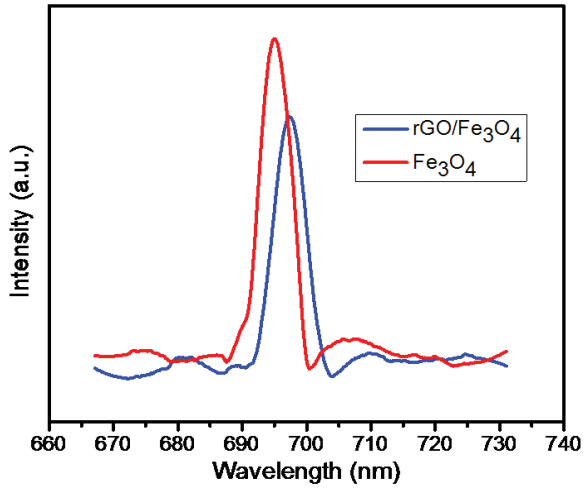

Fig. 5. Photoluminescence (PL) spectra of Fe_3O_4-NPs and rGO/Fe_3O_4-NCs.

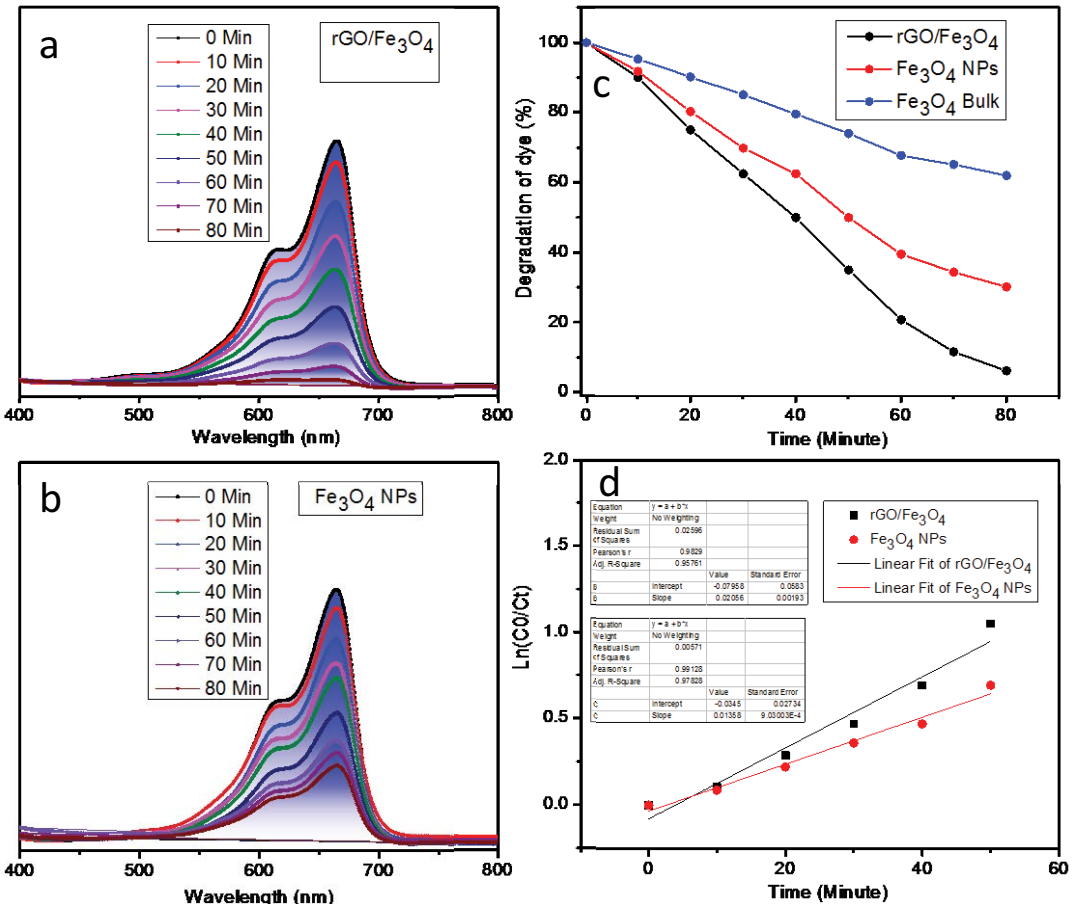

Fig. 6. (a,b) Absorption spectra, and (c,d) percent photo-degradation and linear plots of photo-catalysts for degradation of MBD.

Table 1
Details of experimental conditions and photo-catalytic efficiencies of rGO/Fe_3O_4-NCs, Fe_3O_4-NPs and bulk Fe_3O_4 particle for degradation of MBD

Photo-catalysts	Amount of photo-catalysts	Source of light	Conditions	Irradiation time (min)	% Degradation
rGO/Fe_3O_4-NCs	1.0 mg	Direct sunlight	Air atmosphere, pH = 8	80	~94%
Fe_3O_4-NPs	1.0 mg	Direct sunlight	Air atmosphere, pH = 8	80	~70%
Bulk Fe_3O_4 particle	1.0 mg	Direct sunlight	Air atmosphere, pH = 8	80	~40%

methylene blue with ~92% over the surface of rGO/ZnO nanocomposites.

The photo-catalytic mechanistic pathway to understand the principles has been shown in Fig. 7a. The reactive species including holes (h^+), oxygen radicals ($O_2^{-\bullet}$) and hydroxyl radicals ($OH^\bullet$) play an important role in photo-degradation reactions of MBD. The photo-catalytic activity of rGO/Fe_3O_4-NCs on the photo-degradation of methylene blue under sunlight irradiation shows remarkable suppression over the Fe_3O_4-NPs and bulk Fe_3O_4 photo-catalysts. The photo-generated electrons were excited from valence band to conduction band and then migrated to the surface of the reactive species. The holes were located on valence band and oxidize the MBD directly. During the photo-catalytic process, the $OH^\bullet$ radicals are formed by the splitting of H_2O. The $OH^\bullet$ radicals attack the MBD molecules and oxidize them into the intermediates followed by the generation of inorganic constituents. The following steps could be considered for photo-degradation of MBD:

$$\text{rGO-}Fe_3O_4 + hv \rightarrow \text{rGO-}Fe_3O_4(e^- + h^+)$$
$$\text{rGO-}Fe_3O_4(h^+) + H_2O \rightarrow \text{rGO-}Fe_3O_4 + OH^\bullet + H^+$$
$$\text{rGO-}Fe_3O_4 + O_2 + e^- \rightarrow \text{rGO-}Fe_3O_4 + O_2^{\bullet-}$$
$$\text{MBD} + \text{reactive species} \rightarrow CO_2 + H_2O + \text{intermediate}$$

The enhanced photo-catalytic activity of graphene-based inorganic nanostructured material (rGO/Fe_3O_4) could be ascribed to the surface property of graphene which suppresses

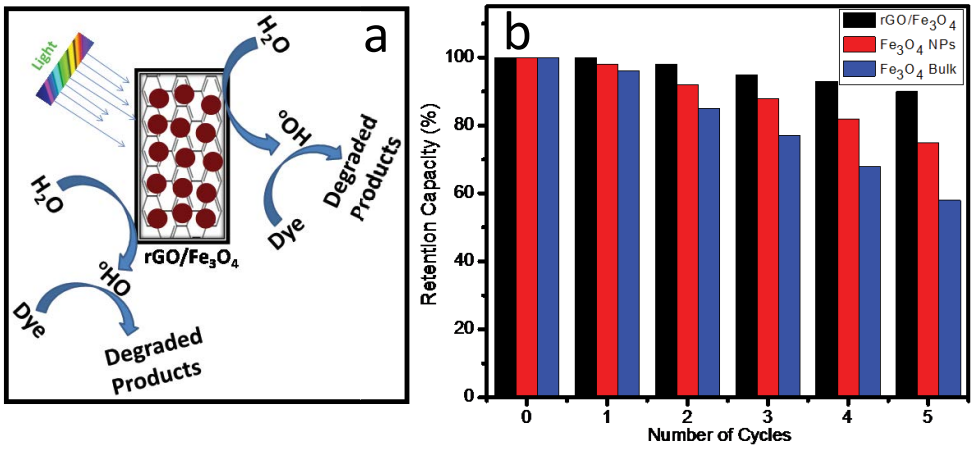

Fig. 7. (a) Photo-degradation mechanism and (b) recycling efficiencies of photo-catalysts for degradation of MBD.

the photo-induced electron–hole recombination by sinking the photo-excited electron from the conduction of Fe_3O_4 and utilizing them in the photochemical reaction. The stability and recycling efficiencies of the photo-catalysts were also evaluated for five times recycled catalysts. The recycled catalyst (rGO/Fe_3O_4-NCs) exhibited excellent photo-catalytic efficiency compared with recycled Fe_3O_4-NPs and bulk Fe_3O_4 particle (Fig. 7b). The rate of photo-catalytic degradation decreases with the recycles, which could be due to the interaction between the surface of photo-catalysts and dye molecules. Note that after completion of each experiment, the catalysts were successfully separated by the permanent magnets and properly washed to clean the surface prior to use for the next experiment. Magnetic separation method is an advantageous way to use and recollect the photo-catalysts easily to avoid the contamination. Therefore, our results demonstrate the enhanced photo-catalytic performance of rGO/Fe_3O_4-NCs with stability and recyclability compared with other photo-catalysts, which were used in the degradation of methylene blue.

4. Conclusion

Excellent stability, recyclable efficiency and catalytic performance of rGO/Fe_3O_4-NCs (~94%) were studied for photo-degradation of MBD compared with pure Fe_3O_4-NPs (~70%) and bulk Fe_3O_4 (~40%). XRD, FTIR and Raman techniques used for structural studies. Electron microscopic studies confirmed that Fe_3O_4 nanoparticles (~10 nm) are very well supported by rGO sheets, that is, rGO/Fe_3O_4-NCs. Excellent photo-stability and recyclable nature of rGO/Fe_3O_4-NCs make them ideal for further catalytic studies or other applications.

Conflict of interest

There is no conflict of interest.

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