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# Properties of $\alpha$-$Fe_2O_3$/graphene nanohydrid synthesized by a simple hydrothermal/solution mixing method

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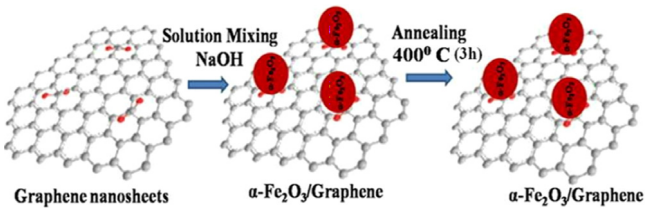
## HIGHLIGHTS

- Preparation of $\alpha$-$Fe_2O_3$/graphene with different graphene nanosheets (GN) compositions.
- Nanohybrid formation is confirmed by XRD, TEM, EDX and FTIR.
- DR-UV spectra suggest that band gap reduces from 1.74(2) to 1.47(5) with GNs composition.
- Saturation magnetization reduces while Morin transition temperature increases with GNs composition.

## GRAPHICAL ABSTRACT

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## ABSTRACT

$\alpha$-$Fe_2O_3$/graphene nanohybrid with different graphene nanosheets (GN) compositions are prepared by a simple hydrothermal/solution mixing method. The XRD patterns reveal that $\alpha$-$Fe_2O_3$ nanoparticles (NP'S) are successfully anchored on the GNs. Suppression of Fe signal and increase of C signal are evidenced from EDX spectra. TEM images show that the as prepared nanohybrids have packed structure of NP'S on GNs with some voids. Vibrational bands in the FTIR studies confirm the fabrication of $\alpha$-$Fe_2O_3$/GNs nanohybrids. DRUV spectra suggest that band gap reduces from 1.74(2) to 1.47(5) with GNs composition. VSM characterization reveals that saturation magnetization shifts toward field axis, while Morin transition temperature increases with GNs composition.



## 1. Introduction

Graphene nanosheet (GN) with two-dimensional honeycomb-like network of carbon atoms, has initiated an explosive interest owing to its prominent thermal stability, superior electronic conductivity, high surface area and structural flexibility [1–3] has many applications in the field of nanotechnology. Numerous GN-based inorganic nanocomposites with metal [4,5] metal oxides [6–14] and sulfide [15,16] have been successfully synthesized and showed enhanced properties of these host materials. There has been a great deal of interest in nanohybrids containing $\alpha$-$Fe_2O_3$ nanoparticles dispersed in GNs with great technological importance for its use in Li-ion batteries [17–20], photoelectrochemical cell [21], photocatalytic activity [22–24] gas sensor [25], biocatalytic activity [26] and supercapacitors [27–30]. The superior performance of the aforementioned applications can be due to the positive synergistic effect between GN and $\alpha$-$Fe_2O_3$ nanoparticles. Although vast research has been carried out to understand the performance in different applications, studies pertaining to magnetism on $\alpha$-$Fe_2O_3$/graphene are not explored. It is well known that besides interesting structural, morphological and optical characteristics of $\alpha$-$Fe_2O_3$/graphene nanocomposites, the magnetic properties are of great interest as they exhibit antiferromagnetism below the Morin transition temperature $T_M$ and weakly ferromagnetic above $T_M$ [31]. It is known that the room temperature weak ferromagnetism (RTFM) of $\alpha$-$Fe_2O_3$ is sensitive to a non-magnetic material anchored on its surface. The uncompensated surface spins of $\alpha$-$Fe_2O_3$ can influence the core spins via exchange coupling interaction, leading to a weak RTFM in the nanocomposite [32]. Moreover, other exciting magnetic properties like saturation magnetization, coercivity and retentivity can be effectively tuned by

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anchoring $\alpha$-$Fe_2O_3$ on graphene due to Ruderman–Kittel–Kasuya–Yosida type interaction between graphene and magnetic ions [33]. Tuning of magnetic parameters can be effectively done by varying the ratio of non-magnetic material in the nanocomposite [34]. It is found that tuning the composition of magnetic nanostructures anchored on graphene could exhibit excellent magnetic, electrical and dielectric performance and finds application in electromagnetic wave absorption, radio-frequency interference, electrochromic devices, Li-ion batteries, sensors and field effect transistors [35]. In this context, it is envisaged to synthesize magnetic $\alpha$-$Fe_2O_3$/graphene nanocomposite with varying graphene composition to investigate the optical and temperature and field dependent magnetizations. These studies further give a clear insight about the interactions of the two distinct materials in the composite that modifies the physical properties. Also, to prepare metal oxide nanocomposites, various synthesis methods including solid state reactions [36], two-step sol–gel process [37], hydrothermal [38,39], microwave assisted fabrication [40], coprecipitation [41] and solution mixing method [42] have been employed. Among these, solution mixing is a simple method to fabricate metal oxide/graphene nanohydrids. The oxygenated functional groups on GO facilitate the uniform distribution of metal oxide under vigorous stirring or ultrasonic agitation [43]. For instance, Mukherji et al. [44] synthesized nitrogen doped $Sr_2Ta_2O_7$/graphene sheets by mixing the graphene oxide dispersion and $Sr_2Ta_2O_{7x}N_x$, followed by reduction of graphene oxide to graphene under xenon lamp irradiation. N. J. Bell et al. [45] prepared $TiO_2$/graphene composites by mixing $TiO_2$ particles and GO colloids ultrasonically, followed by ultraviolet (UV)-assisted photocatalytic reduction. Considering graphene's large network of $sp^2$ hybridized carbon, this material can tend to form strong $\pi-\pi$ bonds with other graphite-like materials. To the best of my knowledge there have been no reports on the synthesis of $\alpha$-$Fe_2O_3$/graphene nanohydrids by hydrothermal/solution mixing method and their detailed magnetic properties. In this present work $\alpha$-$Fe_2O_3$/graphene nanohydrids with different graphene compositions were prepared by hydrothermal/solution method followed by annealing. The influence of graphene composition the structural, morphological, optical and magnetic properties of the $\alpha$-$Fe_2O_3$/graphene nanohydrids have been investigated.

## 2. Experimental

### 2.1. Materials and methods

#### 2.1.1. Preparation of graphene nanosheets (GNs) by Hummer's method

Graphite powder, $<$ 20 μm, synthetic was purchased from Sigma Aldrich, Switzerland. Sulfuric acid (A.R.) was purchased from High media, Mumbai. $KMnO_4$ was purchased from HANS CHEM, India. Sodium acetate ($CH_3COONa$), hydrogen peroxide ($H_2O_2$) and iron (III) nitrate anhydrous ($Fe(NO_3)_3$) were purchased from Merck, Mumbai. GNs were synthesized using a modified Hummer's method [46]. 0.5 g of graphite powder and 0.5 g of $NaNO_3$ were added in 23 mL of 12 M $H_2SO_4$ and stirred in an ice bath for 15 min. Then 4.0 g of $KMnO_4$ was slowly added to the above mixture placed in the same ice bath to yield a purple-green mixture. This suspension was transferred to a 40 °C water bath and magnetically stirred for another 90 min. The dark brown colored paste was diluted with the slow addition of 50 mL of double distilled water (DD) and allowed to stir for a further 10 min. Then, 6 mL of $H_2O_2$ was slowly added to quench the solution and thus a golden-brown sol was obtained. The resultant product was centrifuged and washed with 50 mL of DD water repeatedly. Finally the product was dried at 80 °C for 24 h in an electric oven to collect the graphene powder.

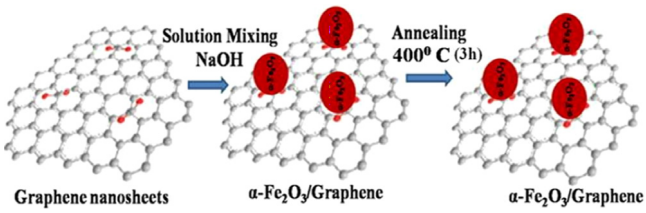


**Fig. 1.** Schematic representation for the formation of $\alpha$-$Fe_2O_3$/graphene nanohybrid.

#### 2.1.2. Synthesis of bare $\alpha$-$Fe_2O_3$ nanoparticles (NP's)

Iron (III) nitrate anhydrous ($Fe(NO_3)_3$) and sodium hydroxide (NaOH) pellets were purchased from Merck, Mumbai. Sodium acetate ($CH_3COONa$) was purchased from Fisher inorganics & aromatics, Madras. $\alpha$-$Fe_2O_3$ NP's were synthesized by hydrothermal method similar to previous work [47]. In this typical method, 0.1 M $Fe(NO_3)_3$ and 0.3 M $CH_3COONa$ were dissolved in 40 mL of double distilled water under magnetic stirring. The above solution was transferred into a Teflon-lined stainless steel autoclave and heated at 160 °C in an electric oven for 24 h. The suspensions were centrifuged with double distilled water several times to collect the reddish brown precipitates. Then the precipitates were air dried in an electric oven (KEMI) at 80 °C overnight to obtain $\alpha$-$Fe_2O_3$ NP's.

#### 2.1.3. Synthesis of $\alpha$-$Fe_2O_3$ NP/GN nanohybrids

$\alpha$-$Fe_2O_3$/graphene nanohybrids with different GNs compositions were prepared through a simple hydrothermal/solution mixing method. First, 5% of GNs were sonicated in 30 mL of DD water for 1 h to achieve uniform dispersions of GNs. Next, $\alpha$-$Fe_2O_3$ NP's were added slowly to the GNs dispersions while stirring. The $\alpha$-$Fe_2O_3$/GO mixture was further stirred for 1 h to ensure complete mixing. Then 10.5 g of NaOH was added to the above solution and stirred for another 10 min. The pH was noted as 14. Again 60 mL of DD water was added and this washing process was repeated several times until the pH reaches to 7. Finally the nano nanohybrids were filtered using a filter paper. The precipitates were dried in an electric oven overnight at 80 °C to collect the powders. In order to achieve a good anchoring of $\alpha$-$Fe_2O_3$ NP's on the surface of GNs annealing was carried out at 400 °C for 3 hrs and the resulting nanocomposite was labeled as $N_1$. Similarly, the compositions of GNs were varied as 10%, 15% and 25% and they were labeled as $N_2$, $N_3$ and $N_4$, respectively. The schematic representation of $\alpha$-$Fe_2O_3$/graphene nanohybrid formation during solution mixing process and annealing is shown in Fig. 1.

#### 2.1.4. Characterizations

X-ray diffraction (XRD) patterns were recorded to confirm the phase purity of the samples by an Xpert'o Panalytical X-ray diffractometer. The morphologies of the nanohybrids and the presence of elements were studied with the help of a TECNAI high resolution transmission electron microscope (HRTEM), equipped with an energy dispersive X-ray spectroscopy (EDX) system. The infrared optical spectra were recorded using a Fourier transform infrared spectrophotometer (FTIR, Perkin Elmer Spectrum Two). The bandgap energies were determined using a UV–vis diffuse reflectance spectrophotometer (Shimadzu UV-2700) and the magnetic properties of the samples were acquired by means of a Vibrating sample magnetometer (Lakeshore 7410).

## 3. Results and discussion

### 3.1. TEM analysis

In order to track the formation of $\alpha$-$Fe_2O_3$/graphene nanohybrids, Transmission Electron Microscopic (TEM) images are