

Synthesis of Magnetic Exfoliated graphene via one pot Electroless Chemical Deposition method

Abdur Rauf,^{a,b} Syed Sohail Ahmad Shah,^{b,c*} Azim Khan,^{b,c} Syed Awaiz Ahmad Shah,^c Khadija tul kubra,^d Akbar Ali,^e and Khalid H. Thebo.^{f*}

^a School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.

^b Center of Excellence in Solid State Physics, University of the Punjab, QAC, Lahore-54590, Pakistan.

^c Institute of Metal research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang, Liaoning, 110016, China.

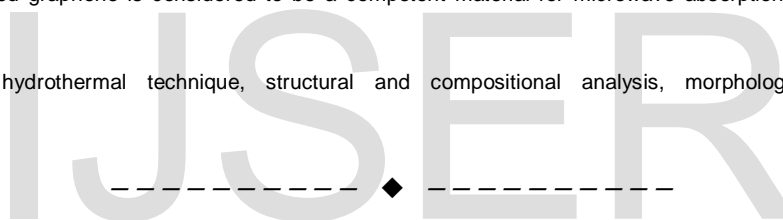
^d Institute of Chemical Science, University of Peshawar, Khyber Pakhtun-khwa, Pakistan

^e National Center for Nanoscience and Technology (NCNST), Chinese Academy of Sciences (CAS), Beijing China.

^f School of Chemistry and Material science, University of Manchester UK, oxford Road, M13 9PL, Manchester UK.*

Abstract— A chemical two-step approach, based on the hydrothermal technique, has been developed to synthesize Fe₂O₃ nanoparticles-decorated graphene. Exfoliated graphene (xG) were purified by acidic treatment, sensitized to attach functional groups. FeCl₃, xG and NaOH were used as a precursor. The reaction temperature of the formation of Fe₂O₃-Graphene was 155 °C. The structural and compositional analysis, morphologies and magnetic properties of the sample were carried out via using different analytical techniques. The formation of maghemite Fe₂O₃ nanocomposites was confirmed by X-ray diffraction (XRD), Raman spectroscopy and value stream mapping (VSM). The particle size of Fe₂O₃ nanoparticles loaded on graphene (as observed from TEM) was found to be smaller than 20 nm. The VSM plot of the sample is a straightforward evidence of the presence of super paramagnetic Iron Oxide nanoparticles. The maghemite Fe₂O₃ decorated graphene is considered to be a competent material for microwave absorption as well as energy storage devices.

Key words: graphene, hydrothermal technique, structural and compositional analysis, morphologies, magnetic properties, nanocomposites.



1 INTRODUCTION

Graphene a nanoscale allotropic form of carbon having quasi-two dimensional lattice structure possesses some interesting and unique properties. It has quite high electron mobility [1], its breaking strength is 200 times greater than steel [2], a high thermal conductivity[3], and has such a high opacity that it can be seen on a suitable substrate with a standard optical microscope [4]. These remarkable properties such as flexible and very strong structure, light weight and electrically super conducting make it a primary component of nanotechnology for next generation devices i.e. Quantum computers and smart phones etc. Unlike CNTs, graphene is a continuous medium hence heating due to the resistance at electrical contact is minimized [5], which make it more suitable in future electronic industry. Recently, more research interests explode towards the decoration of graphene with magnetic nanoparticles due to their extensive potential applications in different applied fields e.g. microwaves absorption and catalysis. Jang et al.

[6] synthesized graphene decorated with ZnO nanocrystals by a facile in situ one-pot hydrothermal route. Teo et al. [7] established a green, cost effective and sufficient method of decorating reduced graphene oxide (r-GO) with magnetic nanoparticles. Ming-Liang Chen et al. [8] reported the synthesis of graphene decorated with Pd, Pt and Fe nanoparticles.

In this paper, we demonstrate the decoration of x-Graphene with maghemite-Fe₂O₃ nanoparticles with a one-pot method by decomposition of iron chloride with x-Graphene in ethylene glycol. Due to high boiling point (197 °C) and appropriate viscosity Ethylene glycol (EG) was chosen as solvent. Furthermore, the structure of EG molecule is ideal to form chelated complexes with metals. Therefore EG can perform as a complexing agent as well as good solvent for the synthesis process. We aim to decorate graphene with metallic magnetic nanoparticles to enhance the absorption and shielding capabilities using a green

* Corresponding author, Tel: +86-15542152720
e-mail address: sohail.sohailshah@gmail.com, khalidthebo@yahoo.com

chemical method. Previous results [1.60] have shown that introducing an appropriate content of magnetic nanoparticles (NPs) has enhanced the EM wave's attenuation. Furthermore, metal-decorated x-Graphene are believed to outperform in biosensors [9-10] i.e. clinical diagnosis, electronics industry specially in field effect transistor (FET), transparent conducting films, Lithium Ion batteries, supercapacitors and ultra-sensitive sensors [9-11].

1. Experimental procedure

All chemicals used in this experiment were of analytical grade and used as received except Graphite powder. Graphite powder (purity > 95%) were obtained from National Center for Physics (NCP) Islamabad, Pakistan. The three step solve thermal procedure was adopted to prepare the sample (Fe₂O₃/ x-Graphene). The three steps process described is shown in figure 1.1 and discussed below:

Graphene oxide (GO) was synthesized from graphite powder using modified Hummer's method. In brief, 1 g of graphite and 1 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid and the solution was cooled to 3-5°C under constant stirring for 30 min. After 30 min, 3 g of KMnO₄ was added gradually to the above solution while keeping the temperature less than 20°C to prevent overheating and explosion. The mixture was stirred at 35 °C for 1 h during which the color of solution changed from black to brown and the resulting solution was diluted by adding 200 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO₄, the suspension was further treated with 30% H₂O₂ solution (10 ml). The resulting mixture was washed with HCl and H₂O respectively, followed by filtration and drying, graphene oxide sheets were thus obtained.

The obtained exfoliated graphene was functionalized in order to make its surface active for metallic group attachments. For this purpose, we used the reflux technique. 2g exfoliated graphene was dissolved in 110 ml HNO₃ in a 200 mL beaker. After this we add 75 ml de-ionized water to dilute the acidic solution and obtained the desired molarity of the solution (12.7 M). Then this mixture was reflux at 200 C° under magnetic stirring for 5 h. After reflux, the sample was washed with de-ionizes water many times for the removal of residue and make its pH value down to 7. The purified sample was then collected by centrifugation at the rate of 6000 rev/min and liquid evaporation was done in a petri dish. The functionalized graphene was then dried in electric furnace. The obtained product was labeled as (functionalized Ex-Graphene).

In third step, 700 mg of functionalized Ex-Graphene and 700 mg of FeCl₃ were dissolved in 15 ml ethylene glycol (EG) to get solution (Sol.1). This solution was sonicated for 20 mints to make the mixture homogeneous. Also separately 120 mg of NaOH was dissolved in 10 ml eth-

ylene glycol (EG) to form solution (Sol.2). The solution of graphene and FeCl₃ (Sol.1) and NaOH solution (Sol.2) was mixed under constant stirring at room temperature for 1 h. After stirring, the mixture was transferred it into Pyrex square glass bottles. The autoclave was sealed and heated in electric oven at the rate of 5 C°/min up to 155 C°. This temperature was maintained for 1 h. When the overnight sample in autoclave was naturally cool down to room temperature, we dilute the solution by adding 20 ml methanol. The obtained sample was again washed with de-ionized water several times. It was collected by centrifugation and dried up in vacuum at 60 C° for 12 hrs to obtain the final black grayish powder.

The prepared sample was then characterized using different analytical techniques and instruments. The structural and phase analysis were investigated using a powder X-ray Diffractometer (Rigaku D/Max-2400). The elemental analyses of the sample were carried out through Proton Induced X-ray Emission (PIXE), at NCP, Islamabad. In order to see the vibrational, rotational and other low frequency modes in the system, Raman spectroscopy was employed. The magnetic properties were determined by VSM (Lake Shore 7400 series) installed at Centre of Excellence in Solid State Physic, University of the Punjab, Lahore. To observe the related Morphologies of the nanostructure Fe₂O₃- Ex-Graphene, the high resolution TEM (JEOL JEM-4000FX) examination was done at Schools of Science and Engineering, Shanghai University, P.R. China.

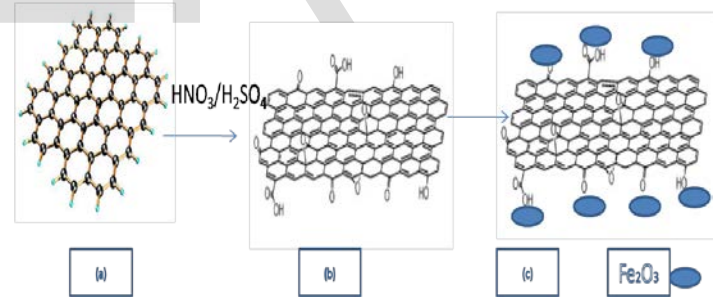


Figure 1: Schematic illustration of electroless Fe-deposition on Ex-Graphene a) Ex-Graphene b) sensitization and activation, (d) electroless attachments of Fe₂O₃ Nanoparticles.

2. Results and Discussion

3.1 Fourier transforms infrared spectroscopy

To find the vibrational spectrum of magnetic Fe₂O₃- Ex-Graphene, FTIR spectroscopy was been used to analyzed the sample. FTIR plots, **Fig. 2a** reveals the presence of different functional groups to MWCNTs. In **Fig. 2a** the absorption peak at 3775 cm⁻¹ indicates the stretching vibration of N-H bond amine. The observe peaks at 3666 cm⁻¹ and 1168 cm⁻¹ shows the stretching vibration of O-H and C-O bond of alcohol respectively attached to MWCNTs. The

nitro group is attached at 1555 cm^{-1} . These attachments have been done after surface activation, modification and sensitization occurs during step 1. **Fig.2b** reveals a strong absorption at wave number 570 cm^{-1} , which is strongly in agreement with the absorption peak of iron particles as well with the previous reports [12-14]. By FTIR analysis it has been confirmed that iron oxide nanoparticles have been attached to the Ex-Graphene after step 2.

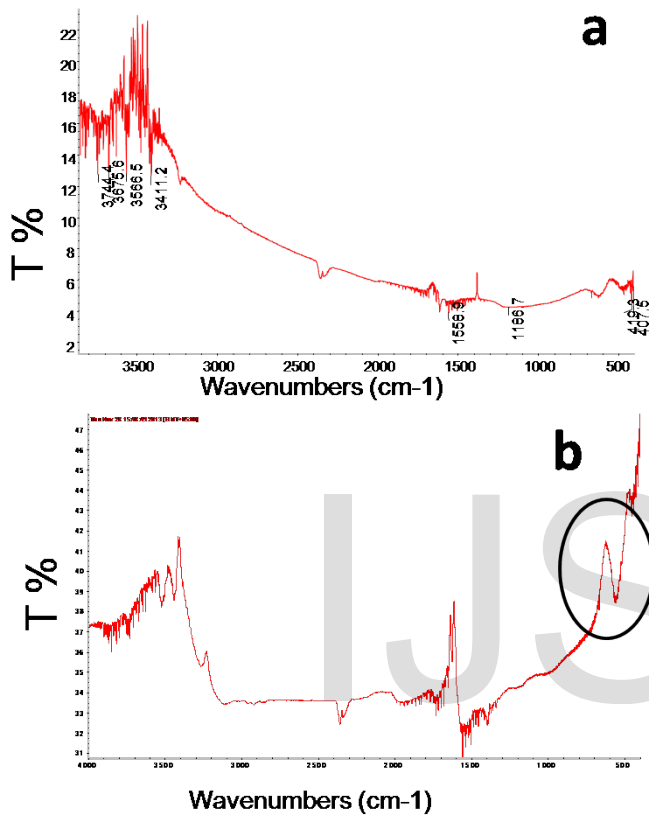


Figure 2.1 The FTIR spectrum of (a) Ex-Graphene (b) magnetic Fe_2O_3 - Ex-Graphene

3.2 Proton induced x-ray emission

The graphical analyses by Proton Induced X-ray Emission (PIXE) are shown in **Fig. 3 (a-b)**. The X-rays were detected between 15° and 30° respectively. The exposure time of sample to proton beam was about 30 minutes. After the attachment of Fe atoms, increases in the number is suggested to the attachment of iron oxide atoms to Ex-Graphene, which is also evident from the peak of iron from graphical view in **Fig 3b**. The number of iron atoms has been significantly increased from 1439 to 24246, which shows the creation and attachment of Fe_2O_3 atoms to Ex-Graphene. By comparison of the two PIXE spectrums of the samples, it can be clearly seen that the Fe peak is dominant in sample (S_2) with increased in count numbers, whereas due to the high sensitivity of the device the elements other than Carbon and Fe have been detected as impurities during sample surface activation and functionalization processes.

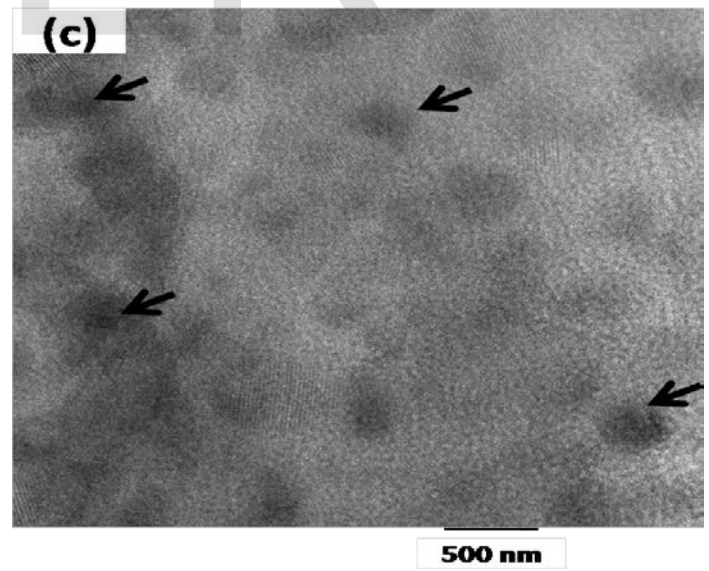
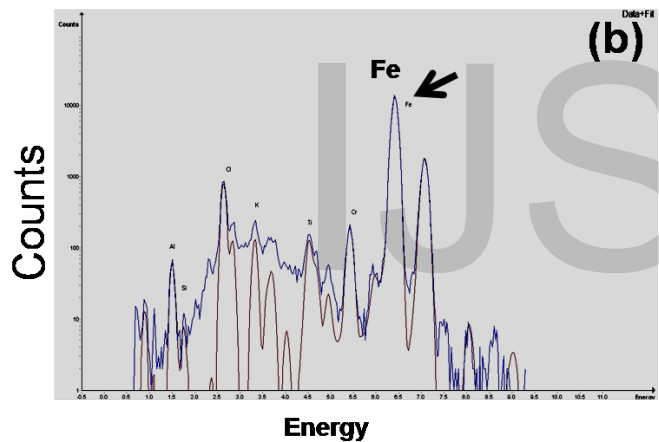
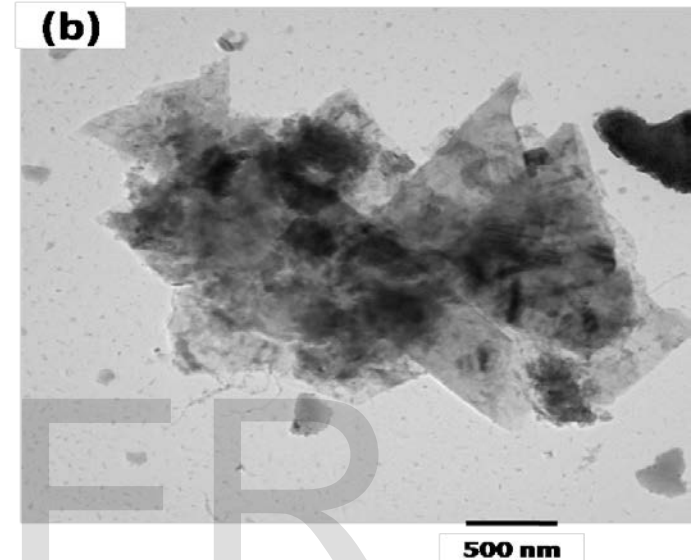
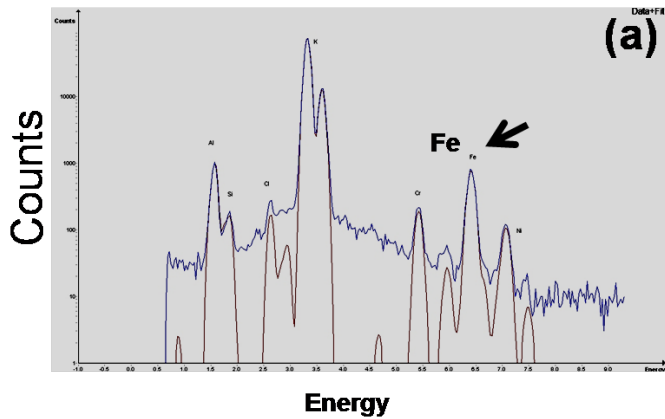
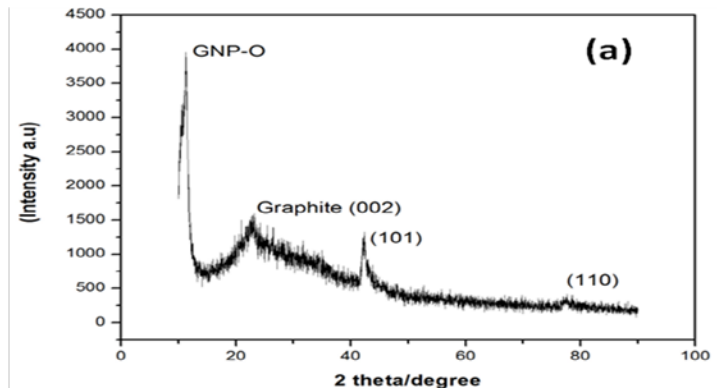
3.4 XRD and Morphological analysis

Fig. 5a reveals the XRD patterns of the as-prepared sample after step 2. The results indicate the mix phase product of Ex-Graphene and maghemite Fe_2O_3 (JCPDS card No. 33-0664.). The diffraction peak at $2\theta = 10.4^\circ$ is the typical Bragg peak of functionalized Ex-Graphene oxide and indexed as (0 0 2) peak of reflection of graphene, whereas the typical graphite peak is present at $2\theta = 26^\circ$. The non carbon related peaks match well with the (1 0 1), planes of the standard XRD data for the maghemite Fe_2O_3 which is also in agreement with the previous literature [12-14], whereas the peak corresponding to impurities was (1 1 0). The XRD results tell the good crystalline structure of the product. As calculated by Scherer's formula, the average crystallite size of the Fe_2O_3 crystals was about 18 nm.

The morphology and size of the as-prepared sample were also investigated by transmission electron microscopy (TEM). The TEM images of Fe_2O_3 -Graphene are depicted in **Fig.4b-e**. These spherical or non-geometrical shaped particles can be clearly seen which are distributed uniformly on the surface and edges of the graphene (**Fig.4b-d**). The average size of Fe_2O_3 nanoparticles loaded on graphene surface ranges between 10-20 nm with narrow size distribution which is in agreement with the XRD result. In some micrographs, the distribution of nanoparticles over graphene surface is non-uniform (**Fig. 4b-d**), rather aggregation of particles occurs. The aggregation is due to immobilization of particles on the surface due to presence of active functional groups (dangling bonds) in the sample or cavitations due ultra-sonication during step two of sample preparation [15]. The loading of nanoparticles on the both the sides of the graphene can be achieved with appropriate functional groups such as hydroxyl, carboxylic groups. Lian et al. [16] have decorated graphene with Fe_3O_4 using a conventional method. Their results also showed a non-uniform distribution (aggregation) of Fe_3O_4 nanoparticles on the graphene surface. To observe the active bands Raman spectrum of Fe_2O_3 /graphene is presented in (**Fig. 4f**). It displays sharp peaks at 1596 cm^{-1} and 2680 cm^{-1} and a small peak at 1354 cm^{-1} which are in good correspondence with graphitic (G) band and disordered (2D) band of graphene sheets[17-18]. The D band is a disordered or defect mode cause by elastically scatter longitudinal optical (LO) phonon to conserve the momentum. This mode is usually located between 1300 and 1400 cm^{-1} frequency range. In the present sample D band can be seen very prominent which is suggested some surface defects which were occurred during sample preparation. In carbon nanotubes, the D band is activated from process of sp^2 -hybridized carbons by the presence of grain boundaries, vacancies, substitutional hetero-atoms, or other defects [19-23].

The peak observed at 1301 cm^{-1} is attributable to a ma-

ghemite due to two-magnon scattering [24]. The 2D-band can be used to determine the number of layer of graphene. As for multi-layer graphene, the shape of 2D-band (G') is different from that in the single-layer graphene i.e. the 2D-band in the single-layer graphene intense and sharper as compared to the 2D band in multi-layer graphene [25]. It is obvious in the plot that the peak corresponding to 2D-band is little bit broader, which is evidence of multilayer graphene.



Sample #	Steps	Elements	Concentrations (part per million)
1	Sample after Surface activation and functionalizations	Al	198
		Si	159
		K	11305
		Cr	234
		Fe	1439
2	Sample after attachment of iron particles	Ni	21
		Al	4034
		Si	12
		K	3
		Fe	24246
		Ti	36

Figure 3.1 Pixe spectra of the Fe_2O_3 - Ex-Graphene nanocomposites: (a) after step 1 i.e. functionalized Ex-Graphene (b) After step 2 i.e. magnetic Fe_2O_3 - Ex-Graphene and its corresponding data table.

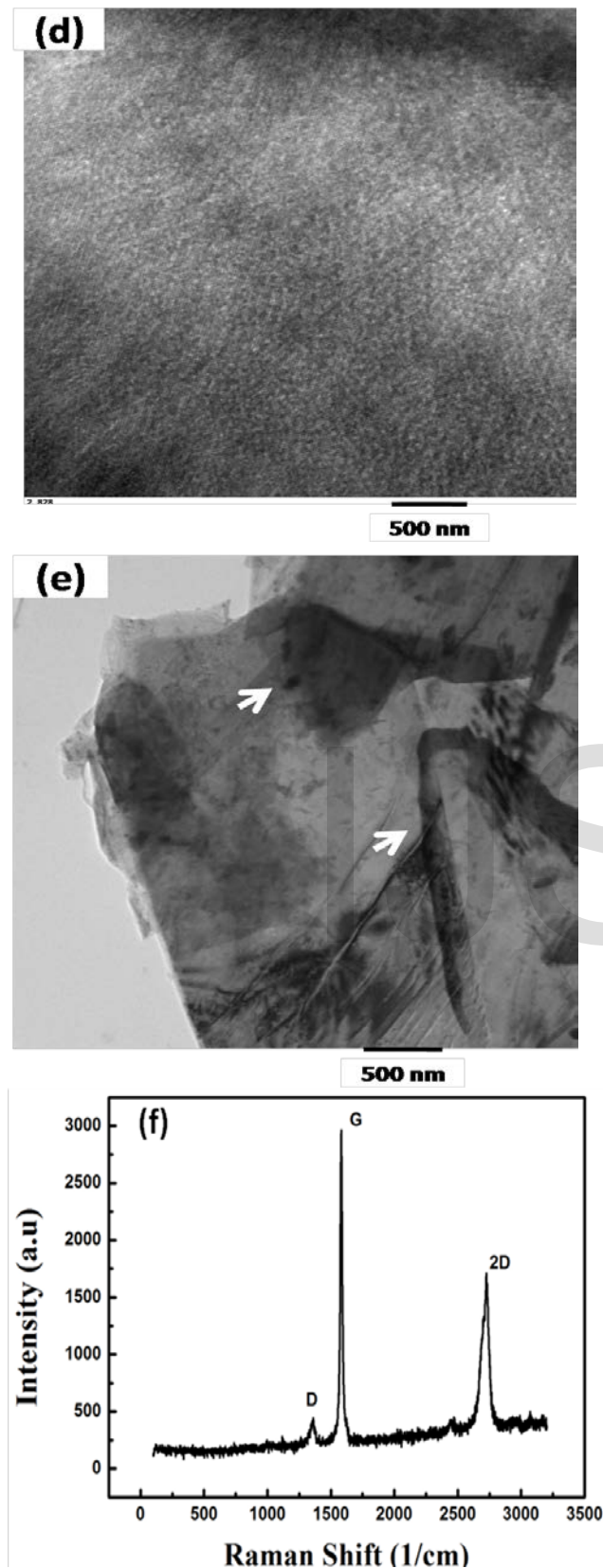


Fig. 4.1 Structural and morphological characterizations of the as-prepared sample (a) XRD pattern; (b-e) TEM images of maghemite Fe₂O₃- Ex-Graphene hybrid materials. (f) The detailed Raman spectrum of the maghemite Fe₂O₃- Ex-Graphene hybrid materials.

3.5. Magnetic Properties

In order to observe the magnetic properties of the as-prepared sample vibrating sample magnetometer (VSM) technique was applied. A hysteresis loop is formed, which is property of ferromagnetic/ super paramagnetic materials [26-27]. As obvious from the characteristics of the plot **Fig. 5**, the samples exhibit super paramagnetic behavior at room temperature with measured values of saturation magnetization (M_s) of $\sim 657.92 \times 10^{-6}$ emu, coercivity (H_{ci}) 375.56 G and retentivity 212.72×10^{-6} emu. Fe₂O₃/Graphene show ferromagnetic behavior even at room temperature i.e. their Curie temperature low. When the magnetizing field is reduced to zero, the sample retains a magnetization (retentivity) with all domains still oriented. Field dependent magnetic moment of Fe₂O₃/Graphene is shown in the **Fig.5**. The sample show ferromagnetic behavior even at room temperature because of the presence of maghemite Fe₂O₃ phases. This unique property makes it ideal to involve in target-drug delivery as well in detection, separations and electromagnetic waves absorption materials. The As-prepared maghemite Fe₂O₃- Ex-Graphene nanostructures can be very easily dispersed in water as shown in (**Fig. 6**). Also as exposed to commercial magnet these magnetic composites could be quickly separated from water, which indicates their feasibility to organize by an external magnetic field.

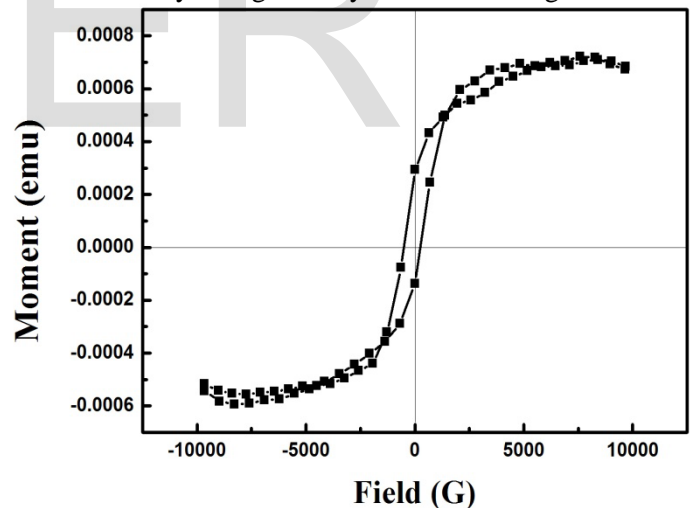


Fig.5. Magnetic hysteresis curves of the maghemite Fe₂O₃- Ex-Graphene hybrid materials.

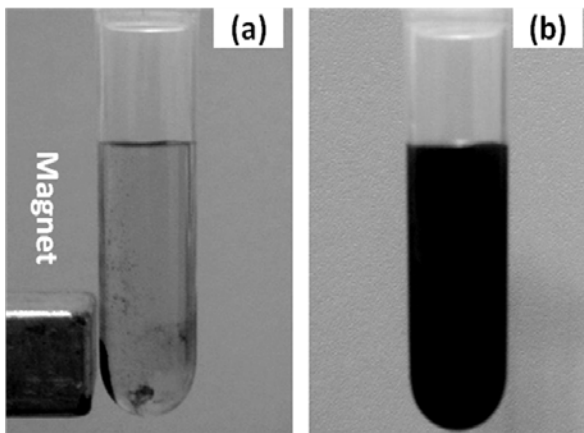


Fig. 6. Photographic view of maghemite Fe_2O_3 -Ex-Graphene nanocomposites: (a) their response to a magnet and (b) dispersed in water

4. Conclusions

In summary, maghemite Fe_2O_3 nanoparticles, with the average size of ~ 10 - 20 nm were successfully attached to the surface of Ex-Graphene using a green, cost-effective and simple two step solvothermal technique. Super paramagnetic properties were introduced which are assumed to enhance Ex-Graphene for biotechnological purposes e.g. (target-drug delivery, detection and separations, and in clinical diagnosis), and microwave absorption as well as energy storage devices (e.g. super-capacitors, Li-ion batteries). The results show that the distribution of the iron additives on MWCNTs powder was achieved. The high thermal stability, mechanical strength of the material and low cost simple procedure invite future investigations on the design of new composites of Fe_2O_3 -Ex-Graphene. The same technique may be employed to attach other metallic nanoparticles like Ni, Co, Cr and Zn etc. and optimize various parameters. The synthesis of these nanoparticles-decorated Ex-Graphene composites can be established in epoxy matrix to demonstrate their application as microwave absorber in radar systems. Ex-Graphene based hybrids are promising material for multifunctional applications.

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