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Synthesis and characterization of graphene-Fe₃O₄ nanocomposite

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Abstract: Novel method to synthesize graphene-Fe₃O₄ nanocomposite is disclosed. Graphene functionalized with carboxylic group was added during the chemical synthesis of Fe₃O₄ nanoparticles by reduction of Fe(acac)₃ using ascorbic acid to get graphene-Fe₃O₄ nanocomposite, wherein the monodisperse spherical nanoparticles of Fe₃O₄ of 10 nm diameter remains attached to graphene surface. Physico-chemical characterization of the synthesized nanocomposite is done using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Raman and Fourier Transform Infra-red spectroscopy in order to understand different physico-chemical parameters and properties of the synthesized material.

Keywords: Graphene, Fe₃O₄ nanoparticles, nanocomposite

1 Introduction: Graphene has attracted lots of attention due to its excellent electrical and mechanical properties, since from its discovery in 2004 [1]. Somani et. al. have demonstrated synthesis of planer nano-graphenes from camphor by CVD method first time in the world [2]. Structure of graphene is a honeycomb lattice which is a two dimensional in which carbon atoms are bonded together with σ bonds [3 - 10]. Graphene is coupled with nanoparticles of other materials for various applications. Deposition of nanoparticles is possible on graphene surface because of its two-dimensional structure and high surface area [11]. Nanoparticles of different materials such as metal oxides [11, 12], metals [13], quantum dots [14], sulfides [15] etc. have been combined with graphene for various applications. This helps in two ways: nanoparticles remains anchored on graphene sheet and do not get agglomerated, and also prevents graphene sheets from their reassembly into graphite or aggregation in a bulky form. Deposition of nanoparticles on graphene is observed to enhance its electrical, mechanical, and thermal properties [16]. Graphene based nanocomposites have also potential applications in biosensing, solar cell, magnetic resonance imaging (MRI), drug delivery, photocatalysis, electrodes of energy storage devices such as that of supercapacitors and batteries [17 - 21] etc.

Fe₃O₄ nanoparticles are of special interest due to their magnetic properties and possible applications in cancer hyperthermia, MRI imaging etc. In earlier studies, Fe₃O₄ nanoparticles have been deposited on graphene oxide.

In these efforts, graphene is first converted into graphene oxide and then nanoparticles are deposited on graphene oxide. Ma et. al. made functionalized graphene-Fe₃O₄ nanocomposite by dispersing graphene oxide, FeCl₃.6H₂O in a mixture of ethylene glycol and diethylene glycol followed by heating at 200 °C for 10 hours [22]. Major drawback of this approach is that the reaction needs very long time. Also the size distribution of nanoparticles is very wide (from 50 nm to 300 nm). Guan et. al. assembled Fe₃O₄ nanoparticles on graphene by stirring Fe₃O₄ nanoparticles and graphene in hexane overnight and then sonicating for 2 hours [23]. However, Fe₃O₄ nanoparticles are not firmly attached to graphene sheet. Poor adhesion between Fe₃O₄ and graphene is a major concern for any realistic applications. In another effort, Li et. al. synthesized Fe₃O₄ decorated graphene oxide sheets by adding graphene oxide in solution containing FeCl₃.6H₂O and FeSO₄.7H₂O under N₂ at 80°C [24]. However, the method has a crucial and difficult step of adjusting the pH of the reaction to 10, throughout the course of the reaction. In yet another attempt, Gan et. al. synthesized Fe₃O₄-(poly(diallyldimethyl ammonium chloride) (PDDA)) core-shell structured nanoparticles and graphene oxide-DNA composite first. In next step both composites were attached together by sol-gel technique. But while doing the synthesis of Fe₃O₄ nanoparticles, FeCl₃.6H₂O and sodium acetate were dissolved in ethylene glycol and obtained solution was heated at 200°C for 8 hours. This kind of method needs long time reaction and high temperature. Also mean Fe₃O₄ particle size was 300 nm [25].

Magnetic Fe₃O₄ nanoparticles are of interest to us for their applications in cancer hyperthermia treatment. Synthesis of monodisperse, small size (less than 10 nm), shape and size controlled, reproducible, and of single phase (without contaminations by other iron oxide phases such as FeO, Fe₂O₃, etc) was a challenge. We developed a method for synthesis of Fe₃O₄ nanoparticles and addressed listed challenges. Fe₃O₄ nanoparticles are synthesized on carboxylic group functionalized graphene in presence of Fe(acac)₃, ascorbic acid, dehydrated ethanol and ultrapure water. In our method, Fe(acac)₃ was reduced by ascorbic acid and hydrolyzed by ultrapure water in presence of surface functionalized graphene for deposition of Fe₃O₄ nanoparticles on graphene. –COOH moieties present on surface functionalized graphene provides attachment site for Fe₃O₄ nanoparticles [26, 27]. The reaction parameters are optimized to obtain monodisperse Fe₃O₄ spherical nanoparticles of 10 nm diameter deposited on surface functionalized graphene sheet. Synthesized nanocomposite is characterized by various physico-chemical characterization techniques and results are reported here.

2. Materials and methods:

2.1.1 Chemicals: Chemicals used in this work were: Graphene (6-8 nm thick × 5 microns wide, Strem chemicals, Japan), Fe(acac)₃ (purity 99 %, Strem chemicals, Japan), ascorbic acid (purity 99.6 %, Wako Pure Chemicals Industries, Ltd., Japan), dehydrated ethanol (prepared and used when required in our laboratory), diphenyl-ether (purity 99 %, Wako Pure Chemicals Industries, Ltd., Japan), and Ultrapure deionized (DI) water.

2.1.2 Functionalization of graphene: Graphene is functionalized with carboxylic group by interacting it with H₂SO₄ and HNO₃ mixture, followed by filtration, washing with ultrapure water and drying at room temperature and at 60 °C.

2.1.3 Synthesis of graphene-nano-Fe₃O₄ nanocomposite: Surface functionalized graphene (0.1 gm) was added in 50 mL of 30 mM Fe(acac)₃ diphenyl-ether solution made (by dissolving Fe(acac)₃ in diphenyl-ether) and the solution was kept under stirring in N₂ gas atmosphere. Temperature was increased upto various temperatures 60 °C, 70 °C, 80 °C. Ascorbic acid solution of 0.025 M in 12 M ultrapure water and dehydrated ethanol was then added at a dropping rate of 2 mL/min when solution temperature reached to 70 °C. After the addition of reducing acid solution, the reaction mixture was heated to 190 °C again and refluxed for 1 hour.

Finally, it was cooled down to room temperature naturally. Product was separated by filtration and washed 4 - 5 times by chloroform to remove any impurities, followed by dried in vacuum. Dry powder obtained is subsequently used for physico-chemical characterization.

2.2 Analysis and characterization

2.2.1 Instruments: Graphene, functionalized graphene and graphene-Fe₃O₄ samples were characterized by X-ray powder diffraction (XRD) using a Rigaku RINT-2100 X-ray diffractometer (Japan). Scanning Electron Microscopy and EDAX analysis was carried out by using JSM-6510LA scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using JEOL JEM-2100F (USA) microscope. X-ray photoelectron spectroscopy (XPS) was done using UIVac Phi Versa Probe CU (Japan). Raman Spectroscopy was also performed using Renishaw InVia Raman Microscope (Japan).

2.2.2 Fourier transform infra-red (FTIR) analysis: The chemical characterization of functional groups on surface of the all samples was studied by a Fourier transform infrared spectrometer in the range 4000 cm⁻¹ - 450 cm⁻¹.

2.2.3 Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) analysis: Scanning electron microscopy was used to visualize the surface morphology of the carbonized and activated products. The samples were coated with gold by a gold sputtering device for a clear vision of the surface morphology. Elements composition of the samples was also observed using scanning electron microscopy equipped with energy dispersive spectrometer. EDAX spectrum showing elemental composition by scanning through surface of samples. The surface distributions were collected from SEM pictures using different magnifications.

2.2.4 X-ray diffraction (XRD) analysis: X-ray patterns of FW, the carbonized and activated products were recorded by X-ray powder diffractometer with Cu K_α radiation (λ = 1.5406 nm).

2.2.5 Transmission electron microscopy (TEM): In order to study the size, shape and surface morphology transmission electron microscopy was done. The images of samples were taken at low and high magnification.

2.2.6 X-ray photoelectron spectroscopy (XPS): To predict the formation of Fe₃O₄(magnetite) nanoparticles and chemical bonds present in sample XPS(X-ray photoelectron spectroscopy) was done.

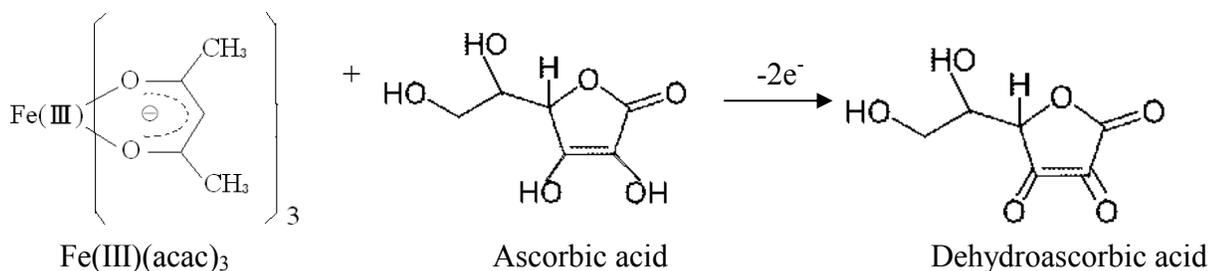
2.2.7 Raman spectroscopy: In order to understand the chemical composition and structure Raman spectroscopy was done (Raman microscope having 532 nm laser wavelength).

3. Results and discussion:

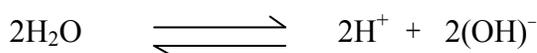
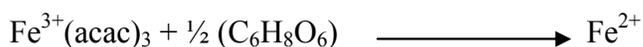
3.1 Mechanism of Fe₃O₄ formation: During the synthesis process, Fe(acac)₃ is reduced by ascorbic acid and hydrolyzed by ultrapure water. Ascorbic acid acts as reducing agent and ultrapure water acts as oxygen supplier. When this reaction occurs in presence of carboxylated graphene, the –COOH moieties provide anchoring site for Fe₃O₄ nanoparticles and graphene-Fe₃O₄ nanocomposite is synthesized. In first step, Fe ions (Fe²⁺ and Fe³⁺) get anchored on oxygen containing groups (-COO⁻) present on graphene sheets. In second step, Fe₃O₄ nanoparticles are generated through heating process in which oxygen is supplied by ultrapure water and Fe-ions gets reduced. The proposed mechanism for Fe₃O₄ formation is as follows:



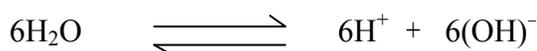
Ascorbic acid reduces the $\text{Fe}(\text{acac})_3$ as follows:



Fe^{2+} is formed because of reduction of $\text{Fe}^{3+}(\text{acac})_3$ by ascorbic acid, and because of ultrapure water $\text{Fe}(\text{OH})_2$ is generated as follows:



And $2\text{Fe}(\text{OH})_3$ is formed as follows:



In general, $\text{Fe}(\text{acac})_3$ is reduced by ascorbic acid and $\text{Fe}_3(\text{OH})_8$ is synthesized as follows :



Heating the reaction mixture results in crystallization of Fe_3O_4 nanoparticles and hydrolysis. The formation of Fe_3O_4 is as follows:



3.2 FTIR spectrum of carboxylated graphene: Figure (1) shows the fourier transform infra-red spectroscopy (FTIR) spectrum of carboxylated graphene. It can be observed that after carboxylation process, $\text{C}=\text{O}$ stretching vibration was observed at 1710 cm^{-1} . Peaks at 3425 cm^{-1} , 1630 cm^{-1} , 1039 cm^{-1} , 1165 cm^{-1} are due to O-H vibrations, C=C vibrations, C-O vibrations and C-O vibrations, respectively.

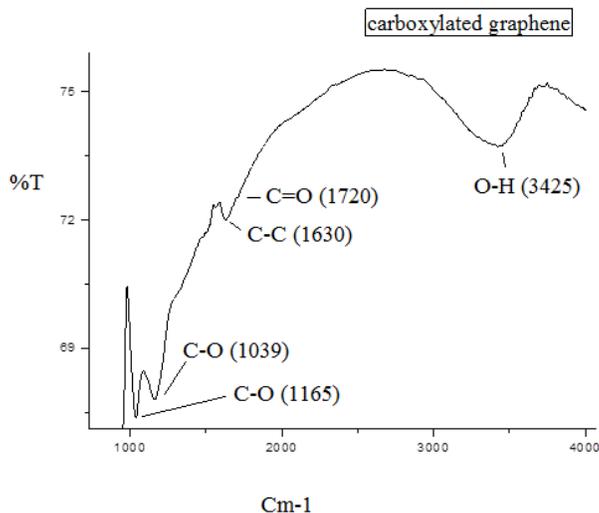


Figure (1): FTIR spectrum of carboxylated graphene.

3.3 Spectra XPS of Carboxylated Graphene: In order to understand the chemical structure of carboxylated graphene, X-ray photoelectron spectroscopy (XPS) study was performed. Figure (2a) shows C 1s region XPS spectrum of carboxylated graphene. C 1s XPS spectrum contained four typical components which corresponds to binding energy peaks centered at 284.5 eV (C-C bond type bonding), 285.61 eV (C-O type bond), 286.75 eV (C=O type bond), and 290.43 eV ($-\text{COO}$ bond). Figure (2b) is carboxylated graphene XPS spectrum of O 1s. It can be observed that O 1s spectrum can be deconvoluted into two peaks centered at binding energy of 530.69 eV and 531.67 eV and 533.43eV; which can be C-O type bonding and C=O bonding and carboxylated carbon (COOH). This indicated that carboxylation of graphene was successfully prepared. The data was consistent with reported data [28 - 30].

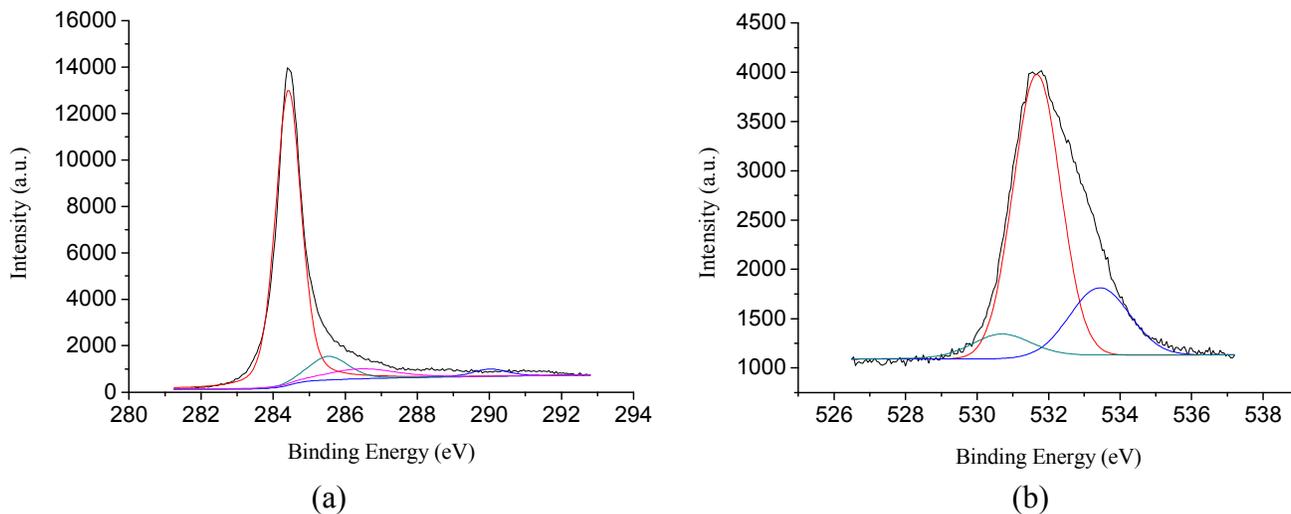


Figure (2): (a) XPS - C1s spectra of carboxylated graphene, (b) XPS-O1s spectra of carboxylated graphene.

3.4 Spectra EDAX of carboxylated graphene: Figure (3) shows the elemental composition of carboxylated graphene studied by Energy Dispersive X-ray Analysis (EDAX). Main elements found were carbon and oxygen. Gold (Au) was also detected which arises due to gold coated samples used for SEM observations.

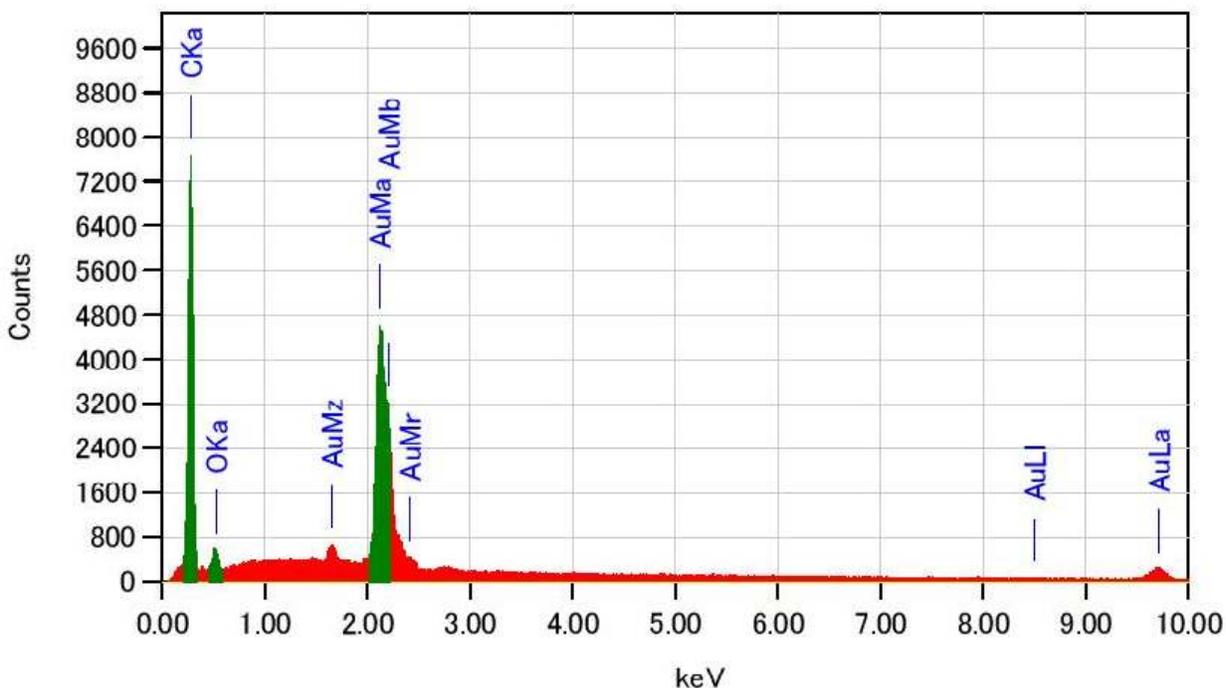


Figure (3): EDAX spectrum of carboxylated graphene.

Table (1): elemental analysis by EDAX of carboxylated graphene.

Element	atomic weight %
C (carbon)	92.40
O (Oxygen)	4.27
Au (Gold)	3.33

3.5 SEM and TEM of carboxylated graphene: Figure (4a) represents SEM image of carboxylated graphene. Figure (4b) shows the transmission electron microscopy (TEM) image of carboxylated graphene in which carboxylated graphene sheets consisting of layers stacked eah other with less wrinkles and foldings. Figure (4c) is the high resolution transmission electron microscopy (HRTEM) image of carboxylated graphene sheet showing the lattice fringes.

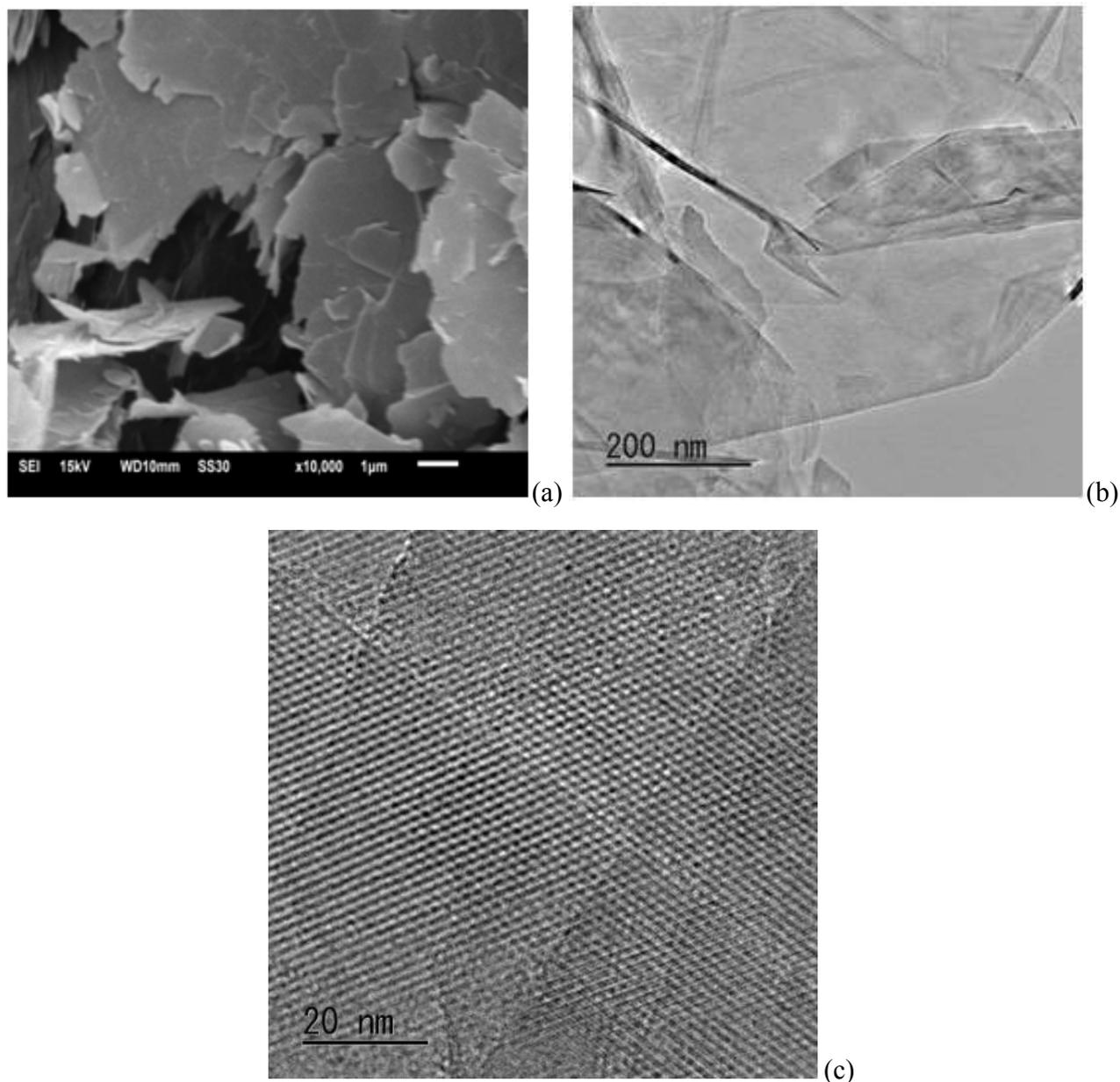


Figure (4): (a) SEM image of carboxylated graphene, (b) TEM image of carboxylated graphene and (c) HRTEM image of carboxylated graphene.

3.6 XPS of Graphene-Fe₃O₄ nanocomposite: Figure (5) represents XPS spectra of as synthesized graphene-Fe₃O₄ nanocomposite. C 1s spectrum (figure 5a) can be deconvoluted into three main peaks at 284.42 eV, 288.43 eV and 285.33 eV attributable to C-C type bond, C-O type bond and C=O type bonding, respectively. O 1s spectrum (Figure 5b) can be deconvoluted into three peaks centered at 531.10 eV, 532.43 eV and 530.04 eV attributable to Fe-O-C bond, C-O bond and Fe-O bond, respectively. The Fe-O-C linkage suggests interfacial interaction between Fe₃O₄ and graphene and ensured the strong interaction, structural stability of graphene-Fe₃O₄ nanocomposite. The results were consistent with reported data [30].

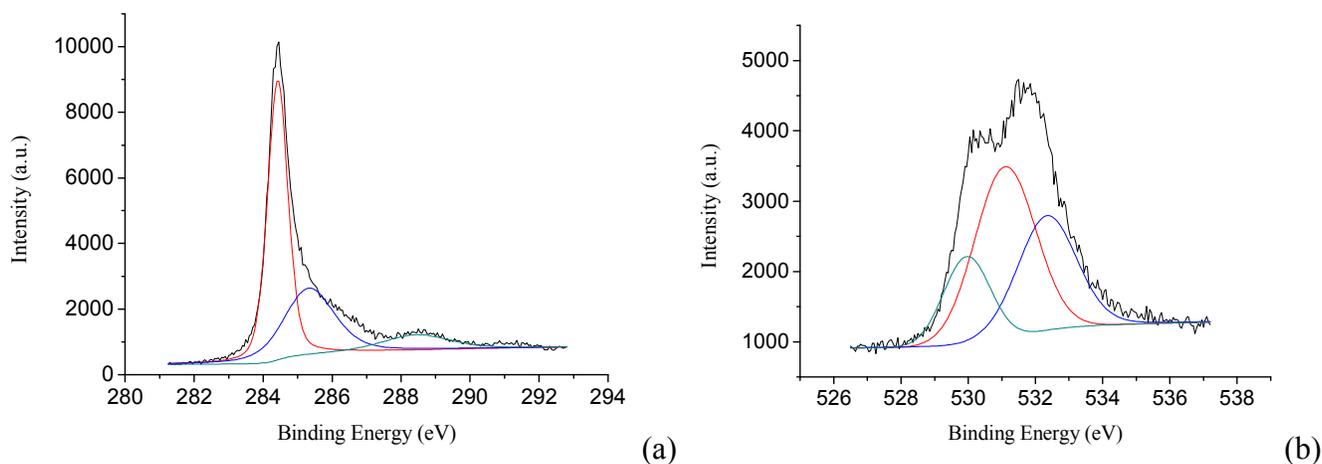


Figure (5): XPS spectrum of Graphene-Fe₃O₄ nanocomposite.
(a) C 1s spectrum and (b) O 1s spectrum.

Figure (6) shows the XPS spectrum of Fe 2p region. The Fe 2p spectrum can be deconvoluted into five peaks at 710.29 eV, 711 eV, 719.06 eV, 722.90 eV, and 724.70 eV. Photoelectron peak at binding energy of 724.70 eV corresponds to 2p_{1/2} of Fe³⁺ ion, the peak at binding energy of 722.90 eV can be assigned to 2p_{1/2} of Fe²⁺ ions. The peaks at 710.29 eV and 711 eV can be assigned to 2p_{3/2} of Fe²⁺ and Fe³⁺ ions. The peak at 719.06 eV is a satellite peak for above four peaks [31].

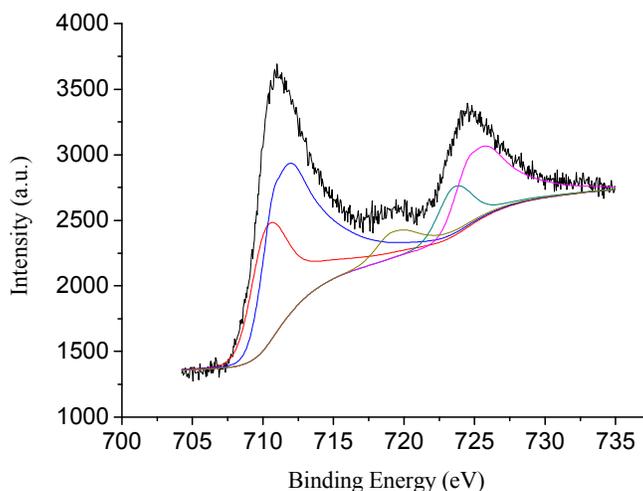


Figure (6): XPS of Fe2p region for Fe₃O₄ nanoparticles.

3.7 TEM and SEM of graphene-Fe₃O₄ nanocomposite and Fe₃O₄ nanoparticles: Size, shape and morphology of graphene-Fe₃O₄ nanocomposite and bare Fe₃O₄ nanoparticles were characterized by SEM and TEM. Figure (7a and b) represents TEM images of graphene-Fe₃O₄ nanocomposite. It is evident that the two-dimensional graphene sheets are decorated by Fe₃O₄ nanoparticles. Average size of Fe₃O₄ nanoparticles was found to be 10 nm. Aggregation of Fe₃O₄ nanoparticles was not observed on graphene sheet. While making the samples for TEM analysis, even after vigorous ultrasonication, Fe₃O₄ nanoparticles were firmly attached on graphene sheets indicating strong interaction between the two. Figure (7c and d) shows SEM image of graphene-Fe₃O₄ nanocomposite. It is observable that Fe₃O₄ nanoparticles are distributed over graphene sheet.

For comparison, SEM and TEM images of Fe_3O_4 nanoparticles synthesized separately (without using graphene) are displayed in Figure (7e and f). Fe_3O_4 nanoparticles of the same size of about 10 nm were obtained. However, aggregation of Fe_3O_4 nanoparticles is observable.

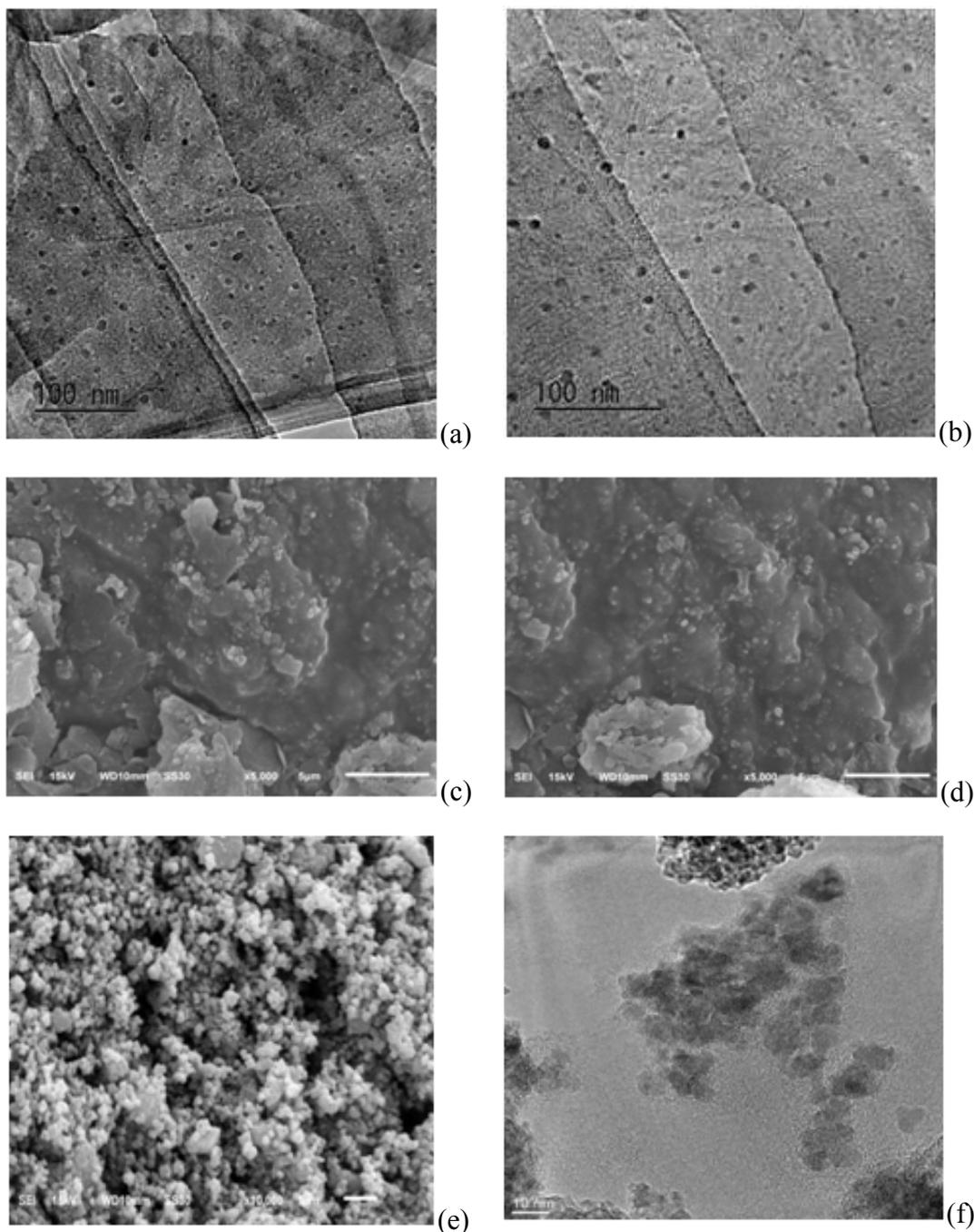


Figure (7): (a, b) TEM images of graphene- Fe_3O_4 nanocomposite, (c, d) SEM images of graphene- Fe_3O_4 nanocomposite, (e and f) SEM and TEM image of bare Fe_3O_4 nanoparticles.

3.8 Raman spectra of carboxylated graphene and graphene- Fe_3O_4 nanocomposite: Figure (8) represents Raman spectra of graphene (Figure 8a) and graphene- Fe_3O_4 nanocomposite (Figure 8b). Raman spectrum of graphene exhibits D-band at 1350 cm^{-1} , G-band at 1580 cm^{-1} and 2D band at 2717

cm^{-1} . Raman spectrum of graphene- Fe_3O_4 nanocomposite shows D-band at 1352 cm^{-1} , G-band at 1581 cm^{-1} and 2D band at 2717 cm^{-1} which is similar to Raman spectra of graphene.

D- and G- bands are corresponding to sp^3 -hybridized carbon and sp^2 -hybridized carbon [32]. It is observed that I_D/I_G ratio of graphene- Fe_3O_4 (0.97) nanocomposite was greater than I_D/I_G ratio of graphene (0.51) which indicates the presence of some unrepaired defects and interaction between Fe_3O_4 and graphene. This is consistent with earlier observations by other researchers [33, 34].

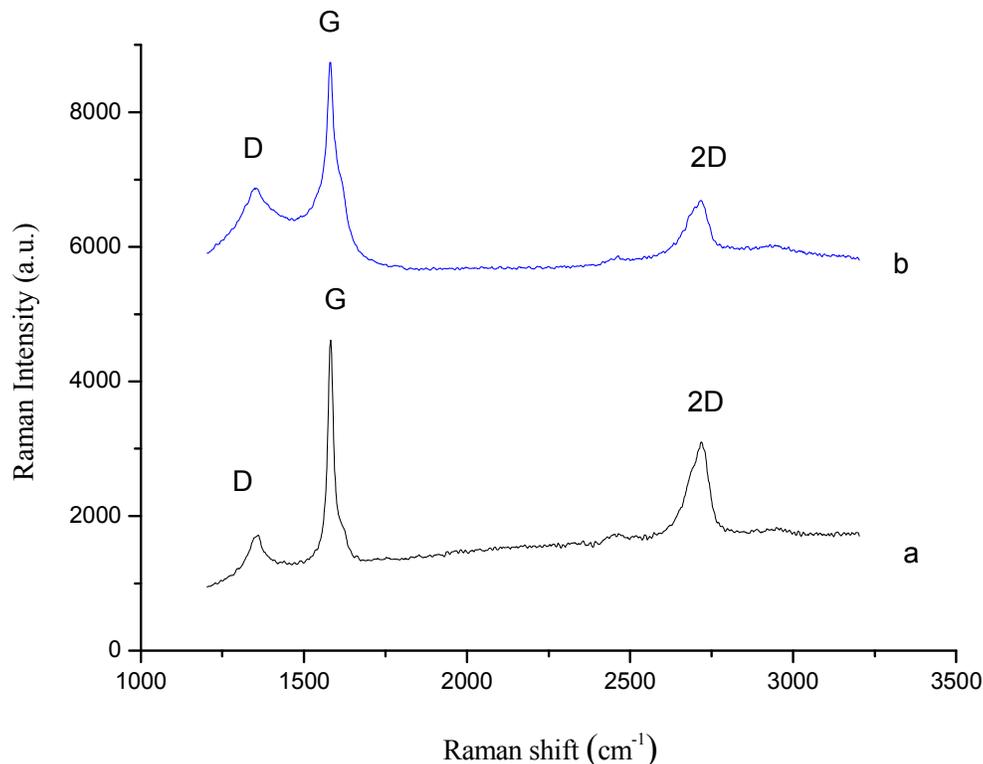


Figure (8): Raman spectra (a) graphene and (b) graphene- Fe_3O_4 nanocomposite.

3.9 EDAX spectra of Graphene- Fe_3O_4 nanocomposite: Figure (9) represents the EDAX spectrum of graphene- Fe_3O_4 nanocomposite. Major elements found are: carbon, oxygen, iron, and gold (which arises due to the fact that the samples were coated with gold for SEM observations).

Table (2): Elemental composition obtained from EDAX.

Element	atomic weight %
C (carbon)	76.94
O (Oxygen)	9.39
Fe (Iron)	10.32
Au (Gold)	3.35

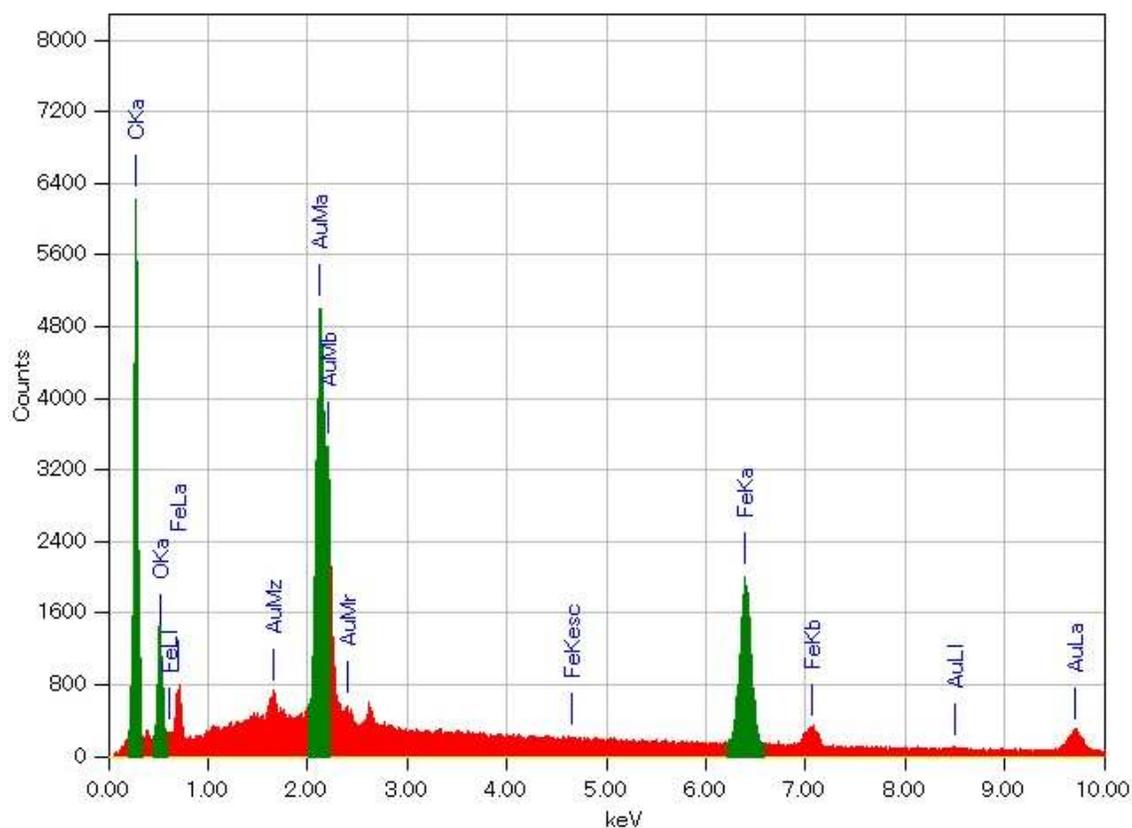


Figure (9): EDAX spectrum of graphene-Fe₃O₄ nanocomposite.

4 Conclusions: A new and simple method has been developed to synthesize graphene- Fe₃O₄ nanocomposite in which ascorbic acid reduces Fe(acac)₃ at a specific temperature in presence of carboxylated graphene and ultrapure water. TEM shows that Fe₃O₄ nanoparticles of about 10 nm diameter were decorated on graphene. FTIR and XPS confirm the carboxylation or surface functionalization of graphene. XPS also confirms formation of Fe₃O₄ nanoparticles and chemical bond between graphene and Fe₃O₄ nanoparticles. Method presented herewith should prove to be useful for synthesis of graphene-Fe₃O₄ nanocomposite for application in cancer hyperthermia. Further uploading of drug molecules on the graphene-Fe₃O₄ nanocomposite should be possible for applications in biomedical science.

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