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GREEN SYNTHESIS OF GRAPHENE SUPPORTED IRON NANO COMPOSITE

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ABSTRACT

Graphene has attracted scientific interest due to its unusual electrical, optical, thermal and mechanical properties. The reduction of graphene oxide (GO) is considered to be easy and cost effective method for large scale production of graphene. But the most of the reducing agents used are toxic and has long lasting environmental impacts. Hence green methodologies involving plant derived reducing agents are preferable as they are less hazardous, cost efficient and eco-friendly. The electronic, magnetic and catalytic properties of graphene can be further improved by incorporating suitable nano materials on the graphene surface which provides surface modification along with exfoliation of layers. The reduction of graphene oxide/graphene in presence of metal ion using phytochemicals provides a convenient one step green route for the metal-graphene composite synthesis. Among the metal nanoparticles, Iron nano particles have excellent applications due its inherent magnetic property and catalytic activity. In this study iron nanoparticles loaded graphene composite was prepared by green reduction of ferric ion in presence of dispersed deoxygenated graphene by phytochemicals present in the pomegranate fruit (*Punica granatum*) juice. The poly functional molecules in the juice function both as a reducing as well as a stabilizing agent for the formed iron nano particles. The prepared composites were characterized by FTIR, UV-vis, XRD, SEM and TEM analysis.

KEYWORDS: Nano Composites, *Punica granatum*, Graphene Oxide, Reduced Graphene Oxide

Graphene is a single layer of carbon atoms or single layer of graphite having sp^2 hybridization has been intensively studied in the last few years. The graphene has unusual chemical, electrical, thermal, optical, physical properties which makes high potential for the enormous applications (Paton et. al., 2014). Graphene is the starting block of all kinds of graphitic materials, because graphite is stacked of many graphene layers. Graphene's unusual properties arise from the unbounded fourth electron in the valence orbital (Potasz et. al., 2012). The experimental studies reveals that the exfoliated graphene sheet has a theoretical surface area of 2600 m^2 $g^{-1}$and a carrier density of approximately 10^{12} cm^{-2} and the highest electrical conductivity of 106 s cm^{-1} at room temperature (Stankovich et. al., 2006). The raw material to the graphene was graphite powder and by using the Modified Hummer's method the graphite oxide was synthesized (Hummers and Offeman, 1958). The properties of graphene can be modified by doping it with suitable nano materials to yield graphene nano composites (Zhou et. al., 2015). The novel electric, thermal and magnetic properties of graphene metal nano composite arise from the interfacial electronic interaction between metal and graphene. It was reported that the interfacial electrical interaction between the Fe and graphene layer improves the dielectric properties of the nanocomposites and exhibits excellent microwave absorption performance in a wide frequency range hence can be used as an excellent Microwave Absorbing Materials (MAMs) (Shen et. al., 2009 & Zhao et. al., 2013). Here we synthesized the graphene supported Fe nanocomposite (Fe/G) via green route and investigated their characteristic properties.

In the last two decades the green chemistry lighten the non toxic, eco friendly, less expensive and novel way of production of chemicals. Further it was found that plant extracts were very effective in reduction and surface passivation of metal ions during the metal nano particle synthesis. The plant extracts, mainly the leaf and fruit extracts carries certain poly phenols, flavonoids etc having reducing and capping ability which helps in the reduction of metal ions to metal nano particles (Zhang et. al., 2012 & Zhu et. al., 2010). The newly formed metal nano particles may have the tendency to get aggregated, but the flavonoids in the plant extract cover the metal and prevent it from aggregation. Here we were interested with pomegranate fruit juice.

MATERIALS AND METHODS

The following chemicals were used without any further purification: Graphite powder, potassium permanganate ($KMnO_4$), Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium nitrate ($NaNO_3$), ethanol (C_2H_5OH), Sulfuric acid (H_2SO_4), Hydrogen peroxide (H_2O_2, 30%), Ammonia solution (NH_4OH, 25%), Hydrochloric acid (HCl), Fresh Pomegranate fruit juice and deionized water.

Specifications of instruments used for analysis are Fourier Transform Infrared spectroscopy (Thermo Nicolet Avatar 370), UV- Visible spectroscopy (Varian Cary 5000), Scanning Electron Microscopy ((JEOL

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JSM390LV) and Transmission Electron Microscopy (JEOL JEM 2100).

Synthesis of Graphite Oxide

The preparation of graphite oxide (GO) was carried out by a modified Hummer's method. In a typical synthesis, 1.0 g of graphite powder was added into 2.5 g of $NaNO_3$ and 100 ml of concentrated H_2SO_4 under stirring in a ice bath. Then 3.0 g of $KMnO_4$ was added gradually to this mixture at 10°C under stirring for 2 h. Then ice bath removed. The resulting mixture was added to 100 ml of distilled water and then heated to 60°C. The obtained mixture was continued to be stirred for 2 h. After that, 10 ml of 30% H_2O_2 was added in the mixture with stirring for 2 h. The color of the mixture changed to bright yellow. Finally, the mixture was filtered and washed with a 5% HCl aqueous solution to remove metal ions, followed by hot distilled water for removal of the acid. The sample is dried in an oven to get graphite oxide.

Exfoliation and Deoxygenation of Graphite Oxide to Graphene

A suspension was obtained by the dispersion of 1g of graphite oxide in 100ml of distilled water with intensive sonication for 2 hour. Then to the well suspended solution added 4 ml of NaOH (8M) solution and applied a temperature field of between 60°C. Then the whole mixture admitted to a mild sonication for 2 hours. The original yellowish-brown color turned black in color. Then the black solid sample dried at 60°C in an oven.

Preparation of *Punica granatum* Juice Extract

About 250g of fresh *Punica granatum* whose grains are red in color and washed it with distilled water. Then its fresh extract is obtained by using a juicer and filtered the extract with a Whatmann filter paper to avoid the solid grains from it. Keep the extract in cold condition.

Synthesis of Iron Supported Graphene Nanocomposite by *Punica granatum* Juice Extract

The iron supported graphene nanocomposite was prepared by a direct method using the *Punica Granatum* juice as the reducing agent. In a typical procedure, graphene (500 mg) was dispersed in distilled water under sonication for 2 hours, and then a mixture of 5ml of pomegranate juice and 5ml of $FeCl_3 \cdot 6H_2O$ (0.1M) was added under ultra sonication for 4 hours. The obtained black solid was centrifuged and washed with distilled water and then washed with ethanol several times to remove residue of plant extract.

RESULTS AND DISCUSSION

FTIR Studies

The dried powders of Graphene oxide and reduced Graphene Iron nano composite were analyzed with Fourier transform infrared (FTIR) spectroscopy and spectrometry within a range of 500–4000 cm^{-1}(Fig. 1). The FT-IR can provide significant information about the graphene sheet and the carbon neighborhood. The graphene oxide spectrum (purple curve) shows dominant peaks at 1715, 1588, 1241 and 1051cm^{-1}. The peak at 1715 cm^{-1} corresponds to a stretching vibration from the C=O carbonyl stretching vibrations. The peak at 1558 cm^{-1} corresponds to a stretching vibration from the C=C bonds. The peak at 1241 cm^{-1} corresponds to a stretching vibration from the C-O bond of ether or epoxy group. The peak at 1051 cm^{-1} corresponds to a vibration from the C-O group. The reduced Graphene-Iron nanocomposite spectrum (red curve) shows dominant peaks at 3446, 1640, 1327, and 1051 cm^{-1}. The peak at 3446 cm^{-1} corresponds to a bending vibration from the O-H groups, may come from the plant extract. The peak at 1640 cm^{-1} corresponds to a stretching vibration of the C=C, the aromatic moiety. The peak at 1715 cm^{-1} corresponds to a stretching vibration from the C=O carbonyl stretching vibrations is missing at the nanocomposite. It indicates the replacement of epoxy or ether group by the Iron nano particles.

UV-vis Spectroscopy

Optical study of UV- vis spectrum of graphene supported Iron is shown in Fig. 2. The UV-vis spectrum of graphene exhibits a characteristic band at 260 nm, indicating the restoration of the extensive conjugated sp^2 carbon network. The peak at 314 nm indicates the adsorption Iron nano particles on the surface of graphene sheet. In the electronic spectrum of the composite, a peak at λ_{max} 390 nm due to the surface plasmon absorption of iron Nanoparticles confirms the nanocomposite formation.

X-ray Diffraction Studies

To support the data obtained by UV-Vis spectroscopy; graphite, graphie oxide, graphene and Graphene - Fe nanocomposite were further characterized by XRD (Fig. 3). The XRD patterns of graphite (Black) showed characteristic peak at 2θ= 26.2°. A characteristic intense peak at 10.4° confirms the increased inter layer placing due to oxygen functionalities in the GO (red). The absence of crystalline peaks in the XRD pattern of graphene (green) confirms complete exfoliation and deoxygenation. The observation of sharp peaks

corresponding to that of beta Ferric Oxide (JCPDS -00-040-1139) in the XRD spectrum of the composite proves the incorporation of Iron nano particle on the reduced graphene (Fig. 4). The average particle size of the iron particle calculated by the Debye- Scherer equation is 28.16 nm.

$$D=K\lambda/(\beta \cos \theta)$$

Where D is the particle size and K is a constant 0.94, λ is the wavelength of X-Ray (λ=1.54AM). β is the full width at half maximum of the peak of XRD pattern.

Scanning Electron Microscopy (SEM)

Surface morphology and distribution were investigated using SEM analysis was conducted and SEM pictures depicts the formation of well dispersed Iron nano composites in which the iron particles are randomly distributed over the graphene layer (Fig. 5)

Transmission Electron Microscopic Analysis

Morphologies of graphene supported iron nanocomposite were determined by TEM analysis (Fig. 6) showed many metal NPs anchored to the surfaces of graphene. The adhered NPs have spherical morphologies, an even distribution, and a homogeneous dispersion on the rGO surfaces; The TEM images also revealed that the graphene layers are transparent enough.

CONCLUSION

This study presents a novel and environmentally friendly method that can be extended to prepare nanocomposites of iron supported graphene by using *Punica granatum* fruit juice as the reducing agent. The Pomegranate extract have been successfully used for the simultaneous reduction of graphene and ferric chloride. The characterization results showed the average crystalline size of 28.16 nm, and thin and transparent nature of graphene sheet.

Conflict of interest: The authors declare no conflict of interest regarding the paper

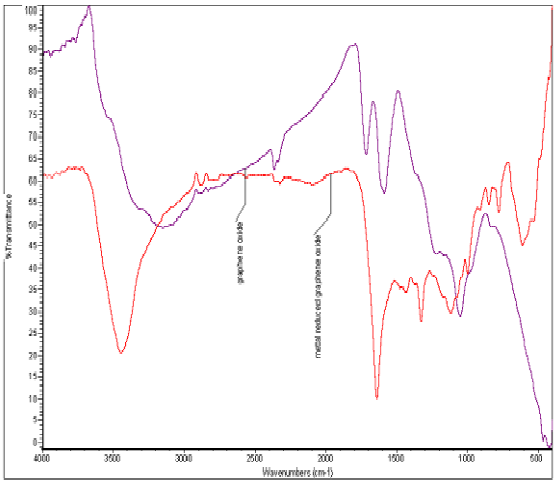

Figure 1: FTIR spectra of Graphene oxide (purple) and reduced Graphene Iron nano composite (red)

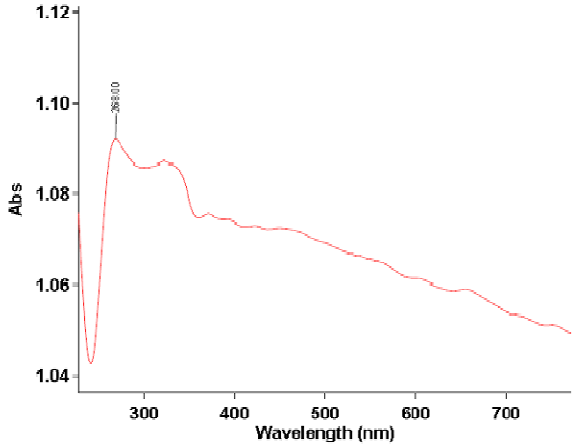

Figure 2: The solid state UV spectra of reduced Graphene - Iron Nanocomposite

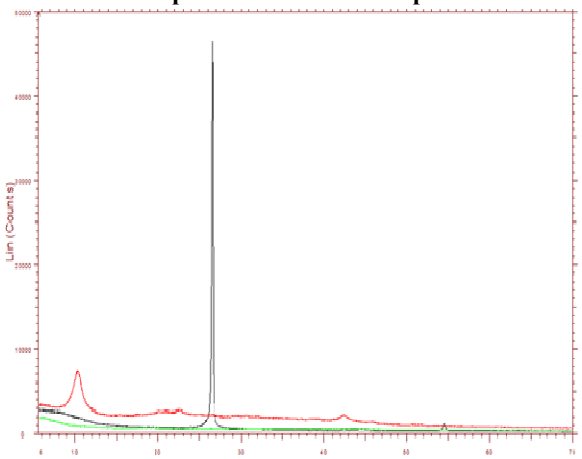

Figure 3: XRD pattern of Graphite (Black), GO (red) and RGO (green)

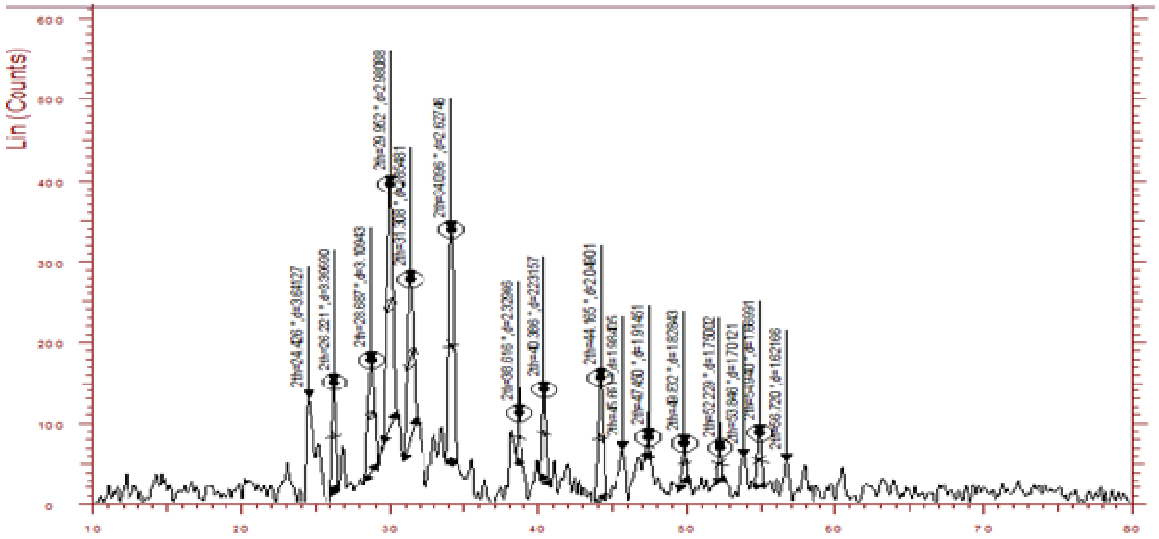

Figure 4: XRD pattern of Iron Doped Graphene

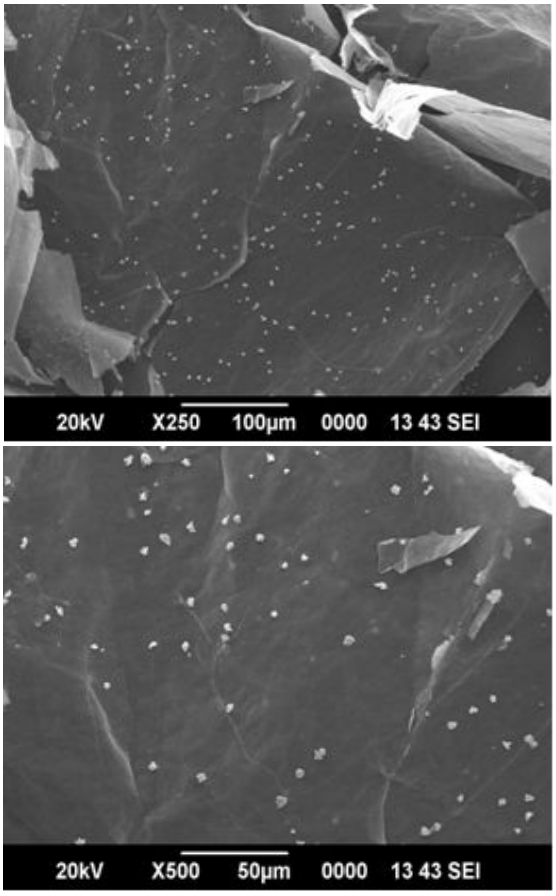

Figure 5: The SEM images of graphene iron nano composite in different magnifications

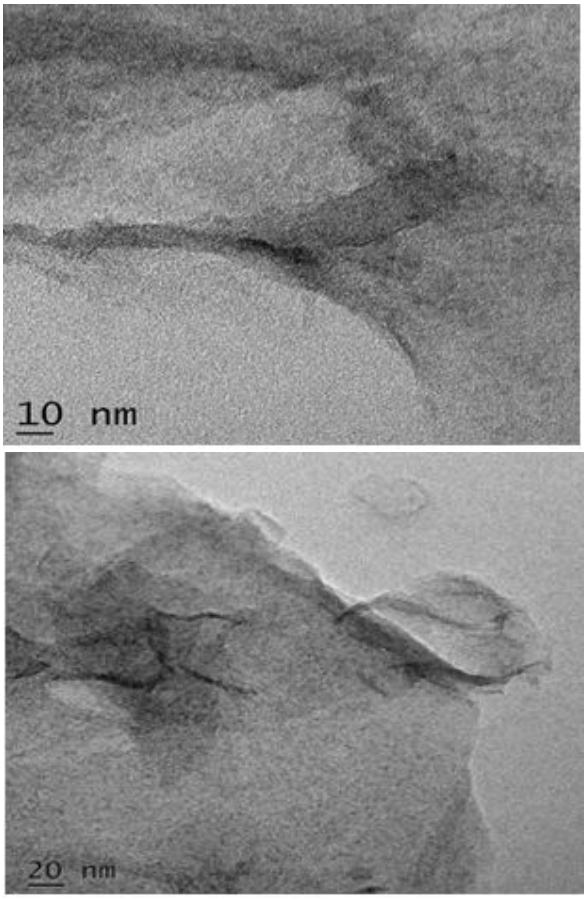

Figure 6: TEM images of Iron supported Graphene sheets

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