



# Graphene/metal matrix material for Supercapacitor applications

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## Abstract

Supercapacitor can store more energy than conventional capacitors and release it with high power, achieve at the same time current density typical for capacitors and unavailable for batteries. Iron oxide is new emerging material for the Supercapacitor application. Its performance is good when it is incorporated with graphene. Iron oxide and Graphene were synthesized by Sono-chemical and hummer's methods respectively. Nanostructured Fe<sub>2</sub>O<sub>3</sub>-graphene composite is prepared by mixing the two samples. Well-crystalline Fe<sub>2</sub>O<sub>3</sub> nanoparticles with 331 nm in size are highly encapsulated in graphene Nano sheet matrix, as demonstrated by employing various characterization techniques like XRD, FTIR, Particle size analysis and SEM with EDAX. In virtue of their superior performance, they will be promising electrode materials for high-performance Supercapacitor applications.

*Keywords: Fe<sub>2</sub>O<sub>3</sub>, Graphene, Nanoparticles*

## I. INTRODUCTION

Iron oxide is a purified natural occurring mineral exists in diversity of structures and occur great in variety of forms from geological to nanoscale technological applications [1] plays a dynamic role in many technological purviews such as biomedical imaging, catalytic applications [2], energy storage devices, sensors [3] biosensors [4]. Metal oxide Nano composites have been used in the fabrication of Supercapacitors [5], batteries [6], solar cells [7].

Nanoparticles with magnetic properties are incorporated with non-magnetic graphene material will provide the remunerations of the both materials unique properties (e.g. electrical conductivity, mechanical strength, high surface area, light weight, high flexibility and magnetization) [8].

Energy storage and conversion is one of the most significant issues in the twenty-first century [9]. Currently, the research and development of energy storage system have achieved low-cost and environmental friendly, which have received a vital attention. Supercapacitors (also called electrochemical capacitors or ultracapacitors), as one of the most promising electrochemical energy storage systems, are promptly acquiring energy, particularly in the field of portable electronic devices, hybrid electric vehicles and electric vehicles due to their high power density and long cycle life when compared with secondary batteries and their higher energy density when compared with electrostatic and electrolytic capacitors [10].

Supercapacitor (SC) is a distinctive electrochemical device which is patterned to possess both high energy and power densities. When integrate into a portable power source that relies on rechargeable batteries, it adds the expertise for meeting the rupture power demands in applications such as electric vehicles and power tools [11]. The material which is used in Supercapacitor application may also require being high surface area, high cycle capability and electrical conductivity. So these efforts have been made to accomplish the objective [12].

Iron oxides have been deliberated as one of the most favorable pseudocapacitor electrode materials with regard to both its specific capacitance and cost effectiveness [13]. Contemporary studies illustrate that hematite (Fe<sub>2</sub>O<sub>3</sub>) nanostructures can be used as electrode materials for Supercapacitors. They found that the electrochemical capacitive performance of the film depends on morphologies. Recently, we developed a morphological-conserved route for the synthesis of mesoporous Fe<sub>2</sub>O<sub>3</sub> nanostructures with manageable contours for Supercapacitors applications [14].

Graphene, a sole single-layer of carbon atoms compactly packed into a two-dimensional honeycomb sp<sup>2</sup> carbon lattice, has attracted remarkable consideration in energy storage devices as a result of its good chemical stability, huge specific surface area and remarkable electrical conductivity [15-18]. The reduced graphene oxide-Fe<sub>2</sub>O<sub>3</sub> composites reveal good cycling performance, large specific capacity and rate capability because of the optimistic synergistic effect of reduced graphene

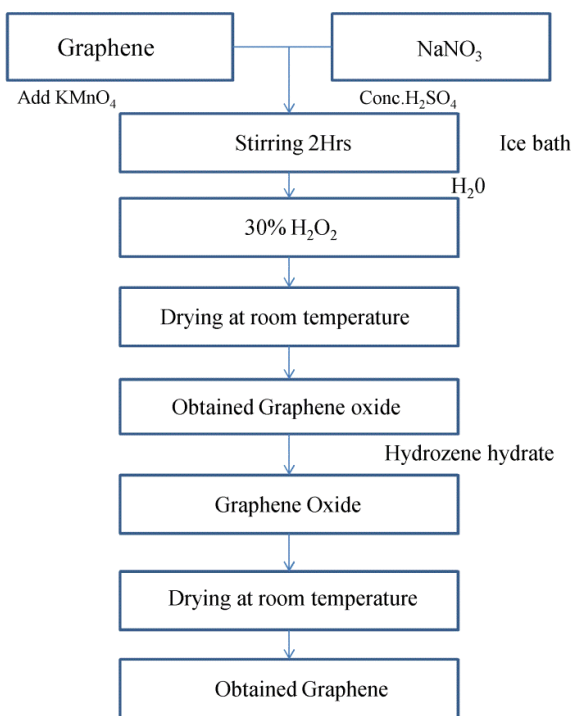
oxide and Fe<sub>2</sub>O<sub>3</sub>. Enlightened by these forge works, it is believed that the nanostructured Fe<sub>2</sub>O<sub>3</sub>-graphene composite will be a promising candidate for great performance Supercapacitors.

**II. MATERIALS AND METHODS**

*A. Graphene Synthesis Methods*

Different techniques have been performed to synthesis graphene sheets such as epitaxial growth by ultra -high vacuum graphitization, chemical oxidation of graphite and further reduction, chemical vapour deposition, solvothermal synthesis, sol-gel, ion-exchange and hydrothermal reduction. Among the various methods of graphene synthesis, electro chemical method is one of the simple and high yielding methods.

**Synthesis**



**Fig 1 Synthesis of graphene**

Graphene was synthesised by several methods, use Hummer’s method to synthesis graphene, 5 g of graphite is added 2.5 g of Sodium nitrate (Na (NO<sub>3</sub>)<sub>2</sub>) and 115 ml of concentrated sulphuric acid. The above mixture was stirred in ice both vigorously. Later the 15 g Potassium permanganate (KMnO<sub>4</sub>) was gradually added to maintain under the controlled temperature 20°C. Now the ice bath was removed, and the temperature was maintained at 35° C for half an hour. 230 ml of H<sub>2</sub>O was added slowly to the mixture and boiled, after 15 minutes, 700 ml of hot water and 12.5 ml of 30% H<sub>2</sub>O<sub>2</sub> is added. The sample solution was continuously stirred at 5 days. The solid mixture was washed with dil.HCl and H<sub>2</sub>O

respectively. The resulting solid was dried at 50°c for 3 days; obtain the fine graphene oxide powder. The obtained graphene oxide (GO) 0.1g was taken in round bottom flank and 1 ml of hydrazine hydrate was added. This solution was reflux at 6 hrs. Finally the black precipitated graphene was obtained .The obtained powder was dried at 80°C.

*B. Iron Oxide Synthesis Method*

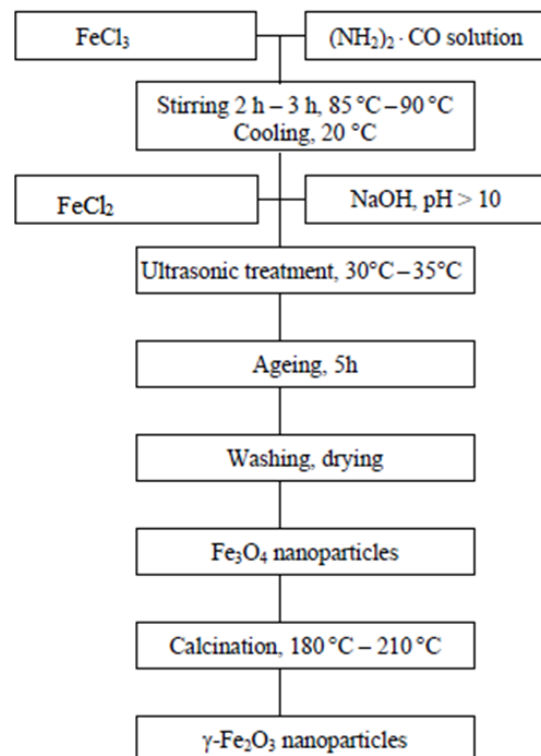
Decomposition (by sonolysis or thermolysis) of organometallic precursor is an important technique for synthesis of iron oxide. Nanoparticle growth can be limited by using polymers, organic capping agents or structural hosts. The very high temperature hot spot generated by rapid collapse of sonically generated cavities which allows for conversion of ferrous salts into magnetic nanoparticles. Oxide formation will also occurs if sonication is done in aqueous solution.

**Reagents used**

- Ferrous chloride
- Ferric chloride
- Urea
- Sodium hydroxide

Wet chemical synthesis of iron nanoparticles was based on hydrolysis of Fe<sup>3+</sup> and Fe<sup>2+</sup> salts in the presence of urea and sodium hydroxide.

**Synthesis**



**Fig 2 Synthesis of Iron oxide**

The  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_2)_2\text{CO}$  were dissolved in water at 85 – 95 °C for 2 - 3 h. The solution of  $\text{FeO}(\text{OH})$  precipitations was cooled down to 20 °C and  $\text{FeCl}_2$  and  $\text{NaOH}$  was added until the  $\text{pH} > 10$ . The  $\text{FeO}(\text{OH})/\text{Fe}(\text{OH})_2$  precipitation was treated by ultrasound in the sealed flask at 30 – 35 °C for 10–30 min in order to enhance interaction between the hydrolysis products. After aging for 5h the obtained black powder was washed and dried. The calcination of the pre-prepared  $\text{Fe}_3\text{O}_4$  powder in air at temperature 180 –210 °C led to formation of  $\gamma\text{-Fe}_2\text{O}_3$ .

### GRAPHENE AND $\text{Fe}_2\text{O}_3$ COMPOSITE PREPARATION

The Nanostructured  $\text{Fe}_2\text{O}_3$  was mixed with graphene in the weight ratio 1:3 to obtain the graphene and  $\text{Fe}_2\text{O}_3$  composite.

### III. CHARACTERISATION

#### Characterisation Techniques

Various techniques were used for characterizing of synthesized nanoparticles. They are X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Particle size analysis, scanning electron microscope (SEM) with EDAX.

#### A. X-Ray Diffraction (XRD) Analysis

The crystalline nature and phases of prepared samples were analysed by X-ray powder diffraction patterns (X' Pert-Pro) using  $\text{Cu K}\alpha$  as a radiation (1.54060) source. The diffract meter was operated at 40KV with a current of 30mA and the scans were performed over a  $2\theta$  range from 10.0251 to 79.9251 with an increment of 0.05. The peak positions and the relative intensities of the powder pattern were identified in comparison with the reference powder diffraction data (JCPDS). The average crystalline size of the samples was identified using Scherer's formula.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is the crystalline size, K is the shape factor (0.9),  $\lambda$  is the wavelength of the X-ray,  $\beta$  is the line broadening at half the maximum intensity (FWHM) in degrees and  $\theta$  is the Bragg's angle in degrees.

#### B. Fourier Transforms Infrared Spectroscopy (FT-IR) Analysis

An FTIR spectrum of synthesized samples were obtained employing Perkin Elmer infrared spectrometer (Perkin Elmer infrared spectrum 100, Waltham, MA) in the frequency range 4000–400  $\text{cm}^{-1}$  using KBr pellet method. The transparent discs of 13mm diameter were made by pressing the mixture, which contains 10 mg of nanoparticles with 100 mg of IR grade KBr at a pressure of about 110Kg/cm<sup>2</sup>. The resulting spectrum with back ground correction of KBr peaks represents the molecular adsorption and transmission of IR waves, thus creating a molecular fingerprint of the samples.

#### C. Particle Size Measurement

The diameter and particle size distribution (d10, d50 and d90) of the prepared HAp and metal doped HAp nanocomposites were determined with a submicron size Particle Size Analyser (PSA) (DLS, Nanophox; Sympatec, Clausthal-Zellerfeld, Germany) through the dynamic light scattering technique. The diameter and distribution of the particles in suspension was measured through this method. The particle size measurements of all the samples were performed in the particle size range of 1-500 nm with a scattering angle of 90°. The particle size and stability of the particle were measured employing the three dimensional cross correlation techniques. The light source used was Helium-Neon (He Ne) laser with a maximum intensity of 10 mw at a wavelength of 632.8 nm. All the prepared samples were dispersed in ultrapure water under sonication prior to its measurement. The particle size for all the samples was measured for the ultrasonically dispersed colloidal HAp solution.

#### D. Scanning Electron Microscope (SEM) with EDAX

The morphology and composition of prepared samples (FT350 and FT 500) was examined using scanning electron microscope (SEM) (JSM-6390LV; JEOL, Japan) and energy dispersive spectrometer (EDAX) (JED-2300; JEOL).

### IV. RESULTS AND DISCUSSIONS

Figure.3 shows the plot of the XRD pattern measured for sample (b) nanoparticle powder. There is a distinct absence of any diffraction peaks in the spectrum, which is indicative of its amorphous nature. In contrast sample (a), exhibited well defined diffraction peaks at diffraction angles of 26.35°, 36.97°, 40.2°, 45.78° and 53.32° corresponding to the crystal planes of (012), (110), (113), (202) and (116) respectively and hence is considered to be representative of an Rhombohedral crystal structure (JCPDS file no:(33-0664)). Moreover no Stacking peak was detected in the composite sample which reveals that the sample is highly disordered stacking with low degree of graphitization. These results show that the composite sample consists of disorderly stacked graphene and well crystallized Iron Oxide nanoparticles. And also shows that the weakening diffraction intensity for composite when compared to the Iron Oxide sample.

Two different types of samples (a) and (b) were subjected into FT-IR spectral measurements, as reported in Figure.4. The plot of the spectral response shows that both the samples (a) and (b) exhibited a characteristic absorbance response at 1652 $\text{cm}^{-1}$ , which is considered to be due to the vibrational stretching of C=C. Furthermore, the absorbance band in wave number region of 1133  $\text{cm}^{-1}$  for the samples (a) and (b), is attributed to vibrational mode of C-O while the sharp absorbance band located in the region of 490-610  $\text{cm}^{-1}$  corresponds to the vibrational stretching mode of Fe-O.

The plot in Figure 5 shows the particle size distribution of the Iron oxide and composite (Iron oxide + Graphene) samples. The plot reveals that the average particles for Iron oxide and

composite samples are 331 nm and 680 nm respectively. The size variation of the particles is due to addition of graphene.

The surface morphology and corresponding elemental analysis for the sample (a) and (b) of iron oxide and its composite (iron oxide and graphene) nanoparticles are shown in figures 6 (a (i, ii) and b (i, ii) respectively. It is apparent from figure 6 (i) that the sample (b), exhibits greater agglomeration of particles, giving rise to a non-uniform surface morphology. In contrast, sample (a) surface exhibits a more uniform morphology with greater degree of long range order, with Nano cluster structure. The EDAX pattern of sample (a) indicates the presence of elements Fe, C, and O. The EDAX pattern of sample (b) shows the presence of elements Fe, C, and O which shows that the sample (b) is much higher purity than the sample (a).

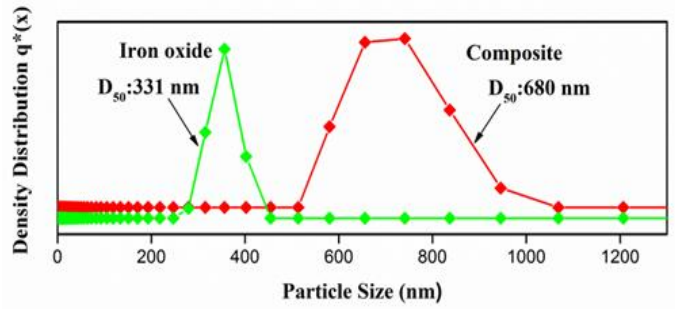


Fig. 5 Particle Size for iron oxide and it’s composite

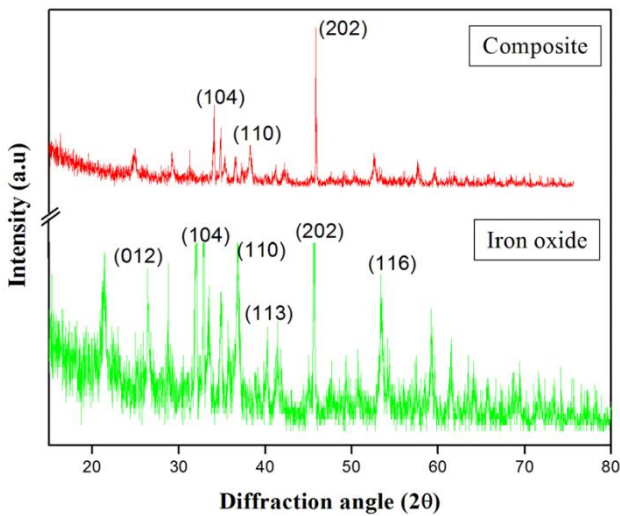
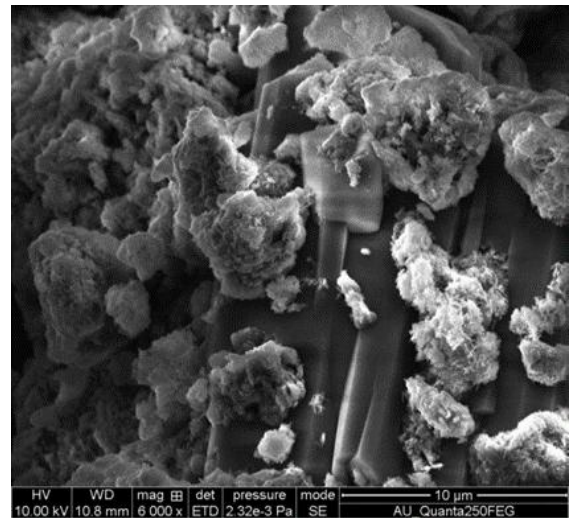


Fig. 3 XRD patterns of the Iron Oxide (a) and composite (b) nanoparticles



(i)

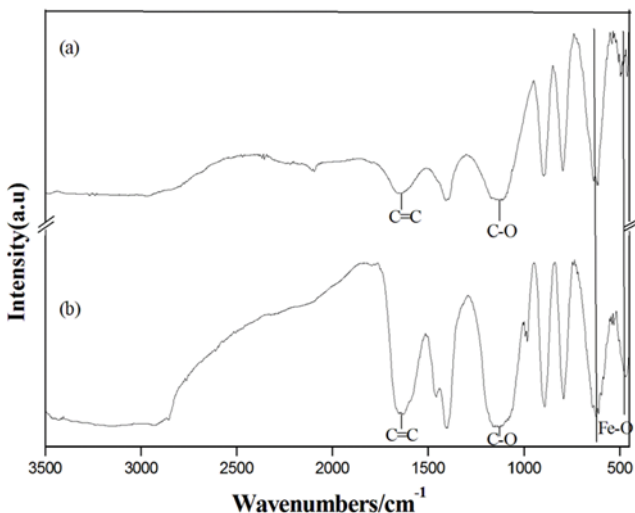


Fig. 4 FT-IR spectra of the Iron Oxide (a) and the composite (b) samples

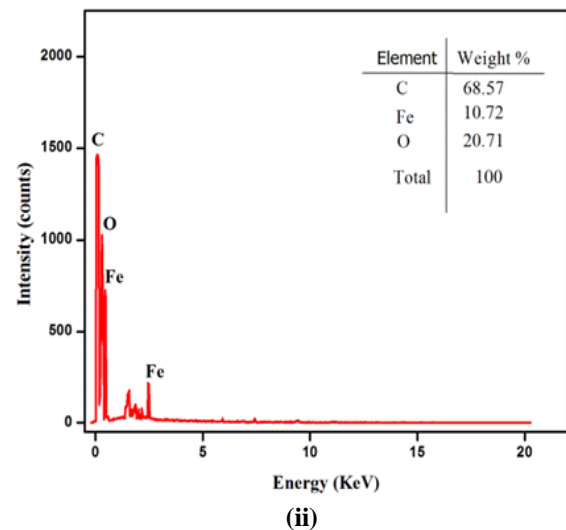
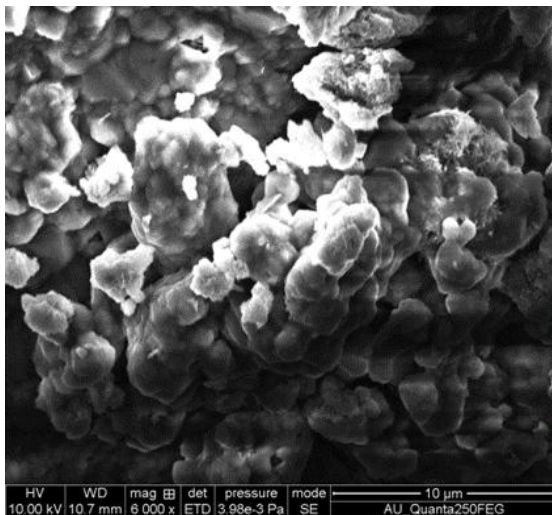
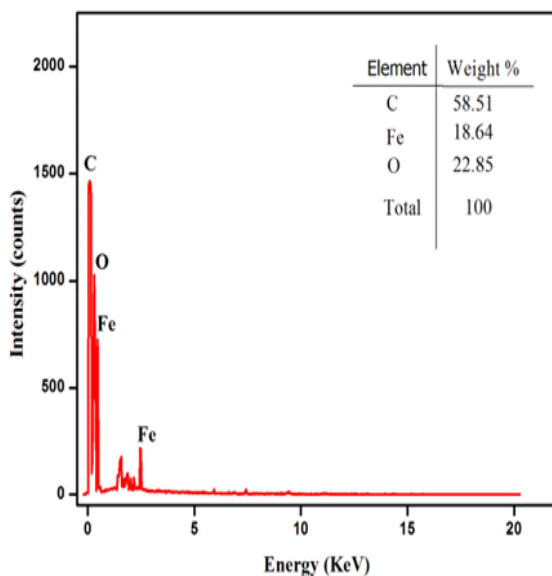


Fig. 6 (a) SEM (i) and EDAX (ii) Pattern of iron oxide Nano particles



(i)



(ii)

**Fig. 6 (b) SEM (i) and EDAX (ii) Pattern of Iron oxide and Graphene composite Nano particle**

## V. CONCLUSION

In summary, we have developed an efficient solution-based route for the synthesis of nanostructured Fe<sub>2</sub>O<sub>3</sub>-graphene composite. Various measurements confirm that well-crystalline Fe<sub>2</sub>O<sub>3</sub> nanoparticles with 331 nm in size are highly encapsulated in a graphene Nano sheet matrix. Results show that the Fe<sub>2</sub>O<sub>3</sub>-graphene nanocomposites exhibits good performance and it is applicable for Supercapacitor application.

The superior performance of the Fe<sub>2</sub>O<sub>3</sub>-graphene is probably attributed to its unique nanostructure, which intimately combines the conductive graphene network with uniformly dispersed Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

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