

## Electronic Supporting Information (ESI)

# One pot synthesis of Graphene /iron oxide nanocomposite by simple ultrasonication followed by microwave irradiation its Application

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### S-1. Experimental

**Chemicals.** Graphitic flakes (Reinste nano ventures), ethanol (absolute, AR, Merck) Iron nitrate nonahydrate (LR, Merck), ethylene glycol LR, Merck), citric acid (LR, Merck), sodium oxalate (AR, Merck), potassium permanganate (AR, Merck), stannous chloride (AR, Merck), mercuric chloride (AR, Merck), manganese sulphate (AR, Merck), phosphoric acid (AR, Merck), conc. sulfuric acid (AR, Merck), conc hydrochloric acid (AR, Merck), potassium dichromate (AR, Merck), potassium iodide (AR, Merck), sodium thiosulphate (AR, Merck), sodium bicarbonate (AR, Merck), starch indicator (AR, Merck), PVAc (Pidilite Industries) was used without further purification.

**Instruments.** Sonication was conducted by using ultrasonication bath (35 kHz, Kudos). Microwave irradiation was carried out by a microwave reactor (make :Raga) ESEM was carried out with Quanta 200, FEI. High resolution transmission microscopy (HRTEM images, EDAX, SAED pattern) characterization was carried out by TACHNAI F-30, FEI with 300 kV field emission gun(FEG). Nano Fe<sub>2</sub>O<sub>3</sub>, graphene and graphene-iron oxide nanocomposite was dispersed in methanol with ultrasonication. The dispersion was placed on TEM grid. Solvent was evaporated by oven drying. Fourier Transform Infrared Spectroscopy(FTIR) were collected by Nicolet 5700, ThermoScientific. Raman traces and mapping were measured by Invia relex micro raman, Renishaw. X-Ray Defraction traces were collected by X- Ray Defractometer D8 advance, Bruker with Cu K $\alpha$  source at measurement angle range  $2\theta=2-90^\circ$  with a scan rate  $2^\circ/\text{min}$ . Differential Scanning Calorimetry (DSC) curves were collected by DSC-7, Perkin Elmer. Thermo gravimetric analysis(TGA) was carried out by Mettler Toledo, Model-TGA/SDTA851. The BET surface area was measured by nitrogen absorption using Gemini VII 2390t surface area analyzer (Micrometric, USA) The sample (0.2 g) was activated by heating at  $250^\circ\text{C}$  for 6 hrs under nitrogen gas purging. The obtained specific surface area (SSA) was converting in to particle size assuming that the particles are closed sphere with uniform surface and uniform size.

$$D_{\text{BET}} = 6000/(\text{SA} \cdot d)$$

Where  $d$  = density of iron oxide in  $\alpha$  phase (5.24 g/cc)

### S-2. Synthesis of nano iron oxide

The process is consists of two steps viz. polymeric gel preparation of citrate followed by gel calcination. Gel preparation is carried out in gel preparation unit and calcination carried out in calcination unit i.e. muffle furnace.

The gel preparation unit is consists of a dissolution vessel (make:PP; cap. 50 Litre, baffles and stirrer) and a cylindrical single jacketed glass vessels (cap. 50 Litre) with bottom discharge valve and multineck lid. The centre neck of the reactor is fitted with stirrer having two impellers with four blades each of hydrofoil design. Side necks of lid are fitted with thermo well, nitrogen blanketing dip tube, slurry feeding neck condenser (vapor neck is fitted with a PTFE below and manually operated reflux divider.

Water produced during the reaction are condensed in the multicoil heat exchanger (HTA~1.5m<sup>2</sup>) and collected in a 10 lit calibrated dean and stark vessel.

A silicon oil heated system with a 60 liter tank fitted with 2x2 kw heaters was connected to the glass reaction vessel for heating of reaction mixture through jacket of the reactor. 100 liter chilling plant is provided for pumping cold water to the heat exchanger. Several toxic gases e.g. Nox, CO, CO<sub>2</sub> are also produced during chemical reaction. These gases were scrubbed out using a unique venturi scrubber. For drying and calcination of polymeric gel, an electrically heated muffle furnace (capacity~ 800 liter) with exhaust system (exhaust duct, ID fan and chimney) was used. Furnace can operate up to maximum temperature of 1000°C with heating rate 5 °C per min.

A typical batch operation is as follows: solid citric acid and ferric nitrate nonahydrate were dissolved in ethylene glycol, in the dissolution vessel to get brown color solution. This solution was fed into the reactor using a dosing pump (wetted part SS316). The solution was slowly heated to 90°C by circulating hot thermic fluid (silicon oil) in the reactor jacket. An initial exothermicity was observed at reaction temperature ~100°C with evolution of NOx fumes which was controlled by stopping the circulation of hot thermic fluid in the reactor jacket. However, exothermicity subsided during the rest of the reaction period. Then hot oil circulation was started to the reactor jacket and temperature of reaction mass was increased from 100°C to 140°C.

Water molecules evolved during the reaction were condensed by a condenser using chilling water circulation in the tubes. Uncondensed gases were scrubbed by venturi scrubber. After collection of ~3.5L condensate, polymeric gel was discharged in SS 310 trays (3 kg each tray). Trays were kept inside the muffle furnace; the gel was first dried at 300°C for 2 hrs. under oxygen-rich atmosphere by purging compressed air. Evolved gases were exhausted through chimney by ID fan. Then dried gel was calcined at 600°C for 6 hours to get pure nano  $\alpha$  Fe<sub>2</sub>O<sub>3</sub>.

S-3:

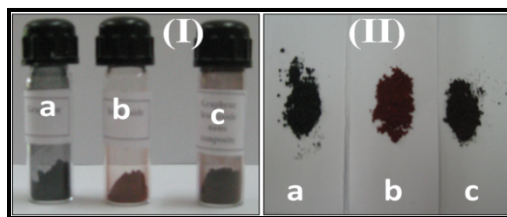
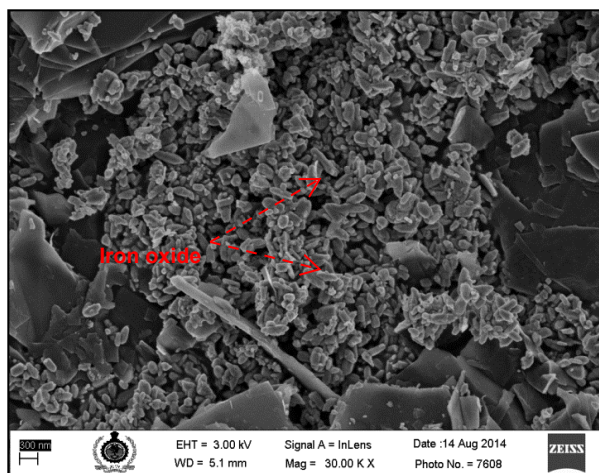
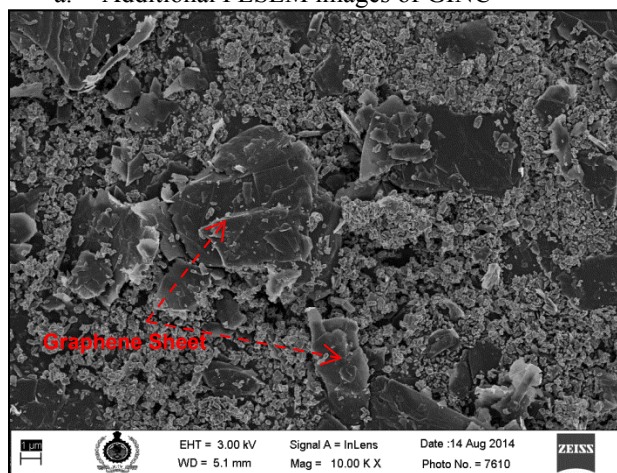


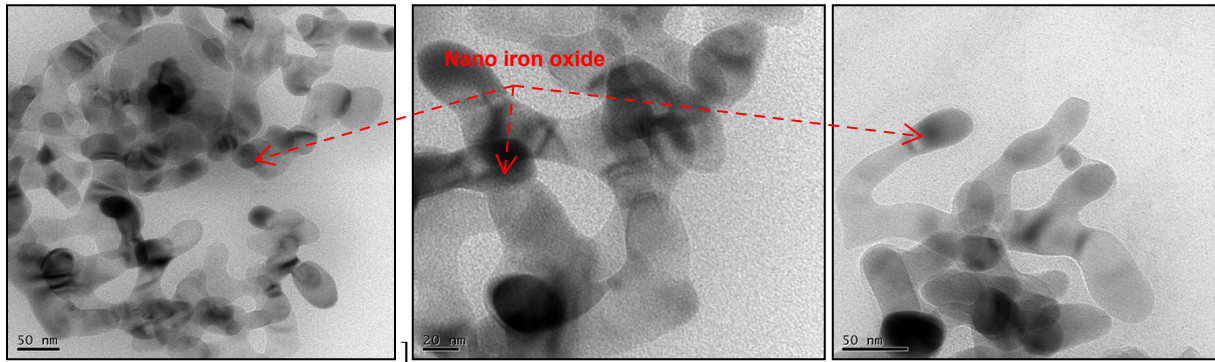
Photo of (a) graphene (black), (b) nano iron oxide (red) (c) graphene iron oxide nanocomposite (GINC, coffee colour)

#### S-4. Additional FESEM images HRTEM images

a. Additional FESEM images of GINC

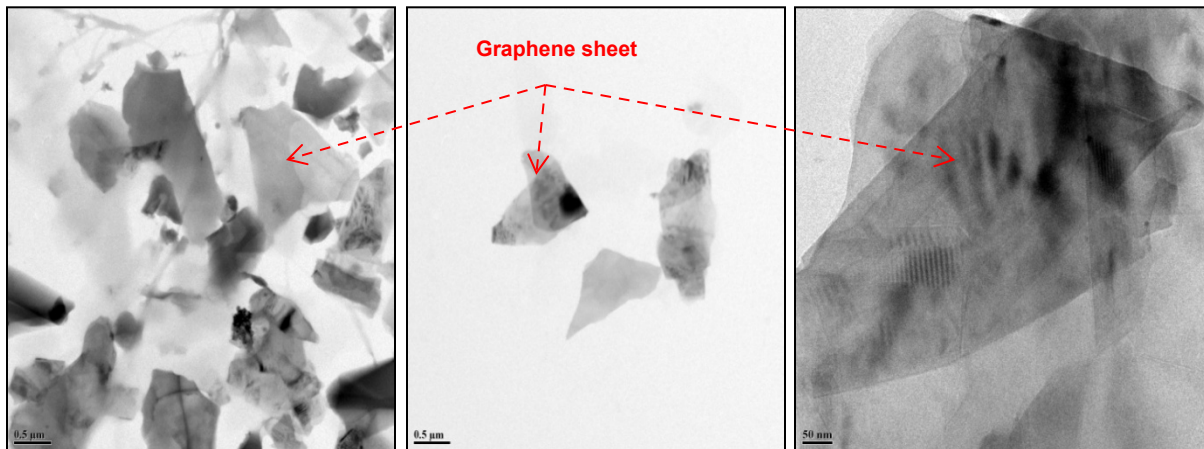


b. Additional HRTEM images of nano iron oxide



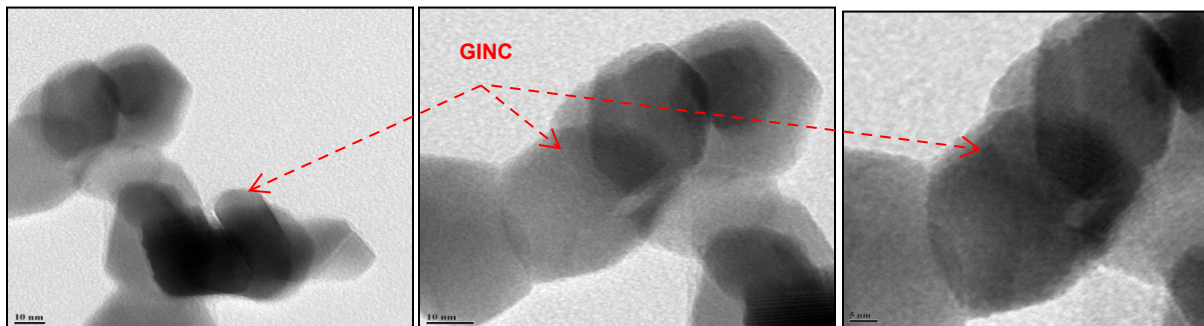
HRTEM images of nano iron oxide

c. Additional HRTEM images of Graphene



HRTEM images of Graphene

d. Additional HRTEM images of graphene- iron oxide nano composite(GINC)



HRTEM images of Graphene ironoxide nanocomposite(GINC)

**S-5. Raman mapping of Graphene iron oxide nanocomposite**

Raman scattering of pure graphene, nano iron oxide and the composite thereof were collected using the In via Reflex Dispersive Micro Raman spectrometer from Renishaw, UK. A 785 nm solid state laser line with 5% input power and 50x objective of microscope were employed to collect the scattered lines in the spectral range of 100 to 3200  $\text{cm}^{-1}$ .

For Raman mapping, data have been collected at  $\lambda = 632$  nm with a magnification of 100X. Mapping has been done over a designated area  $\sim 32$   $\mu\text{m}$ . It indicates following characteristics.

- 1) The major portion (shown in blue color) of the profile indicates  $\text{sp}^2$  bonded zone
- 2) However, the disordered zone (green shed) has been observed in the vicinity of Fe decorated zone (indicated by red color) functionally attached to graphene.
- 3) The zone of functionality seems to be deviated from  $\text{sp}^2$  bonding and varies with shed contrast.
- 4) None the less, in the vicinity of Fe particle, the amount of disorder looks to be very high
- 5) In fact, on the iron cluster, the surface Plasmon resonance seems to be having variable resonant frequencies and indicated by sky blue (at the periphery) and violet ultracore and yellow(core) zones.

Raman mapping helps to get an idea regarding the iron oxide decoration over graphene sheet.

### S-6: BET surface area calculation of Graphene, Iron oxide, and Graphene iron oxide nano composite

#### Analysis of BET surface area

Sr. No	compound	Size (plane), nm	$S_{\text{BET}}(\text{m}^2\text{g}^{-1})$	$D_{\text{BET}}(\text{nm})$	$D_{\text{BET}}/\text{Size}$
1.	Graphene	28 ( $D_{116}$ )	22	55	1.96
2.	Iron oxide	38 ( $D_{104}$ )	24	63	1.65
3.	GINC	<b>34(<math>D_{104}</math>)</b>	<b>46</b>	<b>43</b>	<b>1.26</b>

### S-7: Detail procedure for thermoelectric properties measurement

The electrical conductivity of our samples was measured with four probe instrument ( using Delta mode techniques by coupling Keithley 6220 as current source and Keithley 2182A as nano voltmeter, and labview software). The detail procedure is as follows. Electrical conductivity( $\sigma$ ) is the reciprocal of electrical resistivity( $\rho$ ). Electrical resistivity has been calculated from resistance by following equation

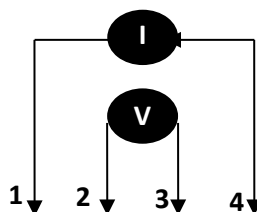
$$\rho = (V/l) / (I/wt)$$

where, V=voltage, l= spacing of the probe tips, w=width, t= thickness, I= current

$$\sigma = 1/\rho$$

where  $\sigma$ = electrical conductivity

Four probe measurement of electrical conductivity is shown in the figure. Though two contact points is necessary for applying current (I) and measuring voltage (V) of the material. But, four probe method eliminate any contact resistance, electrical noise which are the main error during electrical resistivity measurement. The thickness of the sample has been measured by digital micrometer.



**Sample**

**Substrate**

The used probe head set up in this experiments contains four gold pins with a equal spacing.

**S-8:** Summary of thermoelectric properties of the best composite of inorganic and organic materials.

Thermoelectric materials	$\sigma$ , S/m	$S$ , $\mu\text{V/k}$	$\kappa$ , W/mK	Calculated PF ( $S^2\sigma$ ), $\mu\text{W m}^{-1}\text{K}^2$
PANi + SWCNT composites with different SWCNT [Ref. 59]	10-125 (RT)	11-40 (RT)	0.5-1 (RT)	0.5-5 (300K)
PANi+ unoxidized SWCNT [Ref.60]	$5.30 \times 10^4$	33		0.6
PANi+ HCL+ MWCNT(40%) [Ref.61]	$1.71 \times 10^3$	10	--	0.17
PANI+CNT (15.8%) [Ref: 62]	$6.1 \times 10^3$	29	0.4-0.5	PF=5
CNT+graphite+polylactic acid [Ref. 63]	$4.123 \times 10^3$	17	5.5	ZT= $7.2 \times 10^{-5}$ at RT
P3HT+MWCNT (30%) [Ref.64]	11	11.3 at 493K	--	--
P3HT+MWCNT (5%) [Ref. 65]	$1.31 \times 10^{-1}$	131	--	--
P3HT+SWCNT (81%)	$1.8 \times 10^4$	32	0.13	18
P3HT+FeCl <sub>3</sub> + SWCNT (42-81%)	$1.1 \times 10^5$	29	--	95
P3HT+FeCl <sub>3</sub> + MWCNT (10-40%)	$8 \times 10^3$	29	--	6
P3HT+FeCl <sub>3</sub> + MWCNT (50%) [Ref. 66]	$1 \times 10^3$	12	0.16	0.2
PEDOT:PSS+CNT(35%) [Ref. 67]	$4 \times 10^4$	--	0.2-0.4	ZT=0.02
PEDOT:PSS+ SWCNT(20-95%) [Ref. 68]	$6 \times 10^4$ - $3.6 \times 10^5$	15-28	0.56	42-95
Nafion +MWCNT (10-50%) [Ref.69]	0-8	20-26	--	0.5
Nafion +FWCNT (10 -50%) [Ref. 63]	0-13	17-24	--	0-1
Nafion +SWCNT (10-50%) [Ref. 63]	0-1	25-30	--	0.1-0.2
Graphene [Ref. 70]	$10^6$	5000	--	ZT= 0.006 at 300K
PANi/Graphene composite [Ref. 71]				
PANi	$10^3$	14	--	0.2
Graphene	$2 \times 10^4$	15	--	8
<b>Pallet :</b> PANi :Graphene:: 4:1 to 1:1	$1.4 \times 10^3$ - $5 \times 10^3$	20-30	--	0.7-5.6
<b>Film</b> PANi :Graphene:: 4:1 to 1:1	20-700	27-41	--	0.04-1.2
PANi + HCL +Graphene (50%) [Ref. 72]	123	34	3.3	14
PANi+GNP (In situ polymerization with protonation ratio- 0.2)				ZT (300K)=
Neat PANi	150	7	0.6	$3.68 \times 10^{-6}$
Neat GNP	$2 \times 10^4$	5	74	$3.04 \times 10^{-6}$
PANi/GNP (50mM, as made)	5900	33	13	$1.51 \times 10^{-4}$
PANi/GNP (50mM, reprotonated)	$1.74 \times 10^4$	19	15	$1.26 \times 10^{-4}$

[Ref.73]				
PANI + 30% Graphene [Ref. 74] (Insitu polymerization)	$5 \times 10^3$ at 323K	12	--	ZT= $1.95 \times 10^{-3}$ at 453 K
PANI at 420K	500	13	--	0.1
PANI + 5-30% Graphene [Ref. 74].	$700-4.0 \times 10^3$	28-32	--	0.4-2.6
PANI+HClO <sub>4</sub> +Graphite (50 wt.%) [Ref. 75].	$1.2 \times 10^4$	19	1.2	1.2
PEDOT:PSS+GNP(2-3%) [Ref. 76]				
PEDOT:PSS + GN (1-4%)	74-3170	44.75-165.8	0.14-0.30	
PEDOT:PSS/Graphene (1-5%) [ Ref. 77]	52800-63700	21.750-26.778	--	PF= 26.444-45.677

## S-9: References

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