

Supporting Information

Facile synthesis of one dimensional graphene wrapped carbon nanotube composite by chemical vapor deposition

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S1. Detailed Experimental section

Synthesis of Graphite Oxide: Graphite oxide was prepared according to Modified Hummers method.¹ SP-1 (Bay Carbon) graphite was used as the starting material. Briefly, graphite was grounded with NaCl and washed with DI water followed by filtration. After drying, the filtrate was stirred with conc. H₂SO₄ for 8h. 6 g of KMnO₄ was gradually added while keeping the temperature less than 20°C. The mixture was stirred at 35 to 40°C for 30 min and 65 to 80°C for 40 min. 92 ml water was added to the above solution and heated to ~ 100°C. This was diluted by adding 280 ml of water followed by the addition of 30% H₂O₂. The mixture was washed followed by repeated centrifugation and filtration (first by 5 % HCl and then with water). The final product was washed and dried in vacuum.

Synthesis of catalyst for carbon nanotubes (MmNi₃)

CNTs were synthesized using a single stage furnace thermal CVD facility by catalytic decomposition of acetylene over misch metal (Mm) based AB₃ alloy hydride catalyst. These catalysts were prepared through hydrogen decrepitation route by performing several cycles of hydrogenation/dehydrogenation of the alloy using a seiverts apparatus.² Fine powders of alloy obtained after several cycles of hydrogenation/dehydrogenation were directly placed in a quartz boat and kept at the center of a quartz tube, which was placed inside a tubular furnace. Hydrogen (50 sccm) was introduced into the quartz tube for 30 min at 500 °C, and then furnace was heated up to 700 °C, followed by the introduction of acetylene for 30 min with a flow rate of 50 sccm. Acetylene flow was stopped, and the furnace was cooled to room temperature. Argon flow was maintained throughout the experiment.

Synthesis of Graphene

In order to understand the exfoliation of GO at different temperatures, graphite oxide was heated at 240°C and 500°C in hydrogen atmosphere. The resultant graphene samples are designated as graphene-240 and graphene-500.

Synthesis of Smooth Graphene wrapped CNT- Catalyst MmNi₃/GO-500

Fine powders of alloy hydride (MmNi₃) and graphite oxide (1:1) were grinded together in a mortar. The powder was sprinkled over a quartz boat and placed at the centre of the quartz tube in the furnace. Furnace was heated up to 500°C in argon atmosphere. After reaching the set temperature, argon flow was stopped and hydrogen was allowed for 30 min with the flow rate of 50 sccm. This was followed by heating up to 700°C in argon atmosphere. Acetylene was allowed for 30 min with a flow rate of 50 sccm at this temperature. Acetylene flow was stopped, and the furnace was cooled down to room temperature in argon atmosphere. As prepared graphene wrapped CNT was purified by refluxing in concentrated nitric acid at 60°C for 6h. The as synthesized sample is labeled as as-grown graphene-CNT-500 and the corresponding purified sample as graphene-CNT-500.

Synthesis of wrinkled graphene wrapped over CNT-Catalyst MmNi₃/GO-240

1:1 ratio of GO and MmNi₃ kept at the centre of the quartz tube was heated in argon atmosphere up to 240°C. Hydrogen was allowed at this temperature for 30 min with the flow rate of 50 sccm, after stopping the argon flow. The rest of the reaction was performed under similar conditions as specified above. As prepared graphene wrapped CNT was purified by refluxing in concentrated nitric acid at 60°C for 6h. The as synthesized sample is labeled as as-grown graphene-CNT-240 and the corresponding purified sample as graphene-CNT-240.

Characterization

The XRD measurements were performed with a PANalytical X'Pert Pro X-ray diffractometer with nickel-filtered Cu K α radiation as the X-ray source. The pattern was recorded in the 2θ range of 5° - 90° . Field emission scanning electron microscopy (FESEM, Quanta 3D) imaging was used to examine the morphology of the synthesized samples. Samples were mounted on a standard aluminium specimen stub using double sided conductive carbon tape. The microscope was operated at an accelerating voltage of 5-30 kV depending on different imaging purposes. EDX spectra were recorded with Li doped Silicon X-ray detector equipped with FESEM. High resolution micrographs were obtained with FEI Tecnai G² transmission electron microscope operated at 200 keV. The samples were dispersed in ethanol and drop cast over holey carbon coated copper grid (200 mesh). The samples were dried over night in ambient atmosphere. Raman spectroscopy was performed on Witec Raman microscope using green (532 nm) laser excitation. Scans were taken on an extended range (500 - 3000 cm^{-1}) for an exposure time of 60 s. The samples were sprinkled over cleaned glass slides for observation and viewed under a maximum magnification of x20. FTIR was performed on Perkin Elmer spectrum one spectrometer in the range of 400 - 4000 cm^{-1} using KBr pellet method. Thermo gravimetric spectra were recorded with NETZSCH analyzer from ambient temperature to 850°C in air atmosphere with temperature heating of $10^\circ\text{C}/\text{min}$. UV-Vis spectra was recorded with JASCO V-570 spectrophotometer of different concentrations of all samples.

S2. X-ray diffractograms (XRD)

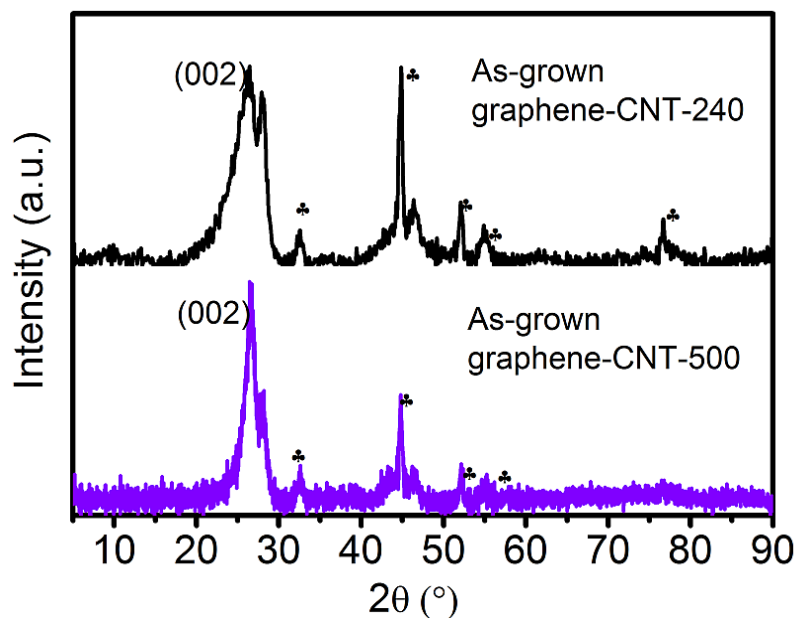


Figure S1: X-ray diffractograms of as-grown graphene-CNT-240 and as-grown graphene-CNT-500.

The XRD of as synthesized samples shown in **figure S1** exhibit peaks corresponding to metal catalyst impurities (denoted with stars) in addition to the graphitic (002) peak. The refluxing in conc. acid for a period of 6h, could completely eliminate the catalytic impurities.

S3. FESEM image and EDX spectrum of GO-MmNi₃ composite

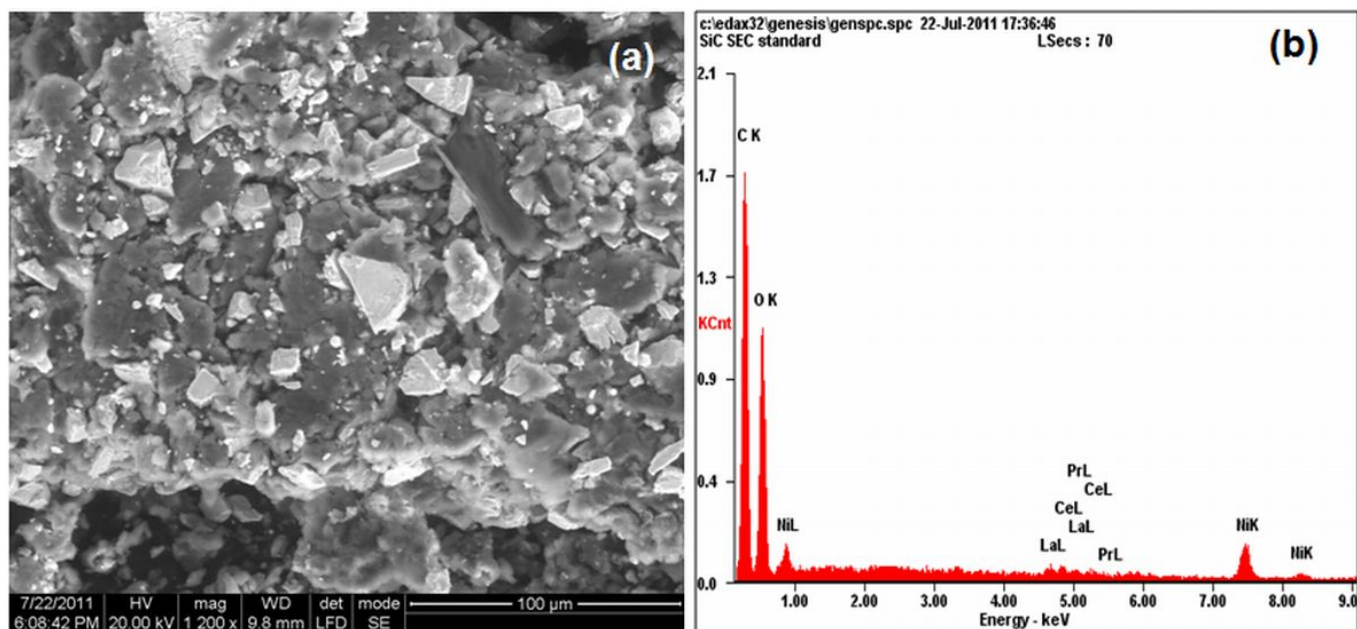


Figure S2: (a) Field emission scanning electron micrograph and (b) EDX spectrum of GO-MmNi₃ composite.

S4. FESEM images of graphene-500 and graphene-240

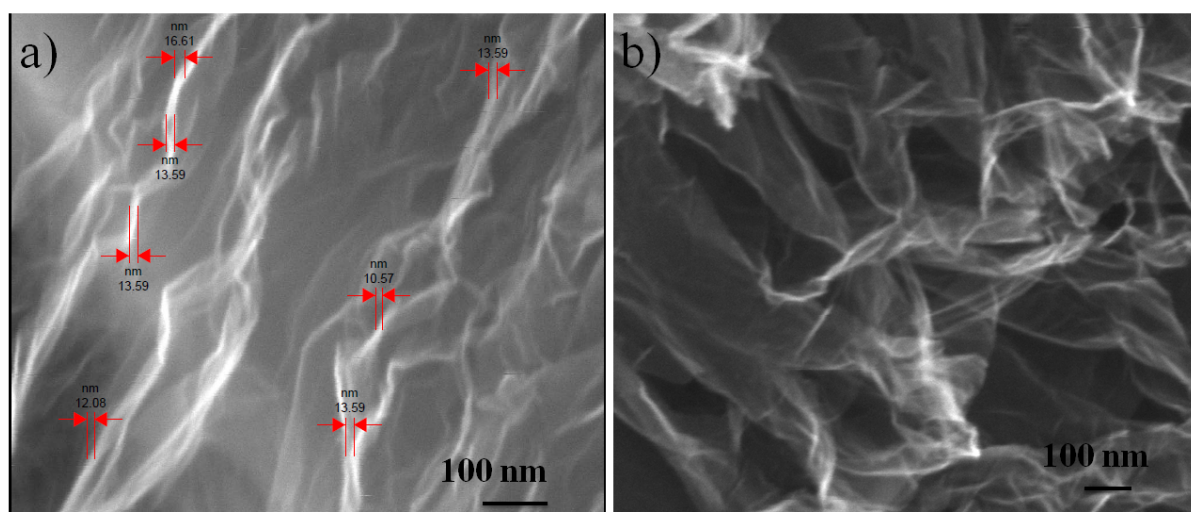


Figure S3: Field emission scanning electron micrographs of the graphene-500 and graphene-240
FESEM image of the graphene exfoliated at 500°C (**figure S2a**) in hydrogen atmosphere clearly reveals the formation of ~10-16 nm thick graphene flakes whereas graphene exfoliated at 240°C (**figure S2b**) exhibits more wrinkled morphology. This difference can be due to the more vigorous reaction of hydrogen with the functional groups present in GO at 240 °C.

S5. Higher magnification FESEM Imaging of graphene-CNT-500 and graphene-CNT-240

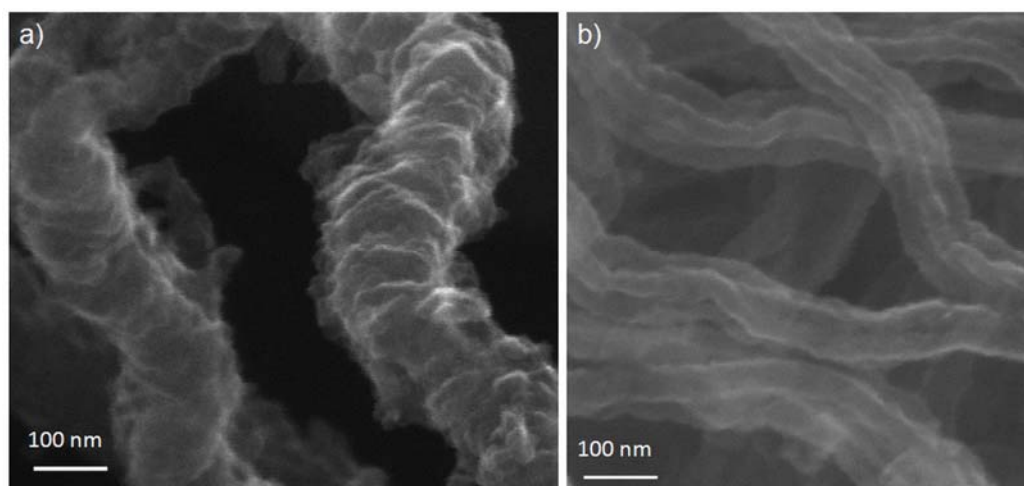


Figure S4: FESEM images of the graphene-CNT-240 and graphene-CNT-500

High resolution FESEM images has been shown in Fig.S3 in order to clearly differentiate the difference in the morphology of coating. The hypothesis of smooth and wrinkled layering of graphene over MWCNT can be obtained by tuning the growth procedures were substantiated by the FESEM images.

S6. TEM and lattice imaging of graphene-CNT-500

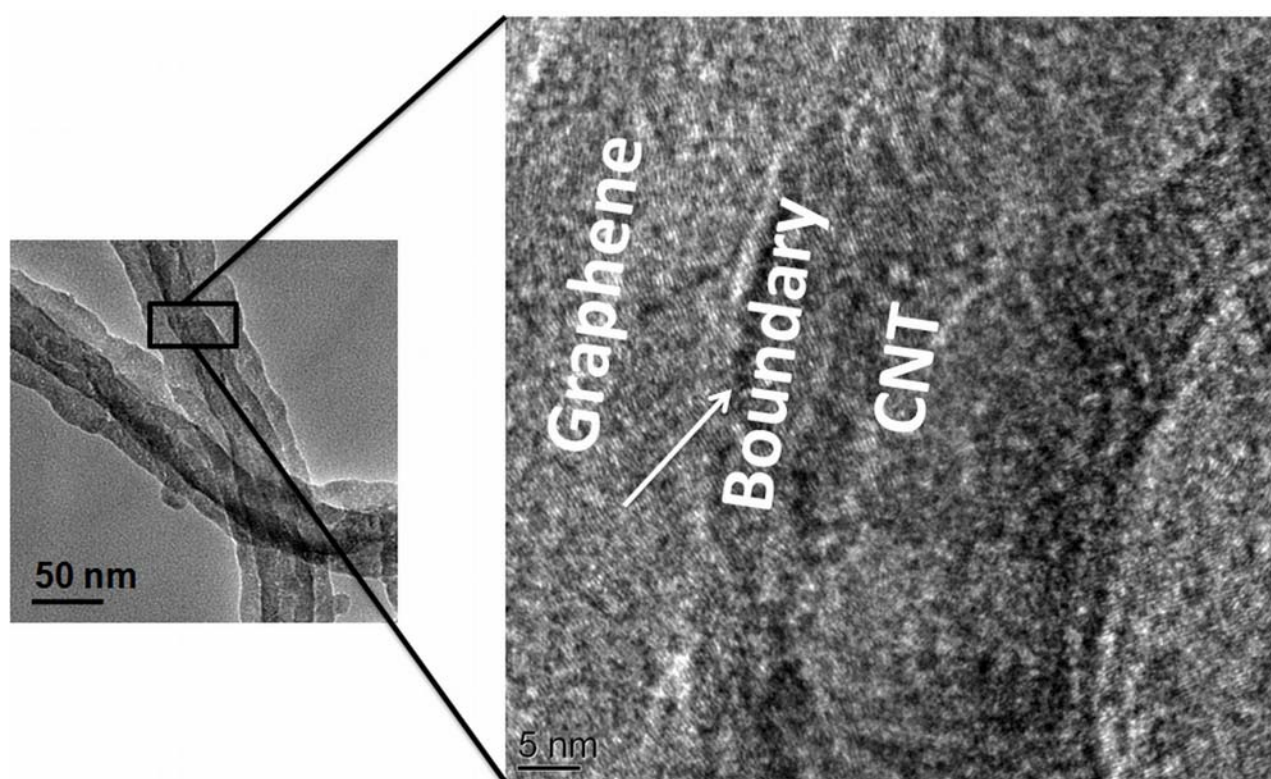


Figure S5: TEM and lattice image of graphene-CNT-500

In order to understand the interface of CNT and wrapped graphene, we have taken TEM micrograph and corresponding high resolution micrograph as shown in **figure S4**. It clearly reveals that the lattice lines of the graphitic structure are visible and we do not observe much changes in interplanar spacing in CNT and graphene region. This suggests that there is a probability of formation of pi-pi bonding between hexagonal network of graphene and CNT.

S7. FTIR spectra of GO, graphene-CNT-240 and graphene-CNT-500

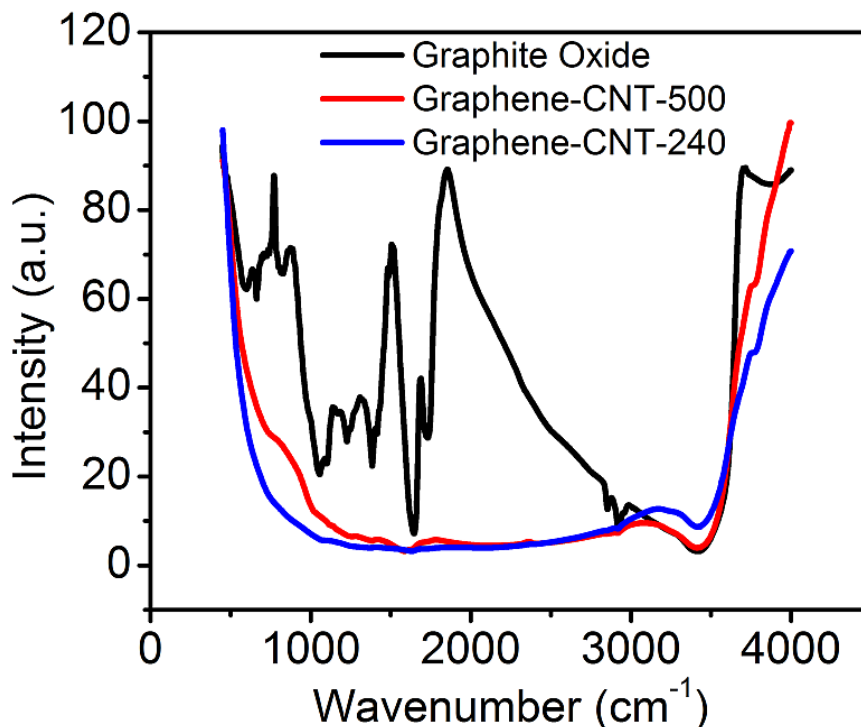


Figure S6: FTIR spectra of graphite oxide, graphene-CNT-240 and graphene- CNT-500

The FTIR spectra of graphite oxide, graphene-CNT-240 and graphene-CNT-500 are shown in **figure S5**. FTIR spectra of graphite oxide shows the most characteristic features at 3430 cm⁻¹ (O–H stretching vibrations) and the bands at 1726 cm⁻¹ (C=O stretching vibrations from carbonyl and carboxylic groups), 1588 cm⁻¹ (skeletal vibrations from unoxidized graphitic domains), 1226 cm⁻¹ (C–OH stretching vibrations), and 1103 cm⁻¹ (C–O stretching vibrations).³⁻
⁵ Thus FTIR spectra confirm the presence of hydroxyl, carbonyl and epoxide groups on basal planes of graphite oxide. The only prominent peak in the purified graphene-CNT-500 and graphene-CNT-240 nano composites is the O–H stretching vibrations at 3430 cm⁻¹. The absence

of any other functional groups substantiate the complete exfoliation of GO during synthesis of the hybrid nano composites.

S8. UV-visible spectrum of graphite oxide

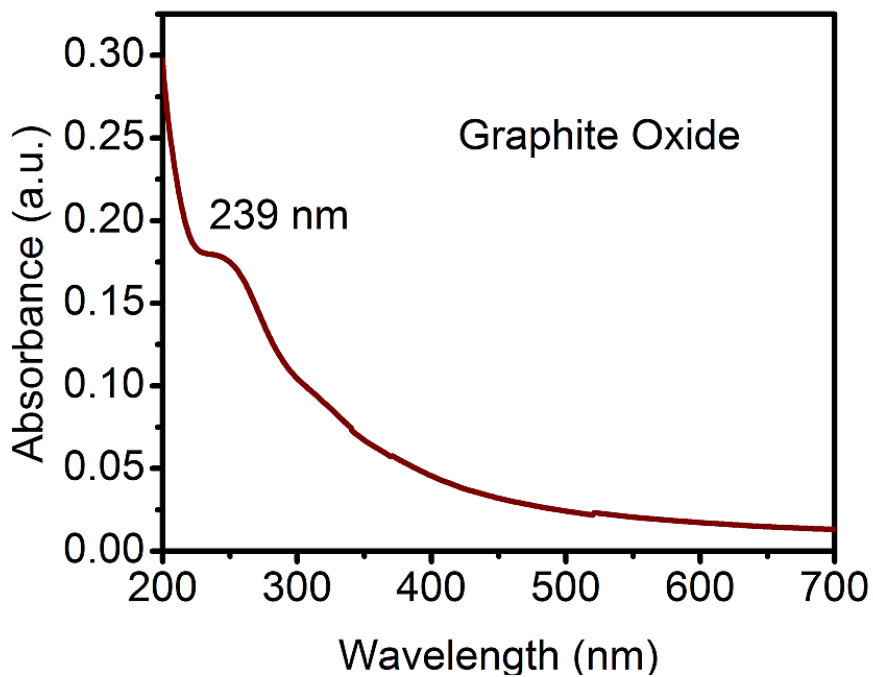


Figure S7: Uv-visible spectra of aqueous dispersions of graphite oxide

The UV-visible spectrum of GO showed a broad peak at 239 nm which after exfoliation shifted to ~285 nm, indicating the electronic conjugation of GO was restored.

S9. TGA and DTG of graphite oxide

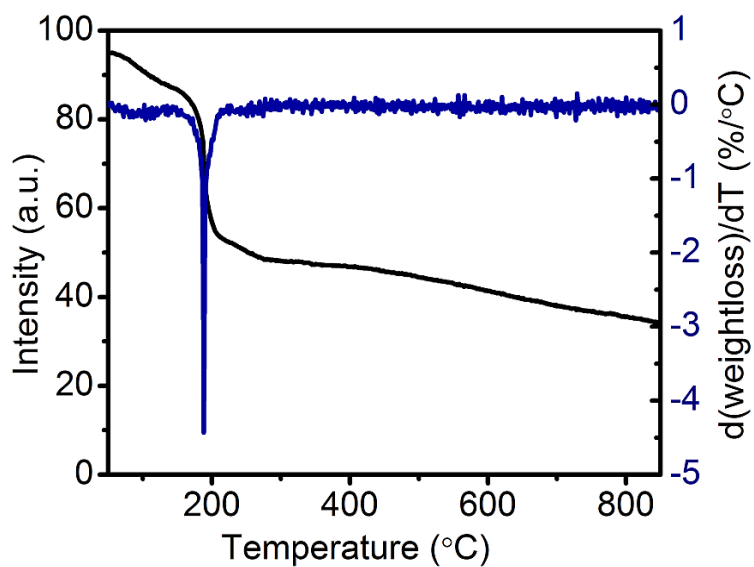


Figure S8: TGA and DTG of graphite oxide in air atmosphere

The TGA of GO exhibits nearly 40 % weight loss at 200°C, indicates the decomposition of labile oxygen functionalities on the basal planes of GO (**Figure S7**).

S10. TGA and DTG of as-grown graphene-CNT-240

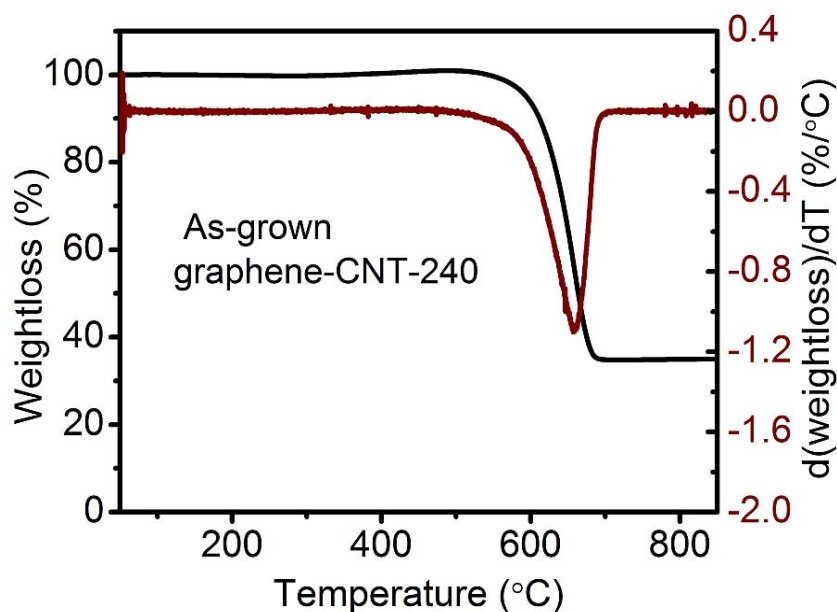


Figure S9: TGA and DTG curves of as-grown graphene-CNT-240.

The TGA of as-grown hybrid materials exhibits better stability as compared to that of precursor GO (**Figure S8, Figure S9**). The weight loss at 200° C was nearly 3% and 2.5% for graphene-CNT-240 and graphene-CNT-500 respectively. The decomposition temperatures also increased considerably from ~200°C for GO to nearly ~560°C for the hybrid nanocomposites, which indicates the highly stable nature of the composites. The purity of the samples were 65% and 60% for graphene-CNT-240 and graphene-CNT-500 respectively. The remaining may be due to metal catalysts and remanent carbon. After acid treatment process, the purity of the samples enhanced considerably to ~ 98 %.

S11. TGA and DTG of as-grown graphene-CNT-500

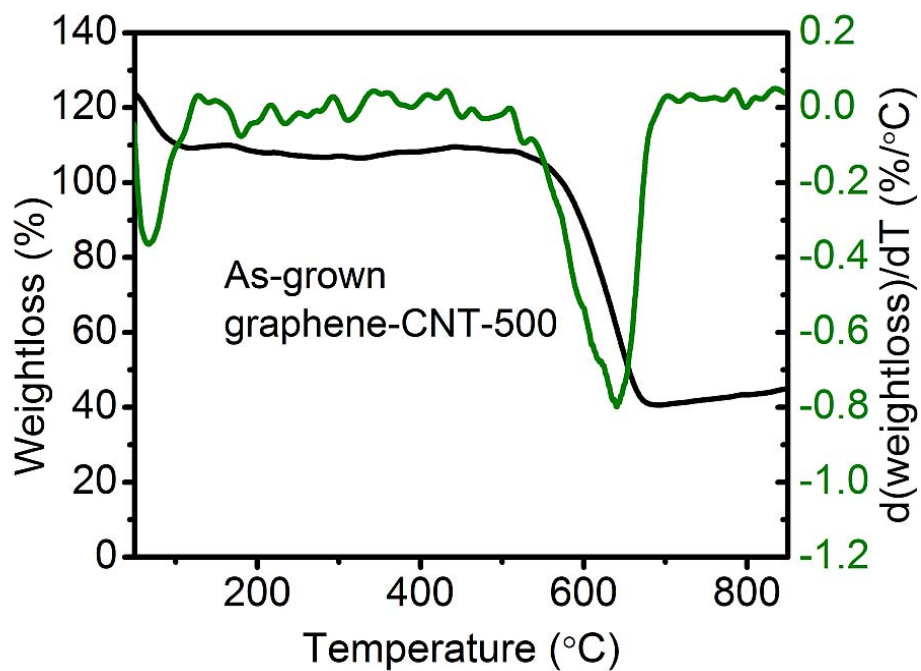


Figure S10: TGA and DTG curves of as-grown graphene-CNT-500.

S12. Raman spectra of as-grown graphene-CNT-500 and as-grown graphene-CNT-240

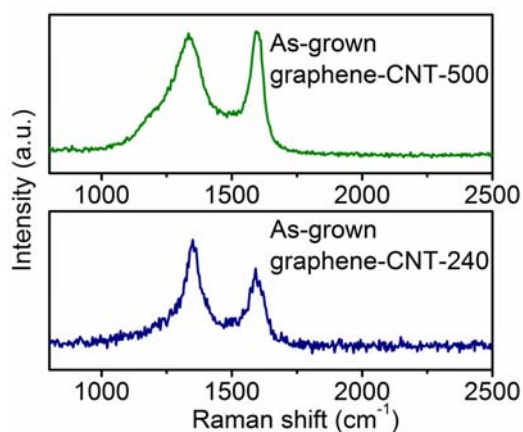


Figure S11: Raman spectra of as-grown graphene-CNT-240 and as-grown graphene-CNT-500

The Raman spectra of as-grown hybrid nanocomposites were shown in **figure S10**. The ratio of intensity of D band to G band for as-grown graphene-CNT-240 and as-grown graphene-CNT-500 were 1.42 and 0.93 respectively .

S13. Digital photographs of graphene-CNT-240 dispersions in DMF, NMP, ethanol and acetone.



Figure S12: Digital photographs of the graphene-CNT-240 dispersions in DMF, NMP, ethanol and acetone.

S14. Digital photographs of graphene-CNT-500 dispersions in DMF, NMP, ethanol and acetone.



Figure S13: Digital photographs of the graphene-CNT-500 dispersions in DMF, NMP, ethanol, acetone.

Figure S11 and figure S12 shows the dispersions of graphene-CNT-240 and graphene-CNT-500 in different solvents viz. dimethyl formamide (DMF), N-Methyl-2-pyrrolidone(NMP), ethanol and acetone. It clearly suggests that stable dispersions can be achieved with these novel hybrid composites of graphene and CNT. This is due to the creation of insitu defects while growing of carbon nanotubes in the presence of exfoliated GO as well as during purification.

S15. EDX spectra of graphite oxide and graphene-500

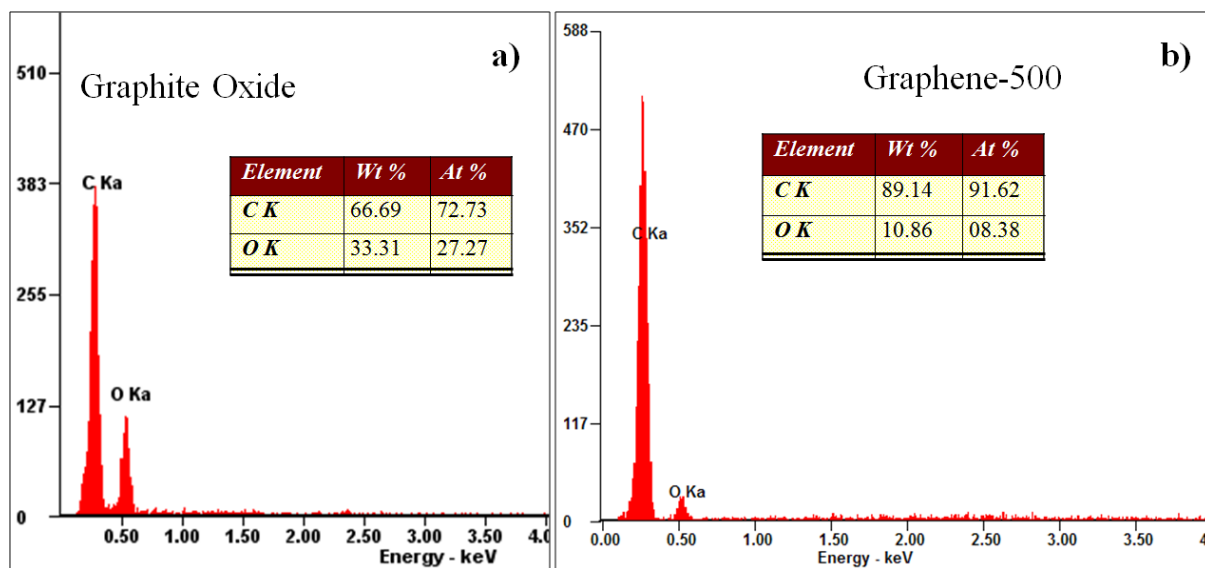


Figure S14: EDX of the graphite oxide and graphene-500.

S16 . EDX spectra of as-grown graphene-CNT-500 and graphene-CNT-500

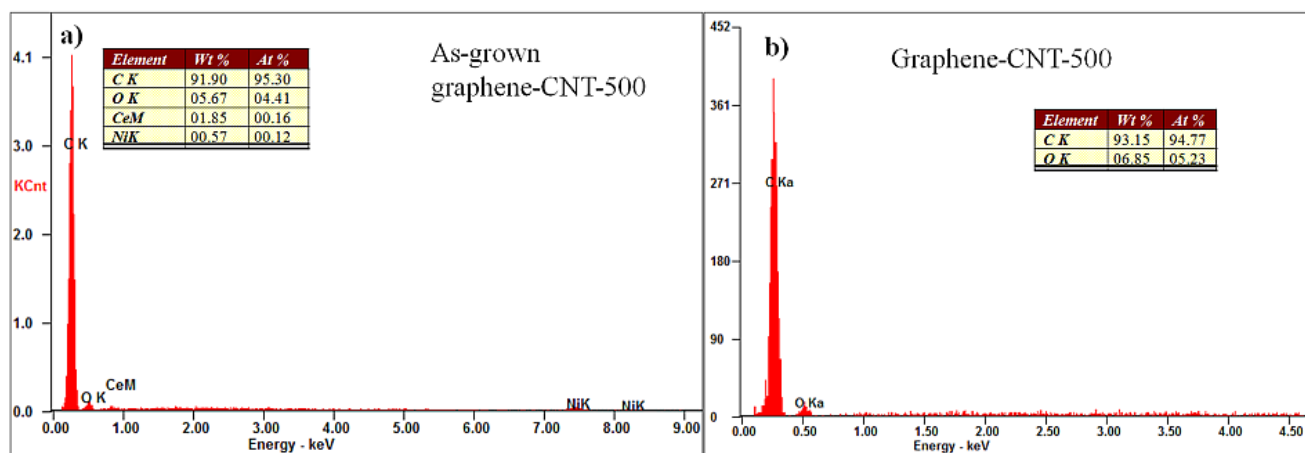


Figure S15: EDX spectra of as-grown graphene-CNT-500 and graphene-CNT-500 nanocomposites.

S17 . EDX spectrum of graphene-CNT-240

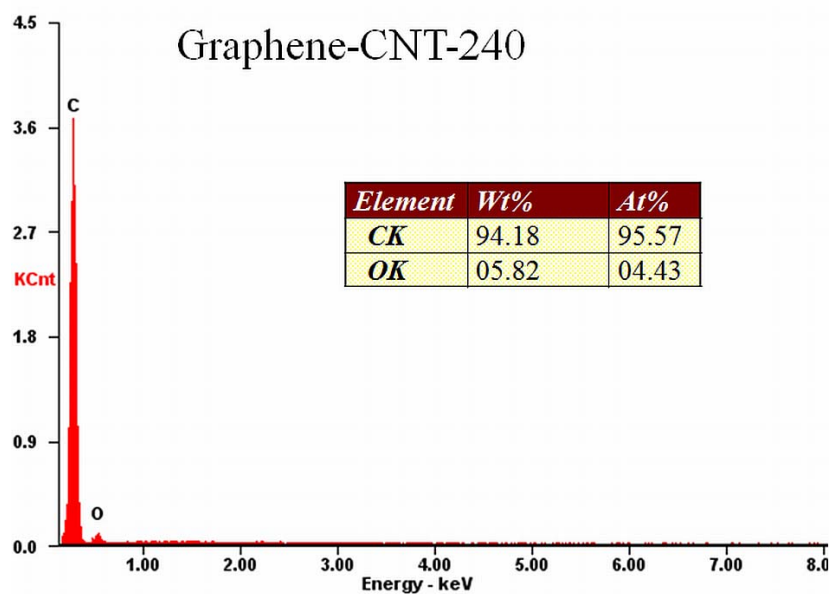


Figure S16: EDX spectrum of graphene-CNT-240 nanocomposite.

The atomic elements present in the as grown and purified samples has been characterized by Energy dispersive analysis of X-rays (EDX). **Figure S13a** shows the EDX spectra of graphite oxide which confirms the presence of carbon and oxygen observed at 0.265 eV (K_{α}) and 0.514 eV (K_{α}). The weight percentage of the oxygen in graphite oxide is ~33% due to the strong oxidation of the graphite structure by the oxidizing agents. After heating GO up to 500°C, the weight percentage of the oxygen shows 10 wt% due to the removal of oxygen functional moieties over graphite oxide (**Figure S13b**). It is similar to the thermal exfoliation but hydrogen was allowed at 500°C in order to understand the morphology and composition of the exfoliated graphite oxide at that particular temperature. **Figure S14a** shows the EDX of the as-grown graphene-CNT-500 hybrid composite which confirm the presence of oxygen, carbon and catalyst particles. After purification, all metal catalyst particles get removed and carbon shows the ~ 93% purity (**Figure S14b**). Similarly the EDX spectra of graphene-CNT-240 under similar conditions shown in **Figure S15** also confirm the purification process.

S18. BET surface area measurements of graphene-CNT-240, graphene-CNT-240, CNT and GO

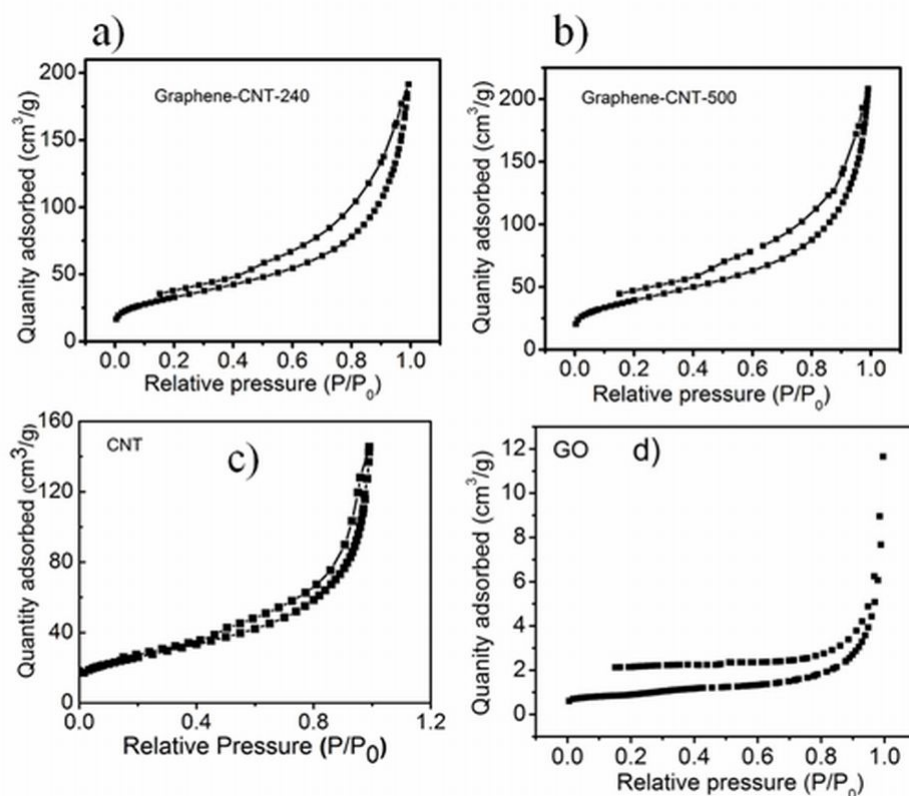


Figure S17: Surface area measurements of graphene-CNT-240, graphene-CNT-500, CNT and GO using Nitrogen adsorption-desorption isotherm curves.

References

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