Graphene Decorated with Hexagonal Shaped M-type Ferrite and Polyaniline Wrapper: A Potential Candidate for Electromagnetic Wave Absorbing and Energy Storage Device Applications

Pallab Bhattacharya,[a] Saptarshi Dhibar,[a] Goutam Hatui,[a] Avinandan Mandal,[a] Tanya Das,[b] Chapal K. Das[a*]

Supporting Information

Materials

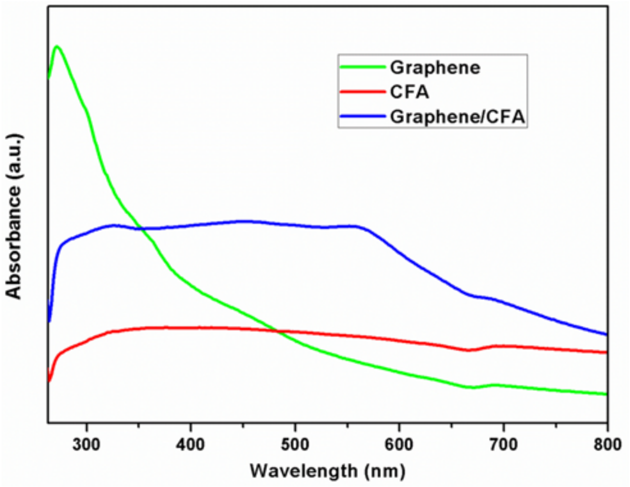
All the required metal nitrates [$Cu(NO_3)_2$, $Al(NO_3)_3.9H_2O$ and $Fe(NO_3)_3.9H_2O$] to prepare CFA, were purchased from Merck Ltd., India. Graphene (Sinocarbon Materials Technology Co. Ltd., China) was used as a component for the preparation of nanocomposites. HNO_3 and H_2SO_4 were used to prepare acid modified graphene and obtained from Loba Chemie Private Limited, India. Tetrahydrofuran (C_4H_8O, E. Merck Ltd., India) was used as a solvent for the preparation of MA. Sodium Hydroxide (NaOH, Loba Chemie Private Limited, India) was used as a precipitating agent. Cetyltrimethylammonium bromide (CTAB) [$((C_{16}H_{33})N(CH_3)_3Br$, Loba Chemie Private Limited, India] has played the role of a surfactant. All the chemicals and materials were used as purchased without any purification unless specified. The TPU (Lubrizol Advanced Materials, Thermedics TM Inc. Polymer Products, USA) used for developing MA belong with commercial medical grade aliphatic, polyether (TecoflexVR EG 80A injection grade). Tecoflex EG 80A (around 35% of hard segments) has shore hardness of 72A, specific gravity of 1.04, and its constituent formulation contains methylene bis (cyclohexyl) diisocyanate (HMDI) as hard segment, and polytetramethylene oxide (PTMO) as soft segment (molecular weight =1000 g/mol), and chain extender 1, 4-butane di-ol (BD). Aniline ($C_6H_5NH_2$) and ammonium persulfate [$(NH_4)_2S_2O_8$] obtained from Merck, India were used as the monomer and oxidant respectively. Hydrochloric acid (HCl) and potassium chloride (KCl) was supplied by Spectrochem Private Limited, India.

Characterization

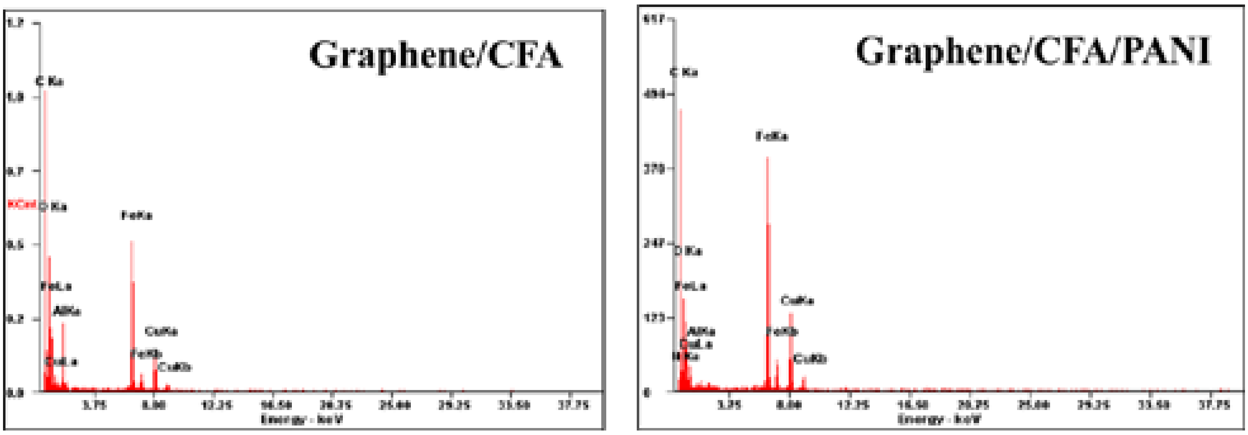
The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray Diffracrometer, ULTIMA III with Cu Kα radiation (λ=1.5418 Å) at a scanning of 1^0/min. X-ray photoelectron spectroscopy (XPS) of the prepared graphene/CFA composite was determined using a PHI Versa Probe 5000 calibrated system with Mg Kα radiation (hν =1253.6 eV). The binding energies (BE) were calibrated using the BE of C1s (284.6 eV). Fourier transform infrared (FTIR) spectra were carried out by using a NEXUS 870 FTIR (Thermo Nicolet) to detect the presence of different functional groups. The samples were prepared by mixing the composites with potassium bromide (KBr) in weight ratio of 1:10 and pelletized. Raman spectroscopic analysis of the prepared samples was performed at room temperature using Bruker Raman spectrometer with the powder samples. The Raman spectra were recorded at an excitation laser wavelength of 514.5 nm. UV-VIS spectroscopy of the samples was done in *N, N-dimethylformamide* (DMF) solvent by using Perkin Elmer, Lambda 750 Spectrophotometer. A Carl Zeiss-SUPRATM 40 field emission scanning electron microscopy (FESEM) with an accelerating voltage of 5 kV was used to understand the morphology of the nanocomposites. The transmission electron microscopy (TEM) images were taken by HR-TEM, JEOL 2100. Energy-dispersive spectroscopy (EDS) attached to TEM was performed to understand the chemical constituents present in the nanocomposites. Thermogravimetric analysis (TGA) of the composites was performed by using Dupont 2100 Thermogravimetric analyzer. The TGA measurements were conducted at a heating rate of 10°C/min under Nitrogen atmosphere from room temperature to 650°C. The magnetic properties were measured using a Quantum design Evercool SQUID-VSM magnetometer with an applied magnetic field strength over the range from −15 kOe to +15 kOe at room temperature. The frequency of VSM used for the measurement is 12.4 Hz. The DC electrical conductivity of the prepared composites was measured by a four probe method using Keithley DMM instrument (Lakeshore Resistivity and Hall measurement set up) having 220 programmable current sources. The frequency dependent AC conductivity was carried out using a computer-controlled precision impedance analyzer (Agilent 4294A) by applying an alternating electric field of 1volt amplitude. The thickness of the disk type materials was 0.5 mm and the electrode diameter was 11.4 mm. The frequency range of the AC conductivity measurement was maintained from 10^1 Hz to 10^6 Hz. Current–voltage (I-V) relationships of the nanocomposites were measured with the pellet samples, using a Keithley 2400 source meter (lab view 18.1 protocol). Microwave absorption study was done by using a two port vector network analyzer (ENA E5071C). Microwave absorption property of the prepared microwave absorbers was measured by using Transmission Line method. Relative complex permittivity (ε_r) and permeability (μ_r) was computed from the measurement of the reflected signal (S11) and transmitted signal (S21). Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) of the materials were carried out on Biologic sp-150 VMP-3 instrument using a three electrode system where platinum and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. CV measurements were performed in the voltage range of -0.8 to 0.8

V versus SCE. For the EIS measurements, a frequency range from 1 MHz to 0.1 Hz was applied.

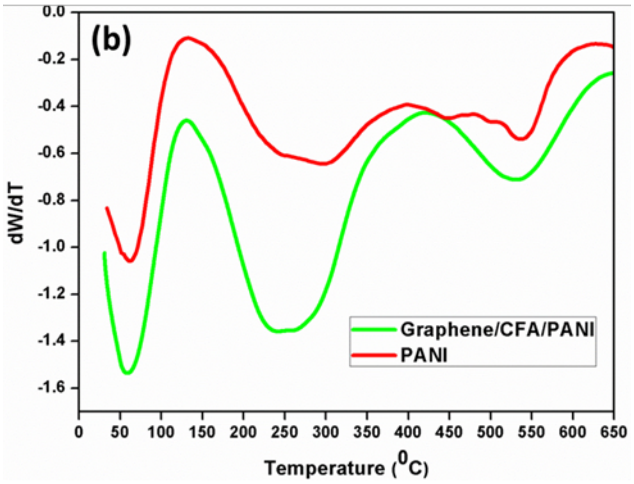
Figures:



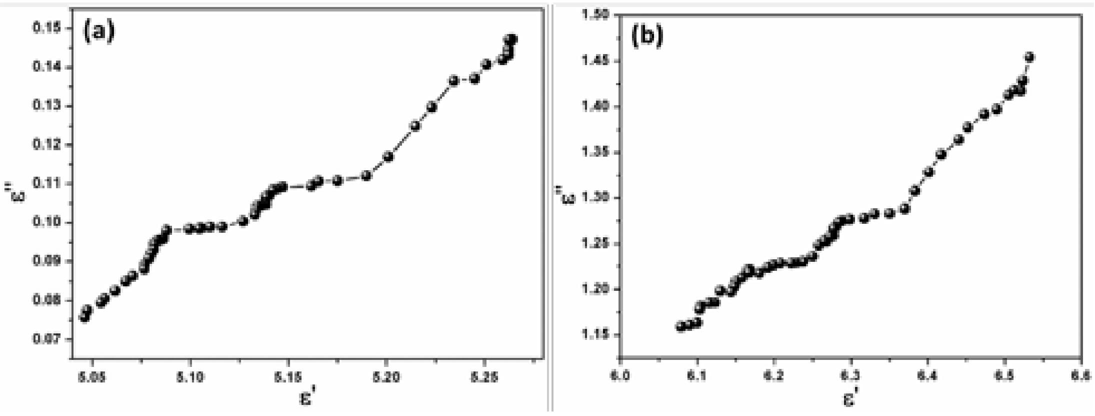
S1: UV-VIS spectra of acid modified graphene, CFA and graphene/CFA composite



S2: EDS Profile of graphene/CFA and graphene/CFA/PANI composite



S3: DTG plot of PANI and graphene/CFA/PANI composite



S4: cole-cole plot of (a) graphene/CFA and (b) graphene/CFA/PANI composite

Tables:

T1: Comparison of results obtained from magnetic measurements

Sample Name	M_s (emu/gm)	M_r (emu/gm)	H_c (Oe)	Reference
CFA	1.23	0.34	2395	[1]
Graphene/CFA	0.96	0.03	40	Present work
Graphene/CFA/PANI	0.76	0.012	21	Present work

T2: Comparison of results obtained from microwave absorbing measurements

Details of the Composites	**Maximum RL (-dB)**	**Thickness**	**Frequency Range Of Study (GHz)**	**Frequency range with R.L. > 10(-dB)**	**References**
Nickel coated graphene	16.5	1.5 mm	2-18	> 5 GHz	[2]
Hexagonal close-packed Ni nanocrystals/graphene nanosheet	17.8	5 mm	2-18	< 2 GHz	[3]
Expanded graphite/PANI/$CoFe_2O_4$	19.13	5 mm	2-18	-	[4]
Graphene/Fe_3O_4/PANI	26	2.5 mm	12-18	-	[5]
Reduced Graphene Oxide/Fe_3O_4	26.4	4 mm	0.5-18	< 2 GHz	[6]
Reduced graphene oxide/Fe_2O_3 Hydrogel	33.5	5 mm	1-18	-	[7]
Graphene/ Fe_3O_4@Fe/ZnO	38.4	5 mm	2-18	-	[8]
Graphene/Fe_3O_4 nanohybrids	40.36	5 mm	2-18	-	[9]
Reduced graphene oxide/PANI/Co_3O_4	44.5	3.3 mm	2-18	4.3 GHz	[10]
$NiFe_2O_4$ nanorod/graphene composites	44.6	4 mm	2-18	-	[11]
Graphene/PANI nanorod arrays	45.1 dB	2.5 mm	2-18	-	[12]
Graphene/$CuFe_{10}Al_2O_{19}$	60.7	2.5 mm	8.2-12.4	Whole X-band	Present Work
Graphene/$CuFe_{10}Al_2O_{19}$/PANI	63.6	2.5 mm	8.2-12.4	Whole X-band	Present Work

References

1. P. Bhattacharya, C. K. Das, *Ind. Eng. Chem. Res.*, 2013, **52**, 9594-9606.

2. J. J. Fang, S. F. Li, W. K. Zha, H. Y. Cong, J. F. Chen, Z. Z. Chen, *J. Inorg. Mater.,* 2011, **26**, 467-471.

3. T. Chen, F. Deng, J. Zhu, C. Chen, G. Sun, S. Ma, X. Yang, *J. Mater. Chem.,* 2012, **22**, 15190.

4. K. Chen, C. Xiang, L. Li, H. Qian, Q. Xiao, F. Xu, *J. Mater. Chem.,* 2012, **22**, 6449.

5. K. Singh, A. Ohlan, V. H. Pham, R. Balasubramaniyan, S. Varshney, J. Jang, S. H. Hur, W. M. Choi, M. Kumar, S. K. Dhawan, B. S. Kong, J. S. Chung, *Nanoscale*, 2013, **5**, 2411.

6. X. Sun, J. He, G. Li, J. Tang, T. Wang, Y. Guo, H. Xue, *J. Mater. Chem. C,* 2013, **1**, 765-777.

7. H. Zhang, A. Xie, C. Wang, H. Wang, Y. Shen, X. Tian, *J. Mater. Chem. A,* 2013, **1**, 8547.

8. Y. L. Ren, H. Y. Wu, M. M. Lu, Y. J. Chen, C. L. Zhu, P. Gao, M. S. Cao, C.Y. Li, Q. Y. Ouyang, *ACS Appl. Mater. Interfaces*., 2012, **4**, 6436-6442.

9. T. Wang, Z. Liu, M. Lu, B. Wen, Q. Ouyang, Y. Chen, C. Zhu, P. Gao, C. Li, M. Cao, L. Qi, *J. Appl. Phys.,* 2013, **113**, 024314.

10. P. Liu, Y. Huang, *RSC Adv.*, 2013, DOI: 10.1039/C3RA43073A.

11. M. Fu, Q. Jiao, Y. Zhao, *J. Mater. Chem. A,* 2013, **1**, 5577-5586.

12. H. Yu, T. Wang, B. Wen, M. Lu, Z. Xu, C. Zhu, Y. Chen, X. Xue, C. Sun, M. Cao, *J. Mater. Chem.,* 2012, **22**, 21679.