A Review of Functionalized Graphene properties and its application

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ABSTRACT: With excellent electrical, optical, magnetic and mechanical properties as well as large specific surface area, graphene has been applied in next-generation nano-electronics, ultra-high frequency device, transparent electrical conductors, composite materials, and superior energy capacitors etc. Functionalization of graphene has become a focus of extraordinary interest, because they cannot only stabilize, but also induce new properties of graphene. This review concise the properties of graphene and enormous application, from a science perspective.

KEYWORDS: Nano-electronics, Ultra-high frequency device, Capacitor, Functionalization.

1 INTRODUCTION

Graphene, which consists of a two-dimensional (2D) sheet of covalently bonded carbon atoms, forms the basis of both 3D graphite and 1D carbon nanotubes. It has attracted massive attention in recent years owing to its large specific surface area and unique electrical, mechanical and thermal properties [1, 2, 3, 4, 5]. It exhibits excellent physical and chemical properties, which makes it promising for variety of applications in the areas such as solar-cells,[6] energy storage,[7] field effect transistors,[8] catalyst support,[9] sensors,[10] and nanocomposites.[11] In 2004, Geim and co-workers at Manchester University first isolated single-layer graphene samples from graphite is shown in **(figure 1)**.

Graphene is a thrilling material. It has a large theoretical specific surface area ($2630 \ m^2 \ g^{-1}$), high intrinsic mobility ($200000 \ cm^2 \ v^{-1} \ s^{-1}$), [12, 13] high Young's modulus (~ 1.0 TPa) [14] and thermal conductivity ($\sim 5000 \ Wm^{-1} \ K^{-1}$), [15] and its optical transmittance ($\sim 97.7\%$) and good electrical conductivity merit attention for applications such as for transparent conductive electrodes, [16 , 17] among many other potential applications. Graphene has been experimentally studied for over 40 years, [18, 19, 20, 21, 22, 23, 24] and measurements of transport properties in micromechanically exfoliated layers [25], of graphene grown on (SiC) [26], large area graphene grown on copper (Cu) substrates.

Graphene has been characterized by a variety of microscopic and other physical techniques including atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM) and Raman spectroscopy [27, 28, 29, 30,2]. This literature is a comprehensive overview of all major recent experimental results related to graphene properties and its applications.

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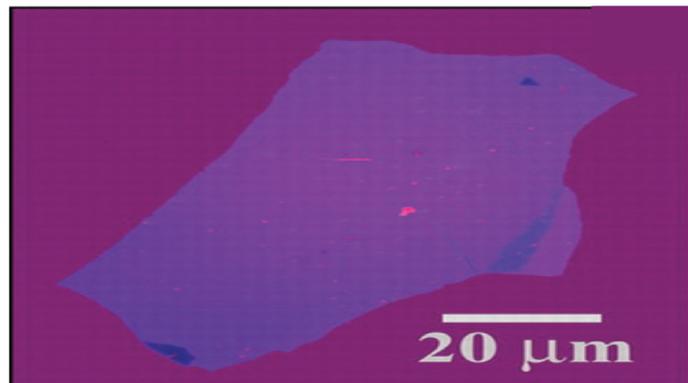
Figure 1. Single layer graphene was first observed by Geim and others at Manchester University. Here a few layer flake is shown, with optical contrast enhanced by an interference effect at a carefully chosen thickness of oxide [1].

2   SYNTHESIS OF GRAPHENE

Researchers are now making rapid progress toward generating process able graphene. After fine-tuning, the technique provided high-quality graphene crystallites up to 100 µm in size, which is adequate for an in-depth study of its properties. So far, several techniques have been established for graphene synthesis. However, mechanical cleaving (exfoliation) [31], chemical exfoliation [32, 33], chemical synthesis [34], and thermal chemical vapor deposition (CVD) [35] synthesis are the most commonly used methods today. Some other techniques are also reported such as unzipping nanotube [36, 37, 38] and microwave synthesis [39] however, those techniques need to be explored more extensively. Mono-layer graphene was first produced and reported in the year 2004, where Mechanical exfoliation using AFM cantilever (adhesive tape) was used to continually slice down the graphene layers on a substrate single-layer graphene is obtained by the reduction of single layer graphene oxide, CVD and other methods besides micromechanical cleavage. Few-layer graphenes are prepared by the conversion of nanodiamond, arc discharge of graphite and other means.
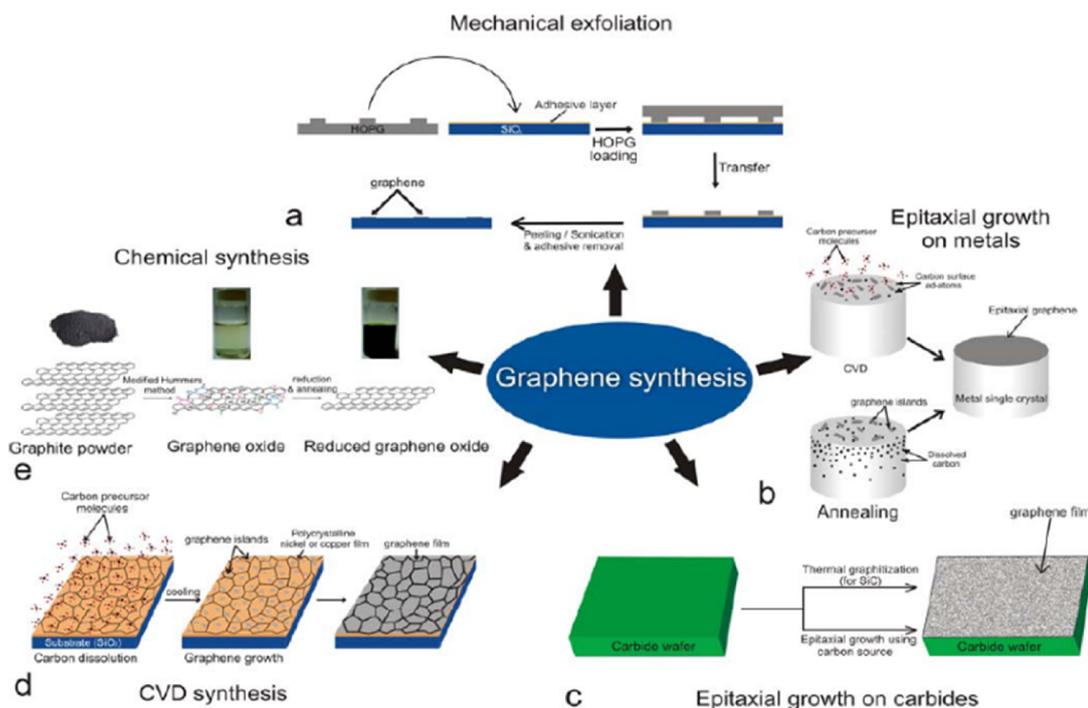
Figure 2. Flow diagram of various methods of synthesis grapheme

3   FUNCTIONALIZATION OF GRAPHENE

Graphene has been functionalized by both covalent and non-covalent means in order to disperse or solubilize them in different solvents [30, 2]. Using covalent modification, Haddon and co-workers had achieved functionalization of graphene by surface –OH and –COOH groups which was first reacted with SOCl$_2$ to create –COCl groups, followed by reaction with a long chain aliphatic amine to obtain the amide derivative soluble in nonpolar solvents [40].Soluble graphene layers in THF can be generated by the covalent attachment of alkyl chains to graphene layers via reduction of graphite fluoride with alkyl lithium reagents [41]. Such covalent functionalization enables solubilization in organic solvents such as CCl$_4$, CH$_2$Cl$_2$ and THF [42]. Graphene can be functionalized through π-π non-covalent modification structure by wrapping with surfactants or through interaction with aromatic molecules such as 1-pyrenebutanoic acid succinimidyl ester (PyBS) and the potassium salt of coronene tetracarboxylic acid [42].Fabrication of graphene-based devices and nanocomposites are exploiting the chemically oxidized graphene, namely graphene oxide (GO) and reduction graphene oxide (RGO).Generally, GO is produced using different variations of the Hummers' methods [43] in which graphite is oxidized using strong oxidants such as KMnO4 , KClO3 , and NaNO2 in the existence of nitric acid or its mixture with sulfuric acid. GO can be exfoliated into single or few layered nanosheets under mechanical forces such as ultrasonication.Thermally reduced GO can be produced by rapid heating of dry GO under inert gas and high temperature. The reduced graphene oxides (rGO) prepared via the two routes shows highly electrical, thermal conductivity, and ambipolarity [44]. Graphene-based polymer nanocomposites can be produced via in situ intercalative polymerization of monomers, melting blending, solution-based processes.

4   ELECTRONIC PROPERTIES

4.1   BAND GAP

Monolayer graphene shows a so-called ambipolar characteristic, where electrons and holes coexist symmetrically against the Fermi level. The first Brillouinzone has two in equivalent points K and K ' (called Dirac points). The tight-binding approach considering only the first nearest neighbor interaction provides the dispersion relation of the electrons near the *K / K '* points [46, 47]. The energy band structures and dispersion relations for graphene are illustrated in (**figure 3**).

$$E \pm (\vec{K}) = \pm t \left(1 + 4 \cos \frac{\sqrt{3k_x}}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2} \right)^{\frac{1}{2}} \tag{1}$$

Where $a = \sqrt{3}a_{cc}$, a_{cc} is the carbon-carbon bonding length (0.142 nm), and t is the transfer integral is the nearest neighbor hopping energy with a magnitude of about 2.8 eV.
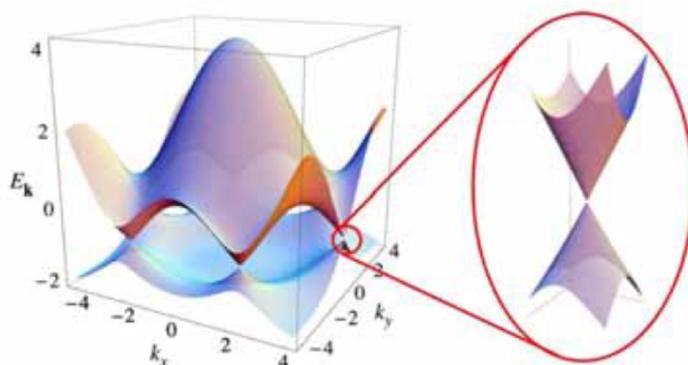
Figure 3. A schematic illustration of graphene's band structure from tight-binding bonding [47].

Due to the honeycomb lattice structure, graphene has two types of carrier transport: one is along with the armchair edge and the other is along the zigzag edge shown in (**figure 4**).
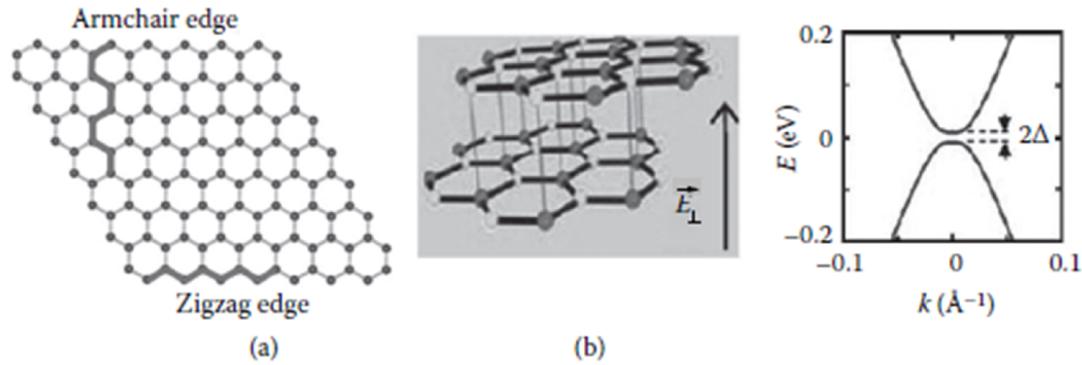
Figure 4. (a) Carrier transport for monolayer graphene and (b) band gap opening for chirally stacked bilayer graphene. [48]

Graphene nanoribbons exhibit an energy spectrum with a gap between the valence and conduction bands for armchair transport depending on the nanoribbon width dr [49].

$$\varepsilon_{p,n}^{\mp} = \pm \upsilon \left\{ p^2 + (\pi\hbar/d_r)^2 n^2 \right\}^{\frac{1}{2}} \qquad (2)$$

where v ≈ 108 cm/s is the characteristic velocity of the electron (upper sign) and hole (lower sign) spectra, p is the momentum along the nanoribbon, ħ is the reduced Planck constant, and n = 1, 2, 3, … is the sub band index. A-B stacked bilayer graphene exhibits an energy gap Eg between the valence and conduction bands [50].

$$E = \frac{edV_g}{W} \qquad (3)$$

Where d ≈ 0.36 nm is the effective spacing between the graphene layers in the graphenebilayer (GBL) which accounts for the screening of the electric field betweenthese layers, W is the distance between the gate and the graphene layer, and Vg is thegate-source voltage.

4.2 ULTRA-HIGH MOBILITY

The mobility of graphene is not significantly depend on temperature in the measurement. Thus, mobility of graphene is found to be ultra-high (exceeding 15, 000 cm^2 V^{-1} s^{-1} at room temperature [5]. In the meantime, theoretically, electrical resistance of grphene calculated from the ultra-high mobility values can be as low as 10^{-6} $\Omega \cdot cm$, which is even lower than that of silver. However, electrical resistance of graphene in real application may not reach its theoretical value due to effect of solid substrats, phone scattering from graphene to environment, so that the mobility and electrical resistance of graphene are usually restricted.

5 MECHANICAL PROPERTIES

The mechanical properties of monolayer graphene including the Young's modulus and fracture strength have been investigated by numerical simulations such as molecular dynamics [51, 52, 53]. Defect-free graphene is the stiffest material, with Young's modulus of 1.0 TPa, ever reported in nature and also has superior intrinsic strength, ∼ 130 GPa [5]. The average Young's modulus and the highest fracture strength of functionalization, assembly, and cross-linking of graphene sheets [54] obtained were ∼ 32 GPa and ∼ 120 MPa [55]. The elastic properties and intrinsic breaking strength of free-standing monolayer graphene were measured by nano indentation using an AFM (atomic force microscope). The mechanical properties of this 'graphene oxide paper' were improved by introducing chemical cross linking between individual platelets using divalent ions[56] and polyallylamine [57]. The mechanical properties as prepared graphene papers were investigated by tensile, bending, indentation, and superior hardness test.

5.1 TENSILE TEST

Stress and strain amounts based on their dimensions and following equations:

$$\varepsilon_x = U_x , \qquad (4)$$

$$\sigma_x = \frac{F}{A} , \qquad (5)$$

$$\varepsilon_x = 1 * \frac{(\sigma_x - \upsilon\sigma_y)}{E}, \tag{6}$$

Where E is the Young's modulus, F the tensile force, A the cross section area, υ the Poisson's ratio, u and ε_x the displacement and the strain in x direction, σ_x and σ_y the stresses in x and y directions. Stress-strain curves of Graphene paper (GP) and Graphene attachment with octadecylamine (G-ODA) shown in (**figure 5**) straightening behavior at the starting roughly linear [58, 59].
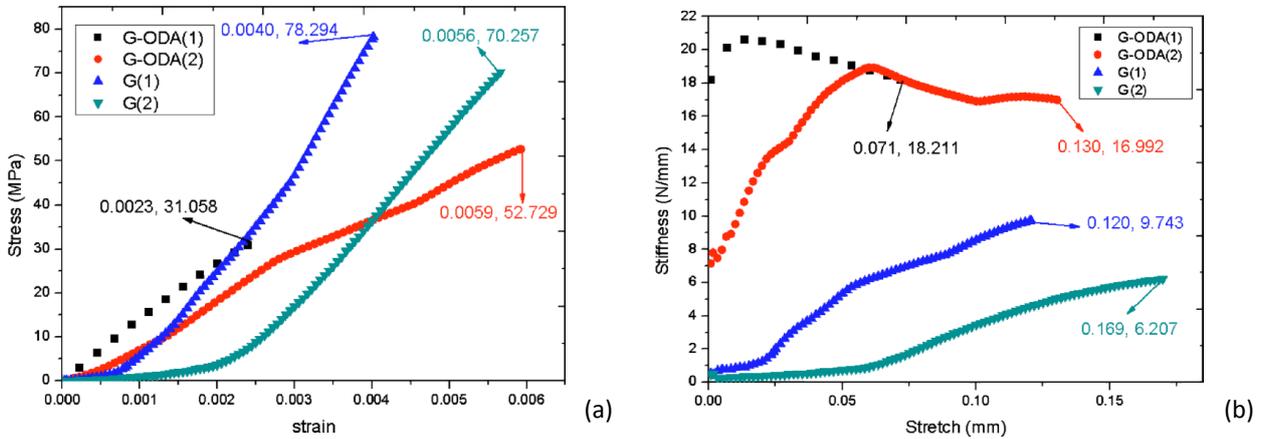
Figure 5. (a) Stress-strain curves of GP and G-ODA strips. (b) Stiffness vs stretch of GP and G-ODA strips. [60]

Stiffness (S) which is an extensive material property, can be defined as a resistance of elastic body to stretch (δ)

$$s = \frac{F}{A}, \tag{7}$$

Relationship between Young's modulus and stiffness is determined as below,

$$F = \frac{AE}{L}, \tag{8}$$

Where L is the length of strip. From (**figure 5.b**) shows that GP has greater Young's modulus and ultimate strength but G-ODA sheets exhibit higher stiffness.

Bucky papers prepared by different synthesize methods; Young's modulus (0.8–24 GPa), ultimate tensile strength (10–74 MPa) and strain (1.5%–5.6%). Maximum Young's modulus and ultimate tensile strength of our GP samples are 31.69 GPa and 78.294 MPa [61]. Young's modulus of 20–40 GPa, ultimate tensile strength of 70–80 MPa, and ultimate tensile strain of 0.3%– 0.4% were stated as mechanical properties of GP and graphene oxide papers [58, 59].

5.2 INDENTATION TEST

Spherical indenter of radius 100 µm as the most suitable indenter for thin films was selected to measure hardness, elastic modulus, yielding strength, and Poisson's ratio of GP, G-ODA. Indentation tests were carried out by an ultramicro indentation system (UMIS) and repeated on several points of GP, heat treated GP (thickness: 3 µm) and G-ODA (thickness: 7 µm) [60]. There followed this equation: [62]

$$\frac{1}{E^*} = \frac{(1-\vartheta^2)}{E} + \frac{(1-\vartheta'^2)}{E'}, \tag{9}$$

$$E = \frac{P_h}{2a}, \tag{10}$$

Hardness is calculated as,

$$H_y = \frac{P}{\pi a^2}, \tag{11}$$

Hardness, yielding strength of materials can be appraised as

Table 1. Dimensions and tensile test results of GP and G-ODA strips [63, 64].

	Length (mm)	Width (mm)	Thickness (µm)	Ultimate strain	Ultimate Strength (MPa)	Young's modulus (GPa)	Stiffness (N/mm)	Maximum stretch (mm)
GP(1)	30	5	3	0.0040	78.294	31.6969	15.8485	0.1205
GP(2)	30	5	3	0.0056	70.257	21.1987	10.5993	0.1697
G-ODA(1)	30	6	7	0.0023	31.058	15.4701	21.6582	0.0715
G-ODA(2)	30	6	7	0.0059	52.729	12.3094	23.4998	0.1302

5.3 BENDING TEST

Modulus of elasticity and bending rigidity of GP and G-ODA sheets were ascertained via bending test. Deflection equation of intensively loaded circular plate is:

$$w = \frac{F}{16\pi D}\left[2r^2 \ln\frac{r}{r_0} + (r_0^2 - r^2)\right], \tag{12}$$

$$D = \frac{Eh^3}{12(1-\vartheta^2)}, \tag{13}$$

Where r_o is the inner radius of ring, r the radial distance of intensive load to the sheet's center, F the concentrated force, D the bending rigidity, E the modulus of elasticity, h the sheet thickness, and w the deflection of sheet. Two flat rings of 3 mm inner radius were prepared; GP and G-ODA sheets with 3 and 7 µm thicknesses were firmly stuck with glue on the flat surface of these rings. For GP bending modulus of elasticity was 3.0440 TPa and for G-ODA was 0.7647 TPa [64, 65].

6 OPTICAL PROPERTIES

One of the most widely renowned optical properties of graphene is that it can act as a strong quencher for various luminescent dyes and nanoparticles [66] .This is accredited to two possible competitive processes: photo-induced electron transfer and intra-molecular energy transfer facilitated by a through-bond mechanism due to covalent binding of the luminophore [67].Graphene's transparency is more closely related to quantum effect than natural material properties. The zerogap Dirac band structure avail a fine-structure constant of graphene which can be expressed by following equation:

$$a = \frac{e^2}{\hbar c}, \tag{14}$$

Where dynamic conductivity (G) of graphene is constant ($e^2/4\hbar$) [68], Transparency (T) and reflectance (R) of graphene can be calculated by following this equation:

$$T \approx 1 - \pi a, \tag{15}$$

$$R = \frac{\pi^2 a^2 T^2}{4}, \tag{16}$$

Its constant transmittance (T ≈ 97.7%) of incident light has been experimentally observed in the visible-infrared range (300–2500 nm) and the transmittance linearly decreases withthe number of layers for n-layer graphene.
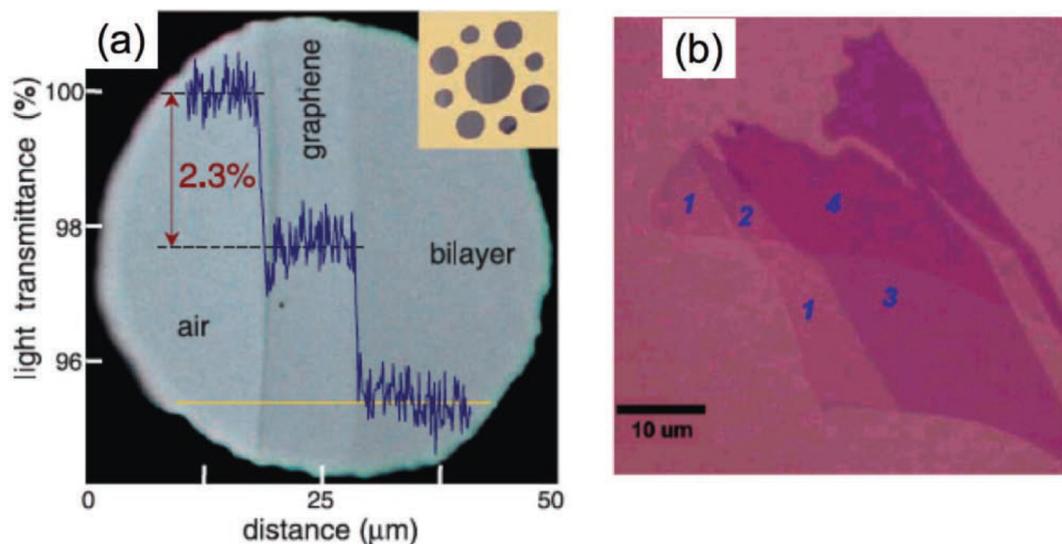
Figure 6. (a) Photograph of a 50-µm aperture partially covered by graphene and its bilayer. The line scan prof le shows the intensity of transmitted white light along the yellow line. Inset shows the sample design: a 20-µm thick metal support structure has apertures 20, 30, and 50 µm in diameter with graphene flakes deposited over them; (b) Optical image of graphene flakes with one, two, three, and four layers on a 285-nm thick SiO_2-on-Si substrate [69,70]

7 MAGNETIC PROPERTIES

Occurrence of magnetism in graphene has been a topic of considerable interest. The magnetism in graphene can be induced by vacancy defects or by hydrogen chemisorption [70]. Some researcher suggest that the zig-zag edges are responsible for the magnetic properties of graphene [71]. Graphene could have certain magnetic features including paramagnetism, spin-glass behavior and magnetic switching phenomena (ferromagnetic or antiferromagnetic) [72].

At room temperature ferromagnetism in graphene samples with very small saturation magnetization values from 0.004 to 0.020 emug−1 after subtracting the diamagnetic background [73] Magnetic properties of graphene samples prepared by EG, conversion of nanodiamond (DG), and arc evaporation of graphite in hydrogen (HG) show divergence between the field-cooled (FC) and zero-field-cooled (ZFC) data, starting around 300 K. In Figure 1(a) shows the temperature dependence of magnetization of EG and HG samples measured at 500 Oe and The graphene samples show magnetic hysteresis at room temperature (Figure 1b) and the MS increases with increase in temperature. HG shows the best hysteretic features with saturation. While DG shows saturation magnetization, MS, it is low when compared to HG.
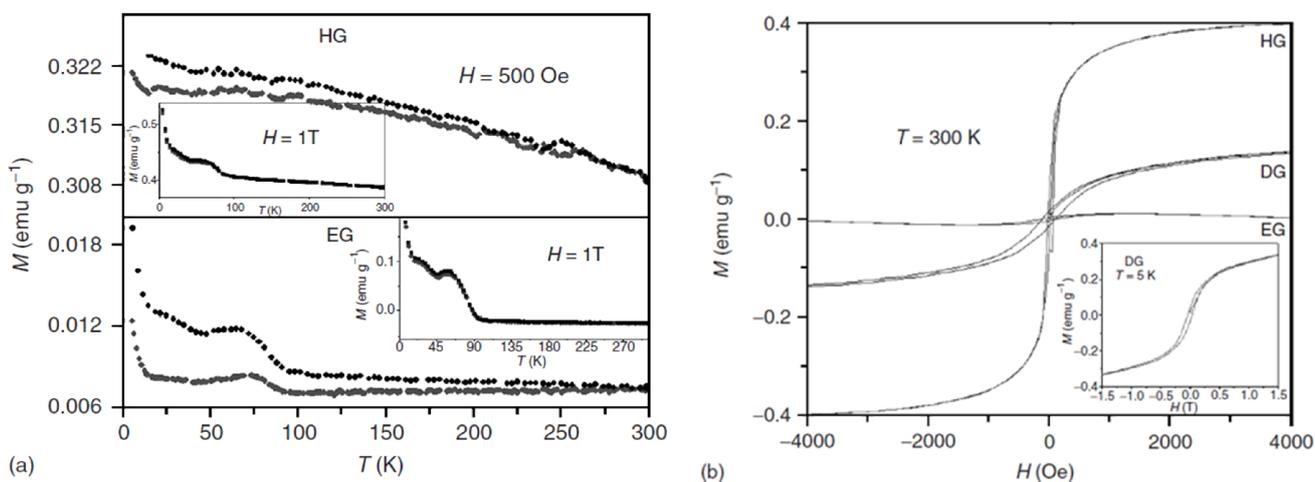
Figure 7. (a) Temperature variation of magnetization of few-layer graphenes EG and HG at 500 Oe, showing the ZFC and FC data. The insets show the magnetization data at 1 T. (b) Magnetic hysteresis in EG, DG, and HG at 300 K. Inset shows magnetic hysteresis in DG at 5 K. [74,75]

Recently modification of graphene with magnetic nanoparticles is usually accomplished by in situ reduction of iron, [76] cobalt [77] or nickel [78] salt precursors, or assembly of the pre-synthesized magnetic nanoparticles [79] on the surface of graphene-based frameworks.

8 SURFACE AREA AND GAS ADSORPTION

Single layer graphene (SG) is theoretically prophesied to have a large surface area of 2600 m^2 g^{-1} [80], however the surface area of few layer graphene (FG) is 270–1550 m^2 g^{-1} [81]. H$_2$ adsorption on FG samples prepared by the EG and transformation from nanodiamond (ND, DG) have revealed a H$_2$ uptake value of 1.7 wt% at atmospheric pressure and 77 K [82]. Adsorption of H$_2$ was found to be directly proportional to the surface area of the samples (**Figure 8a**). A maximum adsorption of 3 wt% was achieved at 298 K and 100 atm for EG. The CH$_4$ uptake of the graphene samples varies between 0 and 3wt% at 273 K and 5MPa. (**Figure 8b**) shows the CO$_2$ and methane uptake of graphene samples as well as activated charcoal against their surface areas.
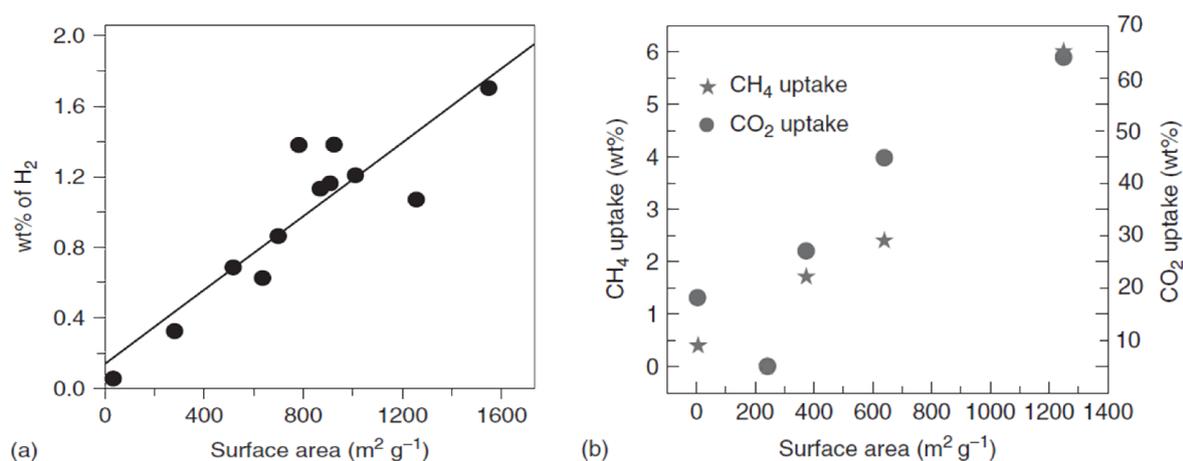
Figure 8.(a) Linear relationship between the BET (Brunauer-Emmett-Teller) surface area and weight percentage of hydrogen uptake at 1 atm pressure and 77 K for various graphene samples.[81] (b) Plot of weight percentage of CO$_2$ uptake (at 195 K and 1 atm) and methane uptake (at 298 K and 5 MPa) versus surface area for different graphene samples. [82]

9 SUPERCAPACITOR

Electrochemical supercapacitors with different graphene samples as electrode materials in aqueous H$_2$SO$_4$ as well as in an ionic liquid (N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, PYR14TFSI) that were used as electrolytes [83] . High-surface-area graphite prepared by ball milling showed a large specific capacitance of 33 F cm^{-2} in aqueous medium, which might be due to high open surface area, lattice defects, and oxygen functional groups in the sample [84]. EG and DG exhibit high specific capacitance in aqueousH$_2$SO$_4$, the value reaching up to 117 and 35 Fg^{-1}. Chemically modified graphene sheets obtained by the reduction of graphene oxide with hydrazine when used as electrode material in supercapacitors gave specific capacitances of 135 and 99 F g^{-1} in aqueous and organic electrolytes [85]. Graphene/polyaniline composites capacitance is 1046 F g^{-1} and Graphene/Co(OH)$_2$ is 972.5 F g^{-1}.

10 OTHER PROPERTIES

Graphene is an inimitable gift of modern century. It have also some remarkable properties like Field Emission and Blue Light Emission [86, 87, 88], Molecular Charge Transfer [89, 90] Decoration with Metal and Oxide Nanoparticles [91].

11 APPLICATION

11.1 ELECTRONIC AND PHOTONIC APPLICATIONS FOR ULTRAHIGH-FREQUENCY GRAPHENE-BASED DEVICES

Due to its unique carrier transport and optical properties, including massless and gapless energy spectra graphene uses in electronic devices is as the channel material in FETs. The optical properties of graphene can provide many advantages in

optoelectronic applications. One typical example is ultrasensitive, ultrafast photodetector and phototransistor operation of graphene in junction and graphene-channel FETs.

11.2 NANOSIZED GRAPHENE IN MATERIAL SCIENCE

Nano-sized graphenes play very significant roles in materials science for its good self-assembling and charge transporting properties, and unusual absorption and emission behavior. Tuning the water solubility and preserving the fluorescence of nano-sized graphenes are the key issues for bio-imaging applications.

11.3 IN CERAMICS

Graphene-incorporated ceramic nanocomposites are also explored for Ni removal from water. MnO_2–graphene composite is studied as an absorbant for removing toxic Ni content from the water through a chemical sorption process. Graphene addition to MnO_2 is stated to enhance the adsorption capacity and mechanical intension of the composite, which improves the Ni adsorption efficiency by 52% over MnO_2 alone [92].

11.4 ANODE FOR LI-ION BATTERY

Graphene has been explored as a second-phase addition to silicon for Li-ion battery anode material [93]. Graphene, as an addition to silicon, is a potential solution to this problem because of its good conductivity, chemical stability, and mechanical properties. The presence of graphene in Si improves its suitability as a Li-ion anode material.

11.5 SUPERCAPACITOR

Due to high surface area of the composite along with the excellent electrical conductivity from both graphene and platinum makes Pt–graphene a very promising material for supercapacitors. Thus composite structure shows 19 times larger capacitance than graphene alone.

11.6 SOLAR CELL

Graphene has been and is being used as a transparent conducting electrode material in various types of inorganic, organic, and dye-sensitized solar cells, and also as counter electrodes in DSSCs (Figure 9).
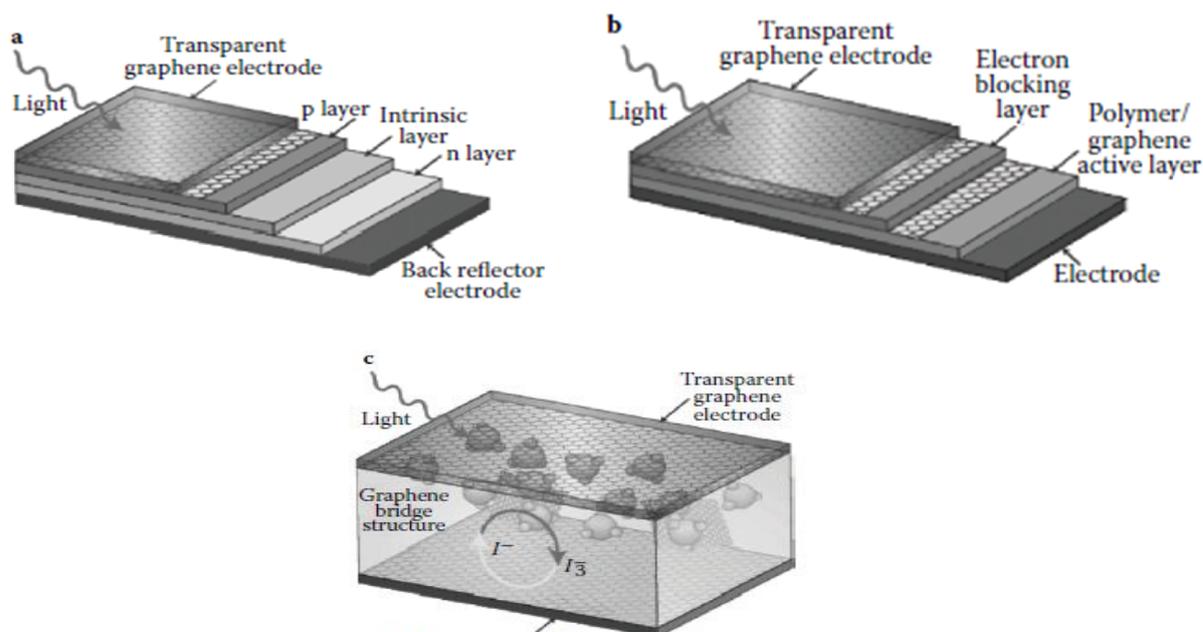
Figure 9.Schematics of graphene-based solar cells: (a) inorganic, (b) organic, and (c) dye-sensitized solar cells. [94]

12 CONCLUSION

In concise, we discuss recent advances in the unique electronic, optical, magnetic, surface area, and mechanical properties of functionalized graphene materials. We should inform that the electrical conductivity of graphene is extremely high, and functionalization of graphene is helpful for the utilization of this property. Various magnetic features of graphene can be induced through both covalent and non-covalent-functionalization (atom adsorption) of graphene sheets. Optical properties of electroluminescence was recently reported in pristine graphene and Optical properties of electroluminescence was recently reported in pristine graphene. Recently Graphene use in LED display, Bullet proof jacket even in medical science.

REFERENCES

[1] A.K. Geim, "Graphene: Status and Prospects", *Science (2009), Vol.* **324**, pp. 1530.

[2] C.N.R. Rao, A.K. Sood, K.S. Subrahmanyam, A. Govindaraj, *Angew.* "*Graphene: The New Two-Dimensional Nanomateria". Chem. Int. Ed. (2009), Vol.* **48**, pp. 7752.

[3] A.K. Geim, K.S. Novoselov, "The rise of graphene", *Nat. Mater* (2007), Vol. **6**, pp. 183.

[4] M. Segal, "Selling graphene by the ton", *Nat. Nanotechnol(2009),vol.* **4**, pp. 612.

[5] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, S.V. Dubonos, I.V. Grigorevia, A.A. Firsov, "Electric field effect in atomically thin carbon films", *Science (2004),vol.* **306**, pp666 .

[6] X. Wang, L. Zhi, K. Mullen, "Graphene-Based Ultracapacitors", *Nano. Lett*. (2008) Vol. **8**, pp.3498 .

[7] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, "Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells", *Nano. Lett (2008),vol.* **8**, pp.323 .

[8] L.A. Ponomarenko, F. Schedin, M.I. Katnelson, R. Yang, E.W. Hill, K.S. Novoselov, A.K. Geim, "Graphene and Emerging Materials for Post-CMOS Applications", *Science (2008),Vol.* **320**, pp.356.

[9] Y. Si, E.T. Samulski, "Exfoliated Graphene Separated by Platinum Nanoparticles", *Chem. Mater*.(2008),Vol. **20**, pp.6792.

[10] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katnelson, K.S. Novoselov, Detection of individual gas molecules adsorbed on graphene. *Nat. Mater* (2007) vol. **6**, pp.652.

[11] S. Stankovich, D.A. Dikin, H.B. Geoffrey Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, "Synthesis, Characterization, and Properties of Large-Area" *Nature* **442**, 282 (2006).

[12] K. I. Bolotin , K. J. Sikes , Z. Jiang , M. Klima , G. Fudenberg , J. Hone , P. Kim , H. L. Stormer ,. "Ultrahigh electron mobility in suspended graphene". Solid State Commun (2008), vol.146, pp.351.

[13] S. V. Morozov , K. S. Novoselov , M. I. Katsnelson , F. Schedin , D. C. Elias , J. A. Jaszczak , A. K. Geim , "Effect of gap opening on the quasiparticle properties of doped graphene sheets Phys." Rev. Lett. (2008), vol.100, pp.016602.

[14] C. Lee , X. D. Wei , J. W. Kysar , J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene." Science (2008), vol.321, pp.385.

[15] A. A. Balandin , S. Ghosh , W. Z. Bao , I. Calizo , D. Teweldebrhan , F. Miao , C. N. Lau, "Superior Thermal Conductivity of Single-Layer Graphene." Nano Lett. (2008), vol.8, pp.902.

[16] W. Cai , Y. Zhu , X. Li , R. D. Piner , R. S. Ruoff, "Graphene and graphene oxide: Synthesis, properties, and applications" Appl. Phys. Lett.(2009), vol.95, pp.123115.

[17] X. Li, Y. Zhu , W. Cai , M. Borysiak , B. Han , D. Chen , R. D. Piner , L. Colombo , R. S. Ruoff, "Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes." Nano Lett. (2009), vol.9, pp.4359.

[18] H. P. Boehm, A. Clauss , G. O. Fischer , U. Hofmann , Z. Anorg. Allg. Chem. "Chemical methods for the production of graphenes" (1962), vol.316, pp.119.

[19] H. P. Boehm, R. Setton , E. Stumpp, "Graphene and Emerging Materials for Post-CMOS Applications" Pure Appl. Chem. (1994), vol.66, pp.1893.

[20] H. P. Boehm, R. Setton , E. Stumpp, "Emerging Two-dimensional Materials: graphene and its other structural analoguesCarbon" (1986), vol.24, pp.241.

[21] J. Wintterlin , M. L. Bocquet, "Graphene Nanoelectronics: Metrology, Synthesis, Properties and Applications" Surf. Sci. (2009), vol.603, pp.1841.

[22] A. J. Vanbommel, J. E. Crombeen , A. Vantooren, "Scanning Probe Microscopy in Nanoscience and Nanotechnology" Surf. Sci. (1975), vol.48, pp.463.

[23] X. K. Lu, M. F. Yu , H. Huang , R. S. Ruoff "Graphene-based and Graphene-derived Materials, Nanotechnology" (1999), vol.10, pp.269.

[24] X. K. Lu , H. Huang , N. Nemchuk , R. S. Ruoff, "Personal perspectives on graphene" Appl. Phys. Lett.(1999), vol. 75, pp.193.

[25] K. S. Novoselov , A. K. Geim , S. V. Morozov , D. Jiang , Y. Zhang , S. V. Dubonos , I. V. Grigorieva , A. A. Firsov "Electric field effect in atomically thin carbon films." Science (2004), vol.306, pp.666.

[26] C. Berger , Z. M. Song , T. B. Li , X. B. Li , A. Y. Ogbazghi , R. Feng , Z. T. Dai , A. N. Marchenkov , E. H. Conrad , P. N. First, W. A. De Heer , J. Phys. "Physical Properties of Ceramic and Carbon Nanoscale Structures", Volume Chem. B (2004), vol.108, pp.19912.

[27] Geim, A. K. and Novoselov, K. S "The rise of graphene", Nat. Mater. (2007), vol.6, pp. 183-191.

[28] Li, D. and Kaner, R. B "Graphene-Based Materials", Science (2008), vol.320, pp. 1170-1171.

[29] Katsnelson, M. I. "Graphene: carbon in two dimensions", Materials Today (2007), 10, pp. 20-27.

[30] Rao, C. N. R., Biswas, K., Subrahmanyam, K. S. and Govindaraj, A. "Graphene, the new nanocarbon", J. Mater. Chem, (2009), vol.19, pp. 2457-2469.

[31] Novoselov, K. S., A. K. Geim, S. V. Morozov, et al. 2004. "Electric field effect in atomically thin carbon films". Science 306 (5696):666–669.

[32] Allen, M. J., V. C. Tung, and R. B. Kaner. 2010. Honeycomb carbon: A review of graphene. Chemical Reviews 110 (1):132–145.

[33] Viculis, Lisa M., Julia J. Mack, and Richard B. Kaner. 2003. A chemical route to carbon nanoscrolls. Science 299 (5611):1361.

[34] Park, S., and R. S. Ruoff. 2009. Chemical methods for the production of graphenes. NatureNanotechnology 4 (4):217–224.

[35] Reina, A., X. T. Jia, J. Ho, et al. 2009. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. Nano Letters 9 (1):30–35.

[36] Jiao, L. Y., X. R. Wang, G. Diankov, H. L. Wang, and H. J. Dai. 2010. Facile synthesis of highquality graphene nanoribbons. Nature Nanotechnology 5 (5):321–325.

[37] Kosynkin, D. V., A. L. Higginbotham, A. Sinitskii, et al. 2009. Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. Nature 458 (7240):872–876.

[38] Jiao, L. Y., L. Zhang, X. R. Wang, G. Diankov, and H. J. Dai. 2009. Narrow graphene nanoribbons from carbon nanotubes. Nature 458 (7240):877–880.

[39] Xin, G. Q., W. Hwang, N. Kim, S. M. Cho, and H. Chae. 2010. A graphene sheet exfoliated with microwave irradiation and interlinked by carbon nanotubes for high-performance transparent flexible electrodes. Nanotechnology 21 (40).

[40] Niyogi, S., Bekyarova, E., Itkis, M. I., McWilliams, J. L., Hamon, M. A. and Haddon, R. C "Solution Properties of Graphite and Graphene", J. Am. Chem. Soc(2006), vol.128, pp. 7720-7721.

[41] Worsley, K. A., Ramesh, P., Mandal, S. K., Niyogi, S., Itkis, M. E. and Haddon, R. C. "Soluble graphene derived from graphite fluoride", Chem. (2007). Phys. Lett., vol.445, pp. 51-56.

[42] Subrahmanyam, K. S., Vivekchand, S. R. C., Govindaraj, A. and Rao, C. N. R "A study of graphenes prepared by different methods: characterization, properties and solubilization, J. Mater. Chem. (2008), vol.18, pp.1517-1523.

[43] Ghosh, A., Rao, K. V., George, S. J. and Rao, C. N. R. "Non-Covalent Functionalization, Exfoliation and Solubilization of Graphene in Water Employing a Fluorescent Coronene Carboxylate." Chem. Eur. J. (2010), vol.16, pp.2700.

[44] W. S. Hummers , R. E. Offeman , J. Am. "Preparation of graphitic oxide" Chem. Soc. (1958), vol.80, pp.1339 – 1339.

[45] O. C. Compton, S. T. Nguyen, "Graphene Oxide, Highly Reduced Graphene Oxide, and Graphene: Versatile Building Blocks for Carbon-Based Materials" Small (2010), vol.6, pp.711 – 723.

[46] P. R. Wallace, "The Band Theory of Graphite" Physical Review (1947), vol.71, pp.622.

[47] A. H. C. Neto, F. Guinea , N. M. R. Peres , K. S. Novoselov ,A. K. Geim, "The electronic properties of graphene" Rev. Mod. Phys. (2009), vol.81, pp.109.

[48] J. B. Oostinga et al. 2008. Nature Materials 7: 151.

[49] V. Ryzhii, M. Ryzhii, A. Satou, and T. Otsuji. "Current-Voltage Characteristics of a Graphene Nanoribbon Field-Effect Transistor." *J. Appl. Phys.* (2008). *Vol.*103, pp.094510.

[50] V. Ryzhii, M. Ryzhii, A. Satou, T. Otsuji, and N. Kirova. Device model for graphenebilayer field-effect transistor. J. Appl. Phys. (2009), vol.105, pp.104510.

[51] G. Van Lier , C. Van Alsenoy , V. Van Doren , P. Geerlings, "Influence of Structural Defects and Chemical Functionalisation on the Mechanical Properties of Graphene" Chem. Phys. Lett. (2000), vol.326, pp.181.

[52] C. D. Reddy , S. Rajendran , K. M. Liew, "Equilibrium configuration and continuum elastic properties of finite sized graphene", Nanotechnology (2006), 17 , 864.

[53] K. N. Kudin, G. E. Scuseria , B. I. Yakobson , "Trends in Nanoscale Mechanics: Mechanics of Carbon Nanotubes, Graphene" Phys. Rev. B (2001), vol.64, pp.235406.

[54] M. Terrones , O. Martín , M. González , J. Pozuelo , B. Serrano , J. C. Cabanelas , S. M. Vega-Díaz , J. Baselga , Adv. Mater. 2011, 23, 5302 – 5310 .

[55] Z. An , O. C. Compton , K. W. Putz , L. C. Brinson , S. T. Nguyen, "Functionalized Graphene Oxide and Graphene" (2010), vol.6, pp.711-723. [53]   [71] S. Park , K. S. Lee , G. Bozoklu , W. Cai , S. T. Nguyen , R. S. Ruoff , ACS Nano 2008 , 2 , 572 .

[56] S. Park , K. S. Lee , G. Bozoklu , W. Cai , S. T. Nguyen , R. S. Ruoff, "Graphene-Based Materials: Science and Technology" ACS Nano (2008), vol.2, pp.572.

[57] S. Park, D. A. Dikin , S. T. Nguyen , R. S. Ruoff , "Graphene Oxide as an Electrophile for Carbon Nucleophiles." Phys. Chem. C (2009), vol.113, pp.3842 – 3846.

[58] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, and R. S. Ruoff, Nature London 448, 457 (2007)

[59] H. Q. Chen, M. B. Müller, K. J. Gilmore, G. G. Wallace, and D. Li, Adv. Mater. Weinheim, Ger. 20, 3557 (2008).

[60] A. R. Ranjbartoreh,B. Wang,1,2 X. Shen, and G. Wang. "Advanced mechanical properties of graphene paper", JOURNAL OF APPLIED PHYSICS 109, 014306 (2011)

[61] L. Berhan, Y. B. Yi, A. M. Sastry, E. Munoz, M. Selvidge, and R. Baughman, "Fabrication of Metal Alloy Deposited Flexible MWCNT Buckypaper for Thermoelectric Applications" J. Appl. Phys. (2004), vol.95, pp.4335.

[62] A. C. Fischer-Cripps, J. Mater. Res. 16, 3050 (2001).

[63] H. Hertz, J. Reine Angew. Math. 92, 156 1881; "Translate and reprinted in English in Hertz's Miscellaneous Papers, Macmillan & Co., London", (1896), Chap.5.; b)H. Hertz, J. Reine Angew. Math. 92, 156 1881; "Translate and reprinted in English in Hertz's Miscellaneous Papers, Macmillan & Co., London", (1896), Chap.6.

[64] S. P. Timoshenko and S. Woinowsky-Kreiger, "Theory of Plates and Shells", 2nd ed. McGraw-Hill, New York, (1959), pp. 51–68.

[65] S. Timoshenko, Strength of Materials, Part II Advanced Theory and Problems D. Van Nostrand Company, Inc. Princeton, (1966), pp. 92–96.

[66] W. Wei , K. Qu , J. Ren , X. Qu , Chem. Sci. 2011 , 2 , 2050 – 2056 ; b) W. Wei , C. Xu , J. Ren , B. Xu , X. Qu , Chem. Commun. 2012.

[67] M. Terrones , O. Martín , M. González , J. Pozuelo , B. Serrano , J. C. Cabanelas , S. M. Vega-Díaz , J. Baselga, "Synthesis Techniques for Polymer Nanocomposites" Adv. Mater. (2011), vol.23, pp.5302 – 5310.

[68] K. P. Loh , Q. Bao , P. K. Ang , J. Yang, "The Chemistry of Graphene - Powerpoint Review" - J. Mater. Chem. (2010), vol.20, pp.2277.

[69] R. R. Nair , P. Blake , A. N. Grigorenko , K. S. Novoselov , T. J. Booth , T. Stauber , N. M. R. Peres , A. K. Geim , Science 2008 , 320 , 1308 .

[70] Yazyev, O.V. and Helm, "Defect-induced magnetism in graphene" L. (2007) Phys. Rev. B, vol.75, pp.125408

[71] Bhowmick, S. and Shenoy, "Graphene: Synthesis, Properties, and Phenomena" V.B. (2008) J. Chem. Phys., vol. 128, pp.244717.

[72] C. N. R. Rao, H. S. S. R. Matte, K. S. Subrahmanyam, "Nanoscience: Nanostructures through Chemistry", U. Maitra, Chem. Sci. (2012), vol.3, pp.45 – 52.

[73] Y. Wang , Y. Huang , Y. Song , X. Y. Zhang , Y. F. Ma , J. J. Liang ,Y. S. Chen , Nano Lett. 2009, 9, 220 – 224.

[74] Matte, H.S.S.R., Subrahmanyam, K.S., and Rao, C.N.R. (2009) J. Phys. Chem.C, 113, 9982.

[75] Z. H. Ni , H. M. Wang , J. Kasim , H. M. Fan , T. Yu , Y. H. Wu , Y. P. Feng , Z. X. Shen , Nano Lett. 007, 7, 2758

[76] T. Szabó , A. Bakandritsos , V. Tzitzios , E. Devlin , D. Petridis , I. Dékány , J. Phys. Chem. B 2008 , 112 , 14461 – 14469
V. K. Singh , M. K. Patra , M. Manoth , G. S. Gowd , S. R. Vadera , N. Kumar , New Carbon Mater. 2009 , 24 , 147 – 152
X. Yang , X. Zhang , Y. Ma , Y. Huang , Y. Wang , Y. Chen , J. Mater. Chem. 2009, 19, 2710 – 2714
C. Gao , H. K. He, ACS Appl. Mater. Inter. 2010, 2, 3201 – 3210.

[77] Z. Ji , X. Shen , Y. Song , G. Zhu, "Classification of Electrochemically Active Polymers" Mater. Sci. Eng. B-Adv. (2011), vol.176, pp. 711 – 715.

[78] B. Li , H. Cao , J. Yin , Y. A. Wu , J. H. Warner , "Aquananotechnology: Global Prospects" J. Mater. Chem. (2012), vol.22, pp.1876 – 1883.

[79] F. He , J. Fan , D. Ma , L. Zhang , C. Leung , H. L. Chan , Carbon 2010 , 48 , 3139 – 3144 ; b) T. A. Pham , N. A. Kumar , Y. T. Jeong , Synthetic Met. 2010, 160, pp. 2028 – 2036.

[80] Peigney, A., Laurent, C., Flahaut, E., Bacsa, R.R., and Rousset, A. (2001) Carbon, 39, 507.

[81] Ghosh, A., Subrahmanyam, K.S.,Krishna, K.S., Datta, S., Govindaraj,A., Pati, S.K., and Rao, "Graphene: Synthesis, Properties, and Phenomena" C.N.R. (2008) J. Phys. Chem.C, vol.112, pp.15704.

[82] Kumar, N., Subrahmanyam, K.S., Chaturbedy, P., Raidongia, K., Govindaraj, A., Hembram, K.P.S.S., Mishra, A.K., Waghmare, U.V., and Rao, C.N.R. (2011) Chem. Sus. Chem., 4, 1662–167

[83] Vivekchand, S., Rout, C., Subrahmanyam, K., Govindaraj, A., and Rao, C. (2008) "Graphene: Synthesis, Properties, and Phenomena" J. Chem. Sci., vol.120, pp.9.

[84] Li, H.-Q., Wang, Y.-G., Wang, C.-X., and Xia, Y.-Y. (2008) J. Power Source, 185, 1557.

[85] Stoller, M.D., Park, S., Zhu, Y., An, J., and Ruoff, "Graphene-Based Ultracapacitors" - Nano Letters R.S. (2008) Nano Lett., vol.8, pp.3498.

[86] Eda, G., Unalan, H.E., Rupesinghe, N.,Amaratunga, G.A.J., and Chhowalla, "Graphene Oxide: Physics and Applications." (2008) Appl. Phys. Lett., vol.93, pp.233502.

[87] Malesevic, A., Kemps, R., Vanhulsel,A., Chowdhury, M.P., Volodin, A., andVan Haesendonck, "Carbon Nanotube and Related Field Emitters: Fundamentals "C. (2008) J. Appl. Phys., vol.104, pp.084301.

[88] Jung, S.M., Hahn, J., Jung, H.Y., and Suh, "Improved field emission of few-layer graphene–carbon" J.S. (2006) Nano Lett., vol.6, pp.1569

[89] Palnitkar, U.A., Kashid, R.V., More, M.A., Joag, D.S., Panchakarla, L.S., and Rao, "Graphene: Synthesis, Properties, and Phenomena" C.N.R. (2010) Appl. Phys. Lett., 97, 063102.

[90] 168. Prashant, K., Panchakarla, L.S., Bhat, S.V., Urmimala, M., Subrahmanyam, K.S., and Rao, C.N.

[91] Subrahmanyam, K.S., Manna, A.K., Pati, S.K., and Rao, C.N.R. (2010) *Chem. Phys. Lett.*, **497**, 70.

[92] Ren, Y., Yan, N., Wen, Q., Fan, Z., Wei, T., Zhang, M., and Ma, J.. "Graphene/δ-MnO2 composite as adsorbent for the removal of nickel ions from wastewater", Chem. (2010).

[93] Chou, S. L., Wang, J. Z., Choucair, M., Liu, H. K., Stride, J. A., and Dou, S. X. "Enhanced reversible lithium storage in a nanosize silicon/graphene composite." Electrochem. Commun (2010), Vol.12 pp.303–306.

[94] Bonaccorso, F., Sun, Z., Hasan T., and A.C. Ferrari. "Graphene photonics and optoelectronics". Nature Photonics (2010), vol. 4, pp. 611–622.