

Hydrogen storage by reduced graphene oxide and graphene-like nanosheets decorated with Fe nanoclusters

M. Sterlin Leo Hudson^{*[*](#),a}, O.N. Srivastava^b, Satoru Simizu^c and S.G. Sankar^c

^aDepartment of Physics, Central University of Tamil Nadu, Thiruvarur-610004, India, msterlinleo@cutn.ac.in

^bDepartment of Physics, Banaras Hindu University, Varanasi-221005, India, heponsphy@gmail.com

^cAdvanced Materials Corporation, Pittsburgh, PA-15220, USA, admin@advanced-material.com

ABSTRACT

Here, we present the high pressure hydrogen sorption isotherm up to 50 bar of graphene oxide (GO) reduced by thermal reduction (TR-GO), chemical reduction (CR-GO) and graphene like nanosheets decorated with Fe nanoclusters (Fe-GS). GO was first derived by thermal exfoliation of graphite oxide, prepared by modified Standermir method; further reduction at 623K under high vacuum yields TR-GO. CR-GO has been produced by reduction of GO using hydrazine. Fe-GS has been synthesized through arc discharge between the ends of two graphite rods with one rod carrying Fe nanoparticles. The surface area calculated from nitrogen adsorption isotherm at 77 K using BET method for GO, TR-GO, CR-GO and Fe-GS are 304, 357, 90 and 185 m²g⁻¹, respectively. The skeletal density of TR-GO, CR-GO and Fe-GS determined through He gas probing are 1.8, 2.0 and 1.05 gcm⁻³, respectively. High pressure hydrogen PCT isotherm of TR-GO, CR-GO and Fe-GS has been determined at 300 K and 77 K. The volume of hydrogen adsorbed by TR-GO, CR-GO and Fe-GS at 77 K and 50 bar is 230 ccstp/gram (2.07 wt.% H₂), 60 ccstp/gram (0.54 wt.% H₂) and 240 ccstp/gram (2.16 wt.% H₂), respectively.

Keywords: helium isotherm, nitrogen isotherm, thermal reduction, chemical reduction, pore size analysis

1. INTRODUCTION

Recently, graphene, the one-atom-thick carbon allotrope has gained wide attention due to its potential applications in several important areas, primarily in electronics and energy storage [1, 2]. Hydrogen storage is one of the interesting topics related with its use as a clean alternative fuel for automobiles [3-7]. Graphene and graphene oxide are capable of physically adsorbing hydrogen in the molecular form and the maximum uptake capacity reported for graphene is 3.1 wt.% H₂ at 300 K/100 bar [8]. Ghosh *et al.* have reported that the hydrogen uptake capacity increases linearly with specific surface area of graphene. i.e. ~0.5 wt.% H₂ per 500 m²/g at 77 K per bar [9]. This is very much higher than the hydrogen physisorption capacity of carbon adsorbents indicated by "Chahine rule" [10]. This rule states that the excess hydrogen physisorption capacity of carbon adsorbents is 1 wt.% H₂ per 500 m²/g at 77 K/40 bar [11].

Recent studies demonstrate that graphene decorated with metal nanoparticles exhibits a higher hydrogen uptake behavior, compared to pure graphene. Huang *et al.* [12] observed only 0.067 wt.% hydrogen uptake by pristine graphene at 303 K/5.7 MPa. whereas graphene samples decorated with Pt and Pd show a relatively high uptake of 0.15 wt.% H₂ and 0.156 wt.% H₂, respectively at 303 K/5.7 MPa. Thus, Pt/Pd decoration is found to increase the hydrogen uptake of graphene by a factor >2. Though, the surface area of graphene decreases after Pt/Pd decoration, the increase in hydrogen uptake capacity was attributed to the effect of hydrogen "spillover" on Pt/Pd particles in graphene [13]. The "spillover" effect provides a mechanism for hydrogen molecule dissociation into hydrogen atoms followed by the migration of hydrogen atoms on graphene layers. More recently, Parambhath *et. al.* [14] reported a much higher hydrogen uptake of 4.4 wt.% at 298 K/ 4 MPa by Pd decorated nitrogen-doped graphene. According to these authors, a more uniform distribution of Pd on the nitrogen-doped graphene is found to increase the hydrogen uptake.

Based on first-principles calculation, Tozzini and Pellegrini have predicted that graphene can efficiently store up to 8 % hydrogen by weight [15]. Recent theoretical studies have indicated that graphene with metal particles incorporated in it exhibits a hydrogen uptake capacity in excess of 10 wt.% [16-18]. Theoretical study by Ataca *et al.* [16] shows that Li-graphene complex exhibits a high hydrogen uptake capacity of 12.8 wt.% H₂. The weak ionic bond, attractive Coulomb interaction between positively charged Li and negatively charged H and weak van der Waals interaction are found to be responsible for the formation of mixed weak bonding between H₂ molecules and Li -graphene complex.

In this paper, we report some interesting experimental results on the hydrogen adsorption isotherms of reduced graphene oxide, derived by thermal exfoliation of graphite oxide and graphene sheets decorated with Fe nanoclusters synthesized by arc-discharge between graphite rods.

2. EXPERIMENTAL

2.1. Synthesis of graphene oxide and Fe nanoclusters decorated graphene

Graphene oxide (GO) has been synthesized by thermal exfoliation of graphite oxide, through modified Staudenmaier's method adopted by Schniepp *et al.* [19]. In

this method, GO was prepared by oxidizing graphite powder (99.99%, Sigma-Aldrich) in concentrated sulfuric acid and nitric acid under continuous stirring. After the graphite powder was well dispersed into a black slurry, potassium chloride was added slowly under an ice cooled water bath. The resulting mixture was kept at room temperature under continuous stirring for 95 hours. Then it was filtered and washed with dilute HCl and distilled water. The resultant powder was dried at 40°C under vacuum for 5 hours. The graphite oxide thus obtained was thermally exfoliated at 1050°C under argon atmosphere for 30 sec in a quartz tube of 1.5 m long and 2.5 cm inner diameter. The as-obtained shiny black material was thermally reduced at 623K for about three hours under high vacuum with an ultimate vacuum of the order of 10^{-7} torr. As evidenced from the mass spectra, during heating, the oxygen functionalities in graphene oxide get removed as CO and CO₂. The resultant graphene sample derived after thermal reduction is termed as thermally reduced graphene oxide (TR-GO). The removal of oxygen from GO may lead to the creation of strains and/or topological defects on C-structure [20]. Alternatively, GO was reduced using chemical reducing agent, hydrazine hydrate [21, 22]. GO reduced through chemical reduction has been termed as Chemically Reduced Graphene Oxide (CR-GO). CRGO thus prepared exhibits some lattice distortion and a large number of structural defects arise due to the removal of oxygen functionalities [23]. Graphene sheets decorated with Fe nanoclusters (Fe-GS) was synthesized in an arc reactor using a pure graphite rod and another graphite rod impregnated with Fe nanopowder (APS 10-30 nm, 99.9%, Alfa Aesar). The Fe nanopowder impregnated graphite rod acts as an anode and the pure graphite electrode acts as the cathode. The arc was generated between the electrodes under ~300 torr argon partial pressure using an applied dc source of ~100A and 25V. After 8-10 minutes of the arcing process, a black flake-like material gets deposited around the wall of the arcing chamber, which was collected and then subjected to characterization. The graphene nanosheets obtained through this process contain very negligible oxygen functionalities [24, 25]. Therefore, we termed it "Graphene Sheets (GS)", whereas GO samples derived by thermal exfoliation of graphite oxide contain a large amount of oxygen functionalities [26].

2.2. Characterization

Structural characterization of the samples was carried out using X'Pert PRO (PANalytical) X-ray diffractometer equipped with a graphite monochromator employing CuK_α radiation ($\lambda = 1.5402\text{\AA}$). Microstructural characterization was done by using Technai 200 kV high resolution transmission electron microscope (TEM). Raman spectra were obtained using Horiba LabRAM HR800.

2.3. Gas Sorption Analysis

Gas sorption behavior of graphene samples were determined using an automated four-channel Sieverts apparatus (Advanced Materials Corporation, USA; www.advanced-material.com). All gases used for sorption analysis are of 99.999% purity. PCT adsorption/desorption isotherms of graphene samples were determined between the pressure range 0.1 and 50 bar at 300 K and at 77 K. About 25 mg of sample was used for each sorption analysis in a leak-tight stainless steel sample chamber. The sample temperature was maintained at 77 K during PCT measurement using liquid nitrogen. Isothermal adsorption kinetics were determined at three different pressures using the *soak* mode available in our apparatus. Prior to gas sorption studies, the samples were outgassed at 523 K for about two hours under high vacuum of the order of 10^{-7} torr, using a turbo-molecular pump (Adixen ATP 80). The effluent gases were analyzed using a residual gas analyzer (SRS RGA 200).

3. RESULTS AND DISCUSSION

3.1. Structural and Microstructural Characterization of Graphene

TEM micrograph and Raman spectra confirm the samples exhibit typical characteristics of graphene. Representative TEM micrographs of GO, TR-GO, CR-GO and Fe-GS synthesized in the present investigation are shown in Fig. 1(a-d).

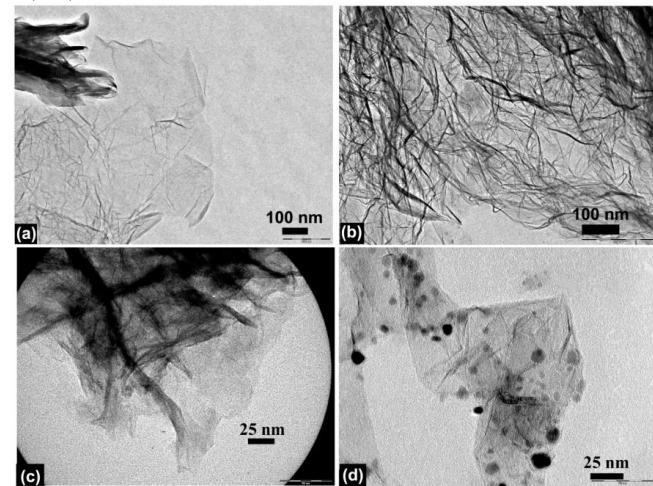


Fig. 1. Transmission electron micrograph of (a) GO (b) TR-GO (c) CR-GO and (d) Fe-GS.

TEM observation shows the as-prepared GO nanosheets shown in (See Fig. 1(a)) are of a few-layers thick and are flat with a dimension $> 1 \mu\text{m}$ length and breadth. The flat GO surface is due to the existence of a large amount of oxygen-containing functional groups on GO [26]. TEM micrographs of TR-GO and CR-GO (See Fig. 1(b) and Fig. 1(c)) indicated that these materials are layer-structured with built-in wrinkles. Corrugation and scrolling suggested the intrinsic nature of graphene, since the 2D membrane

structure would be thermodynamically stable *via* bending and wrinkling [27].

Fig. 2 depicts the Raman spectra of as-prepared GO, TR-GO, CR-GO and Fe-GS.

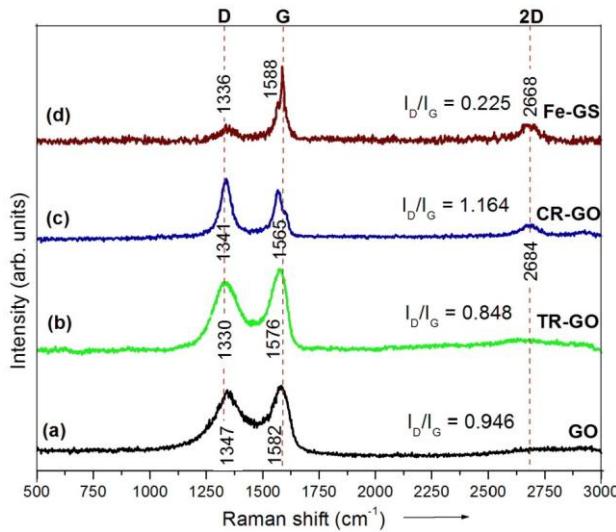


Fig. 2. Raman spectra of (a) GO, (b) TR-GO, (c) CR-GO and (d) CR-GO

The G-band and D-band appear around 1580 and 1350 cm^{-1} , respectively. The G-band is associated with the E_{2g} vibration mode of sp^2 lattice of the graphitic materials. The D-band is due to the breathing modes of six-atom rings, which are associated with the structural defects in sp^2 lattice [28]. Using the D-band and G-band peak intensities ratio (I_D/I_G) of Raman Spectra, it is possible to characterize the level of disorder in graphene. As disorder in graphene increases, I_D/I_G will increase up to a regime of high defect density and then I_D/I_G will begin to decrease due to increasing defect density. This results in a more amorphous carbon structure, diminishing all Raman peaks [29]. The I_D/I_G ratio determined for GO is 0.946 . After thermal reduction of GO, the I_D/I_G ratio corresponding to TR-GO decreases to 0.848 . This slight upshift of G-band and downshift of D-band can be attributed to disorder associated with reduction in the oxygen-defects (i.e., graphitization increases) [30]. However, after chemical reduction of GO (CR-GO), the I_D/I_G ratio increases to 1.164 . This signifies that chemical reduction produces higher level of structural disorder in graphene. The I_D/I_G ratio for Fe-GS is 0.225 . This significant upshift in G-band and downshift in D-band peaks observed for Fe-GS is due to increased defects in the graphene structure due to the interaction of Fe with graphene lattice [31].

3.2. Hydrogen Uptake of Graphene

Isothermal hydrogen sorption analyses of graphene samples were carried out at room temperature (300 K) and at 77 K ,

by measuring the volume of gas adsorbed/desorbed with respect to the applied hydrogen pressure (between 0.1 and 50 bar). It has been noticed that there is hysteresis between adsorption and desorption at 300 K . However, the adsorption- desorption hysteresis was found to decrease at 77 K . A representative hydrogen isotherm of TR-GO, CR-GO and Fe-Gs determined at 77 K and 300 K between the pressures 0.1 and 50 bar are shown in Fig. 3 (a-c).

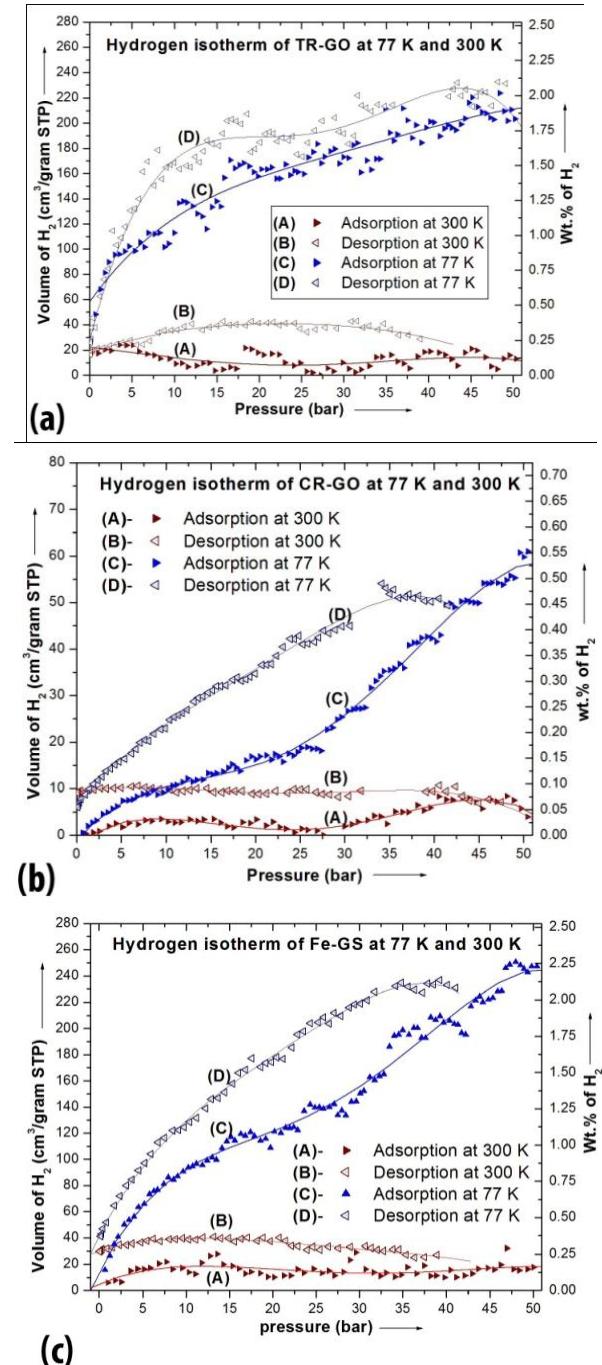


Fig. 3. Isothermal hydrogen adsorption/desorption plots of (a) TR-GO, (b) CR-GO and (c) FeGS

The hysteresis between adsorption and desorption isotherm observed in all the graphene samples signifies its surface heterogeneity [32]. TR-GO exhibits the higher hydrogen uptake capacity of 2.07 wt.% H₂ at 77 K/ 50 bar with less hysteresis between adsorption and desorption among the graphene based samples investigated in this study. The hydrogen uptake capacity determined for different graphene samples is summarized in Table. 1.

Table. 1. Summary of hydrogen uptake capacity determined for graphene samples used in the present study.

Sample	BET surface area (m ² /g)	Hydrogen uptake capacity (wt. %)	Temperature (K)	Pressure (bar)
GO	304	0.17	300	50
Thermally reduced GO	375	0.32	300	50
		2.07	77	50
		0.1	300	50
Chemically reduced GO	9	0.54	77	50
		0.27	300	50
Graphene nanosheets decorated with Fe	190	2.16	77	50

From the hydrogen adsorption isotherms and Raman spectra of these graphene samples, we have observed that the hydrogen uptake capacity of graphene sample depends not only on its surface area but also its defects concentration. Hence, CR-GO with very low surface area and more structural defects show high hydrogen uptake behavior.

4. CONCLUSIONS

Raman spectra shows that chemical reduction and metal decoration produces more structural disorder in graphene. The hydrogen uptake capacity of TR-GO, CR-GO and Fe-GS determined at 77 K and 50 bar are 230 cm³/gram (2.07 wt.% H₂), 60 cm³/gram (0.54 wt.% H₂) and 240 cm³/gram (2.16 wt.% H₂), respectively. We have also observed that the hydrogen uptake capacity of graphene sample depends not only on its surface area but also its defects concentration. More defective graphene surface exhibits higher hydrogen uptake behavior.

REFERENCES

- [1] Chen D, Feng H, Li J. Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications. Chem. Rev. 2012; **112(11)**: 6027-6053.
- [2] Wan X, Huang Y and Chen Y. Focusing on Energy and Optoelectronic Applications: A Journey for Graphene and Graphene Oxide at Large Scale. Acc. Chem. Res. 2012; **45(4)**: 598-607.
- [3] Jena P. Materials for Hydrogen Storage: Past, Present, and Future. J. Phys. Chem. Lett. 2011; **2(3)**: 206-2011.
- [4] Yang J, Sudik A, Wolverton C and Siegel DJ. High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery. Chem. Soc. Rev. 2010; **39(2)**: 656-675.
- [5] Hudson MSL, Dubey PK, Pukazh selvan D, Pandey SK, Singh RK, Raghubanshi H, Shahi RR, Srivastava ON. Hydrogen energy in changing environmental scenario: Indian Context. Int. J of Hydrogen Energy 2009; **34(17)**: 7358-7367.
- [6] Berseth P A, Harter A G, Zidan R, Blomqvist A, Araujo C M, Scheicher R H, Ahuja R and Jena P. Carbon Nanomaterials as Catalysts for Hydrogen Uptake and Release in NaAlH₄. Nano Lett. 2009; **9(4)**: 1501-1505.
- [7] Pukazh selvan D, Hudson MSL and Srivastava ON. Direct synthesis of sodium alanate using mischmetal nanocatalyst. Int. J of Hydrogen Energy 2012; **37(4)**: 3697-3704.
- [8] Subrahmanyam KS, Vivekchand SRC, Govindaraj A and Rao CNR. A study of graphenes prepared by different methods: characterization properties and solubilization. J. Mater. Chem. 2008; **18**: 1517-1523.
- [9] Ghosh A, Subrahmanyam KS, Krishna KS, Datta S, Govindaraj A, Pati SK, Rao CN R. Uptake of H₂ and CO₂ by Graphene. J. Phys. Chem. C 2008; **112(40)**: 15704-15707.
- [10] Benard P and Chahine R. Modeling of adsorption storage of hydrogen on activated carbons. Int. J of Hydrogen Energy 2001; **26(8)**: 849-855.
- [11] Jin Z, Lu W, O'Neill KJ, Parilla PA, Simpson LJ, Kittrell C and Tour JM. Nano-Engineered Spacing in Graphene Sheets for Hydrogen Storage. Chem. Mater. 2011; **23(4)**: 923-925.
- [12] Huang CC, Pu NW, Wang CA, Huang JC, Sung Y, Ger MD, Hydrogen storage in graphene decorated with Pd and Pt nano-particles using an electroless deposition technique, Sep. and Pur. Tech. 2011; **82(27)**: 210-215.
- [13] Contescu CI, Brown CM, Liu Y, Bhat VV and Gallego NC, Detection of Hydrogen Spillover in Palladium-Modified Activated Carbon Fibres during Hydrogen Adsorption.
- [14] Parambhath VB, Nagar R, Ramaprabhu S, Effect of Nitrogen Doping on Hydrogen Storage Capacity of Palladium Decorated Graphene, Langmuir 2012; **28(20)**: 7826-7833. J of Phys. Chem. C 2009; **113(14)**: 5886-5890.
- [15] Tozzini V and Pellegrini V. Reversible Hydrogen Storage by Controlled Buckling of Graphene Layers, J of Phys. Chem. C 2011; **115(51)**: 25523-25528.

- [16] Ataca C, Akturk E, Ciraci S and Ustunel H. High-capacity hydrogen storage by metallized graphene, *Appl. Phys. Lett.* 2008; **93**: 043123.
- [17] Ao ZM and Peeters M. High-capacity hydrogen storage in Al adsorbed graphene, *Phys. Rev. B* 2010; **81**: 205406.
- [18] Zhou W, Zhou J, Shen J, Ouyang C and Shi S. First principles study of high-capacity hydrogen storage on graphene with Li atom, *J of Phy. Chem. Sol.* 2012; **73(2)**: 245-251.
- [19] Schniepp HC, Li JL, McAllister MJ, Sai H, Alonso MH, Adamson DH, Homme RKP, Car R, Saville DA, Aksay IA. Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide. *J of Phys. Chem. B* 2006; **110(17)**: 8535-8539.
- [20] Ganguly A, Sharma S, Papakonstantinou P and Hamilton J. Probing the Thermal Deoxygenation of Graphene Oxide using High Resolution *In Situ* X-Ray Based Spectroscopies. *J. Phy. Chem. C* 2011; **115(34)**: 17009-17019.
- [21] Ren PG, Yan DX, Ji X, Chen T, Li ZM. Temperature dependence of graphene oxide reduced by hydrazine hydrate. *Nanotechnology* 2011; **22(5)**: 055705.
- [22] Park S, Hu Y, Hwang JO, Lee ES, Casabianca LB, Cai W, Potts JR, Ha HW, Chen S, Oh J, Kim SO, Kim YH, Ishii Y, Ruoff RS. Chemical structures of hydrazine-treated graphene oxide and generation of aromatic nitrogen doping. *Nat. Commun.* 2012; **3:638**: 1-8.
- [23] Rozada R, Paredes JI, Villar-Rodil S, Martinez-Akibso A and Tascon MD. Towards full repair of defects in reduced graphene oxide films by two-step graphitization, *Nano Research* 2013; **6(3)**: 216-233.
- [24] Wu Y, Wang B, Ma Y, Huang Y, Li N, Zhang F and Chen Y. Efficient and Large-Scale Synthesis of Few-Layered Graphene Using an Arc-Discharge Method and Conductivity Studies of the Resulting Films, *Nano Res.* 2010; **3(9)**: 661-669.
- [25] Matte HSSR, Subrahmanyam KS and Rao CNR. Systematic Aspects and Selected Properties of Graphene, *Nanomater. Nanotechnol.* 2011; **1(1)**: 3-13.
- [26] Fu C, Zhao G, Zhang H and Li S. Evaluation and Characterization of Reduced Graphene Oxide Nanosheets as Anode Materials for Lithium-Ion Batteries, *Int. J Electrochem. Sci.* 2013; **8**: 6269-6280.
- [27] Wang ZL, Xu D, Huang Y, Wu Z, Wang LM and Zhang XB. Facile, mild and fast thermal-decomposition reduction of graphene oxide in air and its application in high-performance lithium batteries. *Chem. Comm.* 2012; **48**: 976-978.
- [28] Cancado LG, Jorio A, Ferreira EHM, Stavale F, Achete CA, Capaz RB, Moutinho MVO, Lombardo A, Kulmala TS and Ferrari AC. Quantifying Defects in Graphene via Raman Spectroscopy at Different Excitation Energies, *Nano Lett.* 2011; **11**: 3190-3196.
- [29] Childres I, Jauregui LA, Park W, Cao H and Chen YP. Raman Spectroscopy of Graphene and Related Materials: Jang JI editor. *Developments in Photon and Materials Research*, Nova Science Publishers; 2013, ISBN: 978-1-62618-384-1.
- [30] Ambrosi A, Bonanni A, Sofer Z, Cross JS and Pumera M. Electrochemistry at chemically modified graphenes. *Chem.* 2011; **17(38)**: 10763-10770.
- [31] Gutes A, Hsia B, Sussman A, Mickelson W, Zettl A, Carraro C and Maboudian R. Graphene decoration with metal nanoparticles: Towards easy integration for sensing applications. *Nanoscale* 2012; **4**: 438-440.
- [32] Levy AS and Avnir D. Surface Geometry Effects on Adsorption-Desorption Hysteresis, Latent Adsorption and Adsorption-Probability Plots. *Stud. Surf. Sci. and Catalysis* 1993; **80**: 365-372.