

Some notable experiments of graphene

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Abstract : Graphene is an allotrope of carbon where carbon atoms are attached through sp^2 hybridization in a two-dimensional (2D) plane. Based on the structure, graphene can be visualized as a single sheet of graphite. A. Geim and K. Novoselov successfully isolated free standing monolayer graphene from graphite by scotch tape method for the first time in 2004. This discovery won them the Nobel Prize in physics 2010. However, several inception experiments had been carried out much before its birth by other eminent scientists. In fact, several extended experiments have been performed to understand the properties of graphene after its discovery. This article is a collection of some of the notable pre and post-discovery experiments. In addition, it includes some of the experiments those have been carried out at CSIR-NML.

Keywords: Graphene; Bio-polymer; Natural carbon source; Photocatalytic method; Ion-bombardment; Scotch tape method

PRIOR TO DISCOVERY

The first study of graphite exfoliation was reported by the German Scientist C. Schafhaeutl in the year 1840^[1, 2]. He mixed graphite in a solution of nitric and sulphuric acid, subsequently boiled to remove these acids from the solution. He observed that the color of the graphite turned to shiny blue upon reaction with sulphuric and nitric acid. However, this study was limited to observation only without any conclusion. In the year 1859 British chemist Sir Benjamin Brodie aimed to investigate the structure, molecular formula and molecular weight of graphite by studying the reactivity of flake graphite^[3, 4]. In the experimental protocol, he heated lamellar graphite with potassium perchlorate and fuming nitric acid at 60°C for 3 to 4 days and repeated the process 3-4 times to ensure complete oxidation. He concluded the following points; (i) the structure of graphite was uneven and composed of carbon, oxygen and hydrogen, (ii) the size of crystals in the perpendicular direction from the ground was extremely thin and it was not possible to receive any reflection by the thickness measurement instrument, (iii) the ignition of the crystal yielded black residue and (iv) this material was dispersible in pure and basic water. Based on these observations, he determined that the molecular weight of graphite is 33. He says that “*This form of carbon should be characterized by a name marking it as a distinct element. I propose to term it Graphon*”. Subsequently, Frenzel and co-workers studied the structural investigation of those samples reported by Brodie using XRD in the year 1934, and they concluded that the intercalation of graphitic layers takes place during the experiment^[5]. Few years later, Staudenmaier modified the Brodie’s synthesis method, where potassium chlorate was added drop wise to avoid explosion caused by evolution of large amount of gases and heat. In addition, partial amount of fuming H_2SO_4 was added in the place of fuming HNO_3 to enhance the oxidation. So, the modified experiment reduced the release of toxic gases (NO_2 , N_2O_4 etc) and increased the reaction rate and the C / O ratio^[6]. In the year 1957, Hummers reported a new protocol for the preparation of graphite oxide^[7]. This method comprised of the treatment of graphite with the water-free mixture of sulphuric acid, sodium nitrate and potassium permanganate at temperature less than 45°C. This method took less than two hours for complete oxidation of graphite. The color of the graphite oxide solution was footprint to determine the degree of oxidation; yellow bright at high degree of oxidation and green to black hue in the case of poor oxidation. Currently, this is most adoptive method for the conversion of graphite to graphite oxide, which is popularly known as Hummers method.

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In fact, some eminent groups had carried out theoretical studies to understand the properties of individual graphite layer. In the year 1947, P. R. Wallace for the first time calculated the electronic band structure of individual graphite layer^[8]. He reported that in the reciprocal lattice two atoms unit cell constitute the Brillouin Zone with two conical point at the Fermi surface, K and K ϵ known as Dirac points while the π - π^* band touch at a point. Besides, the electron energy is linearly dependent on the wave vector near the Dirac point. Therefore, graphene is a semimetal or zero-band gap semiconductor. Due to this unique band structure charge carrier in graphene mimic the features of zero mass particles. As a result, the electron mobility in individual graphitic layer is just 300 times less than the speed of light. However, Mermin-Wagner theorem suggested that 2-D materials are thermodynamically unstable in any finite temperature^[9], which discouraged the possibility of the formation of individual graphitic layer experimentally. Therefore, the study of Wallace remained just as a fundamental study to understand the electronic properties of individual graphitic layer. In the year 1962 Boehm et al. reduced the suspension of graphite oxide into thin lamellar carbon using hydrazine, hydrogen sulphide in dilute alkaline media. This experiment protocol yielded very thin lamellar carbon with small amount of oxygen and hydrogen^[10, 11]. In addition, TEM data indicated that the thickness of the thin lamellar carbon is around 4.6Å with a little deviation from the thickness of single layer graphene that is observed in the recent studied i.e. 4Å. Though the TEM data suffered some serious experimental errors, Boehm concluded that these films contain single carbon layer.

In 1968 Morgan and Somorjai used low energy electron diffraction (LEED) technique to investigate the adsorption of organic gas on platinum (100) surface at high temperature^[12]. The LEED data revealed that the organic gas converted into single and multilayer graphitic carbon sheets. In contrast to the Mermin-Wagner theorem, this study proposed that platinum surface played an important role to stabilize the single layer of graphitic carbon by minimizing the free energy. The observed single layer of carbon on platinum surface by Morgan and Somorjai can be considered to be graphene based on the structural features, even though the term of graphene was not coined by that time. Next, Blakely and co-workers reported that the dissolved carbon of transition metals at high temperature converted into single and multilayer of carbon sheets at the surface^[13]. In 1975 van Bommel et al. also observed the formation of single layer graphitic structure at the surface when the single crystal silicon carbide was heated under ultra-high vacuum at and below 800 °C^[14]. Around the time of 1980 many reports on single and multilayer carbon with graphitic structure came into lime light. Hence to precise the definition of this material Boehm et al. in 1986 proposed that the single layer of carbon having the graphitic structure or simply the single layer of graphite should be called as “graphene”^[15]. In 1997 IUPAC incorporated the suggestion of Boehm et al. in the Compendium of Chemical Technology, and it was suggested that “The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed”^[16, 17]. Further, Kovtyukhova and co-workers in 1999 made a pretreatment of graphite with H₂SO₄, K₂S₂O₈ and P₂O₅ to increase the extent of oxidation^[18]. In the same year, Ruoff’s group attempted to manipulate the thickness of highly oriented pyrolytic graphite (HOPG) using AFM tip with the goal to achieve single sheet^[19, 20]. The results showed that the thickness of prepared graphite was around 200 nm which is equivalent to 600 layers of graphite. Later, Kim’s group at Columbia studied the prepared sample from HOPG and could obtained information up to 10 nm thick graphite by a tip less cantilever of AFM, which is equivalent to 30 layers of graphite^[21]. Finally, A. Geim and K. Novoselov from the University of Manchester isolated graphene from graphite using micromechanical method or scotch tape method in 2004^[22]. In this method the individual layers were separated out from the HOPG by using a Scotch tape. This is also known as peeling off method as it involves the cleavage of the HOPG layers in to individual layers with the help of a scotch tape. In a typical method the HOPG powder is pressed in the scotch tape and repeated peeling of the HOPG powder bring it down to a single layer. The underlying mechanism of this process is the application of the normal force for several times to peel off HOPG down to single layer. Depending on the extent of cleavage it yielded mono, bi or few layers graphene.

They transferred the individual layer onto silicon wafer and studied the electronic properties. They observed anomalous quantum effect, which is quite similar to those predicted much before theoretically. In addition, they observed that graphene is a semimetal where the conduction band overlaps with the valence band. The mobility and concentration of the charge carrier were determined by the field effect and magneto-resistance measurements. The calculated mobility was 15000 and 60000 cm²/V.s at 300 and 4 K, respectively. The carrier density was estimated to be > 10¹² cm⁻². The Royal Swedish Academy of Sciences awarded the Nobel prize in physics for 2010 to A. Geim and K. Novoselov for their groundbreaking experiments of graphene. After that, graphene drew attention of many research groups worldwide to explore its utilization towards novel and advanced applications such as opto-electronics, energy storage, photo-voltaic, composite materials, bio-medical, corrosion protection etc.

BEYOND DISCOVERY

After its discovery in 2004, researchers had also attempted to exfoliate graphite via liquid phase exfoliation in order to overcome the criticality and challenges for the volume production of graphene. The sonication assisted liquid phase exfoliation method was reported by Coleman's and Geim's group separately in 2008^[23, 24]. The process involved dispersion of graphite flake in solvent like N, N-dimethyl formamide, N-methylpyrrolidone etc. followed by sonication. Solvents were chosen based on whose surface energy is closer to graphite surface energy, so that the mixing enthalpy will be smaller and exfoliation would be easier. This method also produced graphene. The underlying mechanism of the process is based on the principle of liquid cavitation, in which the cavitation induced bubbles in the solution. The bursting of these bubbles generated shock waves on the graphite surface immediately that led to form the compressive wave. Once the compressive wave spread into the free interface of graphite, a tensile stress wave is reflected back to the body. The generation and bursting of numerous bubbles generates enough tensile stress on the graphite flakes that led to exfoliate of graphite flake and produce graphene sheets. This is a much simpler process for obtaining large scale graphene with respect to the mechanical exfoliation process.

In addition, the remarkable thermal conductivity and mechanical strength properties of free standing graphene sheet were reported by the eminent groups. Balandin measured the thermal conductivity of a free standing single-layer graphene at room temperature using a laser based non-contact technique^[25]. In the experiment, the graphene sheet was suspended over a trench of a Si/SiO₂ substrate. The heat was induced by focusing the laser light of excitation wavelength 488 nm at the center of the graphene sheet. The transformation of heat to the Si substrate was negligible as the thermal conductivity of beneath SiO₂ layer is ~1 W/mK. Considering air has negligible thermal conductivity, the following equation was used for determination of the thermal conductivity; $\partial Q/\partial t = -K\phi \nabla T \cdot dS$, where Q is the induced heat transferred over the time t with the cross sectional area S and T is the temperature. The thermal conductivity is found to be ~5.3 x 10³ W/mK. The high value of the thermal conductivity suggested that it could be an excellent material for thermal management in electronic devices.

Lee et al. measured the elastic and strength properties of the monolayer graphene membrane using nanoindentation in an atomic force microscope (Model: XE-100, Park systems)^[26]. The diamond cantilevers with tip radii of 27.5 and 16.5 nm were used for this study. The spring constant of these cantilevers were calibrated with respect to the reference cantilever. Prior to the nanoindentation experiment, the graphene membrane was scanned by non-contact AFM mode and the tip was placed within 50 nm of the center. Mechanical testing measurement was carried out at constant displacement rate. The acquired data showed no hysteresis loop, indicated the membrane is highly elastic. The breaking force value from the experimental data was calculated to be 2890 nN when the tip radii is 27.5 nm. It was noted that the second and third order stiffness constants are $E^{2D} = 340 \pm 50 \text{ N m}^{-1}$ and $D^{2D} = -690 \pm 120 \text{ N m}^{-1}$, respectively. The intrinsic strength was calculated using

the equation; $\sigma_m^{2D} = (F E^{2D} / 4\pi R)^{1/2}$ and the value was found to be $40 \pm 4 \text{ N m}^{-1}$ by considering the thickness of monolayer graphene is 0.335 nm. The Young's modulus and intrinsic stress were estimated to be of $E = 1.0 \pm 0.1 \text{ TPa}$ and $\sigma_{int} = 130 \pm 10 \text{ GPa}$ at a strain of $e = 0.25$. This experiment suggests that graphene is a strongest material ever known in the universe.

EXPERIMENTS MADE AT CSIR-NML

CSIR-NML published the first report of graphene production in 2012 using lotus flower as a carbon source. It was accidental observation made by A. K. Ray. The main intention of the experiment was conversion of NiCl_2 to Ni nanoparticles by plant as the enzyme of plant has ability to reduce metal ions and form nanoparticles. However, it was an unsuccessful experiment to produce Ni nanoparticles at room temperature. In next plan of experiments, it was decided to heat the flower petals at temperature more than 1000°C . The obtained product was characterized first using Raman spectroscopy. The Raman data was surprised to all of us, where 2D peak was more intense than D and G peaks and the data were well matched with the earlier reported data for graphene [27]. After that, we designed several other experiments for the production of graphene in order to understand the conversion mechanism from the constituent cellulose structure to graphene. In fact, the same kind of Raman data was observed in the case of conversion hibiscus flower to graphene (Fig.1).

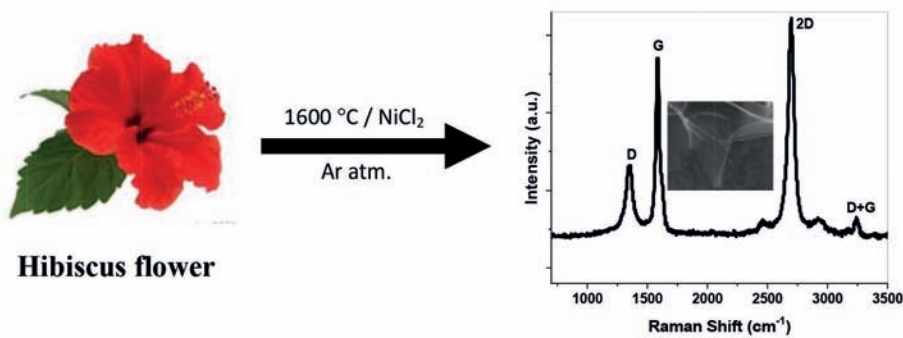


Fig. 1 Experimental protocol and Raman data for the conversion of hibiscus flower to graphene.

We also devised a new experiment for exfoliation of graphene from graphite by photocatalytic reduction [28], where the yellow color graphite oxide solution prepared by Hummers method was reduced using peanut shaped $\alpha\text{-Fe}_2\text{O}_3$ particles under visible light. The monodispersed particles with bandgap $\sim 2.5 \text{ eV}$ was efficient to transfer electrons to the graphite oxide sheet for reduction and exfoliation that led to form large size $\alpha\text{-Fe}_2\text{O}_3$ particles embedded thin graphene sheet (Fig. 2). These particles could also be separated from the graphene sheet by centrifuged the solution at 10000 rpm.

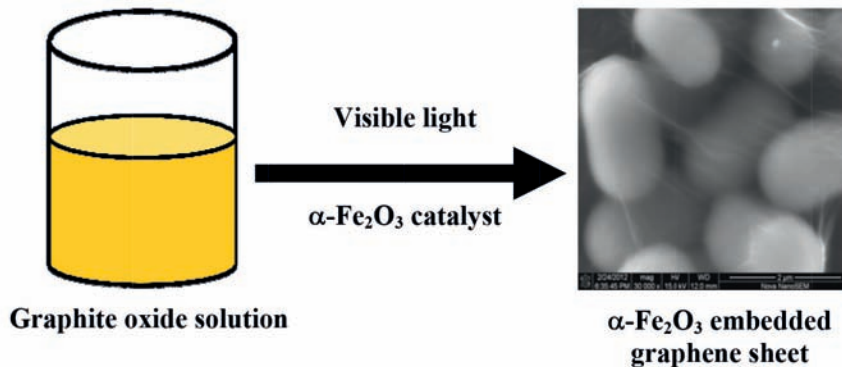


Fig. 2 Experimental protocol for the conversion of graphite oxide solution to graphene sheet by photocatalytic reduction.

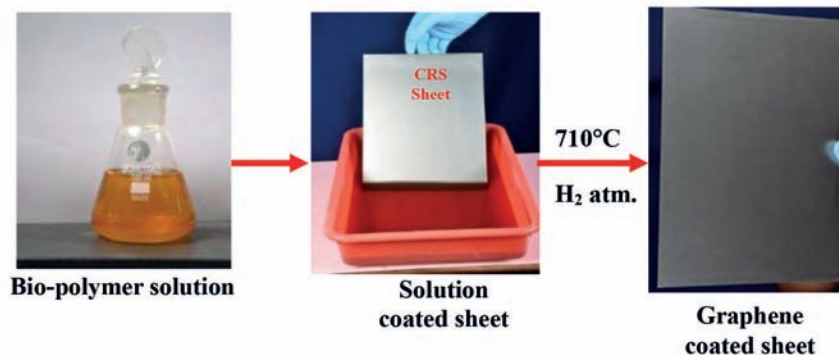


Fig. 3 The schematic representation for the production of graphene coated cold rolled sheet using bio-polymer solution.

Besides, we demonstrated that Ar⁺ ion bombardment could be used for conversion of non-aromatic pyrazoline to aromatic pyrazole N-ring of hydrazine reduced graphene sheet at room temperature^[29]. Such conversion enhanced the conductivity of the graphene film. In 2014, a simple protocol was developed to produce large area graphene coating over steel substrates using shellac bio-polymer as a carbon source under a collaborative project with Tata Steel, Jamshedpur. The existing batch annealing furnace of Tata Steel was used for the conversion of bio-polymer to graphene over a A4 size cold rolled sheet under the heating conditions of 710°C for 24 hrs in H₂ atmosphere (Fig. 3). Subsequent post-treatment of these coated steel products enabled to enhance the corrosion protection in saline environment. This pioneering work received Tata Innovista Award in 2015 from Tata Sons. In addition, NML also initiated collaboration with M/s- John Keells, Sri Lanka for the direct exfoliation of graphite using collagen protein and the produced graphene is suitable for supercapacitor application.

FUTURE ROADMAP AT CSIR-NML

The functional materials group at CSIR-NML is moving towards with the goal of large scale production of graphene from medium purity Indian flake graphite with high energy storage capacity in the wake of indigenously developed energy storage materials will play a pivotal role in fulfilling the sustainable vision set by India for complete mobility to electric vehicle by 2030. Graphite is one of the key materials used in energy storage applications. Despite India is fifth major producers of flake graphite in the world, existing processed graphite materials are unsuited for high performance energy storage devices. The major drawback of Indian graphite is that it contains silica impurity with the average purity of around 90 %. Even after beneficiation of high grade graphite minerals with modified processing technology by some Indian companies it has been achieved maximum purity up to 94%, which is again below then the required purity (~99%) for energy storage applications. In addition, no efforts have been made by Indian industries to improve the energy storage capacity of natural graphite by devising a new strategy, which further increases the dependency of our electric vehicle manufacturing companies on other countries for energy storage materials and devices. However, the energy storing capacity of Indian flake graphite can be enhanced by improving electrical conductivity and surface area through reducing its thickness along the Z-axis down to few layers and converting the silica impurity to Fe, Co, Ni-silicate functionalized phases containing redox ionic pairs. Such anticipated functionalized graphene would provide a strong support for fabrication of high-performance battery and supercapacitor indigenously.

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REFERENCES:

- [1] C. Schafhaeutl: Ueber die verbindungen des kohlenstoffes mit silicium, eisen und anderen metallen, welche die verschiedenen gallungen von roheisen, stahl und schmiedeeisen bilden. *J. Prakt. Chem.* 21: 129-157, 1840.
- [2] C. Schafhaeutl: LXXXVI. On the combinations of carbon with silicon and iron and other metals forming the different species of cast iron, steel and malleable iron. *Phil. Mag.* 16: 570-590, 1840.
- [3] B.C. Brodie: XIII. On the atomic weight of graphite. *Philos Trans R Soc London* 149: 249-259, 1859.
- [4] B.C. Brodie: XXIII.-Researches on the atomic weight of graphite. *Q. J. Chem. Soc.* 12: 261-268, 1860.
- [5] U. Hoffman, A. Frenzel and E. Casalan: Die konstitution der graphitsäure und ihre reaktionen. *Ann. Chem.* 510: 1-41, 1934.
- [6] L. Staudenmaier: Verfahren zur darstellung der graphitsäure. *Ber. Dtsch. Chem. Ges.* 31: 1481-1487, 1898.
- [7] W.S. Hummers and R. E. Offeman: Preparation of graphitic oxide. *J. Am. Chem. Soc.* 80: 1339-1939, 1958.
- [8] P.R. Wallace: The band theory of graphite. *Phys. Rev.* 71: 622-634, 1947.
- [9] N.D. Mermin: Crystalline order in two dimensions. *Phys. Rev.* 176: 250-254, 1968.
- [10] H.P. Boehm, A. Clauss, G.O. Fischer and U. Hofmann: Thin carbon leaves. *Naturforsch* 17: 150-153, 1962.
- [11] H.P. Boehm, A. Clauss, G.O. Fischer and U. Hofmann: The adsorption behavior of very thin carbon films. *Anorg. Allg. Chem.* 316: 119-127, 1962.
- [12] A.E. Morgan and G.A. Somorjai: Low energy electron diffraction studies of gas adsorption on the platinum (100) single crystal surface. *Surf. Sci.* 12: 405-425, 1968.
- [13] J.M. Blakely, J.S. Kim and H.C. Potter: Segregation of carbon to the (100) surface of Nickel, *J. Appl. Phys.* 41: 2693-2697, 1970.
- [14] A.J. van Bommel, J.E. Crombeen and A. van Tooren: LEED and Auger electron observations of the SiC (0001) surface. *Surf Sci* 48: 463-472, 1975.
- [15] H.P. Boehm, R. Setton and E. Stumpp: Nomenclature and terminology of graphite intercalation compounds. *Carbon* 24: 241-245, 1986.
- [16] E. Fitzer, K.-H. Kchling, H.P. Boehm and H. Marsh: Recommended terminology for the description of graphite as a solid. *Pure Appl. Chem.* 67: 473-506, 1995.
- [17] IUPAC in Compendium of Chemical Terminology (Eds.: A.D. McNaught, A. Wilkinson), 2nd ed., Blackwell Scientific, Oxford, 1997.
- [18] N.I. Kovtyukhova, P.J. Ollivier, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva, and A.D. Gorchinskiy: Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem. Mater.* 11: 771-778, 1999.
- [19] X. K. Lu, H. Huang, N. Nemchuk and R. S. Ruoff: Tailoring graphite with the goal of achieving single sheets. *Nanotechnology* 10: 269-272, 1999.
- [20] X. K. Lu, H. Huang, N. Nemchuk and R.S. Ruoff: Patterning of highly oriented pyrolytic graphite by oxygen plasma etching. *Appl. Phys. Lett.* 75: 193-197, 1999.
- [21] Y.B Zhang, J.P. Small, W.V. Pontius and P. Kim: Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices. *Appl. Phys. Lett.* 86: 073104-073107, 2005.
- [22] 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* 306: 666-669, 2004.
- [23] Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, I.T. McGovern, B. Holland, M. Byrne, Y.K. Gun'Ko, J.J. Boland, P.Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A.C. Ferrari and J.N. Coleman: High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat. Nanotech.* 3: 563-568, 2008.
- [24] P. Blake, P.D. Brimicombe, R.R. Nair, T.J. Booth, D. Jiang, F. Schedin, L.A. Ponomarenko, S.V. Morozov, H.F. Gleeson, E.W. Hill, A.K. Geim and K.S. Novoselov: Graphene-based liquid crystal device. *Nano. Lett.* 8:1704-1708, 2008.

SOME NOTABLE EXPERIMENTS OF GRAPHENE

- [25] A.A. Balandin: Thermal properties of graphene and nanostructured carbon materials. *Nat. Mater.* 10: 569-581, 2011.
- [26] C. Lee, X. Wei, J.W. Kysar, J. Hone: Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* 321: 385-388, 2008.
- [27] A.K. Ray, R.K. Sahu, V. Rajinikanth, H. Bapari. M. Ghosh, P. Paul: Preparation and characterization of graphene and Ni-decorated graphene using flower petals as the precursor material. *Carbon* 50: 4123-4129, 2012.
- [28] Y. N. Singhababu, K. K. Sahu, D. Dadhich, A. K. Pramanick, T. Mishra and R. K. Sahu: Capsule-embedded reduced graphene oxide: synthesis, mechanism and electrical properties. *J. Mater. Chem. C* 5: 958-966, 2013.
- [29] Y. N. Singhababu, P. Kumari, S. Parida, R. K. Sahu: Conversion of pyrazoline to pyrazole in hydrazine treated N-substituted reduced graphene oxide films obtained by ion bombardment and their electrical properties. *Carbon* 74: 32-43, 2014.