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**Review** Article

# Graphene: Potential material for nanoelectronics applications

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Owing to Moore's law and the advancements in microelectronics, the industry is shifting to nanoelectronics. The materials used for nanoelectronics applications are termed as nanomaterials recognized as the one which has at least one dimension less than 100 nm. Nanoelectronics allows bottom-up approach in contrast to the top-down approach adopted in microelectronics. So in nanoelectronics, the approach is to design systems using nanomaterials as basic building blocks. The importance of nanoelectronics is that different nanomaterials exhibit certain unusual properties not available at the micro scale. These unusual properties of the nanomaterials are utilized in a wide range of electronic applications like sensors, FETs, photovoltaic cells and many other exotic electronic devices applications. Graphene is one of the most recently discovered nanomaterial known for its exceptional mechanical, electrical, optical properties which are not found in any other material in the world. Being the thinnest, strongest, stiffest and the most conducting material in the world to find a graphene synthesis method which is facile, easy and economical so that graphene can be produced at large scale with least defects. Graphene is ready to replace silicon in almost all the semiconductor devices in order to enhance their capabilities. Till now graphene has been used in electronics applications like Li-ion batteries, photovoltaic cells, supercapacitors etc. In the present paper, various methods of synthesizing graphene, its properties, and work being carried out in the researcher's laboratory is presented.

Keywords: Graphene, Nanoelectronics, Structure, Synthesis and applications

#### **1** Introduction

Before the discovery of graphene in 2004, it was thought that the thermodynamic fluctuation does not allow the existence of two-dimensional crystals. In 2004, a scientist named Andre Geim used mechanical exfoliation method<sup>1,2</sup> to synthesize graphene from graphite.

After Graphene was discovered it was explored for various applications because of its exceptional properties. Graphene is a two-dimensional crystal made up of only carbon atoms as shown in Fig. 1. It is extremely transparent because it absorbs only 2.3% of light falling on it. This property is used in making transparent conducting electrodes. Graphene is known for its exceptionally excellent properties which inspires the scientists to further study this wonderful material. Some of its wonderful properties are its high intrinsic carrier mobility<sup>3</sup> (200000 cm<sup>2</sup>v<sup>-1</sup>s<sup>-1</sup>), high Young's modulus<sup>4</sup> of 1.0 TPa and high optical transmittance<sup>5</sup> of 97.7%. Graphene has the ability to sustain extremely high electric current density around million times more than copper<sup>6</sup>. It is also approximately 100 times stronger than steel<sup>7</sup>. Graphene can be stretched up to 20% of its original length without breaking and therefore used in making the flexible, unbreakable displays which can be twisted easily. It is the best conductor of heat, much better than diamond<sup>8</sup>.

In VLSI (Very Large Scale Integration) circuits as the number of components on a single chip increases the total power dissipation also increases. Graphene, because of its high thermal conductivity, shall be utilized in solving the problem of higher power dissipation in VLSI circuits. Integrated Circuits made up of graphene transistors can easily dissipate heat to the environment and are more durable than conventional Integrated Circuits.

Graphene is a two-dimensional structure made up of carbon atoms with the spacing between each carbon atom 0.142 nm. Other nanomaterials of carbon are one dimensional carbon nanotubes, quantum dots and fullerenes as shown in Fig. 2. In graphene, carbon atoms are bonded in hexagonal structure and any external atom trying to pass through this hexagonal structure will be detected by change in the electrical conductivity of graphene. This property of graphene is used in graphene based gas sensors. ITO (indium tin oxide) is widely used in making transparent conducting electrodes. ITO is easily breakable, costly, rigid and brittle, hence graphene is the most suitable material to replace ITO as a transparent conducting electrode. Graphene can be added to titanium dioxide to increase its conductivity, bringing 52.4 per cent more current into solar cell. So graphene is used to increase the efficiency of the solar cells. Due to its large surface area to mass ratio, it is used in making conductive plates of ultra-capacitors. These ultracapacitors exhibit greater energy storage density than conventionally available.

#### **1.1 Importance of Nanoparticles**

Nanoparticles are the small particles having size between 1 to 100 nanometers. Similarly, nano-size single crystals are called nanocrystals. Nanoparticles are of significant interest because at nano scale unusual and interesting properties are observed as their size approaches the nanoscale. At nanoscale, the percentage of atoms at the surface of material increases. Whereas in case of bulk materials the percentage of atoms at the surface is very less as compared to the number of atoms in the bulk of the material. Nanoparticles possess unexpected optical



Fig. 1 — Graphene honey comb two-dimensional structure



Fig. 2 — Different forms of carbon nano materials

properties. Gold nanoparticles offers low melting point as compared to the gold slab<sup>9</sup>. Photovoltaic cell coated with of nanoparticles absorbs much higher radiation and therefore, enhances the cell efficiency. Zinc oxide is another nanoparticle which is found to have superior Ultra Violet blocking properties therefore often used in the preparation of sunscreen lotions<sup>10</sup>. Nano-structured metal oxide semiconductors are used as window layers in solar cells. Particularly, because of its high transmission, significant surface area of nano-structured titanium oxide porous films are used in dye sensitized solar cells.

# 2 Graphene Synthesis Methods

From the history of graphene synthesis methods, we found that initially mechanical exfoliation method was used to make graphene using scotch tape and solid graphite source. Later on various methods for graphene synthesis, each having its own advantages and disadvantages have been discovered by the researchers. New methods of making graphene from different carbon sources are being investigated by the scientists. Figure 3 shows the graphene synthesis methods most commonly used by the researchers.

## 2.1 Mechanical Exfoliation Method

This is the simplest method known and can be employed in any laboratory to produce graphene sheets from few micrometer to 0.1 mm. The materials required for preparing graphene sheets are scotch tape and thick graphite bar/ sheet having high purity. The



Fig. 3 — Different synthesis methods of graphene

scotch tape is repeatedly used to peel off a layer of graphene from the graphite bar<sup>11</sup>. After a layer of graphene is attached to the tape it is transferred mechanically on to the substrate like silicon, glass etc. The main disadvantage of this method is that it is time consuming process and does not produce uniform quality graphene films. More over the graphene layer developed by this method are very thick.

## 2.2 Chemical Exfoliation Method

This method is somewhat similar to the mechanical exfoliation method except that here the graphite is immersed in a mixture of sulphuric acid and nitric acid in order to increase the spacing between different layers of graphene present in the graphite material, so that these can be extracted easily<sup>12</sup>. By adding layers of atoms between graphite layers facilitates easy peel-off graphene layers and process is termed as intercalation<sup>13</sup>. Other techniques such as ultrasonic heating<sup>14</sup> and acid treatment<sup>15</sup> are generally, used to produce nanoribbons also referred as thin flat graphene wires.

#### 2.3 Chemical Vapour Deposition Method

It is the widely known method to produce graphene on various substrates like Cu, Ni, Co, Si etc. In this method, the substrate is placed in the heated furnace and the carbon source gas is passed through it. The carbon is deposited on the surface of the substrate after chemical reaction. For example a mixture of gases like H<sub>2</sub>, Ar, CH<sub>4</sub> in controlled amount is allowed to flow in a horizontal furnace and the substrate heated to the temperature in the range 750°-1200°C to obtain thin graphene layer as shown in Fig. 4. In this process graphene is formed by hydrocarbon decomposition on the metallic substrates. By this technique, thick layers of graphene can be formed even on insulating substrate. This method is widely used because it is suitable for large scale commercial use. In this method, carbon is adsorbed from the carbon source onto the heated metallic substrate. By this method, graphene has been reported to form on Ni substrate by decomposition of ethylene<sup>16</sup>. Graphene layer formations by CVD technique have also been reported on various metallic substrates like Rh (Ref. 17), Pt (Refs 18-21), Ir (Ref. 22). Further, graphene is also reported to be synthesized on other substrates like Ru (Refs 23-26), Pd (Ref. 27) and Cu foils (Refs 28-31) etc. The various gaseous sources like methane, ethylene etc. have been used for graphene layer deposition using



Fig. 4 — Schematic illustration of graphene layer synthesis by CVD technique

CVD technique. Solid sources like polymethyl methacrylate (PMMA) can be used to synthesize graphene. Recently, scientists have demonstrated graphene layer formation by using simple eatable sugar as a solid source of carbon<sup>32</sup>.

#### 2.4 Epitaxial Growth on SiC

Another method of obtaining graphene is to heat silicon carbide (SiC) to high temperatures usually more than 1100°C to reduce it to graphene. This process produces epitaxial graphene with dimensions dependent upon the size of the SiC substrate. In the present method, the sublimation of the Si atom occurs from the surface<sup>33-35</sup> and the carbon atoms are left to form graphene<sup>36</sup>. The face of the SiC i.e. silicon or carbon-terminated used for graphene formation, influences the thickness, mobility and carrier density of the graphene<sup>37</sup>.

#### 2.5 Graphene Synthesis by Unzipping Carbon Nanotubes

Carbon nanotubes are the one dimensional nanomaterials formed by carbon atoms. When the graphene sheet is rolled up in a cylindrical manner it forms the carbon nanotubes which are known for their great strength and conductivity. By unzipping carbon nanotubes in the solution of potassium permanganate and sulfuric acid graphene can be synthesized<sup>38</sup>.

#### 2.6 Graphene by Langmuir-Blodgett (LB) method

In LB Technique, the raw material derived from re-intercalation and expansion of graphite is dissolved in water insoluble solvent, poured in DI water trough and separation of monolayers are formed based on hydrophilic and hydrophobic molecules. After properly adjusting the surface tension of water trough, the aligned graphene layer is deposited on the substrate. The precise control of substrate movement above water results growth of monolayer of graphene. Thicker graphene films can be produced by repeating the process again. This method produces good quality of thin graphene sheets. Graphene nanoribbons (GNR) have been reported to be produced by sonicating thermally exfoliated graphite in a 1,2-dichloroethane (DCE) solution of poly(m-phenylene vinylene-co-2,5-dioctoxy-p-phenylene vinylene).The LB technique gives low yield, nano ribbons synthesized contained two or more layers<sup>39-41</sup>.

#### 2.7 Hummer's Method

Hummer's method has been widely used by many researchers. The main advantage of this method is that it can give graphene with high yield and can be easily produced in the Laboratory. In Hummer's method, first graphite flakes or powder is mixed with acid and graphite oxide is formed. Then graphite oxide is converted to graphene oxide using sonication. In a typical experiment 2 g of graphite powder is added to 46 ml of sulfuric acid in an ice bath. Then, 6 g of potassium permagnate is added gradually over a period of 30 min with constant stirring in a round bottom flask as shown in Fig. 5. The mixture is stirred for 2 h approximately and 92 ml of water<sup>42</sup> is added. Finally, 280 ml of hydrogen peroxide is added and the reaction is stopped. The mixture is filtered and washed with HCl and dried. This gives the graphite oxide. Sonicating graphite oxide in distilled water gives graphene oxide which is converted to RGO (reduced graphene oxide) by using hydrazine hydrate. Many properties of RGO are similar to graphene, but due to some defects it do not produce hexagonal graphene's structure. The reaction involved in the process is exothermic in nature and releasing lot



Fig. 5 — Hummer's method of graphene synthesis

of energy, therefore, process needs to be handled carefully.

## 2.8 Electrochemical Exfoliation Method

Now a days, electrochemical method is widely used to produce graphene directly from graphite source. In a typical experimental setup, platinum wire is used as cathode and graphite rod is used as anode as shown in Fig. 6. Both anode and cathode are immersed in the electrolyte solution of sulfuric acid so that the minimum distance between both is 2.0 cm (aprox.). A positive voltage of  $\pm 10$  V is applied between anode and cathode<sup>43</sup>. After few minutes, the graphene nanosheets start accumulating in the electrolyte solution from the graphite rod as shown in Fig. 7. The graphene nanosheets from the electrolyte solution is filtered and used for further study/characterization.

# ELECTROCHEMICAL EXFOLIATION METHOD



Fig. 6 — Schematic illustration of graphene synthesis by electrochemical exfoliation method



Fig. 7 — Experimental set-up of graphene synthesis by electrochemical exfoliation method

Different electrolytes which can be used in electrochemical exfoliation method have been reported by the researchers. Some of these are KOH,  $Na_2SO_4$ ,  $K_2SO_4$  and ammonium sulphate.

# 2.9 Sonication assisted liquid phase exfoliation method

Liquid phase exfoliation method is the direct conversion of graphite into graphene in a suitable solvent. Graphite is made up of different layers of graphene attached one over another using Van der walls force of attraction. Sonication is done using ultrasonic bath in which ultrasonic waves are generated which overcome the Van der Walls force in order to separate different layers of graphenes from graphite. The graphite source generally used in this method is fine graphite powder or graphite flakes. It has been observed that interfacial tension between different graphene flakes in graphite plays a key role in deciding the solvent to be used. Solvents with surface tension around 40 mJ  $m^{-2}$  (approx.) were reported to minimize the interfacial tension. Solvents mostly used for liquid phase exfoliation are DMF (*N*,*N*-dimethylformamide), NMP (N-methyl-2pyrrolidone) and ODCB (ortho dichlorobenzene). In a typical experiment around 2 g (approx.) of graphite powder is added to 300 ml of ODCB and the mixture is sonicated in the ultrasonic bath for 3 h 45 min. After that the solvent containing graphene nanosheets is centrifuged using centrifugation machine for 30 min at 4000 rpm. The complete process of graphene synthesis using liquid phase exfoliation is shown in Fig. 8. The precipitates containing graphene is used for further characterization<sup>44</sup>. Figure 9 shows the graphene dispersion obtained by liquid phase exfoliation method using ODCB as solvent.

# **3** Properties of Graphene

There are numerous properties of graphene and intensive investigations are being carried out to explore more exotic properties for future electronic applications. Bi-layer graphene can be used as insulator and biased bi-layer graphene has been reported as tunable semiconductor, a potential material for photo detector application. Because of versatile nature of synthesized graphene, it is considered as designer material and future candidate for nanoelectronics. Few prominent properties of graphene is described below for the benefits of investigators.

## 3.1 Tunable Band gap:

Graphene is known for its zero band gap. Band Gap energy is the criterion of classifying semiconductors,



Fig. 8 — Process route of graphene synthesis using sonication assisted liquid phase exfoliation method

conductors, Insulators. Semiconductors have energy band gap of around 1.0 eV and insulators have band gap energy of around 6.0 eV. Graphene energy band gap can be tuned electrically to result band gap between zero to mid infrared energies. Thus, it makes it most suitable material for making photovoltaic cells under controlled conditions. Figure 10 shows a typical Dirac-Cone structure of graphene possessing zero energy band gap.

## **3.2 Structural Properties**

Graphene is a one-dimensional planar sheet of  $sp^2$ -bonded carbon atoms where the atoms are arranged in a honeycomb crystal structure<sup>45</sup>. The

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Fig. 9 — Graphene dispersion in ODCB (ortho dichloro benzene) solvent obtained by liquid phase exfoliation method



Fig. 10 — Dirac cones showing zero band gap in graphene

length of the carbon–carbon bonds are 0.142 nm and 120 degrees angle apart. The bonds between carbon atoms are responsible for its mechanical and thermal properties. Graphene has the interesting property of repairing any holes in its sheet by itself, when exposed to carbon containing molecules. By bombarding pure carbon atoms on graphene sheet, the atoms perfectly align into the hexagonal structure of graphene, thereby completely filling the holes. Graphene sheet itself is a conductor due to its hexagonal structure but can be made to work as a semiconductor if cut in a zigzag or armchair manner as shown in Fig. 11.

#### **3.3 Mechanical Properties**

The covalent bonds between carbon atoms which hold graphene together and give it the planar structure are the strongest to make graphene one of the strongest materials on earth. The strength of graphene is 200 times that of steel<sup>46</sup>. Graphene has a tensile



Fig. 11 — Zigzag and armchair edges of graphene honeycomb lattice structure

modulus (stiffness) of around 1 TPa. The bond between two carbon atoms in graphene is about 0.142 nm. Graphene sheets stack over each other to form graphite, so that the inter-planar distance between two sheets becomes 0.335 nm approx. These sheets are bound together by the Van der walls force of attraction.

# **3.4 Chemical Properties**

Graphene shows unusual mass-less Dirac-spectrum of the low-energy electronic excitations and this is responsible for excellent chemical sensitivity of graphene. It is very sensitive to the absorption or desorption of a single gas molecule because it make the changes in the conductivity<sup>47</sup>. This gas sensitivity makes it a suitable material for chemical gas detectors. The carbon atoms on the edges of graphene sheets have special chemical reactivity. Other factor which increases its reactivity is the various types of defects present within the sheet. The high chemical reactivity of graphene is because all the carbon atoms are present on its surface; therefore it increases the rate of reaction. In case of other materials more atoms are present inside the bulk rather on the surface; hence only surface atoms take part in the reaction which makes reaction slower.

### **3.5 Thermal Properties**

Graphene is the best thermal conductor known. The exceptionally high thermal conductivity of graphene is because of the strong covalent bonds between the

Table 1 — Comparison of graphene and other semiconductor's properties					
Material	Thermal conductivity (W/cm.K)	Young's modulus (G Pa)			
Graphene	50	1500			
Carbon nanotubes	35	1000			
Diamond	10-22	1050-1200			
Si	1.4	131			
Ge	0.6	103			
SiC	4.1	450			

carbon atoms. The graphene is synthesized from graphite and has thermal conductivity of 5000  $\text{Wm}^{-1} \text{K}^{-1}$ , which is approximately five times that of graphite<sup>48</sup>. The thermal conductivity of graphene is approx. 2.5 times greater than the thermal conductivity of diamond. The thermal conductivity of graphene is isotropic in nature, i.e. it is same in all the directions. The thermal conductivity and Young's modulus of various materials are compared with that of graphene and presented in Table 1.

## **3.6 Optical Properties**

The graphene shows excellent optical properties which help it to be used as transparent conductor in the electronic devices. Firstly, the transmittance in graphene is easily accessible by shining light on a SG membrane<sup>49</sup>. Graphene absorbs only 2.3% of light falling on it and hence it is possible to see graphene by naked eye. Because of the properties like transparency, high conductivity and flexibility, graphene is the right choice for making solar cells, LEDs, OLEDs and other optoelectronic devices<sup>50</sup>.

## **4** Applications of Graphene

Graphene has got applications in various fields like electronics, biological and chemical as shown in Fig. 12. Some of its important applications are described here.

# 4.1 Graphene as Flexible Transparent Conductor

Graphene is used as a flexible transparent conductor and used in making LED, OLED and LCD screens<sup>51</sup>. ITO (indium tin oxide) is used as transparent conducting electrode in electronics devices because of its good sheet resistance. When ITO is sputtered, deposited and annealed near room temperature, it degrades the electrical properties due to its low carrier concentration and high defect densities<sup>52</sup>. Thin films made of ITO are brittle and fragile, and are not suitable for applications that



Fig. 12 — Various applications of graphene in different areas of electronics

require flexibility. Also ITO is sensitive to both acidic and basic environments. Therefore, it is not used for applications which needs chemically inert electrodes like dye-sensitized solar cells<sup>53</sup>. ITO do not posses elasticity along with high transparencies, hence not the best choice for flexible electronics. These limitations are absent in graphene as it is easily stretchable and highly transparent. The sheet resistance of graphene can be adjusted by doping and chemical methods so that it can be made suitable for LEDs, OLEDs etc. Graphene is used as an ideal electrode material in flexible organic field-effect transistors<sup>54-57</sup> due to low contact resistance.

## 4.2 Graphene as Supercapacitor

One of the important applications of graphene is in making supercapacitors. The material used in supercapacitor should have high specific surface area and high conductivity. Other carbon materials used in supercapacitors had high surface area but they had low conductivity. Chemically reduced graphene oxide is reported to be used in making supercapacitors due to its high conductivity, large specific surface area and chemical stability<sup>58</sup>. Solid-state flexible graphene supercapacitor can be fabricated by sandwiching gel electrolyte made of (polyvinyl alcohol) PVA/H<sub>2</sub>SO<sub>4</sub> between two graphene layers as shown in Fig. 13. Aluminium foil is used for making the contacts with for characterization the graphene layers of supercapacitor.

## 4.3 Graphene in Biological Applications

Graphene has been reported as potential material for its uses in tissue engineering applications and regenerative medicine because of its exceptional



Graphene Flexible Solid-state Supercapacitor

Fig. 13 — Schematic diagram of graphene flexible solid-state supercapacitor

mechanical properties<sup>59</sup>. Graphene is used as a transparent conductive support for studying biological molecules by transmission electron microscopy<sup>60</sup>. Graphene has the ability to facilitate the differentiation of stem cells and that too without interfering the growth or alteration of the growth environment of the stem cells<sup>61</sup>. It is because graphene acts as a photocatalytic stimulator in the accelerated differentiation of human neural stem cells into neural networks. The hydrophilic graphene nanogrids exhibited patterned proliferations of stem cells in contrast with the usual random growths occurring on quartz substrates. Chemically modified graphene has helped in the development of biodevices which can detect a single bacterium and that can sense<sup>62</sup> DNA. Chemical modification in graphene is done to change its conductivity by doping different element in it. It is found that by doping with appropriate material graphene can be made to work as a semiconductor, hence its properties can be changed.

## 4.4 Graphene in Li-Ion Batteries

Li-ion battery is another area of application in which graphene is being used. Earlier, graphite was used as anode material in Li-ion battery because of its reversibility and good specific capacity. For making Li-ion batteries of higher energy density and durability, better electrode materials which can provide high charge storage capacity and efficiency. Graphene based anode has been reported for Li-ion batteries because of its better electrical conductivity than graphite. Electrodes made of graphene shall facilitate high surface area and chemical tolerance<sup>63,64</sup>.



Fig. 14 — Schematic illustration of the field effect tansistor (FET) based on graphene

Li-ion batteries made up of graphene electrodes have ten times more charging capacity than the conventional batteries.

## 4.5 Graphene Field Effect Transistors

The application of graphene in FET has opened up a new era of electronics devices. Due to its zero band gap, it cannot be used directly in transistors. For the transistor applications, one-dimensional structure of graphene with narrow widths and smooth edges<sup>65-71</sup> named as graphene nano-ribbons (GNR) have been investigated. These GNRs can behave as a semiconductor or conductor depending upon whether they are of zig-zag or arm-chair types. Therefore, one dimensional GNR become semiconductors with finite energy bandgap. It is found that the band gap up to 400 meV can be introduced by patterning graphene into one dimensional GNR. These GNRs based FET provide excellent switching speed and high carrier mobility<sup>65-71</sup>. IBM has reported a graphene transistor that works at 150 GHz. Graphene is not suitable for digital switches because of the absence of band gap but it is highly suitable for analog electronics specially RF transistors. RF transistors are characterized by cut-off frequency  $f_{T.}$ . Initially, FET operating up to 26 GHz has been fabricated using graphene<sup>72</sup>. Figure 14 shows the schematic illustration of the graphene based FET. Using an organic polymer layer between graphene and the gate dielectrics, further carrier mobility can be manipulated<sup>73</sup>. A cutoff frequency as high as 100 GHz has been reported to achieve by epitaxially synthesized graphene on a 2-inch SiC wafer<sup>74</sup>. A 25-inch touch screen using graphene has also been reported by Samsung to be used as the touch screen of a Computer.

#### 4.6 Graphene as a Gas Sensor

Graphene is known for its large specific surface area and low Johnson noise. There is a transfer of charge at the surface of the graphene causing charge in Fermi level and hence the conductivity of the graphene. The change in the conductivity with the extent of surface absorption makes it suitable material for making sensors for detecting gases and biomolecules<sup>75-78</sup>. The schematic showing the working of a graphene–based chemical gas sensor is shown in Fig. 15. The gas molecules strike on the graphene sheet, making a change in its conductivity which is shown by the ammeter connected in the circuit.

### 4.7 Graphene as a Distillation Agent

The special property of graphene or Reduced Graphene Oxide membrane is that it will not allow any liquids and gases (including helium) to pass through it except water vapours. This property is used for distilling vodka to higher alcohol concentrations because by using graphene filter, water is completely filtered out and pure alcohol remains unfiltered. The advantage of using graphene for distillation is that it can be done at room temperature without the requirement of any heat or vacuum which is normally required in traditional distillation methods<sup>79</sup>. In traditional distillation methods, the purity of ethanol can not be increased more than 95% without involving harmful chemicals but by using graphene pure ethanol can be obtained. Further, graphene can also be used in nano filtration and reverse-osmosis desalination process as filter. The filters used by these plants to separate salt from sea water usually have low permeability. Water flows very slowly through these filters, which makes the filtration process slow. The graphene filters on the other hand are thinner, stronger and can filter much faster. Therefore, graphene membrane based filter demonstrates a high rejection rate of salt and a high flow rate of water. Hence, for filtration of water from either ethanol or salt, graphene is higly efficient.



Fig. 15 — Schematic illustration of gas sensor based on graphene

## 4.8 Graphene as Optical Modulator

Graphene is used in optical modulators as Fermi level of graphene can be tuned to match the optical absorption. At the University of UC Berkeley, a graphene-based optical modulator synthesized is reported to operate at 1.2 GHz without any temperature controller<sup>80</sup>. The bandwidth of the optical modulator made up of graphene was from 1.3 to 1.6 µm.

## 4.9 Graphene as a Piezoelectric Material

Graphene has the property by virtue of which, by creating holes of a certain configuration in the graphene it can behave like a piezoelectric material<sup>81</sup>. Piezoelectric substances generate electricity in response to physical pressure, and vice versa. Graphene in itself is not piezoelectric by nature, but by punching triangle-shaped holes into it and applying pressure it can act as a piezoelectric material. Due to this property of graphene, it is used in applications where we require precise control of mechanical motion like scanning probe microscope and next generation energy harvesters, artificial muscles, sensors and actuators<sup>82</sup>.

## 4.10 Graphene as a Photocatalyst

Graphene used with various nanoparticles works as a good photocatalyst. For example ZnO/graphene nanocomposites perform much better than pure ZnO nanoparticles in the degradation of methyl blue dye under UV light. It is because of the fact that the photo-generated electrons are absorbed by the graphene, hence decreasing the chances of recombination with the holes in ZnO nanoparticles which in turn enhances the efficiency of hole-induced decomposition of dye<sup>83</sup>. Other nanoparticles like Ag, TiO<sub>2</sub> nanoparticles have also been used for making graphene nanocomposites which can help in the photodegradation of methyl orange and methyl blue dyes.

#### 4.11 Graphene in Solar cells

Graphene is a good conductor and highly transparent. By using graphene as the top electrode in solar cell we can increase the efficiency. Unlike silicon, which generates only one current-driving electron for each absorbed photon, graphene produces multiple electrons which increase the efficiency of solar cell. Graphene is added to titanium dioxide to increase its conductivity, which brings 52.4% more current into the solar cell circuit. This increase in current increases the efficiency of solar cell. Further,

Table 2 — Comparison of graphene synthesis methods and its various applications					
Graphene synthesis method	Graphene sheets size	Quality of graphene	Cost of synthesis	Application areas	
Epitaxial growth	More than 50 $\mu$ m	High	High	Transistors, circuits, interconnects	
CVD synthesis	Less than 75 cm	High	High	Touchscreens, smart windows, solar cells, flexible LCD, OLEDs	
Graphene synthesis by Hummer's method	nm to few $\mu$ m	Low	Low	Graphene conductive ink, supercapacitors, sensors, Li-ion battery electrodes	
Liquid phase exfoliation	nm to few µm	Moderate	Low	Transparent electrode, sensors	
Carbon nanotube unzipping	few µm	High	Low	FETs interconnects NEMs	
Electrochemical exfoliation method	Few µm	Moderate	Low	FETs, OLED, Conductive ink	

the high electrical conductivity of graphene sheets allows them to act as bridges, accelerating electron transfer from titanium dioxide to the photo electrode of solar cell. Indium tin oxide (ITO) in organic solar cells and fluorine tin oxide (FTO) in dye-sensitized solar cells can be replaced by graphene<sup>84</sup>. The main component of solar cell where photoelectronic reactions take place can be made by either *n*-doped or p-doped graphene<sup>85</sup>. Organic solar cells made of graphene-electrodes show better performance than those made of ITO electrodes<sup>86</sup>. Because graphene is highly flexible, organic photovoltaic devices made of graphene can survive a bending upto 138° and still function properly. On the other hand, devices made of ITO can withstand a maximum bending upto 36°. Even after hundred of bending cycles, the graphene photovoltaic devices have been reported to function normally<sup>87</sup>. The comparison of various graphene synthesis methods and its applications are summarized inTable 2.

#### **5** Characterization of Graphene

Graphene has been characterized by different methods. Optical microscopy is suitable for characterizing graphene flakes on SiO<sub>2</sub>. In this method, a shadow in the optical image is formed due to the interference between light-beams reflected from graphene and SiO<sub>2</sub> interface<sup>88-90</sup>. The shadow will change the contrast depending upon number of layers of graphene on SiO<sub>2</sub>. Hence, using this method we can distinguish between single layer and multi-layer graphene flakes. Raman spectroscopy is another characterization technique in which the laser light is molecular used. which interacts with vibrations, photons in the material shift the laser photons energy either up or down. This shift in energy gives the required information about the material. This technique is used to determine number of layers



Fig. 16 — SEM results of graphene nanosheets synthesized by liquid phase exfoliation method in investigator laboratory

of graphene<sup>91-93</sup>. Raman spectroscopy also determines the defects present in the graphene hexagonal structure. There are two main peaks in the Raman spectrum known as D and G peaks. The defects in graphene correspond to intensity of D peak. Hence, for high purity graphene low D/G peak ratio is desirable. Another technique used for the graphene characterization is Atomic force microscope (AFM). The AFM can determine the thickness of the layer along with number of layers present in the graphene



Fig. 17 — XRD results of graphite and graphene prepared by electrochemical exfoliation method in the investigator laboratory



Fig. 18 — TEM results showing overlapped graphene nanosheets synthesized using liquid phase exfoliation method in investigator laboratory



Fig. 19 — V-I curve showing conductivity of graphene by Four-Probe method

film. The layer thickness measured by AFM technique depends upon the resolution of machine. X-ray diffraction (XRD) is most popular technique for the identification of graphene structure. XRD gives the interplanar distance between different Bessel planes. Scanning electron microscopy (SEM) is used for measuring the surface profile of graphene layer. The detailed structural characterization is done using transmission electron microscopy (TEM). The sample preparation for TEM analysis is very cumbersome and requires transfer of film on grid structure. The thickness of the graphene sheets can also be estimated from TEM microscopy. Figure 16 shows the SEM results of the graphene nanosheets synthesized using liquid phase exfoliation method. The XRD pattern of graphene and graphite used for making this graphene are shown in Fig. 17. The TEM results of the graphene nanosheets are shown by Fig. 18. The electrical characterization of graphene is done by two probe or four probe method. A constant current source and nano-voltmeter are required to measure the bulk and sheet resistivity of material. Further, graphene as an active device can be characterized by using probe station with inbuilt microscopic arrangement for viewing microstructures. The results of four probe method are plotted in Fig. 19.

# **6** Summary

Graphene is a very exciting material and a potential candidate for nanoelectronics applications. There are various methods used for the synthesis of graphene layer and CVD method is the most suitable for electronic applications. The mechanical exfoliation method is time consuming but simple to perform in any laboratory. Hummer's method is used mostly by the researchers for making graphene as it can give graphene with high yield. Besides, liquid phase exfoliation method and electrochemical methods are also used to prepare graphene from graphite. Graphene has shown exceptional electrical, optical, mechanical, thermal and chemical properties and has excellent potential to be used as transparent electrode, FETs, gas sensors, energy storage devices like supercapacitors and also as catalyst. New methods of synthesizing graphene are being developed to achieve desired electrical properties. In the near future, it is postulated that graphene being designer material shall suitably replace silicon-based electronics. It is expected that future electronic devices based on graphene shall exhibit very high speed of operation, more chemically inert and environment friendly.

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