Available online at www.worldscientificnews.com

World Scientific News

An International Scientific Journal

WSN 143 (2020) 17-27 EISSN 2392-2192

Synthesis, properties and applications of graphene oxide: an overview

Saswati Nanda*, Atirek Gaur, Rajendra Kumar Duchaniya

Department of Metallurgical and Materials Engineering, Malaviya National Institute of Technology, JLN Marg, Jaipur - 302017, India

*E-mail address: saswatinanda58@gmail.com

ABSTRACT

This paper introduces different methods of synthesis of graphene oxide, properties, and applications of graphene oxide (GO). Unique structural, optical, mechanical, thermal, electrical, barrier properties, excellent biocompatibility Broaden the applications of GO in several fields of science and technology. GO a versatile material is a two-dimensional structure contains oxygen-based functional groups. Hydrophilic nature, Corrosion resistance property of GO makes it a hot area of research in nanocomposite coating fields.

***Keywords*:** Graphene Oxide, Brodie's method, Staudenmaier method, Hummer's method, Modified Hummer's method

1. INTRODUCTION

Carbon can able to form different allotropes such as Diamond, graphite, buckminsterfullerene, nanotubes, nano buds, and nanoribbons because of its valency. Diamond, graphite, buckminsterfullerene, nanotubes, nanobuds, and nanoribbons are the allotropes of carbon. Diamond and graphene are existing in a solid-state. In diamond, carbon atoms are bonded to form a tetrahedral lattice while in graphite, carbon atoms bonded to form a hexagonal lattice. Because of stable allotropes and its exceptional electronics, carbon can form sp, sp^2, sp^3

(Received 08 February 2020; Accepted 23 February 2020; Date of Publication 24 February 2020)

network. In sp hybridization s orbital overlaps with p orbital to form two new sp orbitals where the ratio of mixing of s and p orbitals are 1:1 (s:p), hence new hybrid orbital has 50 % of s orbital characteristics and 50 % of p orbital characteristics having bond angle 180 degrees. In sp^2 hybridization one's orbital overlap with two p orbitals to form three new hybrid orbitals where the ratio of mixing of two atomic orbitals are 1:2 (s:p), hence new hybrid orbitals have s and p characteristics about 33% and 66% respectively having bond angle 120 degrees between them. In sp^3 hybridization one's orbital overlaps with three p orbitals to form four new hybrid orbitals where the ratio of mixing of two atomic orbitals are 1:3 (s:p), hence new hybrid orbitals having s and p characteristics 25% and 75% respectively having bond angle 109.5 degrees between them. sp, sp^2, sp^3 hybridization have linear geometry, trigonal planar geometry, and tetrahedral geometry, respectively.

Graphene is a single atomic layer of carbon in which a layer of sp^2 bonded carbon atom arranged in a hexagonal or honeycomb lattice. It is the fundamental structural element of other allotropes, including graphite, charcoal, carbon nanotubes, and fullerenes [1]. Some excellent properties of graphene such as corrosion inhibiting, high mechanical strength, electrical conductivity, high specific surface area that is 2630 m^2/g [2], excellent barrier properties, electron transfer capabilities [3-4], high thermal and electrical stability which make it useful in application in the field of material science, physics, chemistry, biological studies, nanotechnology. Although it is the fundamental basis of different carbon atoms, it was first prepared in 2004, 440 years after the invention of graphene using sticky tape and a pencil. Then graphene can be prepared by several bottom-up synthesis methods [5] such as micromechanical exfoliation, chemical vapor deposition, epitaxial growth, and chemically synthesis, which is difficult for industrial applications. Graphene is also hydrophobic, have poor solubility [6], and forms agglomeration in solution due to its van der Waals interactions [7]. Graphene act as barriers in coating but coating defect such as cracks and defects in graphene film increases corrosion of metal and reduces protection ability. So, another source of graphene has been synthesized from graphite by a top-down approach to overcome the limitation of graphite known as graphene oxide (GO).

Graphene oxide is two-dimensional materials stack together to form graphite oxide is a compound of carbon, oxygen, and hydrogen arranged in variable ratio. It contains a hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), the carboxylic acid (-COOH), and other oxygen-based functional groups [8]. The oxygen-containing functional group introduces both sides of a single graphite sheet and overcome the inter -sheet in van der Waals force and enlarges the interlayer spacing [9] and disturbs the sp^2 bond of graphene so reduces the conductivity of graphene oxide.

Due to its capability to remain exfoliated in water as single atomic layers sheets, higher solubility(hydrophilic), can be produced in large scale by top-down approach from graphite, cast as films, and further, be reduced back to graphene GO, has been successfully used in several applications in electronics, conductive films, electrode materials, and nanocomposites. Synthesis of GO has first done by Brodie, Staudenmaier, and Hummer and Offeman.

2. SYNTHESIS OF GRAPHENE OXIDE

GO can be produced by two routes i.e., top-down method, where layers of graphene derivatives are extracted from carbon source mainly graphite[10-11], and the second method is the bottom-up method, where carbon molecules are used to construct pristine graphene by

chemical vapor deposition, epitaxial growth on silicon carbide wafers[12]. But bottom-up methods have several limitations. However, this method is very much time-consuming.

Hence the top-down method is suitable for graphene oxide production.

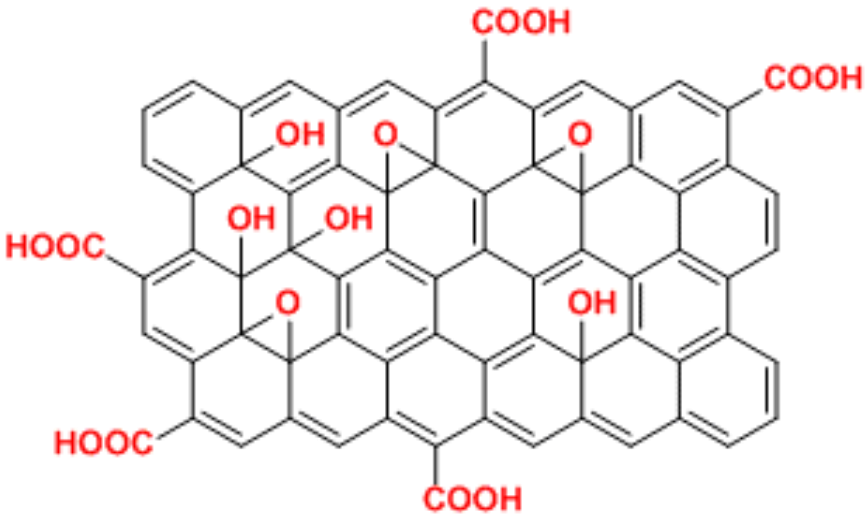

Figure 1. Structure of Graphene Oxide [13]

GO was first reported by Schafhaeult in 1840. It was first prepared by oxford chemist Benjamin C. Brodie in 1859[14]. Brodie reported the synthesis of "paper-like foils" with .5 mm thickness after treating graphite with a mixture of potassium chlorates ($KClO_3$) with fuming nitric acid (HNO_3). Brodie added fuming nitric acid (200 ml) into a flask with a cooling jacket and cooled to 0 degree Celsius in a cryostat bath. Then he added graphite powder (10g) into the flask and dispersed thoroughly to avoid its agglomeration. Then 80 gram potassium chlorate was added slowly in 1 hour and allowed reaction mixture to stir for 21 hours. During the addition of a potassium chlorate explosion may take place, so special precaution is needed. After the reaction has finished, he diluted the mixture with distilled water and filtered in a vacuum until he got the neutral pH of the filtrate.

In 1898, Staudenmaier [15] improved Brodie's method of GO synthesis by adding sulphuric acid (H_2SO_4) to adjust the acid component by using a single vessel to improve processing yield. This method was slowest and gave a light color GO. As $KClO_3$ addition continued over a week, it was the slowest method. This method is also hazardous as it produces toxic gases. So, for safe and large-scale production, it is not an appropriate method.

In 1958 two chemists, Hummer and Offeman from Mellon institution of Industrial Research prepared GO by oxidizing graphite with concentrated sulphuric acid, potassium permanganate, and sodium nitrate mixture [9].

They have taken mixture 2-gram graphene oxide and 2 grams of $NaNO_3$ (catalyst) in 50 ml of H_2SO_4 bath in 1000 ml volumetric flask that kept in an ice bath (0-5 ºC) with continuous stirring for 2 hours. Then they added 6-gram potassium permanganates as oxidizing agents to that mixture very slowly at temp kept below 15 ºC. After sometimes they removed the ice bath and allowed the mixture for stirring at 35 ºC for 48 hours. Then they diluted it with slow addition of water, where the temperature was rapidly increased to 98 ºC. Further, they added 200 ml of

water to dilute it. After some time, he treated the solution with 10 ml H_2O_2 to terminate this reaction. For purification purposes, he centrifuged the mixture with 10 % HCl and then deionized water for several times to get. After filtration, he dried it in a vacuum at room temperature to get powder graphene oxide. Characteristics of graphene oxide are to get the ratio of carbon to oxygen produced is within the range of 1 to 2.1–2.9.

Table 1. Comparison between Hummer's method and Staudenmaier method [16]

Method	% Carbon	% Oxygen	% Water	% Ash	Carbon to Oxygen atomic ratio
Hummer	47.06	27.97	22.99	1.98	2.25
Staudenmaier	52.112	23.99	22.2	1.90	2.89

From the above table, we get that Hummer's method produces more oxygen than the Staudenmaier method. Hummer's method takes less time than the Staudenmaier process but has some disadvantages, such as produces toxic gases like NO_2 and N_2O_4.

Then popular modification of this technique called improved Hummer method where sodium nitrides replaced by phosphoric acid and amount of $KMnO_4$ increased, which can able to reduce the evolution of toxic gases, with more hydrophilic carbon and equivalent conductivity with Hummer's method.

Then modified Hummer's method [9] was proposed, which involved both oxidation and exfoliation of the graphene sheet. It involves several steps such as: - mixing of 2 grams graphite flakes and 2 gram of sodium nitrate ($NaNO_3$) in 90 ml of sulphuric acid (H_2S) in a 1000 ml volumetric flask under ice bath (0-5 ºC) on a magnetic stirrer for continues for 4 hours at this temperature. Then slowly added 12 gram potassium permanganates ($KMnO_4$) to that solution at a temperature lower than 15 ºC. Then dilution was done by adding 184 ml water allowed it for stirring for 2 hours. After that ice bath was removed and again mixture stirred for 2 hours continuously. Then the mixture was kept in a reflux system at 98 ºC for 10 to 15 minutes.

After 10 minutes, the temperature of the solution changed to 30 ºC degree Celsius, and the color changed to brown. Again after 10 minutes, the temperature changed to 25 ºC and allowed it for 2 hours continuous stirring. Finally, the solution was treated with 40 ml H_2O_2, where the color changes to bright yellow. Then 200 ml of water was added to the solution and stirred for 1 hour.

It was kept for 3-4 hours without stirring to settle the particles. Then the resulting mixture was centrifuged rapidly by 10% HCl and then deionized water several times until we get neutral pH. After centrifugation, gel-like substance dried in vacuum at 60 ºC for more than 6 hours to get GO powder.

For characterization of GO we can use several techniques like X-ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM)/Energy dispersive X-Ray spectroscopy (EDS/EDX), Raman spectroscopy, Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Ultraviolet-visible spectroscopy (UV-Vis), X-Ray photoelectron spectroscopy(XPS) [17-19].

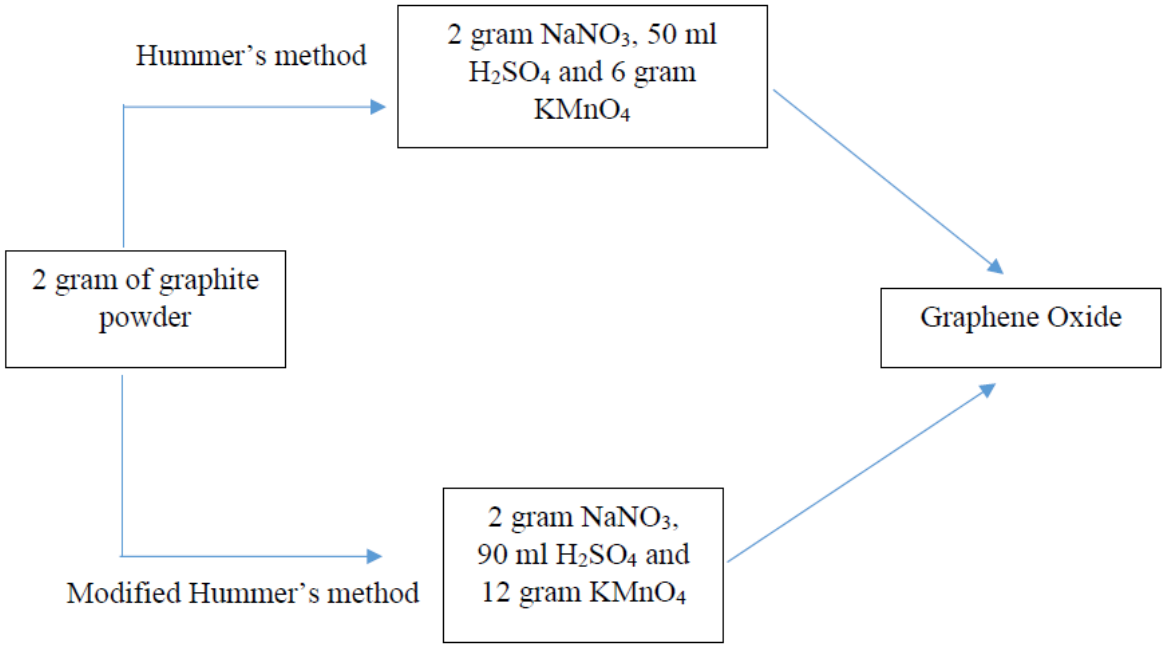

Figure 2. Schematic of Hummer's method and Modified Hummer's method of GO synthesis.

3. PROPERTIES OF GRAPHENE OXIDE

The presence of oxygen functional groups such as hydroxyl, alkoxy, carbonyl, carboxylic acid, etc. in GO expand layer separation and also make it hydrophilic [20], so it can easily disperse in water and organic solvent. It can also mix with a matrix such as a polymer and ceramic to improve their mechanical and electrical properties. It can disperse in water by two methods i.e., mechanical stirring and sonication, but sonication is limited to some applications because it generates defects, so mechanical stirring is a favorable one [21].

GO is hygroscopic that depends on humidity. A strong hydrogen bond is formed between the oxygen functionality of GO and water molecules so that mechanical, electronic, and structural properties get influenced. The increase of humidity content causes swelling of GO films and decrease the tensile modulus [21].

GO flakes are irregular in shape, and size ranges from few nanometres to few mm, depends on domain size of graphite, oxidation procedure, and oxidation time [22]. GO has more surface area, so it is more reactive. So, it can form reduced graphene oxide when reacting with hydrazine derivatives [21].

The thermal conductivity of GO (.5-1 $Wm^{-1}K^{-1}$) is very low as compare to graphite (3000-5000 $Wm^{-1}K^{-1}$). So, in many applications where high thermal conductivity needed, we can't use it. So, the reduction of GO is made to improve thermal conductivity. Because of the low thermal conductivity of GO, it can provide low thermal insulation properties like flame retardants and home insulation [8].

In contrast to graphene having high electrical conductivity (6500 Sm^{-1}) and high electron mobility (25 $m^2V^{-1}s^{-1}$), GO is an electrically insulating material having electrical resistivity around 1.64×10^{-4} because of disruption of Sp^2 bonding orbital of graphene due to presence of

oxygen functionality [8]. Because of less conductivity of graphene oxide reduction of graphene oxide is done to form rGO.

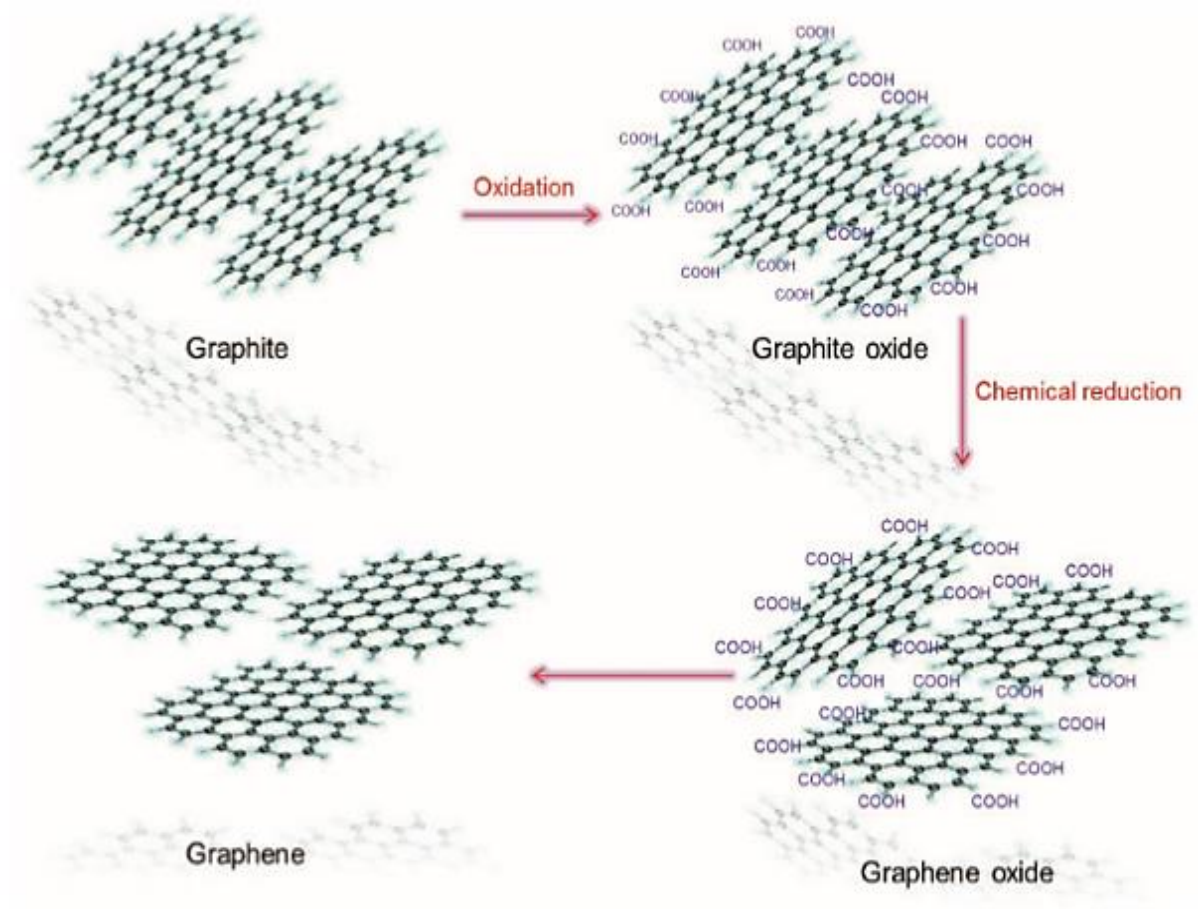

Figure 3. Schematic showing how transformation of graphene from graphite takes place [21]

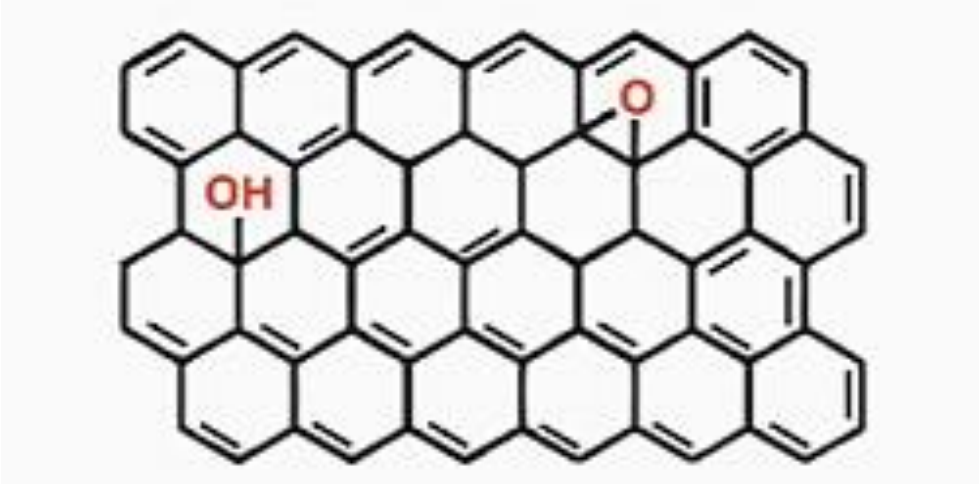

Figure 4. Structure of reduced graphene oxide (rGO) [23]

4. APPLICATIONS OF GRAPHENE OXIDE

Graphene oxide can be used in coating technology, as a film of GO can be deposited on any substrate like steel, aluminium, etc. by different deposition methods like electrodeposition, electroless deposition, electrophoretic deposition technique, etc. After deposition, it can be converted to the conductor, so it is useful in the production of the impermeable and transparent conductive film, which gives better corrosion resistance in dry conditions, but when exposed to water, a smaller than a certain size can allow passing.

GO as a dispersed phase can mix with polymer, ceramic, and some matrix materials and form nanocomposites to enhance mechanical, electrical, and corrosion properties of the matrix phase. GO when dispersing in a polymer matrix to make composite are impermeable to chloride, sulphites, water, and other harmful chemicals and generate a passive layer, so increases corrosion resistance as well as some other properties like tensile strength, electrical conductivity, and young modulus. GO can be form composite with high entropy alloys (HEAs) [24-26], which can be coated on mild steel to improve corrosion resistance, wear resistance, hardness etc. Krishna et al. discussed the utility of GO and rGO in geopolymer composites, the improvement in mechanical, microstructural and thermal properties of geopolymers have observed in their study [27].

Graphene oxide papers can be produced by doing vacuum filtration of water or aqueous disperse graphene oxide flakes and by some other techniques like spin coating and drop-casting. GO papers are mainly insulator, but we can change it to semiconductor and conductor without changing its mechanical properties. GO papers have applied in the water desalination [28] technique, where we can get useful salt and minerals from saline water. Also, the GO paper could be used in reverse osmosis, which is a water purification technique to obtain drinking water.

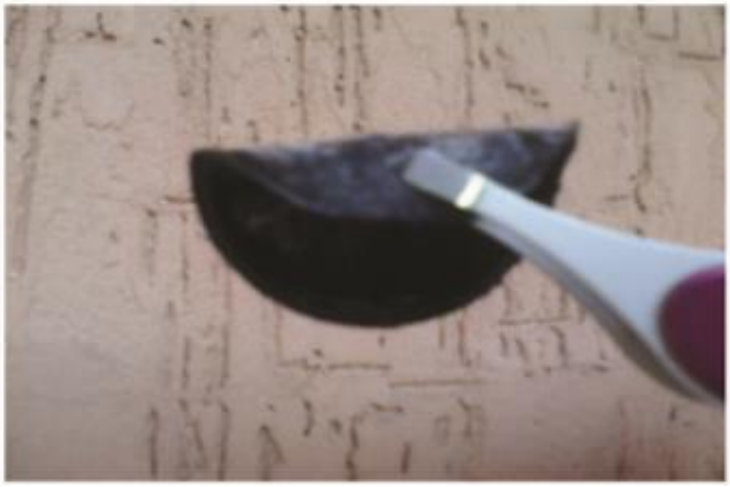

Figure 5. Graphene Oxide paper [21]

GO can be used in the biomedical field because of its biocompatibility nature, as is does not target healthy cell and the presence of oxygenated functional group cause further functionalization and immobilization of nanoparticles on its surface. Its main applications in

biomedical fields are drug delivery, cancer therapy, bioimaging, and biosensor. Some go based nanocomposite have better antibacterial activities. GO was proved as a bioimaging tool for cancer cells. GO as a fluorescent material used as a biosensor for the detection of early disease, find a cure for cancer [29]. It can detect DNA and poor signal. Nanocomposite of GO and silver (Ag) ions use for bacteria detection. GO has fluorescence quenching nature that can improve probe sensitivity.

GO functionalized with glucose oxidase and deposited on the electrode to form an electrochemical glucose sensor. At least one of the components of electronic device fabricates using GO as starting material. rGO that can be produced from GO used as a transparent electrode, hole transport layer in polymer solar cells, and LED [30,31]. GO can be used as tin oxide replacement in touch screens and batteries. We can use rGO as energy storage material in supercapacitors. Zhou et al. [32] fabricated rGO wrapped Fe_3O_4 that can be used as high capacity energy storage in a lithium-ion battery. GO-based microcircuits can be produced by directly visible laser reduction.

Hydrogen can be a better alternative for fossil fuels. Hydrogen can be stored as compressed gas in high-pressure tanks as a liquid form in tanks at very low temperature i.e., -253 ℃ and as solid form by absorbing and reacting with chemical compounds and metals. Hydrogen molecules are stored in an oxygen-based functional group of GO, so it is ideal for hydrogen storage. Zirconia- rGO nanocomposite form by chemical methods serve as good hydrogen storage material [33]. CdS -graphene oxide nanocomposites increased hydrogen production and quantum efficiency.

GO -based electrodes can be used to produce high sensitivity electrochemical immunosensors for detection of binding events between an antibody and antigen. GO based electrode has wide range of applications in electrochemical gas sensors, electrochemical biosensors, electrochemiluminescence, analytical chemistry [34].

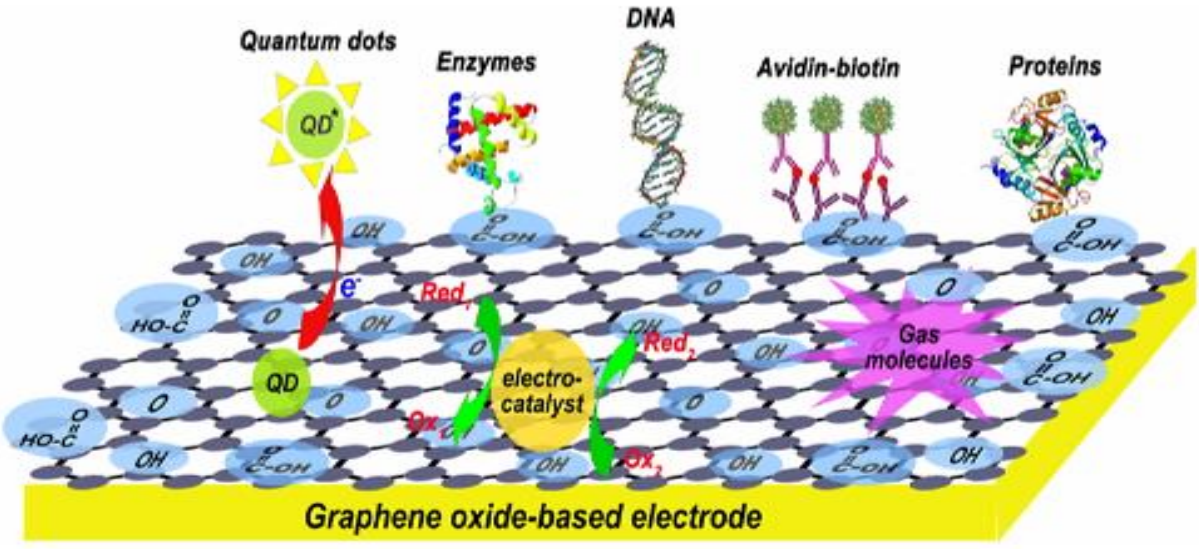

Figure 6. Schematic illustration of GO-based electrode [34]

Graphene Oxide-gold nanocomposites act as absorbent for removal of industrial dyes from aqueous atmosphere and nitro aromatic pollutants [35]. GO lenses based on Fresnel

diffraction model provides high efficiency, high resolution and flexible optical system [36]. GO can dispersed in carbon nanotube to produce GO/CNT hybrid films. GO/PMMA nanocomposite has good thermal stability. GO can also disperse in unoxidized graphene sheets. GO can be used as stabilizing agent in oil-in -water emulsions [37].

5. CONCLUSIONS

GO as a versatile material broadens its application in many branches of science and technology. GO has several advantages over other carbon-based materials such as graphite, carbon nanotube, diamond, pristine graphene Because of its excellent properties like high surface area, excellent biocompatibility, Hydrophilic nature, corrosion resistance, the abundance of the inexpensive source material, easy synthesis.

There are certain issues in the production of graphene from GO because the addition of different chemicals induces impurities that affect graphene oxide's properties. GO with impurities and lattice defects cannot deoxygenate fully. Toxicity is also an issue that limits applications of GO in living matter.

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