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Graphene Oxide and Derivatives: The Place in Graphene Family

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Graphene oxide (GO) is useful and promising material for graphene based applications in electronic, optics, chemistry, energy storage, and biology. At the beginning of graphene history GO was only a simple and cheap step for preparation of single and multilayer graphene films and bulk structures by reduction. The further studies revealed the substantial structure imperfection of graphene oxide derived materials due to the defects in initial graphite and incompletion of reducing process. However, the results of recent research demonstrated a great amount of unique chemical, optical and electronic properties of graphene oxide that allow regarding it as independent nanomaterial possessing a large area of applications. In general, it represents the ultra-large organic molecule containing 2D carbon mesh. Unlike conventional graphene it provides wide range of chemical methods for attachment of various functional groups to its surface for control optical transparency, electrical and thermal conductance. Recently developed methods for preparation of graphene oxide derivatives saturated by carboxyl groups open the new attractive application areas in green technologies including energy storage and utilizing nuclear wastes. The goal of the review is to summarize the results of recent studies of graphene oxide, derivatives and reveal the most promising directions to focus the efforts of researchers.

Keywords: graphene oxide, reduced graphene oxide, synthesis graphene, surface modification, applications

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INTRODUCTION

For the beginning its worth answering question: What is graphene oxide? At first graphene oxide (GO) was regarded as result of chemical exfoliation and oxidizing of layered crystalline graphite (natural or artificial) [1]. Amazingly, at definite conditions of oxidizing graphite carbon atoms conserve integrity 2D structure of layers with oxygen-containing functional groups attached to both sides of carbon plane and to the edges [2]. However quite recent results demonstrated that the same structure could also be obtained using alternative (bottom up) method by hydrothermal treatment of glucose [3] or even by chemical vapor deposition (CVD) technique [4]. Therefore today it worth giving more general definition on the basis of its structure: single atom carbon layer with both surfaces modified by oxygen containing functional groups. Like any 2D carbon GO can have single layer or multilayer structure [5]. Carbon layers in multilayer GO are separated by functional groups bonded to each layer of carbon atoms. Although GO like graphene is two dimensional carbon material, its properties are extremely far from that of graphene. It does not absorb visible light, have very low electric conductance compared to that of graphene and demonstrates significantly higher chemical activity.

For the first time graphene oxide was synthesized by Benjamin Brody in 1859 much earlier than graphene was discovered [6]. He invented method of making the graphite oxide. It consisted in oxidation and exfoliation of natural crystalline graphite and undoubtedly gave a noticeable amount of single layer graphene oxide. Unfortunately, at that time nobody knew about graphene. Only after more than one and half century after "The rise of graphene [7]" the old invention was recollected as an efficient and cheap way of making the new interesting and promising material.

TECHNOLOGY OF GRAPHENE OXIDE

Approaches for Synthesis of Graphene Oxide

The most recent methods of making GO based on the noticeable ability of layered graphite for intercalation. It allows atoms of active metals and some types of oxidation agents to penetrate between flat carbon layers of crystalline graphite increasing interlayer distance and modifying surfaces of layers by chemically bonded functional groups. Finally, the action of suitable oxidation agents causes complete disassembling of graphitic crystal into separate carbon monolayers with chemically modified surface.

The known methods for preparation graphene oxide (by Brodie, Staudenmaier, Hoffman) include application of strong acids (nitric and/or sulfur) and potassium chlorate. The most popular Hummers—Offeman method uses a mixture of concentrated H_2SO_4, $NaNO_3$, and $KMnO_4$. It provides a good yield and requires less time than previous methods. The final product of GO synthesis (**Figure 1A**) is yellow colored aqueous suspension of GO particles [8].

The modern improvements for GO preparations are based on Hummers oxidation and exfoliation of graphite [9]. The detailed review of known methods of preparation GO by oxidation of graphite is given in Singh et al. [10].

It is important to note, that conditions of chemical oxidation of graphite usually requires small ($< 10\,\mu$m) size of particles of the initial material. In order to complete chemical reactions the intensive stirring or even ultra-sonication is usually required. These factors make obtaining large sized GO flakes more difficult. For this reason the mean size of particles in commercially available GO does not exceed several microns.

However main properties of GO itself and especially, colligative properties of macroscopic structures formed by GO (like lamellar films) strongly depend upon the mean size of flakes. Therefore, increase of size of synthesized GO particles remains a challenge for technology. For the reason some recent researches propose the improvements of GO preparation method targeted to obtain large and ultra large sized GO platelets (LGO and ULGO) [11]. The idea of the method is to split GO preparation process into two stages: soft chemical exfoliation of initial graphite into graphene flakes in liquid media and subsequent oxidation of resulting product in mild conditions. In particular using the interaction of crystalline graphite, chromium trioxide and hydrogen peroxide allows obtaining effectively exfoliated graphite at room temperature [12]. The conditions of the process promote conserving the integrity of prepared graphene flakes. Subsequent oxidation of prepared large graphene flakes at reduced (relatively to usual Hummers method) concentration of potassium permanganate allows obtaining large area uniform GO flakes (**Figure 1B**) avoiding formation of oxidation defects [9, 17].

Structure and Composition

Figure 1 illustrates forms and structure of GO. Structure of GO has been studied by broad variety of methods. The results obtained by solid state nuclear magnetic resonance (NMR) [15, 18, 19], X-ray photoelectron spectroscopy (XPS), and X-ray absorption near-edge spectroscopy (XANES) [14, 20–26], Fourier transform infrared spectroscopy (FTIR) [21, 26–28], and Raman spectroscopy [16, 24, 29] suggest that the best description of GO sheet structure is given by Lerf-Klinovski's model [15] updated by Gao et al. [14] (**Figure 1D**). This model represents each GO particle by the basal plane of sp^3 hybridized carbon atoms with chemically bonded hydroxyl and epoxy functional groups situated in close proximity to each other on both sides of the plane. Edges of basal plane are terminated by carboxyl groups five or six membered lactol (O-C-O) rings, ketone and ester of tertiary alcohol. It is important to note that the mean content of edge functionalities inversely depends on the size of GO particles.

Aberration corrected high resolution transmission electron microscopy (HRTEM) images [13] (scheme on **Figure 1C**) as well as results of nanocontact atomic force microscopy (NC-AFM) study (**Figure 1E**) [30] have demonstrated that GO particles always contain some pristine graphene domains. The content and size of domains related to conditions of exfoliation/oxidation process of GO preparation. Content of sp^3 C-O bond that induces structural distortion of basal plane revealed by electron energy loss spectroscopy (EELS) [31] is related to the conditions of making GO and structure of starting graphite.

Perforations in basal plane shown in (**Figure 1C**) also related to defects of initial graphite and conditions of GO synthesis. The perforations are also terminated by the same functional groups that attached to the edges of GO particles.

Properties of Graphene Oxide

Figure 2 illustrates physical properties of GO. GO particles are highly hydrophilic. They form stable aqueous dispersions in wide range of concentrations. They form stable dispersions in a number of organic solvents like ethylene glycol, dimethylformamide (DMF), n-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) [34] owing to hydrogen bonding between hydroxyl groups on their surface and solvent interface [35]. This property allows making films on the variety of substrates even using simple drop-casting method. Thin films of GO exhibit a high optical transparency.

Figure 2A demonstrates optical absorbance spectra of GO film [36]. Due to sp^3 hybridization of the most part of carbon atoms it behaves like wide-band-gap insulator. Electric conductivity of GO is determined by domination of dielectric regions of sp^3 carbon atoms bonded to oxygen containing groups that separate the domains of pristine graphene from each other. As result the conductance becomes less than 10^{-10} S cm^{-1} [14]. **Figure 2B** shows dependence of resistance of thermally reduced GO vs. sp^2 carbon content. The vertical dashed line indicates the percolation threshold at sp^2 fraction of $\sim$0.6.

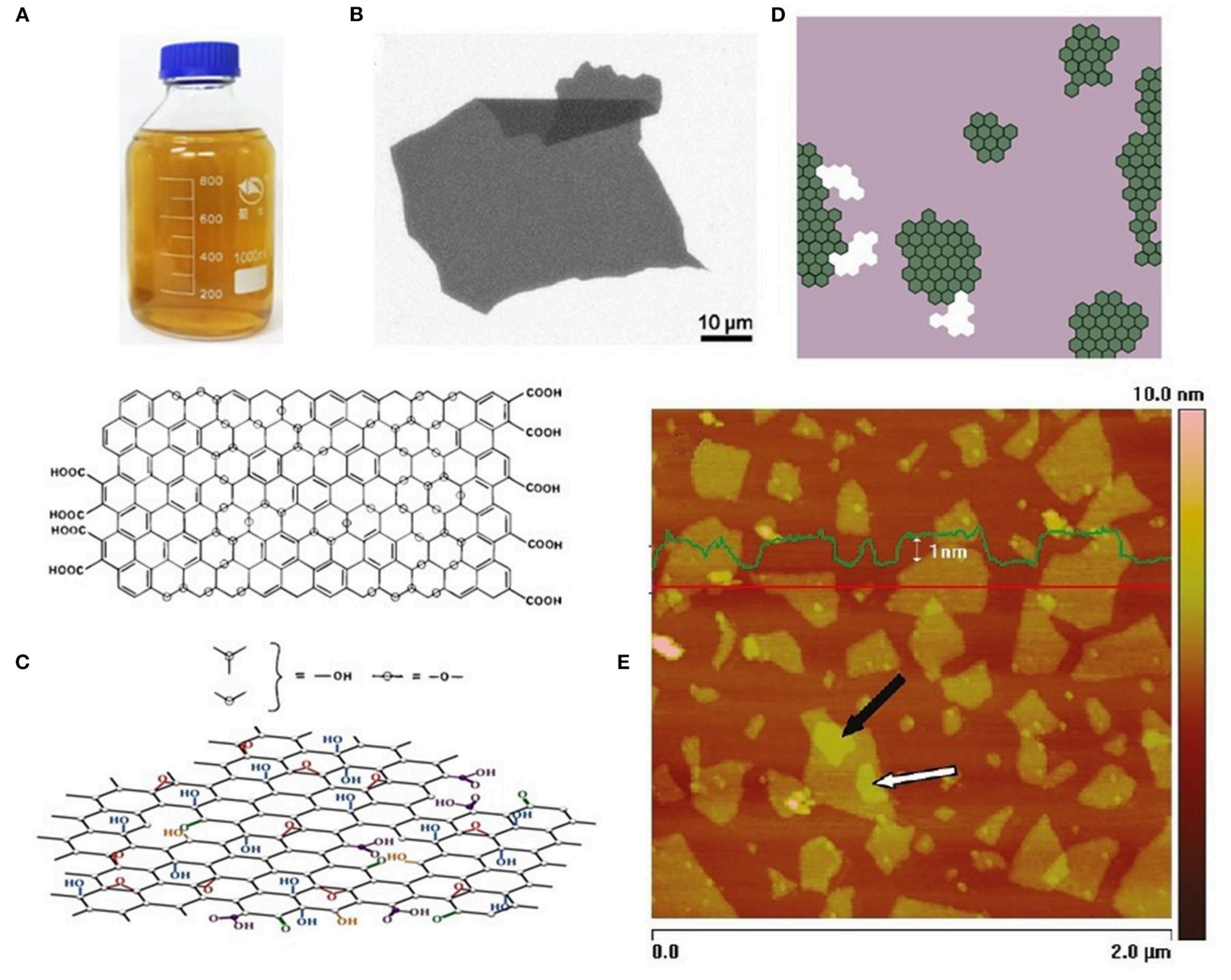

FIGURE 1 | Forms and structure of GO. **(A)** Aqueous dispersion of GO. Adopted with permission from Dong et al. [11] Copyright 2017ACS. Inc. **(B)** SEM image of large GO sheet on Si/SiO$_2$ substrate. Adopted with permission from Marcano et al. [9] Copyright © 2010 ACS. **(C)** Scheme of GO structure accordingly to HRTEM data Ericson et al. [13] of single layer suspended sheet of GO. Pristine graphene regions are indicated by green hexagons, regions containing oxygen functionalities indicated in magenta and holes in basal plane marked by white approximate size is 8 x 8 nanometers. **(D)** Schematic structure of GO accordingly to Lerf-Klinovski model variations indicating ambiguity regarding the presence of carboxylic acids (top) or ester of tertiary alcohol, and ketone groups at the periphery of the basal plane (bottom), accordingly to Gao et al. [14]. Adopted with permission from Lerf et al. [15] Copyright © 1998 ACS. **(E)** AFM image of GO particles on HOPG substrate. Superimposed profile of highs if taken along red line. Adopted with permission from Paredes et al. [16] Copyright © 2009 ACS.

Presence of graphene domains (**Figure 2C**) is the reason for noticeable broadband fluorescence in GO. **Figure 2D** demonstrates PL spectra of progressively reduced GO films. The total time of exposure to hydrazine noted in the legend. Excitation wavelength is 325 nm. It reveals that the most intensive blue luminescence (**Figure 2D**) takes place in weakly reduced GO –about 3 min in hydrazine. The increase of grade of reduction gives dramatic quenching of light emission. **Figure 2E** shows the model for explanation of the observed effect. At top it demonstrates the results of calculation of band gap for the fragments of graphene with increase the size in structure of partially reduced GO. Scheme at bottom of **Figure 2E** demonstrates the transmission of excitation in structure of partially reduced GO between small graphene domains (large band gap) that absorb excitation light and large domains (small band gap) that emit PL photons. Thus the continuous spectrum of domain sizes is the reason for wideband PL and excitation spectra of partially reduced GO [33, 37].

Presence of hydroxyl and epoxy groups on the basal plane of sheets and carboxyl groups at their edges opens the way for chemical modification of as-prepared GO. Various methods of chemical modification of GO using activation of edge carboxyl groups discussed in review [34]. Using activation by thyonilchloryde (SOCl$_2$) and subsequent edition of amines or hydroxyls it is possible to obtain covalently attached various functional groups to GO particles.

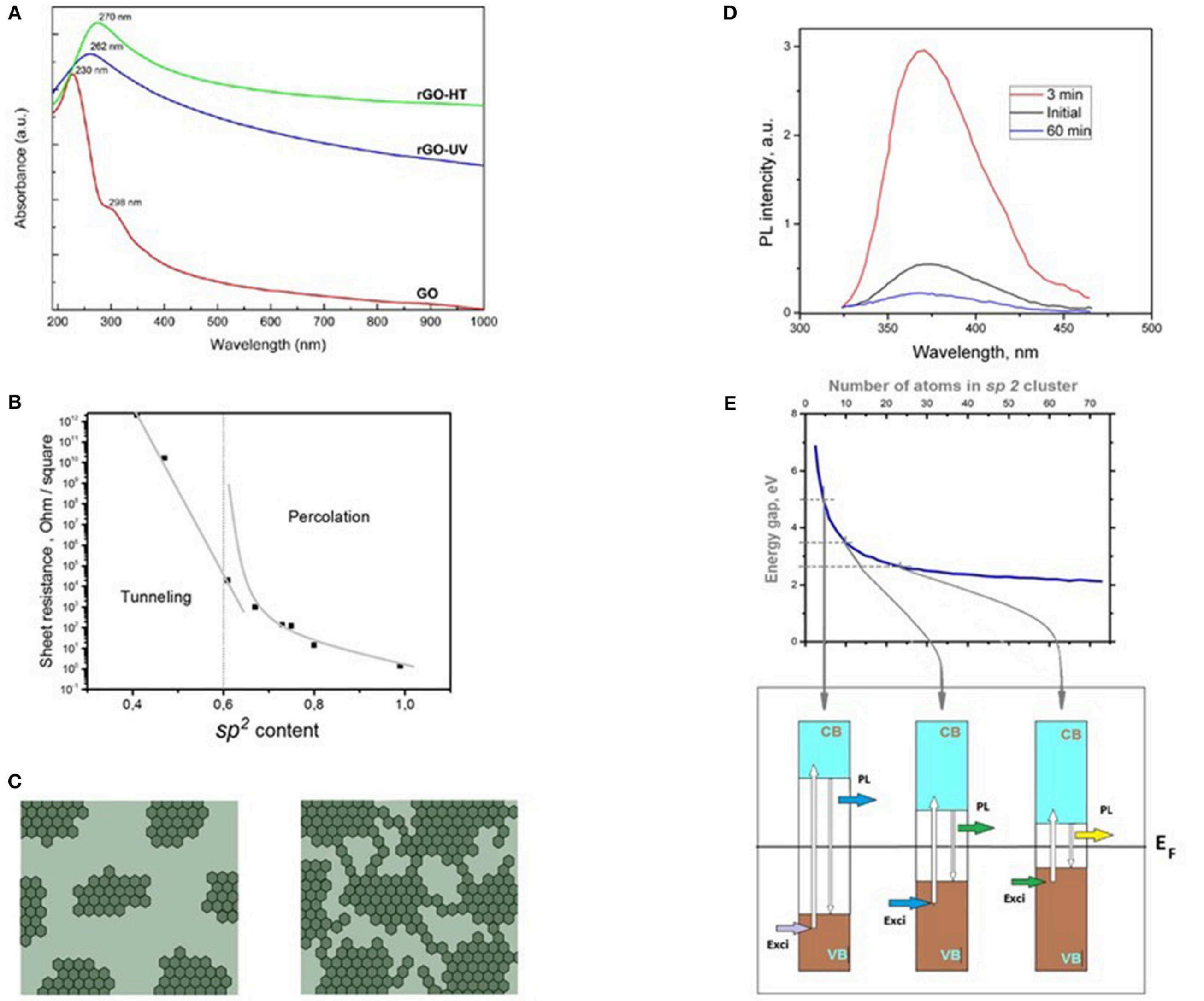

FIGURE 2 | Physical properties of GO. **(A)** Transformation of light absorption spectra of GO under thermal (rGO-HT) and UV reduction (rGO-UV). Adopted with permission from Kumar et al. [32] 2013 Nature. **(B)** Sheet resistance of thermally reduced GO vs. sp^2 carbon content. The vertical dashed line indicates the percolation threshold at sp^2 fraction of ∼0.6. By data from Mattevi et al. [22]. **(C)** Schematic of evolution of GO domain structure at reduction: left—initial GO, right—partially reduced. In dark gray indicated sp^2 graphene regions, in light gray—sp^3 oxygen containing area. Accordingly to Mattevi et al. [22]. **(D)** PL luminescence spectra of progressively reduced GO films. The total time of exposure to hydrazine is noted in the legend. Excitation wavelength is 325 nm. Data from from Eda et al. [33]. **(E)** Explanation of florescence of GO. At top: Estimated energy gap of π-π^* transitions as a function of the number atoms in graphene domain. At bottom: Schematic band structure of GO [blue and brown represent conduction (CB) and valence bands (VB), respectively]. Smaller sp^2 domains have a larger energy gap due to a stronger confinement effect. Photogeneration of an electron–hole (e–h) pair on absorption of light (Exci) followed by relaxation and radiative recombination resulting in fluorescence (PL) is depicted. White arrows denote the transitions of electrons and holes during this process. Accordingly to Eda et al. [33].

Scheme in **Figure 3A** demonstrates as example Isocyanate treatment of GO where organic isocyanates react with the hydroxyl (left oval) at basal plain of GO sheets giving attached carbamate functional groups. Right oval illustrates a reaction with carboxyl groups at the edges of GO platelets giving edge amide functionalization [38]. The approach for targeted covalent functionalization of epoxy groups at basal plane of GO sheets demonstrates **Figure 3B**. Use of amine-terminated ionic liquid (IL) [39] allows carrying out the ring opening nucleophilic reaction between epoxy groups and amine groups attached to ionic liquid. The reaction catalyzed by potassium hydroxide (KOH) gives partially reduced GO modified by IL-NH_2. It improves dispersibility of rGO in wide range of solvents. Similar functionalization of GO could be also carried out by ring-opening reactions with epoxy groups using octadecylamine. Conjugation of targeted functional groups gives opportunities for using GO platelets in various polymer composites [42], drug delivery systems [43], and biodevices [44].

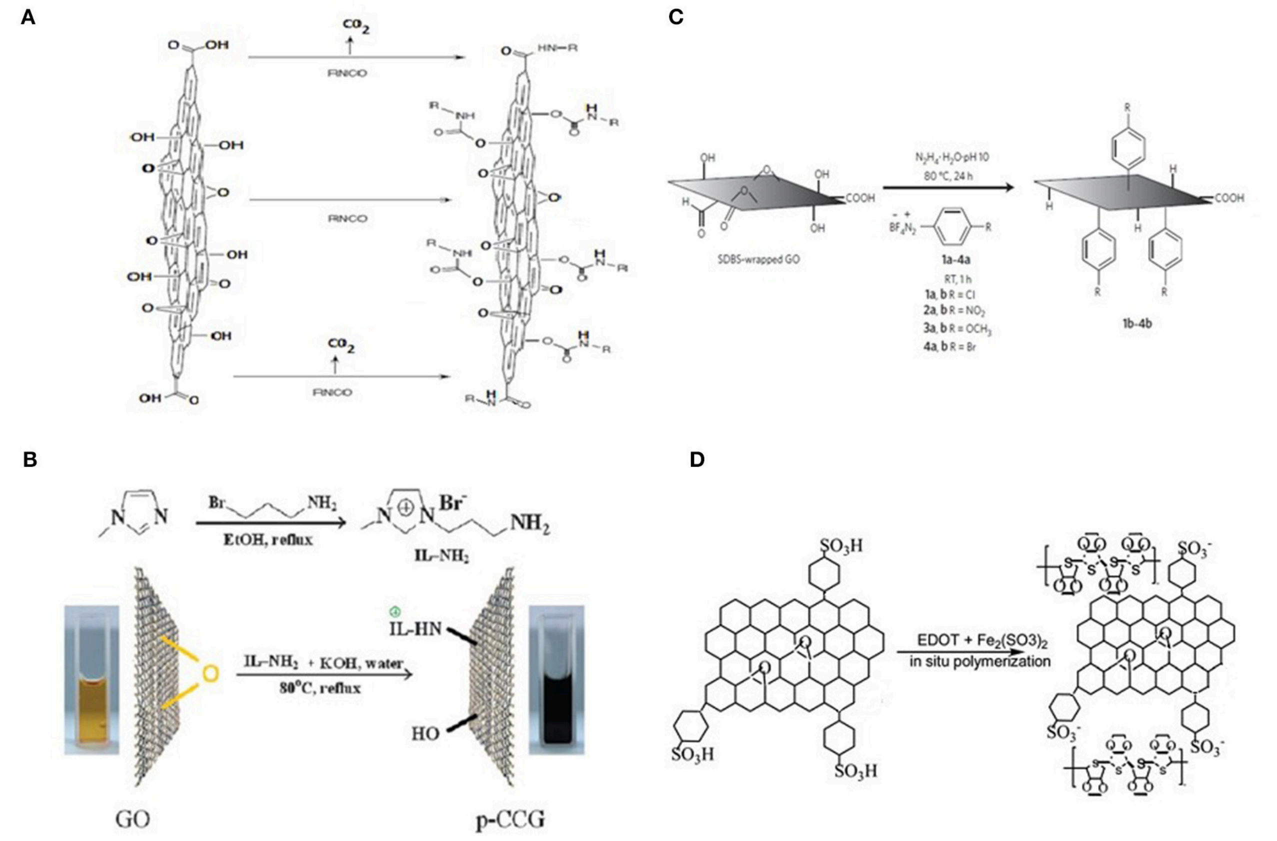

FIGURE 3 | Chemical modification of GO and rGO. **(A)** Isocyanate treatment of GO where organic isocyanates react with the hydroxyl (central arrow) and carboxyl groups (top and bottom arrows) of GO sheets to form carbamate and amide functionalities, respectively. Accordingly to Stankovich et al. [38] Copyright 2006, Elsevier, Inc. **(B)** Covalent functionalization of epoxy groups of GO by an ionic liquid. Adopted with permission from Yang et al. [39] Copyright 2009, RSC. **(C)** Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. GO was treated by sodium dodecylbenzenesulfonate (SDBS) surfactant. Adopted with permission from Lomeda et al. [40]. Copyright 2008 ACS. **(D)** Poly(3,4-ethyldioxythiophene)[PEDOT]/sulphonated graphene nanocomposite Accordingly to Xu et al. [41].

As was previously mentioned in Stankovich et al. [38] it could be useful to enhance solubility of GO sheets in organic solvents or reinforce polymer-GO composites in paper-like structures [45]. Presence of graphene sp^2 domains in structure of GO provides one more way for attachment the required functionality to the basal plane. Non-covalent functionalization (by cation $-\pi$ or van der Waals interaction) makes possible successful attachment of DNA or proteins to the surface of GO film for bio sensing [46].

Reduction of GO

At the beginning of the wave of interest GO was considered only as the way for mass production of cheap graphene. Therefore the most important task of transformation GO was in complete restoring structure and properties of graphene. Structure and chemical composition of GO at high level of oxidation are unstable. The significant part of oxygen containing functional groups can be easily removed from the basal plane of GO particle due to its high surface reactivity. The multiple research proposed broadest variety of methods for GO restoration [8, 47]. The existing methods of transformation GO to graphene could be nominally divided into three groups: physical (thermal), chemical and hybrid, where physical and chemical factors play role simultaneously.

The common feature of thermal methods is heating of GO directly or by irradiation [microwave, infrared visible, or ultraviolet (UV)] in vacuum, inert, or reducing atmosphere. Transformation of GO into rGO is going in wide range of temperatures. The obvious advantage of thermal reduction is simultaneous removal of oxygen-containing groups and restoring structure of GO by thermal annealing. It promotes the restoration of oxidation defects of GO basal plane afloat of sp3-sp2 rehybridization of carbon atoms. Lower temperature limit for GO thermal reduction reported in Kumar et al. [32] is 50°C. At that the reaching of its noticeable level requires several days. In case of GO films on substrate the upper limit of temperature depends mainly upon the substrate material, its thermal stability and chemical interaction with carbon at heating. In case of free membranes the upper level of temperature is limited by evaporation of carbon or destruction of graphene structure due to reaction with reducing atmosphere. Dong et al. [11] report the temperature of thermal reduction exceeding 2400°C obtained by direct Joule heating. This case the time required for full reduction of GO is less 1 min.

At the same time the typical range of temperature for thermal reduction is within 400–1200°C. The choice is determined by reasonable duration of process for required grade of reduction GO. For this reason it is difficult to apply thermal reduction in liquid media or for GO films on organic and most inorganic substrates.

Chemical reduction uses various reactants. The frequently usable reagent for reduction of GO is hydrazine hydrate. Among well-known reactants that effectively restore GO to graphene are Fe powder, sodium borohydride, hydroquinone, hexamethylenetetramine, hydroiodic acid, sodium, and potassium alkaline solutions. It could be carried out in liquid media or vapor atmosphere at moderate or even at room temperature [47]. Catalyst assisted photoreduction methods could also be considered as chemical ones. For instance, presence of titanium dioxide particles effectively assist reduction of GO in aqueous media under UV irradiation [48]. Zinc oxide and bismuth vanadate also demonstrate photocatalyst properties for GO reduction in liquid media [47]. The additional advantage of chemical methods is in opportunity for simultaneous chemical modification of synthesizing material. Worth mentioning example of chemical approach is the group of environmental friendly soft reduction methods applying organic acids, sugars, protein amino acids, and even microorganisms [49]. The comparison of reduction of GO by chemical and thermal methods on obtained residual content of oxygen and sheet conductivity demonstrates the prominent advantage of thermal reduction [19].

The level of reduction achieved by chemical methods can be increased by using solvothermal method—combination of chemical and thermal treatment under supercritical conditions [50]. The similar hybrid approach allows to obtain the nitrogen doping of reduced GO [51, 52] with higher electric conductance. It was demonstrated the controllable perforation of ULGO platelets under soft UV irradiation in argon atmosphere. This method gives simultaneous modification of edges of holes by carboxyl groups useful for chemical sensor application [53]. Functionalization of rGO is based mostly on non-covalent wan der Waals and $\pi-\pi$ stacking interaction of polymers or small molecules with basal plane [36]. Unfortunately increasing concentration of defects of basal plane during oxidation as well as formation highly stable carbonyl and ether groups hinders the complete reduction of GO to graphene [26]. The detailed study has shown that during the reduction GO keeps substantially inhomogeneous structure of basal plane. Area that covered with sp^2 domains increases while oxygen containing sp^3 regions split into the isolated spots due to the energetically favorable diffusion of hydroxyl and epoxy groups [32]. At that a steep rise of conductance at some stage of reduction of GO corresponds to joining of sp^2 domains and overcoming the percolation threshold [22, 52].

Recent reviews suggest that due to incomplete restored structure of initial graphene and therefore to the smaller electrical conductance and electron mobility the reduced graphene oxide (rGO) will probably not substitute epitaxial CVD graphene in active electrical components [10]. At the same time many useful properties of rGO like controllable functionality, high electric and thermal conductance the availability of initial material, cheap and scalable preparation process make GO, and rGO the independent 2D carbon material with broadest variety of applications. For instance, rGO can be successfully functionalized by diazonium salts using preliminary treatment by sodium dodecylbenzenesulfonate (SDBS) surfactant [40] (**Figure 3C**). Sulphonated rGO can also be incorporated into polymer nanocomposite by co-polymerization with Poly(3,4-ethyldioxythiophene) [PEDOT] (**Figure 3D**) [41].

The results of intensive studies of properties and structure GO and rGO carried out at the beginning of this decade established a good base that is sufficient for start of developing the multitude of new technologies [54]. Therefore the research focus in the field of GO and rGO has prominently shifted to application area. The enormous number of research publications on applications of GO and rGO in various technological areas, exceeding 23,000 titles (according to WoS data) for 2 recent years demonstrates this fact.

APPLICATIONS OF GRAPHENE OXIDE

The critical property for significant part of applications of GO based materials is electric conductance. As it was mentioned above GO with high O/C ratio is insulator. Therefore in order to increase the conductance of GO its partial restoration is required. That somewhat sacrifices chemical functionality of the material. Nevertheless, in number of applications mainly chemical and mechanical properties of GO are used. In this case it is important avoiding reduction process of GO.

Conductive Transparent Coatings

Transparent protective and conductive coatings are one of the first and widely discussed applications for rGO [55–58]. Films with thickness of several atomic layers could be easily deposited on any hydrophilic surface by simple drop-casting method or spin coating [59] and subsequent evaporating water. In the case of using electrically conductive substrate the smoothness and density of the film can be enhanced by using electrophoresis [60]. If the surface of substrate is hydrophobic the dispersion in suitable organic solvent can be used. The reduction of GO films to rGO must be carried out avoiding damage of substrate. A suitable method, the most compatible to the substrate could be chosen from the broad variety of physical, chemical, or hybrid methods. The van der Waals adhesion to the substrate in most cases is sufficient for durable rGO films and coatings. It also could be enhanced using chemical bonding to carboxyl groups at the edges of rGO platelets that form a structure of the film. Using GO allows fabrication of transparent graphene electrodes of unrestricted area for displays, solar cells and luminescent light sources [61]. Graphene is less expensive and environmental friendly in comparison with traditional transparent conductor ITO and can successfully substitute it in most applications.

Electronics

rGO transparent films are somewhat less conductive then CVD graphene films fabricated by roll-to-roll technology [62] for the similar applications due to their tile-like structure [63]. At the same time the major advantage of rGO films is their better sustainability for deformation of substrate, which is important for application in flexible electronics. Selective transforming GO-rGO allows formation of electric interconnects on flexible substrates. **Figure 4A** illustrates the patterning process of GO-rGO films on a flexible substrate under UV illumination A homogeneous dispersion of GO + N-Methyl-2-Pyrrolidone (NMP) spin coated and dried at 100 oC, before subjected to UV radiation for 45 min after masking with desired pattern [64]. Another attractive feature of GO is compatibility to ink-jet printing process [68, 69]. It opens the wide area of applications in future electron devices including not only flexible and transparent circuit interconnections [70] but active elements like field effect transistors (FETs) [71, 72] and organic light emitting devices (OLEDs) [73, 74].

The conductance of rGO films with tile-like or paper-like structure determined mostly by contribution of contacts between rGO sheets and less by their own resistance. Thus, development of technology for preparation of LGO and ULGO [12] will help to increase the conductance of transparent rGO electrodes. Correspondingly the additional chemical doping of GO also can help to increase conductance at moderate value of efficient mobility of charge carriers.

For some applications, the discontinuous structure of thin rGO film is critically important. Using rGO films as layers for transparent electrodes incorporated into GaN LED structure allows to increase the output power of LEDs avoiding the local overheating and damage of devices [75–77].

Solar Cells

Large area rGO transparent electrodes can become indispensable component of low cost flexible solar cells based on organic materials. Recently GO and chemically modified rGO were used as components for electron transport layers in new intensively developing organic perovskite based solar cells [78]. Using

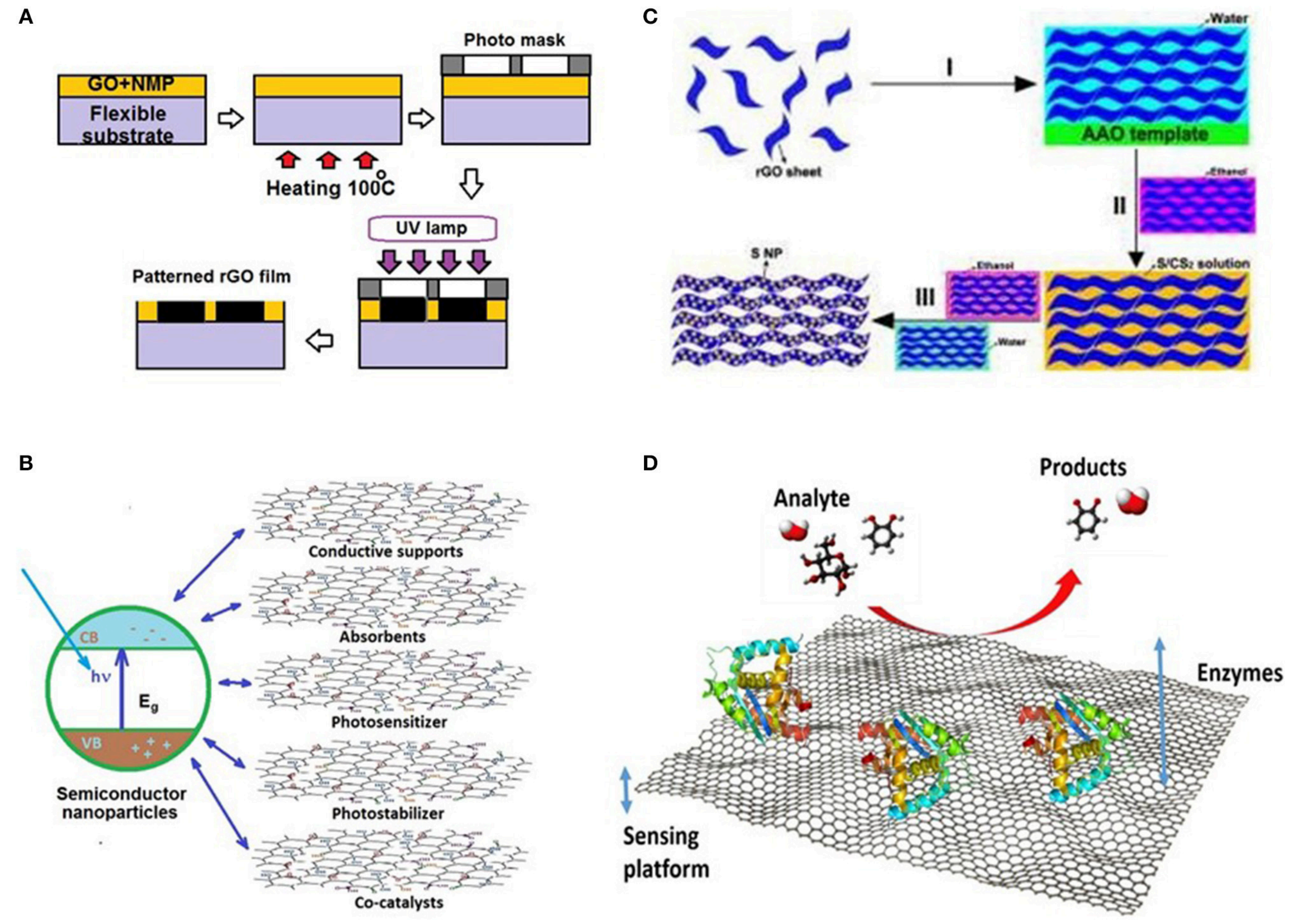

FIGURE 4 | Examples for applications of GO and rGO. **(A)** Schematic for patterning of GO-rGO films on a flexible substrate under UV illumination for applications in flexible electronics. Accordingly to Sonia et al. [64] Copyright 2018, Elsevier, Inc. **(B)** Functions of GO and rGO in graphene based composites for photocatalysts. Accordingly Li et al. [65]. Copyright © 2016 WILEY-VCH. **(C)** Schematic process of fabricating freestanding rGO-S composite films for cathodes of Li-S batteries. Adopted with permission from Luo et al. [66] Copyright 2017, RSC **(D)** Schematic of work process in enzymatic biosensor based of rGO platform. Adopted with permission from Bahamonde et al. [67]. Copyright The Author(s) 2018.

GO and rGO results in noticeable enhancement of quantum efficiency and durability [79–82]. In Kakavelakis et al. [83] has been also demonstrated the effective method of synthesis of nanostructurized TiO_2 (the important component of organic solar cells and photo catalysis systems) applying GO sheets as support and dispersant. GO or rGO are also useful materials for counter electrode in dye-sensitized ultralow cost solar cells based on liquid electrolyte [48].

Photocatalysts

Photocatalysis is one of the intensively developing and demanded technologies in particular for environmental protection [84]. Idea of photo catalyst may be considered as evolution of the organic solar cells concept. It combines solar energy conversion and carrying out the targeted electrochemical reaction. Photocatalysts use same nanoparticles of wide bandgap semiconductor like TiO_2 or ZnO for solar light absorption and utilize the interface with aqueous electrolyte for charge separation of excited electron-hole pairs. It makes possible to carry out electrochemical oxidation of number of hazardous pollutions [84–88]. Incorporation of semiconductor nanocrystals into structure of nanocomposites with chemically modified GO and rGO allows spreading the range of available reactions [65]. Recently developed nanocomposite photocatalysts containing nanodots and transition metal nanoparticles open the way to dissociate even H_2O and CO_2 [65, 89]. GO and rGO in nanocomposite structure of photocatalyst act as binder, electrode and support for external chemical catalyst for carrying on the targeted reactions [85]. Recent publications also report the usage GO and rGO composites with nanoparticles of metals and other functionalization as effective conventional chemical catalyst for a variety of reactions [90–93] including synthesis of biofuel [94] The variety of functions of GO and rGO in nanocomposite graphene-based photocatalysts illustrates **Figure 4B**.

Lithium Batteries

Another focus of research interest in the field of GO and rGO is distinctly associated to electrodes for energy storage systems—supercapacitors and lithium batteries. Today lithium batteries possess maximum energy capacitance. Attention of researchers is attracted to improve anode materials for extension cycle life and electrochemical performance of conventional Li-ion rechargeable batteries [95–99]. At the same time the significant part of research efforts is attracted by Li-S batteries promising theoretical energy density almost order of magnitude higher then contemporary industrial samples [100].

Unfortunately, native sulfur used as cathode material in Li-S batteries brings obstacles on the way of industrial use. The main obstacle is the inherently low electrical conductivity of elemental sulfur used as cathode. Usage sulfur allotropes like S2—S4 chains renders number of technical obstacles including capacity fading and self-discharge. Moreover, the repeated dissolution and re-deposition of sulfur results in rapid destruction of cathode. Therefore, the next step to industrial sulfur batteries requires the perfect host material for sulfur cathode. It must encapsulate elemental sulfur and simultaneously provide high electric conductance. According to the results of recent researches, it probably will be rGO and sulfur particles nanocomposite [99, 100]. **Figure 4C** demonstrates schematic process of fabricating freestanding rGO-S composite films by: I) self-assembling the rGO sheets by vacuum filtration to form solvated rGO films; II) immersing the solvated rGO films into the ethanol and subsequent S/CS2 (10 wt% sulfur) solution to impregnate the sulfur into the interval space of solvated rGO films, III) washing the solvated rGO films with ethanol and water to purge the residual CS2 and ethanol, and freeze drying solvated rGO films with impregnation of sulfur to obtain the freestanding rGO-S composite films [66].

Supercapacitors

Although supercapacitors fall behind lithium batteries in energy capacity they are able to provide much greater peak power. It is important for variety of applications in industry, transport and communications. Supercapacitors store energy in electric double layer (EDLC) [101], formed by ions of liquid, solid or ionic liquid electrolyte accumulated on surface of electrode material. Therefore, the electrode material must be chemically inert, have the largest possible specific area and opened porous structure. It also must have smallest resistance and mechanical durability to provide maximum number of charge—discharge cycles at highest value of current.

rGO is a good candidate for electrode material for new generation of EDLC. The main issue having to overcome is instability of porous structure related to re-stacking of atomically thin rGO sheets [101, 102]. The solution may be in making composite material of GO and conductive nanoparticles that form desirable porous structure and prevent stacking [103–105].

Membranes

The porous structure is of the same importance for GO membrane filters. Today membrane technologies of filtering wastewater and gases for separation heavy metals and CO_2 play more and more significant role in environmental protection.

New results demonstrate successful application of membranes based on functionalized GO composites with polymers for effective separations of gas mixtures CO_2/CH_4 and CO_2/N_2 [106]. The ability of GO membranes for ionic and molecular sieving opens the way for separation of radiochemical wastes [107]. It was also reported that among the graphene-based materials, GO shows the best antimicrobial activity [108]. It was also demonstrated that interlayer spacing of GO based filtering membranes can be tuned trough intercalation by cations [109].

Adsorbents

Besides membranes chemically modified GO and GO based composites are effective adsorbents for removal various pollutions from wastewater [110] including heavy metal ions [111–113]. Moreover the GO based sorbents can be successfully regenerated for subsequent use [114, 115].

Medicine and Biology

The abilities for chemical modification in combination with its low cytotoxicity [116] provide GO broad opportunities for biological and medical applications. Late publications report using chemically modified GO as drag carrier for cancer therapy [117] and tool for gene cancer therapy based on ribonucleic acid (RNA) interference [118]. The combination of GO with quantum dots of AgInZnS produces tunable photoluminescence and can be used for in *vivo* optical imaging of cancer cells and for phototheraphy [119].

Sensors for Chemistry and Biology

The controllable resistivity of partially reduced GO films and good ability for chemical functionalization is the key property for making chemical and biological sensors for broad range of applications [120]. Due to the sharp dependence of resistivity of a few layer GO films from quantity and composition of chemical agents on its surface the sensor design can be very simple. Usually it consists of the film and a couple of metallic contacts. In order to enhance sensitivity more complicated FET structure can be constructed [121]. For selective sensitivity the surface can be modified by catalyst particles or chemical agents to enhance charge transfer from detecting agent to GO layer. It was successfully demonstrated GO is good sensor for hydrogen [122], nitrogen dioxide [123], humidity [124, 125].

Ultrasensitive sensor for environmental monitoring of bisphenols was fabricated with using gold nanoparticles/b-cyclodextrin functionalized reduced graphene oxide nanocomposite as response element [126, 127]. Using a novel Ni(OH)(2)@PEDOT-rGO nanocomposite ultrafast responsive and high sensitive electrochemical glucose sensor was successfully fabricated [128]. Also worth mentioning a beautiful colorimetric pH sensor based on responsive polymer-quantum dot integrated graphene oxide [129]. Using enzyme reactions is a new approach for selectivity bio and chemical sensors. The basic principle of how enzymatic biosensors work is presented in **Figure 4D** [67]. Sensors employing enzymes can detect a variety of compounds with high specificity that would otherwise be difficult to detect in complex mixtures. For example, these sensors can be particularly useful in detecting compounds such as phenols, hydrogen peroxide, 17?-estradiol, glucose, and bilirubin. Obviously the variety of chemical sensors is growing year by year due to unrestricted opportunities for chemical modification of GO and ability for incorporation into nanocomposites.

Microwave Absorbers

One more noticeable branch of GO and rGO contemporary applications are microwave absorbers for electromagnetic interference (EMI) environmental protection. For microwave absorption aerogels of sponges [130] of GO and rGO are used. Results demonstrate 3D composites with carbon nanotubes/zinc ferrite [131], ZnO [132], and with nanosheets of Co_3O_4 [133].

CONCLUSIONS AND OUTLOOK

Although GO (rGO) is the closest relative of graphene, owing to its unique properties it takes the own independent place in graphene family. This material has wide application area and promising future. On **Figure 5** one can see the variety of

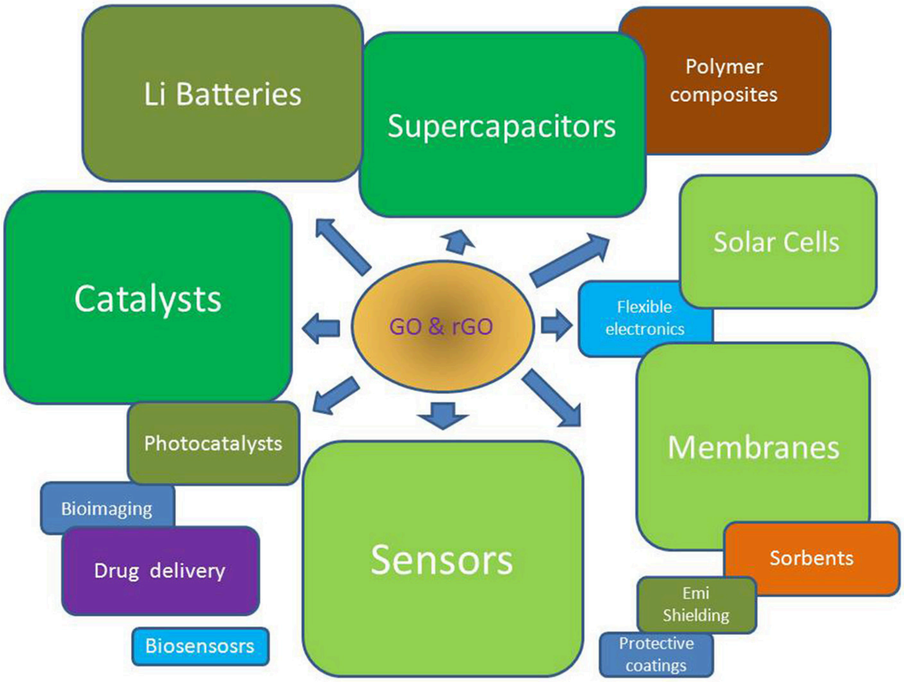

FIGURE 5 | Contemporary and prospective applications of GO and rGO. Size of blocks gives estimation of number of research publications for 2 recent years in corresponding areas. According to the Web of Science.

contemporary and prospective applications of GO and rGO. The brief review is unable to cover the full range of its properties and applications. Its task is in revealing the most promising directions and to focus the efforts of researchers in the field of GO. Undoubtedly, in recent years research focus has shifted to applications of GO and its derivatives. The most promising demanded and supported directions are lying in the area of energy harvesting and storage, environmental protection, biology, and medicine. As it was demonstrated above in the mentioned fields, GO research is most successful and fruitful. However, despite of the good understanding of structure and main properties of GO some questions on basics of reversible transformation of graphene plane to its oxidized state are still waiting the answers.

The important remain problem of a detailed understanding the restoration process of the regular graphene structure at the edges of domains through sp^3-sp^2 re-hybridization during reduction of GO. It probably could help to solve the problem of the defects of graphene plane. It also could help to proximate developing the effective chemical method for preparation of perfect single layer graphene with unrestricted area.

It will extend the area of applications and open the modern industry for graphene technologies.

AUTHOR CONTRIBUTIONS

AD and AV both carefully outlined the contents of the review and wrote the entire manuscript.

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