

# Glimpses of Sulfurized Graphene Oxide: Critical Review Towards Photocatalytic Response

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## Abstract

In this manuscript, we are presenting a review regarding the photo-catalytic response of sulfurized graphene oxide (S@GO). GO is derived from graphite, an allotrope of carbon, which has hexagonal crystal structure. Graphite is a soft material and has implementation in making pencils and as lubricant. Synthesis of GO can be achieved either via mechano-chemical or Hummer's method. The S@GO can be prepared via Staudenmaier, Hummer's, and Hofmann's GO, ball milling method, hydrothermal method, and direct annealing method. While photocatalysis process hydroperoxide radical reduces the pollutant to smaller products, and hydroxyl radical oxidizes the pollutant into smaller products. GO photo-catalyzes resazurin to resorufin, as well as it can be reduced to many azo dyes. The hydro peroxide radical and hydroxyl radical degrade the pollutants to simpler pollutants. Particularly research is going further for the degradation of azo dyes from the polluted water bodies. Because of this, GO, due to its good abilities, is reviewed here. In GO, sulfur atoms get attached to the oxygen sites. S@GO has several applications in making of super capacitor, field effect transistor, batteries, gas sensors, electro catalyst, hydrogen storage apart from being photocatalyst.

## Keywords

Graphene oxide, Sulfur, Recombination, Band gap, Graphite

## Introduction

GO is widely gaining acclaim as it is cost effective and is like an ace material having lots of up to scratch traits and this is why it is used in electronic, chemistry, biochemistry, electronics [1], sensors [1, 2], supercapacitors [1, 3], batteries [1] and mechanical branches of science [4]. GO is an all-round carbon material with a single layer and possesses sp<sup>2</sup> hybridized carbon lattice, retaining electrical, thermal, and mechanical properties [5]. Also, GO is a leading material in photocatalysis field, serving as a magnificent charge carrier at room temperature (200,000 cm<sup>2</sup>/Vs) [5]. GO at molecular level is a monolayer of graphite whose thickness is of one atom; such a layer has sp<sup>2</sup>-bonded carbon atoms which are arranged in a hexagonal lattice [6]. Through the chemical oxidation of graphene, GO is formed [6]. The such formed GO is found to have of several oxygen-containing functional groups such as epoxide (C-O-C), hydroxyl (-OH), carbonyl (C=O) and carboxyl (OH-C=O) groups on its basal plane, which makes its affinitive towards water, permitting better interfacial interaction with polar polymer matrices, leading to more enhanced mechanical and electrical properties following various applications, in which one is that it provides capability to utilize graphene oxide in aquatic and biological environment [6, 7]. Carbon based materials bear a tag for higher adsorption capacity, owing to their high porosity and their electrostatic interaction with adsorbate [8]. Activated carbon is widely

used for adsorption processes, some instances are dye removal, cosmetics, antibiotics, and non-biodegradable chemical compounds like phenol [7]. GO is utilized in plethora of implementations and applications since its discovery. GO can be obtained by oxidizing the very form graphite to graphitic oxide followed by exfoliation [8]. Performing experiments and by theories, it has been established that chemical incorporation of atoms like nitrogen, boron and sulfur can tailor its electronic properties, chemical reactivity and could lead to more fresh possibilities as well [1]. Sulfur has been doped with graphene with interest since doped materials are thought to possess a wider band gap due to the electron-affinitive characteristic of sulfur, as well as these doped materials exhibit electrocatalytic behavior for oxygen reduction reaction [9]. Sulfur and carbon have very little electronegativity difference, therefore, to dope sulfur with graphene becomes difficult. Liang et al. have studied that graphene can act as a good sensor, but sulfur doped graphene is much more reactive and can serve as a better sensor for detecting polluting gases such as NO and NO<sub>2</sub>, the reason being wider band gap opening which modulated its electronic properties [10]. This band opening also has a say on photocatalytic properties [11].

The merit of using nanostructures for photocatalytic utilization is greatly credited to their large surface to volume ratio, high ultraviolet (UV) absorption, and effective separation of electron and hole pair [11]. Sulfur incorporated graphene nanomaterials have excellent electronic conductivity, catalytic activity and electro-chemical properties and have significant implementations in solar cells, batteries, and sensors [12-17].

Feng et al. [18] have reviewed that many of the elements have been embedded with GO but sulfurized graphene is said to have broad energy gap on account of electron affinitive behavior of sulfur, it might lead to potential applications. To bind sulfur and GO requires higher energy to synthesize as compared to boron and phosphorus, so their formation is slightly difficult.

## General Properties of Graphene and Sulfurized Graphene

Shaikh et al. [17] have studied that recently nitrogen and sulfur ( $\chi = 2.58$ ) are embedded due to their analogous atomic sizes and electronegativity with the carbon atom ( $\chi = 2.55$ ) and outermost shell electrons are accessible to form bonds with carbon. Experimentally and theoretically, it has been established that sulfur (or nitrogen or phosphorus) incorporation into graphene (or CNTs) can alter the electrical and chemical characteristics [19]. GO is dispersible in solvents: DMF (N,N-dimethylformamide), NMP (N-methyl-2-pyrrolidone), THF (tetrahydrofuran) and ethylene glycol. Exfoliation can also be done by sonicating its aqueous solution [20].

Additionally, GO is obliging in the photocatalytic mechanism as (a) it resembles as an electron-acceptor, masking the electron-hole recombination, (b) enhancing the adsorption of organic contaminant via  $\pi$ - $\pi$  interactions between the sp<sup>2</sup> region of graphene and the aromatic contaminant [21-26]. Jeon et al. [19] et al. have studied the aftermath of sulfurized graphene. Using the molecular orbital theory, they approxi-

mated highest occupied molecular orbital (HOMO) analogous to electron donor orbital and the lowest unoccupied molecular orbital (LUMO) analogous to electron acceptor orbital distributions for such nanocomposites, which is related to electron transfer during oxygen reduction reactions. Unlike unblended graphene which has uniform distribution, HOMO and LUMO are polarized by covalently bonded sulfur atoms at the edges of graphene, which also behave as active sites for oxygen reduction reactions and high catalytic activity. Also, the position of sulfur attachment has a say upon catalysis rate, the sulfur atom attached at zigzag or armchair edges of graphene is said to display theoretically strong catalysis of oxygen reduction reaction as compared to the sulfur atoms attached on graphene basal plane.

Arvas et al. [27] described that when sulfur is intercalated with carbon, the charge on adjacent carbon varies positively. Sulfur doped carbon-based materials were used as electrodes for electric double layer, and capacitors on account of enhancement in capacitive performances due to sulfur.

Loh et al. [28] have elucidated that band gap of GO alters as oxidation level refashions. Completely oxidized GO behaves like an electrical insulator and partially oxidized GO behaves like a semiconductor [11]. Thangavel and Venugopal [8] have elucidated that adsorption is credited to GO's high surface area and  $\pi$ - $\pi$  interaction witnessed at the uppermost layer of GO. The biphenyl contaminant is terminated accounting to hydrogen bonding of graphene [8].

GO possesses a band gap of 2.2 eV and reduced GO has band gap from 1.00 eV to 1.69 eV [29]. Zhang et al. have mentioned that the UV absorption for graphene oxide is 230 nm in general. It differs with the size of the nanoparticles [30]. The photoluminescence spectra of GO are wide and ranges from 350 nm to 1250 nm and the peak lies between 710 nm on account of radiative recombination in the lower defect states. On reducing the GO, the spectra observe a blue shift.

Peng and Li [5] have developed sulfur doped graphene and studied decomposition of the methyl orange dye, with the consequence that 83% decolorization after 3 h of reaction [31]. Krishnamoorthy et al. [11] have reported illustration of resazurin got reduced to resorufin, and GO is photo-catalyzing the reaction. Electron and hole pairs are formed at the uppermost layer (surface), when GO is imparted energy greater than band gap (3.26 eV). The defect sites in GO behaves as trapping center for the excited carriers and therefore mask the recombination process of the pseudo first order reaction.

The procedure of reduction of resazurin in presence of GO under UV irradiation can be described as follows (Equation 1 and 2) [11]:



Sulfur is an electronegative element and is affinitive to metal ions. Nam et al. described that sulfur doped reduced GO was impinged in an aqueous solution of HgCl<sub>2</sub> while stirring, followed by filtering sulfur doped GO, resulting efficient re-

removal (ca. 94%) of  $\text{Hg}^{+2}$  ions on account of large surface area and sulfur accommodating functional groups on the surface [32].

## Synthesis of S@GO

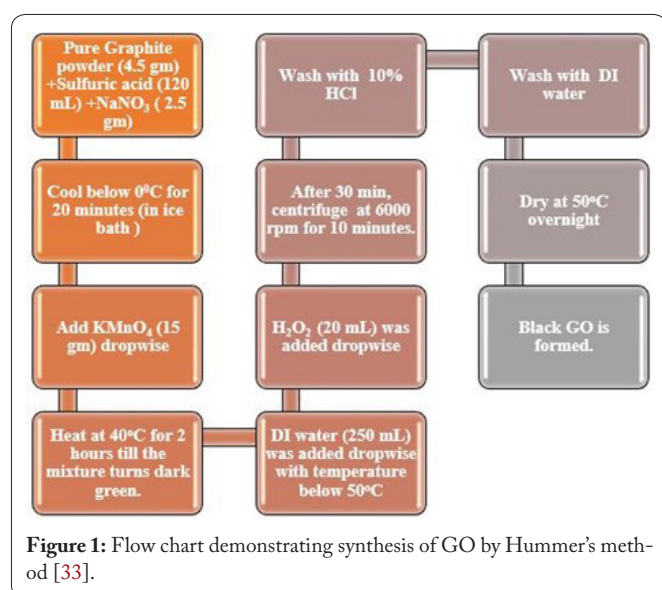
### Preparation of GO

Figure 1 represents the schematic diagram for the synthesis of GO by Hummer's method. Al-Rawashdeh et al. [33] have elucidated the preparation as GO was formed via an improved Hummer's method as illustrated in figure 1. Graphite powder (4.5 gm) was appended to 120 ml of sulfuric acid (96%) composed of 2.5 g of  $\text{NaNO}_3$ . Chilled it to  $0^\circ\text{C}$ , an ice bath solution was utilized, and the resultant was kept as it is for 20 min. 15 gm of  $\text{KMnO}_4$  was appended drop by drop into the solution with intense stirring, utilizing the same  $0^\circ\text{C}$  constant throughout.

Heating at  $40^\circ\text{C}$  for 2 h using stirrer, dark green color is achieved. Adding deionized water (250 ml) drop by drop with temperature lower than  $50^\circ\text{C}$ ,  $\text{H}_2\text{O}_2$  (20 ml), brown color is achieved, which is suggestive of the fact that GO seeds have initiated to form. Centrifugation at 6000 rpm was done for 10 min after half hour. Synthesized GO was washed away with 10% HCl to remove unrequired ions, followed by washing it via deionized water. Leave the sample to dry at  $50^\circ\text{C}$  for one night and henceforth black GO formed in the final step [33]. Guo et al. [34] have mentioned that Hummer's method has a demerit that it becomes hard to remove sodium and nitrate ions from the discarded residue. The second demerit is that whilst using strong oxidants potassium permanganate and sulfuric acid might damage the graphene layers.

### Synthesis procedure of S@GO using Staudenmaier, Hummers, and Hofmann graphite oxide

100 mg of graphite oxide is taken as antecedent and loaded into a quartz glass capsule enclosed by sintered quartz glass filter fronting the way of gas movement [9]. Affixing the capsule to a magnetic manipulator, loaded it into a quartz horizontal reactor in furnace. The system was expelled out of the air and



nitrogen was bled into the system, subsequently the sample was loaded into the warm part of the reactor. Nitrogen and sulfur antecedents were utilized for the sulfonation process. Nitrogen flow (1 L/min) and sulfur antecedents (viz.,  $\text{SO}_2$  and  $\text{H}_2\text{S}$ ) flow (1 L/min) were kept for 5 min to make them steady. The capsule was loaded into furnace for 12 min duration. If  $1000^\circ\text{C}$  were used with  $\text{SO}_2$  antecedent, the exposure time would have been lessened to 2 min. The reason being to avert oxidation and decomposition of graphene. Further,  $\text{CS}_2$  was impinged using a bubbler filled with its liquid form at pressure 1000 mbar and  $17^\circ\text{C}$  temperature. Nitrogen (100 ml/min) was reached as carrier gas after diluting it through measure of 1 L/min, prior to sintering it into the reactor. Exfoliation is done under normal air pressure [9].

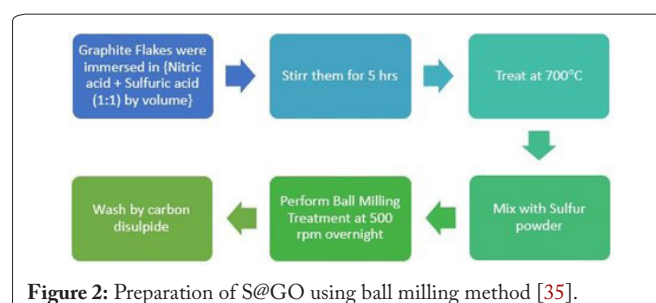
### Preparation of S@GO using ball milling method

Figure 2 represents the schematic diagram for synthesis of S@GO by ball milling method. Graphite flakes were submerged into a mixture of nitric acid and sulfuric acid in equal volumes for 5-h duration. The resulting modified graphite flakes were exposed to  $700^\circ\text{C}$ , which elevates the interlayer distance of graphite [35]. The products along with sulfur powder were blended in a planetary mill at 500 rpm overnight. The planetary mill is made of stainless-steel drum and stainless-steel balls are said to have 5 mm in diameter. Extra sulfur is then washed away using carbon disulfide, the S@GO is received and stored as illustrated in figure 2 [35]. Chua et al. [36] investigated that demerit of using this procedure is that metallic impurities might remain in the prepared samples.

### Preparation of S@GO using hydrothermal method

Figure 3 represents a flow chart for the synthesis of GO by hydrothermal method. GO has been composed from natural graphite using a modified Staudenmaier method. Sulfur doped reduced GO was formed via hydrothermal treatment of the mixed GO and  $\text{Na}_2\text{S}$  solution in a Teflon-lined stainless-steel autoclave as depicted in figure 3 (100 ml in volume).

GO (40 mg) was ultrasonicated in 70 ml deionized water for 30 min duration. Then, 10 ml of  $\text{Na}_2\text{S}$  aqueous solution (40 mg  $\text{Na}_2\text{S}$  dissolved in 10 ml water) was appended drop by drop followed by stirring for 15 min. Further, the final uniform solution was relocated to a Teflon lined stainless-steel autoclave and established at  $120^\circ\text{C}$  -  $180^\circ\text{C}$  for 6 h, and chilled to ambient temperature. Lastly, the resultant solution was segregated out by centrifugation and washed away via distilled water, ethanol, and acetone frequently to detach sulfur appended on the surface, subsequently drying in vacuum oven at  $60^\circ\text{C}$  [37].



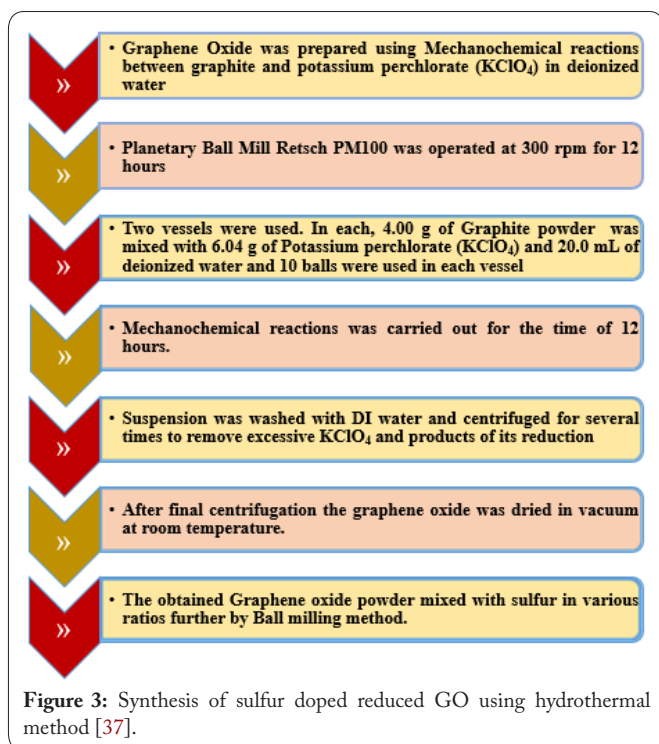


Figure 3: Synthesis of sulfur doped reduced GO using hydrothermal method [37].

### Preparation of S@GO via direct annealing

S@GO can be synthesized by annealing benzyl disulfide (sulfur source) with GO in the presence of inert gas argon. GO and benzyl disulfide were ultrasonicated in ethanol for half an hour to attain uniformly dispersed particles. Subsequently, the solution was poured in evaporating dish and dried. The solid powder was put in quartz tube which had argon and annealing was done at 600 °C - 1050 °C. The mixture was cooled until reaching ambient temperature.

### Photocatalytic Behavior of S@GO

Figure 4 represents photocatalytic degradation mechanism. It was observed that generally GO's behavior as a co-catalyst is better than as photocatalyst in dye degradation [38-40]. The reason which is acknowledged is broader band gap and photo generated charge carriers recombine easily [1]. This dilemma was resolved by doping GO with metal and nonmetal elements which would reduce the early recombination, thereby optimizing photocatalytic activity [1, 41].

IUPAC definition on photocatalyst is as "Catalyst able to produce, upon absorption of light, chemical transformations of the reaction partners. The excited state of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such inter-actions" [42]. Yang et al. has elucidated the very definition of photocatalysts as "the materials which do not change the thermodynamics of the reaction but only changes the kinetics by establishing new reaction routes through absorption of optical energy" [42].

Banerjee et al. [43] have investigated that GO and metal oxide have the same photocatalysis mechanism comparable to other oxides. The GO or the metal oxide is exposed to

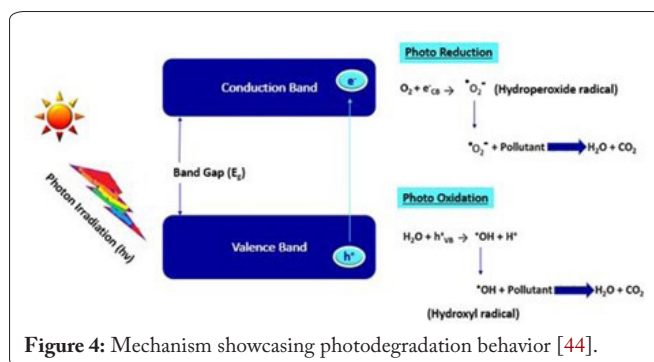


Figure 4: Mechanism showcasing photodegradation behavior [44].

light such that the excitation energy is higher than band gap, followed by relocation of electrons to conduction band (CB) from valence band (VB). In this way, electrons ( $e^-$ ) get formed in the former band and consequently, holes ( $h^+$ ) get formed in the latter band.

The electron-hole charge carriers can recombine, reducing the efficiency of the photocatalytic process and releasing the additional energy via nonradiative mechanisms (Equation 3 and 4) [44].



The electrons and holes which do not participate in the photocatalytic process, go through charge annihilation, they relocate to the surface and start secondary reactions with the surface assimilated products [44].

The photoexcited electrons in the CB can append with oxygen to make superoxide radicals or hydroperoxide radicals ( $O_2^-$ ) and such active superoxide species can take part in the breakage of organic contaminant, whilst positive holes ( $h^+$ ) in the VB can oxidize surface assimilated water or  $OH^-$  as well as form hydroxyl radical (OH), successively oxidizing the biological contaminant (Equation 5 and 6).



The photodegradation of dyes availing semiconductor materials aided by sunrays incidence is the favorable efficacious alternative for dirty water treatment [33], and is inclusive of advanced oxidation processes, which are based on chemical treatment of natural contaminant by oxidation reactions with OH radicals. The high oxidation potential (2.8 V) of OH makes it competent to oxidize natural colorant at ambient temperature wholly.

The degradation reaction materializes by striking the organic materials with  $\bullet OH$  radicals, which can be transformed to lower oxidized smaller products [45]. The photoreduction and photooxidation can be illustrated from figure 4. The reduction of azo pollutants into smaller compounds using photon induced mechanism inside semiconductor materials is the

potent alternative for wastewater treatment [33, 46, 47]. This OH radical is accountable for the fragmentation of the azo adulterant via oxidation [45, 48].

## Applications of S@GO

S@GO has been exercised in oxygen reduction reaction [1, 49] catalytic oxidation reaction [42], esterification reaction [50], and photocatalysis [16] exhibiting pronounced catalytic activity [35]. Sulfur has caught attention due to its use in cathode material for lithium-sulfur batteries since its higher theoretical capacity (~1675 mAh/g) and energy density (~2600 Wh/kg) [51]. Cost effectiveness, scalable, and environmentally friendly production of graphene combined with sulfur acts in reduction process. It has been reported that while exfoliating graphene mechanically through force or by a chemical-based approach, creeping up of defects may be seen into the structure of the material. Some of the major fields of applications are presented in figure 5.

It has been reported by several authors that graphene can act as a gas sensor [10, 52], nevertheless sulfurized graphene is extremely reactive and behaves with efficacious sensing ability for detection of NO and NO<sub>2</sub> [53].

Zhu et al. have investigated that sulfur dopants suppress magnetic ordering in graphene as sulfur modified the magnetic behavior of the samples [53]. Sulfurized graphene shows superconducting behavior below 35 K [54, 55], whilst this superconducting behavior gets eliminated in monolayer graphene as interactions among layer play a key role [56].

Shaikh et al. [17] have investigated sulfur embedded graphene was synthesized using simple chemical method. BMIMPF<sub>6</sub> ionic liquid was used as electrolyte and sulfur embedded graphene was used as electrode. The supercapacitor displayed magnificent capacitive retention up to 95% for 20,000 cycles. Wang et al. [49] have mentioned that sulfur doped GO possesses excellent conductivity, good trapping ability of polysulfides, high cyclability and low degradation rate which led to the promising application in lithium-sulfur batteries. Nair et al. have probed that fluorescent sensor sulfur doped graphene quantum dots which were synthesized using microwave-assisted sono-chemical method detected carba-

mate pesticides carbofuran and thiram successfully [52].

Panda et al. [57] have scrutinized that functionalized graphene layers synthesized using wet chemical method (modified Hummer's route) displayed 71% sensitivity towards 30 ppm carbon monoxide. Panda et al. have also mentioned that reduced GO or graphene sheets synthesized from the raw material graphite can be gathered to form ultrathin sensing layers with the help of number of techniques for instance, spin/drop coating, ink jet printing, casting, layer by-layer deposition and Langmuir-Blodgett technique, which can be further utilized as gas sensors [57]. Tozzini and Pellegrini have reported that hydrogen can be effortlessly adsorbed on graphene surface by physisorption or by chemisorption [58]. Physisorption means interaction via van der Waals forces. Chemisorption means interaction via chemical bonding with C atom [59]. Embedding graphene with alkali atoms, for instance, lithium, sodium, and potassium can enhance the volumetric and gravimetric storage capacity for chemisorption of hydrogen gas onto graphene. Lithium embedded graphene displayed 10% more gravimetric storage capacity as compared to unembedded graphene [60, 52].

Pal et al. [61] have mentioned that pristine graphene is not good in storing hydrogen, nevertheless nitrogen sulfur doped graphene possesses good electrical conductivity, high selectivity, and long durability. Gao et al. [60] have investigated that sulfur doped graphene utilized as bottom gated field effect transistor possessed larger on/off ratio than the pristine graphene and it has been proposed by the authors that sulfur atoms were creating linear nano-domains in graphene's lattice, and they enhanced the electronic transport in graphene.

Park et al. [62] have investigated that sulfur doped graphene behaves as an efficacious electrocatalyst in oxygen reduction reactions of fuel cells. Oxygen reduction reactions are slow in nature, to speed up the reaction, platinum catalysts can be used, but on account of carbon monoxide poisoning and high cost, different substitutes were tried. Liang et al. [63] and Wang et al. [64] have investigated that fabricating sulfur on graphene via annealing GO with benzyl disulfide possessed concomitant catalytic activity in comparison to platinum/carbon catalyst. Gliniak et al. have probed that sulfur doped GO quantum dots were utilized to generate hydrogen gas from photocatalytic water splitting. The amount of gas obtained was maximum when horseradish peroxidase (an enzyme) was added to the solution to be photo-irradiated [65].

## Conclusion

In summary, S@GO nanomaterials can be prepared by ball milling method, hydrothermal method. The sulfur embedment in carbon-based electrode materials is an efficacious alternative to ameliorate their electrochemical executions. The sulfur atoms embedded into the graphene structure reform and brush up the electrical conductivity, attributing to the delocalized electrons along the conjugated backbone of graphene. The disadvantages of graphene such as high production cost, high energy consumption and difficulty in transferring graphene. Also, there are some discrepancies pertaining to the GO adsorption process.

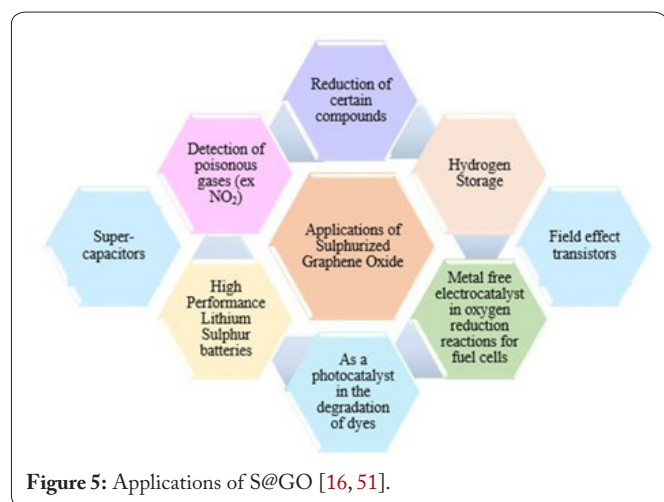


Figure 5: Applications of S@GO [16, 51].

Sulfur doped GO expresses irreversible restacking tendency in solution, resulting reduction in surface charge density, which might lead to precipitation or agglomeration. This limits the practical application of sulfur doped reduced GO. To its remedy sonication, extra stabilizers, and surfactants like SDBS are used. GO has some demerits like high energy consumption, high production cost and difficulty in transferring graphene. Nevertheless, graphene is an excellent material, due to which it has potential promising applications in diverse areas, with a smaller number of demerits.

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## Conflict of Interest

The authors declare no conflict of interest.

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