



Sulfonated graphene nanomaterials for membrane antifouling, pollutant removal, and production of chemicals from biomass: a review

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Abstract

Water pollution and the unsustainable use of fossil fuel derivatives require advanced catalytic methods to clean waters and to produce fine chemicals from modern biomass. Classical homogeneous catalysts such as sulfuric, phosphoric, and hydrochloric acid are highly corrosive and non-recyclable, whereas heterogeneous catalysts appear promising for lignocellulosic waste depolymerization, pollutant degradation, and membrane antifouling. Here, we review the use of sulfonated graphene and sulfonated graphene oxide nanomaterials for improving membranes, pollutant adsorption and degradation, depolymerization of lignocellulosic waste, liquefaction of biomass, and production of fine chemicals. We also discuss the economy of oil production from biomass. Sulfonated graphene and sulfonated graphene oxide display an unusual large theoretical specific surface area of 2630 m²/g, allowing the reactants to easily enter the internal surface of graphene nanosheets and to reach active acid sites. Sulfonated graphene oxide is hydrophobic and has hydrophilic groups, such as hydroxyl, carboxyl, and epoxy, thus creating cavities on the graphene nanosheet's surface. The adsorption capacity approached 2.3–2.4 mmol per gram for naphthalene and 1-naphthol. Concerning membranes, we observe an improvement of hydrophilicity, salt rejection, water flux, antifouling properties, and pollutant removal. The nanomaterials can be reused several times without losing catalytic activity due to the high stability originating from the stable carbon–sulfur bond between graphene and the sulfonic group.

Keywords Sulfonated graphene · Environmental applications · Catalyst · Bioenergy · Economic values

Disclaimer The views and opinions expressed in this review do not necessarily reflect those of the European Commission or the Special EU Programs Body (SEUPB).

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Introduction

Acid catalysts are very important for various chemical and material production processes in the industry (Tawfik et al. 2022a, b). These catalysts can be categorized into homogeneous such as sulfuric, hydrochloric, and hydrofluoric acid and heterogeneous acid catalysts. Graphene and its derivatives are common examples of heterogeneous acid catalysts. The major distinction between homogeneous and heterogeneous acid catalysts is that in homogeneous, the reactant and product phases are the same, but in heterogeneous, they are different (Bohlouli and Mahdavian 2021). Developing heterogeneous acid catalysts with high catalytic activity has recently become a priority for environmental applications (Clark 2002; Farghaly et al. 2017). Graphene nanosheets have exceptional and distinctive mechanical properties, a large surface area and a distinctive two-dimensional structure (Dürkop et al. 2004), which could be easily anchored with highly acidic functional groups (Tawfik et al. 2021b). Hara group attempted the first trial for the treatment of

microcrystalline cellulose with sulfuric acid to synthesize graphene-like amorphous carbon-bearing functional groups of sulfonic ($-\text{SO}_3\text{H}$), hydroxyl ($-\text{OH}$), and carboxyl ($-\text{COOH}$) with unusual catalytic activity required for the cellulose dehydration into glucose (Kitano et al. 2009).

Sulfonated graphene is graphene with numerous sulfonic groups ($-\text{SO}_3\text{H}$) attached to its surface and sheet edges. The sulfonated graphene has the ability to increase the electron-withdrawing from the carboxylic group ($-\text{COOH}$) by increasing the electron density between the sulfur and carbon atoms, enhancing the catalyst stability under severe reaction conditions. Besides, the sulfonic functional group acts as a proton carrier, indicating the material's high density and potential use as a proton conductor (Hara et al. 2004). The sulfonated graphene oxide catalytic activity is 9.1 times greater than that of other solid acid catalysts and traditional sulfuric acid (Tawfik et al. 2022e, f). This high catalytic reactivity is attributable to the formation of hydrophobic cavities on the surface of sulfonated graphene oxide as a result of the combination of graphene nanosheets and oxygen-containing groups, which facilitate the catalyst activity to anchor with substrate/reactants and highly promote the protons' attack (Tawfik et al. 2021a). Several chemical applications have been reported by utilizing graphene and its derivatives. Sugars, such as hexose, glucose, and fructose, were decomposed into levulinic acid using a graphene oxide-based catalyst containing a sulfonic group ($-\text{SO}_3\text{H}$) (Upare et al. 2013). For example, Liu et al. (2012) found that sulfated graphene is highly recyclable for the hydration of propylene oxide. Figure 1 illustrates the properties and applications of sulfonated graphene.

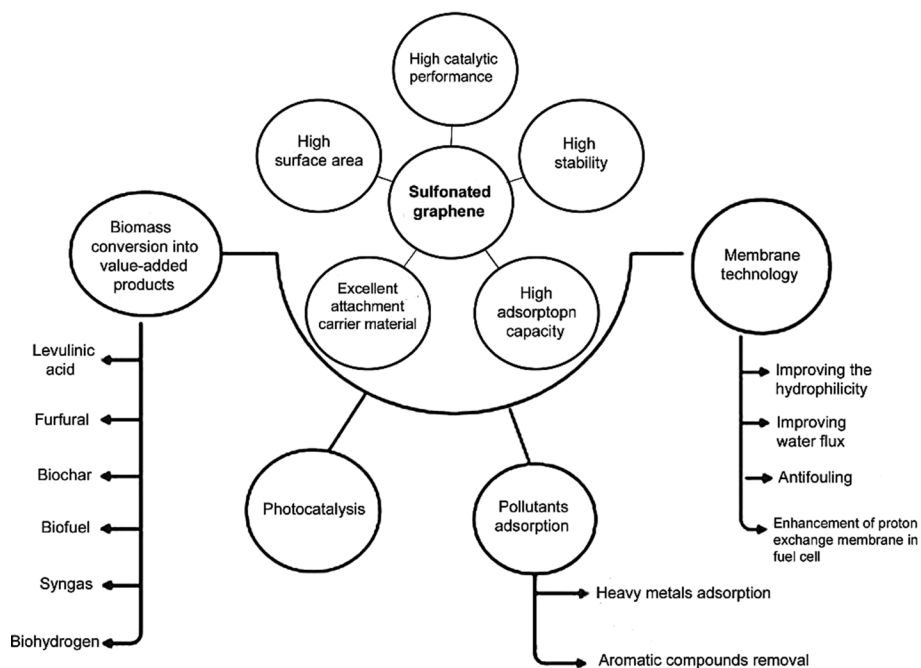
Therefore, this review focuses on the application of sulfonated graphene and sulfonated graphene oxide for biomass valorization, wastewater adsorption, and degradation. The catalyst's role in enhancing the hydrophilicity, salt rejection, water flux, and antifouling properties of membrane units, as well as the proton exchange membrane's performance in fuel cells, was discussed. Photocatalyst degradation of cationic dye and lignocellulosic material conversion to useful by-products were assessed. The economic value of bio-oil derived from the liquefaction of biomass by sulfonated graphene was also evaluated.

Synthesis

Structurally, graphene is hexagonal or honeycomb sp^2 -hybridized two-dimensional carbon sheet with a thickness of one carbon. The physical and chemical properties of graphene have aroused the world's interest in its applications (Tawfik et al. 2021b). Graphene is prepared by reducing graphene oxide and increasing sp^3 -hybridized carbon atoms (Tawfik et al. 2022d). The sp^3 bonding is less stable than sp^2 ; therefore, the attachment of oxygen-containing function groups on the graphene oxide to the organic solvents is variable (Elreedy et al. 2017). The electrical conductivity of the graphene oxide increases with the removal of these functional groups (Lu et al. 2009; Ray et al. 2015).

Graphene is prepared by the reduction of graphene oxide, which was synthesized for the first time in 1859 by Brodie's method through the oxidative exfoliation of graphite with potassium chlorate (in a ratio of 3:1) with fuming nitric

Fig. 1 Properties and applications of sulfonated graphene. The surfaces of the sulfonated graphene oxide nanosheets are modified with carboxylic ($-\text{COOH}$), hydroxyl ($-\text{OH}$), oxygen ($-\text{O}-$), and sulfonic ($-\text{SO}_3\text{H}$) functional groups. These groups increase the catalytic activity, chemical stability, and adsorption capacity, making sulfonated graphene an excellent carrier material. Sulfonated graphene has various applications, e.g., membrane technology, pollutants adsorption, photocatalysis of anionic and cationic dyes, as well as biomass conversion into value-added products



acid at 60 °C. The reaction takes 3–4 days (Brodie 1860). Staudenmaier (1899) used sulfuric acid instead of two-thirds of fuming nitric acid and designed a simple method with a short reaction time. However, the common method for preparing graphene oxide that is still in use was discovered in 1958 (Hummers and Offeman 1958). Simply, hummer's method used 50 g of sodium nitrate, 2.3 L of sulfuric acid and 300 g of potassium permanganate to oxidize 50 g of graphite powder. Permanganate and sodium nitrate were used instead of potassium chlorate and nitric acid fumes, respectively, to prevent explosion during the reaction. Hummer's method occurs in a few hours and is more efficient (Zaaba et al. 2017). Although several modifications were reported, Hummer's method is still common for graphene oxide preparation (Fig. 2).

Sulfonated graphene (oxide) is a graphene derivative and heterogeneous catalyst, which has the merit of being more sustainable and widely utilized in chemical industries and biology (Mostafa et al. 2016a, b; Tondro et al. 2020). Sulfonated graphene is prepared from the sulfonation of the graphene oxide. Various sulfonating agents such as sulfuric acid, chlorosulfuric acid, 2-chloroethane sulfonic acid, and 4-diazobenzenesulfonic acid were involved in the sulfonated graphene preparation (Oger et al. 2016). Oger et al. (2016) described eight preparation routes for sulfonated graphene, as shown in Fig. 2. Briefly, the routes used different oxidizing and sulfonating agents to form sulfonated graphene oxide from graphite and then the reduction reaction to form sulfonated graphene. Sulfonic group $-SO_3H$ loading was changed for each route. Table 1 summarizes the chemicals utilized in all routes of preparation of sulfonated graphene (oxide) from graphite and the loading of the sulfonic group.

In conclusion, graphene oxide has more sp^3 -hybridized carbon atoms than graphene; therefore, the attachment of oxygen-containing function groups on the graphene oxide to the organic solvents is variable. The electrical conductivity of the graphene oxide increases with the removal of these functional groups. Graphene is prepared by the reduction of graphene oxide, synthesized from the oxidative exfoliation of graphite. Sulfonated graphene (oxide) is prepared from the oxidation and sulfonation of graphite powder. The chemical properties of the sulfonated graphene and graphene oxide were affected by the oxidizing and sulfonating agents.

Membranes

Membrane technology has recently become popular in water purification, wastewater treatment, seawater desalination, food, and medicine. The technology is simple with high efficacy, cost-effectiveness, eco-friendly nature, and insignificant chemical consumption (Kang et al. 2019; Tawfik et al. 2022a). However, the membrane still suffered from

various problems for applications that could be overcome by the addition of nanocomposite materials as follows,

Hydrophilicity, salt rejection, water flux and antifouling properties

The nanofiltration process is widely used for water treatment processes. The technology is efficient for heavy metal removal, virus elimination, and metal recovery from wastewater. The nanofiltration produces demineralized water at low pressure (Shon et al. 2013; Zhang et al. 2015; Zhao et al. 2015a). Adding nanoparticles to active polyamide layers could improve the efficiency of the nanofiltration membrane (Ismail et al. 2015; Lau et al. 2015; Hegab et al. 2017). This is an innovative approach to solving the main technical obstacles due to the unusual and unique nanomaterial properties. Hydrophilic nanomaterials, such as zeolite (Dong et al. 2015), cerium oxide (Lakhotia et al. 2018), and carbon nanotubes (Ghanbari et al. 2015), have been successfully embedded in polyamide of nanofiltration membrane layer to improve its performance.

Graphene oxide was used to improve the nanofiltration membranes. The presence of oxygen functional groups (hydroxyl, carboxyl, and epoxy) in two-dimensional graphene sheets and their derivatives are unique materials for improving the hydrophilicity of membranes (Choi et al. 2013; Bano et al. 2015). Incorporating graphene oxide with the polyamide layer of the membrane would improve the water flux and rejection process. Nevertheless, the main problem with graphene oxide nanosheet application in membranes is the difficulty of homogeneously dispersing them in the membrane matrix. Agglomeration of graphene oxide nanosheets easily occurs at high concentrations, and membrane performance is subsequently suffered from a reduction of hydrophilicity and water flux (Mahmoudi et al. 2015). Accordingly, the agglomeration of graphene oxide nanosheets could be reduced by incorporating different extra functional groups in the nanofiltration membrane surface (Liu et al. 2017).

Graphene oxide was functionalized with a sulfonic acid group resulting in sulfonated graphene oxide to improve the negative charge and anti-agglomeration of nanofiltration membrane as well as hydrophilicity enhancement (Ayyaru and Ahn 2017; Kang et al. 2019). The sulfonated graphene oxide enhanced the zeta potential, cross-linking hydrophilicity, salt rejection, pure water flux, and antifouling properties of the thin film nanocomposite membranes. The negative charges of the membrane surface and hydrophilicity were improved by oxygen-containing functional groups of sulfonated graphene oxide, where water flux increased from 6.3 L per square meter per hour in thin film nanocomposite membrane to 11.8 L per square meter per hour in 30 weight percent sulfonated graphene oxide thin film nanocomposite

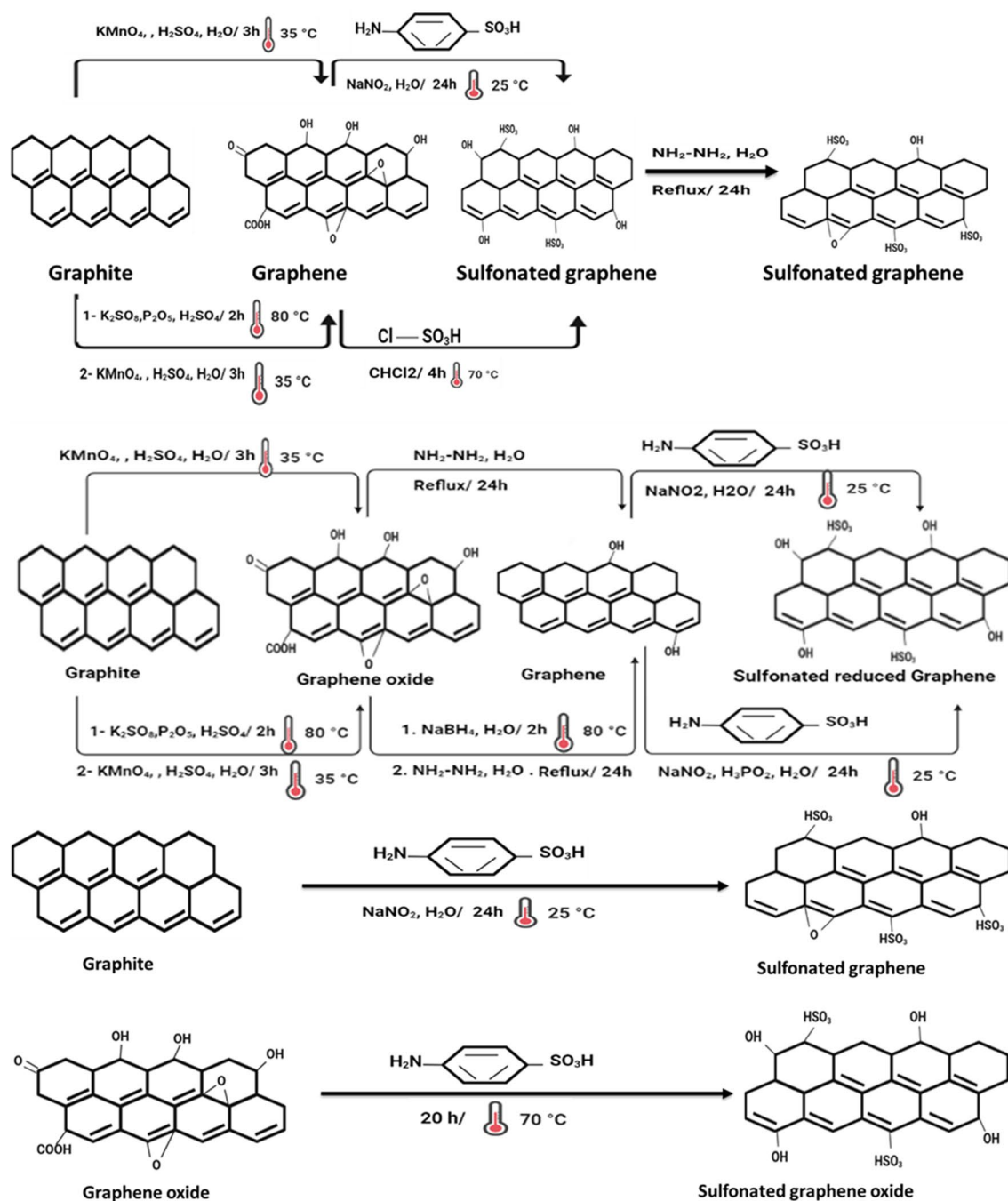


Fig. 2 Preparation routes of graphene derivatives, i.e., sulfonated graphene (oxide) (Oger et al. 2016). Natural sources of rich carbon could be utilized to synthesize sulfonated graphene oxide. The modified sulfonation and Hummer's methods are used to prepare and synthesize solid acid catalysts of graphene oxide and sulfonated graphene oxide

nanosheets. Carboxylic, hydroxyl, oxygen, and sulfonic functional groups are introduced onto the surfaces of the graphene nanosheets. The synthesized sulfonated graphene catalysts are efficient for glycosidic bond hydrolysis and Fischer esterification

membrane. Thin film nanocomposite membranes can highly attract water molecules and facilitate them to pass quickly via the membrane matrix (Zhao et al. 2013). The dispersed, non-uniformly, and excessive dosage of sulfonated graphene oxide highly reduced the water uptake and flux by

a membrane (Bano et al. 2015; Wang et al. 2016). Furthermore, the antifouling property of the membrane was substantially improved by incorporating sulfonated graphene oxide into the polyamide layer, where the sulfonated graphene oxide hydrophilic functional groups increased the

Table 1 Chemicals involved in sulfonated graphene preparation from graphite and the sulfonic group loading value (Oger et al. 2016)

Route	Oxidizing agents	Sulfonating agents	Reducing agents	Sulfonic group loading (mmol/g)
1	Potassium permanganate and sulfuric acid	4-diazoniobenzenesulfonate and sodium nitrite	Hydrazine	0.55
2	Potassium persulfate and phosphorus pentoxide	4-diazoniobenzenesulfonate and sodium nitrite	Hydrazine	0.7
3	Potassium persulfate and phosphorus pentoxide	Chlorosulfuric acid	Hydrazine	0.68
4	Potassium permanganate and sulfuric acid	Hydrazine	4-diazoniobenzenesulfonate and sodium nitrite	1.21
5	Potassium persulfate and phosphorus pentoxide	Hydrazine	4-diazoniobenzenesulfonate and sodium nitrite	1.79
6	Potassium persulfate and phosphorus pentoxide	Hydrazine	4-diazoniobenzenesulfonate and hypo-phosphorous acid	0.8
7	Potassium persulfate and phosphorus pentoxide	Sodium borohydride and hydrazine	4-diazoniobenzenesulfonate and sodium nitrite	<0.1
8	Not applicable	4-diazoniobenzenesulfonate and sodium nitrite	not applicable	0

Potassium permanganate and sulfuric acid are the main oxidizing agents for sulfonated graphene oxide synthesis. 4-diazoniobenzenesulfonate and sodium nitrite are used as sulfonating agents for preparation of sulfonated graphene oxide. Hydrazine and 4-diazoniobenzenesulfonate and hypo-phosphorous acid are used as reducing agents. The sulfonic group loading controls the acidity and reaction activity of the catalyst

hydrophilicity of the nanofiltration membrane. The hydrophilicity surface would highly reduce the adsorption of hydrophobic foulants on the surface of the membrane; thus, high hydrophilicity surface would have better antifouling performance (Choudhury et al. 2018).

In conclusion, supplementing an appropriate quantity of sulfonated graphene oxide to the membrane highly improved the hydrophilicity, salt rejection, water flux, and antifouling properties. Furthermore, the antifouling property of the membrane is improved by incorporating sulfonated graphene oxide into the polyamide layer, where the sulfonated graphene oxide hydrophilic functional groups increase the hydrophilicity of the nanofiltration membrane.

Reduced biofouling in polymeric membranes

Developing polymeric materials would improve membrane performance regarding hydrophilicity, permeability, and separation (Gzara et al. 2016). However, membrane biofouling represents a big barrier to such technology's economic and technological application. Simply, biofouling is the accumulation of foulants (bacterial cells and proteins) present in feeding water on the membrane surface, resulting in deposition, attachment, and metabolites in biofilm formation. Further, biofouling causes solute concentration and nutrient deposits on the membrane (Hummers and Offeman 1958; Tondro et al. 2021), leading to blockage of the pore membrane. This causes salt rejection reduction, dropping permeate flux, and increased pressure

trans-membrane, which requires high energy for water filtration (Neelakandan et al. 2016). Therefore, membrane fabrication modification is necessary to maximize anti-biofouling (Zhao et al. 2015b).

Hydrophilicity and morphology of the membrane are the key parameters for overcoming biofouling phenomena (Banerjee et al. 2011). Cellulose acetate is an employed polymer in fabricating membranes for water treatment. Cellulose acetate has high potential flux and biocompatibility but moderate hydrophilicity. Furthermore, cellulose acetate has poor resistance to fouling processes (Mohan et al. 2015; El-Ghaffar et al. 2020). Biofouling is mainly preferred on polymeric membranes that enjoy a hydrophobic nature. This membrane type has high hydrophobic–hydrophobic interactions with proteins. Thus, improving the morphological and hydrophilicity of a membrane is an innovative approach to the mitigation of biofouling (Rana and Matsuura 2010).

Nanomaterial addition would improve membranes' magnetic, mechanical, morphological, thermal, anti-biofouling, and hydrophilic properties (Madaeni et al. 2011; Vatanpour et al. 2012; Zinadini et al. 2017). Alumina, titanium dioxide, zinc oxide, silica, graphene oxide nanosheets, sulfonated graphene oxide, carbon nanotubes, magnetite, zirconia, and clay nanoparticles were efficiently utilized for the polymer membrane modifications (Liang et al. 2012; Derbali et al. 2017; Tamiji and Ameri 2017; Lim et al. 2020). However, the nanoparticles with a low specific surface area are not preferable due to agglomeration causing the formation of an imperfect pore in the membranes.

The selection of high specific surface area nanoparticles is required, but the low additive dosage is very important (Zhang et al. 2013; Ayyaru and Ahn 2017). The hydrophilic nature of graphene oxide, due to the abundance of oxygen functional groups (carbonyl, hydroxyl, carboxyl, and epoxy), makes the material suitable for membrane modifications (Zhao et al. 2014). The best features of graphene oxide are its easy surface functionalization, high strength, low density and unique planar structure. However, graphene oxide's water uptake ability or hydrophilicity needs improvement (Beydaghli et al. 2014) to mitigate the adsorption/attachment of hydrophobic protein pollutants onto the membrane surface. Microbes and proteins are highly hydrophobic in nature; thus, increasing the hydrophilicity of the membranes would enhance resistance against biofouling (Vatanpour et al. 2011).

The most common problem of using graphene oxide is the poor homogenous dispersion inside the membrane matrix, resulting in high agglomeration. This highly reduces the water flux, hydrophilicity and, subsequently, membrane efficiency. Therefore, the functionalization of graphene oxide with other nanoparticles will minimize the agglomeration problems on the membrane surface (Kang et al. 2019). Cellulose acetate was highly blended and incorporated with sulfonated graphene oxide nanomaterials to improve wastewater treatment's hydrophilicity and antifouling properties (Zahid et al. 2021). The measurement of the contact angle determines the hydrophilicity of the membrane surface. The contact angle of 70° was recorded for a cellulose acetate membrane that was highly reduced up to 50° after supplementation of hydrophilic sulfonated graphene nanofillers indicating better hydrophilicity and water affinity of the membrane. This is linked to the membranes rich with water retention sulfonic acid, carboxylic and hydroxyl moieties on the surface and inside the matrix resulting in hybrid membrane technology. However, the hydrophilicity is highly dependent on the concentration of sulfonated graphene oxide. The addition of sulfonated graphene oxide increased the water flux from 50 for pristine cellulose acetate membranes to 152 L per square meter per hour per hydrolytic pressure for cellulose acetate sulfonated graphene oxide blended membranes.

The presence of sulfonic groups on graphene oxide holds and provides a water-thick layer and subsequently increases the water flow flux. Sulfonated graphene oxide nanofillers reduce the contact angle, positively affecting water permeability (Ayyaru and Ahn 2017). The water flux was slightly decreased at high sulfonated graphene oxide content of 1.4 weight percent, causing agglomeration and pore blockage of the fabricated membranes. The results also showed that the antibacterial activity was increased with increasing sulfonated graphene oxide in the cellulose acetate membrane, indicating the minimization of the fouling process.

The cellulose acetate sulfonated graphene oxide composite surface of the membrane exhibits a negative charge due to the presence of hydrophilic functional groups of sulfonated graphene oxide (sulfonic, carboxylic, and hydroxyl groups) that create highly electrostatic repulsion between the membrane and microbes (Zinadini et al. 2017).

In summary, incorporating sulfonated graphene oxide nanosheets with cellulose acetate polymer decreased the contact angle and hence increased the hydrophilicity, the water flux, and the antifouling properties. The negative charge of the sulfonated graphene oxide function groups creates highly electrostatic repulsion between the membrane and microbes. Therefore, the sulfonated graphene cellulose acetate membrane showed antibacterial activity.

Enhancement of proton exchange membrane in fuel cells

Developing countries prioritize saving renewable energy from natural sources (Tawfik et al. 2022c). Proton exchange membrane fuel cells are a good electricity generation technology and have recently received great attention (Eraky et al. 2022). This technology enjoys low cost, environmental friendliness and high power efficiency (Huang et al. 2016). The proton exchange membranes are the backbone of that fuel cell (Kraytsberg and Ein-Eli 2014). They are mainly utilized for protons' conducting, isolating negative and positive electrodes. Further, the proton exchange membranes must have high hydration ability and unique mechanical properties to avoid conduction proton reduction and water depletion. The non-fluorinated acid ionomer and fluorinated proton exchange membranes have been recently developed, such as sulfonated polyimide-based membranes, polystyrene-based membranes, polybenzimidazole-based membranes, sulfonated aromatic polymer membranes, and polyphosphazene-based membranes (Neburchilov et al. 2007).

Unfortunately, these membranes are not efficient practically due to the deficiency of hydrophilic functional groups and/or the lack of polymer hydrolysis stability (Kumar et al. 2014). The proton exchange membranes must have proper and unique proton conductivity, thermal and chemical stability (Kim et al. 2009). Sulfonated poly(ether ether ketone) has recently gained high attention for application in proton exchange membranes due to its superior chemical stability, low cost, and excellent alcohol resistance (Liu et al. 2015). The presence of a sulfonic acid group ($-\text{SO}_3\text{H}$) in the sulfonated poly(ether ketone) molecules exhibited a low fuel permeability (Zhang et al. 2008). The degree of sulfonation controls the efficiency and performance of the proton exchange membranes. Proton conductivity is increased with an increasing degree of sulfonation. Nevertheless, this provided high permeation of the liquid fuel, reducing the proton exchange membrane structure stability. Inorganic fillers were

proposed to overcome this defect, avoiding the reduction of proton conductivity.

Graphene oxide nanosheets are two-dimensional with high mechanical properties and surface area. Graphene oxide contains oxygen functional groups (hydroxyl, carboxyl, epoxy) (Beydaghi and Javanbakht 2015; Tang et al. 2016) that make graphene oxide sheets hydrophobic. Fortunately, sulfonated graphene was reported to be an excellent inorganic filler of the proton exchange membranes (Gahlot et al. 2014). Graphene oxide sheets lack groups of protons conducting. However, combining those sheets with the sulfonic acid group will highly increase the channels of proton conducting in the membrane matrix and the water retention time of the composite membranes (Xu et al. 2011).

Furthermore, the sulfonic acid group surface in sulfonated poly(ether ether ketone) and sulfonated graphene nanosheets containing oxygen functional groups provides strong interfacial hydrogen bond interaction, reducing the methanol permeability, weakening the membrane expansion, and improving the thermal stability of the proton exchange membranes composite (Fig. 3). Cao et al. (2018) found that increasing the sulfonated graphene in proton exchange membrane provided excellent proton conductivity and electrochemical properties. The 2.0 weight percent of sulfonated graphene loading in the

sulfonated graphene/sulfonated poly(ether ether ketone) composite membrane achieved proton conductivities of 0.063 Siemens per centimeter at a temperature of 54 °C. This value was 1.54 times higher than that of the classical sulfonated poly(ether ether ketone) (0.041 Siemens per centimeter) membranes. Similarly, the methanol permeability of sulfonated graphene/sulfonated poly(ether ether ketone) was 1.834×10^{-9} cm square per second compared to 4.537×10^{-9} cm square per second in conventional sulfonated poly(ether ether ketone) membranes. The composite membranes of the sulfonated graphene/sulfonated poly(ether ether ketone) provided better water uptake and thermal stability than the proton exchange membranes.

In summary, the sulfonated graphene/sulfonated poly(ether ether ketone) composite membranes are novel and exhibit excellent proton conductivity, chemical and thermal stability. Thus, the sulfonated graphene/sulfonated poly(ether ether ketone) composite has great potential application for proton exchange membranes. The sulfonated graphene/sulfonated poly(ether ether ketone) could be widely applied as a new efficient membrane proton exchange in fuel cells. Therefore, a novel proton exchange membrane sulfonated graphene/sulfonated poly(ether ether ketone)-based composite membrane has promising applications from a commercial point of view.

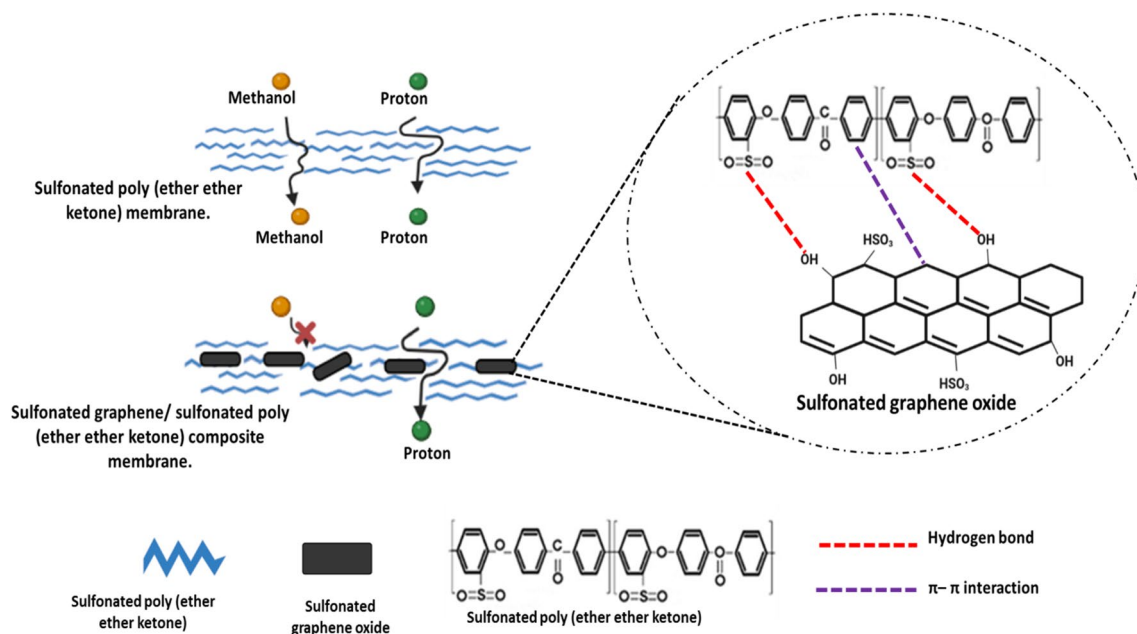


Fig. 3 Proton exchange membrane in fuel cells. Proton exchange membrane fuel cell is a good electricity generation technology and has recently received great attention. These membranes are not practically efficient due to the deficiency of hydrophilic functional groups and/or the lack of polymer hydrolysis stability. Sulfonated poly(ether ether ketone) has recently gained greater attention for application in

proton exchange membranes. The presence of sulfonic acid group ($-\text{SO}_3\text{H}$) in the sulfonated poly(ether ether ketone) molecules exhibited a low fuel permeability. Nevertheless, the degree of sulfonation controls the efficiency and performance of the proton exchange membranes. Proton conductivity is increased with an increasing degree of sulfonation

Pollutants adsorption

Heavy metals and dyes

Recently, various synthetic dyes containing heavy metals have been produced by the most metallurgic industries (Wu et al. 2016), such as printing (Delval et al. 2006), textile (González et al. 2015) and other industries (Pan et al. 2008; Tawfik et al. 2021c). Adsorption of dyes and heavy metals from the wastewater industry has been recently attracted for environmental protection (Allam et al. 2015). So far, conventional absorbent materials such as activated carbon silica, polymer resins, and metal oxides are not efficient (Ismail and Tawfik 2016). Those adsorbents suffered from low removal efficiency and adsorption capacity (Madadrang et al. 2012) due to less active sites, narrow pore diameter, low surface area, and thermal instability (Nguyen-Le and Lee 2015). Graphene oxide's use to remove such pollutants has attracted great attention (Tawfik et al. 2022d). Graphene oxide has various carboxylic acid, epoxide and hydroxyl groups (Wen et al. 2013), which play a role in the contaminants' removal from wastewater (Tan et al. 2015b). However, it is difficult to separate those oxides from the bulking water phase due to high dispersibility (Bai et al. 2015). The functionalization of graphene oxide is usually carried out to overcome the drawbacks of using these nanoparticles for wastewater treatment. Cui et al. (2015) functionalized ethylene diamine tetraacetic acid with magnetic graphene oxide for the adsorption of lead, mercury, and copper from water. Vadahanambi et al. (2013) successfully used three-dimensional graphene and carbon nanotube iron oxide composites to remove arsenic from contaminated water.

Yan et al. (2016) synthesized the chitosan and graphene oxide composite for water treatment.

Graphene oxide functionalization provided unique properties of the adsorbents, such as high adsorption capacity and efficiency (Liu et al. 2014). The oxygen functional groups on graphene oxide sheets facilitate its functionalization and dispersion in an aqueous solution (Qin et al. 2012). It is important to increase the graphene oxide adsorption capacity by functionalization (Shen and Chen 2015). Liu et al. removed organic dyes by functionalizing graphene sheets with beta-cyclodextrins (Liu et al. 2014). Madadrang et al. (2012) eliminated lead from contaminated water using ethylene diamine tetraacetic acid graphene oxide. However, graphene-based materials still suffer from low removal efficiencies and adsorption capacities (Wang and Chen 2015).

Due to its highly rich adsorption sites, sulfonated graphene oxide is an efficient adsorbing capacity material (Shen and Chen 2015). Sulfonated graphene provided a high adsorption capacity of 2850 mg per gram for methylene blue (Wei et al. 2018). The sulfonated graphene oxide electronegative groups are binding sites to adsorb methylene blue. Further, the sulfonated graphene oxide adsorbed lead (415 mg per gram), copper (167.8 mg per gram), lead (209.3 mg per gram), and mercury (65.0 mg per gram) (Table 2). This is linked to the presence of multiple adsorption sites and the good dispersibility of the sulfonated graphene oxide.

The sulfonated graphene oxide adsorption capacity of the cationic dyes could be linked to the presence of oxygen-rich functional groups (hydroxyl, carboxyl, and sulfonyl), which change into oxidized forms in the aqueous solution medium. This will give an electrostatic effect for the adsorption of cationic dye by the ultrathin layer graphene oxide structure. The graphene contains π - π interactions, which can adsorb the cationic dye. The adsorption sites of sulfonated graphene oxide are 2.763 mmol per gram sulfonyl, 3.875 mmol per

Table 2 Adsorption capacity of sulfonated graphene oxide for different pollutants. The absorption capacity of the sulfonated graphene oxide for dyes and heavy metals is quite high

Pollutants	Adsorbing capacity (milligrams per gram)	Interaction type	References
Methylene blue	2850	π - π interactions	Wei et al. (2018)
Lead (II)	415	Electrostatic attraction	Wei et al. (2018)
Copper (II)	167.8	Electrostatic attraction	Wei et al. (2018)
Cadmium (II)	209.3	Electrostatic attraction	Wei et al. (2018)
mercury (II)	65.0	Electrostatic attraction	Wei et al. (2018)
Antimony (V)	158.6	Electrostatic attraction	Wang and Chen (2015)
uranium (VI)	309.09	Electrostatic attraction	Zhang et al. (2016)
1-naphthol	2.407 mmol per gram	π - π interactions	Zhao et al. (2011b)
Naphthalene	2.326 mmol per gram	π - π interactions	Zhao et al. (2011b)

The sulfonated graphene oxide adsorption capacity of the cationic dyes is linked to the presence of oxygen-rich functional groups (hydroxyl, carboxyl, and sulfonyl). Incorporating sulfonic groups with graphene, forming sulfonated graphene, enhanced the adsorption capacity of aromatic pollutants. The main adsorption mechanism is the strong π - π interaction stacking between the sulfonated graphene oxide nanosheets and aromatic molecules

gram carboxyl, 5.592 mmol per gram hydroxyl with π - π interactions. Electrostatic attraction is the main mechanism for the adsorption of heavy metals. The adsorption capacity is quite high for sulfonated graphene oxide due to the functional groups containing sp^3 -hybridized graphene edge (Sun et al. 2017).

In conclusion, the absorption capacity of the sulfonated graphene oxide for dyes and heavy metals (Table 2) was superior compared with other nanocomposite materials. The practical application of sulfonated graphene oxide adsorbents with high adsorption site capacities and simple preparation methods remains challenging. The sulfonated graphene oxide provided outstanding efficiency for removing cationic dyes and heavy metals and could have great potential applications for wastewater industry treatment shortly.

Aromatic compounds

The aromatic pollutants are persistent and generated in the environment by pharmaceuticals, pesticides, and dyestuffs industries (Abdel Maksoud et al. 2021). They are soluble in water; thus, it easily transports into the water ecosystem, causing health harm to the people. Due to its simplistic operation and good removal efficiency, the adsorption technique removes such pollutants from the wastewater industry. However, the adsorption capacities of classical materials are not so high to efficiently remove the highly persistent aromatic contaminants. The development of new adsorbents with high unusual adsorption capacities is needed to remove persistent organic pollutants from wastewater.

Theoretically, graphene has a unique specific surface area of 2630 m square per gram that is highly suitable for excellent adsorption of aromatic compounds from contaminated water (Liang et al. 2009; Su et al. 2009). Graphene nanosheets removed naphthalene and 1-naphthol by 2.3–2.4 mmol per gram (Zhao et al. 2011a). The 1-naphthol and naphthalene adsorption are due to the strong π - π interaction between graphene nanosheets and the aromatic pollutants molecules. Incorporating sulfonic groups with graphene-forming sulfonated graphene enhanced the adsorption capacity of 1-naphthol (Zhao et al. 2011b). The adsorption kinetic capacities of 1-naphthol on sulfonated graphene nanosheets were 2.3 mmol/g at 293.15 Kelvin and 6.4 mmol per gram at 313.15–333.15 Kelvin (Table 2). The strong π - π interaction stacking between the sulfonated graphene nanosheets and aromatic molecules greatly contributed to the adsorption of 1-naphthol adsorption (Sheng et al. 2010; Zhao et al. 2011a).

The planar aromatic molecules are highly inclined to stack on the sulfonated graphene nanosheet surface. Sulfonated graphene not only provided single but multi-layer adsorption of the 1-naphthol due to high dispersion in the reaction medium (Zhao et al. 2011a). Further, the adsorption

of 1-naphthol on the sulfonated graphene increased at increasing temperatures, resulting in the highest adsorption capacity of 6.4 mmol per gram for 1-naphthol. The maximum adsorption capacities of sulfonated graphene were 2.407 mmol per gram for 1-naphthol and 2.326 mmol per gram for naphthalene. This was due to the strong interaction π - π in the form of stacking face-to-face (Zhao et al. 2011a). However, the adsorption of naphthalene and 1-naphthol on sulfonated graphene sheets dropped as the pH in the reaction medium was increased. The sulfonated graphene surface is typically electron depleted at a low pH value, which makes Lewis acid adsorption dominant. Naphthalene/1-naphthol is mainly a Lewis base. Thus, the adsorption capacity of 1-naphthol/naphthalene becomes stronger at decreasing pH due to more electron-depleted surface sites available on the sulfonated graphene. The 1-naphthol interacts with the surface of sulfonated graphene electron depleted at high pH. The n - π electron donor-acceptor for oxygen electron pairs (π -electron donor) of 1-naphthol and the surface of the sulfonated graphene (π -electron acceptor) are proposed mechanisms. This is highly enhanced when more hydroxyl groups are ionized into epoxy groups at high pH.

In conclusion, the sulfonated graphene (oxide) nanosheets would be promising nanocomposite materials for persistent aromatic chemical removal from large volumetric wastewater if these nanocomposite materials could be synthesized in huge quantities shortly.

Photocatalytic oxidation of dyes

The semiconductor photocatalyst titanium dioxide with light has the advantage of degrading recalcitrant toxic compounds (Gar Alalm et al. 2016, 2017). Graphene/semiconductor composite could improve the photocatalytic efficiency by increasing the electron transfer and the light absorption enhancement band range (Zhou et al. 2013; Zhang et al. 2014). Noble metal nanoparticles significantly improved the photocatalytic efficiency of graphene titanium dioxide due to an increase in the ability of light absorption in the visible region (Zhou et al. 2013). These composite materials overcome the electron-hole pair's recombination by transporting photogenerated electrons into the noble metal (Wang et al. 2014b). Nevertheless, graphene/graphene oxide titanium dioxide nanocomposites were destroyed and defected under alkaline operating conditions due to the damage and loss of the interaction between titanium dioxide and graphene/graphene oxide nanosheets (Gao and Sun 2014). This deficiency and drawbacks were overcome in sulfonated graphene/titanium dioxide/silver nanocomposite, which enhanced the stability of graphene, creating electron acceptor, transport channels, and working efficiently in a wide range of pH (Alamelu and Jaffar Ali 2020a).

Sulfonated graphene/titanium dioxide/silver nanocomposite was synthesized and utilized for the photodegradation of anionic dyes such as methyl orange, cationic dyes such as rhodamine B, and 4-nitrophenol. Sulfonated graphene/titanium dioxide/silver could remove 98% of anionic dye (methyl orange) and cationic dye (rhodamine B and 4-nitrophenol) at pH values ranging from 3–7. The photodegradation kinetics of sulfonated graphene/titanium dioxide/silver for all pollutants was four–ninefold higher than titanium dioxide. This is linked to sulfonated graphene/titanium dioxide/silver that extended the capability of light absorption in the relevant visible region, the ability of electron transport and interfacial electron transfer. The maximum photocatalytic degradation of methyl orange (anionic dye) by sulfonated graphene/titanium dioxide/silver occurred at pH (3) and dropped with increasing pH value. The sulfonated graphene/titanium dioxide/silver catalyst surface under acidic pH will bear a positive charge, thus able to adsorb anionic dyes and enhance the fast degradation (Yang et al. 2014). This was not the case for cationic dye rhodamine B removal by sulfonated graphene/titanium dioxide/silver catalyst where the photocatalyst was maximum at pH 7. This is due to the formation of a negative charge on the sulfonated graphene/titanium dioxide/silver catalyst at this pH value.

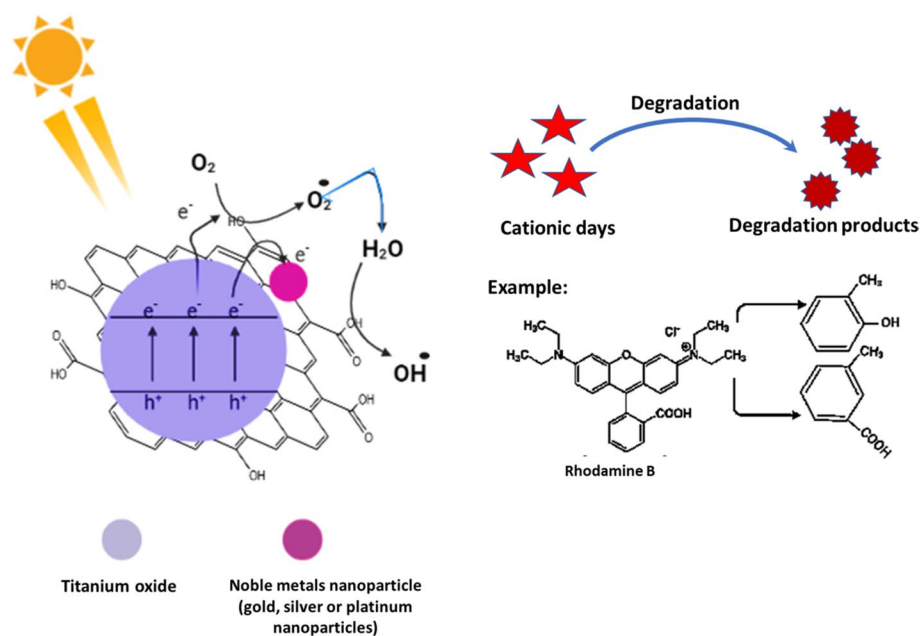


Fig. 4 Mechanism of photoexcited electrons and holes transfer among titanium dioxide and noble metals nanoparticles such as gold, silver or platinum and sulfonated graphene. Incorporating noble nanoparticles into the sulfonated graphene provided more holes and electron generation, which can easily participate in the oxidation/reduction process, improving the photocatalytic pursuance of recalcitrant toxic compounds. Irradiating sulfonated graphene/titanium dioxide/silver by sunlight, the electrons generated in the valance band of titanium

Photocatalytic oxidation of 4-nitrophenol was conducted by sulfonated graphene/titanium dioxide/silver catalyst at a pH range of 3–10. The photodegradation of 4-nitrophenol (97%) occurred at pH (6.5). However, the photocatalysis efficiency of 4-nitrophenol was highly reduced at increasing pH values from 6.5 to 10 due to H_2O_2 instability. The quantity of hydroxyl radicals is decreased with increasing superoxide scavenger radicals (Subbulekshmi and Subramanian 2017). Irradiating sulfonated graphene/titanium dioxide/silver by sunlight, the generated electrons in the valance band of titanium dioxide are highly excited to the conduction band, leaving enormous holes in the valance band (Fig. 4). The electrons of titanium dioxide quickly transfer from the conduction band into the sheets of sulfonated graphene and silver nanoparticles (Tan et al. 2015a). This creates electron–hole pairs required for the photocatalysis process. The generated electrons react with oxygen molecules and reduce them further into superoxide anion radicals that react with protons and electrons to form hydroxyl radicals. Photogenerated holes oxidize water molecules to generate reactive hydroxide radicals. These radicals facilitate the photodegradation of recalcitrant compounds. The synergistic effect of silver, titanium dioxide, and sulfonated graphene highly improved the photocatalytic activity of toxic compounds.

dioxide are highly excited to the conduction band, leaving enormous holes in the valance band. The electrons of titanium dioxide quickly transfer from the conduction band into the sheets of sulfonated graphene and silver nanoparticles. This creates electron–hole pairs required for the photocatalysis process. The generated electrons react with oxygen molecules and are reduced further into superoxide anion radicals that react with proton and electrons to highly form hydroxyl radicals

Sulfonated graphene not only served as the supporting material but also provided a uniform distribution of silver nanoparticles, overcoming aggregation and thus achieving high photocatalytic efficiency. Gold nanoparticles were decorated with sulfonated graphene titanium dioxide nanocomposites to remove p-nitrophenol, rhodamine B, and methyl orange under sunlight irradiation (Alamelu and Jaffar Ali 2020b). Gold/sulfonated graphene oxide titanium dioxide catalyst exhibited 3.2-fold higher than the performance of the pristine titanium dioxide system. This is due to the synergistic effect of raising interfacial electron transfer between composites, reducing the recombination rate of photoexcited holes and electrons and the plasmatic positive effect of gold nanoparticles.

In summary, the sulfonated graphene/titanium dioxide/silver nanocomposite is highly stable for catalytic oxidation of pollutants under a wide range of pH values and could be easily reused several cycles without loss of catalytic activity. Moreover, incorporating silver nanoparticles into the sulfonated graphene provided more holes and electron generation, which can easily participate in the oxidation/reduction process, improving the photocatalytic pursuance of recalcitrant toxic compounds. This renders sulfonated graphene/titanium dioxide/silver a universal and efficient photocatalyst that can be effectively exploited for wastewater industry treatment in real applications.

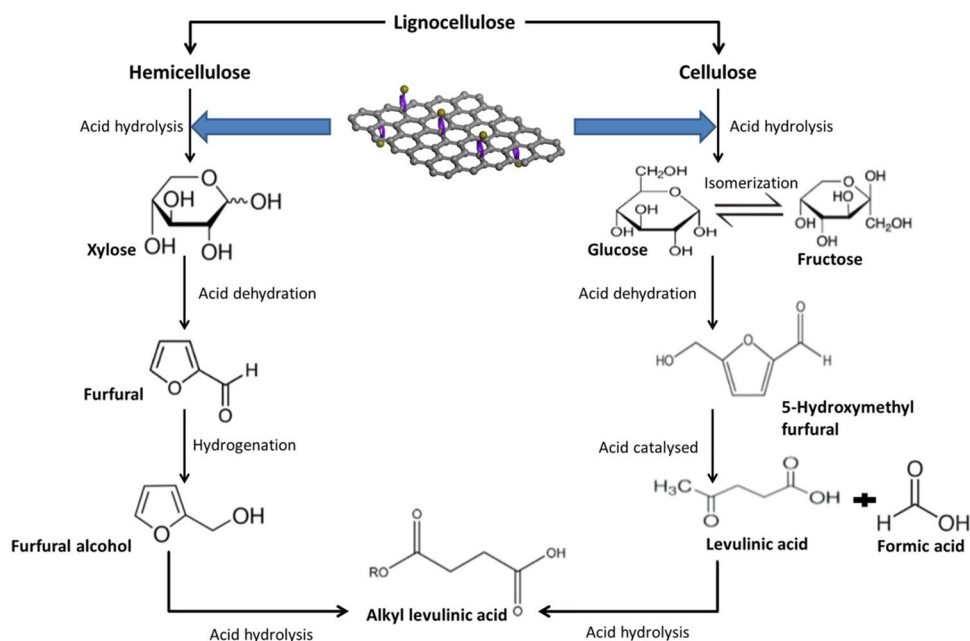
Biomass conversion

Acid hydrolysis of lignocellulosic wastes is efficient and produces chemical by-products (Osman et al. 2021a). The breakdown route of lignocellulosic materials by acidification is presented in Fig. 5. The hemicellulose is hydrolyzed by acid into xylose and terminated with alkyl levulinic acid. Likely, cellulose is converted into glucose and/or fructose that are ended with alkyl levulinic acid by-product.

Transformation of fructose into levulinic acid

Biomass, particularly lignocellulosic wastes, is a renewable resource which could be easily exploited to generate high value-added by-products, such as 5-hydroxymethylfurfural, alcohol, formic acid, furfural, and levulinic acid (Mascal and Nikitin 2010; Upare et al. 2013) (Fig. 6). Production of levulinic acid is a priority that can be further utilized to generate resins, succinic acid, polymers, pharmaceuticals, herbicides, flavoring agents, anti-freeze agents, solvents, biofuels, oxygenated fuel additives, and plasticizers (Braden et al. 2011; Axelsson et al. 2012). Biomass conversion into levulinic acid takes place by multiple steps such as cellulose hydrolysis into glucose, isomerization of glucose into fructose, fructose dehydration into 5-hydroxymethylfurfural, and more hydrolysis to highly form equimolar levulinic acid and formic acid (Alonso et al. 2013). These processes are carried out via enzymatic or chemical routes. The chemical route is preferred for commercial levulinic acid production (Son et al. 2012; Pileidis and Titirici 2016). Homogeneous sulfuric, phosphoric, and hydrochloric acid catalysts were

Fig. 5 Acid hydrolysis of lignocellulosic wastes. The cellulose and hemicellulose are easily acidified and converted into various intermediates chemicals. These chemical by-products could be easily utilized for various applications in the chemical industry



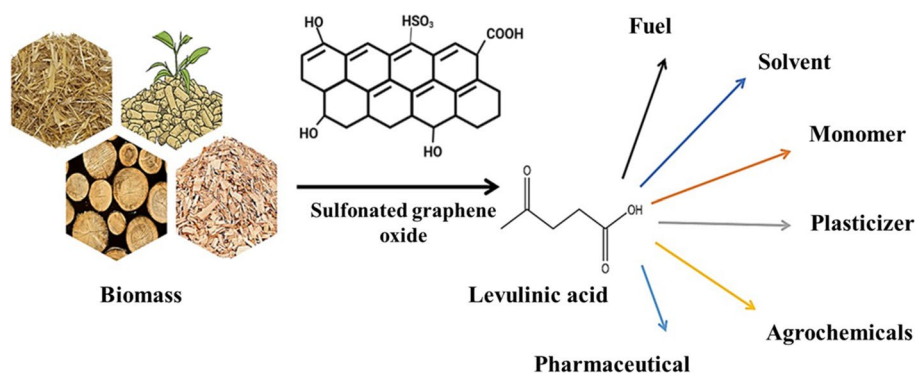


Fig. 6 Sulfonated graphene oxide promotes the conversion of the lignocellulosic biomass into levulinic acid, which can be used in making numerous value-added products. Levulinic acid can be converted into fuel, solvents, monomers, plasticizers, agrochemicals and pharmaceuticals. Biomass conversion into levulinic acid is taken place in

multiple steps. Cellulose is hydrolyzed into glucose, isomerization of glucose into fructose, fructose dehydration into 5-hydroxymethylfurfural, and more hydrolysis to highly form equimolar levulinic acid and formic acid. These processes are carried out via enzymatic or chemical routes

used for levulinic acid production because of their low resistance to mass transfer (Li et al. 2018). Those acidic catalysts are highly corrosive and non-recyclable (Zhao et al. 2016). The grafting of sulfonic groups provided the most catalytic activity providing a high levulinic acid yield due to the high acidity of the catalyst (Pizzolitto et al. 2020).

Graphene oxide is a porous catalyst with a high surface area and functional groups of carboxyl and hydroxyl (Wang et al. 2014a; Farghaly et al. 2016; Mostafa et al. 2016b; Upare et al. 2019). Sulfonated graphene oxide is the most powerful acid catalyst for the conversion of biomass (Tawfik and El-Qelish 2014; Zhu et al. 2015). Grafting sulfonic acid onto the two-dimensional structure of graphene oxide created an accessible active site that aided in the conversion of biomass into value-added chemicals like levulinic acid and its derivatives. A sulfonated graphene oxide catalyst was synthesized and prepared from petrochemical waste oil (Lawagon et al. 2021). Because of its high mesoporosity and the presence of 2.4 mmol per gram sulfonic groups grafted onto its surface, the prepared sulfonated graphene oxide has a high specific surface area (246.2 m square per gram). The sulfonated graphene was successfully used to convert fructose into levulinic acid. The levulinic acid yield was 61.2 mol percent at a temperature of 160 °C for one hour and fructose-to-sulfonated graphene weight ratio of 6.0 g per gram. Fortunately, sulfonated graphene can be reused five times with no severe loss of catalytic activity.

The conversion of 97.0% fructose into levulinic acid was achieved by adding sulfonated graphene (0.2 g) catalyst at a temperature of 200 °C and a substrate concentration of 4.5 g. 5-hydroxymethylfurfural (1.2%) and 26.9% levulinic acid were yielded after 10 min. Complete degradation of fructose into 38.5% levulinic acid occurred by increasing the reaction time to 60 min, and 5-hydroxymethylfurfural was not detected. Nevertheless, levulinic acid and formic acid

were decreased after 120 min, indicating that 5-hydroxymethylfurfural could form humin via hydroxyl and aldehyde reactive sites (Choudhary et al. 2013; El-Bery et al. 2013; Hu et al. 2015).

Sulfonated graphene oxide nanosheets exhibited high mesoporosity, offering a high specific surface area of 246.2 m square per gram. These results show excellent interaction conditions between fructose and catalyst active sites. The presence of oxygen-rich groups would enhance sulfonated graphene oxide surface hydrophilicity, which could be beneficial for the conversion of fructose (Qi et al. 2015). Furthermore, sulfonic groups (2.4 mmol per gram) on the catalyst surface highly enhanced the fructose conversion to levulinic. At a sulfonated graphene catalyst loading of 0.1 g, 100% fructose was transformed into 28.4% of 5-hydroxymethylfurfural and 17.7% of levulinic acid. The sulfonated graphene oxide catalyst of 0.2 g increased the levulinic acid up to 41.2% with a low yield of 5-hydroxymethylfurfural.

Nevertheless, further increases in the sulfonated graphene oxide catalyst loading exerted only a slight increase in the yield of levulinic acid, 5-hydroxymethylfurfural and formic acid. High acidity content can boost the hydrolysis of 5-hydroxymethylfurfural into levulinic acid (Tawfik and Salem 2012; Jung et al. 2021). Nevertheless, excessive sulfonated graphene oxide catalyst loading would promote not only fructose dehydration into levulinic acid but also the degradation of 5-hydroxymethylfurfural and levulinic acid into other unwanted by-products, like humins (Fachri et al. 2015; Velaga et al. 2019). The optimal ratio of fructose to the catalyst sulfonated graphene oxide was 22.5 g/gram, which provided the highest levulinic acid productivity.

In conclusion, the sulfonated graphene oxide derived from petrochemical waste oil is an environmentally benign catalyst for producing levulinic acid from fructose and other classical biomass derivatives.

Dehydration of xylose into furfural

Furfural is mainly derived from hemicellulose degradation and is used as an intermediate for several industrial applications such as pharmaceuticals and polymers (Xing et al. 2010). Nafion, a sulfonated tetrafluoroethylene, was proven an efficient and reusable catalyst for converting xylose into furfural. Nevertheless, this solid acid catalyst uses organic solvents such as toluene and dimethyl sulfoxide, making it complex for industrial application and difficult to separate furfural. Further, those catalysts lose their activity of acidic sites in water. The need for homogenous acid catalysts is urgently important to avoid corrosive chemicals and neutralization prior to disposal. The development of an economical catalyst enjoying high thermal stability and applicable for xylose dehydration into furfural in water is a novel approach. Moreover, the catalyst should be reusable to reduce potential high costs and capital investment.

Carbonaceous materials have recently become very effective for producing solid acid catalysts due to their high chemical and thermal stability and low production costs (Lu and Love 2005; Zhang et al. 2010). Sugar molecules are carbonized in an acid medium to form sulfonate-functionalized carbon nanoparticles. Sulfonated graphene is a water-stabilized catalyst utilized for ethyl acetate hydrolysis (Ji et al. 2011). Graphene oxide, graphene, sulfonated graphene oxide, and sulfonated graphene were synthesized, prepared, characterized, and examined for the dehydration of xylose into furfural in an aqueous solution (El-Gohary et al. 2009; Lam et al. 2012).

The surface area of graphene oxide (318 m square per gram), sulfonated graphene oxide (680 m square per gram), and sulfonated graphene (634.0 m square per gram) were lower than the theoretical specific surface area of graphene (2600 m square per gram) (Stankovich et al. 2006). Sulfonic acid anchored mobile composition of matter number 41 (mesoporous material) was an effective catalyst for the D-xylose dehydration into furfural (Dias et al. 2005). Furfural is converted into formic acid (Antal et al. 1991).

In summary, the graphene and its derivatives' catalytic performance with reusability for the synthesis of furfural from dehydration of xylose is a novel process. Sulfonated graphene oxide is a robust and reusable catalyst that can be repeated several times for xylose dehydration without losing its high catalytic activity. Sulfonic acid groups and carboxylic acids in sulfonated graphene oxide catalysts are potentially highly active sites for the dehydration of xylose. Sulfonic acid groups are thermally stable and have active acidic sites for producing furfural from xylose in water.

Cleavage of the glycosidic bonds of cellobiose

The catalytic hydrolysis of cellobiose by sulfonated graphene oxide and other acid catalysts was investigated by Wei et al. (2014). The cellobiose conversion and glucose yields were 40.5–37.2%, respectively. The sulfonated graphene could be reused several times without losing its catalytic activity due to its high stability that originates from the stable carbon–sulfur bond between the graphene and the sulfonic group. Further sulfonic groups are too hard to be dissolved in the substrate or removed from the graphene nanosheets.

The graphene oxide and sulfonated graphene oxide catalysts have an unusual theoretical specific surface area of 2630 m square per gram (Dürkop et al. 2004). Most sulfonic groups are uniformly distributed and bound to the external and internal surfaces of the graphene nanosheets. This is due to sufficient graphene nanosheet oxidation and large spaces between their layers. This will allow the reactants to easily enter the internal surface of graphene nanosheets and further facilitate contact with active acid sites. Sulfonated graphene oxide is hydrophobic and has hydrophilic groups (hydroxyl, carboxyl, and epoxy), creating cavities on the graphene nanosheet surface. Amouri and Gargouri (2006) found that the hydroxyl groups on carbon nanomaterials effectively bond with the oxygen atoms through a glycosidic bond within hydrogen bonding to adsorb cellobiose.

Sulfonated graphene contains both hydrophobic graphene sheets and hydrophilic oxygen-rich groups (carboxyl, hydroxyl and sulfonic) that produce an adsorbent site to affinity with reactants. This reaction is divided into the following steps, as shown in Fig. 7. The hydrophobic graphene nanosheets of sulfonated graphene provide hydrophobic cavities to the target reactants on the catalyst surface. The hydrophobic portion of the reactants (the carbon ring of the cellobiose molecule) is eventually attracted by the graphene nanoskeleton, and the hydrophilic portion (hydroxyl and epoxy groups) forms hydrogen bonds with the oxygen-rich groups on the graphene surface. Thus, the reactant concentrations around the acid sites of sulfonic groups are increased (Kitano et al. 2009), and the reactive site can be attached by protons and increase the reaction rate and selectivity. A proton ionized from sulfonic groups easily attacks the glycosidic bond to catalyze the cellobiose. Finally, the glycosidic bond of cellobiose is broken and hydrolyzed. The hydrolyzed by-product is subsequently desorbed on the catalyst surface.

Hydrolysis of microcrystalline cellulose

Cellulose is the main component of lignocellulosic biomass and has thousands of glucose molecules linked by β -1, 4 glycosidic bonds that could be easily depolymerized into

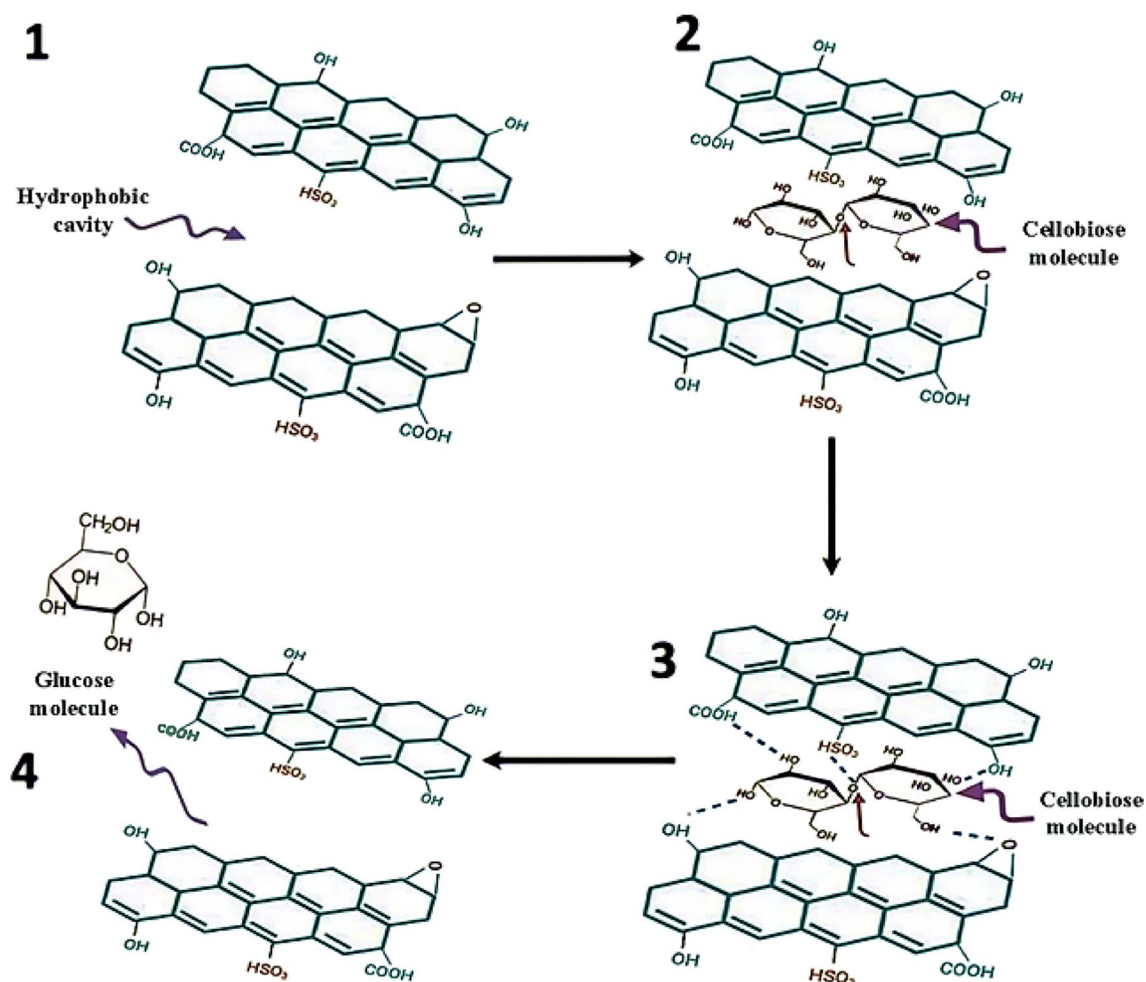


Fig. 7 Mechanism of hydrolysis activity of sulfonated graphene oxide toward cellobiose. The hydrophobic nanosheets of sulfonated graphene oxide provide hydrophobic cavities to the target reactants on the catalyst surface. The hydrophobic portion of the reactants, which is the carbon ring of the cellobiose molecule, is eventually attracted

into the hydrophobic cavity. The hydrophilic portion forms hydrogen bonds with the oxygen-rich groups on the graphene surface as well as the sulfonic group attack and breakdown the glycosidic bond. Glucose is desorbed as a hydrolysis product from the catalyst surface

glucose monomers via catalytic hydrolysis (Lai et al. 2011; Osman et al. 2022). The solid carbonaceous acids could be prepared by hydrothermal carbonization of unwanted biomass as an efficient carbon precursor, followed by surface functionalization of sulfonated acid groups (Ngaosuwan et al. 2016; Shen et al. 2018). Water-dispersible sulfonated graphene oxide is a highly active heterogeneous catalyst for biomass hydrolysis due to its layered structure and abundance of functional groups (hydroxyls, carboxyl, carbonyls, epoxy, and sulfonic).

The nettle-derived sulfonated graphene oxides were successfully used to hydrolyze microcrystalline cellulose in water as a solvent. The nettle-derived sulfonated graphene oxide catalyst has a surface area of 354.9 m square per gram and acidity of 5.47 mmol per gram. The maximum glucose yield was attained at 72.8%, at the nettle-derived sulfonated graphene oxides concentration ratio of 1 g per

gram, with a temperature of 160 °C for a time of 3.0 h (Ton-dro et al. 2021). The microcrystalline cellulose conversion was increased from 8.3 to 42.6% as the temperature range from 130 to 180 °C. The glucose yield was 26.3% at 160 °C at 3 h. This is due to the temperature increase of the contact of β -1, 4-glycosidic bonds of cellulosic chains with the catalyst (Liu et al. 2016). Increasing the temperature by 180 °C resulted in more sugar decomposition into other by-products (Guo et al. 2013).

Glucose dehydration into 5-hydroxymethylfurfural is one of the major by-products of cellulose hydrolysis (Elsayed et al. 2018). 5-hydroxymethylfurfural can rehydrate to produce levulinic, formic acid and humins. The glucose yield was increased from 13.5 to 29.4% as the nettle-derived sulfonated graphene oxide catalyst dose increased from 0.5 to 2.0 g per gram, respectively. The high catalytic activity is related to acidic strength and

available acidic sites required for the microcrystalline cellulose hydrolysis process (Shen et al. 2014; Chen et al. 2019). The highest glucose yield was achieved at the nettle-derived sulfonated graphene oxides to microcrystalline cellulose ratio of 1 g/gram in 0.01 L water. At the nettle-derived sulfonated graphene oxides to microcrystalline cellulose ratio catalyst dose of 0.5 g per gram, the 5-hydroxymethylfurfural productivity was < 1% at 3 h. Increasing the catalyst loading from 1 to 2 g per gram, the 5-hydroxymethylfurfural yield dropped from 4.1 to 3.3% due to the excess of acid active sites, which not only catalyze and dehydration of glucose into 5-hydroxymethylfurfural but also the further 5-hydroxymethylfurfural degradation into other by-products such as levulinic acid, furfural, and humins. Excessive solid acid catalyst provides excess active sites in the reaction medium, which accelerate not only the cellulose hydrolysis into reducing sugars but also the reducing sugars degradation of other by-products.

In conclusion, the optimal required dose of the nettle-derived sulfonated graphene oxides to microcrystalline cellulose for conversion of cellulose into sugars is 1 g per gram, and a temperature of 160 °C, a reaction time of 3 h, resulting in glucose yield and selectivity of 26.3–72.8% respectively. The nettle-derived sulfonated graphene oxides catalyst bears sulfonic, carboxyl, and hydroxyl groups and has a synergy of multilayered structure to facilitate the cleavage of a β -1,4-glycosidic bond of the cellulose into β -1, 4-glucan and glucose (Zhang et al. 2017). The fresh nettle-derived sulfonated graphene oxides to microcrystalline cellulose have a 19.26% sulfonic acid content with a total acidity of 5.47 mmol per gram, which was reduced to 17.10% and 4.63 mmol per gram, respectively, after the fourth reaction cycle at 160 °C for 3.0 h. This implied that the nettle-derived sulfonated graphene

oxides to microcrystalline cellulose are not stable, and further research is needed to stabilize the catalyst.

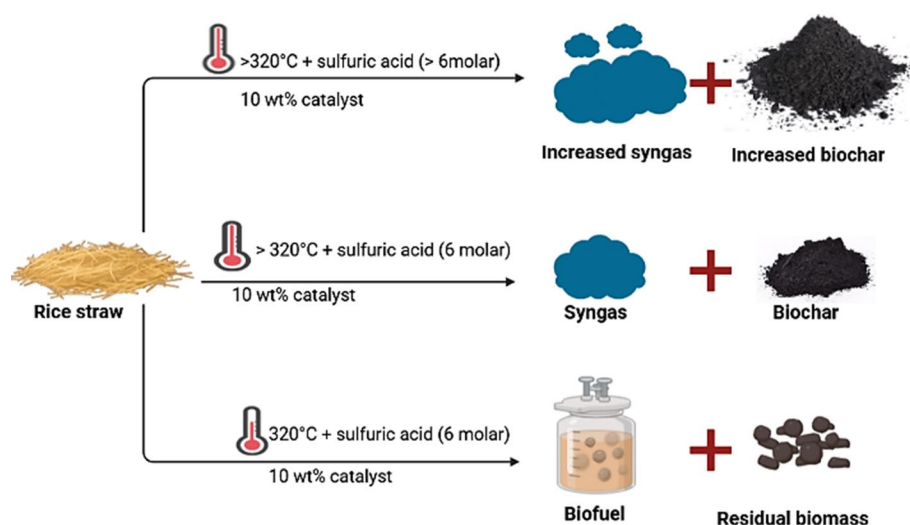
Crude rice straw liquefaction and transformation

Liquefaction of lignocellulosic wastes such as rice straw can be carried out using sulfonated graphene oxide. The latter disintegrates the straw into low molecular levels for further utilization in bioenergy productivity. The acid heterogeneous catalyst (zeolite) promotes the cellulose and hemicellulose disintegration structures of the biomass into biofuel. The available acidic sites of the catalyst are either the Brønsted or Lewis acid types, which are highly responsible for enhancing hydrocarbon productivity instead of ester and ketone molecules.

The alkali heterogeneous catalyst mainly produces ester and ketone molecules, which should be avoided, particularly for bioenergy productivity (Talukdar et al. 2001). The acid sites of the catalyst are further responsible for not only the hydrolysis of cellulosic biomass but also the deamination of the amino acids into fatty acids and glucose. The existence of acidic sites on graphene oxide promotes the cracking reaction of biomass (rice straw) (Browning et al. 2016; Li et al. 2016). The acid sites on the catalyst promote isomerization reactions that transform the biomass composition's straight molecules into branched molecules with a higher tendency to be highly turned into soluble by-products (Soualah et al. 2008; Jörke et al. 2015). However, high catalyst concentration produces unwanted by-products that plug the catalyst sites' pores, negatively affecting the catalytic and biofuel productivity processes. The sulfonated graphene oxide was used for the supercritical liquefaction of rice straw into ethanol (Echaroj et al. 2021).

Graphene oxide was thermally synthesized from humic acid and treated with sulfuric acid using the wet impregnation method. Sulfuric acid exceeded 6.0 molar, causing a

Fig. 8 Rice straw liquefaction by sulfonated graphene oxide catalysts. The supercritical liquefaction of rice straw takes place at 320 °C, with 6.0 molar sulfuric acid and 10 weight % catalyst producing biofuel and biomass, with increasing the temperature. The syngas and biochar are produced from the catalytic conversion of rice straw. The increasing sulfuric acid concentration increases the syngas and biochar yields from rice straw



reduction in biofuel productivity. The biofuel productivity increased dramatically from 3.9% to 24.2% as the catalyst concentration increased from 5 to 10% weight. This is linked to an increase in the number of available active sites for the liquefaction of rice straw. The acidic active sites existed inside the catalytic, causing the breakdown of the lignocellulosic matrix. However, further catalyst increases had no serious effect on biofuel productivity. The formation of other soluble by-products, such as phenols, was gradually increased as the catalyst concentration rose. Moreover, as shown in Fig. 8, the liquefaction reaction for biofuel generation was optimum at a temperature of 320 °C, 6.0 molar sulfuric acid, and 10 weight percent catalyst, resulting in biofuel productivity of 33.4%. The liquefaction of rice straw produced biofuel, biochar, residual biomass, and syngas, which can be calculated as follows,

$$X = \left(\frac{M_f - M_R}{M_f} \right) \times 100 \quad (1)$$

$$\text{Biofuel} = \left(\frac{M_B}{M_f} \right) \times 100 \quad (2)$$

$$\text{Char} = \left(\frac{M_C}{M_f} \right) \times 100 \quad (3)$$

$$\text{Gas} = \left(\frac{M_f - M_B - M_C - M_R}{M_f} \right) \times 100 \quad (4)$$

where X is the percentage conversion of rice straw biomass, M_f is the rice straw weight, M_R is the rice straw remaining weight after the reaction, M_B is the biofuel productivity, and M_C is the char weight.

In conclusion, the sulfonated graphene oxide catalyst can hydrolyze the lignocellulosic portion of the rice straw to produce biofuel, syngas, and biochar. The liquefaction process occurs at 320 °C, with 6.0 molar sulfuric acid and 10 weight percent catalyst. Increasing the temperature and/or the sulfuric acid concentration could increase syngas and biochar production.

Conversion of 5-(hydroxymethyl)-2-furfural

The acid-catalyzed reaction of ethanol with 5-(hydroxymethyl)-2-furfural produces useful by-products of 5-(ethoxymethyl) furfural diethyl acetal, 5-ethoxymethylfurfural, and/or ethyl levulinate. Reduced graphene oxides containing sulfonic acid groups and acid sites of carboxylic acids have superior catalytic efficiency for ethyl levulinate productivity compared to other acid catalysts. This is linked to sulfonic acid content that provides

high-strength acidity. The acidic functionalities are highly bonded to the surface of sulfonated-reduced graphene oxide to increase catalytic reaction stability, allowing sulfonated-reduced graphene oxide's efficient recycling and reuse. Sulfonated reduced graphene oxide (3.0-g catalyst per liter) achieved the highest ethyl levulinate yield of 94% with 100% 5-hydroxymethylfurfural conversion (Antunes et al. 2014). These results are correlated with the acid site quantities in the catalyst.

The partial modification of reduced graphene oxide by sulfuric acid treatment introduces surface sulfonic acid groups, resulting in sulfonated reduced graphene oxide with acid sites of 2.2 mmol per gram (carboxyl, sulfonic and hydroxyl). These functional groups exhibited high catalytic activity for transforming 5-(hydroxymethyl)-2-furfural into 5-(ethoxymethyl) furfural diethyl acetal, 5-ethoxymethylfurfural, and ethyl levulinate in the temperature range of 110–140 °C. Further, sulfonated-reduced graphene oxide with solid acid Amberlyst-15 (4.3 mmol SO_3H per gram) was superior to the modified carbon black and carbon nanotubes for catalytic activities. This could be explained by the unique cooperative effects of the various acid sites and sulfonated reduced graphene oxide two-dimensional structures. The sulfonated reduced graphene oxide acidic surface functionalities are stable and could be reused without losing their catalytic activities.

Conversion of lipids

Biodiesel production using reusable heterogenous acid catalysts is a novel and low-cost approach (Wang et al. 2017; Elsamadony et al. 2021). Sulfonated graphene oxide is a suitable solid acid catalyst for cellulose hydrolysis and chemical reactions (Hara 2010). Solid acid catalysts, namely graphene oxide, sulfonated graphene, sulfonated graphene oxide, and sulfonated active carbon, were used for biodiesel productivity from lipids fractions of wet microalgae (Cheng et al. 2017). The better conversion efficiency of lipids into fatty acid methyl esters was achieved by catalytic oxidation of sulfonated graphene oxide with 84.6% of sulfuric acid. This is mainly due to the higher content of hydrophilic hydroxyl groups in the sulfonated graphene oxide catalyst. The latter achieved higher lipid conversion efficiency by 48.6% compared to sulfonated graphene. However, sulfonated graphene has a higher acidity of 1.69 mmol per gram than that of sulfonated graphene oxide (0.44 mmol per gram). The sulfonic group content was 0.38 mmol per gram in sulfonated graphene oxide, achieving a lipid conversion efficiency of 73.1%. Sulfonated active carbon provided the lowest lipid conversion efficiency.

Cellulose into chemical by-products

Lignocellulosic wastes rich in carbohydrates are abundant in agricultural countries, causing environmental damage (Meier et al. 2020). Direct fermentation of these wastes for bioenergy productivity faces difficulties and challenges (Kumar et al. 2018). This is linked to the structure of lignocellulose wastes, which have five and six polymerized carbon sugars in cellulose and hemicellulose layers embedded in the lignin matrix (Güell et al. 2015). The poor solubility in water and the crystalline structure of lignocellulosic wastes are considered the major obstacles to the slow hydrolysis of glycosidic linkages of the cellulosic chain. The cellulose layer has a partial crystalline shape structure chains containing glucose units with several β -1, 4-glycosidic linkages that are connected by hydrogen bonding (Altaner et al. 2014) (Fig. 9). These cellulosic layers need to be hydrolyzed into sugar monomers (pentoses and hexoses) before the fermentation process, which could be carried out by the destruction of hydrogen bonds (Liu et al. 2016; Osman et al. 2021b).

Sulfonated graphene oxide catalyst is water dispersible and efficient for converting biomass into biofuels (Wei et al. 2014). Sulfonated graphene oxide carries hydrophilic functional groups and offers high chemical activity, high surface area, and thermal stability compared with other solid acid catalysts (Mission and Quitain 2017). The potential application of sulfonated graphene oxide for cellulosic substrate hydrolysis followed by hydrogen fermentative productivity from the harvested hydrolysates using *E. aerogenes* was investigated by Tondro et al. (2020) and is presented in Fig. 9. Graphene oxide sulfonation was carried out using chlorosulfonic acid with an acid density of (4.63 mmol per gram). The glucose yield and total reducing sugars were 454.4 ± 22.20 mg per gram and 682.6 ± 30.67 mg per gram

at operational conditions of 150 °C, 3.0 h, and 250 mg of sulfonated graphene oxide. The maximum hydrogen productivity was 150.0 ± 5.65 ml per gram which was 2.2-fold higher than that obtained from the sample without catalyst addition (67.3 ± 8.84 ml per gram).

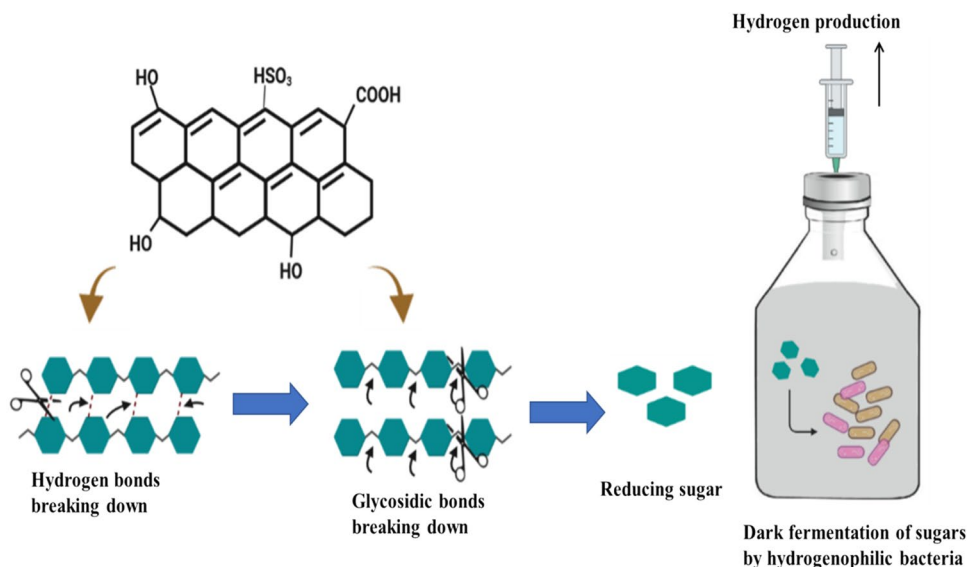
The total reducing sugar productivity from cellulosic materials depends on the probability of collision between the target substrate and the catalyst acid sites (Shuai and Pan 2012; Elsamadony and Tawfik 2018). The solid acid catalytic reaction process occurs via the adsorption of the sugars via the hydrogen bonding interaction between functional groups of sulfonic, carboxyl, and hydroxyl groups of the solid acid catalyst and the oxygen in a β -1, 4-glycosidic (Shen et al. 2018). Furthermore, sulfonated graphene oxide has a high hydrophilicity structure that tends to adsorb the sugars of cellulosic materials via hydrogen bonding.

In summary, the hydrolysis of cellulosic materials by solid acid catalytic reaction performs with great potential, and the resultant hydrolysates are converted by hydrogen producers into useful biofuel. The biohydrogen yield is 153.9 mLg^{-1} with a hydrogen production rate of 7.70 ml per gram per hour from catalytic hydrolysis of cellulosic materials using sulfonated graphene oxide due to the release of the total reducing sugars of 732.0 mg per gram. There is a direct correlation between sugar concentration and hydrogen production.

Economy of oil production from biomass liquefaction

The estimated catalyst cost is a major factor affecting the decision to implement such a catalyst in industrial applications (Tondro et al. 2021). The price of raw materials,

Fig. 9 Conversion route of catalytic oxidation of cellulosic materials into hydrogen energy. Breaking hydrogen bonds and glycosidic bonds resulted in the formation of reducing sugar. Afterwards, hydrogen is produced through the dark fermentation of sugar by hydrogenophilic bacteria. Finally, the biohydrogen produced within the process could be used for multiple purposes



production processes, chemical synthesis route, products and by-product yield, operational cost conditions, disposal, and waste treatment should be considered for economical cost calculations. The graphite price varied from 700 to 1800 dollars per ton in 2019. The overall cost of synthesising graphene oxide from 3.0 g flakes of graphite generates 5.5 g of products, which is estimated to be 4.57 dollars per gram. The total estimated cost for the production of graphene oxide is 4.574 dollars per gram in laboratory preparation, which should be lowered on an industrial scale (Tondro et al. 2021). Reaction temperature of 320 °C, graphene oxide catalyst (10%), and sulfuric concentration of 6.0 mol were used for biofuel production from the liquefaction of rice straw (Echaroj et al. 2021). The heating value of bio-oil was tested by protocol D4809. The bio-oil from the liquefaction of rice straw had a lower and higher heating value than classical gasoline. This is mainly due to the presence of molecules of lighter weight generated from the liquefaction reaction of rice straw. At high temperatures, the liquefaction reaction of rice straw produces cresol and phenol, which reduces the viscosity of the fuel. This indicates that the bio-oil (fuel) from rice straw liquefaction can be efficiently blended with gasoline for transportation services.

Conclusion

Sulfonated graphene (oxide) bears highly abundant functional sulfonic groups of $-\text{SO}_3\text{H}$ that are synthesized by an affordable method. Sulfonated graphene (oxide) is a highly acceptable heterogeneous acid catalyst for the delignification of lignocellulosic wastes compared to traditional minerals and classical solid acid catalysts. The superior sulfonated graphene (oxide) catalytic performance is attributed to the synergistic combination of the water-tolerant, specific structure and the existing highly functional acidic sulfonic groups on its outer surface. These unique features are favorable, particularly the catalyst stability and high mass transfer in the medium reaction. Highly dispersed sulfonated graphene (oxide) sheets were efficient at effectively adsorbing persistent aromatic pollutants from wastewater. Amorphous carbon nanoparticles bearing active sulfonic acid groups undoubtedly exhibit high catalytic efficiency performance for biodiesel productivity via fatty acid esterification and triglyceride transesterification of triglycerides and cellulose hydrolysis. The highly efficient catalytic activity of the carbon material is attributed to the synergetic combination effect of the unique structure and the functional groups. Separable and reusable heterogeneous catalysts are the main superior features compared with homogeneous catalysts. However, the environmentally benign chemical productivity of active heterogeneous catalysts from biomass should be developed in the future, minimizing the synthesis reaction

processes. Discovering more efficient and low-cost production methods of sulfonated graphene oxide is needed, along with improvement of its catalytic stability and acid density.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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