Graphene Aerogel for Wastewater Treatment Applications

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Abstract—Graphene Aerogel (GA) is a novel porous and lightweight material derived from graphene with remarkable properties in various applications, especially in water purification. This review summarizes recent advances in the synthesis, characterization, and wastewater treatment applications of graphene aerogels, including the removal of organic pollutants, desalination, oil-water separation, gas purification, and ion extraction. The challenges and future prospects for GA in this field are also discussed which would provide a comprehensive overview of GA as a promising material for water treatment and inspire further research and innovation.

Keywords—graphene, aerogel, wastewater, water purification

I. INTRODUCTION

Graphene Aerogel (GA), a novel type of porous and lightweight material derived from graphene, which is a single monatomic layer of carbon atoms arranged in a hexagonal lattice [1, 2]. Typically, Three-Dimensional (3D) graphene aerogels are made from Two-Dimensional (2D) graphene sheets, which requires the assembly of 2D graphene sheets into the 3D graphene aerogels with pores and channels [3], which can be achieved by freeze-drying, air drying, and supercritical drying methods [3]. GA has attracted considerable attention in recent years due to its remarkable properties, such as high strength, large surface area, low density, and excellent electrical conductivity [4-6]. These properties make GA a promising candidate for many applications in energy storage, catalysis, degradation, pollutants removal, sensors, supercapacitors, biology, medicine, and other aspects [7–9]. For instance, GA can be used as an electrode material for supercapacitors and batteries with its high specific capacitance and rate capability [10-12]. Wang et al. utilized GA as an absorbent with its pore size, large specific surface area, hydrophilic and hydrophobic properties [13-15]. Due to its high surface area and electrical conductivity, GA attracted extensive research in the application of capacitor deionization system [16–18] and catalyst support for catalysis [19]. Moreover, GA can be used for membrane desalination application due to its high selectivity [9, 20].

However, there are still significant challenges that need to be overcome and further research needs to be done in the synthesis, characteristics, and applications of GA. Applications in different fields of GA have been discussed by a number of authors in literature, this review will focus on the properties and the applications of different categories of GA in water purification, specific applications currently available include: the removal of organic pollutants [21], desalination [9], separation of water and oil, gas purification [22], separation and extraction of certain ions [23]. In general, the wastewater treatment methods can be grouped into traditional methods and novel methods, according to the natural pollutants in the water, the requirements for water quality, and the complexity of treatment and economic factors, etc. Some of the traditional water treatment methods include filtration, sedimentation, and disinfection [24]. Although traditional methods are widely used and well developed, they suffer from high cost and time. Novel water treatment technology summarizes the past experience and uses it to greatly improve the treatment efficiency and shorten the reaction time. Novel methods, include physical methods, chemical methods, biological methods, and electrochemical methods for different applications [25].

In this review, we first describe the preparation of different types of GA from Graphene Oxide (GO) as a common precursor [6]. There are various methods to prepare GA, and the GA prepared by different methods have different properties and application directions. For example, hydrothermal method can produce reduce GO (rGO) with tunable pore size and morphology [15], freeze-drying method can oxidize graphene sheets to produce rGO aerogels with high surface and porosity [3], chemical vapor deposition method can produce carbon nanotube aerogels with high electrical conductivity and mechanical strength [26], and self-assemble method can produce GA with ordered structures and functional properties [3, 6]. Then we summarize the structure, composition, physical and chemical properties of GA with density, surface area, pore size, and electrical conductivity by various techniques [4, 15]. Next, we introduce the influence of referencing other atoms and mixing other inorganics on GA, and compare their advantages and disadvantages. Finally, we explore the currently potential applications of GA in various fields and discuss the challenges and opportunities for future research on GA. Some of the challenges that need to be addressed include control of pore size and thickness [27], homogeneity and stability of graphene flakes [7], functionalization and doping of graphene surfaces, and integration of space-based materials with other materials [28]. These challenges influence the performance and functionality of GA in different applications. Therefore, understanding the structure, synthesis mechanism, porosity of GA, and the properties and relationship between each material is very important for us to study its applications [4, 29].

Numerous studies utilize the conductivity and adsorption properties of GA as an important tool for wastewater treatment, taking different types of aerogels for different pollutants to adsorb or degrade them. GA can oxidize or reduce organic contaminants in water, like removing methylene blue or phenol from water [7, 28]. Due to the simple preparation method, water purification efficiency, low cost, reusable, less pollution, large scalability—can be combined with a variety of inorganic materials to expand into a composite material, GA is considered to be a purification material with great prospects for applications. A series of recent studies have indicated that GA has great potential prospects in many areas [10, 17, 21], we hope this review can inspire new directions and provide comprehensively updated reference for the researchers who are studying in the exploration of GA.

II. WHAT ARE GRAPHENE AEROGELS

GA is a layered porous and ultra-light material derived from graphene, which is a single monatomic layer of carbon atoms arranged in a hexagonal lattice [1]. GA is a synthesized novel nanomaterial with extremely low density, high porosity, and high surface area, forming its outstanding mechanical, electrical, and thermal properties that have potential applications in various fields. Moreover, GA has unique features such as excellent electrical conductivity, high surface-area-to-volume ratio, and sheet-like nanocarbon structures [30].

A. Synthesis Methods of Graphene Aerogels

In most cases, GA is made from GO and rGO as precursor [1]. Researchers first oxidized graphite flakes using sodium nitrate, sulfuric acid and potassium permanganate, then added a small amount of a water-soluble polymer to water to enhance the mechanical strength of the aerogel, and then prepared the GA by reducing the GO to graphene through freezing and heat treatment [30]. There are different preparation methods to synthesize GA, such as hydrothermal method [27] followed by freeze-drying method [31], and self-assemble method [6].

However, in the process of preparing GA, due to the difficulty of controlling the structure of the graphene network, the specific structure of the graphene produced is unpredictable, which limits its potential for development of all aspects [19]. Based on this situation, Zhu et al. proposed a method to solve this problem, using a 3D printing technology called direct ink writing to fabricate GA with microlattice structures (Fig. 1) [19]. They used GO as the ink material and then reduced it to graphene, which can be printed in a variety of structures including tetragonal, cubic, square and diamond. Compared to traditional graphene, 3D printed graphene aerogels can be compressed to ninety percent of their original height and can be reduced to their original state without collapsing during compression like traditional graphene. Moreover, the 3D printed graphene has higher Young's moduli than traditional graphene. Dong et al. found a simple and low-cost way to make highly crystalline graphene from graphite in water without using any chemical additives, which can be easily separated from water and stored, as well as easily re-dispersed into water [32].

B. Types of Graphene Aerogels

Based on the polyfunctional structures of GO and multilayer porous structure of graphene aerogel, it can be hybridized with a variety of organic substances [13], inorganic compounds [33] or metal oxides [7] to form a composite aerogel, which not only retains the unique structure of graphene itself, but also increases the performance of combining the hybrids.



Fig. 1. Preparation of GA with micro-lattice structure by three-dimensional printing using GO as precursor and addition of pyrogenic silica and catalysts. Reproduced from ref [19]. Copyright 2015, Springer Nature.

For example, Li et al. found a scalable and environmentally friendly novel technique that synthesizes an aerogel using Covalent Organic Framework (COF) and Graphene Oxide (GO) as precursors by an effective hydrothermal method (Fig. 2(a)) [1], which has more than 200 times higher absorption capacity than conventional aerogels. COF, which are porous crystalline polymers formed by organic linkers, possess a higher theoretical surface area than that of measured value because of structural limitation, such as dead ends and inaccessible regions, enabling it to exhibit an impressive absorption capacity of 98 to 240 times its own weight for different solvents. By various techniques, including scanning electrons microscopy and nitrogen adsorption-desorption analysis, the synthesis of COF uses polystyrene spheres as templates, resulting in a porous structure with macropores, mesopores, and micropores widely distributed within it (Fig. 2(b)) [1]. Furthermore, Li et al. examined the electrochemical properties of the material, highlighting its excellent electrical conductivity, high specific capacitance (near 270 F/g when its current density is at 0.5 A/g), and outstanding capacitance that can be retained over 95 % after five thousands cycles (Fig. 2(c)) [1] of charge and discharge, which can be used as a raw material for supercapacitors, indicating the potential of the COF/GA composite as a supercapacitor electrode material, thus contributing to advancements in energy storage technologies. COF with low density, good chemical stability, and large surface area can effectively form composites with two-dimensional graphene. The as-prepared aerogel with an equal mass ratio of COF and GO can absorb over 100 times its own weight for various solvents, including silicon oil, toluene, chloroform, etc., due to its large surface area.



Fig. 2. Preparation method and properties of COF/GA. (a) Preparation of GA from COF and GO as precursors. (b) Pore size distribution of frames and hybrid aerogels of GA by the NLDFT method. (c) Relationship between the specific capacitance of COF/rGO and the number of cycles at a current density of 8 A/g. Reproduced from ref [1]. Copyright 2020, Springer Nature.

A number of studies have shown that potassium ferrate can be used as an oxidizing agent to produce graphene oxide in a single layer—a precursor to graphene (Fig. 3(a)) [34]. The method is green and ultralow cost, which can avoid the harmful heavy metals and toxic gasses that are common in other methods, such as KMnO₄, NaNO₃, and Cl₂, at the same time, the method can reuse the sulfuric acid in the process. The obtained graphene oxide powder can be dissolved in water to form liquid crystals and can be further processed into graphene fibers, films and aerogels (Fig. 3(b)) [34]. The process produces a single layer of graphene rapidly in less than an hour compared to other methods, which take several hours or days.

Several studies have shown that hierarchical porous graphene aerogels can be synthesized by creating porous structures on graphene nanosheets using different stencils, such as metal oxide nanoparticles, Polystyrene (PS) spheres, and ice crystals [15]. By various chemical treatment methods, the 3D network of GA will reveal micro-, meso-, and macropore forms.



Fig. 3. Preparation and structural morphology of GO. (a) Potassium ferrate as an oxidizing agent and the process of GO formation. (b) SEM of wet-spun continuous fibres and films made by filtration and their cross sections. Reproduced from ref [34]. Copyright 2015, Springer Nature.

III. RESEARCH BACKGROUND ON GRAPHENE AEROGEL

Water pollution is one of the most serious environmental problems facing mankind today, which not only concerns the survival and development of millions of people around the world but also affects the survival of other organisms and ecosystems in nature. In addition, water pollution is a growing problem and the demand for freshwater is increasing because of natural and human impacts such as climate change, population growth, and industrialization. Therefore, to prevent serious disasters caused by water scarcity in the future, there is an urgent need to develop efficient and sustainable water purification technologies to meet nature's growing demand for clean water [35, 36]. In a variety of water purification technologies, with the increasingly high requirements for water purification, traditional water purification methods such as filtration, precipitation, etc. can no longer meet the needs of the current society, scientists are committed to researching novel water purification technologies suitable for the current development. Such as seawater desalination [17], the use of adsorbents to remove various types of pollutants in water [37], oil-water separation in industrial production [38]. As a result, various water purification materials and technologies based on GA show great potential in removing various types of pollutants in water, such as organic dyes, oils, heavy metals, and other pollutants.

IV. APPLICATIONS OF GRAPHENE AEROGEL FOR WATER PURIFICATION

According to the type, structure and mechanism of action of GA, its water purification type can be classified into four categories: adsorption [39], oil-water separation [40], electrochemical degradation [27] and capacitive deionization [41].

A. Adsorption Capacity of Graphene Aerogels

Due to its high specific surface area and low density, GA can quickly adsorb various types of organic pollutants [12]. The adsorption capacity of GA depends on several factors, such as the pore size, and surface modification of the nanosheets [42]. So based on some previous studies, some important properties of GA adsorption were found. In previous studies, researchers have mostly ignored the influence of nanoscale structural units on the adsorption capacity of graphene aerogels. However, in one study, they are working to study the effects of structural unit-wall thickness and pore size on the adsorption capacity of aerogels [42]. The work explored a novel method that used a freezing-drying process to prepare graphene aerogels with different wall thicknesses and pore sizes, finding that by adjusting the grain size of the ice crystal during the freezing process, the contact area between the graphene sheets and the enhancement of the bonding strength caused by the grain refinement can produce ultra-light, ultra-elastic and high-strength graphene. The wall thickness can significantly influence the graphene adsorption capacities for oil solvents, making the graphene have a super-high adsorption capacity for oil substances. Due to the large surface area and pore volume of the aerogel with more spaces and channels for oil molecules, oil molecules have more space and channels to pass through, which allows aerogels with the thinnest wall thicknesses (about 10 nanometres) to adsorb more than 1,270 times their own weight of oil solvents, much more than other adsorbent materials.

As antibiotics are increasingly polluting the globe, Yao et al. have been urgently looking for a solution to this problem, so a novel organic aerogel was prepared [13]. The organic aerogel is fabricated by a one-step ultrasonication method (Fig. 4(a)-(d)) [13], which involves the dispersion and assembly of cellulose nanofibril and graphene oxide nanosheets in water that are bonded through hydrogen bonds, exhibiting a three-dimensional network microstructure. It has high porosity and large surface area due to its unique structure of three-dimensional network microstructure. This study tested the adsorption properties (Fig. 5(a)) [13] of the hybrid aerogel by removing 21 different antibiotics from water, indicating that the aerogel has a high removal percentage for the antibiotics (Fig. 5(b)) [13], with values exceedingly nearly 70 %. Moreover, the study demonstrated that the aerogel will not degrade significantly in adsorption performance and it can be regenerated and reused for up to ten cycles.



Fig. 4. Process for the preparation of cellulose aerogel and binding method. (a) Schematic of the preparation process of cellulose aerogel. (b) Combination of CNF and GO. (c) and (d) 3D structure of CNF/GO. Reproduced from ref [11]. Copyright 2017, Springer Nature.



Fig. 5. Adsorption capacity and specific process of cellulose aerogels. (a) Adsorption isotherms and pore size distribution curves of cellulose aerogels. (b) Schematic representation of the absorption of antibiotics by cellulose GA. Reproduced from ref [13]. Copyright 2017, Springer Nature.

One study has found that GO nanosheets and starch nanoparticles can be combined to synthesize a composite aerogel (Fig. 6) [12]. The starch nanosheets can enhance the mechanism strength of the aerogel and help itself stay apart and strong to prevent them from clustering together acting as a crosslinker and stabilizer. Various studies have shown that this composite aerogel can be used as a supercapacitor electrode due to its excellent electrochemical properties, as well as its highly porous structure, large specific surface area, and good electrical conductivity. The researcher compared the individual properties of this composite aerogel with those of the conventional RGO aerogel, finding that the specific capacitance of the composite aerogel is 118 F/g higher than that of the RGO aerogel at a current of 1 A/g and has higher cyclic stability and faster adsorption rates. This aerogel does not pollute the environment and can be reused after washing with ethanol or water, making it a promising material for water purification.



Fig. 6. Preparation process and structure of starch/GA. Reproduced from ref [12]. Copyright 2019 American Chemical Society.

Similar to GA, Graphene Hydrogel (GH) also has excellent adsorption properties. Ma et al. applied a green and efficient hydrothermal reduction method to prepare GH by rGO (Fig. 7(a)–(c)) [43]. GH is a porous material that can be used to remove contaminants from water like antibiotics. However, it may cause bad environmental problems to prepare GH that requires harsh chemicals or high temperatures, Ma et al. selected ciprofloxacin, a common antibiotic pollutant, to determine the adsorption properties and capacity of GH. By comparing the adsorption capacity (Fig.7(d) and (e)) [43] of GH and GA to ciprofloxacin, they found that the existence of water is the key that GH granules show better advantages than GA granules for ciprofloxacin removal. GH showed excellent adsorption capacity with near 236 mg/g and a fast adsorption rate with ninety percent removal within thirty minutes. GH has a three-dimensional porous structure with a large surface area and a high moisture content of more than 100 wt% which is prepared by reducing GO in water at 180 °C for 12 h through a simple and low-cost process. The study explored the effects of temperature, pH, ionic strength (Fig. 7(f)) [43], and coexisting substances on the adsorption process by various techniques, finding that the environment has little effect on the adsorption capacity of GH and GH are stable and effective under different environmental conditions.





Fig. 7. Structure of GO, comparison of adsorption capacities of GH and GA, and factors affecting GH. (a), (b) and (c) Morphology of graphite oxide, graphene oxide, and GO hydrogel under TEM. Insert: digital photo of respective substance. (d) and (e) Comparison of the morphology of GH particles and blockages, the equilibrium adsorption isotherms of GH and GA. (f) Adsorption performance of GH as a function of pH and ionic strength curves. Reproduced from ref [43]. Copyright 2015, Springer Nature.

B. Applications of Graphene Aerogel for Oil-Water Separation

With the development and utilization of oil, the problem of global industrial pollution is becoming more and more serious, so it is very necessary to solve this problem. Due to the high porosity, hydrophobicity, and oleophilicity of GA, it can be used as an effective material for oil-water separation. Therefore, GA can effectively separate oil substances and water molecules, selectively adsorb various oils in water and repel water molecules at the same time [44]. GA is considered to be an ultra-light material with the density of 5.0 mg/cm³ and a superhydrophobic material that could repel water completely [14]. Through various techniques, Wang et al. have discovered some outstanding properties of GA. First of all, aerogels have an ultra-low density, making them very lightweight, as well as a large specific surface area, which effectively improve oil-absorbing properties. can Furthermore, aerogels are completely hydrophobic, effectively blocking water droplets from entering the material. Secondly, the aerogel also exhibits super lipophilicity, meaning it has a strong affinity for oil and organic solvents, giving it great potential for oil absorption. Further, the researchers measured the adsorption capacity of the GA and found that each gram of aerogel can adsorb more than 100 grams of organic solvent.

To solve the problem of oil spills, a study found a new stable and recyclable graphene container made of graphene oxide foam that can autonomously and selectively separate and spill oil from seawater [45]. Previous researches have utilized a variety of organic solutions to prepare superhydrophobic and lipophilic elastic GA by the Pickering emulsion method, which can absorb various organic solvents and oils close to 40 times its own weight [5, 46]. Graphene materials for oil-water separation can be made from reduced oxides and polyurethanes into three-dimensional porous GA, which is highly reusable and superhydrophobic [47]; a new type of graphene container can be made from graphene oxide

foam, which is superhydrophobic and lipophilic on the surface, and can autonomously and selectively separate oil from seawater and oil spills [45]; and a single layer of carbon-atomic graphene can be made into a modified three-dimensional spongy GA, which is highly hydrophobic and lipophilic, and can absorb up to 100 times its own weight of a variety of organic solvents and oils [48].

However, conventional GA has low adsorption capacity and single function, to solve this problem, scientists have researched modified aerogel. For example, one study has combined a mixture of graphene oxide and alginate by freeze-drying to prepare a porous lightweight material that repels oil and absorbs water under saline conditions and has excellent mechanical strength [38]. Others have used a simple hydrothermal freeze-casting process to incorporate Enteromorpha, a green alga, into graphene to develop a novel modified aerogel that is compressive, ultralight, and amphiphilic [44]. This technology enhances hydrophobicity and oil absorption and is abundant and biodegradable, leading to efficient oil-water separation. By adjusting the amount of Enteromorpha and the freezing temperature, Ji et al. found the conditions required when the modified aerogel had the strongest adsorption capacity. The results showed that the modified aerogel performed best when the amount of graphene was twice that of Enteromorpha and the freezing temperature was -50 degrees Celsius. This study provides a promising material for efficient oil/water separation, and the unique properties of aerogels make them a potential solution for environmental remediation and wastewater treatment.

C. Degradation Capacity of Graphene Aerogels

The degradation capacity of GA has great potential for pollutant removal, and its adsorption capacity and photocatalytic activity can be significantly enhanced by introducing certain functional groups and heteroatoms [49].

Due to the increase in global water pollution and water scarcity, it affects the ecosystems and millions of organisms living in nature. And the increase in demand and decrease in supply of fresh water, traditional desalination methods are no longer able to meet the demand for fresh water, Seo et al. are working on developing a new desalination method using graphene membranes to solve these problems, which provides high characteristics, low energy consumption, excellent efficiency, fouling resistance, environmental sustainability, and membrane fouling resistance [9]. This methodology was developed by developing a process to synthesize graphene films via a centimeter-scale chemical vapor deposition process (Fig. 8(a)) [9]. The graphene membrane is a sustainable and low-cost source of carbon fabricated from renewable oil with nanochannels formed by overlapping graphene grains in different orientations and sizes (Fig. 8(b)) [9], which allow water vapor to pass through while blocking salt and other contaminants.



Fig. 8. Synthesis of graphene films and morphology of nanoorbitals. (a) Synthesis of graphene using soybean oil and other substances and testing of its desalination properties. (b) Nanomorphology of graphene film particles under TEM. The inset represents a schematic representation of the most representative overlapping domain boundaries. The three small figures below show the graphene morphology with different rotation axes. Reproduced from ref [9]. Copyright 2018, Springer Nature.

Seo et al. demonstrated the characteristics and performances of the graphene membrane such as antifouling capability and effectiveness by various techniques and simulation experiments. By comparing with other commercial distillation membranes (Fig. 9(a)) [9], they found that the graphene membrane has higher water vapor flux and salt rejection rate, and even higher resistance to oil-based substances. They also tested graphene membranes over a long period of time using real seawater (Fig. 9(b)) [9] and concluded that graphene membranes can produce high-quality fresh water, which reduced water vapor flux by only 4 L/m²/h three days. Some studies have demonstrated that organic pollutants can also be removed from water by reducing GO and magnetic nanoparticles using the chemical reaction-Fenton [21] and by preparing a hybrid aerogel by hydrothermal reduction of GO with urea as the nitrogen source [49]. This hybrid aerogel of reference N consists of a three-dimensional interconnected network structure with a high BET surface area close to 500.00 m²/g and a high nitrogen doping content of more than 5.90-7.40 at %. Three nitrogen adsorption configurations were identified by various techniques: graphite, pyridine, and pyrrole. Ren et al. investigated the mechanism of phenol degradation by the hybrid aerogel through a number of experiments and identified the reactive species in the catalytic oxidation process. They also conducted adsorption experiments to evaluate the contribution of adsorption to phenol removal, and the results showed that adsorption significantly improved the catalytic performance of the hybrid aerogel, reducing the phenol degradation time from 30 to 10 minutes. In addition, this work explored the catalytic performance of hybrid aerogels for phenol degradation in aqueous solution and compared different factors such as pH, catalyst dosage, temperature and initial phenol concentration to find the optimal conditions for phenol removal. The optimum conditions were found when the pH was 3, the temperature was 25 °C, the catalyst dosage was 0.1 g/L and the initial phenol concentration was 50 mg/L. The results showed that the catalytic performance of phenol degradation in industrial production solution was satisfactory. This type of hybrid aerogel is mainly used for the removal of phenol pollutants csaused by industrial production [49].



Fig. 9. Comparison of graphene films with other distillation films and a study of their testing. (a) Comparison of water vapor flux and salt removal with commercial distillation membranes. (b) Pictures of field process of taking sample water, comparison of salt rejection and water flux by commercial MD film and graphene film. Reproduced from ref [9]. Copyright 2018, Springer Nature.

Graphene is an excellent adsorbent, which can efficiently desorb ions from their surfaces but difficult to remove ions from its surface. One study developed a new method that adds AI^{3+} (Fig. 10(a)) [23] to displace the adsorbed ions in water [23]. The research also introduced a new process that measures the ion release of different graphene-based materials by using a laser technique. Xia *et al.* compared the new material with other traditional materials and found that it can desorb ions up to one hundred times faster than the traditional materials. This method has a high adsorption capacity for ions and can achieve near 98% adsorption in less than a minute, which is mainly used to enrich 60Co (Fig. 10(b)) [23].



Fig. 10. Ion adsorption resolution of graphene and graphical representation of enrichment of 60Co. (a) Comparison of adsorption properties of graphene for various ions in the presence and absence of Al ions. (b) Schematic representation of graphene enrichment for 60Co. Reproduced from ref [23]. Copyright 2022, Springer Nature.

Organic solvents in the air are very harmful to organisms and cause many health problems and environmental problems. Therefore, some studies have investigated many methods to remove organic solvents from air using adsorption techniques. Among them, the method using aerogels as adsorbents has shown high adsorption capacity and adsorption efficiency in recent years, and revealed its adsorption mechanism. For example, adding α -MnO₂ nanofibers to graphene to adjust the electronic structure of its surface, using water and electricity, and making graphite into GO by hydrothermal and annealing methods (Fig. 11(a)) [27] can decompose ozone efficiently and stably [27]. Zhu et al. have studied the adsorption of different alkali metal cations in the pores of graphene, and the results show that the adsorption capacity is directly proportional to the ionic radii of the metal ions, and is closely related to the pore size is closely related to the pore size. They also investigated the working principle and ozone decomposition performance of the material, and the results showed that the material has stability and high ozone removal efficiency. In addition, they compared this fiber with other catalysts (Fig. 11(b)) [27] and found that it could convert up to 80 % of ozone at a relative humidity of 20 % (Fig. 11(c)) [27]. Electro degradation of GA by immersion in a salt solution produces electrical energy by transporting electrons through the movement of dissolved ions [50].



Fig. 11. GO synthesis process, comparison of fiber aerogels with other catalysts and ozone conversion of fiber aerogels. (a) Schematic representation of the process of GO preparation by hydrothermal and annealing methods. (b) Comparison of the reaction and ozone conversion of cellulose with other types of catalysts. (c) Relationship between ozone conversion and reaction time at different relative humidities. Reproduced from ref [27]. Copyright 2021, Springer Nature.

Catalytic degradation using light is also a new direction of current research, which can enhance the degradation ability of GA, for example, porous aerogels of graphene oxide, titanium dioxide and silver prepared by sol-gel and freeze-drying processes can degrade formaldehyde in the air with high efficiency, stability and reusable properties [33]; hybrid aerogels combining graphene and bismuth phosphate can be purified by hydrothermal and freeze-drying methods for organic pollutants in water, with high adsorption capacity, efficient photocatalytic activity and excellent stability of the hybrid aerogel's performance and structure [31]; synthesized a new composite material by combining titanium dioxide and graphene oxide through solvothermal and calcination processes, which can degrade methylene blue dye in water [28].

D. Capacitor Deionization Properties of Graphene Aerogels

In recent years, scientists have explored a low-consumption, low-cost, and low-pollution desalination technology-Capacitive Desalination (CDI) technology. However, the efficiency and stability of CDI technology largely depend on its electrode materials. Therefore, they have developed a variety of novel aerogels (GA) as capacitor electrodes to improve their deionization capability and to address the impact of freshwater scarcity on human beings. CDI is an electrochemical water treatment technology that uses porous carbon electrodes to remove ions from salt water by adding it with an external electric field, the performance of which depends on the structures and properties of electrode materials, such as surface area, pore size, and electrical conductivity [11]. Graphene can be the optimal material due to its high surface area, tunable pore structure and excellent electrical conductivity. However, graphene is prone to stacking and aggregation during the preparation process, so it has been demonstrated that the reference of nitrogen atoms in it can change the structure of graphene and improve its stability and hydrophilicity. Xu et al. used graphene oxide and urea as precursors to fabricate the nitrogen doped graphene sponge by a simple hydrothermal method (Fig. 12(a)) [11], which has a three-dimensional porous structure with large pores and interconnected networks. The sponge has a high specific surface area of exceeding 550 $m^{2/g}$ and a high nitrogen content of nearly 10.0 %. Then they tested its electrical adsorption performance in NaCl solutions (Fig. 12(b)) [11] with different concentrations, indicating that the graphene sponge has the highest adsorption capacity of 21.0 mg/g in 500 mg/L NaCl solution. Further, a binder-free aerogel can also be made in combination with inorganic compounds and graphene to serve as an electrode for the CDI system to enable the absorption or release of Na⁺ or Cl⁻ ions in the presence of an electric current [17]. The desalination capacity of this system can reach more than 107.0 mg/g far more than other systems compared to conventional systems, and it has excellent cyclability with no loss of desalination capacity after hundreds of cycles. The system has high ion storage capacity and efficient salt removal, which can be used for renewable energy sources. It is also possible to combine 3D graphene and metal oxides to form a new compound as its electrode, combining the advantages of both materials [8]. Sasidharan et al. studied the deionization performance of this hybrid material, comparing different hydrothermal reaction times and the adsorption performance of other materials, and showed that the compound has better performance than other materials suitable for electrodes. The compound has a higher desalination capacity, with the adsorption capacity of the mixture being 1.36 times higher than when the two materials are separated; better stability, with the specific capacitance remaining unchanged after thousands of cycles; and faster desalination, which is four times faster than that of activated carbon. In addition, they explored the mechanisms by which the hybrid materials can improve the performance of the technology, noting that the compounds' large surface area, high electrical conductivity, and the combined effect of graphene and metal oxides are critical. Aerogels synthesized from reduced Graphite Oxide (rGO) and dissolution-like material (RF) precursors heated in an oven can also serve as an excellent electrode [41]. RGO is a chemically modified graphene, the improvement can increase its conductivity and stability. RF is a polymer, a porous network of carbon formed by thermally treating. Wang et al. used various techniques to characterize the structure, morphology, and properties of rGO-RF and compared with other electrode materials-rGO and activated carbon, showing that rGO-RF has higher specific area and pore volume with more storage space for ions, higher electrosorption capacity with excellent salt removal, higher capacitance with efficient ion removal. Furthermore, they investigated the effect of voltage and initial concentration of rGO on electrosorption during CDI processes, which shows that these factors are directly proportional to the electrical adsorption capacity of CDI. Lithium and boron present in brine can also be recycled and used in other ways, for example, a novel hybrid aerogel was developed by combining oxygen-rich vacancy Co compounds on a 3D graphene aerogel through a facile hydrothermal and phosphorization process as a CD electrode, which is characterized by a high specific capacitance, a fast ionic diffusion, and a high adsorption affinity for lithium and boron ions in brine. This hybrid material has high selectivity and efficient recovery performance for lithium and boron [18].



affecting performanc e of CDI, preparation process of nitrogen-ref erenced graphene sponge, and electrosorpt properties

12.

in NaCl solution. (a) Schematic diagram of the preparation process of nitrogen-referenced graphene sponge. (b) Electrosorption properties of nitrogen-referenced graphene sponges in NaCl solutions of different concentrations. Reproduced from ref [11]. Copyright 2015, Springer Nature.

Due to the performance of graphene-based devices depending on the interaction of water and ions with graphitic interfaces, the ion selection in graphene capacitors determines their capacitance performance and has a great impact on their applications in supercapacitors and desalination. A study was conducted on how different types of ions affect the interaction of graphene with water at an applied voltage [20]. Zhan et al. emulate the different voltages, pore sizes, ion concentrations of the ion-graphene system using a molecular dynamics simulation, finding that ion adsorption on graphene is proportional to ion size but also to pore size. Water and ions form layers of different densities and orientations on the graphene surface, thus affecting the electrical potential and charge distribution across the interface. Furthermore, ions can change the capacitance and resistance of the layer by absorbing on the graphene surface or entering the graphene pores (Fig. 13(a)) [20]. The scientists explored that the capacitance of graphene is affected by changes in voltage, pore size (Fig. 13(b)) [20] and ion type. For small pores, larger ions are more adsorbable because of the stabilizing hydration shells formed by their close proximity to the pores; conversely, smaller ions are more absorbable because of the higher number of hydrogen bonds they form with water on the graphene surface (Fig. 13(c) and (d)) [20]. For different ions, there are significant differences in the charge conversion between the ions and the graphene surface, with some ions providing electrons to graphene and others receiving electrons from graphene at different voltages and pore sizes, which affects the capacitance of graphene interface. This research provides new ideas on the molecular mechanisms of cation-graphene interactions, but further exploration is needed to explore the interactions between anions and other types of ions at the interface with graphene.



Fig. 13. Effects of ions on graphene pores, causes and results. (a) Factors and Schematic of the Effect of Ion Size on Graphene. Inset: schematic of charge transfer on graphene electrodes. (b) Reasons and Schematic of the Effect of Ion Size on Graphene. (c) and (d) Effect of voltage, pore size and ion type variation on graphene capacitance, and schematic representation of charge transfer and adsorption sites of graphene for various ions. Reproduced from ref [20]. Copyright 2019, Springer Nature.

V. CONCLUSION

GA has attracted much attention due to its great potential in wastewater treatment, and has a wide range of applications in environmental remediation and wastewater utilization [2, 7, 9]. Due to its high surface area, high electrical conductivity, and high porosity [4-6], GA has excellent adsorption capacity and can remove toxic substances such as organic pollutants [49], heavy metals [34], and antibiotics [13] from wastewater. GA can be synthesized by a variety of methods and hybridized with inorganic compounds [17], metal oxides [31] and organic frameworks [1], which can significantly enhance their properties and stabilize their structure. GA has excellent performance in removing pollutants such as high removal rate, low pollution and reusability [7, 46]. However, to further improve the efficiency of GA wastewater treatment, there are some challenges and difficulties, such as expanding the scale of

industrial production of GA, optimizing the structure and porosity of GA, researching new aerogel with multiple functions, and enhancing the stability and efficiency under harsh conditions. Therefore, this review provides a comprehensive overview and useful reference for researchers interested in developing novel wastewater treatment aspects of GA.

CONFLICT OF INTEREST

The author declare no conflict of interest.

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