INTERFACE SCIENCE AND TECHNOLOGY

Advanced Low-Cost Separation Techniques in Interface Science

Edited by
George Z. Kyzas
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Advanced Low-Cost Separation Techniques in Interface Science

Interface Science and Technology

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Chapter 8

Graphene aerogels for oil absorption

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1. Introduction

As the world becomes more industrialized, new environmental challenges arise as well. Most of the world's energy demands are being met by fossil fuels, which can potentially harm the environment either during their production and processing or through their use. One of the most devastating environmental events that fossil fuels can cause is oil spills. A major incident can possibly release millions of barrels of oil into the environment, in a short amount of time, which can prove catastrophic for the local ecosystem. For that reason special attention is given to oil spill cleanup techniques. One promising way to fight oil spills and restrict their effects is oil absorbers. Such substances can absorb the oil, be recovered, and then be reused. With technology's progress in materials science, new materials are constantly available for such roles. One such material is graphene, which shows many extraordinary properties in itself and for absorption purposes. Its aerogel form provides many advantages that can be exploited as an oil absorber.

1.1 Oil spill pollution

Oil propelled humanity into a new age of prosperity but at an environmental cost, not just from its actual use but also from accidental discharges onto the environment while transporting or producing it (Fig. 8.1).

With over 85 millions of barrels (in 2009 [1,2]) of oil used every day, it is to be expected that some eventually leaks to the environment. These leaks are usually small and can happen both by production and consumption reasons.

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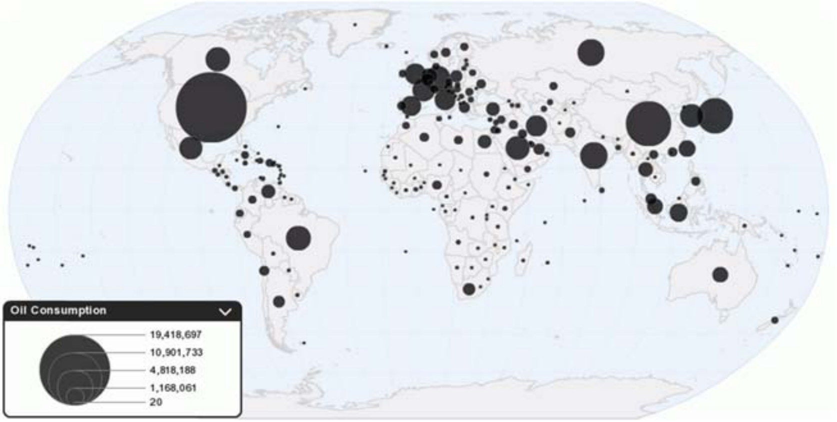

FIGURE 8.1 Daily oil consumption in barrels [1,2].

These small discharges, such as urban run-off, refinery effluents, nautical vessels, etc., along with the larger scale oil spills amount to about 1.2 million tonnes annually. It needs to be mentioned though that an oil spill can measure anywhere from a few barrels to even millions of barrels (Lakeview Gusher, Deepwater Horizon, to name a few) that has a really adverse impact.

While most man-made oil spills are very small, the majority of the oil leakage comes from major incidents. From Fig. 8.2, we can see that 93.7% of

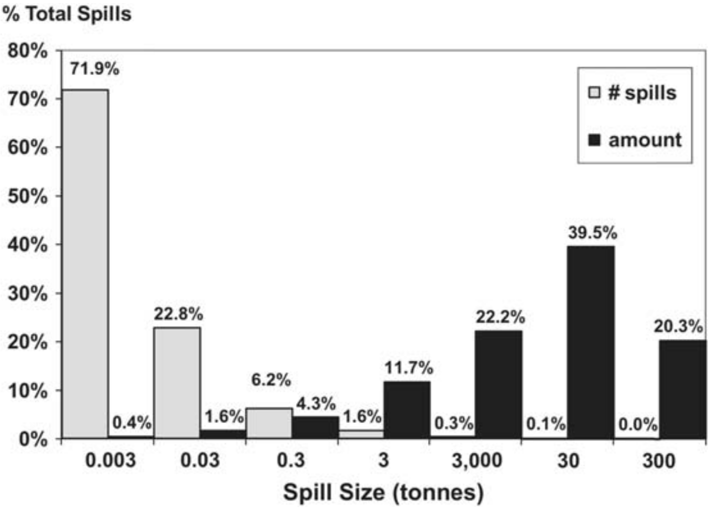

FIGURE 8.2 Size classes of US marine oil spills, 1990–99 (ERC data) [3].

spilled oil came from 0.4% of spill incidents. So it is imperative that these large spills are taken care of, as to impact the environment as little as possible.

1.2 Oil spill response methods

1.2.1 Physical responses

1.2.1.1 Booms

Containment includes the process of confining the oil so that it would not spread or to concentrate in an area so it can be further processed. The main way of containing the oil is via oil booms. A boom is a mechanical barrier, resembling a vertical curtain that extends both under and over water. They can be effective with low waves but as the wave height increases, oil can easily go over the top of the boom. Booms are usually used in a U, V, or J configuration.

Other technique's using booms include the following:

- Diversion (The boom is used to redirect oil from one location or direction of travel to a specific site for recovery.)
- Deflection (The boom is used to redirect oil away from a location to be protected or simply to change the course of the oil slick. The main difference of deflection with diversion is that diversion is not done with the purpose of recovering the oil.)
- Exclusion (The boom is in a fixed position and simply prevents oil from entering an area.) (Fig. 8.3)

1.2.1.2 Skimmers

A skimmer is a machine that removes the oil from the surface of the water. Usually skimmers perform better when the oil is more concentrated and

FIGURE 8.3 Oil boom in V configuration guiding oil to a skimmer [3].

viscous. For that reason, booms are used first to gather the oil. Skimmers are often placed in front of booms or wherever the oil has the most concentration as to remove as much oil as possible.

- A weir skimmer uses gravity to recover the oil from the water surface to a tank under the water. The most simple of these skimmers are made of the weir, the holding tank, and a pipe to some pump to extract the oil. Weir skimmers exist in many builds and models.
- Suction or vacuum skimmers use vacuum to remove oil from the water surface. These skimmers act exactly like an enlarged home vacuum and suck the oil with the addition of a floater to keep them afloat.
- Elevating skimmers make use of conveyors to move oil from the surface to another location. The conveyor belt moves the oil above the water level and into another recovery device or location.
- Submersion skimmers are like elevating skimmers but do the opposite. They have a downward incline and push the oil deeper. The oil is removed from the conveyor by scraping it. After it is removed from the conveyor, it goes up assisted by gravity into a collection well and is then pumped away from there.

Both skimmers and booms could possibly include sorbent materials to modify or enhance their scope (Fig. 8.4).

1.2.1.3 Manual recovery

Manual recovery is the arduous process of using tools such as rakes, shovels, hoses, pumps by people to clean up a beach or some other location from debris

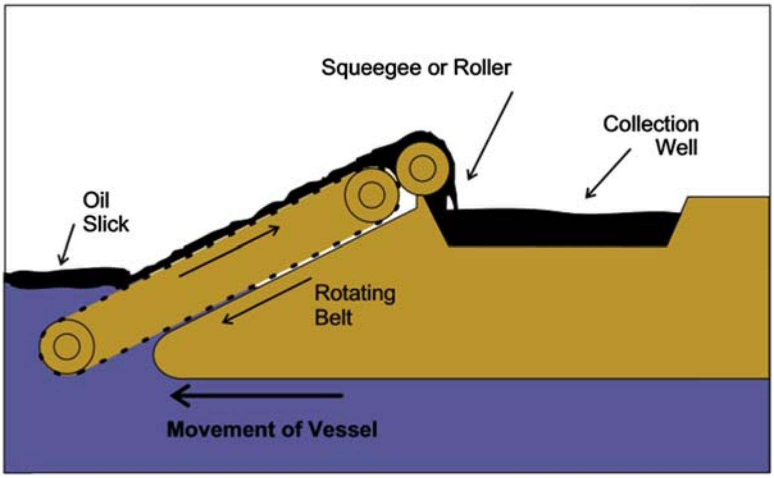

FIGURE 8.4 Elevating skimmer concept [3].

and oil. The collected materials can be sent for further processing. Manually removing the oil is hard and not very efficient but creates less waste that other cleanup methods. Heavier oils are easier to remove than lighter oils. By using this method a lot of water is collected too, requiring more storage capacity.

1.2.2 Chemical responses

1.2.2.1 Dispersants/thickeners

Dispersants are chemicals that include surfactants, emulsifiers, and solvents that cause the oil to form small droplets and help it disperse throughout the water. On the other hand there are thickeners (herding agents) that increase the surface tension between oil and water that prevents the oil spreading or facilitates easier recovery. The use of dispersants/thickeners has caused controversy over their usefulness due to their toxicity and cost [4].

1.2.2.2 Surface washing agents

Surface washing agents act in a different way than dispersants. They act like normal detergents act on stains. Surface washing agents are supposed to be used on contaminated locations to release the oil from their surface. While toxicity has been an issue, there are indeed surface washing agents that present little aquatic toxicity.

1.2.2.3 Bioremediation

The US EPA has defined bioremediation agents as microbiological cultures, enzyme additives, or nutrient additives that significantly increase the rate of biodegradation to mitigate the effects of an oil spill [5]. While bioremediation agents might perform well in laboratory studies, the same cannot be said for field studies [6–9].

1.2.2.4 Emulsion breakers and inhibitors

Emulsion breakers and inhibitors break emulsions and prevent them from forming. Water-in-oil emulsions are problematic because they can triple the volume of material that has to be processed, making storage, and disposing it harder. Water-in-oil emulsions also make it harder for pumps and skimmers to function due to increased viscosity.

1.2.2.5 Recovery enhancers

Recovery enhancers are substances that try to improve the recovery efficiency of other recovery devices such as skimmers by increasing the adhesiveness of the oil. The efficiency for sorbent surface skimmers can be increased 10-fold for nonadhesive materials like diesel. The effect on naturally adhesive substances is highly diminished.

1.2.2.6 Solidifiers

Solidifiers are used to change liquid oil to a solid state that can be easily collected by mechanical means. These are also called gelling or collecting agents. Gelling agents are the opposite of dispersants and are still in an experimental state. These agents contain cross-linkers or polymerization catalysts that cause the oil molecules to be linked together by stronger bonds and thus turning solid. They are usually in the form of powder that when used it is fused with the oil. Depending on the agent, 1/10—1/4 of the oil's mass is required for solidification.

1.2.2.7 Sinking agents

Sinking agents absorb the oil in the water and then sink. These sinking agents are a major environmental concern and most countries do not allow their use. These agents jeopardize aquatic life, and the oil can eventually be released back into the water.

2. Graphene aerogels as oil sorbents

2.1 Sorbents as an oil spill response method

Another physical response to oil spills is sorbents. Sorbents are materials that can recover oil either via adsorption or absorption. Currently, they provide a powerful tool against oil spills and have multiple uses:

- As a response for absorbing the final traces of oil spills
- As an addition to other response means, such as sorbent skimmers and booms for very small spills
- As a primary response for very small incidents
- For passive cleanup

One such example of passive cleanup is exclusion sorbent booms that absorb any remaining oil from the shoreline and stop any more oil from entering the protected site.

There are natural and synthetic sorbents:

- Natural sorbents can be made of organic materials, such as peat moss or wood products, and inorganic materials, such as vermiculite or clay.
- Synthetic sorbents are man-made materials with excellent sorbing capabilities. They are often used to clean other equipment. For cleaning equipment, they mostly come in the form of sheets or rolls.

Sorbents exist in many forms but usually in the form of granules or powder and are contained inside some kind of bag. Some other forms include pads, rolls, blankets, and pillows. A specific type of plastic sorbent be processed into flat strips or "pom-poms" that excel at absorbing heavy oil.

A significant advantage of synthetic sorbents is their potential for reusability. Synthetic sorbents can often become reusable by compressing them and recovering the oil but most sorbents show reduced performance after some cycles, and it could potentially be more expensive to recover the oil than simply using new sorbent. Additionally, sorbent filled with oil is harder to handle and can potentially leak back oil during transportation or processing.

The sorption capacity of a sorbent depends on many properties of the sorbent. One main property is the amount of surface area to which the oil can adhere to as well as the type of surface. A sorbent with complex porous structures and capillaries with high surface area is generally more fit to absorb lighter oils. Sorbents with a coarser surface are best suited for recovering heavier oils. Pom-poms that are used to recover heavy oil are made of flat plastic strips that contain no capillary structure. Another very important property is oleophilicity and hydrophobicity of the sorbent. Some sorbents that are not inherently oleophiles or hydrophobes can be treated with oleophilic and hydrophobic agents to improve the material's absorption capabilities. Natural sorbents are a prime candidate for treatment since they usually absorb large quantities of water along with the oil.

The performance of sorbents is measured in both oil recover and water intake. "Oil recovery" is the weight of the recovered oil compared with the original weight of the sorbent. It is possible for the best synthetic sorbents to potentially absorb many times their own weight in oil. It is important to also have a low water intake, with the best sorbents not absorbing any water.

Sorbents have their disadvantages though and should be used with care. Excessive use of sorbents at an oil spill, especially those that are very fine, can create problems and render skimmers inoperable at the site. Sorbents may cause plugging in pipelines or in pumps. Just like sinking agents, sorbents that sink should not be used and could possibly create similar issues. Many kinds of sorbents have problems with sinking, such as untreated peat moss, some inorganic sorbents, and many wood products. Sorbents that sink in the water are forbidden to use on most countries because both the oil and the sorbent can be harmful to the environment. For that reason, it is important to consider the recovery, transport, and final disposal of the oiled sorbent. The sorbent must be able to retain the oil inside it until the sorbent has been properly disposed (or until the oil is recovered).

Lots of promises are given by new synthetic products that show extraordinary properties that could create impressive sorbents. One such material is graphene.

3. Graphene and its synthesis

Graphene is an allotrope of carbon consisting of a single layer of carbon atoms in a hexagonal lattice, essentially a 2D material. The lateral dimension of graphene can be in nanoscale or macroscale. Graphene is considered to be the thinnest and lightest material yet. It also exhibits fantastic mechanical properties, making it stronger than diamond and 100 times stronger than steel. It even exhibits elasticity up to 20% strain [10].

While graphene was theorized even from 1947 [11], it was not separated from graphite until 2004 [12] for which Geim and Novoselov won the 2010 Nobel Prize in Physics.

These unique properties have led to graphene being used in medicine [13], mechanical design [14], electronics [15], and optics [16].

Smalls quantities of high-quality graphene can be acquired by chemical vapor deposition (CVD) and on Si or on metal substrates [17]. The "Scotch Tape" technique (mechanical exfoliation) [12] and vapor deposition provide a very small amount of graphene, though. For large-scale production, a chemical approach is usually used such as the Hummer's method [18] from which graphene oxide can be acquired [19] and subsequently graphene. The disadvantages of Hummer's method include reactions inducing high temperatures and toxic fumes, for that reason a modified version has arisen [20] which removes the need for $NaNO_3$ (Fig. 8.5).

3.1 Chemical vapor deposition

In general, graphene production via CVD follows a two step process. The first step is the dilution of carbon into the metal, in which the precursor carbon is decomposed to carbon radicals at the metal substrate surface. Gas is fed inside the reactor, and it reacts with the carbon on the surface, resulting in mono or

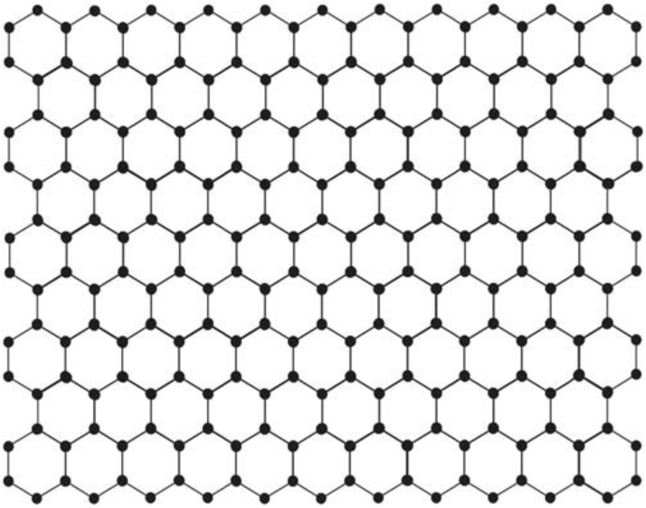

FIGURE 8.5 The honeycomb lattice of graphene [10].

few layers of graphene. The metal substrate acts as a catalyst to lower the energy barrier of the reaction and also determines the graphene deposition mechanism, which in the end affects the final quality of the graphene. Many metal substrates can be used for CVD synthesis of graphene, but Ni and Cu metal substrates are mostly used [21].

3.1.1 Carbon precursors

Many precursors can be used including solids, liquids, and gasses. Hydrocarbon gasses are a popular precursor because of its higher purity as compared with other liquids and solids. Though recently, more studies are being made into liquid precursors. Methane is one of the most common gaseous precursors to grow graphene films.

3.1.2 Graphene synthesis on Ni

First, a polycrystalline Ni film is thermally annealed (900−1000°C) in H_2 in order to increase the grain size. After that an H_2/CH_4 gas mixture is introduced. The methane is decomposed and carbon is dissolved into the Ni film forming a solid solution. The material is then cooled in Ar atmosphere. While the temperature drops, carbon atoms are diffused from the solution and precipitated on the Ni film.

Different cooling rate have a great effect on the quality and thickness of the graphene since it controls the diffusion and precipitation process, with the best results being had with medium cooling rates. Also the crystals of the Ni film seem affect the final product. It is suggested that, the graphene film on the Ni surface is not broken until it reaches some defect on the Ni structure which is on the grain's borders. If the Ni is annealed in H_2 then the grain size is increased and removes some impurities in the Ni film [22].

3.1.3 Graphene synthesis on Cu

In general, Cu foil is first annealed in hydrogen atmosphere at about 1000°C, and then a mixture of H_2/CH_4 mixture is introduced, similarly to Ni. After the graphene creation process is complete, the sample is cooled down.

Graphene grown on polycrystalline Ni exhibits multilayer flakes, while graphene grown on polycrystalline Cu is more uniformly monolayer. For graphene CVD on Ni, it has been suggested that it is a segregation process.

Cu has an extremely low carbon solubility as opposed to Ni, which means that regardless of the H_2/CH_4 concentration or reaction time, there will be a very small amount of carbon dissolved into the Cu since the carbon is originated from the catalytic decomposition of the hydrocarbon gas on the metal film.

As such, it is easier to grow monolayer graphene on low carbon solubility metals, like Cu, as opposed to fast cooled graphene growth on high carbon solubility metals like Ni since it is harder to control the growth of monolayer graphene through fast cooling processes on high-solubility metals, like Ni.

More research is put into graphene CVD, but it is still impossible to create completely uniformly monolayer graphene. It is not known how the metal crystal structure affects the segregation of carbon from the metal to form the graphene film. Also the effect the transition metal has during the connection of two graphene islands is unknown. More problems arise with the fact that graphene CVD requires very high vacuum and temperature conditions making the process more expensive. New studies show that it is possible to do graphene CVD in atmospheric pressure but results in inferior quality graphene. Also the use of valuable transition metals such as Ru, Ir, Pt, and Pd is impractical and those catalysts cannot be reused. Constant recycling of the transition metal is required to reduce the production cost and be more scalable.

3.2 Mechanical exfoliation

The idea of mechanical exfoliation is that the graphene is peeled from graphite one layer at a time. Essentially, the van der Waals forces between the flakes is overcome in a mechanical manner. The two ways to overcome these forces is via applying normal or lateral force. An example of applying normal force is through the Scotch Tape method. Due to the self-lubricating ability of graphene, it is also possible to apply lateral force to peel away layers. Another facet of mechanical exfoliation is the fragmentation of the graphite. While applying force during exfoliation, it is possible to break large graphite and graphene layers to smaller pieces. While this is unwanted for creating large area graphene, it does reduce the height of the layers and smaller graphite particles are easier to process due to smaller van der Waals forces in the smaller particles.

3.2.1 Micromechanical cleavage

With this technique one exerts normal force over the graphite to cause cleavage of layers from the main graphite bulk. Doing this repeatedly for many times, the graphite gets thinner and thinner resulting in graphene. The Scotch Tape method is an example of this. The exfoliation mechanics are dominated by a normal force. Using micromechanical cleavage, it is possible to produce high-quality and large-area graphene at the cost of intense labor and time. Hence, it is limited to producing graphene for research purposes and is not possible to be scaled for mass production.

New techniques involve feeding graphite into an oscillating lathe like diamond edge which can result in nanometers-thick graphene sheets and the usage of a three roll mill that uses Polyvinylchloride (PVC) dissolved in dioctyl phthalate (DOP) as an adhesive. While the three roll mill machine is well used in an industrial setting, the problem of residual PVC and DOP still remains. They need to be completely removed, and this is no easy task.

3.2.2 Sonication

Coleman et al. [23] were the first to achieve production of graphene using exfoliation via sonication in 2008. Graphite powder was dispersed in N,N-dimethylformamide and N-methylpyrrolidone, which was sonicated and centrifuged afterward.

While this method is an easy way to create large amounts of low-cost graphene, it does have disadvantages. When the technique first came out, the concentration of graphene was very low (0.01 mg/mL) which was far from enough for actual use. Researchers have tried to improve the concentration by changing parameters such as the sonication time, the initial graphite concentration, adding surfactants, and polymers, using solvent exchange methods, mixing solvents, etc.

Also, it has been shown that graphene synthesized through sonication is of inferior quality, exhibiting more defects than normal. This is suggested to happen due to the sonication-induced cavitation. Even though cavitations assist the exfoliation process, they can be an intense process resulting in high local temperature, pressure, and rapid heating/cooling rate.

3.2.3 Ball milling

Ball milling is a way to exfoliate graphite using lateral force, as opposed to the Scotch Tape or sonication that mainly use normal force. Ball mills, like the three roll machine, are a common occurrence in industry, for the production of fine particles. During the ball milling process, there are two factors that contribute to the exfoliation. The main factor contributing is the shear force applied by the balls. Using only shear force, one can produce large graphene flakes. The secondary factor is the collisions that occur during milling. Harsh collisions can break these large flakes and can potentially disrupt the crystal structure resulting in a more amorphous mass. So in order to create good-quality, high-area graphene, the collisions have to be minimized.

3.2.4 Fluid dynamics

Using fluid dynamics, exfoliation can be achieved while the graphite is inside a moving fluid. While sonication is an intense process, leading in cavitation, fluid dynamics can be tuned for a milder exfoliation process.

One such example of a milder fluid dynamics exfoliation process is using the vortex fluidic film method. It uses a rapidly revolving tube with the graphite inside a fluid. This method achieves exfoliation in two ways, partial lifting and slippage of the graphite layers on the walls of the tube. Parameters like the speed or orientation of the tube can be manipulated to change the fluidic film. Due to the centrifugal force, graphite flakes will start going toward the wall and because of the fluidic flow will start to get partially lifted. After the partial lift, slippage begins to occur. The graphite flakes are pushed against the tube wall by the centrifugal force and experience a shear-induced displacement along the tube, resulting in exfoliation at the tube surface.

3.3 Reduced graphite oxide

Graphite oxide (GO) is a product of using methods, such as Hummer's, to oxidize graphite. This introduces oxygen-containing groups (epoxide and hydroxyl) to the graphite crystal structure. These oxygen groups interact with the water, making the GO hydrophilic. Due to GO being hydrophilic, water is introduced between the GO sheets and causing them to disperse. It is possible to restore a big part of the graphitic network by thermally annealing or chemically reducing the GO. This method is extremely scalable and cheap. Graphite is very cheap and abundant and can easily create large amounts of reduced GO. As a final note, GO also shows promise as a material for composites.

3.4 Organic synthesis of graphene

While reducing graphene oxide, one can chemically produce micrometer-thick graphene, but there is still need for smaller molecules. While not exactly graphene, "graphene-like" polycyclic aromatic hydrocarbons (PAH) fill that niche by having just the right size between "molecule" and "macromolecule." It is possible to insert aliphatic compounds inside the aromatic structure to tune the solubility of PAHs, but they still have a really limited molecular weight range. Increasing their molecular weight reduces their solubility considerably and increases the occurrence of unwanted side reactions. Hence, tuning solubility and still keeping the wanted planar orientation is still problematic.

4. Graphene aerogels

While the exact definition of a gel might be a bit undecided, all attempts [24–26] usually follow some common ground: A gel comprises a solid and a liquid component, and it exhibits properties of a solid or a semisolid.

According to IUPAC [27], a gel is a nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid. An aerogel is a gel which its fluid component is a gas.

While graphene exhibits some extraordinary properties, it performs below its theoretical performance when inserted into polymers [28–36]. As such, it is hard to fully exploit graphene's capabilities in 3D structures. One structure that shows promise and has received plenty of studies are graphene aerogels (GAs) [37–47]. Aerogels in general show high porosity, extremely low density, low thermal conductivity, low refractive index, and low dielectric constant [48].

GO is used to synthesize GAs due to the reasons explained earlier, such as its scalability, low cost, and properties. GO is often produced by oxidation of graphite flakes or powder using oxidants via a modified Hummers' method [20].

4.1 Graphite oxide synthesis (Hummer's and improved Hummer's)

Graphite flakes/powder and sodium nitrate are stirred into sulfuric acid, while being stirred potassium permanganate is added slowly. An ice bath is used to keep the temperature low. After some time, water is added and the solution is finally treated with hydrogen peroxide to finish the reaction. The color of the resulting solution shows the degree of the oxidation of the graphite, with bright yellow denoting higher oxidation over green and black colors.

In improved methods there are a few modifications, the most major being that no sodium nitrate is used, which produces toxic gases. Also the acid mixture now comprises sulfuric and phosphoric acid.

After the GO is purified (rinsed, centrifuged, etc.) one can proceed in a multitude of ways to the next step, which is creating a graphene hydrogel. Ways of GA synthesis include hydrothermal reduction [45], chemical reduction [43], cross-linking [49–53], and template-directed reduction [54,55].

4.2 Graphene aerogel synthesis methods

These techniques can be used separately, or in tandem, to achieve different results.

4.2.1 Hydrothermal reduction

Hydrothermal reduction is a common way to produce a graphene gel. After the reduction, freeze drying the gel creates a GA. Hydrothermal reduction [56–58] requires high temperature and high pressure, while the solution is sealed. This provides a controllable gel rate and retains the gel integrity. During the hydrothermal process, GO self-assembles to a 3D porous structure due to $\pi-\pi$ stacking and van der Waals forces. On the other hand, $\pi-\pi$ stacking also causes the conjoining of layers which can reduce porosity and absorption capabilities. As such hydrothermal techniques often produce less than perfect graphene, but it still remains a popular choice.

4.2.2 Chemical reduction

This method treats the GO with some reducing agents like vitamin C or sodium ascorbate [59–62] and is considered to be better than hydrothermal reduction, which can require chemical cross-linkers and high temperatures and pressures [63]. Electrochemical reduction of GO is an easy way to create graphene [64,65].

4.2.3 Template-directed reduction

This method is favorable for creating porous GA due to the fact that it reduces the occurrences of random interconnections while also aiding to the creation of controllable and uniform macropores and tailorable microstructures [66]. Another method is ice template−directed method [55] which uses freeze drying. Porous GA in aqueous solutions [67,68] is produced this way, whose porosity can be controlled via the cool rate and temperature.

4.2.4 Cross-link

GO is hydrophilic and forms a stable solution in water [69], but this is not true in acidic solutions due to insufficient mutual repulsion [70]. In general, cross-linking aids the gelling of GO layers by increasing the bond forces between them. Cross-linkers usually used on GO are hydroxyl [55], oxygen-containing, or nitrogen functional groups [70]. Cross-linked GO sheets have uses in other areas too [71].

4.3 Freeze and supercritical drying

After the GO hydrogel has been formed, it is necessary for the water to be removed in order to be modified into an aerogel. This is usually accomplished by freeze drying. In products containing water, direct transition of water from liquid to gas could potentially damage them. While the water is being evaporated, the liquid body pulls against any solid structures the liquid might is in contact with and the surface tension can destroy sensitive structures.

4.3.1 Freeze drying

Freeze drying (sometimes also called lyophilization or cryodesiccation) is a dehydration technique which instead of facilitating high temperatures to evaporate water uses low temperatures to freeze the product. After freezing it, the pressure is lowered and the ice is sublimated into steam, essentially removing the water. By avoiding the use of high temperatures, sensitive products (mainly food or other biological matter) can be safely dehydrated with minimal loss of quality.

4.3.2 Supercritical drying

Some products though are so structurally sensitive that even just the creation of large ice crystals or the process of sublimation could potentially damage or alter their structure. Supercritical drying solves this by going through the supercritical region of the phase diagram. Each substance has a critical point with specific temperature and pressure in which there is no distinct liquid and gas phases. While at the critical point, the substance behaves both as a gas and a liquid, and both the liquid and the gas phase have the same properties. By increasing both the pressure and temperature, the water can go from liquid to gas through the supercritical area.

4.4 Graphene aerogels as oil sorbers

Depending on the production method of the GA, its properties vary and could lead to different applications, from supercapacitors or electrodes to absorbing oil and other organic wastes.

GAs provide an excellent candidate as oil sorbers due to the fact that they can be created to be both highly hydrophobic and highly oleophilic. Along with GA's durability, reusability, and high absorption per weight ratio, they show lots of promise for use as a waste sorber.

There are plenty of recent studies [72–93] showing off GA's excellent properties for oil absorption. These GAs show high absorption rate (~100–250 times their weight depending on substance absorbed and the GA at hand), low density, high porosity, and high reusability with minimal performance loss. It needs to be noted though, that ultralight graphene assemblies have a natural advantage on the absorption rate due to the way it is calculated (i.e., oil weight absorbed/GA weight).

Cheng et al. [72] in 2013 reported a way to prepare a new type of highly hydrophobic and ultralight 3D porous GA with GO as a precursor and melamine formaldehyde microspheres as a spacer and pore forming agent, followed by hydrothermal reduction, freeze drying, and calcination process. It resulted in the creation of a GA that famously won the Guinness World Record for lightest material. Its absorption capacity was 230 times its weight for diesel oil and retained 91% of its absorption capabilities after 10 cycles.

Hong et al. [73] reported creation of functionalized GA with high porosity and hydrophobicity that is prepared by surface modification of self-assembled graphene oxide aerogels. Fluorinated functional groups are introduced into the surface of three-dimensional macroporous GA through a one-step solution immersion method. The functionalized GA shows low density, high porosity, mechanical stability, and hydrophobicity. Its absorption capacity for various types of oils and organic solvents was reported for up to 112 times its weight.

Zhao et al. [74] report graphene/carbon nanotube aerogels that are prepared through hydrothermal reduction, freeze drying, and high temperature heat treatment with the blending of GO and carbon nanotubes. They choose ascorbic acid as a reduction agent to explore the best preparation process. When the carbon nanotube content is 50%, these aerogels show the best performance. Its absorption capacity was reported at 100 times its weight.

Luo et al. [75] report polyurethane sponge-reinforced GAs with low surface energy, high sorption capacity, and excellent recyclability for use as oil sorbents. They used waste sponges from plastic production plants to prepare spongy GAs via precompaction and ice-templated assembly. Its absorption is up to 29–54 times its own mass. They found that this GA has selective and high-volume absorbability (>100%) and can efficiently separate oil from water under continuous pumping action.

Xu et al. [76] report a GA that was prepared by the one-step chemical reduction–induced assembly of graphene oxide with L-phenylalanine as the reducing agent in a simple and scalable process. The resulting GA had an absorption capacity of 100–260 times its weight for organic solvents, mainly depending on the density of the solvent.

Liu et al. [77] report a highly compressible 3D with anisotropic porous structure that is fabricated by directional freezing of graphene hydrogel using anisotropically grown ice crystals as templates followed by freeze drying. This anisotropic GA exhibits high compressibility and can be recycled by burning, distilling, or squeezing. Its absorption capability was shown to be ~150 times its weight for n-heptane and n-hexane.

Xiao et al. [78] report the synthesis of a GO/nanofiber aerogel. Cellulose acetate nanofibers are introduced into the GO suspension and freeze dried. Cellulose acetate was chosen due to its abundance, hydrolytic stability, and eco-compatibility. One of their samples was modified using vapor deposition of hexadecyltrimethoxysilane. While that sample shows extreme absorption capabilities for some organic solvents (up to ~700–800 times its weight), its n-hexane capability is around ~200–240 times which is still impressive.

Huang et al. [79] report a GA that was synthesized via an ethylenediamine-ammonia double hydrothermal reduction approach, with an absorption capacity of up to 130 times its weight for oil. Most importantly though it kept the same absorption capabilities despite the density of oil.

Wang et al. [80] report the synthesis of an ultralight, hydrophobic GA in a very simple process via reducing GO using only ammonia in an autoclave, freeze drying, and finally thermal annealing. While the thermally annealed GA performed better on all absorption tests than the nonannealed sample, it requires very high temperatures (750°C) compared with the 90°C needed for just the autoclave. Their absorption capacity for oils was ~150 times its weight while the annealed sample reached 200–250 times. They found the best way to recycle this particular GA was through squeezing it, instead of burning or distilling it.

Wan et al. [81] studied the effect of the reducing agent, reaction time, and temperature have on the hydrothermal formation of GAs focused on oil absorption. Namely, the reduction agents they tested were vitamin C, ethanediamine, and ammonia (in decreasing reduction potency) at temperatures ranging from 80 to 180°C and reaction times ranging from 4 to 24 h. The samples exhibited different mechanical properties again with vitamin C having the best and ammonia the worst, which is important because they can affect their reusability. On the other hand, absorption capacity was best for ammonia and worst for vitamin C, but again ammonia was the most sensitive to temperature and reaction times. The more intense reduction caused by vitamin C to the GO's oxygen groups seem to make the resulting aerogel's walls more compact.

While not strictly only applicable to oil absorption, Han et al. [82] created a GA via ammonia reduction. They found that the concentration of ammonia solution is crucial since it differentiates the density and volume of the GA. An increase in ammonia concentration corresponds to a volume decrease while the macropore walls of the material become thicker, giving it a larger porosity.

Mi et al. [83] synthesized a highly compressible elastic anisotropic cellulose/GA through a bidirectional freeze drying process. The resulting aerogel was then grafted with long carbon chains via CVD, making it hydrophobic. It displays excellent mechanical properties, which allow up to 85% of the absorbed oil to be removed via compression and with minimal loss of absorption capacity over several cycles. Its absorption capacity for gasoline was 100 times its weight.

Shafiq et al. [84] studied the effects of oil viscosity, agitation speed, and oil—sand wettability on the adsorption efficiency of heavy crude oil from contaminated sand using GA. They contaminated sand with heavy oil and tried adsorbing it using pre-bought GA. It seems to be a two step process, where the oil rapidly adheres to the surface of the GA and then followed by a slower diffusion through the pores of the GA. This effect is more prominent on heavier oils. Increased oil viscosity negatively impacts the process, while agitation speed and oil—sand wettability both have a sweet spot for best results. Their adsorption kinetics study suggests that for spilled heavy viscous oils, the GA should be in smaller pieces to increase its total surface area in contact with crude oil for better adsorption.

Cao et al. [85] created a GA by using polyvinyl alcohol and stearic acid as cross-linking agents to construct a framework of reduced graphene oxide via a hydrothermal reduction process. Its absorption capacity for hexane is 115 times its weight, reaching 100 times after 10 cycles of mechanical compression.

Rahmani et al. [86] reported hydrothermal method using pyrrole as a doping agent to achieve a hydrophobic hydrogel to remove oil from oil/water systems. They also studied the effects of salt and temperature on the adsorption process. Benefiting from the abundant porous architectures, the prepared aerogels exhibited high adsorption capacity. Doping of graphene with heteroatoms such as N, B, S, and P is becoming more commonplace to enhance its properties. It showed excellent absorption capacity at 210 times its weight for crude oil. Due to the high selectivity of the GA, capacity did not change much after adding salt. They tested temperatures of 25, 45, and 65°C and found a very slight decrease in the adsorption capacity with increasing temperature due to the changing density and viscosity of the oil.

Chen et al. [87] created graphene/cysteamine aerogels using cysteamine at various concentrations as a covalent cross-linker under a mild heating process at 90°C and subsequent freeze drying. The GO was partly reduced by the cysteamine. Its absorption capacity was ~150 times its weight for diesel.

Li et al. [88] synthesized a peanut hull/GA, which uses an agricultural waste to create a cheaper alternative for oil absorption in a simple hydrothermal process. Its absorption capacity is 60 times its weight for diesel.

Ren et al. [89] reported on a sulfur and nitrogen codoped GA with an additional GO membrane on it, added via an electrostatic spraying method. Due to its low density and hydrophobicity, the nonsprayed GA can fly up from the water surface with strong winds. This codoped GA has extreme Janus wettability allowing it to remain on the interface despite harsh conditions. It is noted that the hydrophobic mechanism of this GA is due to the changes of surface electrostatic potentials and charge densities due to the codoping into the graphitic structure and the decrease of oxygen-containing functional groups. Its absorption capacity is ~80 times its weight for diesel.

Luo et al. [90] describe a step-by-step in situ biosynthesis process to create a highly porous, robust, and ultralight GA. It involves the self-assembly of 2D few-layered reduced graphene oxide into 3D monolithic bacterial cellulose network. Since bacterial cellulose is produced in very large quantities, this process can potentially be cheaper than pure graphene GAs or other hybrid aerogels. Its absorption capacity is 340 times its weight for diesel and 250 times for gasoline.

Dong et al. [91] created a GA by reducing GO using vitamin C. They heeded special care on specific parameters like the carbon size, GO concentration, GO/vitamin C ratio, and the PH of the solution, with optimal results for pump oil absorption at 500 mesh, 2.5 mg/mL, ≤ 2.5, and natural pH, accordingly.

Ren et al. [92] reported on a GA created using Pluronic P123 copolymer as a template and a novel drying process. P123 has been widely used to prepare mesopore core–shell structures. Both freeze and vacuum drying were attempted resulting in different pore results, with vacuum drying generally resulting in better oil absorption capabilities.

Yang et al. [93] developed a way to create a structurally intact macrostructure of GA about 1 square meter via a surfactant-foaming sol–gel method. They also achieved this using a simple fridge and air drying, further reducing down the cost for energy and special equipment. Essentially, they added a foaming agent to introduce nanobubbles as to obtain uniform large GO crystals using eco-friendly alkyl polyglucoside. This allowed the heterogeneous GO liquid crystals to reform to a more homogenous state, facilitating the creation of a macroscopic assembly with less structural damage. Its absorption capacity for gasoline is 300 times its weight and retains elasticity up to 99% strain. Also this process should be easily scalable for mass production.

5. Conclusions

Ever since graphene's isolation, the scientific community has been interested by graphene's extraordinary properties, and more effort is constantly put forth into graphene and its products. With an ever-increasing need to protect the environment, GAs could potentially provide a feasible alternative way to ameliorate oil spill treatment and restrict damage caused by massive oil spills by sorbing unwanted oil and wastes, after which it is possible to recover both the GA and large portion of the spilled oil. It is important to also notice that the same hydrophobic and oleophilic GAs can also be used for the treatment of organic wastes in general, further increasing their potential.

While GAs exhibit extremely valuable properties for sorbing oil, their use in actual spills still remains to be seen. They possess huge absorbing capacity for oils (up to 300 times their weight) and can be recycled multiple times using compression, distilling, or simply even burning. Most are also very mechanically sound and can withstand many times their weight in force and keep their elasticity for huge amounts of strain (50%−99%). Their problem lies in their expensive synthesis process and general inability to easily scale it to industrial sizes. Important steps for the creation of a GA for oil absorption are (1) creation of GO; (2) reduction of GO; (3) forming of hydrogel; (4) hydrogel drying; (5) thermal annealing. Hummer's method for creating GO has received modifications over the years to make it more eco-friendly and safer by removing $NaNO_3$ and adding phosphoric acid.

The reduction of GO is usually achieved by using ammonia, vitamin C, ethylenediamine, hydrazine, or some other reduction agents and can be assisted by a hydrothermal process. The reduction of the GO's oxygen-containing groups is very important since they are hydrophilic. Higher degrees of reduction generally correspond to better mechanical properties but reduced absorption capacity. It is very important to monitor all aspects of the reduction like agent concentration, temperature, and reaction time. It is possible to use a template to guide the creation of the GA. The template can range anywhere from cheap bacterial cellulose to polymers or nanobubbles. A sufficiently reduced GO should form a hydrogel by itself. Adding cross-linkers or acidizing the mixture will aid the gelation process. Drying the GA is a necessary step and usually requires special equipment to perform freeze or supercritical drying. New techniques are arising, that allow vacuum or air drying. Thermally annealing the GA is optional, but it enhances its properties and requires very high temperatures. In the end, improving any of these steps will improve the whole process. If GA is to be used commercially for oil spills, the economic factor has also to be considered. Every step of the synthesis has to be simplified, and expensive additional materials be avoided as much as possible. It is possible that a simple GA created by reducing GO using ammonia is the best solution instead of more expensive GAs with better properties. It all comes down to the scalability and how easy it would be to produce larger quantities of GA.

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