

# A perspective on graphene based aerogels and their environmental applications

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## ARTICLE INFO

### Keywords:

Aerogels  
Graphene oxide  
Wastewater treatment  
Environmental protection

## ABSTRACT

Various developments are taking place in the field of environmental protection driven by the world today requirements and by the growing attention to the environment. Aerogels systems are for sure one of the most important novelties in the field thanks to their multiple properties and versatility. In this context graphene-based aerogels emerged as innovative devices characterized by large surface area, soft nature, mechanical resistance, responsive and selective behavior. These features have guaranteed them great recognition as sorbent material of contaminants of different nature, as well as smart systems for diagnostic and monitoring. The aim of this review is to focus on graphene-based aerogels fabrication and characteristics together with their unique characteristics in environmental protection, monitoring and safeguarding. In particular strong attention will be devoted on how even small variations on the aerogel formulation used can determine important effects on the real performances of these devices.

## Introduction

With the rapid evolutions of technology and the continuous growth of the demand for daily supplies worldwide, the environment is subjected to huge threats due to different forms of pollutions. In particular, the past two decades witnessed the massive development in both industrial and agricultural sector, graving on the pollution level of water bodies and landfills [1]. The environmental stress is evident in terms of water quantity and quality. Factors like climate change, population growth, rising standards of living and uneven distribution of water are strictly related to competition over water resources, water scarcity, poor waste quality and variability of hydrological events. It was reported that about 300–500 million tons of waste are released into the environment every year [2]. Even if most of the harmful chemical wastes are filtered, the presence of leakages into the environment seems sometimes inevitable, causing serious problems and often wielding significant influences towards the global health; these compounds can be accumulated by the organisms living in the environment and then biomagnified via food chains. The main types of pollutants present in water can be distinguished into inorganic and organic pollutants and examples are nutrients, such as nitrogen or phosphorous components that cause the eutrophication of water bodies threatening the aquatic life, or carcinogenic organic pollutants directly affecting the human health [3]. The

major contributors to this type of pollution are the paper industries, metal-plating industries, mining operations, fertilizers industries, agricultural waste, and dyeing industries [4]. There are different types of pollutants each one with a lot of varieties, such as organic dyes, phenols, biphenyls, pesticides, fertilizers, hydrocarbons, plasticizers, detergents, oils, greases, pharmaceuticals, proteins, carbohydrates, and many others. For example, industrial organic dyes chemicals released in water can absorb sunlight leading to an increase of the temperature or to affect the growth of aquatic bacterial species, disrupting the ecological balance. The organic dyes are even more harmful than other pollutants due to their chemical stability that makes them not easily degradable in water [5]. There are more than 100 000 commercially available dyes, with over  $7 \times 10^5$  tones produced annually. Indeed, they are common compounds used for many different fields, such as textile and food industries.

To avoid such environmental repercussions, efficient water purification methods must be considered. Therefore, many studies on the removal of organic dyes from water were conducted in the last years. More precisely, three major water purifications methods have been developed, including adsorption, precipitation, and filtration. The former is the simpler and more efficient considering the cost of the materials and the operation. Adsorption is based on the accumulation of the target compound on the surface of an adsorbent, generally

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characterized by high surface area due to a porous structure. Among the adsorbent materials, aerogels are emerging exponentially. Aerogels are commonly identified as synthetic materials characterized by low density and high porosity obtained through freeze drying from precursor hydrogel systems [6]. They present soft and stretchable nature, high surface area, low thermal and electrical conductivity and ability to respond to external stimuli depending on the materials of which they are made [7]. They can so serve as a simple, potentially low cost, sustainable and safe technology able to adsorb numerous types of contaminants in wastewater. Among them, in the last years, great interest arose around graphene and graphene oxide-based system thanks to the unique properties of these molecules. Specifically, graphene oxide, an oxidized form of graphene made of a single monomolecular layer with various oxygen functional groups, presents great elasticity and flexibility, great mechanical resistance, adsorbent features, and unique surface properties and represents an ideal candidate for aerogels synthesis [8,9]. Because of this, many different systems of this kind have been designed in recent years for environmental applications and represent the core of this review.

### Aerogels: Common characteristics and synthesis

As said aerogels are porous solid materials obtained from organic, inorganic or hybrid molecular precursors [10], through a sol-gel process and an appropriate drying technology that led to the formation of a three-dimensional structure characterized by a porosity of about 80–99.8 %, high specific surface areas, low bulk density, electric resistivity, and adjustable surface chemistry.

The porous microstructure can be modified by both the sol-gel parameters and the drying process. Moreover, the abundant functional groups such as the  $-OH$ ,  $-NH_2$  and  $COOH$  groups on the surface of sol particles composing the aerogels can modify the aerogels' properties [11]. The first aerogel specimens appeared in the first decades of the twentieth century, and they were firstly introduced by S. Kistler in 1931 [12], when he extracted the solvent from the pores of wet gels using a supercritical drying approach. Its inventor named them as "aerogels" (air + gel) because it replaced the liquid component with the air without damaging the solid microstructure [13]. They were manufactured based on silicon dioxide ( $SiO_2$ ) and their structure is shown in Fig. 1: the system is composed of small spherical  $SiO_2$  clusters 3–4 nm in diameter that are linked to each other and form chains, which in turn form a spatial grid with air-filled pores [14].

Apart from  $SiO_2$ -based aerogel, aerogels are currently produced using other materials including inorganic (such as  $SiO_2$ - derived from various alkoxysilanes,  $TiO_2$ ,  $Al_2O_3$ ,  $ZrO_2$ , etc.), organic (i.e. resorcinol-formaldehyde (RF), polyurethane, polyimide, polystyrene, etc.) and carbon (i.e. carbon, carbon nanotubes, graphene), semiconductor chalcogenide (i.e.  $CdS$ ,  $CdSe$ ,  $PbTe$ ), natural based aerogels (i.e. cellulose and other polysaccharides and various proteins), and more recently  $SiC$ -

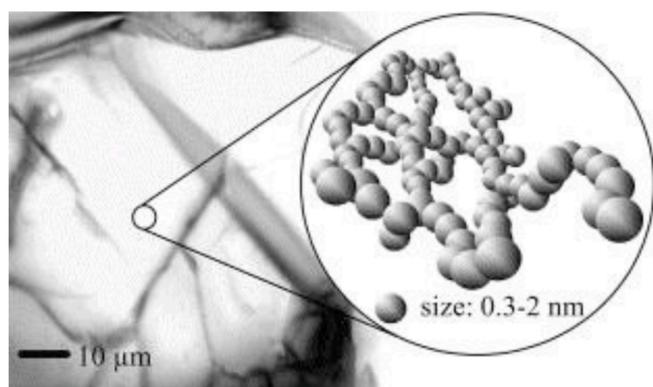


Fig. 1.  $SiO_2$  aerogel's structure, reprinted with permission from [8].

based aerogels [15]. One of the features most widely studied is the low thermal conductivity due to which aerogels have been used in thermal insulation with high performances [16,17].

For instance, silica aerogel is a super thermal insulator characterized by a thermal conductivity lower than  $12 \text{ mWm}^{-1}\text{K}^{-1}$ . Compared with conventional insulators, this lower value is due to the small pore size that could limit the gas phase conduction [18]. Aerogels can also be used in many different fields like heavy metal removal [19], gas absorption [20], radioactive waste confinement [21], drug delivery [22], sensors [23], nuclear particle detection [24], optics [25], electronic devices [26], catalysis [27], and surface coatings [28] (self-cleaning coatings, chemical resistant coating, etc.). Together with high advantages, these materials also present some disadvantages, such as fragility, rigidity, dust formation, bulkiness, which still limit their applications on a large scale and necessity other research efforts before they reach the market [28].

### Aerogels classification

The microstructure and the surface groups of aerogels are extremely important for the potential applications of these materials. Consequently, it is vital to select a right condition to model the properties necessary to meet the target application requirements. The critical synthetic steps in aerogel preparation are essentially three: sol-gel process, aging and drying [15,28]. Aerogels can be classified according to different basis [29].

#### Drying process

According to this classification, aerogels can be distinguished into real aerogels, obtained by supercritical drying, xerogels, obtained by ambient pressure drying, and cryogels, obtained by freeze drying.

#### Polarity and surface functionality

They may be hydrophilic, hydrophobic, amphiphilic, oleophilic or oleophobic.

#### Type of precursor

They are classified into organic, inorganic or hybrid. The former consists of carbon-based organic materials such as cellulose, biochar, graphene, polymers and chitosan.

The inorganic aerogels are composed by transition metal oxides and metals, i.e. silica and aluminum, gold, silver, copper, titanium, zinc, nickel, cobalt, etc [30]. Metal-based aerogels [31,32] are of fundamental importance for their excellent electrical conduction properties.

They have received intense attention in recent years due to their higher surface area and ultralow densities. In an experimental study, Qian et al. reported the synthesis of ultralight gold aerogel monoliths with tunable pore densities and structures [33]. The last category is the one of hybrid aerogels that are prepared by the combination of organic and inorganic materials, showing the properties of both types.

A schematic representation of the classification of the aerogels is reported in Fig. 2.

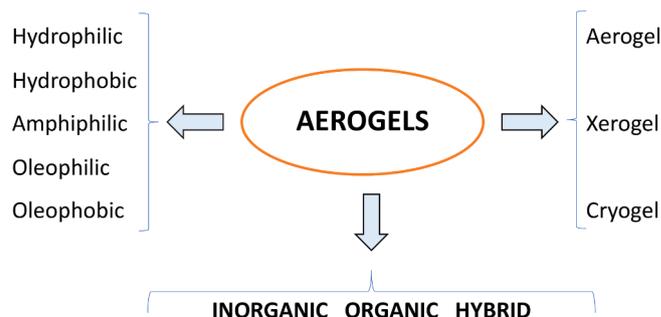


Fig. 2. Schematic representation of the classification of the aerogels.

## Common examples of aerogels formulations

### Silica-based aerogels

As previously mentioned, silica-based aerogels (SBA) were the first inorganic aerogels synthesized by Kistler in 1931 [34]. SBA are characterized by unique features, e.g., high porosity (80–99.8 %), specific surface area (500–1200 m<sup>2</sup>/g), low density (about 0.003–0.5 g/cm<sup>3</sup>) and thermal conductivity (0.005–0.1 W/mK) as well as ultra-low dielectric constant ( $k = 1.0$ – $2.0$ ) and low index of refraction (about 1.05) [18].

Up to now, the synthesis of SBA has been accomplished mainly through the sol–gel method with the controlled condensation of small colloidal particles in an alcohol aqueous solution, followed by a supercritical drying process. As reported, the most widely used precursors in the preparation of SBA are silicon alkoxides that can be acquired with high purity specification. They possess numerous important properties for a wide range of applications in various fields. The small size and the surface interface of these materials provide unique optical properties that can be changed by adding other organic compounds and inorganic metals [35,36]. Thanks to the nanoporous network structure, the heat conduction is reduced, so they are widely used as adiabatic materials [37]. Material having good thermal insulation properties can be made from a mixture of a silica aerogel and a ceramic fiber material or an opacifier. Alumina can be added to those mixtures, e.g. in the form of alumina particles or alumina fibers [38]. Wang et al. have incorporated alumina-silica ceramic fibers (Al<sub>2</sub>O<sub>3</sub>: 43–45 %; SiO<sub>2</sub>: 49–52 %; Fe<sub>2</sub>O<sub>3</sub>: 0.5–0.8 %) and TiO<sub>2</sub> particles (30 % TiO<sub>2</sub> + 3 wt% ceramic fibers) in the silica aerogel matrix, and the resulting material reached a thermal conductivity of 38 mWm<sup>-1</sup>K<sup>-1</sup> at 800 K, while that value for a conventional insulating material, such as an alumina-fused brick, is around 100 mWm<sup>-1</sup>K<sup>-1</sup> [39]. Moreover, the low dielectric constant makes silica aerogels excellent dielectrics in supercapacitors [40]. On the other hand, the structure of silica aerogels composed by cross-linking nanoparticles and weak connections is rigid and brittle, and their mechanical strength still is not adequate for them to resist and remain monolithic in some practical applications. Since their birth, researchers have studied to improve their mechanical properties. With diversified properties and functionalities, the precursors for preparing SBA, such as tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), polyethoxydisiloxane (PEDS), methyltriethoxysilane (MTES), methyltrimethoxysilane (MTMS) and their mixtures, have been extensively investigated by various research team [41]. The hybridization of silica aerogels has been presented as a possible solution for strengthening purposes, by promoting the co-gelation of the silicon alkoxide with hybrid precursors such as poly(dimethylsiloxane) (PDMS).

Gels obtained in this way are termed “ORMOSIL” (ORganically MODified SILica) hybrids. This method leads to a dramatic increase of tensile strength and robustness of the aerogels. Moreover, incorporation of various fibrous supporting materials, such as polymeric fibers, carbon nanofibers, and fiberglass, into the aerogel systems, was also found to be quite effective in improving the mechanical properties of aerogels [42].

### Carbon aerogels

Carbon aerogels (CAs) are another class of material that is considered very attractive especially for high-temperature insulation applications in non-oxidizing atmospheres or vacuum [43,44]. They have received widespread attention since they were firstly obtained due to their fascinating properties including an open, porous, solid structure consisting of three-dimensional network of the spherical, interconnected primary particles, high electrical conductivity, good chemical stability, and environmental compatibility. The number of publications related to them has increased exponentially in the last period since they represent an important option able to sufficiently meet most of the high-performance applications requirements [45]. They are generally obtained by carbonization through a four-step procedure, composed by (1) preparation of the sol mixture and further gelling, (2) curing of the gel,

(3) drying of the wet gel, (4) carbonizing of the dried gel and further activation [28]. As previously mentioned, also in this case, by varying the synthesis condition it is possible to regulate and control the average pore diameter and the particle size in the range of several micrometers, making the CAs suitable for thermal insulation applications, especially at high temperatures [44], and for catalysis and electrodes in supercapacitors [46]. They have been involved in many other fields of application, such as biosensors [47,48], hydrogen storage [49], and adsorption. Many researchers are focusing their attention on the development of carbon aerogel (CA) electrodes for biosensors, due to their important properties such as the electric double layer performance, the porous structures, the high surface area, and transportation channels for electrolyte ions.

The electrical and chemical performance can be enhanced by modifying these CA electrodes can be modified with different nanoparticles (e.g. Ni, Pd, Ag<sub>2</sub>S, CuS, CdSe, WO<sub>3</sub>, Au, PtNi, NiCo<sub>2</sub>S<sub>4</sub>).

Silver sulfide (Ag<sub>2</sub>S) is an important nontoxic semiconductor recognized for its optical and electrical properties. Martinez et al. [50] proved that the Ag<sub>2</sub>S nanoparticles (NPs) on carbon aerogel increase the absorption of visible and near-infrared light, improve electric conductivity and REDOX reactions reversibility. Ag<sub>2</sub>S -CA electrodes were analyzed by SEM, XRD. The NPs size and size distribution are parameters that must be considered when a working electrode is designed because when these parameters are modified, their optical and electric properties can be enhanced. The average of the size of Ag<sub>2</sub>S -CA NPs obtained was in the range of 8.65 nm to 21.35 nm. Since there is less silver available for the sulfur-silver reaction, it has been found that NPs size decreases as silver deposition time decreases. The sulfidation temperature and time are also important parameters in controlling the dimensions through the nucleation and the growth process.

### Graphene-based aerogels

Graphene is a material at the center of intense research since its discovery due to its excellent electrical, thermal, and mechanical properties [51]. Graphene is characterized by a single-layer structure, leading to a structure in which all atoms are surface atoms. The available surface area of graphene is higher than that of carbon nanotubes and the adsorption kinetics is generally faster than on the traditional adsorbents. Properties such as its high strength/strain-to-failure, high surface area and chemical stability have attracted more and more attention, leading to the synthesis of graphene-based aerogels (GBAs) [52]. From many studies, it is not difficult to find that GBAs extensively improve the physical and chemical properties, such as excellent dielectric properties, high specific surface area, and high adsorption efficiency of aerogels [53]. Also, graphene aerogels can become lighter than air, and this is the reason why graphene has been proposed as a substitute for the relatively rare and expensive helium [54].

Often, however, when graphene is used to produce composite materials, their properties are lower than theoretical predictions. This is related to poor dispersion of graphene in the polymeric matrices and the resulting agglomeration due to  $\pi$ - $\pi$  stacking interactions between graphene sheets [55].

For this reason, to fully exploit the properties of graphene certain methodologies must be used to convert the 2D material to 3D structures. Generally, graphene oxide (GO) is the appropriate precursor to prepare 3D graphene assemblies due to its high dispersion in aqueous media and its functionality. Also, GO is very useful as starting material in synthesizing GBAs, because the oxygen atoms present can react covalently with different compounds and thus yield new materials with properties that can be tailored to specific applications. Among these compounds, biopolymers can be immobilized covalently onto GO sheets and that enhances their biocompatibility without affecting their overall performance. It has been shown that GO can be reduced to graphene via a hydrothermal process or by appropriate reducing agents yielding (by self-assembly) a 3D structure with pore sizes in the sub-micron to micron range. This assembly is achieved through careful modulation of the

hydrophobic/hydrophilic balances in the GO solution through either non-covalent or covalent interactions [56].

### Production and general features of graphene-based aerogels

GO-based aerogels are the most common three-dimensional graphene structure synthesized because of their facile synthetic route and the control of pore morphology that they provide. As previously mentioned, GO has a lot of hydrophobic basal plane and hydrophilic oxygen-containing groups, like hydroxyl, epoxy, carbonyl and carboxyl groups, that facilitate GO to be functionalized through covalent and non-covalent bonding and facilitate the possibility to have self-assembly of the graphene sheets. The most used routes for producing GBAs are divided in four categories: hydrothermal reduction, chemical reduction, cross-linking and template reduction methods.

#### Hydrothermal reduction

This method is also known as the self-assembly method under high temperature and pressure, and it is essentially composed by two steps: the preparation of the graphene oxide and the synthesis of the reduced graphene oxide aerogel. GO can be prepared using the modified Hummers' method [57], in which natural flake graphite powder and  $\text{NaNO}_3$  are added to  $\text{H}_2\text{SO}_4$  under stirring, while the temperature is kept at  $0^\circ\text{C}$  using an ice bath.  $\text{KMnO}_4$  is slowly added under the same conditions. The flask was subsequently maintained at  $35^\circ\text{C}$  under stirring. The solution is subsequently diluted with distilled water to avoid excessive stirring, and the reaction was finally completed by adding 30 %  $\text{H}_2\text{O}_2$  until the gas evolution stopped. Repetitive washing of the solution with distilled water are performed until the solution has become neutral. The acquired solid GO can be recovered under vacuum and dried. Following the work of Garcia-Bordejé et al. [58], to carry out the hydrothermal treatment, a GO aqueous dispersion is introduced into a Teflon lined autoclave at  $180^\circ\text{C}$ , where it remains for a certain time. After the hydrothermal reaction begins, the graphene oxide gradually becomes hydrophobic. With the process of transforming graphene oxide from hydrophilic to hydrophobic, weakening the hydrogen bonds in the water. The partially reduced GO nanoplatelets aggregate, resulting in a phase separation to form the hydrogel that takes the shape of the container vessel. By subsequent freeze-drying of the hydrogel, the aerogel has been obtained. The standard GO concentration employed in this work was 2 mg/mL. Different experiments were performed using also 1 mg/mL GO and it has been found that gelation did not lead to a single monolithic hydrogel but to numerous small agglomerates. Therefore, a limiting minimum concentration, between 1 and 2 mg/mL, was necessary to form a single monolithic hydrogel. The reason behind this could be that at enough high concentrations, the sheets are attracted to each other by the Van der Waals forces, forming a three-dimensional porous structure.

#### Chemical reduction

As the hydrothermal method, the chemical reduction method is still based on the self-assembly of graphene and graphene oxide, but it uses mild reduction agents like hydrazine, vitamin C and sodium ascorbate. For this reason, it is suitable for large scale production. Xu's team firstly prepared superhydrophobic pure graphene aerogel by simple chemical reduction of graphene oxide dispersion. They synthesized GO by improved Hummer method [59]. Then, they chemically reduced GO with L-phenylalanine and induced GO self-assembly to form a mixture. They treated the mixture by ultrasonic treatment, oil bath soaking and freeze drying to obtain graphene aerogel [53]. The process of chemical reduction of graphene-based materials often leads to a small surface area since the graphene layers restack through a  $\pi$ - $\pi$  interaction during the process.

#### Cross-linking method

Another synthetic strategy involves the use of chemical cross-linkers to promote gelation of GO sheets by strengthening the bonding force between the sheets. As previously mentioned, the formation of a three-dimensional network derives from the large and flexible two-dimensional structure of GO sheets and the force balance between their static repulsion and bonding interaction. The GO network can be reinforced, inducing GO gelation and precipitation, by increasing the bonding or decreasing the repulsion force between the sheets. This can be tuned by adding cross-linkers. Common cross-linkers are hydroxyl, oxygen-containing, or nitrogen functional groups. It has been found that the self-assembly and gelation of GO sheets are promoted also by divalent and trivalent ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ , as shown by Hua Bai et al. [60]. The picture in Fig. 3 reports the GO dispersions after adding different metal ions. Monovalent ions (e.g.,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ) cannot induce GO gelation, while divalent and trivalent ions (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ) can promote the formation of GO hydrogels.

Because the pH value of GO solution is affected by the presence of the metal ions, their coordination with hydroxyl and carboxyl groups on GO sheets is considered the main driving force able to lead to the assembly of GO sheets. Multivalence transition-metal ions usually have larger coordination stability constants than those of alkali metal and alkaline-earth metal ions. Thus, the former ions also have stronger cross-linking abilities. To prove the role of metal ions as cross-linkers in the hydrogels, a chelating agent, ethylene diamine tetraacetic acid (EDTA), was added into the GO/metal hydrogel to remove them. After the addition of EDTA, the hydrogels decomposed quickly. This phenomenon also confirmed that GO sheets contact with each other in their concentrated solution and small metal ions can interact with individual GO sheets to form 3D networks.

#### Template-directed reduction

Template-directed reduction is a useful method for obtaining porous GBAs because it reduces the random interconnections, favoring the formation of controllable and tunable micropores and adjustable structure. An example can be found in the work of Chen et al [61]. The GO hydrosol was mixed with a PMMA spheres suspension.

Subsequent vacuum filtration was then conducted to realize the sandwich type assembly of PMMA spheres and GO sheets. A composite film was removed from the filter, air dried and calcinated to remove the PMMA template and thermally reduce GO into graphene simultaneously. From the thermogravimetric results, it was found that the oxygen-containing functional groups of GO are removed at  $230^\circ\text{C}$ , while the PMMA spheres are pyrolyzed and removed at  $400^\circ\text{C}$ . Graphene was finally derived with the PMMA spheres acting as the interlayer spacer. A similar method is ice template-directed method that takes advantage of



Fig. 3. Photographs of 5 mg/mL GO solutions mixed with different metal ions: 1, 20 mM  $\text{Li}^+$ ; 2, 20 mM  $\text{K}^+$ ; 3, 20 mM  $\text{Ag}^+$ ; 4, 15 mM  $\text{Mg}^{2+}$ ; 5, 9 mM  $\text{Ca}^{2+}$ ; 6, 3 mM  $\text{Cu}^{2+}$ ; 7, 3 mM  $\text{Pb}^{2+}$ ; 8, 3 mM  $\text{Cr}^{3+}$ ; 9, 3 mM  $\text{Fe}^{3+}$ . Reprinted with permission from: [60].

the freeze-drying approach. Luis Estevez et al reported the synthesis of multifunctional hybrids in both films and bulk form. [62] The hybrids are synthesized by a two-step process composed by the ice templation of an aqueous suspension of Nafion, graphite oxide, and chloroplatinic acid to form a microcellular porous network and the mild reduction in hydrazine or monosodium citrate which leads to graphene-supported Pt nanoparticles on a Nafion scaffold. Other templates methods are the chemical vapor deposition (CVD) and the stencil sintering. CVD method is based on lamellar stacking, that allows the formation of an aerogel characterized by less interface and higher electrical conductivity with respect to the other methods.

However, the construction of 3D GBAs by CVD technology still faces many challenges in mass production: CVD on large scale produce defects such as grain boundaries and lamination. While the GBAs prepared by stencil sintering are characterized by unique mechanical properties and functions. They are prevalently applied in the fields of supercapacitors and energy storage [63,64]. To conclude, a recent progress on GBAs synthesis is represented by the 3D printing-freeze drying, that is a revolutionary manufacturing process that has great potential for example in the field biological bone repair. The wet gel after printing is directly subjected to freeze-drying or hydrothermal treatment, obtaining an elastic aerogel that can withstand high temperature. The problem of the 3D printing of GBAs is associated to the difficulty in the use of graphene ink, and in the necessity to adjust its viscosity, one possible strategy is to cross-link GO with  $\text{Ca}^{2+}$  ions, forming a colloidal ink that can be used for printing [65].

In the Fig. 4 a schematic illustration of 3D printing process is reported:  $\text{CaCl}_2$  is added to the GO solution, that is extruded through a robot-assisted nozzle to construct a 3D structure. The product is then freeze dried to obtain the solid GO aerogel and further reduced by HI to get neat graphene-printed aerogel microlattice.

#### Environmental applications of graphene-based aerogels

Over the past few decades, the exploitation of the planet and the

environment have increased very fast [66], and the need to try to slow down and avoid the pollution of the environment, have led to develop technologies able detect, adsorb, and reduce environmental pollutants. Examples include water treatment, air cleaning and sound absorption. As previously mentioned, graphene adsorbents have attracted great interest recently due to the fantastic properties and potentiality to be used for environmental applications [67]. For instance, among the graphene adsorbents, graphene oxide (GO) shows the highest performance in treating heavy metal ions and cationic dyes. However, the problem of the pure GO is related to the fact that its separation after adsorbing pollutants is very difficult.

Indeed, GO disperses very well in water, and this requires high speed centrifugation to precipitate, limiting the applicability: the high-speed centrifugation is unpractical for water treatment, due to the large quantity of wastewater involved. The fact that GO can loss the surface area during the drying is another drawback of GO adsorbents. The reduced surface area leads to the decrease of adsorption capacity. For this reason, the most promising forms thank to which all the properties of GO can be efficiently explored are hydrogel and aerogel, that are not dispersible in water, thus they could be separated easily by filtration or low speed centrifugation. As explained above, the GBAs can be produced by different methods that leads to final materials with enhanced properties such as high electrical conductivity, high mechanical strength, thermal stability and high adsorption capacity for dyes, oils, organic solvents, and inorganic ions. Thus, the GBAs can be exploited in a whole range of applications, and they have become increasingly employed especially for environmental pollution control and monitoring, such as water treatment [68] and pollution degradation [69,70]. The other advantage that makes GBA so interesting in environmental applications is the reusability and the recyclability of these materials [71,72]. In the work of Ren et al. [73] a robust reduced graphene-based aerogel (rGBA) was synthesized and used as an efficient and recyclable sorbent for oils and organic solvents: it shows highly efficient absorption of various oils and organic solvents (up to 19–26 times of its own weight) and excellent recyclability (>5 times) by heat treatment, maintaining a stable

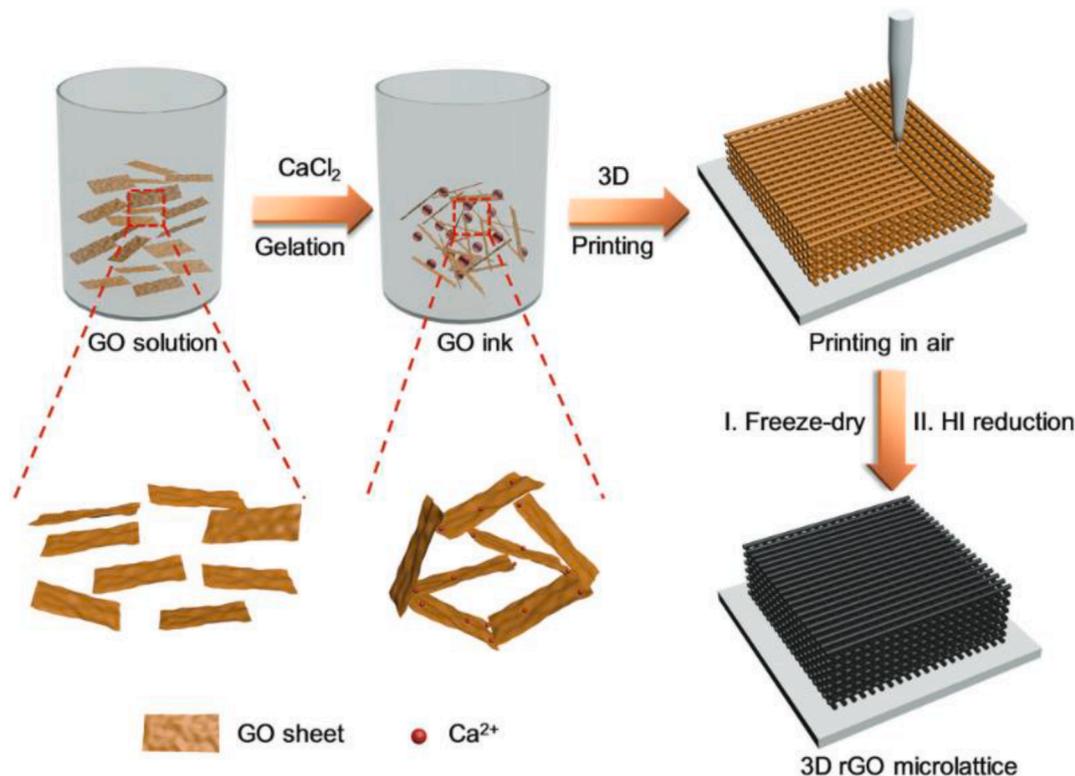


Fig. 4. Schematic illustration of 3D printing process. Reprinted with permission from [65].

adsorption capacity in the cycle experiment. Therefore, functional GBAs are an effective means of solving environmental problems, that continue to affect the daily life of people. The types of applications that will be treated in this chapter are related to the removal of metallic ions, the removal of organic compounds, environmental monitoring, and the removal of polluted exhaust.

#### Adsorption of heavy metals ions

In recent years, the increasing wastewater containing heavy metal ions has caused great harm to environmental safety, due to their extreme toxicity, not biodegradability, and tendency to be accumulated in body via the food chain, causing the long-term adverse threat to human health and natural ecosystems [74,75]. Therefore, a variety of remediation techniques have been developed to efficiently remove these heavy metal ions, including ion exchange, coagulation–precipitation, membrane filtration, reverse osmosis, adsorption, and so on.

The doping of  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions in industrial wastewater requires electrochemical treatment, that is expensive and does not meet the energy conservation and the green production concepts. The use of adsorption materials, including aerogels and in particular graphene-based aerogels, to remove these ions from water is an important topic in current research. There are many reports according to which GBAs have an excellent effect on the adsorption of  $\text{Cu}^{2+}$  ions. Yu et al. has reported the fabrication of GO-chitosan (CS) aerogel by lyophilization for the removal of  $\text{Cu}^{2+}$  ions [76]. Chitosan has been recently studied and applied in water treatment and is regarded as a green adsorbent due to its excellent biocompatibility and biodegradability. To prepare GO–CS aerogel, GO was dispersed in deionized water and CS was added dropwise under vigorous stirring. The composite material was washed with deionized water for three times and then lyophilized for 3 days.

The GO–CS aerogel is formed by the non-covalent interaction between GO and CS, leading to the formation of a three-dimensional porous structure, characterized by a surface area of  $345 \text{ m}^2/\text{g}$ . The adsorption data on GO–CS were well fitted by the Langmuir model, with a maximum adsorption capacity of  $2.54 \times 10^1 \text{ mg/g}$ , close to the experimental value of  $2.16 \times 10^1 \text{ mg/g}$ . The adsorption kinetic of  $\text{Cu}^{2+}$  is shown in Fig. 5.

The adsorption capacity increases fast in the first 5 h, and then become slower. Pseudo-first order and pseudo-second order were adopted to analyze the data, using the equations (4) and (5):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The pseudo-first order was not ideal for describing the adsorption

process and this was consistent with the results in literature, where the pseudo-second order model is proven to be better. The experimental ( $2.16 \times 10^1 \text{ mg/g}$ ) and calculated ( $2.08 \times 10^1 \text{ mg/g}$ ) equilibrium adsorption capacity ( $q_e$ ) values showed very good consistence. The small rate constant of adsorption ( $k_2$ )  $4.14 \times 10^{-3} \text{ min}^{-1}$  was compatible with the relatively slow adsorption process.

The efficiency of adsorption is closely related to temperature and pH value. It is higher in an alkaline environment with high pH, while the decrease in ionic strength and the temperature growth also contributed to the adsorption of  $\text{Cu}^{2+}$ .  $\text{Cu}^{2+}$  ions are not the only ones adsorbed by GBAs. The efficient removal of hexavalent chromium ( $\text{Cr(VI)}$ ) with high toxicity has attracted widespread concern since it causes serious harm to ecological environment and public health [77–79].

In 2021 Wang et al proposed the synthesis and application of a novel polyethyleneimine functionalized chitosan aerogels with highly porous network for the adsorption of  $\text{Cr(VI)}$  [80].

The kinetic studies showed how the  $\text{Cr(VI)}$  adsorption followed the pseudo-second order model, indicating the adsorption dependence from the chemical reaction between the ions and the aerogel. High maximum adsorption capacity ( $445.29 \text{ mg/g}$ ), resulting from the fitted Langmuir model, were observed, exceeding those of similar chitosan adsorbent reported in literature. Similarly, Liu et al. fabricated three-dimensional (3D) graphene/ $\delta$ - $\text{MnO}_2$  aerogels via self-assembly and reduction of graphene oxide, followed by in situ solution-phase deposition of ultrathin  $\delta$ - $\text{MnO}_2$  nanosheets [81]. Due to the unique structural characteristics, the resulting 3D aerogels exhibited fast adsorption kinetic rate and superior adsorption capacity toward heavy metal ions, such as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ . A schematic representation of metal ions adsorption on graphene base aerogels is reported in Fig. 6.

The heavy metal ions were not only adsorbed on the surface of graphene/ $\delta$ - $\text{MnO}_2$ , but they penetrated also into the interlayer gaps of  $\text{MnO}_2/\text{GA}$ , revealing the synergistic effect of the static electrical attraction, surface complexation and ion exchange. Furthermore, the regenerated aerogels after the initial HCl and subsequent KOH treatment kept their original shape, so they were repeatedly reused for more than eight cycles without degradation of performance. More importantly, the hybrid aerogels were easily separated and did not generate secondary contaminants.

High removal efficiency, fast adsorption kinetics, excellent regeneration and reusability, and ease of separation operation make these hybrid aerogels an ideal candidate for heavy metal ions decontamination in practical application. In addition, in the field of removal of heavy metals from radioactive wastewater like Iodine 129 and cesium is still and unsolved challenge [82,83]. In particular cesium removal is very important for nuclear energy sustainable development and public health. In this direction chitosan was added to GO to form a three-dimensional macroporous structure with excellent sorption properties

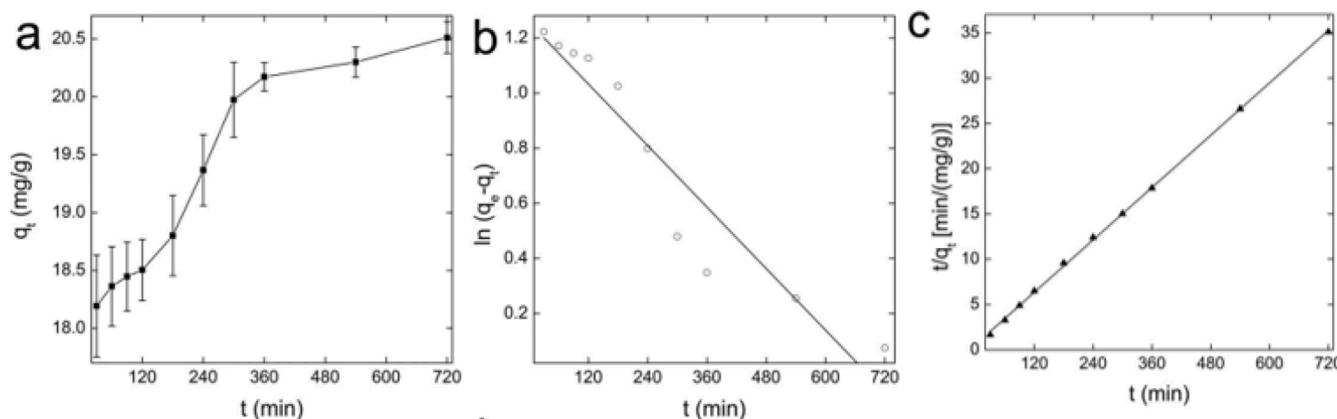


Fig. 5. Kinetic analysis of the adsorption of  $\text{Cu}^{2+}$  on GO–CS at 303 K: (a) Adsorption as a function of contact time; (b) the pseudo-first-order model; (c) the pseudo-second order model; and (d) intraparticle diffusion model. Reprinted with permission from: [76].

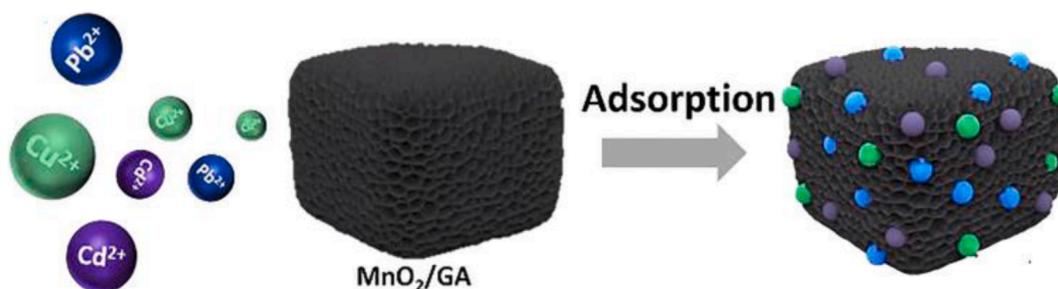


Fig. 6. Schematic overview of adsorption of metal ions on GBAs. Reprinted with permission from: [65].

with ultrafast kinetics thanks to the electrostatic attraction between  $\text{COO}^-$  and C-OH groups [82]. 3D porous graphene based aerogels were also used to explore antimony removal potential from wastewater with very good selectivity among competing ions and reusability with 95 % efficiency [84].

#### Removal of organic compounds

With the rapid development of industrialization, oil spillage and chemical leakage accidents have occurred frequently during exploration and transportation processes, resulting in severe environmental pollution. Therefore, many processes, such as chemical precipitation, physical adsorption, biodegradation method, and membrane separation, have been developed to address oil spill pollution. Among these methods, the use of adsorption materials is considered one of the most promising methods for the removal of oils [85,86] and organic solvents, such as dyes [87] and antibiotics [88,89]. GBAs are widely applied for the adsorption of these organic matters. Chen et al. [90] reported a GA prepared by hydrothermal treatment and the freeze-drying method for oil absorption; its absorption capacity could reach 224–522 times its own weight. Hong et al. [91] prepared functionalized GA (FGA) by surface modification of GAs for adsorption of oils and organic solvents. Xiao et al. [92] developed a graphene/nanofiber aerogel (GNA) for dyes adsorption derived from homogenized suspensions of graphene oxide and cellulose acetate nanofibers. The GO/ nanofiber suspensions were transformed into high-porous (>99 %) and ultralight (minimum density of  $1.8 \text{ mg/cm}^3$ ) hybrid aerogels after freeze-drying as shown in Fig. 7.

In the graphene/nanofiber aerogel, the flexible GO sheets can wrap nanofibers tightly, leading to several sheets/nanofibers combinations and increasing the mechanical robustness and the shape stability. The construction of interconnected porous network is favored by the long nanofibers that can bridge several GO sheets. The dye adsorption experiments were performed by adding graphene/nanofiber aerogel (5

mg) and dye solution (20 mL) into a polypropylene centrifugal tube in a constant temperature vibrator under shaking at 200 rpm at  $30^\circ\text{C}$  and  $\text{pH} = 7$ . These GNAs exhibited excellent underwater stability and high adsorption capacity (>800 mg/g) towards cationic dyes, due to the strong electrostatic attraction between the negatively charged GO sheets and the cationic dyes. The adsorption was analyzed to determine the dye concentration according to a calibration curve pre-established using UV–Vis absorption spectra as reported in Fig. 8.

Zhao et al. [93] synthesized a porous graphene oxide-chitosan (PGO-CS) with hydrothermal method and lyophilization to be used as a recyclable adsorbent material for the antibiotic tetracycline. Antibiotics are among the most important pollutants to water nowadays, due to their unavoidable release during their use and production. They can induce serious consequences, such as toxicity to animals and human beings, influence on aquatic photosynthetic organisms and disruption of indigenous microbial populations. The results showed that PGO-CS could be used as a recyclable adsorbent for tetracycline removal with a huge adsorption capacity of  $1.13 \times 10^3 \text{ mg/g}$ . The adsorption kinetics was well described by the pseudo-first-order model and the intraparticle model. Higher pH, ionic strength and temperature facilitated the adsorption. Moreover, as a practical application, the implementation of adsorption columns has been proven to be an efficient wastewater treatment method, due to low cost of adsorbent, simplicity of preparation and high removal efficiency. In the work of Vo et al. [94] the preparation of an eco-friendly graphene oxide–chitosan (GC) composite hydrogel column (GCCHC) has been presented together with its application as a broad-spectrum adsorbent for wastewater treatment. The GCCHC is characterized by a high removal capacity towards different contaminants including both cationic dyes, such as methylene blue and rhodamine B, and anionic dyes, like methylene orange and congo red.

The removal capacity changes with the composition of the composite hydrogel, for example, increasing the GO content leads to a higher dye removal capacity towards cationic dyes, whereas increasing the CTS

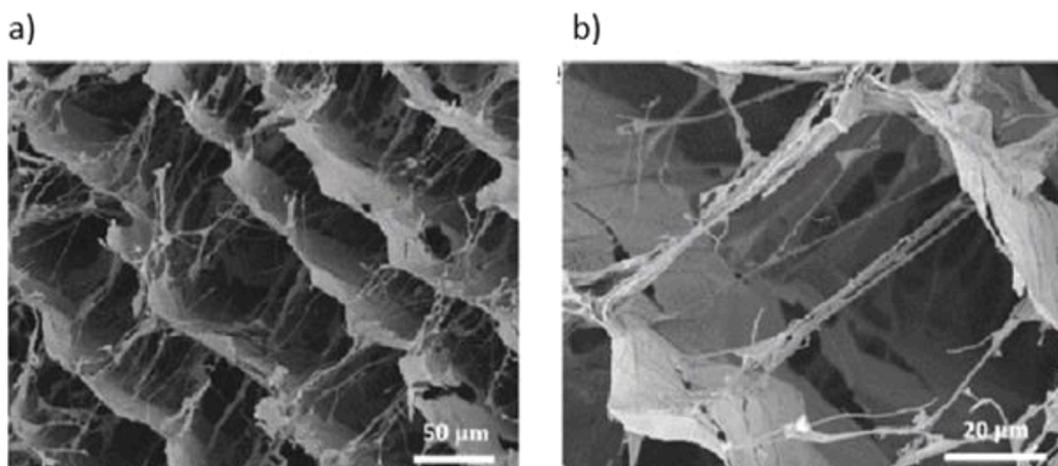


Fig. 7. SEM images of GNA showing the porous structure. Reprinted with permission from: [92].

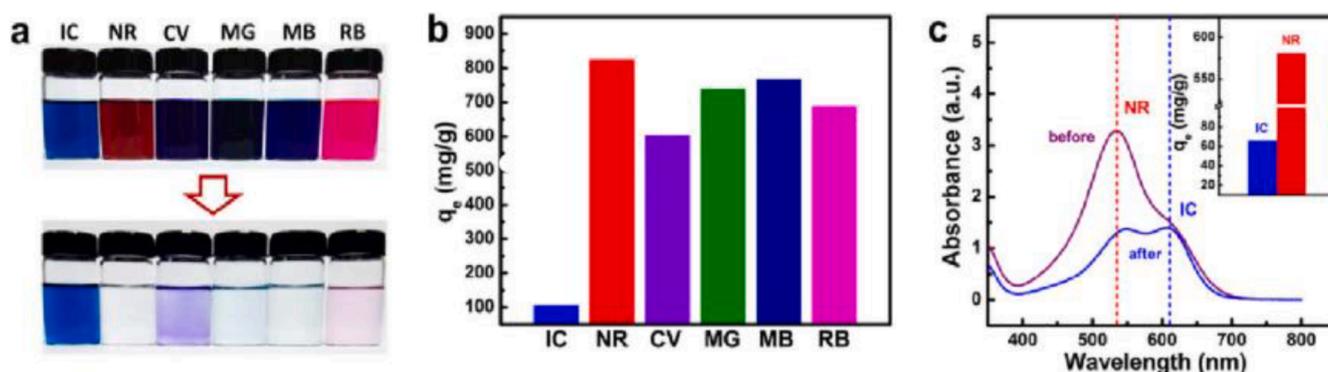


Fig. 8. A) photographs of various dye solutions (100 mg/L) before and after adsorption using GNA ( $\rho = 18.3 \text{ mg/cm}^3$ ,  $f = 0.4$ ). b)  $q_e$  of GNA for different dyes (500 mg/L). c) UV-Vis spectra of NR/IC binary dye solution before and after adsorption. Reprinted with permission from: [92].

content increases the removal capacity towards anionic dye. In parallel the use of *Nicandra physaloides*(L.) Gaertn seed gum with GO aerogels enhanced the removal of methylene blue [95]. The samples can be regenerated and recycled without loss of contaminant removal capacity over four successive adsorption and washing cycles. An other harmful organic compound is represented by perfluorooctanoic acid (PFOA) due to its high stability and consequent not degradability. To efficiently remove PFOA Liu et al [96] functionalized GO aerogels with Cu nanoparticles and fluorine with consequent enhanced 2.68-fold respect to neat GO aerogels and high possibility to reuse them several times. The improvement is ascribed to better ligand exchange reaction and hydrophobic interactions.

#### Environmental monitoring

In the recent years, the need of rapid and continuous measurements has made sensors of fundamental importance in different areas such as process control, product quality control, medical diagnosis, environmental monitoring, safety alarms and automotive. These devices can collect from the surrounding environment information about a physical parameter such as temperature, mass, pressure, charge, magnetic field, distance and position, or chemical parameter, usually a concentration, and to transform it into an analytical signal. Thanks to all the features described above, aerogels can be used as sensing materials that are able to recognize a physical, a chemical or a biological stimulus. Graphene nanosensors have been subjected to a rapid growth in the last years, being used as electrochemical sensors, molecular sensors, gas sensor, and smart wearable pressure sensors [97,98]. Thanks to the relatively simple production methods, graphene aerogel sensing components can be quickly produced with different shapes by freeze-drying or 3D printing, leading to the formation of large porous structure, which changes its potential when it is subjected to an external pressure.

On the other hand, the large specific surface area significantly increases the adsorption rate and it indirectly increases the sensor's sensitivity reducing the detection limit. Drogoman et al. [99] developed a high-pressure (>100 kPa) sensor based on an highly compressible graphene aerogel functionalized with  $\text{SnO}_2$  or GaN thin films, formed from aggregate nanoparticles that are piezoelectric. For graphene aerogel functionalized with  $\text{SnO}_2$  or GaN nanoparticles, there is a clear dependence of the almost linear I-V characteristics on pressure. In both cases the dependence of  $\Delta R$  on pressure is uniform, so that the pressure can be determined from electrical measurements. This is a consequence of the piezoelectric behavior of  $\text{SnO}_2$ , which significantly enhances the pressure sensing properties of graphene aerogel at high pressures. Indeed, tin oxide ( $\text{SnO}_2$ ) is a *n*-type metal dioxide with rutile structure and a wide band gap of 3.6 eV at 300 K [100], that has been widely used for different types of gas sensing applications, such as ethanol, nitric oxide, formaldehyde, etc., due to its properties, such as high physical and chemical stability, nontoxicity, and low cost. As shown before, its

electrical conductivity varies with different types of target gases, increasing when it is exposed to reducing gases and decreasing in oxidizing atmosphere. On the other hand, its use to produce  $\text{SnO}_2$ -based sensor is limited by the tendency of the nanoparticles to agglomerate during the synthetic process, reducing the specific area and thus the sensing performance. This drawback can be limited by depositing  $\text{SnO}_2$  nanocrystals on a conductive and stable support and graphene has been widely used for this purpose. Lei et al. [100] reported a facile hydrothermal method to prepare three-dimensional rGO-based aerogels with dispersed  $\text{SnO}_2$  nanocomposites by using different metal salt precursors. The working principle is shown in Fig. 9: the sensing performances of the gas sensors fabricated from the prepared 3D  $\text{SnO}_2$ /rGO hybrid aerogel were evaluated by their resistance changes upon exposure to  $\text{NO}_2$  gas with a controlled concentration at different operation temperatures. At the optimal operating temperature of 55 °C, the  $\text{SnO}_2$ /rGO aerogel demonstrated high sensitivity ( $0.001 \text{ ppm}^{-1}$ ), low detection limit (2 ppm) and a wide linear range.

There are many examples in literature where graphene-based aerogels have been synthesized for gas sensing purpose: Taher et al. fabricated very sensitive ammonia gas sensor with three-dimensional thiourea-treated graphene aerogel [101]. It was demonstrated that by treating graphene in the presence of thiourea it is not only improved the sensing sensitivity of the graphene aerogel but its selectivity for ammonia gas is also made remarkably better. The developed sensor showed very low detection limit and short response time to ammonia without requirement to thermal shock or vacuumed condition for recovery of the sensor response.

#### Removal of polluted exhaust

In recent years, scientists have also considered the use of aerogel materials with a large surface area in the removal of harmful exhaust gases from the air, such as NO or  $\text{SO}_2$ , that can cause for example acid rain. As a new type of waste gas treatment material, graphene-based aerogels are not only used for simple adsorption of small molecules, but also for catalyzation of  $\text{CO}_2$  to CO or nitrogen-containing waste gas using light energy. Catalytic conversion of  $\text{CO}_2$  to CO and to other organic compounds has been explored as an alternative to its mere capture and storage [102]. Graphene and GO three-dimensional microstructure can act as substrate for the growth of catalytic nanoparticle, providing active sites for the conversion of  $\text{CO}_2$  to other organic compounds (Fig. 10). Nanoparticles with catalytic activity that can be used are Ag,  $\text{Cu}_2\text{O}$ , and  $\text{TiO}_2$ .

An amine-functionalized GO-TiO<sub>2</sub> nanohybrid were synthesized by one-step aerosol technique and used for adsorption of  $\text{CO}_2$  in the form of alkylammonium carbamate and its photoreduction to CO under ultraviolet light [103]. After the evolution of CO by photoreduction, the amine groups are regenerated, resulting in a three-dimensional microstructure that can be used for multiple cycles.

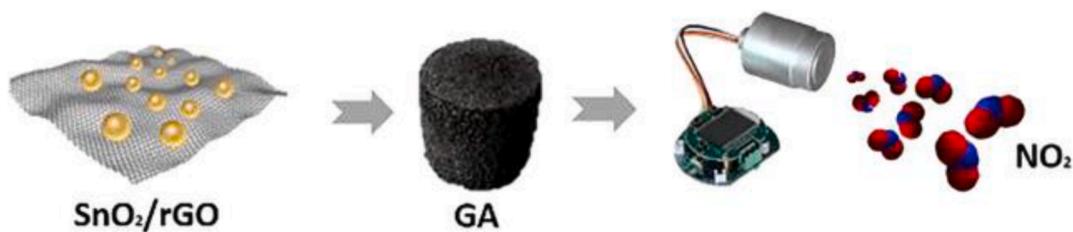


Fig. 9. SnO<sub>2</sub>/rGO aerogel for gas sensing application. Reprinted with permission from: [100].

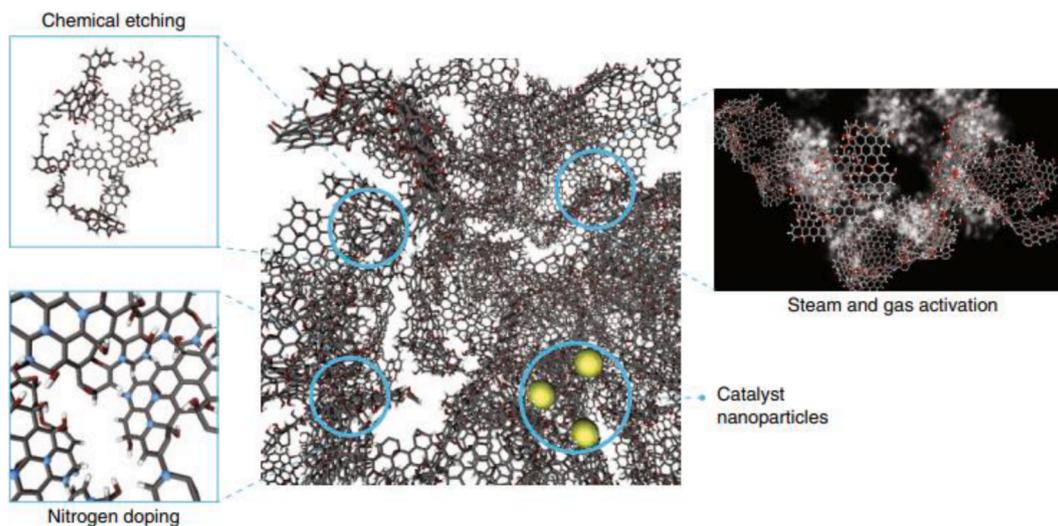


Fig. 10. 3DMs for air treatment. Reprinted with permission from: [104].

Another example where graphene-based aerogels have been used as a catalyst for gas removal is the one proposed by Jiang et al. [104] prepared with a three-dimensional flexible Pt-promoted graphene aerogel monolith. Ethylene glycol was employed as the reducing agent and the solvent, accelerating the in-situ reduction of GO and metal ions during the solvothermal process, leading to the cross-linking of GO to form a three-dimensional network. The Pt-promoted graphene aerogel monolith exhibited excellent flexibility and mechanical properties and it is characterized by low density of 20 mg/cm<sup>3</sup> and a compression

modulus of 0.6 MPa. It also showed a high performance for the catalytic oxidation of CO, HCHO and C<sub>2</sub>H<sub>4</sub> with 100 % conversion at room temperature, with an excellent stability longer than 72 h. The schematization of the working principle of these aerogels is reported in Fig. 11.

Similarly, Jundie et al. proposed the synthesis of a functional graphene aerogel PICNGA using graphitic-carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) modified with a perylene imide (PI) and graphene oxide (GO) [105]. These photocatalysts displayed excellent activity because of their strong visible-light absorption, good charge transport properties, and large

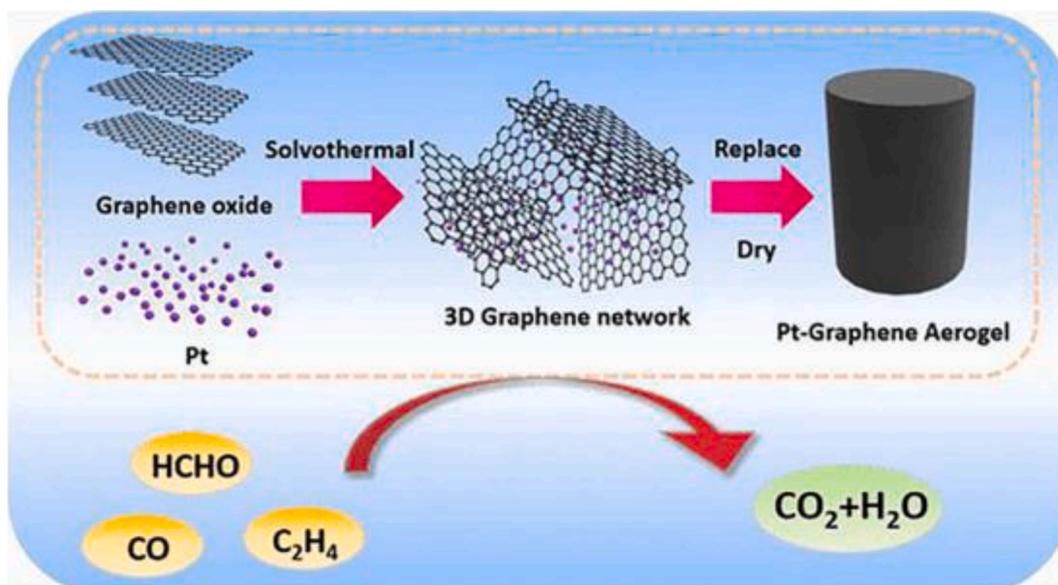


Fig. 11. Principle diagram of flexible Pt-promoted graphene aerogel. Reprinted with permission from: [104].

specific surface area. These materials are able to adsorb NO and absorb visible light, converting NO to NO<sub>3</sub>. The optimal ratio of PICN to GO to maximize photocatalytic activity was 3:1. The PICN(S)GA aerogel containing thiophene proved to be the best photocatalyst of the series, with an NO removal ratio of 66 %. The primary mechanism was to illuminate the imide with visible light and catalyze part of the NO and then transfer the energy to C<sub>3</sub>N<sub>4</sub>. The oxygen catalyzed the conversion of most of the remaining NO to NO<sub>3</sub>.

## Perspective and conclusions

Despite the very promising results also some challenges still remain in the field and should be overcome before reaching the final market. The advancement in novel aerogels should firstly consider material science of adsorbents to have better performances respect to the actual solution used in terms of fast response, reliability, easy to use, easy to reuse and final recyclability.

The following issues should be taken under strong attention in order to have: i) processes with responsible resources management; ii) competitive cost of production and iii) new raw materials. In this direction a critical study on aerogel sources, that consider both wastes and by-products, coming from nonrenewable sources should be done. In addition also efforts on best working practice, facilities and expertise is fundamental to move from lab to industrial scale. In summary there is strong need of multidisciplinary able to translate advances on aerogels into scientific, technological and regulatory improvement to reach the final market with suitable commercial products. Graphene-based aerogels have gained in the last years great considerations and their application in the environmental field is always more important. Their properties are for sure an incentive in this kind of employment: high surface area, sorbent ability, good mechanical resistance, soft nature and responsive behavior are an excellent and effective compromise for multiple uses. Their versatility is testified by the wide range of devices presented, employed not only in the removal of contaminants but also in the monitoring of the environment. In this context great effort is made to develop and test new formulations to properly combine polymers and graphene and obtain final effective devices also combining micro and nano moieties to obtain specific properties in the final system.

## Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Filippo rossi reports financial support was provided by Polytechnic of Milan. Filippo rossi reports a relationship with Polytechnic of Milan that includes: employment.

## Data availability

No data was used for the research described in the article.

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