
Carbon Nanotube and Graphene Aerogels – The World’s 3D Lightest Materials for Environment Applications: A Review

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To cite this article:

Phan Ngoc Hong, Dang Nhat Minh, Nguyen Van Hung, Phan Ngoc Minh, Phan Hong Khoi. Carbon Nanotube and Graphene Aerogels – The World’s 3D Lightest Materials for Environment Applications: A Review. *International Journal of Materials Science and Applications*. Vol. 6, No. 6, 2017, pp. 277-283. doi: 10.11648/j.ijmsa.20170606.12

Received: August 25, 2017; **Accepted:** September 13, 2017; **Published:** October 29, 2017

Abstract: Carbon Nanotube and Graphene Aerogels (CNTAs & GAs)- the world’s lightest 3D materials (GA is seven times lighter than air - a cubic meter weighs just 160 grams) attracted widespread attention due to their excellent mechanical compressible properties, high temperature and thermal stability, recyclable and highly efficient organic pollutants adsorption capability (GA can absorb up to 900 times its own weight in oil and do so quickly, with one gram of Aerogel able to absorb up to 68.8 grams of organics per second). In this review, we present briefly recent progress in synthesis methods for fabrication of 3D CNTAs and GAs and their emerging applications in the field of environmental protection such as removing oil, organic pollutants, arsenic ions and other toxic metals from water. Furthermore, to assist advanced research for practical applications of these 3D materials, the technical challenges are discussed, and future research directions are proposed.

Keywords: Carbon Nanotube Aerogels, Graphene Aerogels, 3D Materials, Environment Protection, Applications

1. Introduction

Aerogels are a diverse class of ultralow density and extremely porous solids with properties unlike anything else. These materials are synthesized from a gel, in which the liquid component of the gel has been replaced with a gas by different techniques. The first aerogel was invented by Samuel Stephens Kistler in 1931, which were made from silica and later work involved aerogels based on alumina, chromia and tin dioxide [1]. Silica aerogel is the most common type of aerogel and the most extensively studied. Due to its translucent nature and the way light scatters in the material, silica aerogel is also called “frozen smoke”, “solid smoke”, “solid air”, or “blue smoke”. The lowest-density of the recorded silica aerogel is 1,900 g/m³ with the remaining 97% of the volume composed of air in extremely small nanopores, extremely low thermal conductivity, from 0.03 W/m.K in atmospheric pressure down to 0.004 W/m.K in

modest vacuum. Its optical transmission is very high and the refractive index is of ~1.05. Until 2011, the silica aerogel held 15 entries in Guinness World Records for material properties, including best insulator and lowest-density solid [2]. Owing to these extraordinary properties, silica aerogel has been intensively studied and successfully used in various application fields, such as thermal and acoustic insulation in building construction, modern-day products manufacturing like shock-absorbers in cars, cradling aircraft flight data recorders, protecting fragile laptop computer hard drives and super light-weight and warm ski jackets and so on.

Up-to-now several types of aerogels such as metal oxide aerogels, organic/polymer aerogels, carbon aerogels, CNTs/graphene aerogels have been studied and developed. Figure 1 shows the types of aerogel and their evolution timeline.

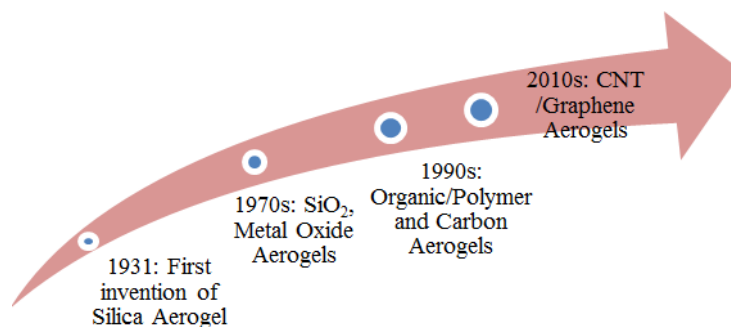


Figure 1. Types and evolution timeline of the aerogels [3].

Among the types of aerogel denoted in Figure 1, CNT and graphene aerogels have attracted considerable attentions for investigation because of their prominent properties: well-defined and controlled pore structure, large surface area, high electrical conductivity, heat- & fire-resistance and thermal/mechanical stability, which make them innovative and promising materials for various applications.

Herein, we review recent research achievements on three-dimensional (3D) CNT and graphene aerogels for purposes of environment protection applications including removal of oils, organic pollutants and heavy toxic metal

ions from contaminated water and adsorption of toxic gases in air.

2. Methods for Synthesizing Aerogels

2.1. General Method for Synthesizing Aerogels

Aerogels have been fabricated using traditional organic sol-gel chemistry. A procedure of aerogels preparation in general, carbon nanotube (CNT) and graphene aerogels, in particular, is shown in the Figure 2.

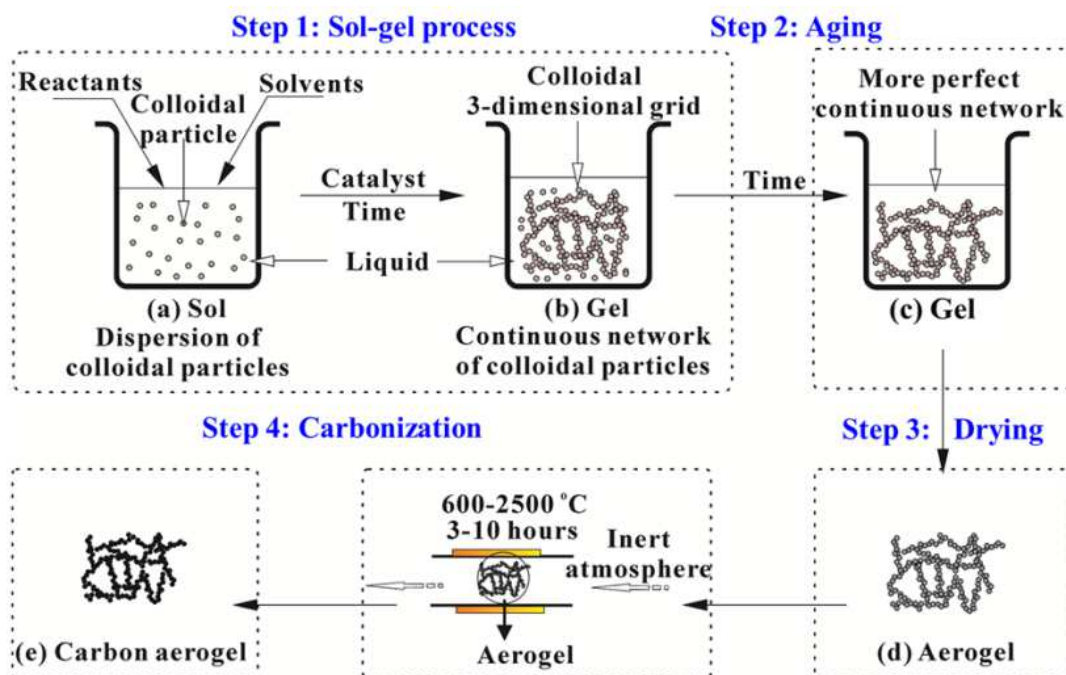


Figure 2. A general procedure for aerogel preparation [3].

The procedure consists of 04 main steps as follow: (1) Step 1: Sol-gels preparation; (2) Step 2. Aging of the sol-gels; (3) Step 3: Drying which may be performed using one of the following techniques: (i) Direct evaporation from liquid phase to gas phase causes collapse to the gel network due to the effect of surface tension, (ii) Supercritical drying (CPD) process: the temperature and pressure of liquid are raised above its critical point to form a supercritical fluid. By slowly releasing the pressure, the hydrogels are dried to

aerogels with well-preserved networks, and (iii) Freeze drying is a common method to create aerogels. During this process, the samples are fast frozen and then placed in a vacuum under raised temperature to allow the ice to sublime; (4) Step 4. Carbonization: The aerogels are carbonized at high temperature in an inert atmosphere for several hours to form carbon-based aerogels [3].

To produce CNT and graphene aerogels the following materials are usually used (1) Nanomaterials: CNTs (MW or

SW), graphene sheets, graphene flakes, graphene oxides (GO), reduced graphene oxide (RGO), metal/metal oxide nanoparticles and organic/polymers (for fabrication hybrid nanocomposite aerogels); (2) Solutions and catalysts: ID water, various kind of chemical compounds. There are several techniques for fabrication of CNT & graphene aerogels. However, in framework of the review, in the next section we will briefly describe only a room temperature freeze gelation (RTFG) technique for fabrication of multiwall carbon nanotube (MWCNT) Polyvinyl alcohol (PVA) hybrid aerogel since this method is rather simple and promised to be able to produce inexpensive aerogels in large scale. The same technique can be used to produce hybrid graphene aerogels.

2.2. Room Temperature Freeze Gelation (RTFG) Technique for Synthesizing MWCNT-PVA Hybrid Aerogels

Room-temperature freeze gelation (RTFG) was originally developed by Halloran and co-workers for the manufacture of ceramics [4] and has been recently used by Lizeng Zuo

and his co-authors to fabricate polymer/carbon-based hybrid aerogels [3]. This processing route is similar to conventional aqueous freeze gelation (or freeze casting) but with the water replaced by an organic solvent selected to have a melting temperature greater than room temperature and a high vapor pressure. The material to be processed is mixed and dispersed in the solvent above its melting point, typically in the temperature range 50–120°C and cooled to form a solid at room temperature. The solvent is selected to have a high vapor pressure above the solid at room temperature and thus rapidly sublimates at room temperature under ambient atmospheric conditions, leaving a porous solid of the original material.

In our study we used phenol (C_6H_6O) melting at low temperature 40.5°C with the addition of polyvinyl alcohol (PVA) in solution to increase the strength of the resulting aerogel. The sol-gel solidification and phenol evaporation can be performed at room temperature. A schematic of how the RTFG process is used for MWCNT aerogel preparation is illustrated in Figure 3 [5].

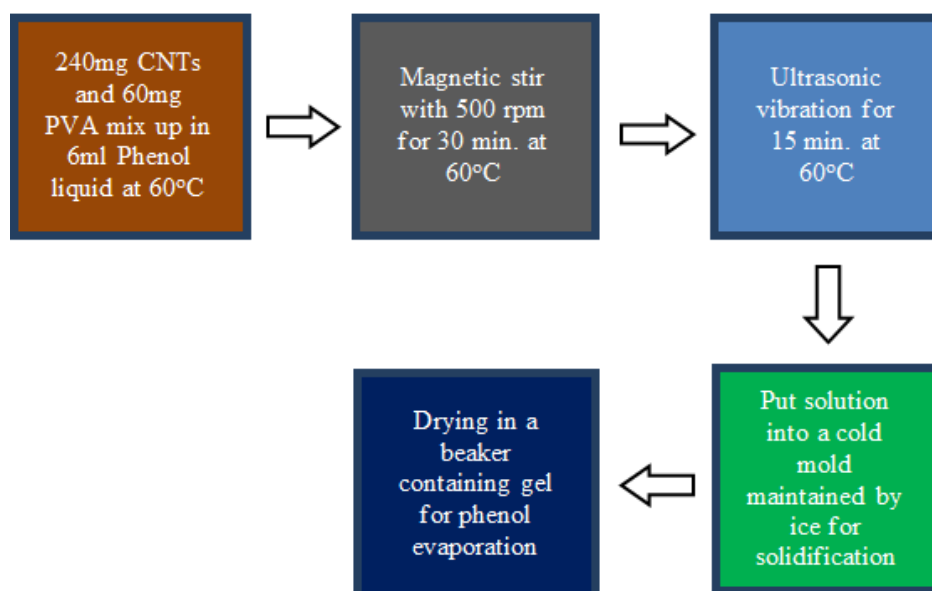


Figure 3. Schematic of the room-temperature freeze gelation (RTFG) process [5].

Briefly, the preparation procedure of MWCNT/PVA aerogel is following: MWCNTs are dispersed to the required concentration in an appropriate solvent at 60°C, using magnetic stir with 500 rpm for 30 min. and ultrasonic vibration for 15 min. to form a stable dispersion. This dispersion is then used with an appropriate forming method,

e.g., molding and cooled in ice to promote solidification. The resulting waxy solid contains a uniform suspension of MWCNTs. The solvent sublimates at room temperature leaving a porous MWCNT aerogel. The optical image and microstructure of RTFG MWCNT aerogel obtained is shown in Figure 4.

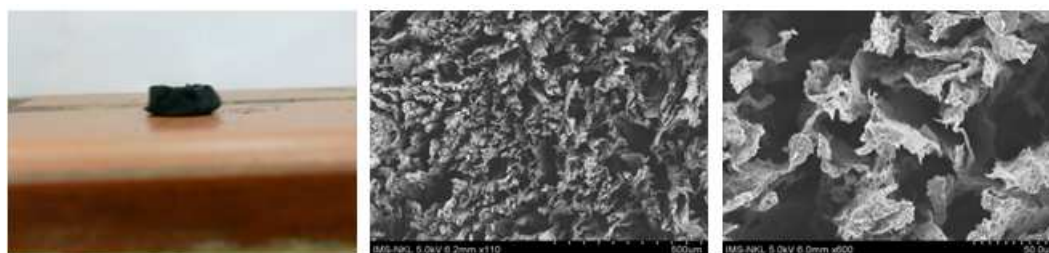


Figure 4. An optical image (Left) and microstructures (Right) of RTFG MWCNT aerogel [5].

With the same procedure, Yue Lin, *et al.* have recently successfully produced the RTFG aerogel using mixtures of graphene flakes and MWCNT, mixtures of rGO and MWCNT with the addition of polymers in solution to increase the strength of the resulting aerogel [6].

3. Specific Properties of CNT and Graphene Aerogels

CNT and graphene aerogels are solid, rigid, and dry materials that do not resemble a gel in their physical

properties. The name comes from the fact that they are made from gels. They exhibit extraordinary properties that do not have any other materials.

- a). They are the world's lightest materials ever known: The density of GAs synthesized by a chemical reduction method and dried with supercritical CO₂ is 14.1- 52.4 mg/cm³ [7], and according to the report of Chinese researchers at Zhejiang University, the lowest-density of the recorded graphene aerogel is 0.16 milligrams/cm³, seven times lighter than air (air density is - 11,8 mg/cm³) [8, 9]



Figure 5. The graphene aerogel is so light that a cube inch of the stuff can be balanced on a blade of grass (Left) and sitting on top of a plant's leaves (Right) [10].

- b). They are the most porous solid network that contains air pockets, with the air pockets taking up majority of space within the material, therefore aerogel is a material that is ~98.2% air;
- c). Their surface area is very high ranging between 400–1,000 m²/g [2].
- d). They exhibit extremely low thermal conductivity because they are composed almost entirely of gas, which are very poor heat conductors. At room temperature the lowest thermal conductivity of CNT Aerogel $K = 0.01 \div 0.1$ (W/m.K) [2] and of graphene aerogel $K = 4.7 \times 10^{-3} \div 5.9 \times 10^{-3}$ (W/m.K) [8], much lower than pristine CNT and Graphene $K = 2,000 \div 5,300$ (W/m.K) (Silica aerogel is especially good because silica is also a poor conductor of heat; CNT and graphene aerogels would be less effective, but on the other side, they exhibit excellent heat and fire resistant properties).
- e). They are mechanically strong and extremely elastic, bouncing back after being compressed. The graphene aerogel can recover completely after more than 90% compression [5]. Recently, Cheng *et al.* reported that 75.0 mg graphene aerogel cylinder could support a 2kg counterpoise, at least 26000 times their own weight as can be seen in the figure 6 [11].



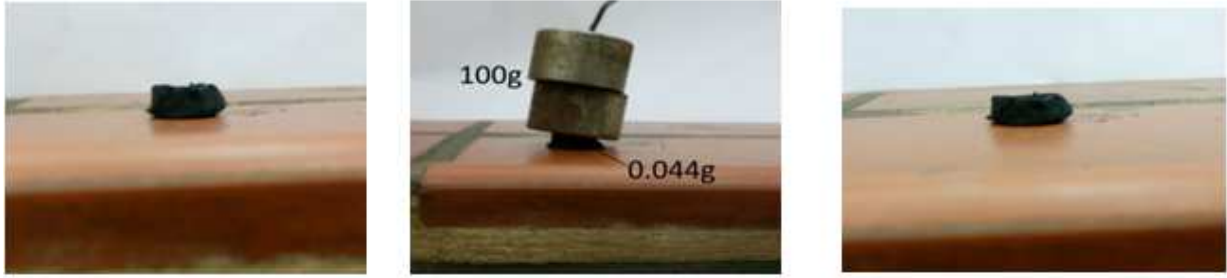


Figure 6. CNT & Graphene Aerogels are extremely elastic, bouncing back after being compressed [5, 11].

- f). They exhibit excellent properties of hydrophobicity and adsorption of oils, organic pollutants, heavy metal ions, toxic gases.

Hence, it is no surprise that CNT and Graphene aerogels provide some of the most amazing benefits that may see them being used soon in most industries and environment applications. In the framework of this review, we present a brief description on some attracted applications of CNT and graphene aerogels only for environment protection.

4. Applications for Environment Protection

Environmental pollution especially oils, organic pollutants, heavy metal ions, toxic gases in water and air, caused by industry and agricultural activities, severely affects ecological balance and human health, and has received extensive attention worldwide. It is why research for finding new materials and methods for effectively removing these pollutants in water and air is necessary and urgent.

Currently, many adsorbents and materials have been

researched and developed. Among them, nanomaterials, especially, carbon nanotube and graphene in general, and their aerogels in particular, have been considered as the most perspective materials for various environment protection applications.

4.1. Removal of Oils and Organic Pollutants from Water

The hydrophobicity of MWCNT and graphene aerogels makes them good candidates for removing oils and organic pollutants from water. Lizeng Zuo *et al.* reported that the uptake capacity of a thermally treated MWCNT hybrid aerogel is up to about 37 times of its weight for various lubricating oils, and to about 23 times for vegetable oils [3]. Recently, Luo *et al.* successfully synthesized superhydrophobic spongy graphene aerogels which is able to adsorb up to 29–54 times its own mass with the slightly lower density than other aerogel composites ($24 \pm 2 \text{ mg cm}^{-3}$) (figure 7 and 8a-b) [12]. An ultralight GA with density $< 3 \text{ mg cm}^{-3}$ reported by Zhang *et al.* shows very high n-hexane absorption capacity ($Q = 226$) (figure 8c) [13].

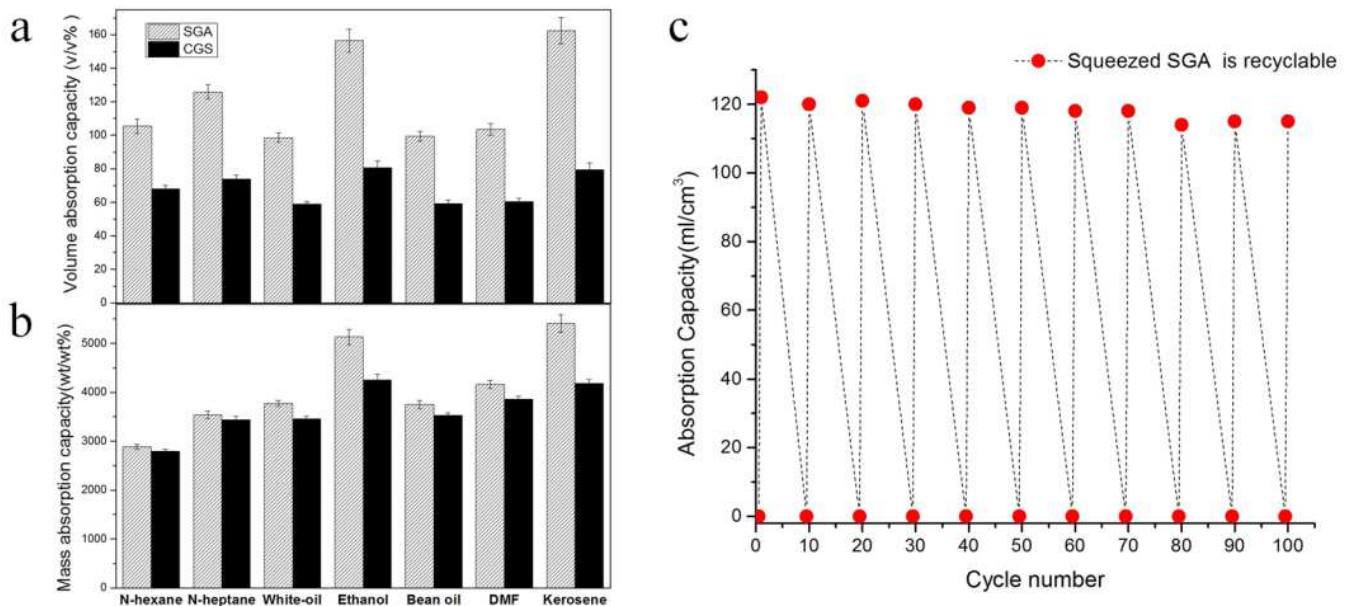


Figure 7. The absorption capacities of different organic liquids on (a) mass basis and (b) volume basis, (c) The high absorption recyclability of GA with n-heptane [12].

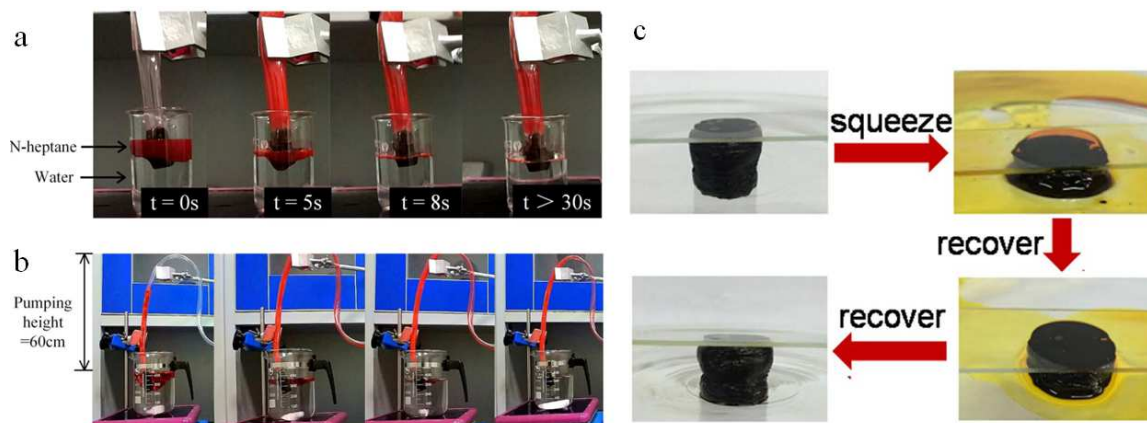


Figure 8. (a) The selective absorption of GA in an oil-water mixture with pump. (b) The continuous removal of n-heptane using a 120-W pump [12], (c) GA shows excellent repeated absorption of n-hexane after multiple times of being compressed above 90% of its initial height [13].

4.2. Removal of Lead, Arsenic and Other Heavy Metal Ions from Contaminated Water

Heavy metal ions, such as lead (Pb^{2+}), cadmium (Cd^{2+}), chromium (Cr^{3+} , Cr^{6+}), mercury (Hg^{2+}), copper (Cu^{2+}) and arsenic (As^{3+}), have severe risks to environment and human health, and need to be removed from water. Zhuo Han *et al.* reported the adsorption capacity of GA for Pb^{2+} from aqueous solution up to about 80 mg g^{-1} , which could reach as high as 5000 g m^{-3} per unit volume [14]. Mi *et al.* prepared a GO aerogel with highly oriented porous structure from GO nanosheets by the freeze-drying method [15]. The obtained aerogel can act as a good adsorbent of Cu^{2+} in aqueous solutions with fast adsorption rate, which attributed to its interconnected pore structure being conducive to the diffusion of Cu^{2+} . Yan Ye *et al.* reported that the three-dimensional $\text{Fe}_3\text{O}_4/\text{GA}$ is an excellent material for removing arsenic (As) ions from water [16]. This material shows that iron oxide nanoparticles are decorated on graphene with an interconnected network structure and therefore $\text{Fe}_3\text{O}_4/\text{GA}$ own a capacity of As ions adsorption up to 40.048 mg/g due to their remarkable 3D structure and existence of magnetic Fe_3O_4 nanoparticles for separation.

It is very interesting to note that owing to the excellent adsorption capability of Pb^{2+} and As^{3+} ions and other heavy metals ions, GAs can be used to easily and effectively separate these metal ions from water, indicating the potential applications in water treatment.

4.3. Air and Gas Purification

Air pollution is currently one of the most serious environmental problems. Gas and air purification represents a major challenge in a time of concerns for growing air pollution based on emission of gases (especially toxic and greenhouse gases) from various industrial sources.

Regarding the greenhouse gases, the subject of carbon dioxide (CO_2) capture, utilization, and storage has received widespread attention because of the interest in reducing the amount of released CO_2 as a greenhouse gas. The amount of CO_2 present in the atmosphere contributes to 60% of global warming effects.

Related to this issue, porous carbons play an important role in CO_2 adsorption and separation due to their high porosity, excellent stability, wide availability, and tunable surface chemistry. They are mainly classified into the following categories: conventional activated carbons (ACs), renewable-resources-derived porous carbons, synthetic polymer-based porous carbons, graphitic porous carbons, CNT/graphene-based porous materials including aerogels and etc. Among them, aspen and CNT/graphene aerogels for CO_2 capture are being created at an increasing rate and are highlighted in the last few years.

Related to the quality of indoor and outdoor air environment, to overcome the drawbacks of current air cleaners in the market, new materials and methods for air purifying are needed. In this aspect, the combination of adsorption and photocatalysis is definitely a competitive and applicable way of air cleaning. The adsorbents could concentrate the pollutants around TiO_2 to facilitate the photocatalytic reaction, while the photocatalytic oxidation serves as regeneration way of the adsorbents. In this aspect, ultralight, high porosity and highly compressible CNT and graphene aerogels are expected to be the best support for TiO_2 . Based on this idea, Xicheng Xiong *et al.* have developed porous graphene aerogels added with TiO_2 nanoparticles for air cleaner filters [17]. For cleaning air exhausted from other objectives such as solid waste incinerators, vehicles and motorcycles, it is suggested that one can use CNT and graphene aerogels functionalized by catalyst nanomaterials, such as Zirconium Oxide (ZrO_2), Cerium Oxide (CeO_2), Rhodium Oxide (RhO_2) and platinum (Pt). Three-dimensional printing technology is recommended to be used to create graphene aerogels with a highly ordered pore structure and highly transported gas flow thus more effective air cleaning [18].

5. Conclusion

Carbon nanotube and graphene aerogels, the world's latest materials, have attracted widespread attention due to its excellent mechanical strength, super compressibility offering up to 90% compressive strain and high surface area, low

thermal conductivity and stability, and adsorption capability. With their excellent multifunctional properties, they can be promising candidates for several applications.

However, the greatest obstacle to the widespread use of 3D aerogels is cost. The cost of these aerogels is not inherent in their composition, but it results from the time and energy used for their production. Therefore, other ways may be found to make three-dimensional CNT more efficiently.

Acknowledgements

The authors acknowledge financial support from the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.99-2012.35 and from Center for High Technology Development, Vietnam Academy of Science and Technology.

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