

Aerogels Based on Graphene Oxide with Addition of Carbon Nanotubes: Synthesis and Properties

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Abstract

Nowadays numerous sorbents based on graphene and other carbon nanomaterials have been synthesized for the removal or collecting of oil remains due to its unique physico-chemical properties. Obtaining of aerogels based on graphene oxide and carbon nanotubes with addition of chitosan solution as a binder component is shown in this paper. Aerogels were synthesized by reduction of aqueous dispersion of graphene oxide using the reducing agents, followed by ultrasonic and thermal treatment. Ultrasound destroys the graphene layers, decreasing them in size, thereby exposing new layers to form edges that already have no stabilizing carboxyl groups, which are located at the edges, and participate in the formation of bonds. The surface morphology of obtained aerogels was studied by SEM. The study of the sorption capacity showed that graphene/CNTs aerogel is characterized by short absorption time and high sorption ability that depend on densities of the used solvents. All experimental results show the possibility of using the aerogels based on graphene and CNTs as sorbents for collection of oil residues.

Introduction

Currently in world science there are researches in the field of creation of carbon nano-aerogel using carbon nanomaterials (graphene, nanotubes, activated carbon). This scientific direction is being intensively developed in such countries as the USA, China, and the United Kingdom. For the Republic of Kazakhstan this research area is also important and promising due to large deposits of oil which are situated on Caspian shelf and mining and transportation of oil in some cases can cause oil spills on water and earth. In future these aerogels can be used as a selective reusable sorbent for oil with high sorption properties.

By definition, a gel is a type of colloidal systems, represented as a slurry of liquid particles in a solid phase. The amount of a solid component in a gel is much smaller by volume than a liquid one, gel consists of nanometer-sized particles that contact with each other followed by formation a branched network of chains and sheets continuously penetrating the entire volume of the gel.

The first carbon aerogel was obtained by Professor Pekala using carbonization of resorcinol-formaldehyde (RF) aerogel. In its turn, it is usually regarded as a kind of highly porous amorphous graphite foam. The main idea of obtaining of RF-aerogel was that high temperature pyrolysis (1000-1200 °C) was carried out at high pressure or in the atmosphere of inert gas. In 1996, Hanzawa et al. developed a new approach for obtaining of carbonized RF-aerogel with ultrahigh surface area by activating the carbon skeleton under the influence of carbon dioxide [1].

Synthesis of graphene-based aerogels is one of the new directions in the field of production of carbon aerogels, for the first time they were synthesized by the group of Professor Wang in 2009 [2]. The dispersion of graphene oxide was transformed to graphene aerogel by a jellification process under the influence of ultrasonic waves with subsequent drying and thermal treatment.

The authors [3] stated that graphene aerogels also possess pronounced superhydrophobic properties due to a specific morphology of their surfaces. It

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is shown that graphene aerogels show natural hydrophobicity because of defects on their surfaces, an after their treatment with fluorinated silane, they start showing the superhydrophobic properties, with the contact angle with water reaches 160° . In view of these specific characteristics these aerogels can be applied as self-cleaning or water – repellent surfaces with a low volume density and the method of obtaining them excludes stages of complex chemical vapor deposition or supercritical drying, as in case with other analogs.

These results support the potential application of graphene-based aerogels as a selective sorbent for elimination of the oil remains, thus the high sorption rate of organic substances is observed at the simultaneous repulsion of water due to high hydrophobicity [3].

In the paper [4] the preparation of ultralight graphene/carbon composite aerogels with high surface areas and porosity, good conductivity and well-defined bulk shape by assembly of graphene oxide and resol-type phenolic prepolymers is demonstrated. By studying the observed structures and properties of aerogel the adsorption-assembly mechanism for the assembly of GO sheets and resol prepolymers under hydrothermal conditions is proposed. It is shown that, due to its high porosity, the obtained aerogels is a fast sorbent for organic solvents with high adsorption efficiencies, capable of absorbing 400 times its weight of chloroform.

As a type of three-dimensional (3D) structure the authors [5] fabricated a robust superhydrophobic and superoleophilic carbon nanotube/poly (dimethylsiloxane)-coated polyurethane sponge for the continuous absorption and expulsion of oils and organic solvents from water surfaces. The paper [5] stated that the sponge in conjunction with a vacuum system could separate great amounts of oil – up to 35000 times its own weight - from water in a one-step process and could also separate surfactant-free water-in-oil emulsions with high efficiency (oil purity: >99.97 wt.%), making it a promising candidate material for use in oil-spill cleanups.

One of the most important properties of graphene aerogels is elasticity, therefore these lightweight materials, which are subjected to compression with subsequent elastic recovery of its original shape, are widely used. The authors [6] synthesized the aerogel based on carbon nanotubes and graphene by pre-coating of carbon nanotubes containing aerogel with polyacrylonitrile, and then after a two-stage pyrolysis graphene was introduced into the structure of aerogel. The density of aerogel based on carbon nanotubes was 8.8 mg/ml, but after introduction of graphene it increased to 14 mg/ml, that in its turn

increased the volume fraction from 0.0067 to 0.009 with porosity more than 99% .

The synthesized aerogel based on carbon nanotubes and graphene does not change its shape after more than 13106 cycles of loading, and its original shape is quickly restored after compressions. Moreover, graphene has no effect on structural integrity of nanotubes or compressibility and porosity of the network of nanotubes. Introduction of graphene also increases the Young's modulus, and power storage unit with the coefficient $6 \sim [6]$.

3D architectural structures are of great interest in field of electronics, catalysis and various sensors. Nevertheless, a very topical issue is synthesis of such structures based on graphene under the conditions that do not require expensive and special equipment. In paper [7] the methods for synthesis of 3D structures based on graphene using the process of self-assembly at soft chemical reduction at 95°C in the atmospheric pressure without stirring are investigated. These methods do not require a high pressure.

In the research [7] NaHSO_3 , Na_2S , vitamin C, HI or hydroquinone were used as reducers of graphene oxide in the process of hydrogel formation. As is shown, it is possible to synthesize both graphene hydrogels and graphene aerogels, and by vary their shapes by changing the type of reactor. The obtained three-dimensional structure has a low density, high mechanical properties, heat resistance, high conductivity, and also high sorption capacity that make it a potential candidate to be used in supercapacitors, hydrogen storage and as a support for catalysts.

In the sphere of synthesis of 3D graphene-based aerogels by chemical reduction the authors [8] used a combination of oxalic acid and sodium iodide as a reducing agent. The studied reducing agent is novel and characterized by environment-friendly medium. The results of research show that the using the combination of oxalic acid and sodium iodide as a reducing agent for synthesis of graphene-based aerogels allows to obtain them from GO suspension with a wide range of concentrations (0.1 to 4.5 mg mL $^{-1}$) and also to control their volume. The resulting 3D graphene-based aerogels is characterized by low density, highly porous structures, and electrically conducting properties.

The purpose of this work is to synthesize aerogel based on graphene and carbon nanotubes with chitosan as a binder and triethylenetetramine as a reducing agent for graphene oxide, to study morphology of the surface of obtained aerogels, the average pore size and the sorption capacity for determining the possibilities of its application as a sorbent for collecting oil remains.

Experimental

SLGO and carbon nanotubes used in this research were bought in CheapTubes.com (physical address is 3992 rte 121 STE 3 Cambridgeport, VT 05141).

Synthesis of aerogel based on reduced graphene oxide and carbon nanotubes.

A weighed portion of graphene oxide (GO) and carbon nanotubes (CNT) with masses of 0.014 and 0.007 g, respectively were added into aqueous solution of chitosan with a concentration of 3 mg/ml and total volume of 5 ml (pH = 9-10). Further a measured amount of triethylenetetramine as a reducing agent for GO were poured into obtained dispersion of GO and CNTs in aqueous solution of chitosan. The resulting dispersion was subjected to ultrasonic treatment in an ultrasonic bath (Elma D-78224 Singen/Htw, Germany) for 4 h at the frequency of 50-60 Hz. Then the dispersion was placed in a water bath and heated for 5 h at 95-98 °C, whereby the hydrogel based on reduced GO bound with CNTs was synthesized.

For complete removal of water from the hydrogel, it was subjected to freeze-drying for 48 h.

Freeze drying is the process of removing the solvent from the frozen solution of gels, suspensions based on sublimation of the solidified solvent (ice) without formation of macro amounts of a liquid phase; also it can be defined as the transfer of a substance from the solid phase directly to a gaseous state, bypassing the liquid. Hydrogel in a special vessel was placed in the volume of liquid nitrogen with the purpose of its rapid freezing, and then this vessel was connected to a pump for pumping gas (Fig. 1).

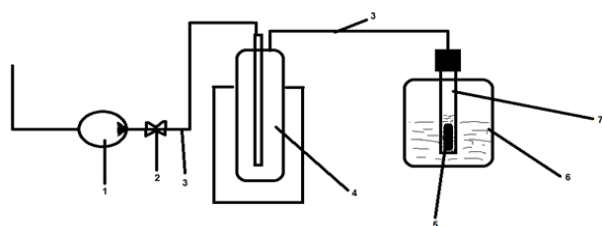


Fig. 1. Principal scheme of installation for freeze-drying of hydrogel based on reduced GO and CNTs: 1 – vacuum pump; 2 – vacuum supply valve; 3 – vacuum hose; 4 – trap for gases with liquid nitrogen; 5 – frozen hydrogel; 6 – a vessel filled with liquid nitrogen; 7 – a special vessel for hydrogel.

After 48 h of freeze-drying, the ultralight aerogel based on reduced GO and CNTs was obtained.

To stabilize the obtained aerogel, it was subjected to thermal heating to 900 °C for one hour at an average heating rate of 5 °C/min in inert

atmosphere of argon with average flow rate of 100 ml/min. Stabilized graphene/CNTs aerogel was obtained after thermal heating.

The surface morphology of the synthesized aerogel was studied using scanning electron microscopy (Quanta 3D 200i) with an accelerated voltage of 20 kV and a the pressure of 0.003 Pa at National nanotechnological laboratory of open type of Al-Farabi Kazakh National University. Sorption capacity (BET), average size and pore volume were determined on the device Sorbtometr - M. Relative density and porosity of aerogel were determined by numerical methods.

Results and Discussion

The formation of the structure of hydrogel based on reduced GO and CNTs involves the process of its jellification under the effect of ultrasonic treatment. Under the effect of ultrasound irradiation there takes place the process of destruction of the graphene layers, followed by decreasing them in size and due to that the obtained new layers of graphene form edges that already don't contain stabilizing carboxyl groups which are located at the edges, and participate in the formation of bonds.

Jellification occurs after 30 min of ultrasonic treatment, but such a short time of ultrasonic treatment results in formation of a weak gel. With a longer ultrasonic treatment (180-240 min), formation of more stable and strongly bound hydrogels is observed.

Visual analysis of the resulting aerogel (Fig. 2) showed that the sample is of a rich black color with a characteristic luster; the surface is rough, with numerous defects. During mechanical loading there takes place a little decay that can be explained by incomplete stabilization of aerogel during the thermal treatment.

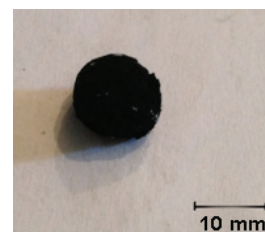


Fig. 2. Picture of graphene/CNTs aerogel sample.

The resulting graphene/CNTs aerogel doesn't exhibit elasticity possibly due to introduction of CNTs forming a rigid frame of the aerogel as well as chitosan acting as a binder.

Relative density of aerogel that amounts to 7.3 mg/cm³ was determined by numerical method taking into account its mass and the relative volume.

Calculation of porosity of graphene/CNTs aerogel sample was carried out by the following equation, taken from paper [9]:

$$\varepsilon = 1 - \rho / \rho_0$$

where ε is porosity of the sample; ρ is relative density of synthesized aerogel; ρ_0 is density of graphite, which is conventionally taken as 2.2 g/cm³.

The surface morphology of the synthesized graphene/CNTs aerogel was examined by scanning electron microscopy. As is seen in Fig. 3, the obtained aerogel has a porous surface where the layers of graphene oxide and CNTs are linked, and also there appear chemical covalent bonds caused by introduction of the chitosan solution. CNTs are mounted on the surface of walls of the graphene aerogels.

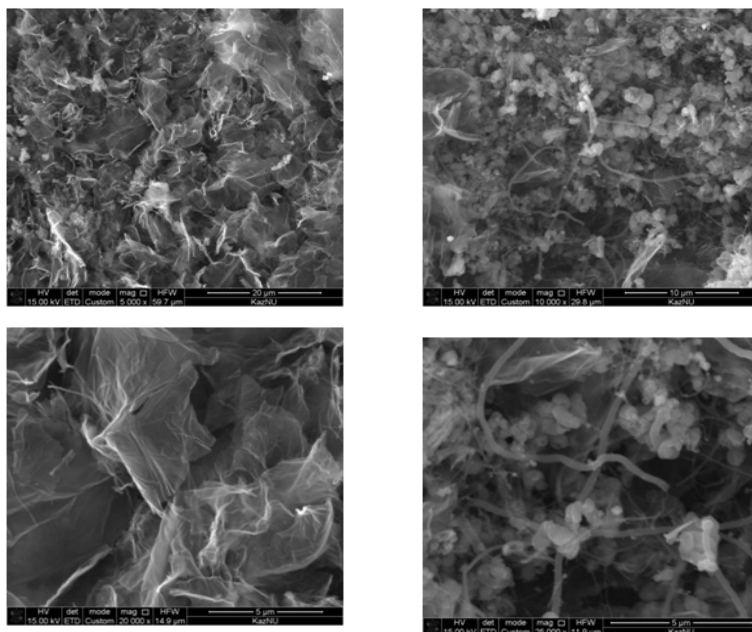


Fig. 3. SEM images of the surface of graphene/CNTs aerogel.

Huge deposits of oil are concentrated in Republic of Kazakhstan, especially at the Caspian shelf, where continuous production and transportation of oil is performed. In this case, oil spills present a great threat to nature's ecosystem and the environment of the region, as a result the question of timely purification of oil-contaminated surfaces arises. This problem can be solved using the technology for obtaining sorbents, aerogels based on carbon materials due to its simplicity and convenience and possibility of re-using them.

For their application as oil sorbents, these aerogels must demonstrate superhydrophobic (oil spills on water) properties, high pore volume, large pore size and high compressibility. These physico-chemical characteristics are achieved by careful selection of the necessary conditions of synthesis, as well as a crucial step is the flow conditions of freeze-drying the aerogel.

During the freeze-drying the solvent reaches a critical state in which it is easy for it to leave voids of hydrogel, and at the same time a stable frame of anhydrous gel is formed. As a result, the structural

voids of hydrogel contain no solvent and it consists of 88-98% of pores and ~ 12% of the material substance.

As is seen from Table 1, the synthesized aerogel based on reduced graphene oxide and CNTs with addition of chitosan solution, has an average value of the specific surface area – 489.5 m²/g and pore volume, that can be related to difficulties of freeze-drying in a continuous mode, which in its turn affects the formation of pores of aerogel.

The obtained aerogels have a macroporous structure with a large pore volume imparts good absorbing properties to aerogel. The prepared graphene/CNTs aerogel has a low density 7.3 mg/cm³, so approximately 98% of aerogel can be filled with air, which is of great advantage for absorption applications. To evaluate the absorption ability of the aerogels, we put the sample of aerogel into a special glass vessel and using a special syringe with a measured volume we flow drops of organic solvent onto the surface of aerogel till its full saturation. The solvent-filled aerogels were taken out and then weighed. The absorption capacities were calculated

as the ratio of the mass of absorbed organic solvent to the mass of aerogel (M_{OS}/M_{AG}) or the ratio of the volume of the absorbed organic solvent to the mass of aerogel (V_{OS}/M_{AG}).

Table 1
Properties of graphene/CNTs aerogel

| | |
|------------------|--------------------------|
| Size | 100×70 mm |
| Density | 7.3 mg/cm ³ |
| Porosity | 88-98% |
| Pore volume | 0.859 cm ³ /g |
| Specific surface | 489.5 m ² /g |

The absorbing ability of aerogels was measured several times for different solvents, especially for benzene, toluene and chloroform. During the experiment it was stated, that absorption rate is rather high: 2 sec for benzene and toluene, and 5-6 sec for chloroform.

Figure 4 shows that obtained graphene/CNTs aerogel can absorb the organic solvents. The sorption capacitance is presented in two variants: M_{OS}/M_{AG} is mass of organic sorbent adsorbed by 1 g of aerogel and V_{OS}/M_{AG} is the volume of the absorbed organic solvent by 1 g of aerogel. As is seen from the bars of Fig. 4, 1 g of obtained graphene/CNTs aerogel can absorb about 26 ml of benzene and toluene and 14 ml of chloroform. While measuring the sorption capacitance by mass we found that the weight of full saturated aerogel with chloroform is much higher than it saturated with benzene and toluene – 24 to 16, respectively. This phenomenon can be explained by the density and nature of the adsorbed organic solvents.

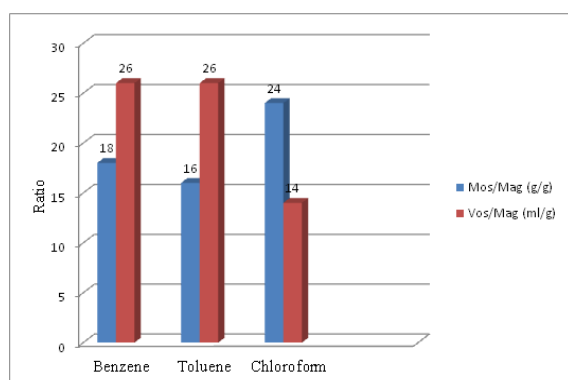


Fig. 4. Diagram of absorption capacities of 1 g of graphene/CNTs aerogel for organic solvents.

It is also interesting to see that the volume-based capacity for toluene and benzene is higher than that for chloroform, because the aromatic solvents have

higher affinity for graphene-based aerogels and wet them better than the aliphatic solvents.

Conclusion

As a result, aerogels based on reduced GO and CNTs were obtained by the gelation process under the conditions of ultrasonic treatment. Physico-chemical characteristics of aerogels, their surface morphology, relative density and porosity were determined. The experimental data show that the obtained samples of aerogel have an average value of the specific surface area – 489.5 m²/g, that is primarily determined by the conditions of continuous freeze drying, resulting in formation of a porous structure. We found that 1 g of obtained graphene/CNTs aerogel can absorb about 26 ml of benzene and toluene and 14 ml of chloroform, it is clear that density and nature of organic solvents also influence on sorption capacitance of graphene/CNTs aerogel. This fact shows the possibility of their application as a re-usable sorbent for collection of oil residues. In future we plan to work on optimizing the process of freeze-drying and synthesis conditions for increasing the specific surface area and pore size of aerogels, the sorption capacitance of aerogels, because all these factors are very important for their application as sorbents for collection of oil residues.

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