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Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142,
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Editorial address: Institute of Organic Catalysis and Electrochemistry named after D. V. Sokolsky
142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22,
e-mail: orgcat@nursat.kz

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АЭРОГЕЛИ НА ОСНОВЕ МНОГОСТЕННЫХ УГЛЕРОДНЫХ НАНОТРУБОК И ХИТОЗАНА

Ф.Р. Султанов^{1,2}, А.А. Уразгалиева^{1,2}, Б. Бакболат^{1,2}, З.А. Мансуров^{1,2}, Shin-Shem Pei³

¹Институт проблем горения, Алматы, Казахстан;

²Казахский национальный университет имени аль-Фараби, Алматы, Казахстан;

³Хьюстонский Университет, Центр перспективных материалов, Хьюстон, США
fail_23@bk.ru

Ключевые слова: аэрогель, карбонизация, сорбция, хитозан, сублимация

Аннотация. Данная статья посвящена синтезу и исследованию аэрогелей на основе углеродных наноматериалов. Аэрогели на основе графена и других углеродных наноматериалов представляют собой класс ультралегких систем, в которых жидкая фаза полностью замещена газообразной. Гомогенизацию углеродных нанотрубок с хитозаном проводили посредством ультразвуковой обработки, после чего для удаления воды из структуры геля применяли сублимационную сушку. Сублимация льда проводилась при температуре -15°C и давлении 40-50 Па. По окончании сублимации, которая в среднем длится 20 часов, полученные аэрогели были карбонизованы при температуре 800 °C в атмосфере инертного газа. Морфология поверхности полученных аэрогелей была исследована методом сканирующей электронной микроскопии. Была исследована гидрофобность и сорбционная емкость полученных аэрогелей по отношению к органическим жидкостям различных плотностей.

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MULTIWALLED CARBON NANOTUBE/CHITOSAN BASED AEROGELS

F.R. Sultanov^{1,2}, A.A. Urazgaliyeva^{1,2}, B. Bakbolat^{1,2}, Z.A. Mansurov^{1,2}, Shin-Shem Pei³

¹Institute of Combustion Problems, Almaty, Kazakhstan;

²al-Farabi Kazakh National University, Almaty, Kazakhstan;

³University of Houston, Center for Advanced Materials, Houston, USA

Keywords: aerogel, carbonization, sorption, chitosan, sublimation

Abstract. This paper is devoted to synthesis and investigation of aerogels based on carbon nanomaterials. Graphene and other carbon nanomaterials based aerogels represent a class of ultra-light materials in which the liquid phase is completely substituted by gaseous. Aerogels were synthesized by homogenization of carbon nanotubes and chitosan under ultrasonic treatment and active stirring, followed by freeze-drying in order to remove the liquid from its structure. Freeze-drying was carried out at temperature of - 15°C and pressure of 40-50 Pa. After freeze-drying which lasted for 20 hours, the as-obtained aerogels were carbonized at temperature of 800 °C in an inert atmosphere. Surface morphology of resulting aerogels was studied using scanning electron microscopy. The hydrophobicity and sorption capacity to organic liquids that are characterized by different densities were investigated.

Introduction. Aerogel is a synthetic porous ultralight material derived from a gel, in which the liquid component of the gel has been replaced by a gaseous. These materials are characterized by extremely low density and exhibit a number of unique properties: toughness, transparency, heat resistance, very low

thermal conductivity. Among them are well known aerogels based on amorphous silica alumina, chromium and tin oxide. At the beginning of the 1990s the first aerogel based on carbon was synthesized [1].

The first carbon based aerogel was obtained in 1989 (Prof. Pekala) by carbonization of resorcinol-formaldehyde (RF) aerogel. In turn, it is usually treated as a kind of highly porous amorphous graphite foam. The basic idea of obtaining of RF-aerogel lies in high-temperature pyrolysis of resorcinol-formaldehyde (1000-1200 °C) at high pressure or in an inert gas atmosphere. In 1996 Hanzawa et al. developed a new approach in obtaining of carbonized RF aerogel characterized by ultrahigh surface area via activation of its carbon skeleton by using carbon dioxide [1].

In view of a huge variety of aerogels, for further investigation it is more perspective to study the carbon nanomaterials based aerogels because of its unique properties - extremely low density, low thermal conductivity, high elasticity (ability to recover its shape after repeated compression and expansion) and the ability to absorb organic liquids. The latter property can be used for oil spill recovery [2].

A huge number of researches are devoted to study of the phenomenon of synthesis of ultra-light, flexible and ultraporous aerogels based on carbon nanomaterials (CNM). The perspective and interesting is the study of the influence of the original type of CNM that used in the synthesis of 3D structures to the physic-chemical properties of the final products.

Nowadays there are many different approaches in synthesis of 3D porous materials. The most perspective and interesting to explore are the following areas of synthesis of aerogels:

1. Chemical reduction of graphene oxide followed by formation of a three-dimensional porous structure [3-5];
2. Composite aerogel based on carbon nanotubes (CNT) and graphene formed by chemical reduction of graphene oxide or using different chemical binders [6-8];
3. The chemical vapor deposition (CVD) method for the formation superhydrophobic aerogels and sponges using high temperature, metal substrate and gas vapours [9-10].

Graphene is a two-dimensional nano-material with a thickness of just one atom that contains sp²-hybridized carbon. Graphene is of great scientific interest because of its unique properties: surface area - 2600 m²/g [11], high thermal conductivity [12], high mechanical stiffness with Young's modulus of about 1000 GPa, [13], an unusual electrocatalytic activity [14] and optical properties [15].

More often in modern literature a great amount of articles are devoted to the area that is associated with the use of graphene oxide as a raw material for the synthesis of aerogels. The group of scientists [16] has done a detailed research in the field of producing of ultra-light and flexible (capable to restore the original shape after mechanical loadings) aerogel based on graphene oxide using its chemical reduction by ethylenediamine (EDA). A certain amount of reducing agent was added to the aqueous dispersion of graphene oxide. The resulting mixture was sealed in a glass vessel and heated for 6 hours at 95 °C, while the bonds were forming and resulted to the overall structure of the hydrogel. During the chemical reduction of graphene oxide, the OH-groups that are on a surface of graphene layers are reduced by functional amino-groups, and this in turn also has an effect on the structure of the graphene layers that are formatting the connection between each other.

After the formation of hydrogel it was freeze-dried for 48 hours while the whole solvent was completely removed from of hydrogel thus formatting the functional aerogel. For stabilization of aerogel, it was placed in a quartz tubular reactor and flashed with argon for 20 minutes until full deaeration. Once all the air has been forced out of the reactor by the stream of argon, aerogel was subjected to Microwave Irradiation (MWI) to carbonize and form the structure of resulting aerogel [16].

An innovative and easy-to-use method of synthesis of composite aerogels based on graphene and CNTs was proposed by Professor Qiu in [17]. Often superhydrophobicity occurs in the conditions of increased roughness, which results in the minimization of the contact between the surface and water due to entrained air [18, 19]. Given this fact, CNTs, or more exactly their vertically stacked arrays, were examined for the possibility of creating of superhydrophobic surfaces due to their large aspect ratios, chemical inertness and natural hydrophobicity [20]. In [19] composite aerogels based on graphene and CNTs were obtained by rapid microwave irradiation, in which the layers of graphene are vertically "carpeted" by aligned arrays of CNT, which in turn forms the superhydrophobicity of material. The resulting aerogel based on reduced graphene oxide [18] was immersed to a solution of acetone with ferrocene and dried. After that it was subjected to microwave irradiation for rapid growth of the nanotubes within the structure of the aerogel due to the decomposition of ferrocene. For the growth of CNTs within

the structure of the graphene aerogel, particles of iron and cyclopentadienyl served as the catalyst and the carbon source, respectively.

Experimental

Multiwalled CNTs were purchased in Nanostructured & Amorphous Materials, Inc. (Houston, USA), a purity of 95% and the outer diameter 20-30 nm. Chitosan was purchased in Alfa Aesar (USA). The purchased chemicals were used without further purification.

Synthesis of MWCNT/chitosan based aerogels

A weighted amount (0.05 g) of multiwalled carbon nanotubes were dispersed in 50 ml of a 1% solution of acetic acid under ultrasonic treatment for 60 minutes. Then, during a vigorous stirring, a certain amount of chitosan was added to the resulting dispersion and stirred under heating for 120 minutes until the chitosan is completely dissolved. The resulting homogeneous mixture was poured into special glass flask and frozen in a volume of liquid nitrogen and freeze-dried. While hydrogels were freezing in liquid nitrogen the particles of ice were formed thus forming the porosity of the whole structure of aerogel.

The as-obtained MWCNT/chitosan based aerogels were carbonized in electrical oven for 60 minutes at the temperature of 800 °C in atmosphere of inert gas. The average heating rate is 5 °C/min.

Study of sorption capacity and hydrophobicity of aerogels

The sorption capacity of aerogels have been studied for a number of organic liquids. Samples were immersed into organic liquids for 60 seconds and then removed by shaking the residual amounts of the organic liquid and weighed. The adsorbed mass of organic liquid was calculated by calculation the difference in mass of the sample of the aerogel before and after the immersion.

The hydrophobicity of resulting aerogels was studied by measuring the contact angle between water drop and a surface of aerogel.

Freeze-drying installation

Using freeze-drying the solvent was completely removed from hydrogel thus giving rise to MWCNT/chitosan based aerogel. Freeze-drying is characterized by a certain ratio of pressure and temperature at which the solid phase, in our case - the ice, turns into a gas without passing through a liquid phase. Freeze-drying was carried out at a temperature of -5 °C and a pressure of 30-80 Pa.

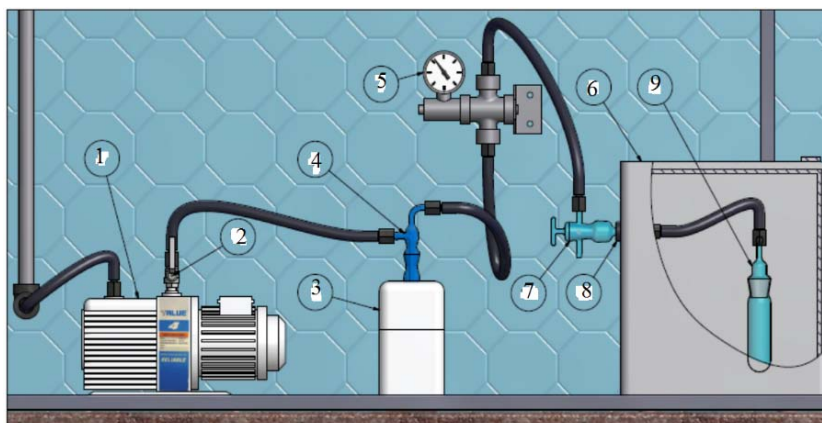


Figure 1 – The scheme of installation for freeze-drying of samples:

1 - the vacuum pump VRD - 4; 2 - ball valve; 3 - a vessel filled with liquid nitrogen; 4 - Glass trap placed in liquid nitrogen to condense water vapor coming from sublimation of ice; 5 - Vacuum gauge; 6 - freezer Exquisit; 7 - the vacuum valve; 8 - a rubber stopper; 9 – flask with frozen hydrogel

Results of research and its discussion

The resulting aerogel based on carbon nanotubes and chitosan is a porous 3D-structure of bright-saturated black color (Fig. 2a). The mechanical properties of aerogel depends on amount of chitosan. Increasing of amount of chitosan improves the mechanical strength of aerogel, but at the same time, the

density also increases what leads to decreasing of its porosity and sorption capacity. It was found that after thermal heating aerogel shrinks in size for 33% (Fig. 2 b, c).

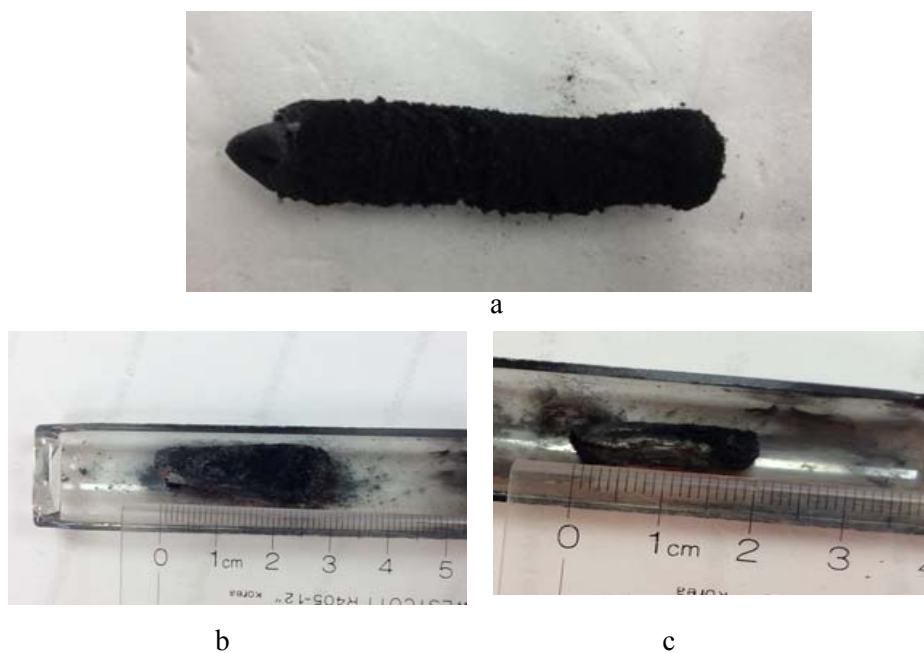


Figure 2 – Image of aerogel based on carbon nanotubes (a); image of aerogel sample before thermal heating in an argon atmosphere at 800 °C (b); image of aerogel sample after a thermal heating in an argon atmosphere at 800 °C (c)

The phenomenon of shrinkage of aerogel was studied. It was found that a pressed tablet of chitosan after annealing to 800 °C in inert atmosphere is carbonized and shrinks in size. The carbonization of chitosan followed by shrinkage in turn leads to shrinkage of aerogel in size (Fig.3)

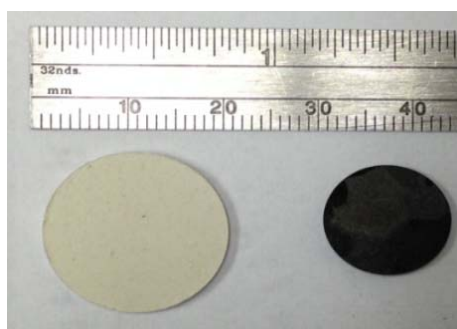


Figure 3 - A pressed tablet chitosan before (left side) thermal treatment at 800 °C and after (right side) of thermal treatment

Table 1. Physical properties of MWCNT/chitosan based aerogels with various chitosan content

Type of aerogel (MWCNT to chitosan ratio)	Relative density of , mg/cm ³	Shrinkage, %
1:2	7,32	33,3
1:10	20,31	30,6
1:20	29,96	27,2

For better sorption of organic liquids, aerogels has to be porous with a low density. As was said above, the increasing of chitosan content increases the density and at the same time that is also adversely affects the sorption capacity of the sample. However, on another hand, the less chitosan we use the mechanically weaker is the obtained sample. In that case, it was important to optimize the amount of chitosan to perform better mechanical strength and sorption capacity. The data of Table 1 shows that with

increasing of amount of chitosan the relative density of resulting aerogels also significantly increases, but the shrinkage of the aerogel structure decreases. According to obtained results, the following investigation of properties was performed using aerogel with MWCNT to chitosan ratio 1:2 because of its low density and higher sorption activity.

For further investigation of the hydrophobicity and the ability of these aerogels to sorb organic liquids their surface morphology was studied by scanning electron microscopy (Fig.4). From scanning electron microscope images can be seen that the surface of the aerogel is presented by a system of macropores, ranging in size from a few tens to hundreds of micrometers (Fig. 4a). Multiwalled carbon nanotubes that have an average outer diameter of 20-30 nm, are localized on the surface of carbonized chitosan skeleton, thereby forming microdefects (Fig. 4 b). This phenomenon may explain the superhydrophobicity of obtained aerogels.

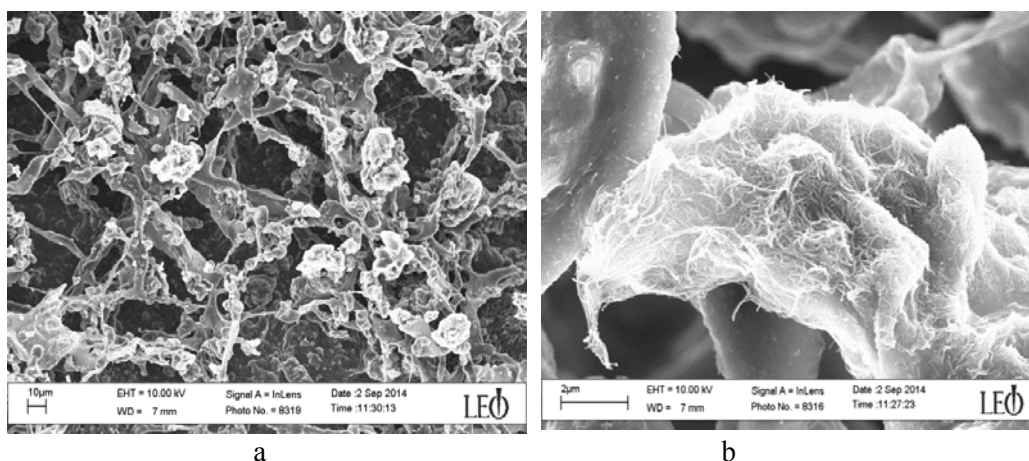


Figure 4 - SEM images of surface of MWCNT/chitosan based aerogels

The presence of MWCNTs on the surface of aerogel's skeleton that is formed by carbonized chitosan particularly forms the hydrophobicity of the surface of the whole aerogel. It was found that the synthesized aerogels exhibit a strong pronounced superhydrophobicity with a contact angle between water drop and a surface of aerogel over 140° (Fig. 5)

It is known that due to its low density and ultra-porosity the aerogels based on carbon nanomaterials exhibit high sorption capacity to organic liquids, oil and petroleum products. Given the fact that their surface is superhydrophobic, i.e. they have the ability to repel the water while adsorbing organic liquid, there appears a promising possibility of its application as a sorbent for collection of oil and petroleum products from the surface of the water. This potential application is also improved by the possibility of its recovery and re-use by a simple squeezing or heating that is followed by evaporation of all amount of adsorbed organic liquid from the structure of the aerogel.

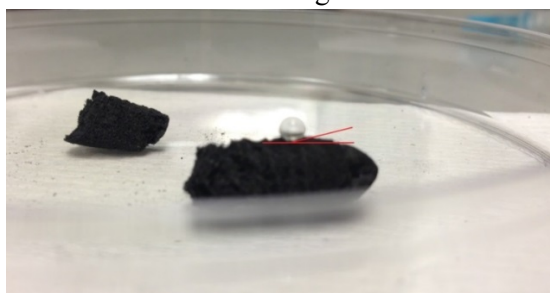


Figure 5 - The image of a water drop on the surface of synthesized MWCNT/chitosan based aerogels with indicated contact angle

Table 2 shows that the samples of MWCNT/chitosan based aerogel exhibits high sorption capacity to organic liquids of different densities. The highest sorption capacity for organic liquids has the aerogel which is characterized by the lowest content of chitosan as well as its density is much lower comparing to

others samples. It has been established that 1 g of that aerogel is capable to adsorb up to 87 grams of diesel.

Table 2 - Quantitative values of sorption of organic liquids by MWCNT/chitosan based aerogels

Type of aerogel, 1g (MWCNT : chitosan ration)	Mass of absorbed n-hexane, g	Mass of absorbed n-octane, g	Mass of absorbed gasoline, g	Mass of absorbed diesel, g	Mass of absorbed pump oil, g
1:2	29,3	58,7	41,3	87,2	82,1
1:10	27,1	30,4	31,3	52,3	51,1
1:20	18,7	19,5	23,3	33,1	28,9

The established high sorption capacity of obtained aerogels to organic liquids, primarily defined by their low density and a well-developed porous surface.

Conclusion

Aerogels based on MWCNTs and chitosan, which acts as a binder, were prepared by creation of MWCNT/chitosan dispersion via ultrasonic treatment, followed by freeze-drying and carbonization at 800°C for 60 minutes under an inert atmosphere of argon. Due to its unique porous structure, these aerogels are characterized by ultraporosity, superhydrophobicity and high adsorption capacity to organic liquids. The investigated properties of MWCNT/chitosan based aerogels provide the opportunity to talk about the prospect of their use as a water-repellent, regenerable sorbent for oil, petroleum products and other organic liquids.

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КӨПҚАБАТТЫ КАРБОН НАНОТҮТІКШЕ МЕН ХИТОЗАН НЕГІЗІНДЕГІ АЭРОГЕЛЬДЕР

Ф.Р. Султанов^{1,2}, А.А. Уразгалиева^{1,2}, Б. Бакболат^{1,2}, З.А. Мансуров^{1,2}, Shin-Shem Pei³

¹Жану Проблемалары Институты, Алматы, Қазақстан

²әл-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан

³Хьюстон университеті, Перспективті Материалдар Орталығы, Хьюстон, АҚШ

Түйін сөздер: аэрогель, карбондау, сорбция, хитозан, сублимация.

Аннотация. Берілген мақала көміртекті наноматериалдар негізіндегі аэрогельдердің синтезі мен зерттелуіне арналған. Графен және басқа көміртекті наноматериалдар негізіндегі аэрогельдер - сұйық фазасы толығымен газ тәріздімен алмастырылған ультражеңіл жүйелер тобы. Көміртекті нанотүтікшелердің хитозанмен гомогенизациясы ультрадыбыстық өңделумен жүргізілді, кейін гель құрылымындағы судан арылу үшін сублимациялық кептіру қолданылды. Мұз сублимациясы -15⁰С температура мен 40-50 Па қысымда жүргізілді. Сублимацияның орташа уақыты 20 сағатқа созылады. Сублимациядан кейін алынған аэрогельдер 800⁰С температурада инертті газ атмосферасында карбонизацияланды. Сканерлеуші электронды микроскопия көмегімен алынған аэрогельдер бетінің морфологиясы зерттелді. Алынған аэрогельдердің әр түрлі тығыздықты органикалық сұйықтарға қатысты гидрофобтылығы және сорбциялық сыйымдылығы зерттелді.

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