

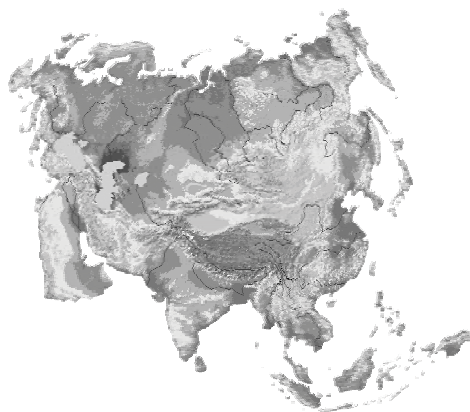
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Study of Sorption Capacity and Surface Morphology of Carbon Nanomaterials/Chitosan Based Aerogels

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Abstract

In this research aerogels were synthesized by homogenization of carbon nanotubes and chitosan under ultrasonic treatment and active magnetic stirring, followed by freeze-drying in order to remove the liquid from its structure. 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 $-15\text{ }^{\circ}\text{C}$ and a pressure of 30–40 Pa. After freeze-drying which lasted for 20 h, the as-obtained aerogels were carbonized at temperature of $800\text{ }^{\circ}\text{C}$ in an inert atmosphere. Surface morphology of resulting aerogels was studied using scanning electron microscopy. The hydrophobicity and sorption capacity of these aerogels to organic liquids characterized by different densities were investigated. In addition, composite aerogels with the presence of graphene nano-platelets in the structure were obtained and the influence of introduction of graphene nanoplatelets on aerogel's properties was analyzed. It was found that composite aerogels based on graphene and carbon nanotubes with chitosan as a glue matrix are characterized by a better-developed porosity of surface with a smaller pore sizes, and their sorption capacity for organic liquids is higher compared with the aerogels based on carbon nanotubes.

1. Introduction

Aerogels represent a class of materials – gels in which a liquid phase is completely substituted by 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 ($1000\text{--}1200\text{ }^{\circ}\text{C}$) 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].

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;
2. Composite aerogel based on carbon nanotubes

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(CNT) and graphene formed by chemical reduction of graphene oxide or using different chemical binders;

3. The chemical vapor deposition (CVD) method for the formation of superhydrophobic aerogels and sponges using high temperature, metal substrate and gas vapours.

Graphene is a two-dimensional nano-material with a thickness of just one atom that contains sp^2 -hybridized carbon. Graphene is of great scientific interest because of its unique properties: surface area – 2600 m^2/g [2], high thermal conductivity [3], high mechanical stiffness with Young's modulus of about 1000 GPa, [4], an unusual electrocatalytic activity [5] and optical properties [6].

In paper [7] three-dimensional graphene aerogels–mesoporous silica frameworks were successfully fabricated. The resulting aerogels exhibited narrow mesopore size distribution (1.87 nm), high surface area (1000.80 m^2/g), and hierarchical macro- and mesoporous structures. These wonderful features made obtained aerogels as a promising adsorbent for the removal of hazardous phenols from wastewater. The adsorption study implied that the novel materials exhibited superior adsorption capacity of phenols to such as phenol, catechol, resorcinol and hydroquinone, with removal efficiencies of 68.6%, 86.6%, 91.1% and 94.7%, respectively.

Authors [8] has a facile, template-free and low-cost strategy has been developed to construct a 3D nitrogen doped graphene aerogel by the incorporation of dopamine which can be served as a highly efficient electrocatalyst in the reduction of H_2O_2 , which is then applied in the nonenzymatically electrochemical determination of H_2O_2 . Electrocatalytic activity of these aerogels was investigated by cyclic voltammetry and chronoamperometry, exhibiting a direct for the reduction of H_2O_2 at -0.5 V. This constructing sensor was applied in detection of H_2O_2 with a detection limit of 0.05 mM, a linear detection range from 0.2 to 35 mM. Due to superior catalytic performance and low cost of obtained aerogels based electrode, it shows great potential in applications for direct sensing of H_2O_2 .

Graphene-based nitrogen self-doped hierarchical porous carbon aerogels were synthesized for supercapacitor electrode application by using chitosan as a raw material through a carefully controlled aerogel formation-carbonization-activation process [9]. Electrochemical investigation measurements showed that the N-doped graphene-based hierarchical porous carbon aerogel represents a good electrode candidate for construction of a solid symmetric supercapacitor, which displays a high specific

capacitance of about 197 F/g at a current density of 0.2 A/g. In addition, the solid state supercapacitor displayed excellent cyclability with a capacitance retention of about 92.1% over 10,000 cycles.

Considering the huge variety of aerogels and their different areas of applications it is clear that carbon nanomaterials based aerogels are more perspective for further investigation and development due to its unique properties – extremely low density, low thermal conductivity, high elasticity (ability to recover its shape after repeated compression) and the ability to absorb organic liquids. The latter property can be used for oil spill recovery [10–11].

The aim of this research is synthesis of highly hydrophobic and porous aerogels based on carbonized chitosan with addition of carbon nanomaterials and study of its surface morphology and sorption capacity to organic liquids for determination of ability of use these aerogel as a water-repellent sorbent.

2. Experimental

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

Graphene nano-powder was obtained by Electron Cyclotron Resonance Chemical vapor deposition [12] at 400 °C using additional microwave irradiation on non-metallic substrate by researchers of Mechanical and Systems Research Laboratories of Industrial Technology Research Institute (Chutung, Hsinchu 31040, Taiwan) and characterized as a high quality of graphene nano-platelets with an average thickness of two layers with a small size of the nano-platelets, its BET surface area is 2041 m^2/g .

2.1. 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 min (35 kHz, 80 W). Then, during a vigorous stirring, a certain amount of chitosan was added to the resulting dispersion and stirred under heating for 120 min 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

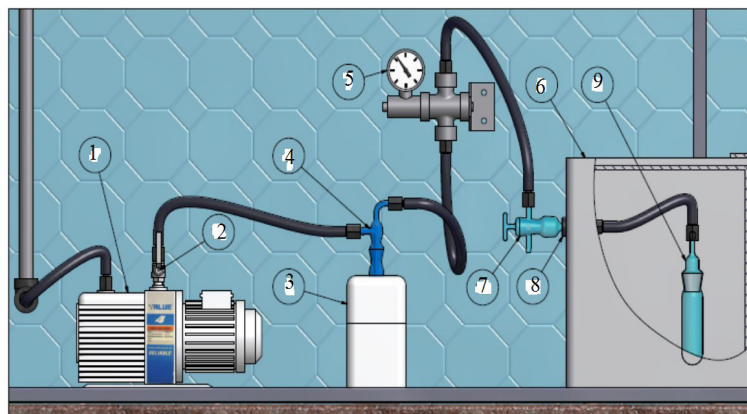


Fig. 1. The scheme of installation for freeze-drying of samples: 1 – the vacuum pump VRD-4; 2 – ball valve; 3 – a vessel filled with liquid nitrogen; 4 – Glass trap placed in liquid nitrogen to condense water vapor coming from sublimation of ice; 5 – Vacuum gauge; 6 – freezer Exquisit; 7 – the vacuum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

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 min at the temperature of 800 °C in atmosphere of inert gas. The average heating rate is 5 °C/min.

2.2. Synthesis of MWCNT/graphene/chitosan aerogels

A weighted amount of MWCNTs were dispersed in 50 ml of a 1% solution of acetic acid under ultrasonic treatment for 60 min. Then under a vigorous magnetic stirring a certain amount of chitosan was added to the resulting dispersion followed by stirring of mixture for 120 min until the chitosan is completely dissolved. With the dissolution of chitosan a weighted amount of graphene nanopowder was added to resulting homogeneous mixture and stirred. The samples were freeze-dried in liquid nitrogen and freeze-dried to remove the solvent. After the process of carbonization of chitosan by heating to 800 °C in atmosphere of argon in electric oven was carried with obtaining of aerogels.

2.3. 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 –15 °C and a pressure in interval of 30–40 Pa (Fig.1).

2.4. 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 sec 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.

3. Results and Discussion

Carbonized chitosan is hydrophobic material by itself, but unfortunately the contact angle between its surface and water drop is not large enough, it is close to 109 ° (Fig. 2 a). The use of carbon nanomaterials as additives which are able to increase the hydrophobicity of a surface is one of the way of creation of superhydrophobic surfaces. In this study we are obtaining superhydrophobic spongy 3D materials with high sorption capacity to organic liquids.

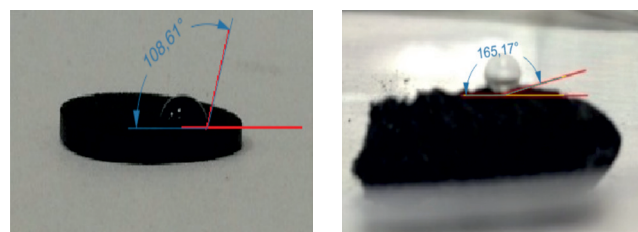


Fig. 2. The image of a water drop on the surface of carbonized chitosan (a) and synthesized MWCNT/chitosan based aerogel (b) with indicated contact angle.

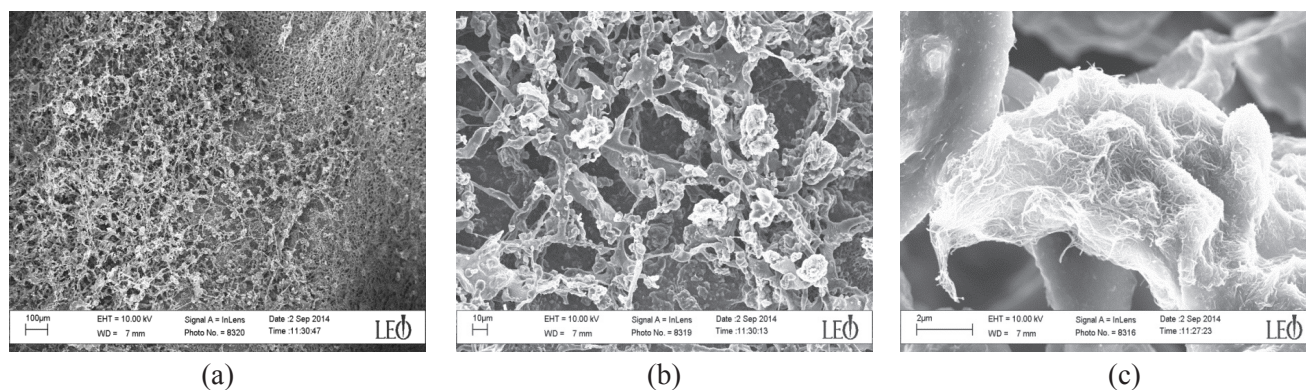


Fig. 3. SEM images of surface of MWCNT/chitosan based aerogels.

Table 1

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

Type of aerogel, 1g (MWCNT : chitosan ratio)	1:2	1:10	1:20
Density of sample, mg/cm ³	7.81	19.23	29.33
Mass of absorbed n-hexane, g	29.3	27.1	18.7
Mass of absorbed n-octane, g	58.7	30.4	19.5
Mass of absorbed gasoline, g	41.3	31.3	23.3
Mass of absorbed diesel, g	87.2	52.3	33.1
Mass of absorbed pump oil, g	82.1	51.1	28.9

The presence of MWCNTs on the surface of aerogel, which structure is formed by carbonized chitosan is definitely improves the hydrophobicity of the whole surface of aerogel. It was found that the resulting samples are characterized by superhydrophobicity with contact angle between a water drop and surface of aerogel larger then 165° (Fig. 2 b).

For further explanation of superhydrophobicity and the ability of these aerogels to absorb the organic liquids the surface morphology of MWCNT/chitosan based aerogels was studied using SEM (Fig. 3). SEM images show that the surface of aerogels is represented by macropore system with the pores ranging in size from a few tens to hundreds of micrometers (Fig. 3 a, b). The MWCNTs with an average outer diameter about 20–30 Nm are located on the surface of carbonized chitosan thereby forming the microdefects of the surface (Fig. 3 c). This phenomenon serves as a key for explanation of the superhydrophobicity of aerogels.

Table 1 shows that aerogels based on MWCNT/chitosan are characterized by high sorption capacity to organic liquids of different densities. Aerogel with a less amount of chitosan shows the highest sorption capacity, because its density is much lower comparing to the other samples. It was found that the increasing of the amount of chitosan leads to

the increase of the density of sample and also to decrease of its sorption capacity. It is established that 1 g of the low density aerogel can absorb about 87 g of diesel.

The density of the samples was calculated by dividing the weight of resulting aerogel to its volume. The samples are synthesized in a cylindrical shape, so the volume of cylinder was taken in account. The results in Table 1 show that with increasing the amount of chitosan the density of aerogel rises greatly while the sorption capacity decreases. Regarding this the optimal ratio of MWCNT to chitosan was taken as 1:2.

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

For the further investigation of the influence of the addition of carbon nanomaterials on the structure and properties of the resulting aerogels the introduction of graphene into the structure of MWCNT/chitosan based aerogels was studied (Fig. 4). Used graphene nano-platelets are characterized with an average thickness of two layers with a small size of the nano-platelets, its BET surface area is 2041 m²/g, were obtained by Electron Cyclotron Resonance Chemical Vapor Deposition [12].

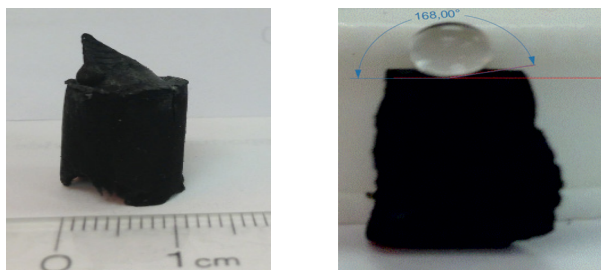


Fig. 4. The image of a water drop on the surface of synthesized MWCNT/graphene/chitosan based aerogels with indicated contact angle.

The study of the surface morphology and sorption capacity of MWCNT/graphene/chitosan based aerogels showed that the resulting aerogels are more resistant to external mechanical influences compared with aerogels based on MWCNTs and chitosan while the both types of aerogels are characterized by the same content of chitosan in the structure. The contact angle between a water drop and surface of ECR CVD graphene/MWCNT's/chitosan based aerogel is 168° (see Fig. 4), its surface is superhydrophobic. It is shown that aerogel based on ECR CVD graphene/MWCNTs/chitosan with own weight 0.09 g is able to carry 110 times higher weight on its surface without any destruction of the structure, while aerogel based on MWCNTs/chitosan which is characterized by approximately same weight is crashed after loading of 10 g on its surface (Fig. 5 a, b). It is possible to make an assumption that the introduction of graphene layers into structure of aerogel enhances stability of its structure to different loadings.

SEM images of the surface of MWCNT/graphene/chitosan based aerogels are presented on Fig. 5. It is shown that introduction of graphene influences on the surface thereby forming more developed pore system that is different to the surface of the MWCNT/chitosan based aerogel (see Fig. 3 a, b). It is also important that graphene affects the average pore sizes, which significantly decreased from a few microns to a dozen (Fig. 6 b). It is



Fig. 5. a – picture of aerogel based on ECR CVD graphene/MWCNTs/chitosan (weight-0.09 g) with loading of 10 g; b – picture of aerogel based on MWCNTs/chitosan (weight-0.085 g) with loading of 10 g.

evident that layers of graphene are vertically located on the surface of the carbonized chitosan thereby forming pores.

It has been found that the introduction of graphene nano-platelets into the structure of MWCNT/chitosan based aerogels is also beneficial to their sorptive properties. Table 2 shows that 1 g of composite aerogel with the ratio of MWCNTs to graphene 1:5 is able to absorb about 101.3 g of diesel. All values of sorption capacities of MWCNT/graphene/chitosan based aerogels to organic liquids is much higher compared to MWCNT/chitosan based aerogels.

4. Conclusion

The as-obtained composite aerogels are characterized by high porosity, superhydrophobicity, high sorption capacity to organic liquids of different densities. It is found that the composite aerogels based on MWCNTs, ECR CVD graphene nanoplatelets and chitosan, which serves as a glue matrix, exhibit stronger stability to weight loadings than aerogels without addition of graphene nanoplatelets. Introduction of graphene layers increases the overall porosity of the structure as well as their sorption capacity to organic liquids. The properties of aerogels studied in this research provide the opportunity to talk about the prospect of their use as a water-repellent, regenerable sorbents for oil, oil products and other organic liquids.

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

Type of aerogel (MWCNT: graphene ratio), 1 g	1:1	1:2	1:5	1:10
Mass of absorbed n-hexane, g	30.2	32.1	36.2	35.9
Mass of absorbed n-octane, g	59.3	59.2	64.1	62.1
Mass of absorbed gasoline, g	43.2	44.4	48.7	48.5
Mass of absorbed diesel, g	90.2	91.3	101.3	100.9
Mass of absorbed pump oil, g	87.8	88.4	99.3	99.4

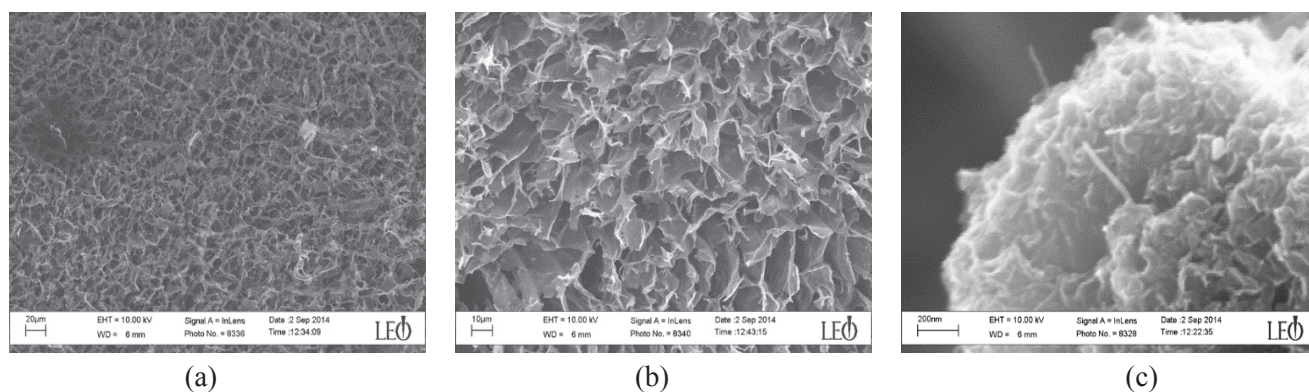


Fig. 6. SEM images of surface of MWCNT/graphene/chitosan based aerogels.

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