Nanoparticle – Based Materials for Various Applications

Zulkhair Mansurov

The Institute of Combustion Problems, 050012, Bogenbay batyr str. 172, Almaty, Kazakhstan

Abstract

The paper reviews recent scientific developments at the Institute of Combustion Problems. The hydrophobic sponges were obtained by coating polyurethane and melamine sponges with carbon nanomaterials. They are excellent water-resistant sorbents for oil, petroleum products and other organic liquids of various densities. Another interesting development is concerned to the synthesis of multiwalled carbon nanotubes on a glass-cloth by use of cobalt oxide catalyst nanoparticles obtained by solution combustion and production of the smart-textile on its basis. A model of soldier with heated jacket based on electroconductive smart-textile was made. The textile showed good electroconductive properties and effective Joule heating by externally applied current. Studies on the development of nanostructured carbon materials and their application as high-performance active components for the electrodes of advanced energy storage systems, in particular electric double layer capacitors were carried out. 2D heterostructures based on graphene and dichalcogenides of transition metals were derived. The epitaxial and single crystals of graphene were synthesized by the CVD-method separately on a copper foil. Two dimension WS_2 layers were synthesized using sulfurization of thin WO_3 films deposited by thermal evaporating on the FTO substrate. A setting time of concrete mass, which could be used as a construction material for 3D printing technology was determined. It was found that calcium chloride decreased the setting time up to 10 min, which is sufficient for the intended application.

1. Introduction

Nanotechnology is one of the most actively discussed directions of scientific and technological investigations which is being highly developed in the recent years and on which the hopes of a wide circle of scientists and technologies anchor their hopes. This direction is considered as a basis of a new industrial revolution which must lead to the abundance of products principally new by their possibilities. On the terms of its logical structure, the term «nanotechnology» must refer to the technology of production of materials and items based on the use of nanosize objects [1].

Nanosubstances are also used as porous materials for chemical and petrochemical industry (catalysts, adsorbents, molecular filters and separators), they are used for production of microelectromechanical devices, fuel elements, electric accumulators and other transformers of energy, they are able to impart new properties (for example, noncombustible nanocomposites on polymer basis or biocompatible tissues for transplantation), they serve as a transport means for delivery of medicinal drugs, etc. [2, 3].

Prof. Pekala has synthesized first carbon aerogel in 1989 via thermal treatment of resorcinol-formaldehyde (RF) – high-temperature pyrolysis in inert medium. In 1996 a scientific group headed by Hanzawa has developed a novel technique for synthesis of RF aerogel using its carbon skeleton activation by CO_2.

Aerogels were synthesized using the following steps: 1) homogenization of carbon nanotubes, and chitosan under ultrasonic treatment and active magnetic stirring; 2) freeze-drying for 20 h in order to remove the liquid from its structure; 3) carbonization at 800 °C in an inert atmosphere.

Surface morphology of the resulting aerogels was studied using scanning electron microscopy.

---

*Corresponding author. E-mail: zmansurov@kaznu.kz

The hydrophobicity degree and sorption capacity for organic liquids of various densities were investigated [5, 6].

Smart-textile was obtained by deposition/in situ synthesis of multiwall carbon nanotubes on glass-cloth-based catalyst decorated with cobalt oxide nanoparticles obtained by solution combustion. The method of solution combustion was applied for coating cobalt oxide nanoparticles on the surface of glass-cloth. The structure and morphology of the smart textiles were evaluated using X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) [7, 8].

Nanostructured carbon materials and their applications as high-performance active components for the electrodes of advanced energy storage systems, in particular electric double layer capacitors (high-power electrical devices designed for various applications including the launch of power installations, wind turbines and electric substations) have been investigated [9].

Coal and petroleum pitch are the main sources of raw materials for production of activated carbons. The wasted biomass can be also used successfully as carbonaceous precursors. The main factors determining selection of a carbon precursor are availability, quantity, value, and cost. The quality of resulting activated carbon depends on the nature of the precursor and on the conditions of thermal and oxidative processes, which occur during carbonization and activation of a biomass material [10–12].

New 2D optoelectronics, sensors, and many other devices can be created by integrating various 2D materials in heterostructures with unique characteristics. However, the controlled synthesis of graphene and related materials and the creation of 2D heterostructures based on them remain to be a challenge. Therefore, the development of new methods is a target area of research. Chemical vapor deposition (CVD) is considered as the most effective synthesis method of graphene and many other 2D materials. However, the structure grown by the CVD method has mainly polycrystalline characteristics. The electrical characteristics of the developed prototypes were evaluated by taking into account their textural features. It was stated that the development of methods for synthesis of individual 2D crystals and of heterostructures based on them is an important task in the field of 2D devices with the intended various applications [13–15].

3D printing technology is developing rapidly, conquering the world. In fact, in this regard a real technological revolution occurs right in front of our eyes. Methods of creating a layered object based on its volumetric 3D model have been wide-ly used in mechanical engineering, electronics and medicine. Even though the production of prosthetic hands, skulls and other parts of the human body by volumetric printing method is widely used, the application of such technology for the construction is sometimes questionable. Behrokh Khoshnevis was one of the first researchers who announced the possibility of applying this technology for the project Contour Crafting – Roboting Construction System [16]. According to his idea, the installation of a great 3D printer resembles the dockside crane mounted on a pre-cleared land. The construction of the house starts from the basement. For this purpose, facility operator gives the appropriate command to the machine, and the workers have to ensure the continuous supply of a special wet and quickly solidifying concrete. 3D printer for construction has a nozzle or extruder that extrudes fast-hardening mixture [17, 18].

2. Investigation of properties and morphology of aerogels

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

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. After freeze-drying which lasted for 20 h, the as-obtained aerogels were carbonized at the temperature of 800 °C in an inert atmosphere.

For applications as oil sorbents, these aerogels or sponges must have a high pore volume, a large pore size, high compressibility and superoleophilicity. This research considers the development of the technology to remove oil spills on the surface of water, where superhydrophobicity is also required. In particular, a filtration system using a water pump and a synthesized carbon nanomaterial filter, which separates organic compounds (oil and other oil products) from water by rejecting water is developed. CNMs based aerogels and sponges have demonstrated both superhydrophobicity and superoleophilicity and are attractive filter materials due to their simplicity, convenience, environmental friendliness, and the ability of reuse.

Carbonized chitosan is a hydrophobic material by itself, but unfortunately, its wetting angle is

close to 109°. The use of CNMs as additives which increase hydrophobicity of the surface is one of the ways of creation of superhydrophobic surfaces.

The resulting composite aerogels based on MWCNTs and chitosan are highly hydrophobic with contact angle of 165°. This strong hydrophobicity is mainly caused by existence of MWCNTs on the surface of carbonized chitosan.

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

To evaluate the influence of the addition of carbon nanomaterials on the structure and properties of the resulting aerogels, graphene was introduced into the structure of MWCNT/chitosan based aerogels (Fig. 1). The graphene nano-platelets are characterized by an average thickness of two layers with a small size of the nano-platelets, its BET surface area was 2041 m²/g.

Aerogel based on MECVD graphene/MWCNTs/chitosan with own mass of 0.09 g is able to carry 110 times higher mass on its surface without any destruction of its structure, while aerogel based on MWCNTs/chitosan which is characterized by approximately the same weight is crashed after loading of 10 g on its surface. The study of mechanical properties of MECVD graphene/MWCNT/chitosan based aerogels showed that the resulting aerogels are more stable to external mechanical influences compared with aerogels based on MWCNTs and chitosan while the both types of aerogels are characterized by the same concentration of chitosan.

SEM analysis of composite MECVD graphene/MWCNTs/chitosan based aerogels indicates that existence of graphene layers improves the porosity of the surface, the pore size decreased from dozen to few microns and the system of connected pores were created.

The study of sorption capacity of both types of composite aerogels based on MWCNTs/chitosan and MECVD graphene/MWCNTs/chitosan based aerogels showed that aerogels with addition of are characterized by higher sorption capacity in regard to organic liquids of different densities. The sorption capacities of composite aerogels based on MWCNT/chitosan and MECVD graphene/
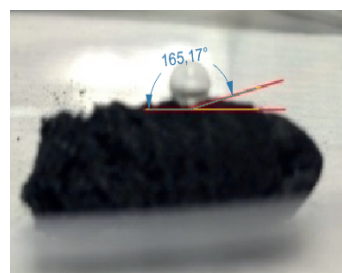

Fig. 1. The image of wetting angle of MECVD graphene MWCNT/chitosan aerogels with the indicated contact angle.
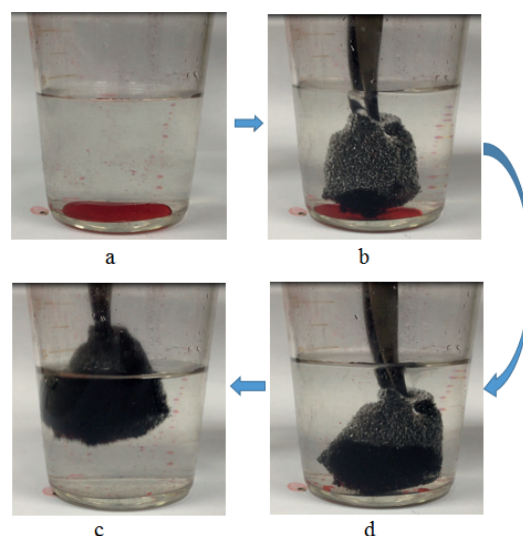

Fig. 2. Illustration of sorption of drop of chloroform, dyed with Sudan, under water by superhydrophobic sponge coated with carbon nanotubes.

MWCNT/chitosan (1 g) in regard to diesel is 87.2 and 101.3, respectively.

Considering the said above, aerogels composite aerogels based on MECVD graphene/MWCNTs/chitosan are highly porous, superhydrophobic and mechanically strong materials with high sorption capacity to organic liquids of different densities. The existence of MECVD graphene nanoplatelets in the structure of composite aerogel improves its porosity, mechanical stiffness and increase its sorption capacity.

The essence of the process of obtaining the hydrophobic sponges lies in coating of sponge's walls, which surface entity of a specific porosity with pore sizes up to 50 μm. Gaphene layers or carbon nanotubes can be used to make the sponges superhydrophobic.

The dip-coating method was used to coat the walls of sponges. The pre-cleaned by an ultrasonic treatment sponge was placed in a dispersion of carbon nanotubes in ethyl acetate, kept inside for an arbitrary chosen length of time, and then removed

and dried to constant weight. The sponge by itself is lyophilic, i.e. actively adsorbs both organic liquids and water. And when absorbing ethyl acetate, carbon nanotubes also deposited and accumulated in its structure. This process was carried out multiple times followed by measuring the weight of the dried sample to determine the degree of loading of carbon nanotubes into the sponge's structure of the sponge.

Figure 2 illustrates sorption of chloroform drop colored with "Sudan red" placed at the bottom of a beaker with water (Fig. 2a). Its density is higher than that of water. The Fig. 2b shows that the hydrophobic sponge completely repels the water due to formation of air particles on its surface, but actively adsorbs the drop of chloroform on the bottom of the beaker (Fig. 2d). The sorption time of drop of chloroform is 5 sec.

3. Electroactive textile produced by coating carbon nanotubes on glass-cloth-based catalyst prepared by solution combustion synthesis

A number of studies have been carried out to obtain electroconductive smart-textile. Smart-textile was obtained by synthesis of multiwall carbon nanotubes on glass-cloth-based catalyst with cobalt oxide nanoparticles.

Cobalt oxide nanoparticles were deposited on the surface of the glass-cloth matrix. In accordance with the weight and moisture capacity of the glass-cloth sample, solution of cobalt nitrate and glycine was prepared. $C_2H_5NO_2$ – glycine acts as a reducing agent. In this experiment content of cobalt oxide was 5 wt.%. The glass-cloth samples of definite sizes were impregnated with an aqueous solution containing stoichiometric amounts of cobalt nitrate and glycine. After that, the dried samples were placed in a muffle furnace or drying oven and heated at 500 °C for 1 h. At this temperature, self-prop-

agating high temperature synthesis takes place. It is seen as a weak bluish glow above the sample. As a result of the reaction, 30–100 nm cobalt oxide nanoparticles were formed.

Synthesis of carbon nanotubes was carried using a classical installation for chemical vapor deposition. The gas flow is He – 650 cm³/min, H_2 – 150 cm³/min, and C_2H_2 – 19.5 cm³/min. The temperature – 710 °C, time of synthesis – 20 min. For investigation of the structure and morphology of the carbon nanotubes and glass-cloth-based catalyst with Co_3O_4 X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used. Obtained carbon nanotubes have diameter of about 23–26 nm.

Current-voltage characteristics of glass-cloth with synthesized CNTs were measured. Pure glass-cloth is dielectric. The sample of CNT on glass-cloth has a resistance R = 0.3636 Ω/cm². Figure 3 shows the current-voltage characteristics of glass-cloth and changing the temperature of glass-cloth with CNT sample at different values of power.

The results show that at the current of 1.25 A the temperature of the sample is 100 °C. The increase of current to 3.25 A the temperature of the sample to 380 °C. As can be seen from the above data, the glass-cloth with CNTs has good electrical conductivity properties. Thus, glass-cloth – CNT composite has a number of advantages.

Studies on the current-voltage characteristics of glass-cloth with carbon nanotubes on Co_3O_4 showed that this material has semiconductor properties. Therefore, glass-cloth with carbon nanotubes is electro-conductive smart-textile and may be used for manufacturing flexible and strong heating elements. To manufacture flexible heating elements electro-conductive cloth electrodes from metal wire were made and connected to the battery. The prototype of a heated warfighter jacket based on conductive smart-textile was made (Fig. 4).
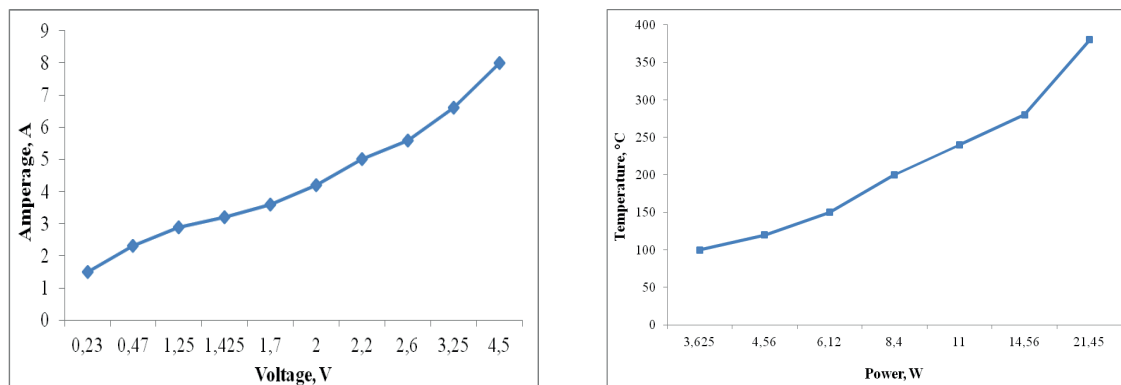

Fig. 3. Current-voltage characteristics and the change of temperature of glass-cloth with CNT sample at different values of power.
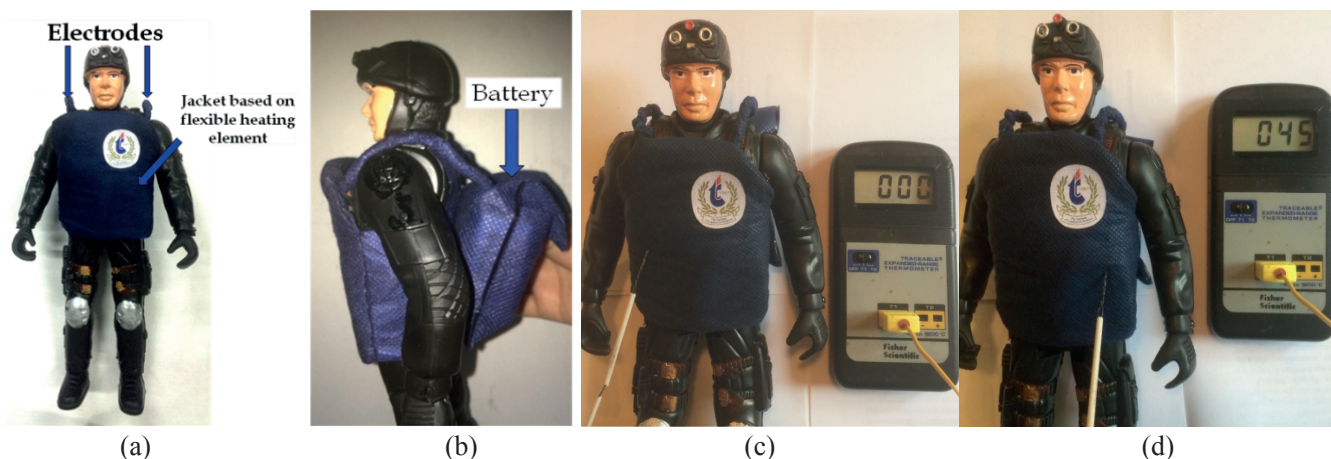
Fig. 4. Images of a soldier model with a jacket based on flexible heating element (glass-cloth and CNTs) (a, b); the images show the temperature of the jacket before applying power (c) and after applying power.

The heating efficiency of the flexible element at low temperature was tested. The temperature of the jacket before applying power was 0 °C. After applying power the temperature of the jacket increased to 45 °C.

The potential of applying the cobalt oxide nanoparticles as catalysts in the carbon nanotube growth process by CVD process was shown. Current-voltage characteristics show good electro-conductive properties of CNT deposited on glass-cloth. A prototype of soldier model with a heated jacket based on electro-conductive smart-textile was made. The heating efficiency of the flexible heating element at low temperature was tested. Before applying power, temperature of the jacket was 0 °C. After applying power the temperature of the jacket increased to 45 °C. Smart-textile based on glass-cloth showed good electro-conductive properties and effective Joule heating by externally applied current. This type of conductive glass-cloth with CNT can be used for various functional applications.

4. Some aspects of research and development of electrode materials for electric double layer capacitors

The Institute of Combustion Problems is also involved in research and development of nanostructured carbon materials and their utilization as high-performance active components for the electrodes of advanced energy storage systems, in particular electric double layer capacitors. These products are high-power electrical devices designed for various applications including the launch of power installations, wind turbines and electric substations.

Activated carbons are universal materials applied as effective adsorbents, catalyst carriers, and for preparing electrodes for electrical double-layer capacitors (EDLCs). The main raw materials for production of ACs are fossil coals, bitumen, petroleum pitch and plant biomass, the latter being a renewable source. It is expedient to use quite dense and strong materials as an initial biomass, among which hard breeds of wood, nut shells and fruit stones are usually chosen.

Selection of the carbonaceous precursors, optimization of energy-intensive methods of their processing and their surface modification methods are actual and most important challenges. In this regard production of high-quality activated carbons derived from rice husk is of great commercial interest. Rice husk is an abundant waste product which is still has no decent application in the Central Asia region. Moreover, this material has shown an outstanding performance in electrochemical capacitors.

Rice husk is lignocellulose biomass which can be converted into high quality activated carbons (ACs). Activated carbons derived from rice husk by using different chemical activation methods such as phosphoric acid, zinc chloride and potassium hydroxide primarily have a developed nanoporous structure. The nitrogen adsorption isotherms measured at 77 K on rice husk activated by phosphoric acid are represented by a combination of Type I and Type IV isotherms (Fig. 5a). This indicates the existence of micropores and mesopores (>2 nm pore diameter), which can provide the capacitance retention at the high scan rates. Electrolyte can freely diffuse inside and penetrate to micropores, where charge accumulation takes place. BET Specific surface area estimated value for the rice husk based carbons activated by phosphoric acid is equal to 1600 m^2/g and pore size distribution represented on Fig. 5b shows heterogeneity of pore sizes.
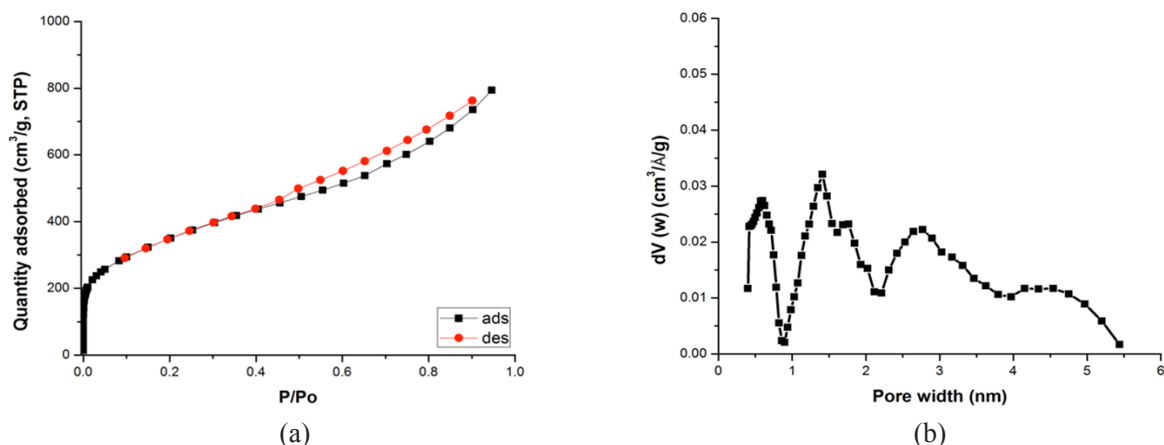
(a)   (b)

Fig. 5. (a) Nitrogen isotherms and (b) DFT pore size distributions of rice husk activated with H_3PO_4.
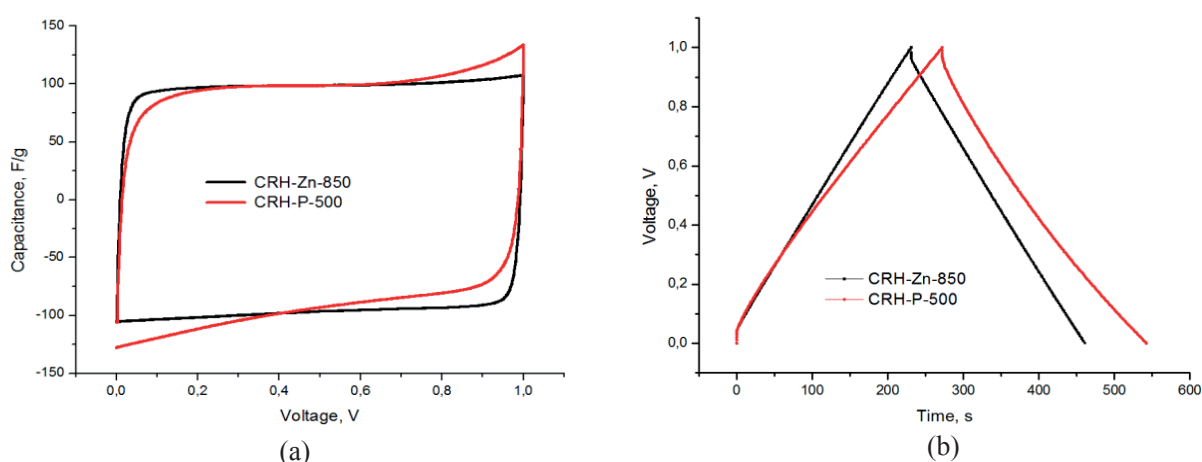

(a)   (b)

Fig. 6. Electrochemical performance of activated carbons derived from rice husk measured in two-electrode cells in $1 \, mol \cdot L^{-1} \, Li_2SO_4$.

The cyclic voltammograms in $1 \, mol \cdot L^{-1} \, Li_2SO_4$ for the zinc chloride activated rice husk carbons are presented in Fig. 6. The rectangular cyclic voltammogram was measured, typical for an ideal electrical double-layer capacitor. This sample shows an excellent charge propagation. On the other hand, the activated carbons derived from rice husk obtained using phosphoric acid as an activation agent exhibits more resistive character of cyclic voltammogram.

Galvanostatic charge/discharge cycling carried out at current load of 200 mA g^{-1} for carbons prepared from rice husk by using different activating agents showed a moderate Ohmic drops. The carbon obtained by phosphoric acid activation has a bigger discharge capacitance in $1 \, mol \cdot L^{-1} \, Li_2SO_4$ which is equal to 110 F g^{-1}. The carbon obtained using zinc chloride activation has more symmetrical discharge curve and its capacitance reaches 100 F g^{-1}.

In Raman spectra of the electrode materials before and after cycling tests at high current loads up to 5000 mA/g indicate a high stability of activat-

ed carbons derived from rice husk, particularly the one activated with zinc chloride (Fig. 7).

5. Synthesis and development of 2D hetero-structures based on graphene and transition metals dichalcogenides

Epitaxial graphene was synthesized on copper foil. 2-D WS$_2$ layers were synthesized using sulfurization of thin WO$_3$ films deposited by thermal evaporation on the FTO substrate.

Synthesis of graphene was carried out in a tubular vacuum CVD quartz reactor installed in a 3-zone high temperature furnace. Methane gas (CH$_4$) was used as a carbon source. Graphenes were synthesized at atmospheric pressure, at 1050 °C, and the ratio of H$_2$: CH$_4$: Ar – 0.2: 0.4: 3 for 20 min.

PMMA layer was coated with graphene by spin coater setup, and separated from copper foil by wet transfer procedure and then moved to the FTO substrate (Fig. 8). This process is very important, as it significantly effects the parameters of portable
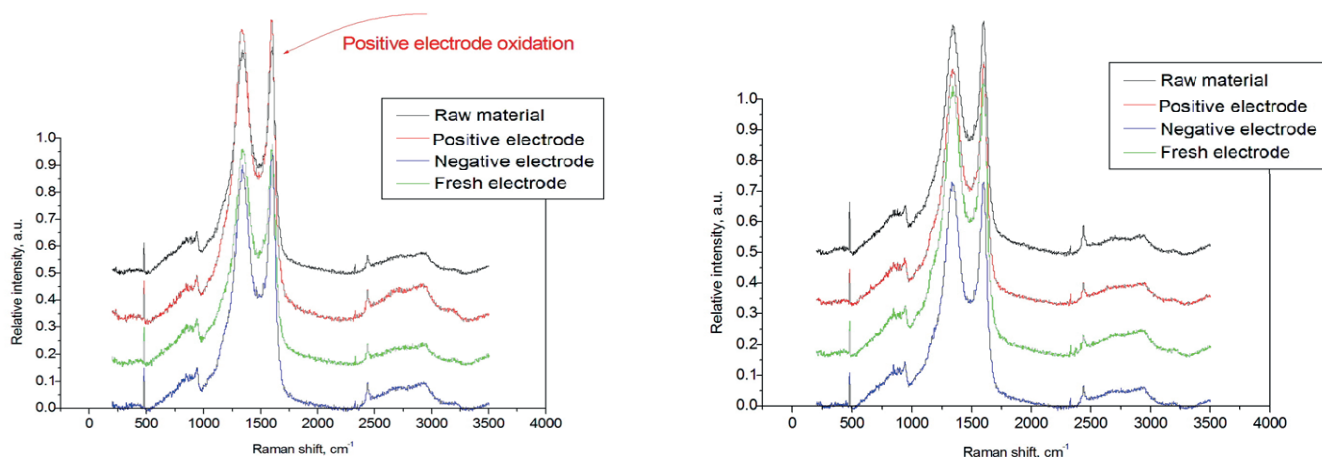
Fig. 7. Raman shift for the carbons activated with KOH (left) and ZnCl₂ (right).
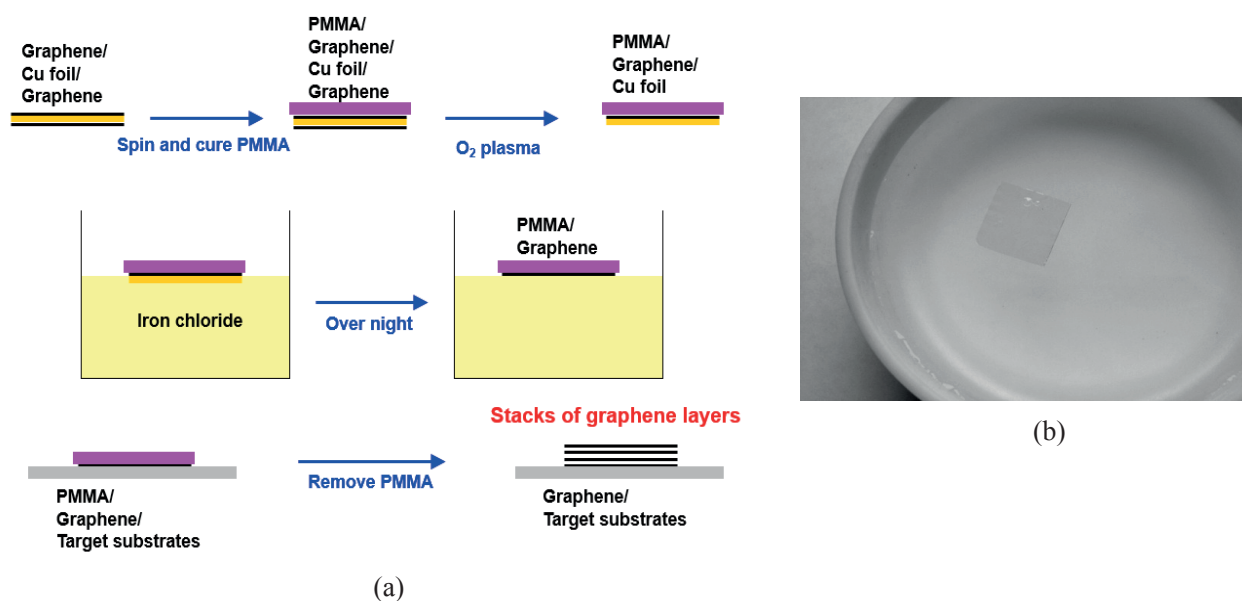

(a)

Fig. 8. a) PMMA assisted wet-transfer; b) graphene layer – coated PMMA.

layers. Copper foil was etched in a solution of iron nitrate. The resulting graphene-coated PMMA layer was deposited on the surface of FTO, after the polymer was washed out with acetone.

Synthesis of WS_2 was performed by sulfurizing WO_3 layer, that was previously deposited on the FTO substrate by thermal evaporation. The deposition of WO_3 on the FTO substrate was performed by vacuum thermal evaporation using ZHD-300M2 equipped with a resistive heater. Synthesis of WS_2 was performed in a quartz vacuum CVD reactor. The process was carried out in argon atmosphere, where the argon molecule acted as carrier material for sublimed sulfur into the reaction zone 2, where the FTO/WO_3 substrate was present. The temperature of the heating zone with sulfur has 120 °C operating system for sulfur sublimation, synthesis zone heated to 750 °C operating systems.

Figure 9 shows a micrograph of the WS_2 surface after synthesis in the CVD reactor by sulfurization. The microstructure has a similar structure of crystalline structures with geometric shapes in the form of triangular crystals at a temperature synthesis 750 °C.

Figure 10 shows Raman spectrum of WS_2 obtained by sulfurization at 750 °C. Peaks of E_{2g} modes and A_{1g} – typical for the WS_2 crystals are visible. Peak intensity is almost the same. The positions of the peak indicate that the thickness of the grown 2D WS_2 is more than 6 layers.

Epitaxial graphene and 2D WS_2 have been synthesized by CVD. Future works will deal with the development of heterostructures by layering obtained 2D materials. The obtained results are of a great interest in the field of photocatalytic water splitting in the visible spectrum as well as in many applications of micro- and nanoelectronics.
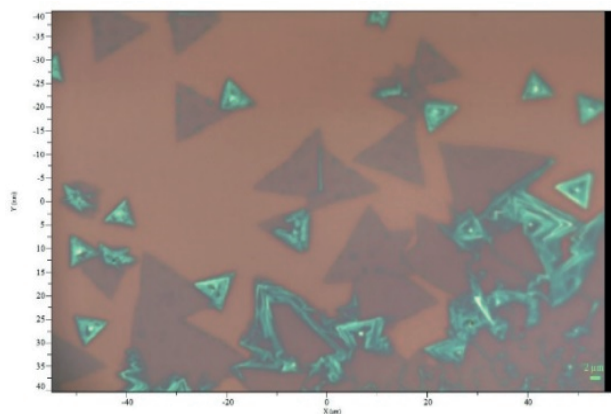
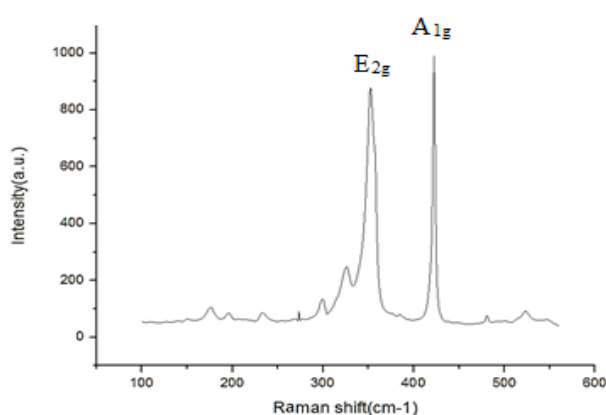Fig. 9. SEM micrograph of the WS_2 crystals synthesized at 750 °C.

Fig. 10. Raman spectra of WS_2 layer.

6. Determination of certain nanostructured additive particles that accelerate the setting time of concrete mass for 3D printing

3D-printer in building construction production robotization is a kind of a conveyor. Naturally, all the branches in this chain must be interrelated, in first place the structure of the printer itself, extruder software, working mixture production, solving of TSP problem, logistics (if solution is prepared near the construction object then the delivery is not needed. Undoubtedly, all these and other issues will be solved due to 3D printing technology. Volumetric printing technology experts are very active. 3D technology are being introduced into life. Presentation of B. Khoshnevis, held in 2012, years 2017–2020 were cautiously called the threshold of the building robots operation, in reality, already in February of 2014 a series of real houses was printed in China.

Nanostructured additive particles for accelerating the setting time of concrete have been known for several decades. There are institutions involved in the solution of various problems of this technology. The main problem is finding the optimal composition for concrete of the desired properties, which were mentioned above. To obtain these properties, a complex mixture of various additives was used. To develop the technology of preparation of fast-hardening mixture the nature of action of hardening accelerator depending on the point of it feeding into the process of preparation of the cement solution was investigated. For the preparation of fast-hardening concrete, cement sand and chemicals were used as a feedstock.

Comparing the obtained test results of additives accelerating setting of concrete samples , the composition of a complex additive (PID-1) was determined. The use of calcium chloride for instance can cause corrosion of reinforcements that is unacceptable for construction of houses.

Table 3 shows that the use of a complex of nanostructured additive particles of PID-1 not only speeds up the setting time of concrete, but also increases the compressive strength.

Then a series of experiments on Vick instrument were conducted for which cement blocks of a definite size were made (State Standard 24211-91). The weight ratio of cement, sand and chemical reagent was 120 g/ 240 g/ 7.2 g, 10.8 g and 14.4 g

Table 2
Characteristics of concrete mass with accelerators

Additive	Characteristics of concrete mass		Amount of additive, % Cement mass
	Water/Cement	Fluidity, cm	
HK (Calcium chloride), HA (Calcium nitrate)	0,35..0,75	0...5	1…2
TNF (Threenatriumphosphate)	0,35..0,75	0…4	2…3,5
NK (Sodium nitrite), NNHK (Nitrite-nitrate calcium chloride)	0,35..0,75	0…6	1,5...2,5
NN (Nitrite-nitrate), NNK (Calcium nitrate-nitrite)	0,35..0,75	0…3	2,5…3

Table 3
Concrete mass strength determination using different kinds of nanostructured additive particles

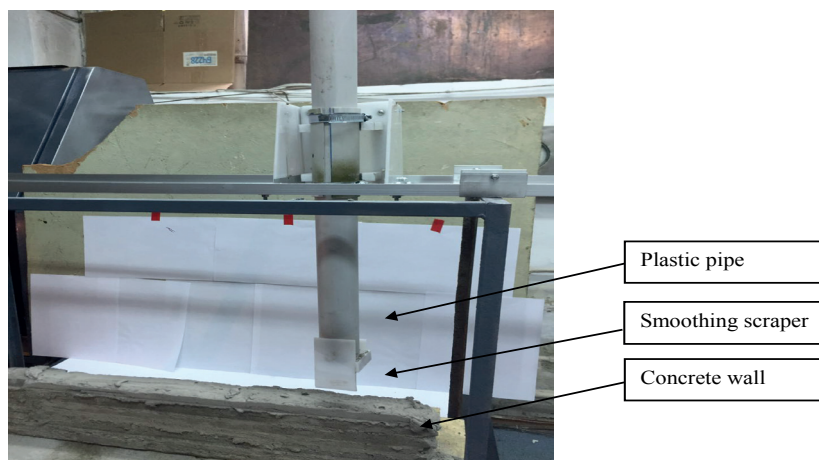| Additive type	% of additive, by weight of cement	Water/Cement	Compression strength [kg/cm²] at the age (in days)		
			3	7	28
NNK	3	0.44	75	90	157
	7	0.44	130	130	165
	10	0.44	125	125	155
	15	0.44	120	120	170
PID-1	3	0.44	130	170	225
	7	0.44	150	165	185
	10	0.44	150	150	185
	15	0.44	150	150	180
NNHK	3	0.44	40	57	122
	7	0.44	65	83	112
	10	0.44	56	80	112
	15	0.44	57	80	112
TNF	3	0.44	90	135	165
	7	0.44	95	122	150
	10	0.44	90	120	150
	15	0.44	100	120	150

Fig. 11. Experimental setup.

respectively. After testing all types of reagents the best result was shown by PID-1 with the percentage of 3–15% of the total cement mass. It is shown that addition of PID-1 in the amount of 3–15% reduces the setting time and makes it sufficient for the technological needs of a cement solution using 3D printer (Table 2).

An experimental setup for testing the mechanical properties of the solution was constructed. The picture of the experimental setup is shown in Fig. 11.

This installation allows to print walls with the thickness of 4 cm and length of 80 cm and a height of 60 cm. Squeezing of solution occurs by force of gravity of the mixture itself. Since the plastic pipe was used in this pioneering design, it is worth mentioning that there is no vibration, because such pipe greatly dampens vibrations.

The thickness of each layer was 2 cm. Figure 12 shows the front side of the wall. It should be noted that there was not any treatment for each layer, which proves the correctness of the selected additives. The installation design allows a slight smoothing of a single layer. The time interval between layers was 10–15 min. The pictures below show the inner side of the wall where each layer can be clearly seen.

Fig. 12. The square of cement walls, printed on the pilot setup.

Moreover, due to this installation a 35×35 cm square with the height of about 14 cm was made. It is worth noting that in order to achieve all the desired properties of the concrete mix a complex of additives should be used. The mass of all additives in the aggregate does not exceed 4% of the weight of concrete solution (Fig. 12).

It is planned to use plasticizers that are polar compounds of carbon radical having hydrophobic and hydrophilic groups with polarizing properties. The percentage content of plasticizing agents is less than 1% of concrete mass.

The use of plasticizers is planned in combination with PID-1. Such additives represents polar carbon radical compounds, which possess hydrophobic properties and polarizing groups with hydrophilic properties. As a result, the composition of nanostructured additive particles increase setting time of concrete mix was identified. The setting time was determined by penetrometer in accordance with the State Standards of the Republic of Kazakhstan. The use of calcium chloride reduced the setting time up to 10 min, which is sufficient for the use of such composition for the buildings construction using 3D technology. The assembled experimental setup allowed demonstrating the process of setting and hardening of concrete without the use of formwork.

7. Conclusions

The article presents the results of investigations carried out at the Institute of Combustion Problems (Kazakhstan) in the field of nanotechnologies and nanomaterials. One of the new directions in the field of carbon nanomaterials is to obtain graphene aerogels and sponges. It has been found that the introduction of graphene nano-platelets into the structure of MWCNT/chitosan based aerogels is beneficial for the development of sorption properties. Accordingly, 1 g of composite aerogel with the ratio of MWCNTs to graphene 1:5 is able to absorb about 101.3 g of diesel oil. The dip-coating method was used to coat by the CNTs and graphene the walls of sponges. Obtained hydrophobic sponge completely repels the water due to formation of air particles on its surface, but actively adsorbs the chloroform. Smart-textile was obtained by synthesis of MWCNT on glass-cloth-based catalyst with cobalt oxide nanoparticles. Synthesis of carbon nanotubes was carried using CVD process. Obtained carbon nanotubes have diameter of about 23–26 nm. Results of current-voltage characteristics investigation shows that the glass-cloth with CNTs has good electrical conductivity properties and effective Joule heating by externally applied current. A prototype of soldier model with a heated jacket based on electro-conductive smart-textile was made. The Institute of combustion problems is also involved in research and development of nanostructured carbon materials and their utilization as high-performance active components for the electrodes of particular supercapacitors. Nanostructured carbon material obtained from rice husk with various activators were tested. The carbon obtained by phosphoric acid activation has a bigger discharge capacitance in 1 $mol \cdot L^{-1}$ Li_2SO_4 which is equal to 110 F g^{-1}. The carbon obtained using zinc chloride activation has more symmetrical discharge curve and its capacitance reaches 100 F g^{-1}. Epitaxial graphene was synthesized on copper foil. 2-D WS_2 layers were synthesized using sulfurization of thin WO_3 films deposited by thermal evaporation on the FTO substrate. Results of investigations show that the microstructure has a similar structure of crystalline structures with geometric shapes in the form of triangular crystals. In the 3D printing technology the use of plasticizers in printing process was tested. As a result, the composition of nanostructured additive particles increase setting time of concrete mix was identified. The use of calcium chloride reduced the setting time up to 10 min, which is sufficient for the use of such composition for the buildings construction using 3D technology.

References

[1]. Z.A. Mansurov, T.A. Shabanova, N.N. Mofa, Sintez i tehnologii nanostrukturirovannyh materialov [Synthesis and technologies nanostructured materials]: Textbook. – Almaty: Kazak University, 2012. – 318 P. (in Russian).

[2]. Z.A. Mansurov, Full scheme for fullerene, graphene, and soot formation in flame. Program Book: Carbon-2016. – Pennsylvania. USA. – P. 11.

[3]. K. Arivalagan, S. Ravichandran, K. Rangasamy and E. Karthikeyan, Int. J. Chem. Tech Res. 3 (2) (2011) 534–538.

[4]. Y. Hanzawa, K. Kaneko, R. Pekala, M. Dresselhaus, Langmuir 12 (1996) 6167–6169.

[5]. F.R. Sultanov, Shin-Shem Steven Pei, M. Auyelkhankyzy, B.T. Lesbayev, Z.A. Mansurov, Eurasian Chemico-Technological Journal 16 (4) (2014) 265–269.

[6]. Z. Mansurov, Fail Sultanov, Shin-Shem Pei, Su-Chi Chang, Sirui Xing, Francisco Robles-Hernandez, Yu-Wen Chi, Kun-Ping Huang. Microwave Plasma Enhanced CVD graphene-based aerogels: synthesis and study // Proceedings of conference "Carbon 2015", Dresden, July 12-17, 2015, Germany, P. 2327.

[7]. G.T. Smagulova, S. Kim, N.G. Prikhod'ko, B.T. Lesbayev, A.V. Mironenko, A.A. Zakhidov, Z.A. Mansurov, Int. J. Self-Propag. High-Temp Synth. 25 (3) (2016) 173–176.

[8]. G.T. Smagulova, N.B. Mansurov, N.G. Prikhodko, A.V. Mironenko, A.A. Zakhidov, Z.A. Mansurov, Synthesis of carbon nanotubes on catalysts prepared by solution combustion on glass-fibers // European Combustion Meeting, Budapest, Hungary. – 30 March-2 April. 2015. – P. 117–118.

[9]. Z.D. Kovalyuk, S.P. Yurtsenyuk, V.M. Bodyarashek, V.V. Netyaga, N.S. Yurtsenyuk, Electrochemical energy 10 (4) (2010) 208–213.

[10]. Z.A. Mansurov, V.V. Pavlenko, M.A. Bijsenbayev, A.P. Kurbatov, A.A. Zakhidov, N.G. Prikhodko, P. Cleszyk, F. Beguin, Gorenie i Plazmohimija [Combustion and Plasmochemistry] 2015, P. 176–179 (in Russian).

[11]. V. Pavlenko, M. Biisenbaev, A. Zakhidov, F. Béguin, Z. Mansurov. Development of active carbons' porous structure for their application in supercapacitors // Proceedings of conference "Carbon 2015", Dresden, July 12-17, 2015, Germany.

[12]. V. Pavlenko, Q. Abbas, M. Biisenbaev, K. Fic, A. Zakhidov, F. Béguin, Z. Mansurov. Electrochemical performance in supercapasitors of carbon prepared from rice husk. Program Book: Carbon-2016. – Pennsylvania. USA. – P. 232.

[13]. R. Beisenov, Z.A. Mansurov, R. Ibrahim, D. Muratov, S.Zh. Tokmoldin and A. Ignatiev. Gorenie i Plazmohimija [Combustion and Plasmochemistry] 2015 – P. 76-78 (in Russian).

[14]. R. Beisenov, Z.A. Mansurov. Karbid kremnija: Osnovnye harakteristiki, metody poluchenija i primenenija [Silicon Carbide: Basic characteristics, methods of obtaining and application] // "Kazakh University". - 2015. – 150 p. // ISBN 978-601-04-1182-1 (in Russian).

[15]. R. Beisenov, Z.A. Mansurov. Epitaxial growth of graphene and dichalcogenides of transition metal by CVD method // All-Russian school-conference with international participation. – Abstracts book. «Chemistry and physics of combustion and dispersed systems». – 2016. – P. 14–17.

[16]. B. Khoshnevis, Automat. Constrtion. 13 (1) (2004) 5–19.

[17]. Bethany C. Gross, Jayda L. Erkal, Sarah Y. Lockwood, Chengpeng Chen, and Dana M. Spence, Anal. Chem. 86 (2014) 3240−3253 // doi.org/10.1021/ac403397r

[18]. Ch. Daulbayev, M. Rodin, Y. Aliyev, Z. Mansurov. Determination of certain additive that accelerates the setting time of concrete mass for 3D printing. Conference abstracts of 5th International conference ZEMCH 2016 (Zero Energy Mass Housing), Malaysia. P. 108-114.