Diatomite: a natural occurring bioinspired nanomaterial with complex-shaped and its application

A. Zhalgasbaikyzy[1], M. Nazhipkyzy[1,2*], A. Nurgain[1,2], A.A. Zhaparova[1,2], Z.A. Mansurov[1,2]

[1]Institute of Combustion Problems, 172 Bogenbai Batyr Str., Almaty, Kazakhstan,
[2]Al-Farabi Kazakh National University, 71 Al-Farabi Ave., Almaty, Kazakhstan

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Abstract

This paper presents the results of the study of natural diatomite of the Mugalzhar region by physico-chemical methods of analysis. Natural diatomite was used as a substrate for the synthesis of multi-walled carbon nanotubes (MWCNT). Cobalt chloride was used as a catalyst. Elemental analysis of obtained multiwalled carbon nanotubes was performed using an attachment to a scanning electron microscope (SEM) using energy dispersive X-ray spectroscopy (EDS) on an EDAX setup (AMETEC Materials Analysis Division, USA).

Keywords: Diatomite, Multiwalled carbon nanotubes, Heavy metal

1. Introduction

Engineers of nanomaterials can have dreams of inorganic nanoparticles which spontaneously are going to desirable three-dimensional structures with hierarchically located patterns from nanometer scale to macroscale.

Ideally this process will happen in the conditions of the environment, in water solution at a neutral pH and to receive material with desirable properties. Actually, such ascending self-assembly of the nanostructured materials is already reality. Organisms which biosynthesize minerals based endo-or exo-skeletons (biominerals), give numerous examples of three-dimensional inorganic materials with hierarchical structure. It is much more difficult than structure of biominerals, than their geological and synthetic analogs that perfectly illustrates as superiority of process of a biomineralization over abiotic mineralogenesis, and our incomplete understanding of mechanisms of biological self-assembly. Now about 70 various biomineral chemicals are known with a calcium carbonate (for example, sinks of mollusks), calcium phosphate (for example, bones) and silicon dioxide (for example, cellular walls diatom frustules) [1]. And one of them is diatomite or diatom silica and about 20 countries own diatomite deposits around the world [2].

The reserves of diatomite make more than three billion tons where about 1% is annually mined. Kazakhstan is particularly rich in the diatomite resources and to the southeast of Emba, right by the railway, there is the Utesay field of diatomite with an area of almost 100 km^2. Here in the 60-ies of the twentieth century, two deposits - Utesay and Kirghiz - with reserves of several million tons were explored. The thickness of the diatomite layer is more than 8 meters. The resources for this field are estimated at more than 1 billion tons of diatomite.

To the north-east of the town of Emba, in the interfluve of the rivers Aula, Kundyzdy and Emba, the Zhalpak, diatomite field is 84 km^2. Here, diatomite is exposed in the form of spectacular white cliffs up to 20 m in height and form a plateau with overlapping diatomite cover of later rocks with a thickness of 0.5-1 m. The thickness of the productive diatomite layer here is up to 40 m, and the estimated resources are 1.8 billion tons of diatomite [3].

So, why we should pay attention to diatomite and what exactly is? Diatomite ($SiO_2 \cdot H_2O$) also known as the diatomaceous earth, kieselgur or Celite, is represents some kind of siliceous sedimentary breed created throughout centuries by siliceous diatom skeletons of single cell photosynthetic microalgae and the diatomite of the seaweed besieged at the bottom of lakes or which are present at the marine environment found in the nature. Diatom frustules, are one of the most impressive examples of biologically received nanostructured materials and each of the estimated 100 000 types the diatom of species has the special cover from silicon dioxide called by a frustules with the characteristic form decorated with the unique drawing of nanodimensional signs, such as time, ridges, thorns and patterns [4].

*Ответственные авторы
E-mail: meruert82@mail.ru (M. Nazhipkyzy)

Diatomite consists a wide range the diatomaceous of forms and the sizes, usually from 0,4 nanometers to 200 mm, in the structure containing up to 80-90% of emptiness [5].

The structure of each frustules has several hierarchical layers of the porous membranes or structures differing in forms, the sizes and patterns. From the Fig. 1, which is SEM pictures of diversity of shapes and 3d structures in diatoms and Fig. 2, which is Optical microscopy photographs, can be seen a remarkable variety the diatom of forms, morphology and porous architecture in which some of the most widespread examples the diatom forms are visibly presented. This variety of forms and ordered porous structures incontestably shows the accuracy and gloss of natural design on micro and nanoscale, giving a huge opportunity to use this material for broad application.

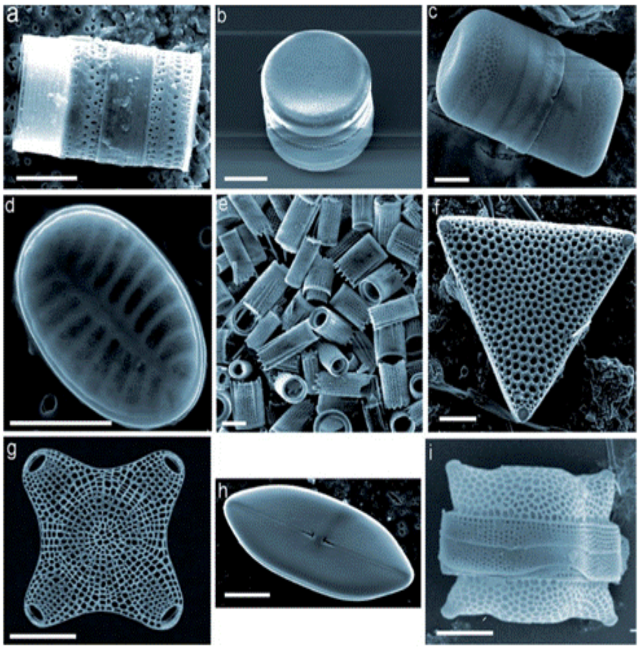


Fig. 1. Extaordinary diversity of shapes and 3d structures in diatoms built by silica.

As diatomite is extracted from geological deposits, it may contain several impurity, such as organic substances and oxides of metals, namely: Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O and P_2O_5 that can have an adverse effect on its properties of application. Thus, various ways of cleaning, such as thermal preliminary calcination and washing of HCl, were usually applied to improvement of distribution of the sizes of a time on diatomite by restoration of impurity from the truncated cones [6].

Diatomite possesses a unique combination of physical and chemical properties, that is high permeability, high porosity, small sizes of particles, big surface area, low heat conductivity and chemical inertness [7].

This sedimentary silica powder has received great attention and has been used in various applications, such as the filtering environments for various inorganic and organic chemicals, as absorbents, carriers of catalysts, fillers and also in pharmaceutical area [8-10].

Besides, the surface of diatomite is characterized by existence the silanol groups which are the adsorption sites for an immobilization of chemical compounds. Thus, diatomite is special interest among natural sorption materials. Concerning the applications connected with adsorption researches for determination of potential of the raw diatomite for restoration of heavy metals in water have been conducted [11-14].

Thanks to the hydrophilic property, existence of a large number in many regions of the world, chemical stability, extremely low cost and not toxicity this fossil material can be the ideal added component.

However, despite the unique combination of physical and chemical properties and large amount of deposits of diatomite, its use as adsorbent for water treatment and as a catalyst carrier or support still has not been investigated properly in Kazakhstan.

That's why, the purpose of our laboratory is studying the chemical nature of and texture of Kazakhstan's diatomite and fabricating sorbents

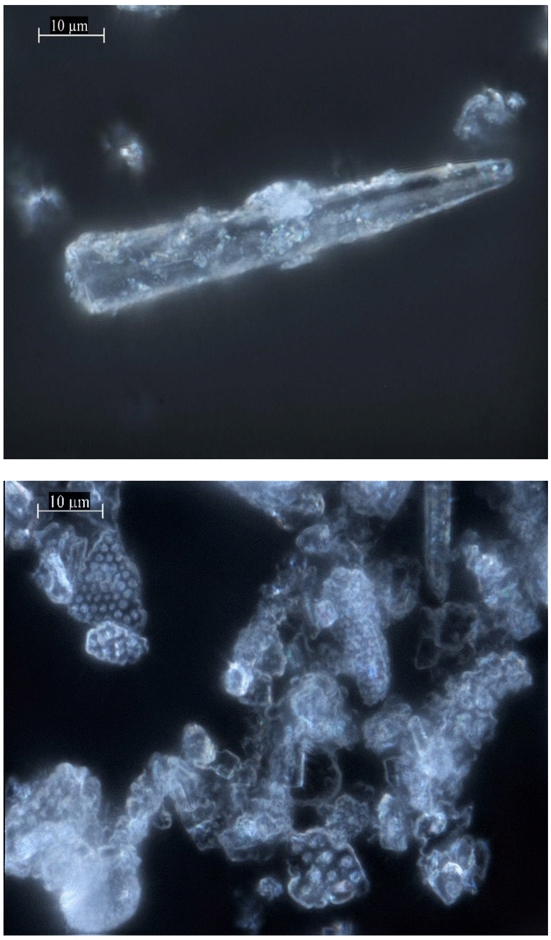


Fig. 2. Optical microscopic images.

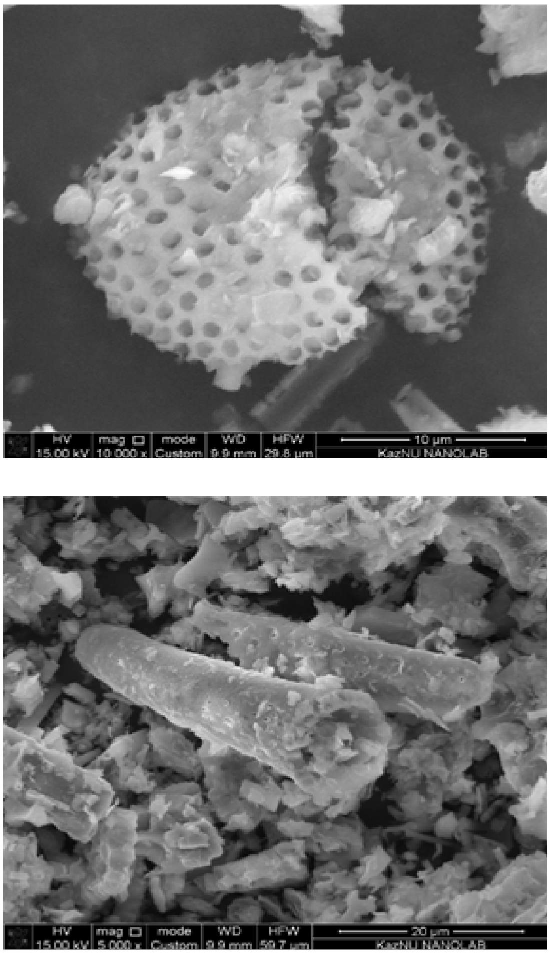


Fig.3. Scanning electron microscopic images of diatomite.

from diatomite and currently, our laboratory working on application of diatomite for synthesis of CNTs, further using them in water remediation. For this porpoise diatomite samples were investigated by Optical microscopic images show the mineral composition of the diatomite original sample, the form and the appearance of the frustules.

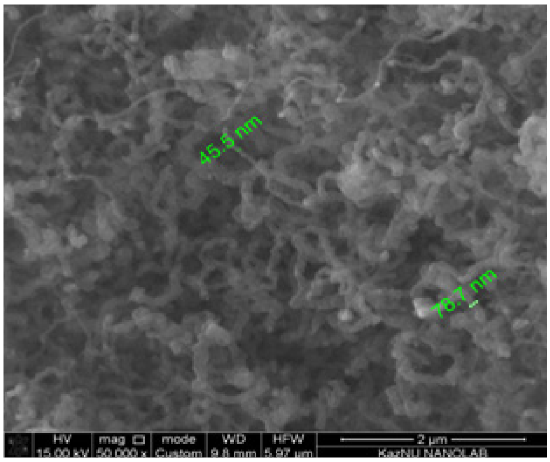
2. Results and discussion

Figure 3 shows a snapshot of natural diatomite, where you can clearly see the skeletons of diatom algae and broken particles of the remains of diatom algae, also in the figure there are particles that differ from the skeletons and represent foreign minerals present in the diatomite.

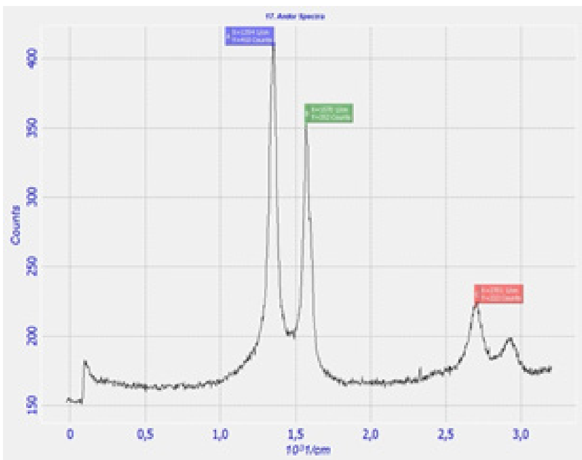
The structure of each truncation has several hierarchical layers of porous membranes or structures, differing in shapes, sizes and patterns. According to some literary sources, diatomite has a large inner surface, contains up to 80–90% of voids. SEM observations of natural diatomite show a clean surface with open pores and associated channels, micropores of varying shapes, sizes, and pore spaces.

From Fig. 3 has been seen certain diatom pores, a high density of regularly ordered pores with a diameter of 1 to 3 µm is seen. The pores are arranged in parallel sets with uniform pores that create the structure of honey combs. You can also see macropores in the size of 0.9 µm. When analyzing the figures, we can say that the surface of diatomite has a heterogeneous structure with local clusters and «clogged» pores, which are caused by the heterogeneity of the composition and the natural origin of diatomite.

In this regard, multiwalled carbon nanotubes (MWCNTs) was synthesized on catalyst system that prepared from natural biomaterial generated from single cell algae, diatomite and by immobilization of Co catalyst particles on to diatomite substrate. A new approach for obtaining MWCNTs by using silica diatomite with natural pores structure has been developed and employed. The resulting carbon nanotubes were examined using a scanning electron microscope, and Raman spectroscope (Fig. 4). According to Raman spectroscopy results, the position G of the peak in the range 1570-1580 cm^{-1} is characteristic for carbon nanostructures of the graphite group, and the shift to the low-frequency region is most characteristic of carbon nanotubes.



(a)



(b)

Fig. 4. The SEM pictures (a) and Raman shifts (b) of MWCNTs on diatomite substrate and Co based catalyst at 800 °C (b).

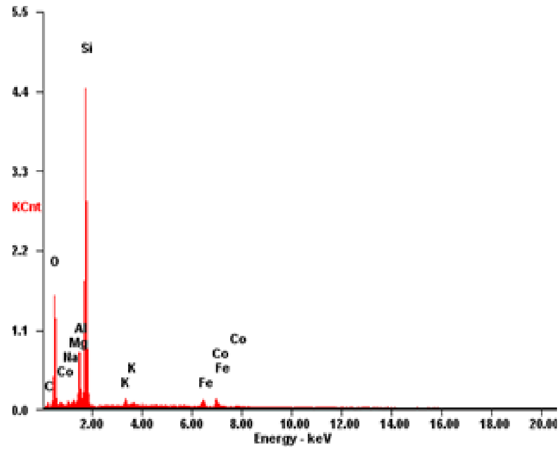


Fig. 5. The EDAX analysis of MWCNT.

The increase in the intensity of the 2D peak in the region 2710-2715 cm^{-1} indicates an increase in the orderliness of the structure of the material. While the peaks D at 1350-1360 cm^{-1} and G + D in the region of 2940 cm^{-1} arise as a result of the disorder of the structure.

For conclusion, a novel approach was developed for synthesis CNTs on diatomite supported catalytic system by CVD method. The result of Raman spectroscopy revealed that the synthesized CNTs on both Co precipitated samples are multiwalled material, however the ratio of the intensities of the peaks $I_{(2D)}/I_{(G)}$ is much high, which indicates a fairly high degree of ordering of the sp^2 carbon structure under investigation. Elemental analysis of obtained MWCNT was performed using an attachment to a scanning electron microscope using energy dispersive X-ray spectroscopy (EDS) on an EDAX device (AMETEC Materials Analysis Division, USA). K, Fe, Co (Fig. 5).

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Диатомит: природный возобновляемый наноматериал с комплексной формой и его применение

А. Жалгасбайкызы[1], М. Нажипкызы[1,2],
А. Нургаин[1,2],А.А. Жапарова[1,2],З.А. Мансуров[1,2]

[1]Институт проблем горения, Алматы, Казахстан
[2]КазНУ имени аль-Фараби, Алматы, Казахстан

Абстракт

В данной работе представлены результаты по исследованию природного диатомита Мугалджарского месторождения физико-химическими методами анализа. Природный диатомит использовался в качестве подложки для синтеза многостенных углеродных нанотрубок. В качестве катализатора использовался хлорид кобальта. Элементный анализ проводился с помощью приставки к сканирующему электронному микроскопу методом энергодисперсионной рентгеновской спектроскопии на устройстве EDAX.

Ключевые слова: диатомит, многостенные углеродные нанотрубки, тяжелые металлы

Диатомит: кешенді пішіні бар табиғи жаңаланатын наноматериал және оның қолданылуы

А. Жалғасбайқызы[1], М. Нажипқызы[1,2],
А. Нұрғаин[1,2], А.А. Жапарова[1,2], З.А. Мансуров[1,2]

[1]Жану проблемалары институты, Алматы, Казахстан
[2]Әл-Фараби атындағы ҚазҰУ, Алматы, Казахстан

Абстракт

Ұсынылып отырған жұмыста Мұғалжар өңірінің табиғи диатомитін физико-химиялық талдау әдістерімен зерттеудің нәтижелері келтірілген. Табиғи диатомит көпқабатты көміртекті нанотүтікшелерді синтездеу үшін табақша ретінде қолданылды. Катализатор есебінде кобальт хлориді қолданылды. Элементтік талдау сканирлеуші электрондық микроскоптың қосымшасы энергодисперсионды рентгендік спектроскопия әдісімен EDAX қондырғысында жүргізілді.