UDC 613.26/.29:664

Aluminosilicatehalloysite nanotubes as a tool of modern nanocomposites for food safety

Haiuk N., **Tsekhmistrenko O.**, **Seleznyova A.**

Bila Tserkva National Agrarian university

E- mail: Haiuk N. gayukn_14@ukr.net, Seleznyova A. alexselena@ukr.net

OPEN ACCESS

Гаюк Н.В., Цехмістренко О.С., Селезньова О.О. Алюмосилікатні нанотрубки галуазиту, як інструмент сучасних нанокомпозитів для харчової безпеки. Збірник наукових праць «Технологія виробництва і переробки продукції тваринництва», 2023. № 1. С. 105–113.

Haiuk N., Tsekhmistrenko O., Seleznyova A. Aluminosilicatehalloysite nanotubes as a tool of modern nanocomposites for food safety. «Animal Husbandry Products Production and Processing», 2023. № 1. PP. 105–113.

Рукопис отримано: 10.03.2023 р.
Прийнято: 24.03.2023 р.
Затверджено до друку: 25.05.2023 р.

doi: 10.33245/2310-9289-2023-178-1-105-113

Nanoscale natural clay minerals, which include Si, O, Al, and Mg, are a class of environmentally safe inorganic materials with unique structures and diverse morphologies, including nanorods, nanofibers, and nanotubes. Aluminosilicatehallusite nanotubes (HNTs) are relatively new objects of research in materials science, they have a number of environmental and economic advantages compared to carbon nanotubes (CNTs), as well as fullerene and graphene. Natural halloysites are an order of magnitude cheaper than their synthetic counterparts. The location of halloysite is quite common, for example, in the KryvyiRih region and other places in other countries. Due to their high environmental friendliness and bioavailability, HNTs can be used in medicine, including as drug carriers with controlled release. HNTs can also exhibit (photo) catalytic properties, have high adsorption properties in relation to heavy metals Cu(II), Pb(II), Cd(II), Zn(II), Cr(IV) and Co(II) and solutions, containing dyes, pesticides and some other organic pollutants, as well as toxic gases (ammonia, hydrogen sulfide). HNTs in combination with other metals, such as Mn, Ti, acquire various practical applications. HNTs were introduced to ensure better functional photo(electro)catalytic properties of composites that can be a substrate, especially in the case of nanotube oxide decoration. For example, titanium, a white pigment, non-toxic, is included in the list of food additives and is designated as E171. Contained in food products: candies, cookies, cakes, chicken fillet, crab sticks, chewing gum, chocolate products. Although the addition of titanium dioxide in food products is permitted by many official documents, there is insufficient data in the scientific literature regarding the potential danger of titanium dioxide to the human body.

Increased interest in TiO_2 is due to its high photocatalytic activity, which allows to realize processes of destruction of organic compounds, including ecotoxicants, into safe products. HNTs, or materials based on them, have found many useful applications in the treatment of drinking water and industrial wastewater. The structural features of HNTs make it possible to obtain new composite materials based on them, such as, for example, imohalite nanotubes (INTs) of a wide functional purpose and to determine the physicochemical patterns of their formation.

Therefore, the relevance of the work lies in the combination of hallusite nanotubes and titanium dioxide as composite materials using electrosynthesis, and the analysis of the influence of the phase composition, photocatalytic activity of the composite material on the safety of its practical use, including in the food industry.

Key words: aluminosilicates, nanotubes, nanomaterials, inner surface, safety, halluasite, titanium dioxide, composites, nanocomposites, synthesis.

The objects of research are titanium dioxide andhallusite nanotubes.

The aim of the research is to study the influence of the phase composition and activity of halloysite and titanium dioxide on the functional properties of wastewater destruction (purification). To determine the prospects of using nanocomposites with hallusite nanotubes and titanium dioxide.

The main tasks of the research:

– to characterize materials using electron microscopy and quantitative photometric analysis.

– to summarize data on the influence of photocatalytic and photoelectrocatalytic properties on the functionality of titanium dioxide and HNTs in food products and wastewater treatment.

– comparative characteristics of various modifications (rutile/anatase) of titanium oxide in electrosynthesis.

Problem statement and analysis of recent research. Today, countries with developed economies focus on the development and greening and application of nanotechnology as a promising industry. Every year, the amount of funding for research and new developments increases. Nanoproducts are already used in the energy, chemical and construction industries, the production of cosmetics, and the food industry. The introduction of nanomaterials into medicine and pharmacology has begun. The use of nanotechnologies and nanomaterials in environmental protection and the food industry is also promising.

Halloysite is an aluminosilicate, a natural, environmentally friendly nanomaterial with the chemical composition $[Al_2Si_2O_5(OH)_4 \cdot 2H_2O]$. The dimensions of hallusite nanotubes (HNTs) vary in length – from tens of nm to several microns, sometimes even reaching >30 microns [1], in outer diameter from 30 to 190 nm, in inner diameter – from 10 to 100 nm [2].Interlayer water is removed with slight heating (100–120 °C), while the distance between the layers decreases from 1 nm to 0.7 nm [4].

Fig. 1. **Appearance of HNTs (hallusite nanotubes).**

The folding of halloysite into a tubular (Figure 2a) structure occurs due to the mismatch in the rows of the tetrahedral layer of SiO_2 and the adjacent layer of Al_2O_3 with an octahedral structure [5]. As a result, a layered hallusitenanotubular structure is formed, which has the formula $[Al_2Si_2O_5(OH)_4 \cdot 2H_2O]$.

Si−O−Si groups are placed on the outer surface of the nanotubes, Al−OH groups are located on the inner surface, as a result of which positive and negative charges appear on the outer and inner surfaces, respectively, in the ratio Al:Si1:1 (Figure 2в) [6]. The surface thus represents a potential area for deposition of nanoparticles [7]. It is known that HNTs have occupied an important niche in modern nanotechnology with applications ranging from electronics, ultralight structural materials, energy conservation, to catalysis and electrochemistry. They reveal (photo)catalytic properties that have not yet been sufficiently studied, especially in combination with innovative technologies of oxide materials, and are a window of new opportunities for the creation of functional materials with specified properties [17].

There are two types of hydroxyl groups in halloysite that maintain the shape of the nanotube: one is internal hydroxyl groups, the other is external HO-groups(Figure 2c).

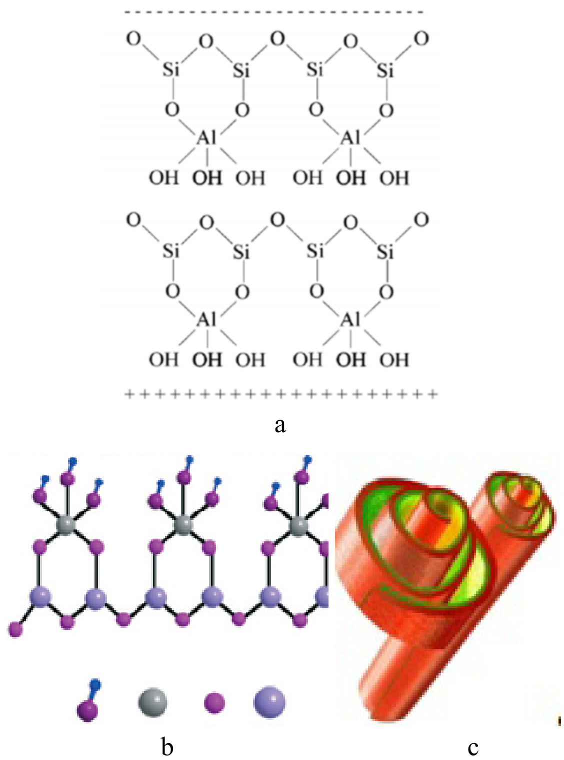


Fig. 2. **a) chemical structure of halloysite[8]; b) structure of the halloysite layer;c) halloysite nanotubes: on the outer surface of the Al−OH group (green color), on the inner surface of the Si−O−Si group (red color) [10].**

Internal HO-groups are located inside the lumen, and external groups are located on the edges and corners of the tubes [3]. Due to the multi-layered structure, most of them are internal groups. The density of surface hydroxyl groups is lower [12].

Thus, halloysite has a different composition of internal and external surfaces. Unlike halloysite, most of the described non-clay nanotubes, such as carbon nanotubes, have the same internal and external chemistry, which makes it difficult to selectively modify their lumen [10]. In addition, halloysite is an alternative to much more expensive carbon nanotubes.

The advantages of halloysite are its high specific surface area (up to 100 m^2/g) [5], high ion exchange capacity, chemical and thermal stability [1]. Halloysite is actively used as fillers of polymer nanocomposites [14], highly effective sorbents, catalysts, sensors [9]. HNTsare non-toxic [11], do not undergo biodegradation and are biocompatible, which leads to wide possibilities of their use in medicine, cosmetology, veterinary medicine and food additives. The outer surface of HNTs is covered with hydroxyl groups, making them amenable to water-phase treatment and compatible with hydrophilic materials, as well as with the surface of materials capable of forming hydrogen bonds with functional groups of other materials.

Pure titanium dioxide is a solid colorless crystalline substance, in a finely ground state it is a white powder. Despite being colorless, in larger quantities, well-purified TiO_2 is the most stable (non-volatile, insoluble in acids, alkalis and solutions under normal conditions) of all known white pigments (practically does not absorb any incident light in the visible region of the spectrum)[21].

Titanium dioxide exists in the form of several crystalline modifications, anatase, rutile and brookite can be found in nature. It should be noted that brookite is almost never used industrially, and is rarely found in nature.

The use of titanium dioxide in the food industry is very wide. E171 can be used in almost any products that require white color for an aesthetic appearance. Here are some of the areas of use: caramel, chewing gum, powdered and refined sugar, frogs' legs, chicken, pork and beef tongues, suckling pigs, flour, dough, sugar glaze, jams, milkshakes, cottage cheese, whey, condensed milk, any fish and sea products etc. Application in the fish processing industry includes bleaching of all types of fish mince, fillets, semi-finished products, surimi, pâtés and other products (for example, squid, fish waste, crab sticks etc.) Depending on the degree of bleaching, the dosage is regulated from 0.1 to 1% of the weight of the product [22].

We have conducted experimental research on establishing the conditions for the electrocrystallization of titanium oxides from suspension electrolytes using electrolytic doping approaches for the production of multicomponent composite materials TiO_2/HNTs. The main task in the planning of the experiment is the strategy regarding the concentration, the nature of additives in the electrolyte, its ligand composition to ensure the given phase composition of manganese (IV) oxide, as well as the functionality of other components.

An important task in this study is to ensure the maximum uniform distribution of all components with the maximum degree of homogenization, dispersion of components and controlled agglomeration. For photo (electro)catalytic applications, where the surface is involved, its maximum development and the presence of nanotubes must be ensured, which, according to literature data [24], contributes to the coverage of near-surface layers in mass (charge) transport. Aluminosilicate nanotubes in this sense have been relatively little studied. Photocatalytic "coupling" effects are possible under these conditions when titanium dioxide is combined with manganese dioxide, provided that the band gap is much smaller.

A stable ratio of the content of ions in the anode product is achieved when the ratio of the concentrations of the corresponding ions in the electrolyte remains unchanged. Changes in the ligand composition of the electrolyte are an additional tool for influencing the ratio of cations in the anodic product, which allows to bring together/dilute the release potentials of the corresponding oxide phases in conditions where co-crystallization of components is possible [14].

We solved the task of electrocrystallization of TiO_2/MnO_2/HNTs composites by introducingTiO_2as a suspension electrolyte component. The maximally even distribution of HNTs in the product should ensure their introduction into the electrolyte composition with an additional vacuum stage (for HNTs).

The suspension of anatase and/or rutile under the conditions of an electrocrystallization experiment in a fluorine-containing electrolyte exhibits the ability to dissolve. Therefore, it was of interest to study and use the features of this process. Spectrophotometric methods were used for this. Titanium (IV) forms a complex compound in an acidic environment with the addition of hydrogen peroxide:

$$TiO^{2+} + H_2O_2 = [TiO(H_2O_2)_2]^{2+},$$

colored yellow. This reaction is used in the quantitative photometric analysis of solutions containing titanium. The optical density of the titanium complex solution is measured at λ=400–500 nm

[25] on a KFK-2 photocolorimeter. Similar complexes are also formed when titanic acid H_2TiO_3 is dissolved in solutions containing H_2O_2. At pH>10, in solutions containing hydrogen peroxide and titanium ions, other complexes are present – $[Ti(O_2)_2(OH)_2]^{2-}$ or $[TiO(O_2)(OH)_2]^{2-}$. They are prone to polymerization and the formation of gels or precipitates [26].

The possibility of crystallization of oxides in the lumen (internal space) of HNTS was considered. However, this version of ASNT interaction with manganese dioxide was not confirmed during further electron microscopic studies. The role of halloysite nanotubes in suspension electrolytes also requires detailed consideration.

Halloysite has a positively charged inner lumen (lumen) of the aluminate layer and a negatively charged outer surface due to silanol groups. It belongs to the number of rare nanotubes with a different composition of the inner and outer surfaces. The inner space of nanotubes reaches up to 50 nm in diameter.

Material and methods of research. To increase the degree of filling of the internal cavities of the nanotubes with a composite (Mn/Ti) and to release the cavities of the nanotubes from air, vacuuming of the HNTs suspension in a sealed flask, a vacuum pump VVN 1–1.5 with a power of 5.5 kW and a residual pressure of 0.4 bar was used (Figure 3). The use of a fluorine-containing electrolyte helps to increase the size of the internal space of HNTs, due to the removal of the internal aluminate layer. For vacuuming, 0.1M HF was used as part of the HNTs suspension. We have worked out a technique for introducing nanotubes into the electrolyte using ultrasonic treatment in a VK-9050 ultrasonic bath with a power of 50 W and a duration of 30 minutes, with exposure for 3 hours. under a vacuum pump.

The HNT preparation procedure included:

• 0.6 g was dispersed in 200 ml of 0.1M НЫ electrolyte using ultrasonic treatment in a VK-9050 ultrasound bath with a power of 50 W for a duration of 30 min;

• exposure for 3 hours under a vacuum pump;

• mixing on a magnetic stirrer and adding portions of 20 ml to electrolytes № № 4, 5, 7, 10.

We synthesized composite materials (table 1), to compare their characteristics, we used different masses of TiO_2 when introduced into the electrolyte, as well as different modifications of TiO_2 (rutile/anatase), and to compare the characteristics of composite materials, they were introduced into the electrolyte with/without salts $(NH_4)_2SO_4$and investigated three-component composites of manganese dioxide/titanium with hallusite nanotubes, including functionality in photo(electro)catalytic processes of destruction and purification of wastewater.

Table 1 – **Conventional designations, composition and introduced additives in the electrolyte and characteristics of electrocrystallization conditions containing 0,1M HF, 0,7M $MnSO_4$**

№	TiO_2rutile, g/l	TiO_2anatase, g/l	(HNTs) g/l	$(NH_4)_2SO_4$ 1,5mol/l	V of electrolyte, l	Time, min
4.		10	0,15	1,5	0,4	180
5.	10		0,15	1,5	0,4	180
7.	8		0,15		0,4	180
10.		8	0,15		0,4	180

а б

Fig. 3. **Installation for vacuuming HNTs in electrolyte.**

It is known that HNTs have occupied an important niche in modern nanotechnology with applications ranging from electronics, ultralight structural materials, energy conservation, to catalysis and electrochemistry. They reveal (photo) catalytic properties that are not yet sufficiently studied, especially in combination with innovative technologies of oxide materials.

Research results and discussion. Therefore, according to our research in a fluorine-containing electrolyte, taking into account the dissolution effects of titanium dioxide and the corresponding electrode processes accompanied by the formation of Ti^{3+}, the resulting composite was not a mechanical combination of two components with known properties. The rather complex behavior of titanium dioxide/manganese suspension electrolytes in a fluorine-containing electrolyte, regardless of the phase composition (anatase/rutile), is a window of new opportunities for the creation of functional materials with specified properties.

Due to the multi-stage process of electrocrystallization of titanium dioxide, one of the most important problems is obtaining products with specified properties. At the same time, the issue of directed synthesis of oxide composite materials remains open, since the influence of synthesis parameters on the composition and physicochemical properties of the resulting composites is not sufficiently studied.

Electrosynthesis in the composition of a fluorine-containing suspension electrolyte with titanium/manganese (IV) oxide as a result of anodic deposition is considered. The directed introduction of NH_4^+cation additives into the composition of the electrodeposition electrolyte can be the basis of the design of the oxide matrix of a certain macro-, micro- and mesostructure. The paper examines the influence of ammonium cation additives on the formation of not only phase equilibria of the system, but also the interaction of components in the formed composite. When preparing fluorine-containing suspension electrolytes, titanium (IV) oxide of the anatase/rutile structure, as well as titanium (IV) oxide from different manufacturers, were introduced. The commercial photocatalyst TiO_2 P25 (EvonikIndustrials, Germany), consisting of an amorphous phase and an anatase/rutile mixture in the proportion of 80/20, exhibits greater activity in photocatalytic processes than pure crystalline phases of anatase [27]. Therefore, the task of the research was to study the properties of titanium dioxide from different manufacturers.

In the scientific literature, we did not find data on the electrocrystallization of composite titanium oxides with halloysite. The above-mentioned components are of interest as components of composite materials that should exhibit improved photo(electro)catalytic properties. Taking into account the polymorphism of the titanium (IV) oxide system, which can manifest itself depending on the cationic composition of the electrolyte and other process parameters, it is possible to control various phase and defect states of the product. The synthesized series of samples contained composites based on introduced halloysite with a concentration of 0.015 g/l and titanium dioxide 8–10 g/l, formed in the process of interaction with the electrolyte and as a result of electrocrystallization during the galvanostatic process of electrolysis of different durations (1, 2, 3 hours).

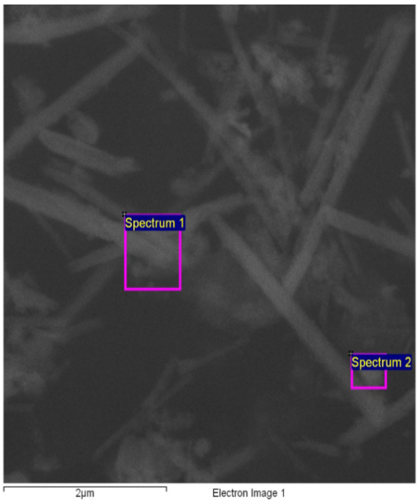
The method of electron microscopy shows that halloysite nanotubes are occluded by manganese (IV) oxide sediment and titanium dioxide nanoparticles actively interact with the surface of nanotubes in the composition of three-component composites.

The authors [15] applied anatase TiO_2 to the surface of HNTs for adsorption and photodegradation of methylene blue. As expected, the HNTs/TiO_2 composite showed an advantage of the dual mechanism of dye adsorption and degradation compared to the adsorption method. It is also about a significant improvement of thermal and mechanical properties when adding hallusite nanotubes to polyethylene products.

HNTs exhibit low electrical thermal conductivity and strong hydrogen interactions, due to which the internal hydroxyl groups show greater stability than the surface hydroxyl groups. The results of the scanning electron microscopy analysis of the elemental composition of HNTs indicate the presence of oxygen, aluminum and silicon in HNTS, which is shown in the table in Figure 4.

Research of the topology and morphology of the surface, identification of the elemental composition of selected areas of the surface, their quantitative composition, is specified in the table. The research of microstructures and microtexture, orientation of crystallites was carried out on a TescanMira 3 LMU electron scanning microscope (Figure 5) with the following technical characteristics: spatial resolution of 1 nm (under conditions of an accelerating voltage of 30 kV), 2 nm (3 kV); working pressure in the chamber ≈ $9 \cdot 10^{-3}$ Pa

Translucent images were obtained at magnifications up to x250,000, and electron diffraction (ED) images were obtained using a limiting diaphragm with a diameter of 0.4 μm. Image registration was carried out in electronic format on the EPOM (Figure 6).



Spectrum	O	All Al	Si
Spectrum 1	84.322	7.46	7.06
Spectrum 2	85.60	3.83	4.10

Fig. 4.**The results of energy dispersive analysis of the elemental composition of halloysite samples, which are indicated in the Figure 1.**

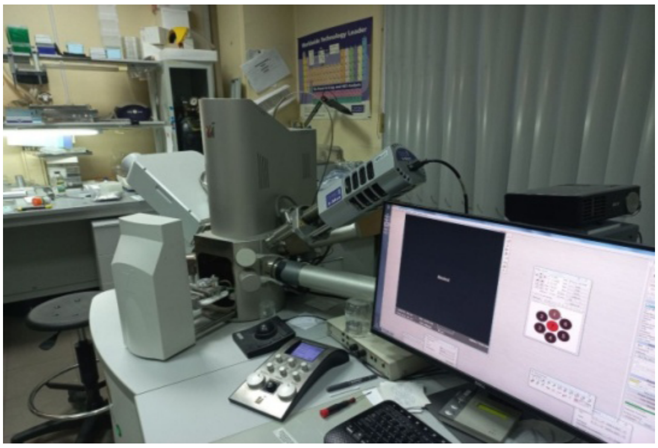


Fig. 5. **Scanning electron microscope Tescan Mira 3 LMU.**

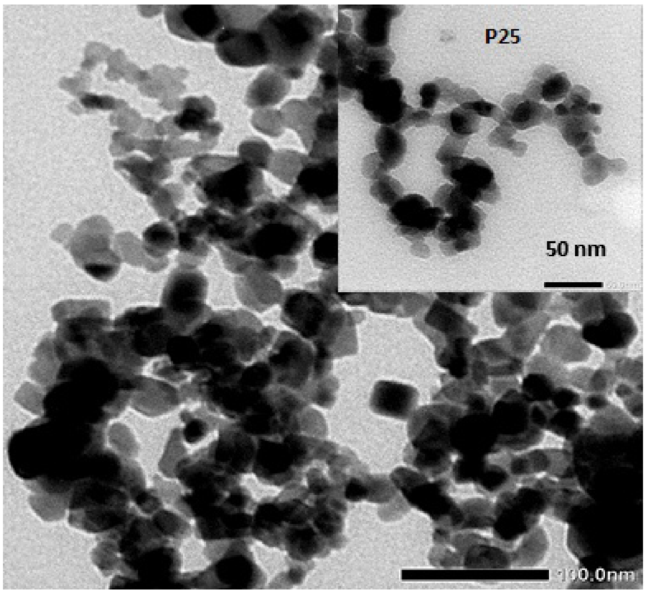


Fig. 6. **Electron microscopic image of powder particles TiO_2 (P25 Evonic).**

HNTs are of special importance for nanomedicine and pharmaceuticals. Works [10] give an example of the use of halloysite nanotube cavities for loading, storage, and controlled release of medicinal and biocidal preparations, DNA, proteins, and enzymes. The release rate of biologically active substances adsorbed by HNTs into the solution is 50–100 times lower than for other nanocarriers [19].

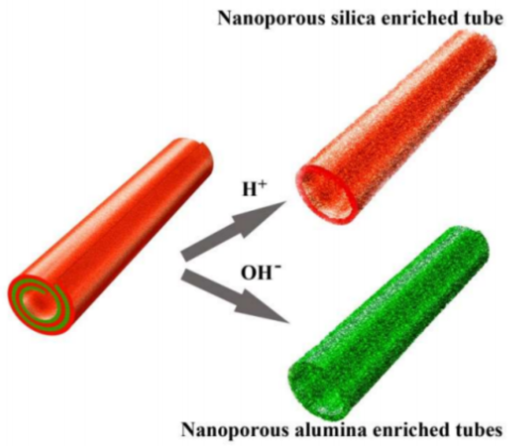
There are various methods to functionalize and improve the properties of HNTs, such as acid activation, intercalation, heat treatment, and chemical modification [15].

Treatment with acid or alkali (Figure 7) of HNTs (pH = 2 or 12) allows selective removal of aluminium or silicon oxides, which helps to increase the volume of the internal lumen without changing the external diameter [10]. Such HNTs can be used as containers of increased capacity.

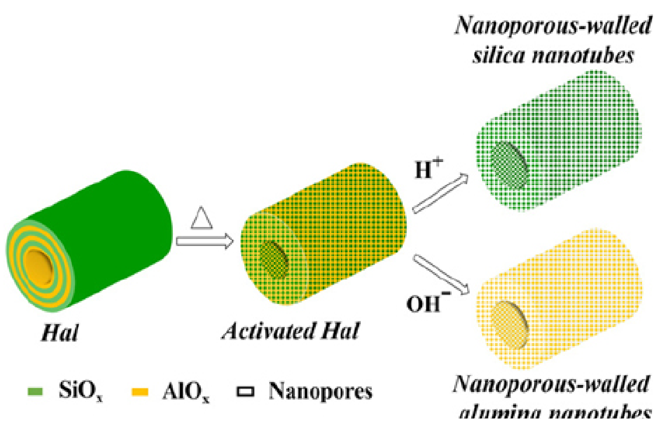
Annealing of halloysite at 800 °C followed by etching allowed the authors to synthesize new effective adsorbents – SiO_2 and Al_2O_3 nanotubes with nanoporous walls with a specific surface area of 414 m^2/g and 159 m^2/g, respectively (Figure 3, a) [20].

Halloysite has high adsorption properties in relation to heavy metals Cu(II), Pb(II), Cd(II), Zn(II), Cr(IV) and Co(II) and solutions containing harmful hydrocarbons (benzene), and as well as toxic gases (ammonia, hydrogen sulfide) [12].

A group of researchers, led by Professor Giuseppe Lazzara (University of Palermo, Italy), [16] use aluminosilicate nanotubes (Figure 1) in their work and prove their significant potential in various processes [4] by changing the surface charge of HNTs (Figure 7) with an increase in pH>7.



а



б

Fig. 7. **a) etching of HNTs with acid [H^+] and alkali [OH^-] [10], б) formation of nanopores in the walls of HNTs during activation (annealing) and subsequent etching with acid [H^+] and alkali [OH^-] [15].**

Conclusions. Titanium dioxide is produced annually in big quantities, including for applications in the food industry for wastewater treatment. TiO_2 is one of the most active photocatalysts that destroys organic compounds to CO_2 in the presence of UV radiation. The rather complex behavior of suspension electrolytes of titanium dioxide/manganese in a fluorine-containing electrolyte, regardless of the phase composition (anatase/rutile), is a window of new possibilities for the creation of functional materials with specified properties.

New intelligent so-called "smart" materials should not only additively combine the properties of components, composites ofTiO_2/MnO_2/HNTS, composition, but also provide certain synergism of properties. Aluminosilicate nanotubes are relatively new objects for research. It is shown that halloysites have a natural origin, a unique structure and morphology, special physicochemical properties and ecological advantages. Due to their hollow tubular structure, different external and internal surface charges, halloysites represent a potential area for the deposition of nanoparticles and provide opportunities for controlled release and delivery of active components, nanocontainers etc.

Based on the above, we consider it expedient to create new promising composites of transition metal oxides with hallusitealuminosilicate nanotubes using electrolytic doping approaches for the degradation of various hazardous objects.

REFERENCES

1. Joussein, E., Petit, S., Churchman, J., Theng, B., Righi, D., Delvaux, B. (2005). Halloysite clay minerals – a review. Clay Minerals, no. 40 (04), pp. 383–426. DOI:10.1180/ 0009855054040180.

2. Yuan, P., Southon, P. D., Liu, Z., Green, M. E. R., Hook, J. M., Antill, S. J., Kepert, S. J. (2008). Functionalization of halloysite clay nanotubes by grafting with γ-aminopropyltriethoxysilane. J. Phys. Chem., vol. 112 (40), pp. 15742–15751. DOI:10.1021/ jp805657t.

3. Yuan, P., Ta, D., Yuan, P., Annabi-Bergaya, F., Yan, W., Liu, D., Liu, Z. (2013). From platy kaolinite to aluminosilicatenanoroll via one-step delamination of kaolinite: effect of the temperature of intercalation. Appl. Clay Sci., vol. 83, no. 84, pp. 68–76. DOI:10.1016/j.clay.2013. 08.027.

4. Lvov, Y., Aerov, A., Fakhrullind, R. (2014). Clay nanotube encapsulation for functional biocomposites. Adv. Colloid Interface Sci., no. 207, pp. 189–198. DOI:10.1016/j.cis.2013.10.006.

5. Bates, T. F., Hildebrand, F. A., Swineford, A. (1950). Morfology and structure of endellite and hallosite. American Mineralogist, vol. 35(7–8), pp. 463–484.

6. Abdullayev, E., Joshi, A., Wei, W., Zhao, Y., Lvov, Y. (2012). Enlargement of Halloysite Clay Nanotube Lumen by Selektive Etching of Aluminum Oxide. ACS Nano, no. 6, pp. 7216–7226. DOI:10.15587/25198025.2017.113525.

7. Wang, L., Chen, J. L., Ge, L., Zhu, Z. H., Rudolph, V. (2011). Halloysite-nanotube-supported Ru nanoparticles for ammonia catalytic decomposition to produce CO – Free hydrogen. Energy Fuels, vol. 25, no. 8, pp. 3408–3416. DOI:10.1021/ef200719v.

8. Nicholson, J. C., Weisman, J. A., Boyer, C. J., Wilson, C. G., David, K. (2016). Dry Sintered Metal Coating of Halloysite Nanotubes. Mills. Appl. Sci., no. 6(9), 265 p. DOI:10.3390/ app6090265.

9. Liang, Yu., Huixian, W., Yatao, Z., Bin, Z., Jindun, L. (2016). Recent advances in halloysite nanotube derived composites for water treatment**.** Environ. Sci.: Nano, no. 3, pp. 28–44. DOI:10.1039/ C5EN00149H.

10. Lvov, Y., Wang, W., Zhang, L., Fakhrullin, R. (2015). Halloysite Clay Nanotubes for Loading and Sustained Release of Functional Compound. Advanced Materials. no. 28(6), pp. 1227–1250. DOI:10.1002/ adma.201502341.

11. Abdullayev, E., Lvov, Y. (2013). Halloysite clay nanotubes as a ceramic “skeleton” for functional biopolymer composites with sustained drug release. Journal of materials chemistry B., 1 (23), pp. 2894–2903. DOI:10.1039/C3TB20059K.

12. Sakiewicz, P., Nowosielski, R., Pilarczyk, W., Gołombek, K., Lutyński, M. (2011). Selected properties of the halloysiteasa component of Geosynthetic Clay Liners (GCL). Journal of Achievements in Materials and Manufacturing Engineering, Vol. 48, pp. 117–191.

13. Sayah, J., Farh, L., Kouch, H., Challioui, A. (2018). Electronic and Optical Properties of Ramsdellite TiO2through mBJPotential. International Journal of Nanoelectronics and Materials, Vol. 11, no. 1, pp. 25–32.

14. Pavlidou, S., Papaspyrides, C.D. (2008). A review on polymer-layered silicate nanocomposites. Progress in Polymer Science, Vol. 33, pp. 1119–1198. DOI:10.1016/j.progpo lymsci.2008.07.008.

15. Skibińska, M. (2019). The sorption capability of halloysite. Annales Universitatis Mariae Curie-Sklodowska, sectio AA – Chemia, vol. 74, no. 2, 147 p. DOI:10.17951/aa.2017.72.1.47.

16. Massaro, M., Riela, S., Cavallaro, G., Colletti, C. G., Milioto, S. (2016). Ecocompatiblehalloysite/cucurbituril hybrid as efficient nanosponge for pollutants removal. Chemistry Select., vol. 1 (8), pp. 1773–1779. DOI:10.1002/slct.201600322.

17. Lisuzzo, L. (2019). Layered composite based on halloysite and natural polymers: A carrier for the pH controlled release of drugs. New Journal of Chemistry, vol. 43, no. 27, pp. 10887–10893. DOI:10.1039/C9NJ02565K.

18. Massaro, M. (2017). Halloysite nanotubes as support for metal-based catalysts. Journal of Materials Chemistry A, vol. 5, no. 26, pp. 13276–13293. DOI:10.1039/C7TA02996A.

19. Unuabonah, E. I., Taubert, A. (2014). Clay-polymer nanocomposites (CPNs): Adsorbents of the future for water treatment. Applied Clay Science, vol. 99, pp. 83–92. DOI:10.1016/j.clay. 2014.06.016.

20. Liang, Yu., Huixian, W., Yatao, Z., Zhang, B., Jindun, L. (2016). Recent advance of halloysite nanotubes derived composites in water treatment. Environ. Sci.: Nano., no. 3, 28 p. DOI:10.1039/C5EN00149H.

21. Ni, M., Leung, M. K. H., Leung, D.Y.C. (2007). A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. Renewable and Sustainable Energy Reviews, vol. 11, pp. 401–425. DOI:10.1016/j.rser.2005.01.009.

22. Doncova, T. A., Bredyhin, I. V. (2013). The mechanism of photocatalysis on the surface of TiO2. Scientific news of the National Technical University of Ukraine "Kyiv Polytechnic Institute", no. 3, pp. 114–118.

23. Suprun, N. P., Bereza-Kindzerska, L. V., Brychka, A. V., Brychka, S. Ya. (2016). Synthesis of agar-agar gels filled with aluminosilicate nanotubes for wound dressings. Bulletin of the Kyiv National University of Technology and Design. Technical sciences, no. 4 (100), pp. 49–55.

24. Meo, P., Lazzara, G., Liotta, L., Noto, R. (2014). Cyclodextrin–calixarene co-polymers as a new class of nanosponges. Polymer Chemistry, 5 (15), pp. 4499–4510. DOI:10.1039/ C4PY00325J.

25. Kostenko, E. E., Drokov, V. G. (2009). Analytical chemistry. Kyiv: NUHT, 184 p.

26. Horoshchenko, Y. G. (1970). Chemistry of titanium. Kyiv: NaukovaDumka, 415 p.

27. Ohno, T., Sarukawa, K., Matsumura, M. (2001). Direct observation of suppressed recombination of electron-hole pairs in the TiO_2 nanopowders with anatase-rutile interface: in-situ NEXAFS study under UV irradiation. J. Phys. Chem, vol. 105, pp. 2417–2425. DOI:10.1109/ NMDC.2006.4388962.

Алюмосилікатні нанотрубки галуазиту, як інструмент сучасних нанокомпозитів для харчової безпеки

Гаюк Н.В., Цехмістренко О.С., Селезньова О.О.

Нанорозмірні природні глинисті мінерали, до складу яких входять Si, O, Al та Mg, належать до класу екобезпечних неорганічних матеріалів з унікальною структурою та різноманітною морфологією, зокрема нанострижнів, нановолокон та нанотрубок. Алюмосилікатні галуазитні нанотрубки (ГНТ) є порівняно новими об’єктами дослідження в матеріалознавстві, мають ряд екологічних та економічних переваг, порівняно з вуглецевими (ВНТ), а також фулереном, графеном. Природні галуазити на порядок дешевші за свої синтетичні аналоги. Місця знаходження галуазиту досить поширені, наприклад, у районі Кривого Рогу та інших місцях, в інших країнах. ГНТ, внаслідок високої екологічності та біодоступності, можуть застосовуватися у медицині, в тому числі як носії лікарських засобів з контрольованим виведенням. ГНТ також можуть виявляти фотокаталітичні властивості, мають високі адсорбційні властивості по відношенню до важких металів Cu(II), Pb(II), Cd(II), Zn(II), Cr(IV) і Co(II) та розчинів, що містять барвники, пестициди і деякі інші органічні забруднювачі, а також токсичні гази (амоніак, сірководень). ГНТ у поєднанні з іншими металами, такими як Mn, Ti, набувають різноманітних практичних застосувань. ГНТ вводили для забезпечення кращих функціональних фотоелектрокаталітичних властивостей композитів, що можуть бути підкладкою, особливо у варіанті декорування оксидами нанотрубок. Наприклад, титан, білий пігмент, нетоксичний входить до списку харчових добавок та позначається як Е171. Міститься в продуктах харчового призначення: цукерках, печиві, тістечках, курячих філе, крабових паличках, жувальних гумках, шоколадних виробах. Хоча добавки діоксиду титану в харчових продуктах дозволені багатьма офіційними документами, в науковій літературі недостатньо даних щодо потенційної небезпечності діоксиду титану для організму людини.

Підвищений інтерес до TiO_2 обумовлений його високою фотокаталітичною активністю, що дозволяє реалізувати процеси деструкції органічних сполук, в тому числі екотоксикантів, у безпечні продукти. ГНТ, або матеріали на їх основі, знайшли багато корисних застосувань в очищенні питної води та промислових стічних вод. Структурні особливості ГНТ дозволяють отримати на їх основі нові композиційні матеріали такі як, наприклад, імогалітні нанотрубки (ІНТ) широкого функціонального призначення та визначити фізико-хімічні закономірності їх утворення.

Отже, актуальність роботи полягає в об’єднанні галуазитних нанотрубок та діоксиду титану як композитних матеріалів, використовуючи електросинтез, та аналізі впливу фазового складу, фотокаталітичної активності композитного матеріалу на безпечність його практичного застосування, в тому числі в харчової промисловості.

Ключові слова: алюмосилікати, нанотрубки, наноматеріали, внутрішня поверхня, безпека, галузит, діоксид титану, композити, нанокомпозити, синтез.

ORCID iD:
Haiuk N. https://orcid.org/0000-0002-5466-7084
Tsekhmistrenko O. https://orcid.org/0000-0003-0509-4627