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OPTICAL PROPERTIES AND ADHESIVE ABILITY OF HYBRID VIRUS NONORGANIC COMPLEXES TMV-AU

One of the promising methods to create nanomaterials reduces to applying of viruses, whose virions, due to their high spatial symmetry, can serve as effective matrix templates that allow assembling of noble metals, in particularly Au, nanoparticles. In the connection with the above mentioned fact, it becomes interesting to investigate physical properties of materials synthesized by virus involving technology, depending on the determined virus-matrix. This paper presents some results of the study of optical and adhesive properties of gold nanoparticles in complexes with the tobacco mosaic virus
Key words: virus-inorganic complexes, tobacco mosaic virus, optical spectra, adhesion ability

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ОПТИЧНІ ВЛАСТИВОСТІ І АДГЕЗІЙНА ЗДАТНІСТЬ ГІБРИДНИХ ВІРУС-НЕОРГАНІЧНИХ КОМПЛЕКСІВ ВТМ-AU

Одним із перспективних методів створення наноматеріалів є використання вірусів, віріони яких, завдяки високій просторовій симетрії, можуть служити ефективними матричними шаблонами, які дозволяють реалізувати ассамблер наночастинок благородних металів, зокрема золота. В зв'язку з цим стає актуальним дослідження фізичних властивостей синтезованих в такий спосіб матеріалів залежно від вибраного вірусу-матриці. У даній роботі наведено результати дослідження оптичних і адгезійних властивостей наночастинок золота в комплексах з вірусом тютюнової мозаїки
Ключові слова: вірус-неорганічні комплекси, вірус тютюнової мозаїки, оптичні спектри, адгезійна здатність.

Reviews of recent studies and formulation of problems

One of the most difficult problems to resolve in nanotechnology is production of nanoobjects with the same geometrical form and size. As some intensive researches [1] show the very promising approach to treat the problem is the use of Tobacco Mosaic Virus (TMV). The TMV can be chemically and genetically modified in order to alter its physical properties and adapt them to demanded technologic applications. Currently, vast researches directed on the implementation of TMV based methods in the fabrication of nanowires, nanostructured thin films, highly effective microbatteries, solid-state nanoelectronics and biosystems engineering are being carried out in the world. The intensity of these studies is due to the microelectromechanical systems field is more and more developing and allows us to advance in effective miniaturization of functional devices and integrated systems [2–6].

However, some fundamental restrictions of microtechnologies do not permit to ultra pass well-known dimension limits. That is why the integration of nanostructured objects with many functional devices to continue to be a serious problem which is a long way to its complete resolution by conventional methods and materials [7–9].

Tobacco mosaic viruses have a specific structure. It is similar to a nanocabel consisting of hollow protein tubes, inside which the RNA passes. The length of the virus is about 300 nm, its outer diameter is equal to 18 nm, while the inner cavity has a diameter of 4 nm. The virus capsid consists of 2130 molecules of protein (monomers), which, like helicoids wrap around the RNA molecule. The protein monomer consists of 158 amino acid residues [10]. It is able to withstand the temperature about 60° C during 30 minutes.

Down-up self-assembling is the basic method to synthesize nanodimensional devices. Contemporary synthesis methods allow to realize precise control over the size and shape of nanoparticles produced by applying biomatrix technology. In comparison with semiconductors their fundamental features reveal increasing structural and functional versatility, self-assembly on the surface and predicted controllability of properties. These advantages in combination with the low cost of production predict a revolution in today's technogenic environment.

Modern technology involves biological objects such as DNAs [11–16], peptides [18], bacteria [17–20] and proteins [21] to create various nanostructures, in particular nanofibers, nanoparticles, and quantum dots. One of the most promising categories of biological nanotemplates which provides exceptional functional opportunities of applications is reduced to plants and bacterial viruses. These particles are formed from high-molecular nucleic acid aggregates, consisting of many copies of the protein shell. Above mentioned molecules demonstrate some essential advantages: they exhibit exceptional stability over a wide range of temperatures and pH-factor values and the ability to withstand influence of denaturation by organic water-soluble mixtures [22].

Between the available viruses, the tobacco mosaic virus is one of the most widely studied filiform structures. The properties of TMV that are extremely useful for nanobiomaterials integration into microsystem devices reduce to well-studied three-dimensional structure [23–26], a large amount of bio-physical information on the characteristics of TMV self-assembly on various substrates [27], discovery of a number of infectious clones from virus of RNA. These and other features allow to create new viral structures and surfaces by applying well-

studied methods of genetic modification [28, 29], a expansive quantity of existing examples of a protein shell with a wide scale of self-assembly properties [30]. Beside it possibilities to receive viruses and protein shells from infected plants in an unlimited amount [31–33] and TMV structural strength make it suitable for use in conventional microelectronics technologies methods [31, 34, 35].

The advantages of using TMV's are that all particles of the same type have got identical structure, shape and size; TMV's virions (that is mature viruses) show capacity to self-assemble and form certain self-organized structures connecting their ends, for example, chains or rings; finally they are highly stable both in chemical and physical senses, and also they can be coated with metals, silicon dioxide and semiconductor materials [36–40].

The surface of the virus consists of repeating amino acid chains. The inner cavity consists predominantly of glutamine and aspartic acids, and the outer surface is composed of a large number of lysine and agrinic radicals. This fact is favourable for the virus surface to react with nanoparticles of metals (gold, silver) [37–39, 41].

The connection of different nanoparticles with the virus molecule can be controlled during the syntheses by changing the chemical parameters of environment (pH, the presence of oxidizing /reducing agents) [42–54].

Investigation of optical properties of vtm-nano-particles of metals

The method of obtaining silver hydrosoles is based on the restoration of silver nitrate by tannin in the presence of a buffer solution of sodium tetraborate and sodium hydroxide (pH = 9.8). In the reaction volume containing the buffer solution (pH=9,8) the tannin solution was added under the room temperature. Then the solution of $AgNO_3$ undergoing to uninterrupted stirring was introduced at a rate of 1.3 ml / min. For the synthesis water solutions of silver nitrate and tannin with following compositions of agents were used: 1) with equimolar ratios, 2) with the excess of tannin ten times, and 3) with the tenfold excess of silver nitrate. The Fig. 1 shows optical spectra of soles which were situated in quartz cuvettes. The optical path length was of 10 mm and the wavelength interval was about 350-600 nm. On the curves the formation of plateau can be observed. If the excess of silver takes place clearly distinguished band at λ=420 nm can be detected too.

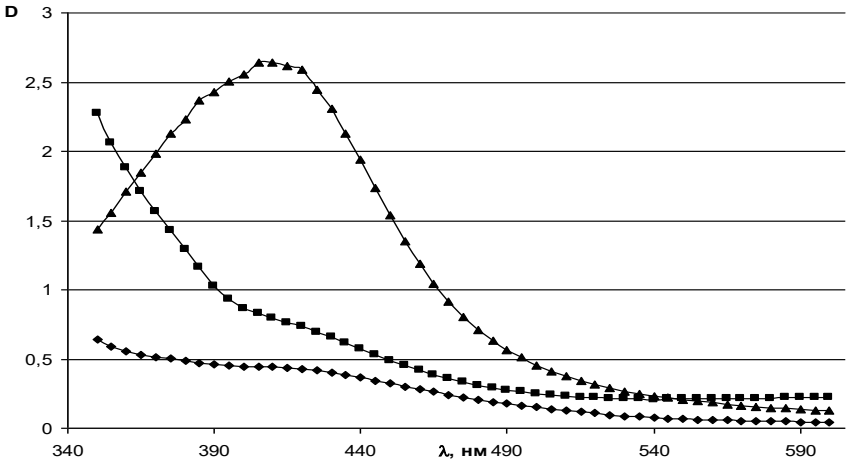


Fig. 1. Optical spectra of silver hydrosoles, obtained: ♦ in equimolar ratios of silver nitrate and tannin; ■ in excess of tannin; ▲ in excess of silver

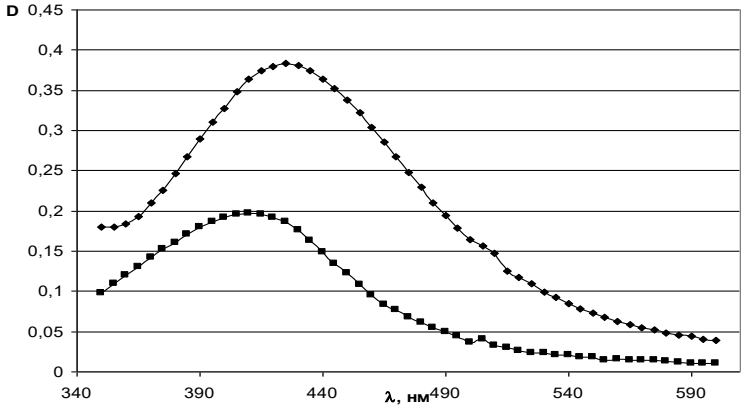


Fig. 2. Optical spectra: ♦ - silver sol in ethanol; ■ - silver hydrosol

Characteristics of soles demonstrate certain level of sensibility in relation to proprieties of solvent. In order to verify this suggestion the effect of solvent type on optic parameters of soles the synthesis of nanosized silver particles was carried out with using of 96% ethanol solution. The maximum of optical absorption band in ethanol

turns out shifted to the long wave part in comparison with the hydrosol optical spectrum (Fig. 2).

The study of the obtained nanowires was carried out in the ultraviolet and visible interval of wavelengths on the two-beam spectrophotometer SPEKOL One only maximum at 540 nm has been observed on the graphs of the optical density of nanowires dependence on wavelength. This fact doubtless points out on the optical activity of the nanowires in this wavelength segment. It should be important to sub line that there are no peaks of absorption for pure viruses (Figure 3).

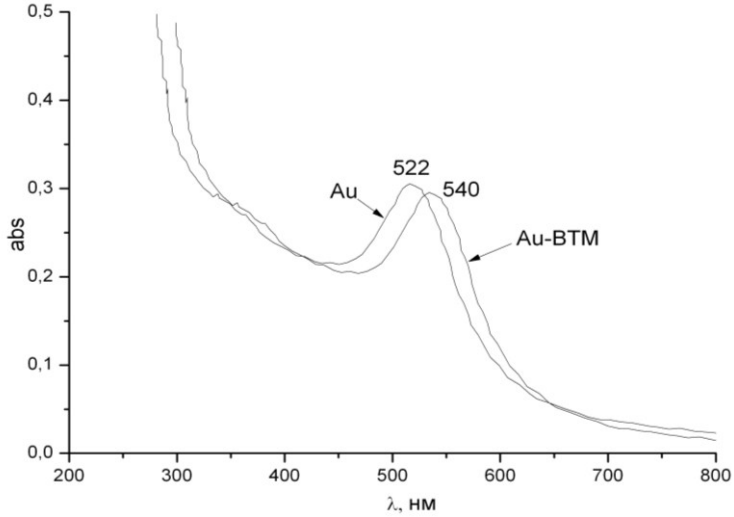


Fig. 3. Optical spectra of pure nanoparticles and nanowires TMV-Au

The our results clearly indicate on existing of optical anisotropy and they have been confirmed by the data of work [54]. The TMV is a rod-shaped virus consisting of a right screw single-breasted ribonucleic acid and demonstrate a positive peak in the spectrum of circular dichroism (CD) at 190 nm and a negative peak at 209 nm due to excitation and the transition from π to π * with optical dipoles perpendicular to axis and parallel to the same axis respectively [54].

On the CD spectra peaks correspond to gold nanoparticles in the wavelength interval of 200-300 nm are not observed. Concerning the TMV-Au complex there is a negative peak of the CD at 222 nm and a maximum of 540 nm on the optical spectra. This fact can be interpreted as manifestation of the correlation between circular dichroism and plasmon resonance spectra of TMV-Au and the correlation of plasmon resonance and optical activity, as well as the presence of two types of chiral structures in the TMV-Au complex: right amino acids, and right α-helix consisting of the amino acids. Thus the TMV-Au admits to be treated as a chiral medium in which the refractive index for right and left-hand polarization in the direction of propagation + x is n +; n-, respectively. Given that the refractive index depends on the direction of propagation these indexes for the right-hand (left-hand) polarized light in the direction -x, were designated respectively as n + (n-). The established difference in the refractive index plays a significant role in interpreting of the obtained, namely, the chiral medium can be referred to the normal medium with the refractive index n. The length of the normal and chiral component of the medium l and L-1, respectively. The ratio of the transmission coefficient for the right-hand polarization t + and the left-hand polarization t- is determined by the method of transfer matrices. Then the ratio t- / t + can be expressed as

$$\frac{t_-}{t_+} = e^{-2i(\theta_+ - \theta_-)} \times \frac{A_{+-}}{A_{-+}} \tag{1}$$

where

$$A_{+-} = (\cos\theta - \frac{i}{n}\sin\theta) \times \left[n_+ e^{i\alpha_{+-}} + n_- e^{-i\alpha_{-+}} + n_+ n_- (e^{i\alpha_{+-}} - e^{-i\alpha_{-+}}) \right]$$

$$+(\cos\theta - ni\sin\theta) \times (e^{i\alpha_{+-}} - e^{i\alpha_{-+}} + n_- e^{i\alpha_{+-}} + n_+ e^{-i\alpha_{-+}})$$

and

$$\theta = kl / n, \theta_{+,-} = kl / n_{+,-} \quad \alpha_{+-} = kl / n_+ - kL / n_-.$$

The first factor of the right-hand side of the equation (1), that is $e^{-2i(\theta_+ - \theta_-)}$ gives an optical activity without the influence of the normal medium. The second one, that is A_{+-} / A_{-+} corresponds to the effect of connecting the normal segment to the chiral part of the system, and it is responsible for the optical activity

$A_{+-} / A_{-+} \neq 1$. This term describes the modification of optical activity. The plasmon frequency A_{+-} / A_{-+} has got significantly high value due to plasmon resonance leading to a notable increase in optical activity. On the other hand, in the UV region, $A_{+-} / A_{-+} \sim$ 1. Therefore the optical activity of the complex is increasing too. Thus the optical activity of the complex in the UV region is not less than that of the chiral medium. This simple model provides a consistent explanation of the experimental results and opens up the possibility of using the TMV-Au complexes to create 3D metamaterials.

Investigation of adhesive and oxidizing properties of tmv virion on the surface of silicone crystal

The adhesion properties of a tobacco mosaic virus on the surface of silicon spraying with gold were investigated by atomic force microscopy. A continuous coating of the surface of the TMV by gold nanoparticles was established. These nanoparticles of gold, unlike ones obtained by chemical synthesis, are localized near the viruses, mostly in the ends of the viruses and less often at their edges. The height of the synthesized wires, determined on the base of the received images, was 10.5 ± 0.9 nm, which, within the measurement error, correlates quite well with the value of the TMV particles diameter evaluated by other methods (Fig. 4).

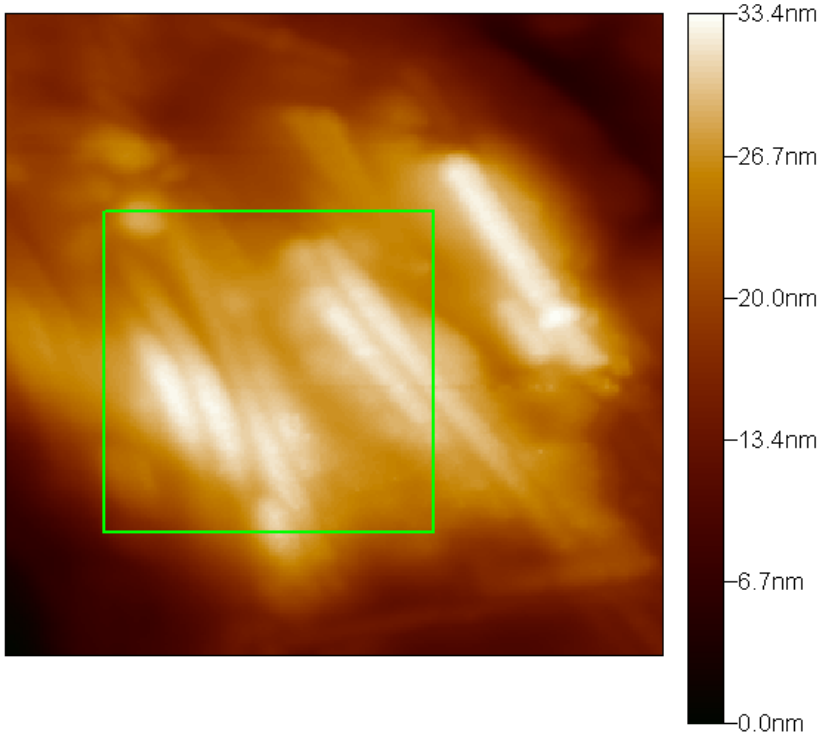


Fig. 4. AFM image of TMV-Au nanowires on the (111) surface of Si monocrystal

The presence of particles whose length is nearly two times larger then the length corresponds to the maximum (300 nm) was observed. This fact indicates the ability of the virions to form «face to face" bindings. If the increase of the concentration of TMV takes place beside of the "face to face" junction an aggregation of "side-to-side" viral particles is also detected with participation about dozen particles in such interaction (Fig. 5).

Appearance of aggregates in the form of islands on the silicon substrate gives ground reasons to suppose that some cooperative mechanism of binding among virus particles has to exist. As it was established, a preferred direction in the orientation of TMV particles on the surface of silicon repeats the direction of the silicon crystallographic axes.

For nanowires obtained by application of the method of the thermal deposition of gold the strength of binding of viruses to the surface of metals and semiconductors was determined with using atomic force microscopy.

After removing TMV from the surface of gold, a study of morphology of surface by atomic force microscopy was performed. The carried out investigations showed a significant change in the relief of gold.

The depth of formed cavity reached 2 nm, and its width was about 18 nm, These date suggest that discussed cavities were created by viruses (Fig. 6). The sub lined result is of great interest because of well known low level of passivation of gold. There are several assumptions about the nature of the interactions of virions with gold. Concerning the nature of interaction between virions and gold surface one can choose from two types, namely, a physical adsorption or chemical one. Physical adsorption is the result of van der Waals forces action and reduces to creation of hydrogen and other electrostatic bonds. As far the chemical adsorption it occurs due to chemical interactions between substances.

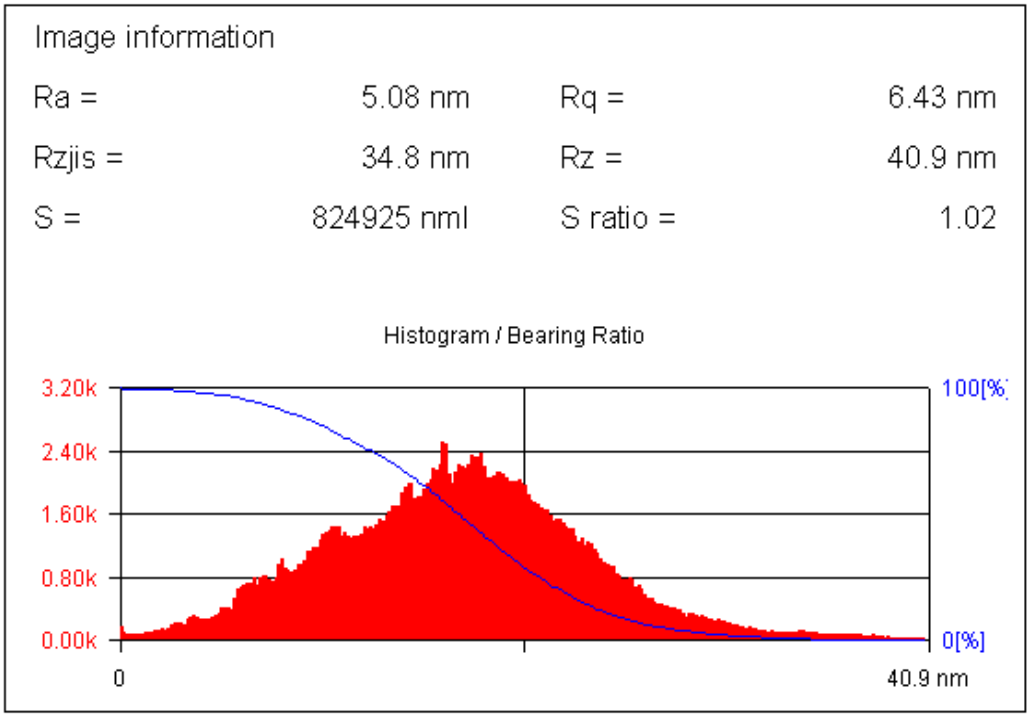


Fig. 5. Distribution of dominated location of nanowires in green squares of Fig. (4)

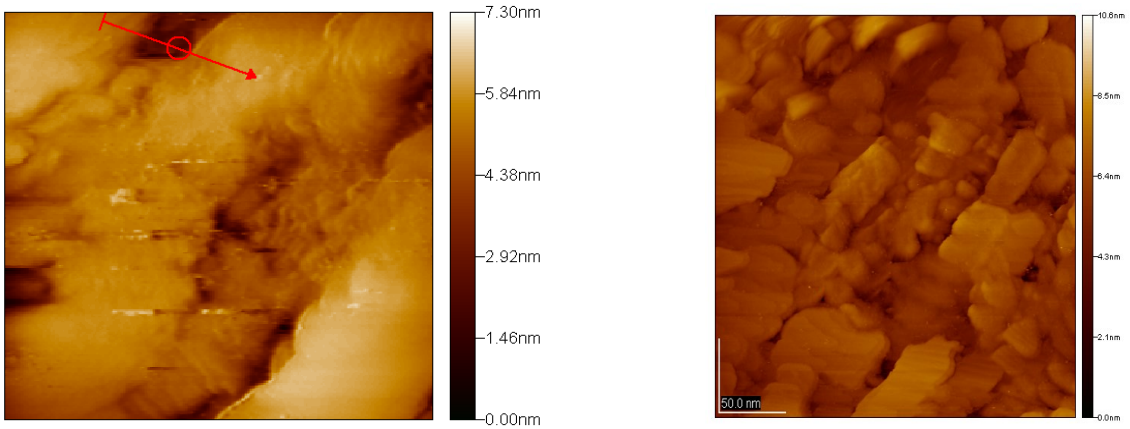


Fig. 6. The image of the surface of gold after removing of the TMV

The presence of characteristic grooves produced by virions indicates a high chemical activity of TMV virions (Fig. 7) and points out on the chemical adsorption as dominated type of interaction.

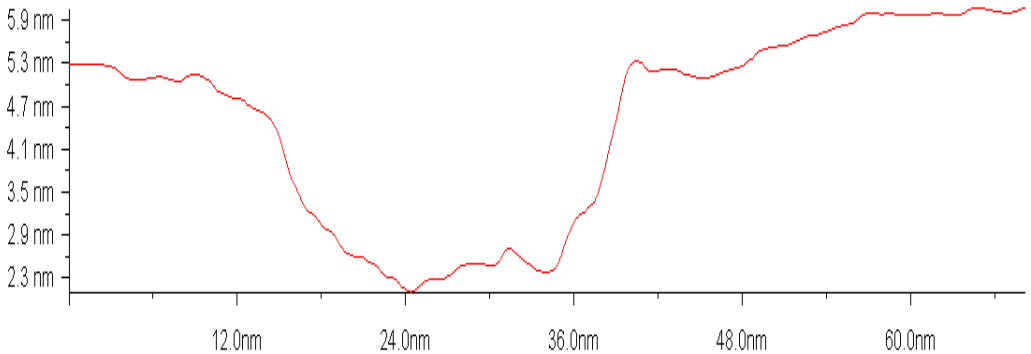


Fig. 7. Characteristic profile of cross section of the cavity on gold surface after the virions of the TMV was taken off

Behaviour of tmv and amv virus in interaction with antibodies

The viruses consist of nucleic acid and globular protein molecules and are the simplest forms of living organisms. The viral particle does not have its own reproduction tools, however, penetrating into the cell, provides its own replication due to the synthesis of viral proteins by infected cell. The size of the viral particles varies from 15 to 1200 nm. In addition to their biological features (reproductive ability, infectivity, contaminative intensity),

viruses have a lot of other properties. In particular, viral particles can form periodical structures with useful optical properties. The presence of a large number of charges on the internal and external surfaces of the virions allows producing nanoparticles by applying the biomimetic method. The ability of viruses to penetrate inside the cell can be used to create the most progressive intracellular nanoprobes and nanosensors. The most promising applications in nanotechnology are plant viruses, since they are safe for humans and animals and can be obtained in large quantities and can withstand various modifications.

To investigate the behaviour of rod-liked viruses with helical symmetry of their protein subunits, in particular, tobacco mosaic virus and alfalfa mosaic virus (AMV), a high-resolution probing microscopy method was used.

TMV suspensions at a concentration of 12 mg / ml and AMV at a concentration of 10 mg / ml were used. The suspensions were deposited on the surface (111) of a silicon monocrystal by applying a microsyringe. After drying of the Si (111) surface into a streaming beam of dry nitrogen the sample was put in the atomic force microscope (AFM) working chamber. The residual pressure in the chamber of probing was 3.0×10^{-8} Pa. For the surface exploring cantileveres fabricated from nitride of silicon, that is Si_3N_4 , have been used. The study of the virus on the surface of a monocrystal was carried out in a contactless AFM mode with atomic resolution.

During the experiment, the interaction of TMV with the surface of Si (111) was investigated for two different conditions. The first corresponds to the fresh virus suspension and the other one referred to the suspension taken 4 months after it has been prepared. The obtained results were compared with ones corresponding to the study of the AMV interaction with identical surface.

The most significant problem reduces to mechanism counteracting to the virion aggregation. In attempt to resolve the problem, we have investigated the behaviour of viruses on the surfaces of a silicon monocrystal with the preliminary vaccination them with antibodies. Figure 8 shows the behaviour of AMV viruses on the (111) silicon monocrystal surface.

The application of a suspension of AMV virions to the (111) surface of Si (111) was accompanied by the aggregation of virions in dense aglomerations and a decrease in height of obtained clusters from 19 nm to 9 nm. In this case, the formation of multilayer disordered clusters of virions was predominantly observed (Fig. 8).

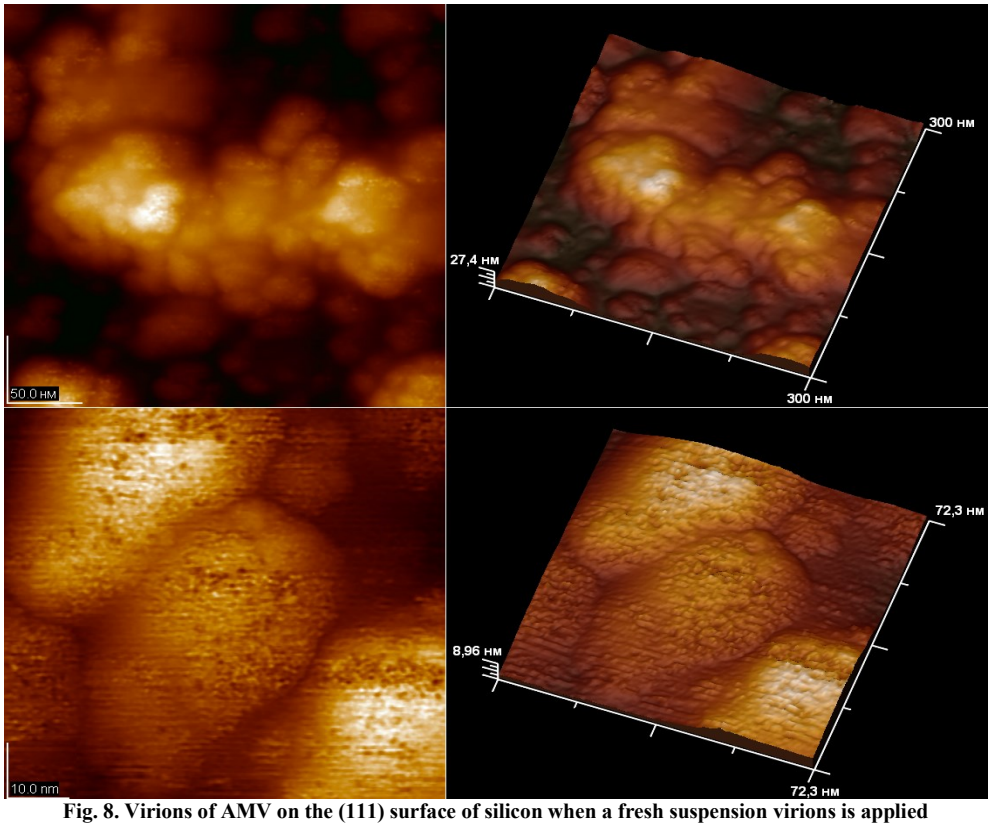


Fig. 8. Virions of AMV on the (111) surface of silicon when a fresh suspension virions is applied

There are two types of adsorption: 1) physical - occurs due to dispersion (Van der Waals) forces, the formation of hydrogen and other electrostatic interactions; 2) chemical - due to the formation of chemical bonds between adsorbate and adsorbent. As is known, the outer and inner surfaces of the virus capsid due to the presence of positively and negatively charged groups in the composition of the amino acid side radicals, carry charges of the opposite signs. However, the (111) surface of silicon has no charge. Therefore interaction of a capsid with this surface can not be related to electrostatic attraction. Consequently the electrostatic nature of such interactions has to be eliminated. Chemical adsorption has also to be excluded, since silicon does not form chemical bonds with any component of viral capsids. Therefore, the most probable processes in the adsorption of virions on the (111) surface silicon are van der Waals interactions and creation of hydrogen bonds with the surface. Van der Waals interactions

dominate for adsorption of virions on the surface of graphite. This material has strong developed hydrophobic properties. That is why the formation of stronger hydrogen bonds turns out impossible. The energy of Van der Waals interactions is the lowest (~ 2 kJ) among others. Therefore the Van der Waals interactions are very weak and are not accompanied by significant changes in the conformation of the molecules. As a result, there is no change in the height of the TMV virions on the surface of graphite.

On the contrary, the adsorption of TMV virions on the (111) surface of silicon, is accompanied by significant changes in virions conformation and a decrease in the height of the virions to 11.7 nm was clearly established. An identical result was obtained in the study of the behavior of alfalfa mosaic virus (AMV) on the surface with the same geometry. Adsorption of AMV virions was accompanied by a decrease in their height from 19.0 nm to 9.0 nm.

It is obvious that such changes in the conformation of the virions are due to the amino acid composition of the outer surface of the capsid. As the negatively charged amino acid residues containing hydroxyl and carboxyl groups (serine, threonine, tyrosine, asparagine and glutamic acid) are concentrated on the outer surface, they can provide virion adhesion by forming hydrogen bonds with the surface. By comparing amino acid content of the side chains of the above enumerated groups, that is in capsid proteins AMV and TMV (AMV-CP and TMV-CP, respectively), one comes to conclusion that content of such amino acids in AMV-CP is greater - Table 1.

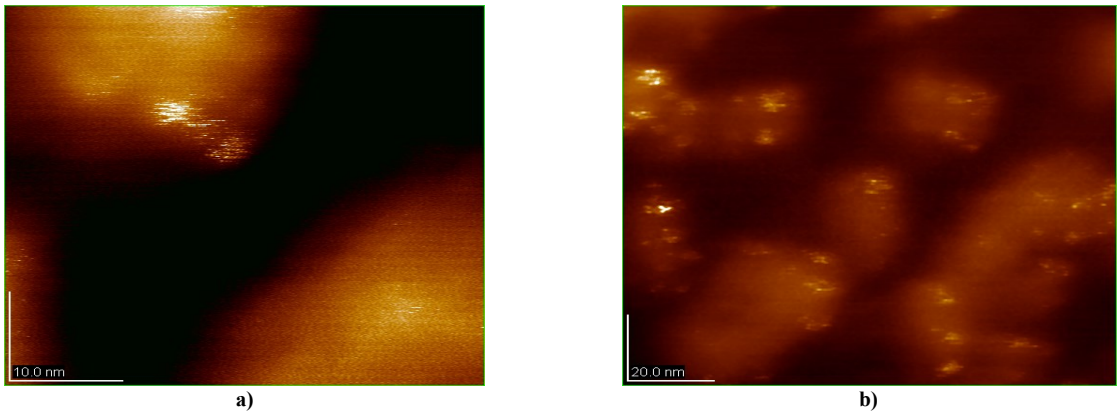
Table 1

The content of amino acids carrying hydroxyl and carboxyl groups in capsid proteins of TMV and AML

AVINOCYLATE	AMV-CP	TMV-CP
Serine	15	16
Treonin	13	16
Aspartic acid	11	8
Glutamic acid	11	6
Tirosine	4	4

Thus, adsorption of the tobacco mosaic virus and alfalfa mosaic virus on the surface of Si (111) is accompanied by variations in accommodation of the virions due to formation of hydrogen bonds and van der Waals interactions. The change in accommodation concludes in reducing of the virions height due to the interaction of amino acid residues on the outer surface of the capsid with silicon atoms on the surface of Si (111). The adsorption of TMV virions is accompanied by appearance of mono-layer films, while multi virion layers observe if the adsorption of TMVs on the surface of Si (111) occurs.

Investigation of the suspension of AMV virions and complexes of antybodies on the surface of Si (111) showed that the antibodies are specifically linked on the surface of the AMV virions (Fig. 9). This binding is accompanied by the aggregation of virions in dense agglomerations and reduction in their height from 19 nm to 9 nm. In the appointed case, predominant formation of multilayer disordered clusters of virions has taken place. Consequently, the binding of antibodies prevents the aggregation of virions. The suggestion can be confirmed by the specific distribution of virions on the Si(111) surface and decrease in the height of the viral particles clearly visible in the picture.



a) **b)**

Fig. 9. Suspensions of AMV virions and antibody complexes on the (111) surface of silicon

CONCLUSIONS

Nanowires of different types were synthesed and investigation of their physical, physico-chemical properties and morphology by applying probe microscopy and atomic resolution spectroscopy has been carried out. It is confirmed that the geometry of VTM's particles can be controlled by special preparing and dirigible alternation of chemical and mechanic environment parameters.

The optical activity of the TMV-Au complex with the maximum on wavelength 540 nm is detected. The

dependence of the optical absorption spectra intensity on the orientation of the polarization vector is observed. Established circular dichroism, opens up the possibility to use the TMV-Au complexes for smart materials creation.

In the study of nanowires electronic properties by the method of probe tunnelling spectroscopy, it has been found that spontaneous and induced transitions to a state with relatively high electrical conductivity take place in the voltage tension from 0 to 6 Volts. To our knowledge this effect is not observed for pure TMVs.

In the connection with the VTM's shell genetic programming, Tobacco Mosaic Virus derivatives can be manufactured with increased selectivity to inorganic materials or substrates. The latter fact allows us to obtain efficient self-assemblies of nanosized biostructures for many functional microdevices.

As it has been proved aggregation and clusterization of composite nanoparticles due to interaction of plant viruses with antibodies are absent.

However, superficial destroying of gold is observed if the TMV's nanoparticles have been removed from gold surface.

The proposed method for the synthesis of nanowires represents perspectives for significant improvement of useful technologies for production nanomaterials based on plant viruses. Knowing to combine TMV with inorganic and organic materials traces the route for developing a wide scale of interesting composites and hybrid materials like those which have been discussed here. Beside it TMV's templates manifest such level of reliability that allows to explore them under so hard conditions that ultra pass capabilities of traditionally used biological molecules.

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