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The Influence of Laser Irradiation and Ultrasound on the Structure, Surface Condition and Electrical Properties of TiS_2/C Composites

I.M. Budzulyak, L.S. Yablon*, R.V. Ilnytskyi, O.V. Morushko, O.M. Hemiy

Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., 76018 Ivano-Frankivsk, Ukraine

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The structure, morphology and electroconductive properties of TiS_2/C composite irradiated with laser and ultrasound are investigated in this work. It has been established that the conductivity of $TiS_2/C = 50/50$ composite obtained by ultrasonic dispersion in acetonitrile at room temperature is 290 $(\text{Ohm}\cdot\text{m})^{-1}$, which is in 10^6 higher than that value for pure titanium disulfide under the same conditions.

Keywords: Composite, Tungsten disulphide, Nanoporous carbon, Laser irradiation, Ultrasonic dispersion, Conductivity.

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1. INTRODUCTION

Nowadays, the significant efforts of scientists and technologists are aimed at finding the solution of the problem of creating high-performance devices for the needs of small energy. Special attention in this perspective is paid to high-power devices capable of delivering significant energy in a short period of time. There is no doubt that the solution of this problem lies in the electrode materials, which, along with high conductivity, must possess a number of other properties necessary for efficient functioning in electrochemical devices such as: presence of guest positions, chemical resistance, low cost and environmental safety. Therefore, the search for new and modifications of the already existing materials of molecular electronics devices today is one of the priority areas of physical material science. However, it is quite problematic to combine all the main characteristics in one material, therefore, current conductive additives are used and various composites are formed on its basis to overcome the problem.

Researchers` special attention is paid to developing methods for obtaining and modifying low-dimensional hybrid structures, which are a composition of two or more different materials. The main requirement for such materials is the high power of the unit of mass and volume, which to some extent correspond to natural minerals with a layered structure, in particular, tungsten disulphide, which, by conduction mechanisms, belong to dielectrics or semiconductors. They can serve as one of the components of the nanocomposite, as the capacity of the devices created on their basis is provided not only by the capacity of the electrical double layer (EDL), but also by rapid reversible Faraday reactions, which results in a significant increase in the amount of accumulated charge due to the diffusion of the electrolyte ions into the layered structure.

One of the components of these nanocomposites is nanoporous carbon material (NCM), atoms of which have the unique ability to form valence states with different hybridization of atomic orbitals and this capacity creates the preconditions for the formation of various nanocomposites on its basis, which may even contain nanoclusters of metals [1]. Of particular interest are nanoporous carbon structures of the a - C type, which contain a mixture of nanosized fragments from sp^1, sp^2 and sp^3-bonds, as these structures are of considerable scientific and practical interest as a material for extra-large capacity condenser systems.

The behavior of nanocomposites subject in action in the conditions of laser irradiation deserves significant attention, which at certain threshold values of energy in the pulse, as a rule, initiates the formation of point defect clusters, namely: pores, dislocation loops of various types, as well as ordered structures (superlattices) in volume and on the surface of solids. Another effective way of modifying nanocomposites is ultrasonic grinding of substances, which are in a state of colloidal solution [2], as a result of which it is possible to obtain nanoparticles of these substances, which leads to a change in their structure, and, consequently, in physical and electrochemical properties of materials.

2. MATERIALS AND METHODS

According to the optical data [3], TiS_2 is a broad-band semiconductor and its conductivity is low (10^{-2} - 10^{-1} $\text{Ohm}^{-1}\text{cm}^{-1}$), therefore there are corresponding difficulties in its use in devices for storage and accumulation of electrical energy, because such a system will have a high resistance, and, accordingly, a small efficiency factor.

In order to improve the physical properties (in particular, electroprotection), we formed TiS_2/C composites, in which the carbon has been obtained by the hydrothermal carbonization modified by our method [4]. The $YAG{:}Nd^{3+}$ laser was used in the research, which emits in the near infrared region of the spectrum (1.06 μm) and operates in the modulated Q-factor mode with a pulse duration $f = 10^{-2} - 10^{5}$ $\tau = 15\text{ns}$, impulses repetition frequency $f = 28\text{Hz}$, the energy in the impulse $E = 0.01\,\text{J/cm}^2$, and the irradiation time was 3 –

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[*] yablon_lyubov@ukr.net

7 minutes. Ultrasonic dispersion was carried out for 25 minutes in water and acetonitrile with the help of ultrasonic disperser UZDN-A, operating frequency range of which was 20 – 25 kHz. The crystalline structure of the resulting composite was studied using an X-ray diffractometer (CuK$_\alpha$-radiation) in the range of $10^o < 2\theta < 90^o$ angles. The conductivity of the studied materials was studied using the AUTOLAB PGSTAT12 measuring system. The measurement of the real Z' and imaginary Z'' parts of the integrated resistance $Z = Z' - jZ''$ was carried out in the frequency range $f = 10^{-2} - 10^5$ Hz at a voltage of 1 mV.

3. DISCUSSION OF RESULTS

Before and after laser irradiation the X-ray diffraction patterns of titanium disulphide, obtained by the method of analysis and investigation of the intensity of X-rays scattering in Cu(Kα)-radiation, indicate the presence of intense peaks at $2\theta = 15.5^o$, 34.6^o, 44.1^o, 53.63^o, 56.28^o , $57.54°$ and weakly intense peaks at $2\theta = 31°$, $31.7°$, $47.8°$, corresponding to the reflexes characteristic of the crystalline structure of 1T- TiS_2. This structure belongs to the hexagonal system, the spatial group of symmetry $P\bar{3}m1$ with the following cell parameters: $a = 0.3407$ nm, $c = 0.5691$ nm. The presence of intense peaks (101) and (001) indicates a strict orientation along the axes *a* and *c*.

On the diffraction reflection curves for TiS_2/C composites obtained by the mechanochemical method, before (a) and after (b) laser irradiation, except for peaks corresponding to the structure of 1T-TiS_2, an amorphous halo is observed at the angles $2\theta = 17 - 28$ °, with the presence of carbon in the composites [5].

It should be noted, that the intensity of the peaks corresponding to the crystalline structure of 1T-TiS_2 decreases in the composites, which indicates its distortion. Such a reorientation of the structure involves the fluctuations of the angles and lengths of the S–Ti–S connection and the disturbance of the ordering between the layers along the axis *c*, which leads to a change in the parameters of the lattice. The analysis of the received diffractograms with the help of the PowderCell program allowed to estimate changes in parameters of the crystalline lattice (Table 1) of titanium disulfide and its composites before and after laser irradiation.

Table 1 – The values of the parameters of the TiS_2 and TiS_2/C crystalline lattice before and after laser irradiation

Samples	TiS_2		TiS_2/C = 50/50		TiS_2/C = 20/80	
crystal lattice parameters	*a*, nm	*c*, nm	*a*, nm	*c*, nm	*a*, nm	*c*, nm
before laser irradiation	0.3409	0.5705	0.3420	0.5776	0.3423	0.5820
after laser irradiation	0.3408	0.5702	0.3431	0.5852	0.3430	0.5845

With the increase in the content of the NCM, the peak of the plane (001) (Fig. 1), shifts towards smaller angles, indicating an increase in the distance between the layers of titanium disulfide [6], while, as can be seen from the Table 1, the parameters of the lattice are increasing, especially for a stable lattice *c*.

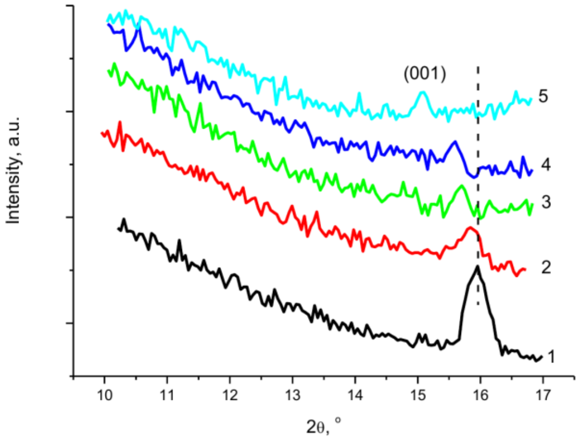


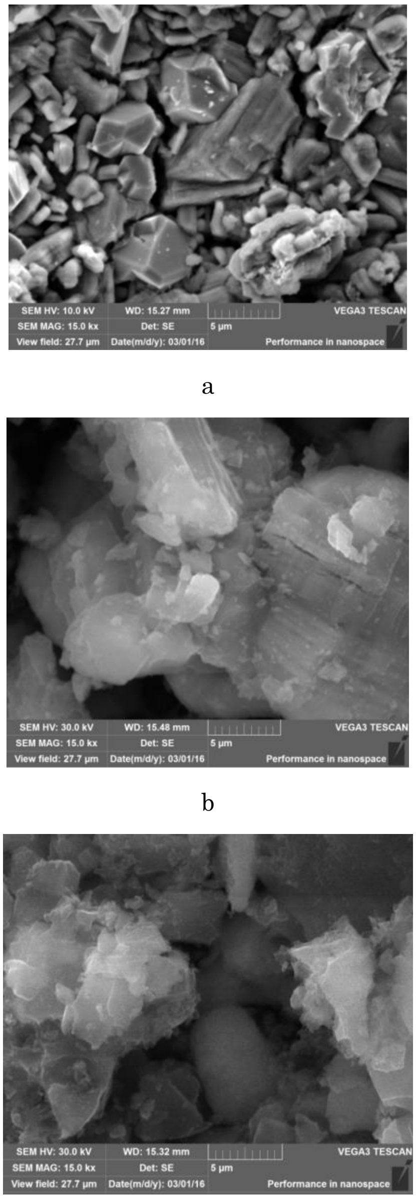
Fig. 1 – Fragments of X-ray diffractograms: 1 – TiS_2, 2 – TiS_2/C = 50/50, 3 – TiS_2/C = 20/80, 4 – laser irradiation TiS_2/C = 20/80, 5 – laser irradiation TiS_2/C = 50/50

The laser irradiation of titanium disulphide results in a decrease in the parameters of the crystalline lattice, and for the composites with the content of NCM, respectively, 50 and 80 %, these parameters increase, which can be explained by the thermal action of the laser beam, as a result of which the lattice passes into an elastically deformed state. After the termination of laser irradiation, the relaxation of the matrix takes place along with returning to a different energy state. Probably, under the influence of laser irradiation, the sublimation of sulfur also takes place, and there is the possibility of replacing sulfur with oxygen, namely the formation of titanium dioxide (rutile, anatase), which leads to a decrease in the period of the crystal lattice, whereas, as it is known [7], the interatomic distance of Ti – S is 0.2424 nm, and of Ti – O – 0.1977 nm. Thus, as a result of laser irradiation, the defect of the structure increases, and, consequently, the number of guest positions in which the ions of the electrolyte can be intercalated also increases.

As the phase analysis has shown, both for disulfide of titanium and its composites on its basis are characterized by the presence of anatase and rutile phase of titanium dioxide. Moreover, after the laser irradiation, the intensity of the corresponding peaks increases slightly, and this fact confirms the assumption that laser irradiation leads to a violation of the coordination of atoms Ti – S.

SEM image of pure disulfide of titanium and its composites before and after laser irradiation are presented in Fig. 2, which show that the powder of pure TiS_2 are crystals with well-defined edges, while the surface of the TiS_2/C composites are agglomerated layered particles. The laser irradiation leads to a sharp change in the morphology of the surface of composites, in particular, the particles of the composite are of lamellar shape with their simultaneous grinding.

The X-ray diffraction patterns of the composite TiS_2/C = 50/50 obtained by ultrasonic dispersion, where water or acetonitrile appeared as a solvent (Fig. 3, curves 1, 2), do not fundamentally differ from each other. The intensity of the peak (001) for the composite



a

b

c

Fig. 2 – SEM image surface, and a – TiS_2 to laser irradiation, b and c – composite TiS_2/C (50:50) before and after laser irradiation

obtained in acetonitrile is greater, and this probably indicates a better structuring of the material obtained [6], as this solvent is highly polar and has a higher affinity for the proton than water. This leads to the ionization of compounds, and its high dielectric permeability (38.8) contributes to their significant dissociation. The data obtained from measurements of magnetic susceptibility, allowed to conclude that acetonitrile can be considered as a ligand, which can form a weak π-bond. Thus, using ultrasound dispersion to obtain a TiS_2/C composite, there is a probability of formation of layered nanosized particles. This assumption can be confirmed by SEM images (Fig. 4), according to which this material is an aggregate of particles of a scale-like shape with dimensions of 50 – 500 nm.

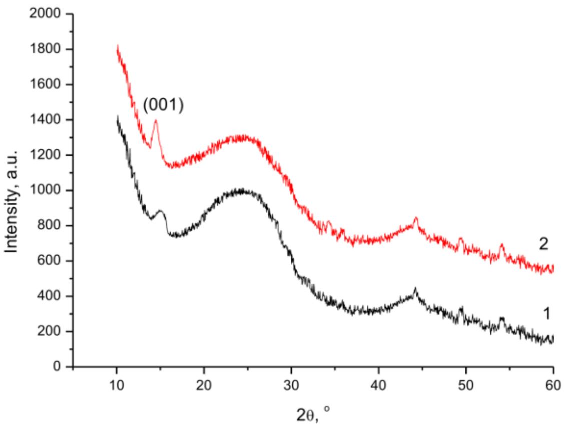


Fig. 3 – X-ray diffraction patterns of TiS_2/C = 50/50, composite obtained by ultrasonic dispersion in 1 – water, 2 – acetonitrile

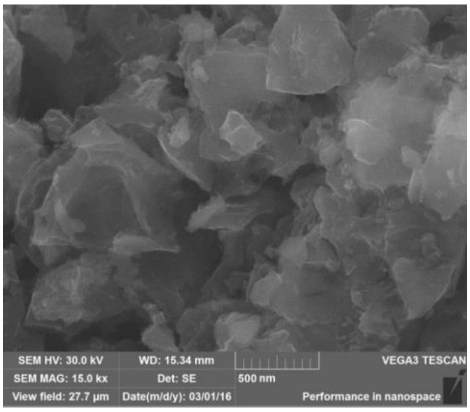


Fig. 4 – SEM image of the surface of composite TiS_2/C = 50:50 obtained by ultrasonic dispersion in acetonitrile

As it can be seen from Fig. 5, which depicts the dependence of electrical conductivity for pure titanium disulfide from the frequency at various temperatures, the electrical conductivity increases, when the temperature rises and reaches the maximum value of 323 K.

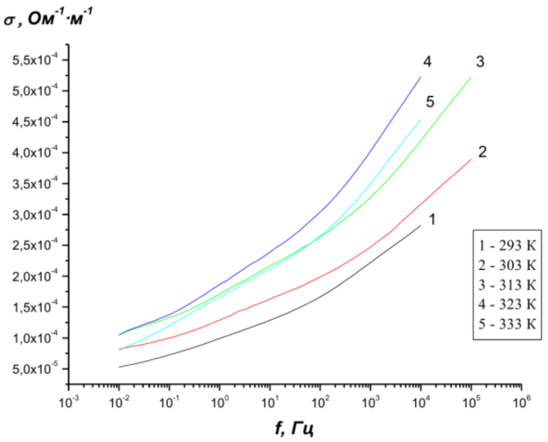


Fig. 5 – Frequency dependences of total electrical conductivity for pure titanium disulphide at different temperatures

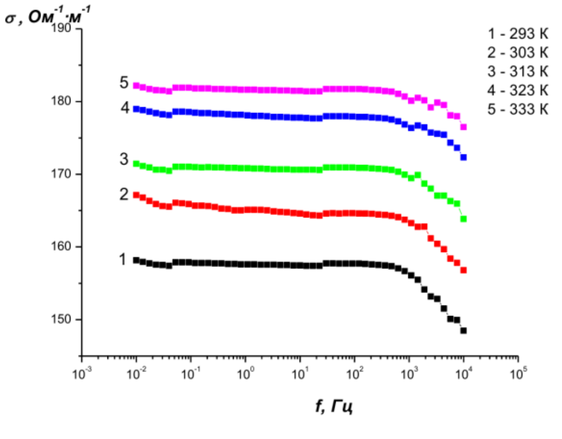
Reducing of electrical conductivity at a temperature of 333 K can be attributed to the reduction of relaxation time scattering of charge carriers when temperature rises.

As the X-ray analysis shows, the parameter *c* of the crystalline lattice increases with the addition of NCM, and this gives reason to believe that the carbon atoms increase the number of charge carriers, due to the transfer of electrons from the interlayer space to the layers of the S–Ti–S, which leads to an increase in the specific conductivity of composites (Fig. 6). The transport of electrons from the interlayer space into layers is confirmed by literary data [8]. In [8] thermoelectric properties of $(MS)_{1+x}(TiS_2)_2$ (M = Pb, Bi, Sn) were studied, which are composites with mutually placed layers of TiS_2 та MS. The number of electrons was estimated, according to the concentration of carriers and lattice parameters, transferred from MS layers, attributable to titanium atom. It was found that for $(BiS)_{1,2}(TiS_2)_2$, $(SnS)_{1,2}(TiS_2)_2$ and $(PbS)_{1,18}(TiS_2)_2$ it is 0.45, 0.16 and 0.2 respectively. Apparently, more electrons are transferred to $(BiS)_{1,2}(TiS_2)_2$, that authors [8] explain with the valence of the bismuth: as Bi^{3+}, we can conclude that one electron can be transfered from one BiS layer to two TiS_2 layers. This leads to the conclusion that each atom Ti receives 0.6 electrons, which, in reasonable limits, is consistent with the above assessment.

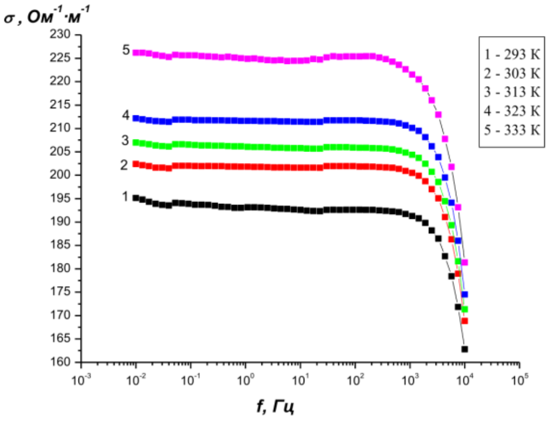
As can be seen from Fig. 6, an increase of carbon content in composites leads to a sharp increase of electrical conductivity. In particular, for a composite containing NCM at 80 % at room temperature, the electrical conductivity value is ~ 192 (Ohm·m)$^{-1}$, that in 10^6 exceeds this value for pure titanium disulfide under the same conditions.

As the temperature rises (Fig. 5, 6), a slight increase in electrical conductivity is observed (up to ~ 225 (Ohm·m)$^{-1}$), the magnitude of which affects both the charge carrier concentration and their mobility. It is likely that the concentration of free charge carriers increases faster than their mobility decreases.

A sharp decrease in electrical conductivity at frequencies above $0{,}5\cdot10^4$ Hz, which is the characteristic of carbon [9], was probably caused by redistribution of heights of jump barriers for transporting charges (tunneling), due to the formation of a porous structure and the decrease of the free-electron mileage, as a result of the formation of dielectric layers by oxygen hetero atoms, conductive breaks and the formation of closed pores.



a



b

Fig. 6 – Frequency dependences of total electrical conductivity for TiS_2/C at different temperatures: a – TiS_2/C = 50/50; b – TiS_2/C = 20/80

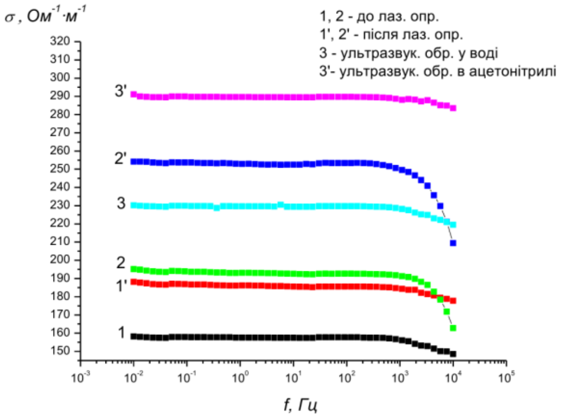


Fig. 7 – Frequency dependencies of conductivity for composites: 1 and – TiS_2/C = 50/50; 2 and 2' – TiS_2/C = 20/80; 3 and 3' – TiS_2/C = 50/50, obtained by ultrasonic dispersion respectively in water and acetonitrile.

Laser irradiation leads to a local increase in composites` temperature, which, in turn, stimulates the nucleation of graphite inclusions in NCM, and the further formation of ordered graphite layers. As the size and orientation of crystallites determine the texture of the material and the mechanisms of electrical conductivity, of NCM, and, consequently, the composite as a whole, which manifests itself in the growth of electrical conductivity (Fig. 7).

In addition, as can be seen from Fig. 7, the value of electrical conductivity for composite TiS2/C = 50/50, obtained by ultrasonic dispersion in acetonitrile exceeds this value for a laser-irradiated composite of the same composition obtained by the mechanochemical method and is about 290 (Ohm·m)$^{-1}$.

4. CONCLUSIONS

It was found that the effect of laser irradiation results in the growth of the parameters of the crystalline lattice of TiS_2/C composites, which results in the lattice passing into an elastic-deformed state, that is, the defect of the structure increases, and, consequently, the number of guest positions into which the ions of electrolyte can intercalate, can be increased. The surface of the composite TiS_2/C, obtained by ultrasonic dispersion, is a collection of nanosized particles of a scale-like shape with dimensions of 50-500 nm. It has been established that the conductivity of $TiS_2/C = 50/50$ composite obtained by ultrasonic dispersion in acetonitrile at room temperature is 290 $(\text{Ohm}\cdot\text{m})^{-1}$, which is in 10^6 higher than that value for pure titanium disulfide under the same conditions.

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