V.M. Boychuk[1], L.O. Shyyko[2], V.O.Kotsyubynsky[1], A. Kachmar[1,3]

Structure and Morphology of MoS₂/Carbon Nanocomposite Materials

[1]Vasyl Stefanyk Precarpathian National University, Shevchenko str. 57, 76018 Ivano-Frankivsk - Ukraine,
vmbojchuk@gmail.com, kotsuybynsky@gmail.com
[2]Precarpathian Eco-Energy Cluster, PEEC.org.ua, lyudmylas13@gmail.com
[3]Institute of Metal Physics named after G.V. Kurdyumov, National Academy of Sciences of Ukraine,
Akademika Vernadskogo boulevard, 36, Kyiv, 02000, Ukraine, andrij,nj.@gmail.com

The paper presents the experimental results of the hydrothermal synthesis composite materials based on the MoS₂ and carbon using different types of detergents (cetyltrimethylammonium bromide and Triton-X) or microporous carbon. The synthesized material was studied by XRD, TEM, and EDS. The investigation of structural and morphological properties of the obtained nanocomposite material shows that the nanoparticles (the average size of about 40 nm) obtained by detergent-assisted procedure have a multilayer crystal ordered superficial layers where quasi-two-dimensional MoS₂ layers alternate with amorphous carbon. The annealing at 500°C in argon caused the formation turbostratically stacked layers of crystalline MoS₂ with amorphous carbon located in the interlayer space. The core-shall morphology (carbon nanoparticles on the surface of MoS₂ clusters) was observed for composite materials synthesized on the base of microporous carbon.

Keywords: molybdenum disulfide, mesoporous carbon, hydrothermal synthesis, nanocomposite.

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Introduction

The layered metals chalcogenides MX_2 (M = W, Mo, Ti, X = S, Se) due to a combination of structural and electronic properties extensively studied for different applications. Nanostructured molybdenum disulfide (MoS_2) was successfully used as an electrocatalysts for splitting of water by the hydrogen evolution reaction [1], photocatalyst for the reduction of organic molecules [2], biomedical application [3], electrode material for lithium [4] and sodium [5] power sources, supercapacitors [6]. The crystal structure of MoS_2 consists of S-Mo-S packages stacked together in atomic layers bonded by van der Waals interactions. As a result, the 2D (thin graphene-like layers) and 3D (fullerene-like and multiwall complexes) morphology of nanoparticles will be thermodynamic preferable. The morphological properties of MoS_2 depend on the synthesis method – from physical and chemical [7] vapor deposition and to sol-gel [8] and hydrothermal [9] methods. The sphere of practical application of ultrafine MoS_2 can be greatly expanded by obtaining of composite systems with carbon nanomaterials (carbons [10], graphene [11], reduced graphene oxide [12]). The main reason for hybrid system formation is the enlarging of electric conductivity of MoS_2 as a wide band semiconductor that has great importance for some applications. The synergetic effects between chemically and electronically coupled MoS_2 and carbon components of composites obtained at simultaneous synthesis can cause novel properties formation. MoS_2/carbon has great potential as an active electrode material for hybrid supercapacitors with different complementary mechanisms of electric charge storage – formation of electric double-layer and pseudocapacitive mechanism with faradaic charge transfer processes due presence of several oxidation states of Mo ions. The development of effective synthesis approaches of MoS_2 / carbon materials obtaining with controllable morphological and structural properties have a great importance. In this work we have investigated and compared different variants of nanocomposite MoS_2/C obtaining and the influence of synthesis conditions on its characteristics.

I. Experimental Details

Three systems MoS_2 / carbon composite materials (S1, S2 and S3) were synthesized. At the first stage, the ammonium molybdate $(NH_4)_2MoS_4$ as an precursor for

MoS_2 obtaining was prepared. The following steps were realized. $(NH_4)_2MoO_4$ (6 g) was mixed with 40 ml of 20 % aqueous solution of $(NH_4)_2S$ with continuous stirring at the room temperature with the formation of a dark yellow precipitate of $(NH_4)_2MoS_4$:

$$(NH_4)_2MoO_4 + 4(NH_4)_2 \rightarrow (NH_4)_2MoS_4 + 8NH_4 \cdot OH$$

The obtained colloidal solution of $(NH_4)_2MoS_4$ was mixed with 2 ml of hydrazine hydrate $N_2H_4 \cdot N_2O$ and 100 ml of distilled water. The final pH = 7.5 of the reaction medium was adjusted by the adding of an aqueous solution of 0.01 M HCl. Different types of surfactants – cetyltrimethylammonium bromide $C_{19}H_{42}BrN$ (cationic) and Triton-X (non-ionic) were used as morphology-formed agents and carbon sources (systems S1 and S2, respectively). System S3 was prepared on the base of the specially obtained microporous carbon. Colloidal solutions of components for each system were loaded to Teflon autoclave and treated at the temperature of 220 °C for 24 hours. The black precipitates were centrifuged, washed with distilled water and ethanol and dried at 80°C. Additional annealing at 500°C for 2 hours in an argon atmosphere was used for each material.

The microporous carbon was obtained on the base of plant feedstock using carbonization and chemical activation procedures. The dry apricot seeds (fraction size of about 0.35 - 0.9 mm, 50 g) were mixed with 500 ml 30 % phosphoric acid (H_3PO_4). The resulting mixtures were stirred for 2 hours, dried to the constant weight at 90 °C and annealed in an argon atmosphere at 600 °C (heating rate of 10 °C min^{-1}) for 1 hour. The obtained powders were mixed with HNO_3 as nitrogen source with the continuous stirring at 50 °C under N_2 flow. The synthesized materials were washed to neutral pH and dried at 90 °C up to constant weight. The average nitrogen content in carbons was up to 2.0 wt%.

The crystal structure and phase composition of obtained materials were investigated by XRD and SAXS

(Cu (Kα) radiation). Morphological characteristics and chemical composition were obtained by TEM and EDS (FEI Technai G2 X-TWIN microscope).
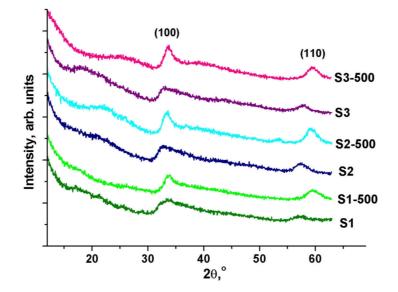
II. Results and discussion

MoS_2 has a hexagonal structure (P63/mmc symmetry group JCPDS 37-1492). XRD patterns of obtained materials are presented on Fig. 1. The state of all as-synthesized (dried at 80°C) samples are close to amorphous and corresponds to powder diffraction of turbostratically stacked layers [13]. The increasing of X-rays intensity at the 2θ ranges of 30 - 38° and 56 - 59° correspond to (100) and (110) reflections of bulk 2H-MoS_2. The missing of the (002) reflex and the appearing of diffraction response for (110) plane indicate the presence of single atomic layers of S-Mo-S structural units without considerable interstacking between them and the formation of graphene-like structure [9].

The annealing procedure causes the structural transformation for all systems of samples. The shifts of (110) reflex positions to higher angles at about 2θ = 2.2° were observed without change of (100) peak position. This result indicates the decreasing of interatomic distances within (001) crystallographic plane along the layers formed by trigonally linked S-Mo-S chains. At the same time accordingly to XRD data annealing did not significantly affect the nanocomposite morphology and composition.

Transmission electron microscopy (TEM) is a good instrument to identify and study of low-stacked MoS_2 layers. It was observed that S1 sample is formed by spherical-like particles with an average size of about 40 nm. The superficial layers of these particles have a crystalline ordering when the inner spaces are amorphous.

Surface layers of the particles consist of 7 - 9 layers formed by S-Mo-S packages. The average interlayer distance is about 0.95 nm that is much more than

Fig. 1. XRD patterns of MoS_2 / Carbon composite materials (system S1, S2 S3) before and after annealing at 500 °C.

0.62 nm for bulk MoS$_2$. The most probable reason for this effect is the presence of amorphous carbon layer between two planes formed by crystalline 2D-MoS$_2$ [14]. This hypothesis is confirmed by the energy dispersive X-ray spectroscopy data. It was determined that the average
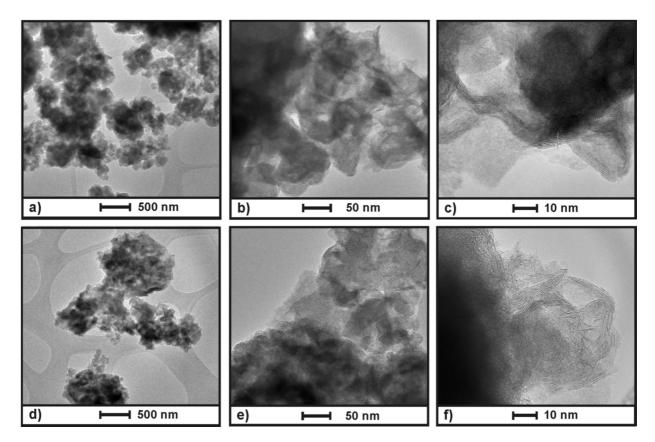

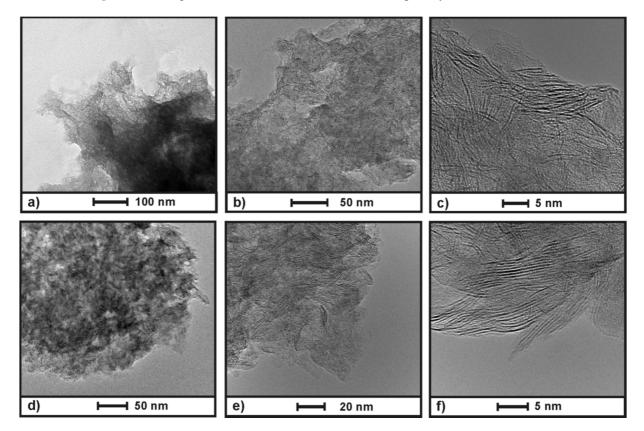**Fig. 2.** TEM images of S1 (a, b, c) and S1-500 (d, e, f) samples (synthesis with CTAB).

Fig. 3. TEM images of S2 (a, b, c) and S2-500 (d, e, f) samples (synthesis with Triton X-100).
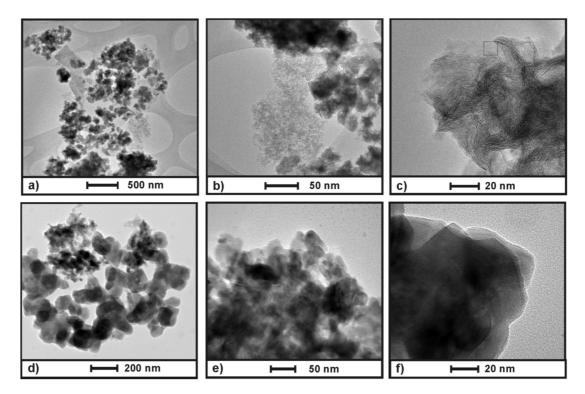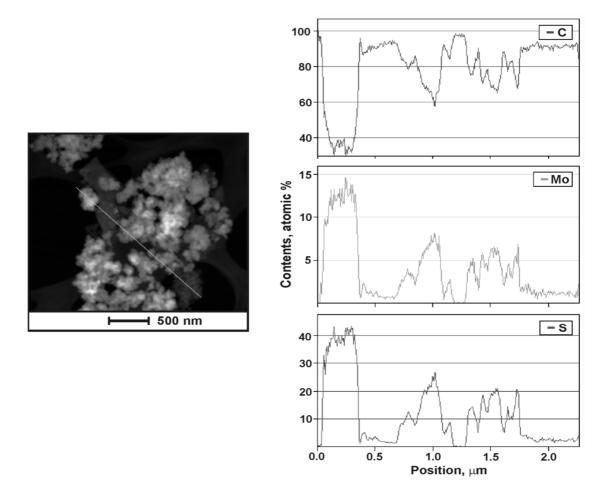
Fig. 4. TEM images of S3 (a, b, c) and S3-500 (d, e, f) samples (synthesis with mesoporous carbon).

Fig. 5. The TEM image of S3-500 sample and atomic content of C, Mo and S components for the material along the line of 2 μm obtained by energy dispersive spectroscopy.

contents of molybdenum, sulfur, and carbon for superficial layer of S1 sample are (15.8 ± 0.6) at. %, (27.0 ± 0.6) at. % and $(46.8 \pm 0.4$ at. %). At the same time, the presence of oxygen (about 10.4 ± 0.2 at. %) was detected. In any case, the surface layers are enriched with molybdenum ions (the ratio S/Mo is 1.71), respectively. Thermal treatment at $500\,^{\circ}C$ leads to increasing of structural ordering for separate packages with the simultaneous disordering and particle's destruction. S1-500 sample consists of turbostratically stacked layers of crystalline MoS$_2$ with amorphous carbon located in the interlayer space. The average interlayer distance is about 0.90 nm but the range of its variation is very broad. The relative contents of molybdenum, sulfur, carbon and oxygen in the S1-500 sample are about (13.0 ± 0.6) at. %, (23.0 ± 0.5) at. %, (53.9 ± 0.5) at. %, and (10.1 ± 0.2) at. %, respectively. We can make a conclusion about a little the annealing effect on the ratio between sulfur and molybdenum (1.71 and 1.77, respectively) that is evidence of temperature stability of the structure.

The using of nonionic surfactant Triton X-100 (sample S2) leads to respectively lower crystal ordering with the formation of a sponge-like morphology (Fig. 3). As-synthesized sample consists of highly disoriented S-Mo-S packages without saving of interplanar distance stability.

The relative contents of molybdenum, sulfur, carbon, and oxygen for a superficial layer of S2 sample are (11.2 ± 0.3), (27.8 ± 0.3), (52.9 ± 0.3) and (8.1 ± 0.1) at. %. The annealing at $500\,^{\circ}C$ leads to decreasing of average carbon content to (26.4 ± 0.1) at. %. At the same time relative contents of molybdenum, sulfur and oxygen atoms for S2-500 sample are (18.3 ± 0.3), (41.3 ± 0.3), and (14.0 ± 0.1) at. %. The ratios of molybdenum and sulfur are very close before and after thermal treatment.

The as-synthesized S3 nanocomposite consists of packages of turbostratically stacked nanosheets of MoS$_2$ with the respectively low ordering and the presence of amorphous regions which corresponds to carbon fragments (Fig. 4). The annealing causes the agglomeration of particles with the formation of carbon shells around the MoS$_2$ spherical particles.

This conclusion is based on the results of EDS analysis the relative content of carbon atoms along 2 μm. It was determined that the average carbon content is about 35 - 40 at %.

Conclusions

The three different types of MoS$_2$ / carbon nanocomposites were obtained via hydrothermal synthesis in the close conditions at the presence of ionic (cetyltrimethylammonium bromide) and non-ionic (Triton-X) surfactants and also microporous carbon. Micelles of cationic and non-ionic morphology-determined additives played the role of templates and initial shape and size of molybdenum disulfide particles. It is shown that the resulting material has consisted of MoS$_2$ layers alternate with amorphous carbon. It was determined the increasing the interatomic distances within the (001) crystallographic plane for MoS$_2$ nanoparticles and shown the presence of single atomic layers formed by S-Mo-S structural units without considerable interstacking. The annealing at $500\,^{\circ}C$ leads to the destruction of crystal ordering for MoS$_2$ for composite materials obtained by surfactant-assisted methods. The atomic ratio between Mo atoms and S atoms did not change indicating the temperature stability of the materials. The nanocomposite obtained on the base of microporous carbon consists of turbostratically stacked nanosheets of MoS$_2$ with the respectively low ordering separated by amorphous carbon fragments. The annealing at $500\,^{\circ}C$ leads to the agglomeration of MoS$_2$ particles and the formation of carbon shells around them.

Boychuk V.M. - candidate of chemical sciences, associate professor of the department of theoretical and experimental physics, associate professor of the department of physics and teaching methods;
Shyyko L.O. - candidate of physical and mathematical sciences, head of the Precarpathian eco-energy cluster;
Kotsyubynsky V.O. - doctor of physics and mathematics, professor of the department of materials science and new technologies.
Kachmar. A. - leading specialist of the joint educational and scientific laboratory of magnetic films.

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В.М. Бойчук[1], Л.О. Шийко[2], В.О. Коцюбинський[1], А. Качмар[1,3]

Структура і морфологія нанокомпозитного матеріалу MoS₂ / Карбон

[1]ДВНЗ "Прикарпатський національний університет імені Василя Стефаника", вул. Шевченка, 57, 76018 Івано-Франківськ – Україна, vmbojchuk@gmail.com, kotsuybynsky@gmail.com

[2]Прикарпатський еко-енергетичний кластер, PEEC.org.ua, lyudmylas13@gmail.com

[3]Інститут металофізики імені Г. В. Курдюмова НАН України, бульвар Академіка Вернадського, 36, Київ, 02000, Україна, andrij.nj.@gmail.com

Стаття присвячена експериментальному вивченню впливу умов гідротермального синтезу на структуру та морфологію нанокомпозитних матеріалів на основі MoS₂ та вуглецю за умови застосування при отриманні різних типів поверхнево-активних речовин (цетилтриметил амонію бромід та Тритон-X) або ж мікропористого вугілля. Отримані матеріали вивчалися методами рентгеноструктурного аналізу, трансмісійної електронної мікроскопії та енергодисперсійної спектроскопії. Встановлено, що матеріали отримані за участю поверхнево-активних речовин, формуються з наночастинок розміром близько 40 нм, приповерхнева зона яких складається з кристалічно-впорядкованих шарів 2D-MoS₂, розділених аморфним вуглецем. Відпал при 500°C в атмосфері інертного газу викликає руйнування частинок та утворення турбостратично-організованих пакетів MoS₂, оточених аморфним вуглецевим матеріалом. Для нанокомпозитів MoS₂ / вуглець зафіксовано утворення оболонок з наночастинок аморфного вуглецю навколо частинок дисульфіду молібдену.

Ключові слова: дисульфід молібдену, мезопористий вуглець, гідротермальний синтез, нанокомпозит.