

Assembling of MoS₂-based photosensitive organic-inorganic nanocomposites by exfoliation-restacking technique

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New nanocomposite compounds containing alternating layers of molybdenum disulfide and organic compounds (dyes, polyvinyl alcohol) have been synthesized using single-layer dispersions obtained by exfoliation of bulk MoS₂ crystals. The formation mechanism of those compounds as well as their structure are discussed. The data on photoelectric sensitivity of the systems consisting of MoS₂-polyvinyl alcohol nanocomposite and some photoconductive polymers are reported.

Новые нанокompозитные соединения, содержащие чередующиеся слои дисульфида молибдена и органических соединений (красители, поливиниловый спирт), синтезированы с использованием монослоевых дисперсий, полученных расщеплением массивных кристаллов MoS₂. Обсуждается механизм образования и строение этих соединений. Приводятся данные по фотоэлектрической чувствительности систем, состоящих из нанокompозита MoS₂-поливиниловый спирт и некоторых фотопроводящих полимеров.

The efficient collection and conversion of solar energy into electricity has become an important problem. This stimulates a search for new approaches for designing materials for photovoltaic devices which can be an alternative to a widely used silicon-based solar cells. The highest power conversion efficiency (η) (10.4 % for AM 1.5 solar radiation) equivalent to that of the silicon-based cells is achieved in photoelectrochemical cells [1] consisting of inorganic semiconductor TiO₂ nanophase sensitized to visible light by means of organic compounds and immersed into a redox electrolyte solution. In these cells, the TiO₂ nanophase provides a large surface area for contact with sensitizing agent and a high carrier mobility inherent in inorganic semiconductors. However, the presence of liquid electrolyte in these cells makes them difficult in operation. On the other hand, the more processable, inexpensive, more simple in manu-

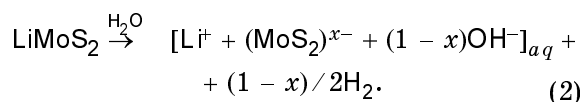
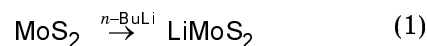
facturing photovoltaic cells with large working area can be obtained based on photoconductive polymers [2]. The latter cells exhibit a high charge carrier photogeneration quantum yield, but provide relatively low power conversion efficiency ($\eta = 0.1-0.2$ %) due to a low charge carrier mobility and intensive volume recombination. Among the systems combining inorganic semiconductors and polymers, those based on CdS and CdSe nanoparticles are studied most intensively [3]. In this respect, molybdenum disulfide is of particular interest as a component of such photovoltaic cells since the bulk crystals of this inorganic semiconductor exhibit a wide interband absorption spectrum (200–1040 nm) which covers almost the whole solar radiation range [4]. Another attractive feature of molybdenum disulfide is its layered structure and possibility to exfoliate its bulk crystals in liquid medium to separate the layers by means of

solvent molecules with formation of single-layer dispersions [5]. The layers in the dispersions can further be restacked in the absence or absence of additional organic compounds. The former makes it possible to obtain the ultra-dispersed particles of molybdenum disulfide itself while the latter has been found to provide assembling of the hybrid hetero-layered compounds containing alternating S–Mo–S layers and the monolayers of organic component (e.g., aromatics, alkyl ammonium cations) [5]. In this work, we have studied the preparation peculiarities of new MoS₂-based hybrid compounds which show promise for photovoltaics (the compounds with organic dyes and polyvinyl alcohol) and photoelectric properties of some systems containing the particles of restacked molybdenum disulfide.

Lithiation and exfoliation of MoS₂ (DM-1) to single-layer dispersions (1 g/l) was carried out according to the procedure described in [6]. In method A, the exfoliation was performed in water or in water-ethanol (4:1 v/v) solutions for the reactions with polyvinyl alcohol (PVALc) and dyes, respectively. Then, solutions of 6g rhodamine perchlorate, 1-oxazine perchlorate, thionine acetate and PVALc in the above-indicated solvents were added in the ratio 0.5 (dyes) and 0.9 (PVALc) mol per 1 mol of MoS₂. In method B, MoS₂ obtained by acidifying the dispersions with HCl, was washed and suspended in water (PVALc) or acetonitrile (dyes) solutions of the reagents taken in the same molar ratios as in method A. After stirring during 1 day, the precipitates were filtered off, washed, and dried in vacuum. The guest content was calculated from the elemental analysis data. To prepare the films for photoelectric measurements, the suspensions of restacked MoS₂ (1–90 %) in aqueous PVALc solution were deposited onto ITO support followed by drying at 100°C during 5 hours. To obtain bilayer samples, the first layer was coated by photoconductive layer consisting of polyimide based on triphenylamine derivatives (PI-1, *p*-type) [7] or by poly(epoxy)propyl carbazole doped (50 %) with perylene diimide derivative (PEPC-PDI, *n*-type) [8]. The film thickness (*d*) varied in the range of 2–4 microns. Photoelectric sensitivity *S* was measured by electrophotography on the films charged in the field of positive or negative corona discharge. To evaluate the effect of MoS₂-containing layer, the sensitivity of the blank samples without this layer (*S*_c) was measured and the difference Δ = *S* – *S*_c was determined. X-Ray powder diffraction patterns were recorded using a DRON-3 diffractometer (Cu

K_α-radiation, Ni-filter). Absorption spectra were recorded using a "Specord" spectrophotometer.

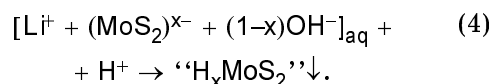
The exfoliation process of bulk MoS₂ crystals includes lithiation of the initial material followed by hydration of the resulting compound with the assistance of ultrasound (Eqs.1, 2) [6, 9].



The so-called single-layer dispersions obtained in this way are ionic systems which contain solvated lithium cations, hydroxide anions and macroanions (MoS₂)^{x-}, retaining partial negative charge. According to the recent studies [5], introduction of organic species (cationic, or capable to be protonated in reaction medium) into the dispersions induces assembling of hybrid materials containing the organic layers included between the inorganic layers of the host (Eq.3).



However, acidifying of the reaction medium causes precipitation of the ultra-dispersed particles of restacked MoS₂ (or perhaps H_xMoS [5]) without the guest (Eq.4).



In order to compare the reactivity of single-layer dispersions and restacked MoS₂, the solutions of polymer or dyes were added directly to the dispersions (method A) as well as to the powdered restacked material (method B). According to diffractometry data, intercalation of MoS₂ occurred in both procedures (Fig. 1). The clearly seen set of 00*l* reflections in the X-ray diffraction patterns of the substances obtained displays their layered structure and allows calculation of the interlayer spacing expansion (Δ*c*) with respect to the initial MoS₂ interlayer distance (*c* = 6.15 Å) (Table). Note that the starting crystalline MoS₂ did not react under these conditions.

As can be seen in Table, both intercalation methods of the dyes result in nearly the same lattice expansions and guest contents. It should be mentioned that the Cl content determined for the materials obtained using perchlorate salts (rhodamine,

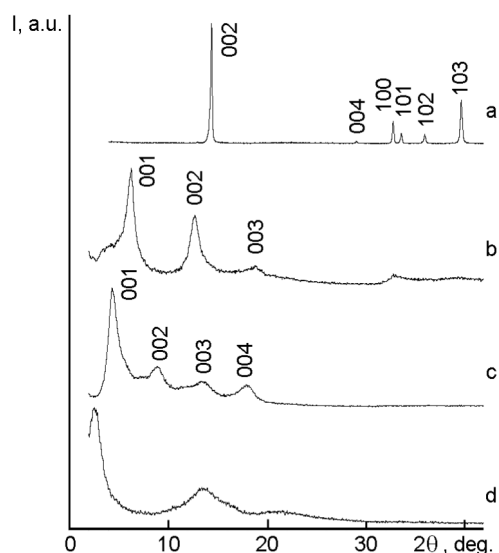


Fig. 1. X-Ray diffraction patterns of initial crystalline MoS_2 (a) and MoS_2 intercalated with rhodamine (b), and PVALc (c, d) prepared by method A (c) and B (b,d).

oxazine) does not exceed 0.02 mol/mol MoS_2 for both methods, thus indicating that the main part of the cationic guest dye molecules contains the $(\text{MoS}_2)^{x-}$ anionic layers as the counter-ions. This means that the intercalation proceeds via ionic mechanism (Eq.3) for both the dispersions and restacked MoS_2 and, consequently, the latter compound should be in ionic form. It appears that these results prove the H_xMoS_2 description for the restacked MoS_2 . Though the precipitated MoS_2 shows no visible interlayer spacing expansion with respect to the crystalline one, this fact does not contradict the presence of hydrogen ions in its structure as it was demonstrated for the related NbSe_2 structure [10].

The intercalation of polymer molecules is also achieved by both procedures studied, but the Δc values differ by two times between methods A and B. Besides, the method A provides more uniform filling of

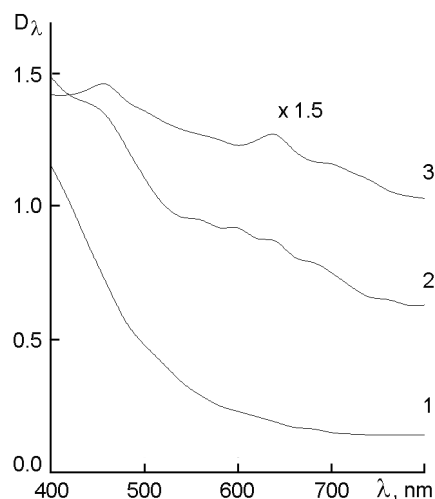


Fig. 2. Absorption spectra of MoS_2 -PVALc films with various MoS_2 concentrations (per cent): 2 (1), 40 (2), 100 (3).

the interlayer spaces resulting in the appearance of four 00l reflections in the diffraction patterns, while in the case of method B, only two broad reflections are present: one (corresponding to 6.2–6.4 Å) can be assigned to a turbostratically stacked non-intercalated MoS_2 , and the other single reflection in a low-angle-region (35 Å) is indicative of mesoporous rather than regular intercalated structure. It should be noted that porous structure could augment the contact surface area of the MoS_2 particles with the other components of photovoltaic cells. For that reason, the films of MoS_2 -PVALc prepared according to method B and combined with transport polymers were tested for photoelectric sensitivity.

Absorption spectra of the MoS_2 -PVALc films obtained from aqueous suspensions and containing MoS_2 particles in different concentrations ($C = 2$ –100 % w/w) are shown in Fig. 2. The spectrum of the film consisting of restacked molybdenum disulfide only ($C = 100$ %) covers a broad region

Table. Thickness of the guest monolayers (Δc) and compositions of the $(\text{guest})_x\text{MoS}_2$ compounds

Guest	Method A		Method B	
	$\Delta c, \text{Å}^*$	Guest/host mol/mol	$\Delta c, \text{Å}^*$	Guest/host mol/mol
Rhodamine 6g	7.4	0.07	7.8	0.07
Oxazine 1	8.1	0.11	6.1–7.5	0.08–0.11
Thionine	3.5	0.15	4.2	0.16
Polyvinyl alcohol	14		29**	0.88

* the difference between interlayer distance of hybrid compound and non-intercalated MoS_2

** additional phase of non-intercalated MoS_2 is observed.

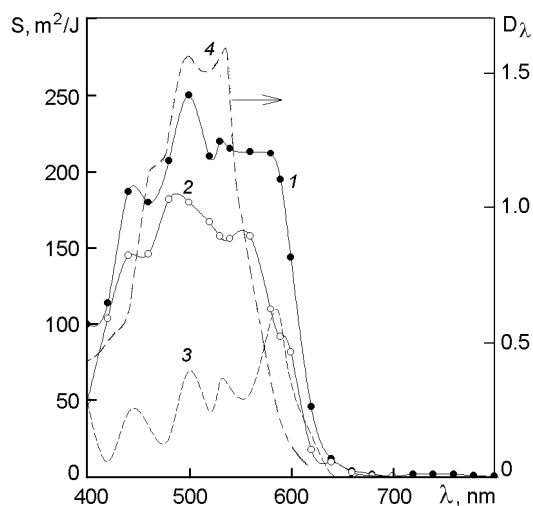


Fig. 3. Spectral dependences of photoelectric sensitivity for bilayer sample $\text{MoS}_2(90\%)$ -PVALc + PEPC-PDI (S) (black circles), for PEPC-PDI (S_c) (open circles) under frontal excitation and negative charging, the difference spectrum (dashed line 3) and absorption spectrum of PEPC-PDI (dotted line 4).

as in the case of bulk crystals. As compared to this spectrum, a pronounced shift to the short-wave region is observed when MoS_2 particles obtained from dispersions are immersed in PVALc and their concentration is lower than 40 %. This shift is indicative of a quantum-size effect and points to the presence of MoS_2 particles of very small sizes ($r = 3$ –10 nm) in the films [4, 11]. Absorption of more voluminous particles ($r > 10$ nm) is known to be closer to that of bulk crystals [4, 11]. For that reason, the appearance of additional shoulder in the 500–800 nm region when C increases to 40 % indicates that, starting from this concentration, aggregation of the particles in the film takes place. Taking into account such absorption behavior, the films with a high concentration of MoS_2 in PVALc were chosen for testing in photosensitive nano-heterophase compositions.

The MoS_2 -PVALc films themselves exhibited a very low photoelectric sensitivity (S). However, bilayer samples prepared by covering MoS_2 -containing film deposited on the ITO support by a layer of photoconductive polymer (PI-1 or PEPC-PDI) showed a significant sensitivity which exceeded noticeably that provided by photoconductive polymer itself (S_c) (Figs. 3–5). The sensitivity was found to depend on the sign of the carriers generated under corona discharge and its value increases when the sample is charged correspondingly to the sign of the major carriers of transport polymer. For in-

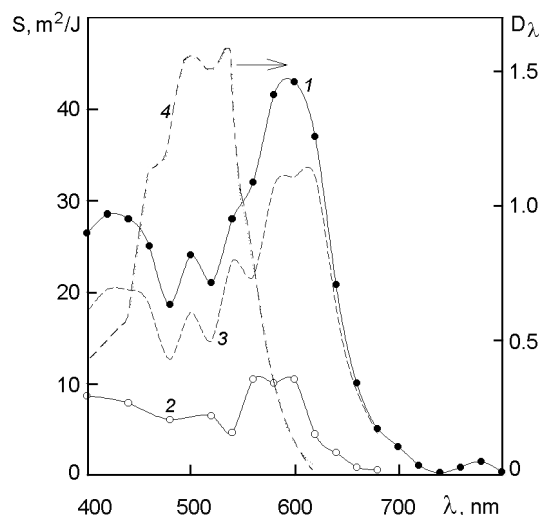


Fig. 4. Spectral dependences of photoelectric sensitivity for bilayer sample $\text{MoS}_2(90\%)$ -PVALc + PEPC-PDI (S) (black circles), for PEPC-PDI (S_c) (open circles) under frontal excitation and positive charging, the difference spectrum (dashed line 3) and absorption spectrum of PEPC-PDI (dotted line 4).

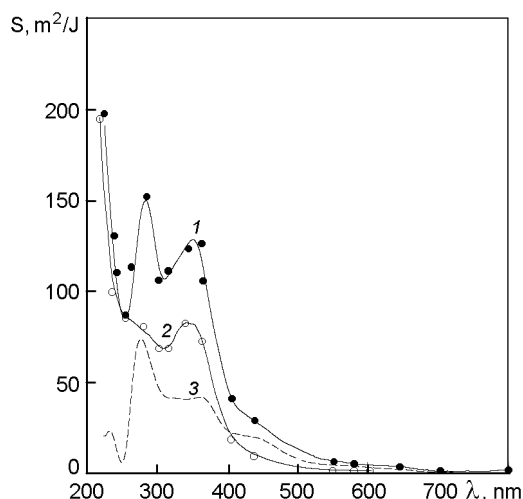


Fig. 5. Spectral dependences of photoelectric sensitivity for bilayer sample $\text{MoS}_2(90\%)$ -PVALc + PI-1 (S) (black circles), for PI-1 (S_c) (open circles) under frontal excitation and positive charging and the difference spectrum (dashed line).

stance, in the case of frontal (through the additional polymer layer) excitation of the sample covered by n -type polymer (PEPC-PDI), the negative charging (which implies the drift of electrons) results in an increased S (ca. $250 \text{ m}^2/\text{J}$) and Δ (ca. $100 \text{ m}^2/\text{J}$) values as compared to the positive charging, which provides the sensitivity $S \approx 45 \text{ m}^2/\text{J}$ and $\Delta \approx 35 \text{ m}^2/\text{J}$ (Figs. 3, 4).

Note that the maximum Δ values are attained at excitation in the polymer absorption band under the condition $D_\lambda = k_\lambda d \sim 1$ (where D_λ and k_λ are optical density and absorption coefficient of the conductive polymer, respectively), when the excitation intensity at the interface between MoS₂-containing layer and transport polymer is essential. These facts are consistent with the photogeneration of charge carriers at the interface between MoS₂-containing phase and transport layer, for instance, due to formation of the hybrid electron-hole pairs which can then dissociate, providing the charges remained in the MoS₂ particles and those capable of drift through a polymer layer. Noteworthy, the significant Δ values are observed for the systems containing not only *n*-, but also *p*-type polymers along with a MoS₂ layer. In the latter case, the maximum S and Δ values are increased to ca. 150 m²/J and 75 m²/J, respectively (Fig. 5). In the framework of hybrid pairs model, this means that MoS₂ particles can accept holes or electrons, depending on the transport agent nature. Though the reason of such dual behavior is expected to be clarified in further investigations, it can be supposed that it may be caused by different properties of the particles of different sizes or perhaps by the presence of MoS₂ particles intercalated with PVAlc along with non-intercalated ones, as follows from X-ray diffraction data.

Thus, the exfoliation-restacking of semiconductor bulk MoS₂ crystals provides preparation of ultra-dispersed particles of this material as well as a large variety of the MoS₂-based heterolayered structures which include the organic components suit-

able for designing nano-geterophase photovoltaic cells. In testing the biphasic systems containing MoS₂ nanoparticles intercalated with polyvinyl alcohol and photoconductive polymers, these systems exhibited a significant photoelectric sensitivity (up to 250 m²/J) exceeding the proper sensitivity of organic components by a factor of 1.5–4.

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Складання фоточутливих органіко-неорганічних нанокмполімерів на основі MoS₂ методом розшарування-перепакування

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Нові нанокмполімерні сполуки, які містять переміжні шари дисульфиду молібдену та органічних сполук (барвники, полівініловий спирт), синтезовано з використанням моношарових дисперсій, одержаних розшаруванням масивних кристалів MoS₂. Обговорюється механізм утворення та будова цих сполук. Подано дані про фотоелектричну чутливість систем, що складаються з нанокмполімеру MoS₂-полівініловий спирт та деяких фотопровідних полімерів.