

Transition Metal Trichalcogenides as Novel Layered Nano Species

V.E. Fedorov¹, S.B. Artemkina¹, E.D. Grayfer¹, Y.V. Mironov¹, A.I. Romanenko¹, I.V. Antonova²,
M.V. Medvedev³

¹ *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Science,
3, Acad. Lavrentiev prospect, 630090, Novosibirsk, Russian Federation*

² *Rzhanov Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Science,
13, Acad. Lavrentiev prospect, 630090, Novosibirsk, Russian Federation*

³ *Samsung Advanced Institute of Technology, Suwon, South Korea*

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In search for new materials for nanoelectronics, many efforts have been put into development of chemistry and physics of graphene, and, more recently, of other inorganic layered compounds having a bandgap (*h*-BN, MoS₂ etc.). Here we introduce a new view on the family of transition metal trichalcogenides MQ₃ (M=Ti, Zr, Nb, Ta; Q=S, Se), which were earlier considered as quasi-one-dimensional systems, and demonstrate that they also may be regarded as layered species suitable for exfoliation by a chemical method. Stable, concentrated colloidal dispersions of high-quality crystalline NbS₃ and NbSe₃ nanoribbons down to mono- and few-layer-thick are prepared by ultrasonic treatment of the bulk compound in several common organic solvents (DMF, NMP, CH₃CN, *i*PrOH, H₂O/EtOH). The dispersions and thin films prepared from them by vacuum filtration or spraying are characterized by a set of physical-chemical methods. Current-voltage characteristics of the NbS₃ films show that charge carrier mobility is as high as 1200 – 2400 cm²V⁻¹s⁻¹, exceeding that of MoS₂ and making NbQ₃ promising potential candidates for field-effect transistors.

Keywords: Niobium Trichalcogenides, Nanocrystals, Colloids, Semiconductors, Thin films

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1. INTRODUCTION

Discovery of graphene has prompted a great interest in other inorganic layered compounds. Although graphene possesses extremely high carrier mobility and other remarkable properties, zero energy gap retards its application in logic electronics. In search for suitable materials, some well-known layered materials including *h*-BN, transition metal dichalcogenides MQ₂ (M=Nb, Ta, Mo, W; Q=S, Se), and Bi₂Q₃, were reconsidered in the context of the present-day knowledge of low-dimensional systems [1-13]. In the present work we focused on the niobium trichalcogenides NbQ₃ (Q=S, Se). During several decades, trichalcogenides of niobium and tantalum have attracted considerable attention in the fundamental research as quasi-one-dimensional systems with intriguing structural and electronic properties including Peierls instability, formation of charge density waves and some related unusual phenomena [14-15]. Although NbQ₃ were considered traditionally as quasi-one-dimensional (1D) systems because of their high anisotropic electronic and chain-like structural properties, they may also be regarded as members of the group of layered materials. The crystal structures of MQ₃ consist of one-dimensional distorted trigonal (wedge-shaped) prisms with metal atom close to the center of each prism (Figure 1 a). The prisms are bonded additionally in two prism layers; thus, the same packing may be considered as a layered structure (Figure 1 b).

In contrast to graphene and some of its inorganic analogues, very few attempts have been made to exfoliate NbQ₃. This may be explained by the fact that NbQ₃ crystals grow in the form of wires with very narrow widths that makes it difficult to apply mechanical exfoliation techniques. Therefore, we suggest an alternative way to exfoliate NbQ₃ in liquid phase and assemble it into thin

films suitable for nanotechnology devices. We showed that NbS₃, NbSe₃ and other trichalcogenides may be efficiently exfoliated down to mono- and few-layers in many common organic solvents resulting in high-quality crystalline nanoribbons stably dispersed in colloids. Liquid-phase exfoliation technique is versatile, scalable, and well-suited to obtain NbQ₃ thin films on a variety of substrates. The process may be potentially extended to all the transition metal trichalcogenide family with their rich variety of properties. Thin films produced from these dispersions possess excellent characteristics of transport and charge carrier mobility making them promising candidates for future electronics.

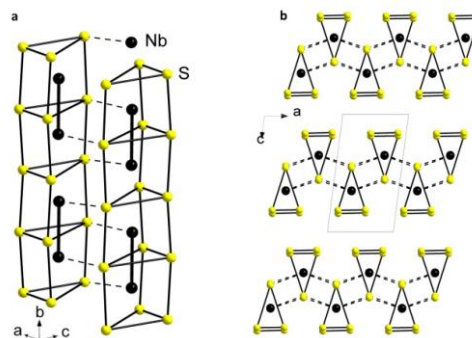


Fig. 1 – Structure of triclinic niobium trisulfide: *a* – two wedge-shaped columns of sulfur atoms with paired niobium atoms inside; *b* – the structure view on crystallographic *ac* plane demonstrating prism bonding into layers.

2. EXPERIMENTAL

2.1 The Synthesis of NbQ₃

The synthesis of triclinic NbS₃ and monoclinic NbSe₃

was carried out using high temperature ampoule method starting from high purity elements. The stoichiometric mixtures of Nb:Q=1:3 were loaded into ampoules which were evacuated to 10^{-5} bar, sealed under dynamic vacuum, heated in electrical furnace at 600°C during 160h, and then cooling to room temperature for 5 h.

2.2 Preparation of Colloidal Dispersions of NbQ₃

Bulk powdered samples of NbS₃ or NbSe₃ (0.5 – 0.7 g) were sonicated in Elmasonic S40 ultrasonic bath (120 W) in 80–100 ml of organic solvents for several hours. The resulting mixtures were centrifuged at 2600 rpm at ambient temperature to remove large (heavy) particles.

2.3 Preparation of Thin Films of NbQ₃

The films of NbS₃ and NbSe₃ were prepared from colloidal dispersions by their filtration using membrane filters Whatman Anodisc with pore size of 0.02 μm and by spray method.

3. RESULTS AND DISCUSSION

3.1 Preparation and Characterization of NbQ₃ Colloidal Dispersions

Bulk samples of triclinic NbS₃ and monoclinic NbSe₃ were sonicated in a number of organic solvents (DMF, acetone, acetonitrile, water, ethanol, water-ethanol 55/45 vol.% mixture, isopropanol or 1-methyl-2-pyrrolidone) in order to achieve exfoliation. NbQ₃ concentration was determined by filtering the dispersions, and weighing of the filtered mass, or by UV-vis spectral analysis. Dynamic light scattering (DLS) measurements yielded an average effective hydrodynamic diameter of particles ~150-200 nm. High-resolution TEM images and associated Fourier transforms proved that the particles in dispersions retained good crystallinity with triclinic NbS₃ or monoclinic NbSe₃ cells undamaged during liquid-phase exfoliation process.

3.2 Preparation and Characterization of NbQ₃ Films

For integration of materials into nanotechnology devices it should be in the form of thin films rather than

bulk powder. As we have noted earlier, mechanical exfoliation of NbQ₃ appears difficult due to their geometry, and in this work colloidal solutions were used for preparation of thin NbS₃ and NbSe₃ films. The films were prepared by two methods: (i) filtration of colloidal dispersions through 0.02 μm membrane filter “Whatman Anodisc”; and (ii) spraying colloidal dispersions on heated substrates (~ 200–250°C). The later method is more flexible as it allows to prepare coatings of different complex configurations. The thin films prepared by both methods are quite smooth and transparent. The films were studied by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), Raman and IR spectroscopies. According to PXRD data, the films are characterized by strongly textured nature with high intensity of 00l Bragg reflections. This fact may be expected from general structural consideration, but experimental evidence of such oriented packing is important. Raman and IR spectra of bulk powder NbS₃, NbSe₃ and thin films prepared from their dispersions are in close agreement with each other and with reported data. All methods, XRD, XPS, IR and Raman spectroscopies, confirm phase composition of the films: they are composed of well-crystallized trichalcogenide nanoparticles, which are highly oriented in the film along 00l planes.

The measurement of transport properties of NbS₃ films was carried out in the temperature interval of 4.2 – 500K using standard four-probe technique. Resistivity of NbS₃ film grows exponentially with temperature decrease (Figure 2 a). This growth can be fitted by fluctuation model of tunneling.

The current-voltage characteristics ((Figure 2 b) of thin NbS₃ film (~ 0.5–1 μm) deposited from colloidal dispersions by spray technology on a SiO₂/Si substrate were investigated in transistor configuration with the use of Si substrate as a gate. The electron (μ_e) and hole (μ_h) mobilities were determined as 1200 – 2400 cm²V⁻¹s⁻¹. High value of carrier mobility in NbS₃ film exceeds similar characteristics measured on MoS₂ single- and multi-layers mechanically exfoliated from bulk MoS₂ crystals. This is an important property for use in field-effect transistors since film production from colloidal solutions is a simpler and more practical technology comparing to mechanical exfoliation of single crystal samples.

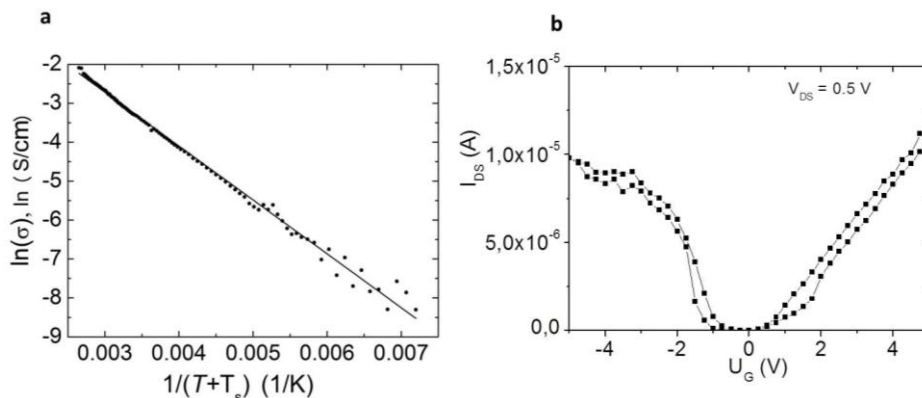


Fig. 2 – a – temperature dependence of resistivity vs. reciprocal temperature for NbS₃ film in coordinates $\ln[\sigma(T)] - T/(T+T_s)$. The straight line is an approximation by equation $\sigma(T) = \sigma_0 \exp[T/(T+T_s)]$, where $T_t = 1384$ K (0.12 eV), $T_s = 80$ K (0.007 eV); b – $I_{ds}(V_g)$ characteristics for NbS₃ films obtained from an alcohol/water solution measured with used of Si substrate as a gate.

4. CONCLUSIONS

We have suggested to reconsider transition metal trichalcogenides with quasi-one dimensional electrical properties as novel layered species for nanotechnology and demonstrated their exfoliation in common organic solvents. Thin films of NbS₃ in the form of ~ 1 – 4 layer-thick high-quality crystalline nanoribbons with advanced characteristics for field-effect transistors were prepared: electron and hole mobility was estimated as 1200 – 2400 cm²V⁻¹s⁻¹. We believe that this work presents a fresh view on the family of transition metal

trichalcogenides and opens up a wealth of new opportunities with potential in future nanoelectronics and other technological areas yet to be discovered.

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