Low-dimensional materials

NANOSTRUCTURED CHALCOGENIDES OF THE EARLY TRANSIENT METALS

Low-dimensional chalcogenides of the early transition metals

M_2Q_3	MQ_2	MQ_3	MQ_4	MQ_5
M^{3+}	*M^{4+}*	*M^{4+}*	*M^{4+}*	*M^{5+}*
$M_2(Q^{2-})_3$	$M(Q^{2-})_2$	$M(Q^{2-})(Q\text{-}Q^{2-})$	$M(Q\text{-}Q^{2-})_2$	$M(Q\text{-}Q^{2-})_{2.5}$
Mo_2S_3	MoS_2 WSe_2	TiS_3	VS_4	MoS_5
Nb_2Se_3	NbS_2 $TiSe_2$	$ZrSe_3$		WS_5
		NbS_3, $NbSe_3$		WSe_{5-6}

monochalcogenides

polychalcogenides

Layered or quasi-layered structures
Semiconductors, semimetals

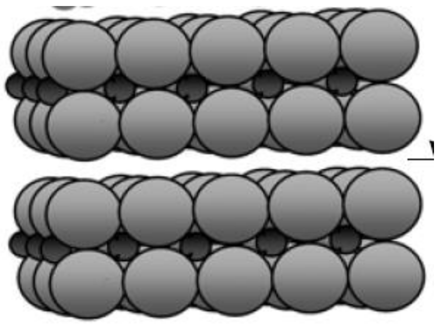
Quasi-one-dimensional (chain) structures
Semiconductors, semimetals
Peierls Transitions
Charge density waves

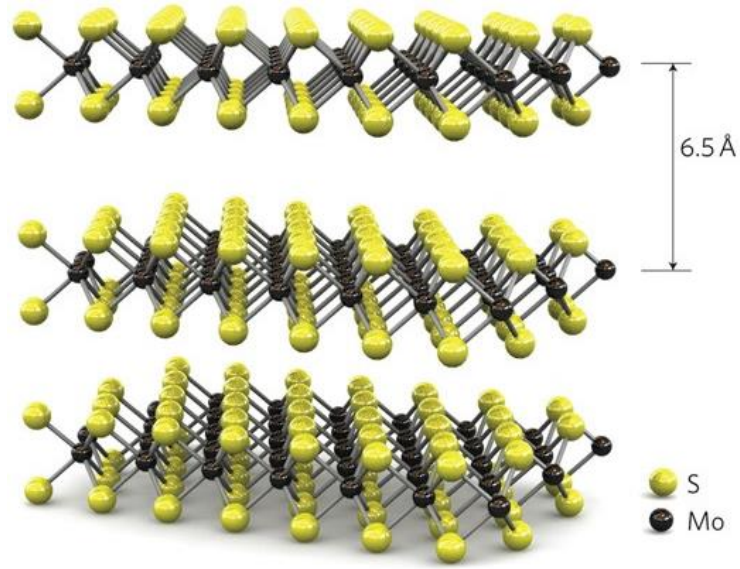
Electronic character of different layered TMDs

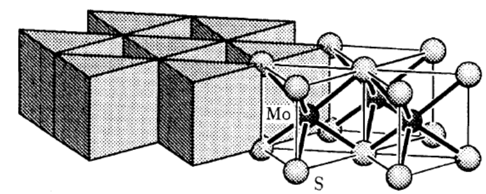
Group	M	X	Properties
4	Ti, Hf, Zr	S, Se, Te	Semiconducting (E_g = 0.2~2 eV). Diamagnetic.
5	V, Nb, Ta	S, Se, Te	Narrow band metals (ρ ~10^{-4} Ω.cm) or semimetals. Superconducting. Charge density wave (CDW). Paramagnetic, antiferromagnetic, or diamagnetic.
6	Mo, W	S, Se, Te	Sulfides and selenides are semiconducting (E_g ~1 eV). Tellurides are semimetallic (ρ ~10^{-3} Ω cm). Diamagnetic.
7	Tc, Re	S, Se, Te	Small-gap semiconductors. Diamagnetic.
10	Pd, Pt	S, Se, Te	Sulfides and selenides are semiconducting (E_g = 0.4eV) and diamagnetic. Tellurides are metallic and paramagnetic. $PdTe_2$ is superconducting.

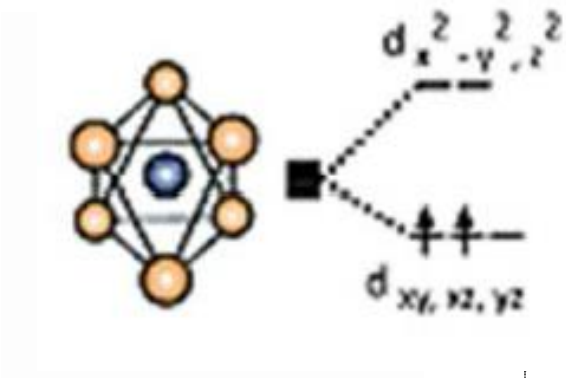
ρ, in-plane electrical resistivity.

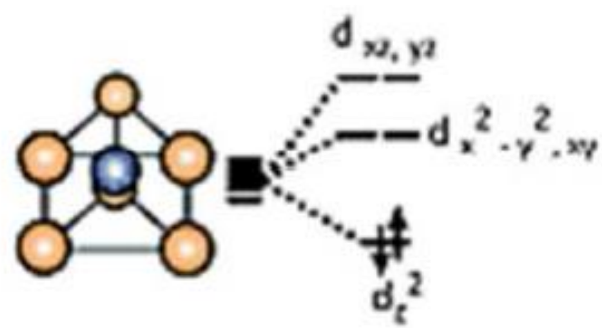
Layered transition metal dichalcogenides





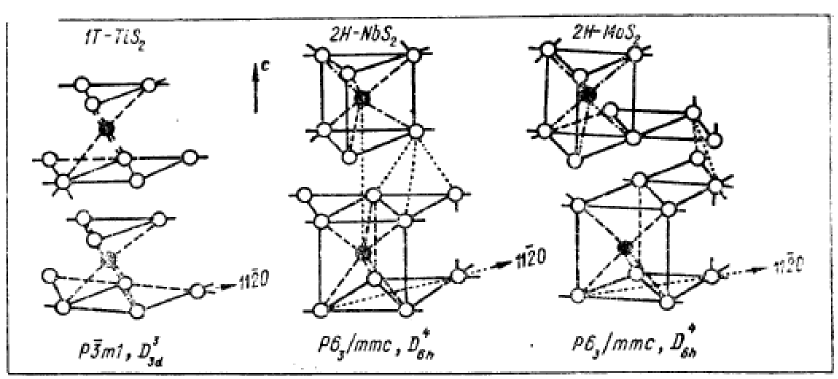






1 T

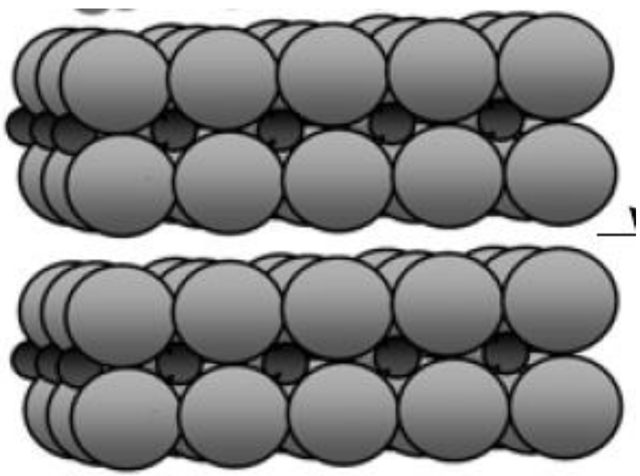
Octahedral coordination of metal atoms



2 H

Trigonal-prismatic coordination of metal atoms

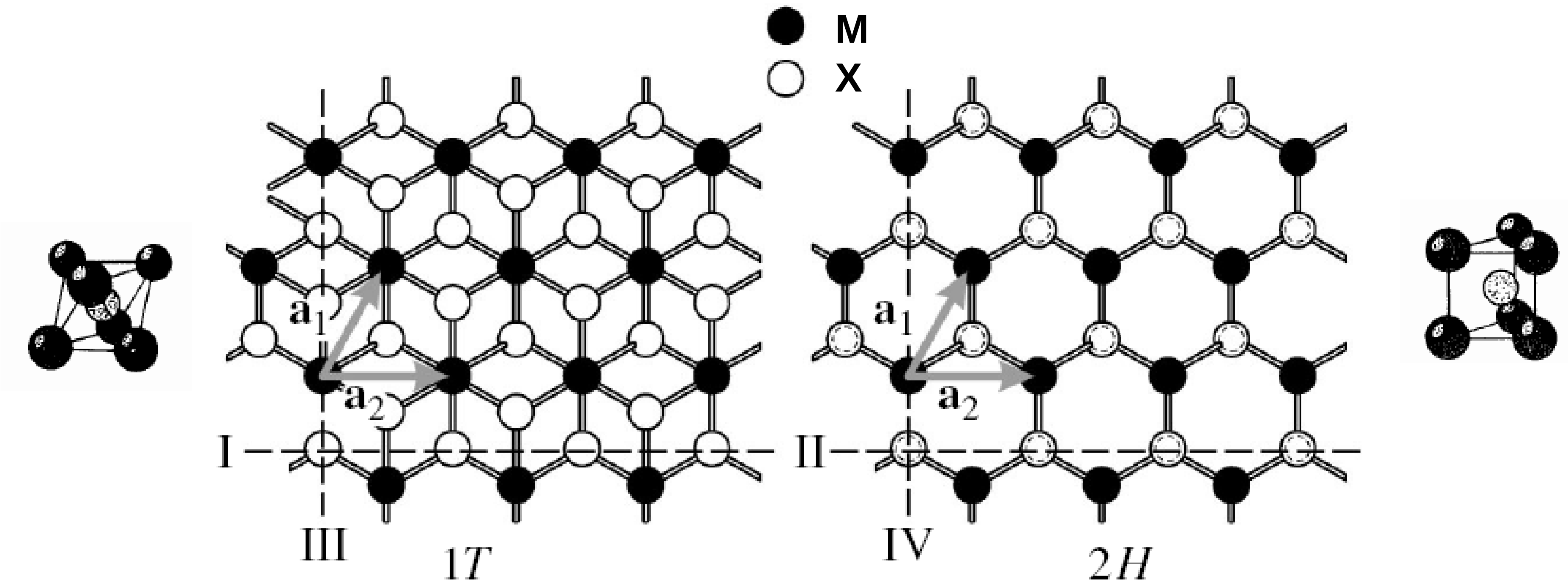
MX_2 (X=S, Se, Te)



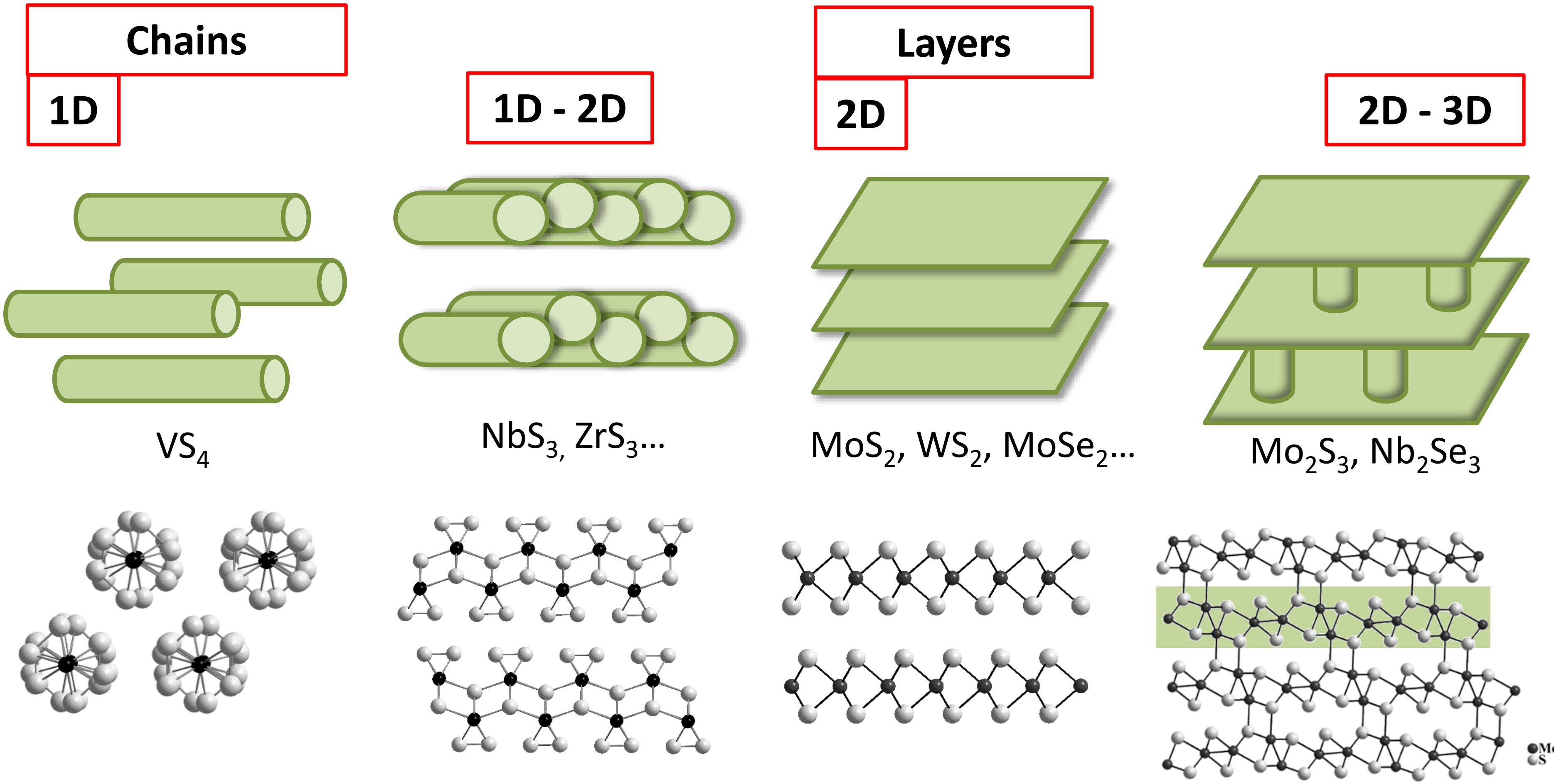
Ionic radii for M^{4+} (Å):

d^0	Ti^{4+}	0.61				
d^1	V^{4+}	0.58	Nb^{4+}	0.68	Ta^{4+}	0.68
d^2			Mo^{4+}	0.65	W^{4+}	0.66
d^3					Re^{4+}	0.63

The ionic radii of various metals are very close.



Structural features of low-dimensional chalcogenides



Transition metal chalcogenides of groups 4-6

2D **MQ_2**

MoS_2, $MoSe_2$, WS_2, …

Semiconductors, semimetals

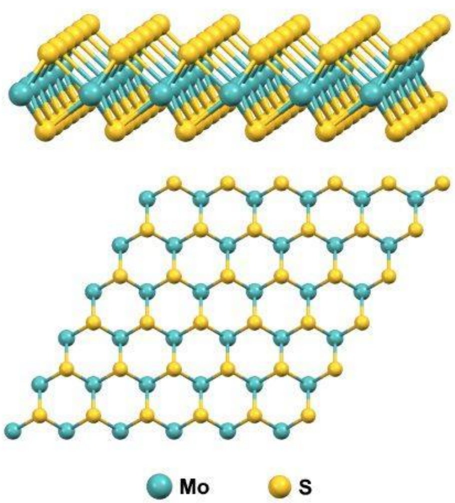
1D **MQ_3**

NbS_3, $NbSe_3$, TaS_3, ZrS_3, …

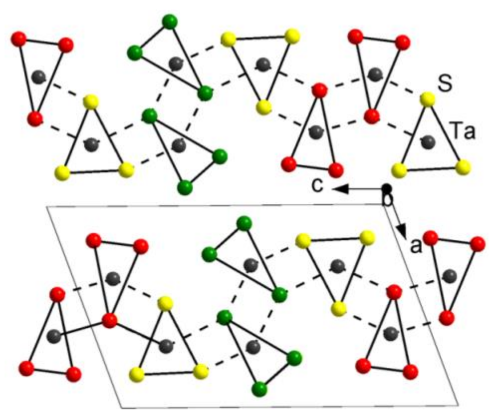
Semiconductors, semimetals

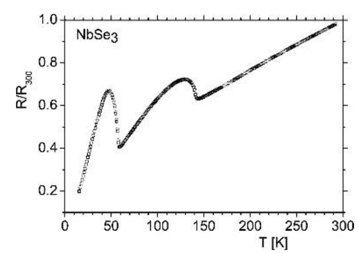
Peierls Transitions
Charge density waves

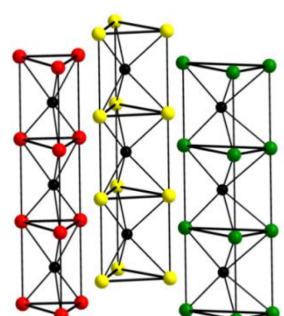
MoS_2



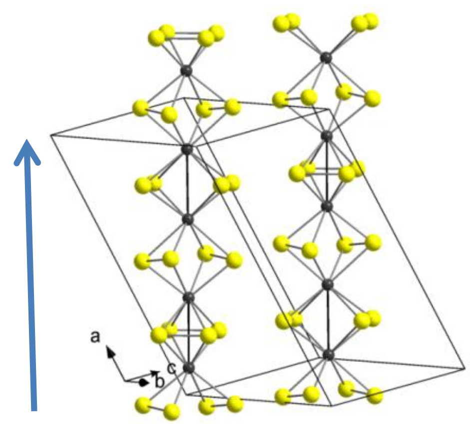
$NbSe_3$, TaS_3







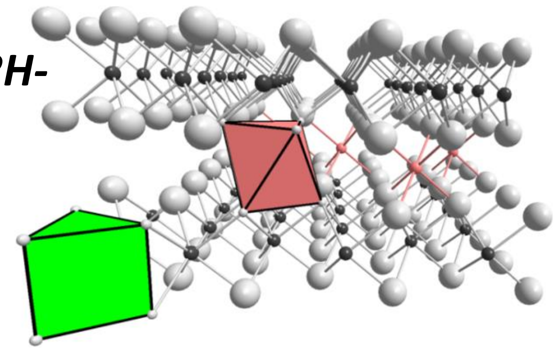
VS_4

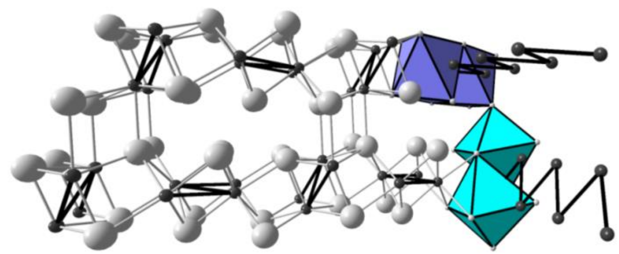


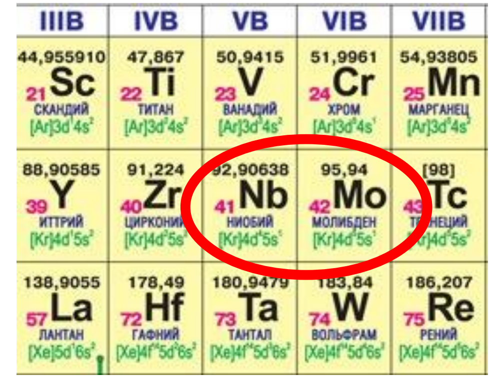
M_2Q_3 chalcogenides: 2 types of structures

I	II

2H-







***$M_{1.33}Q_2$* intercalate:**
***M* atoms between the layers**
$2Nb + 3Q = 1.5\ Nb_{1.33}Q_2$
(Q = S, Se) (1100°C)

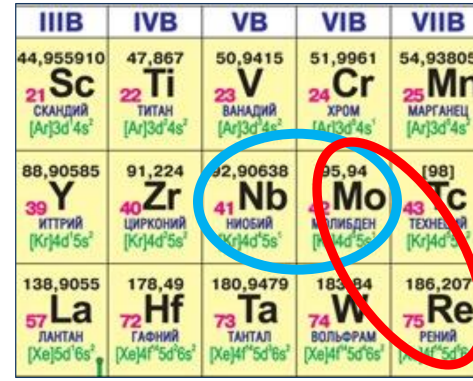
***M_2Q_3* quasi-layered framework:**
chains –M – M – M–
$2Mo + 3S = Mo_3S_2$ (1100°C)
$2Nb + 3Se = Nb_2Se_3$

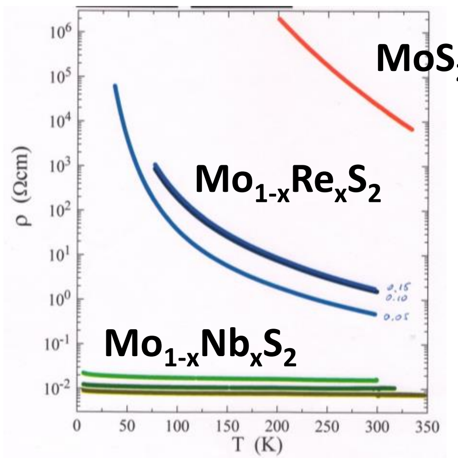
M.N. Ivanova, A.N. Enyashin, E.D. Grayfer, V.E. Fedorov, *Phys. Chem. Chem. Phys.* **2019**

Known compounds / thermodynamic stability (DFT GGA)

		Mo / S	Mo / Se	Nb / S	Nb / Se
I	*$M_{1.33}Q_2$* *intercalate*	X	X	$Nb_{1.33}S_2$	$Nb_{1.33}Se_2$ Slow cooling ↑
II	*M_2Q_3* framework	Mo_2S_3	X $MoSe_2$, Mo_6Se_8	X NbS_2, Nb_3S_4	Nb_2Se_3 (hardening)

Non-Isoelectronic doping MoS_2: $Mo_{1-x}M_xS_2$ (M= Nb, Re)

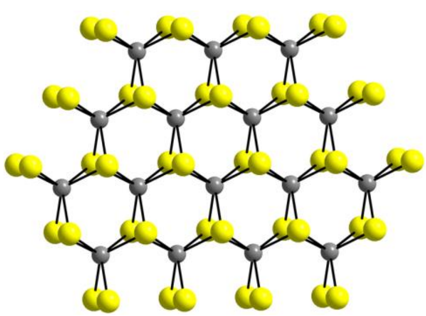




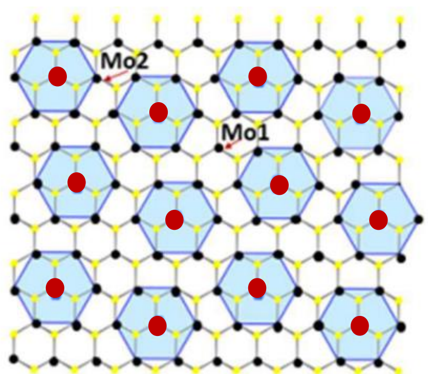
x = 0.05, 0.10, 0.15

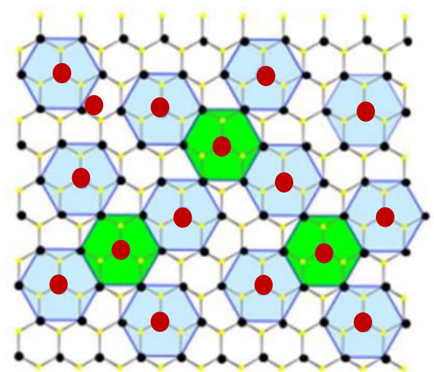
$$(1\text{-}x)Mo + xM' + 2S = Mo_{1-x}M'_xS_2$$
x = 0.05, 0.10, 0.15

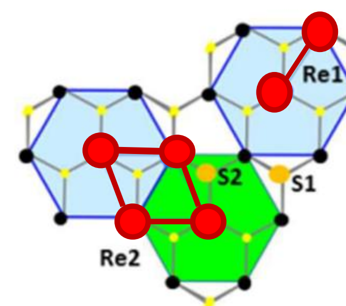
Variants of embedding rhenium atoms in the lattice MoS_2

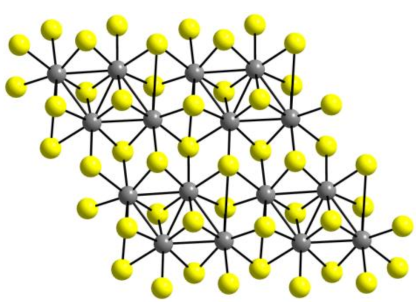


MoS_2
NbS_2









ReS_2

model of single Re atoms surrounded by Mo (not implemented)

… + n Re

cluster "Re_4"

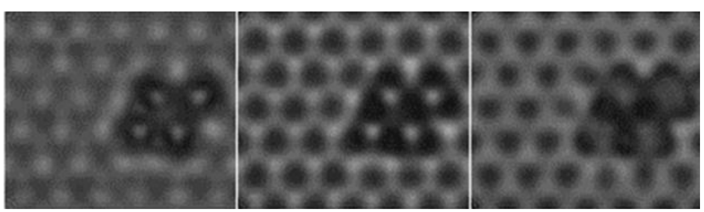
$Mo_{1-x}Re_xS_2$: theoretical calculations and electron microscopy

при T = 0

$$\Delta H_{mix} = \frac{H(Mo_{1-x}Re_xS_2) - H(MoS_2) - H(ReS_2)}{100x}$$

1) $Mo + 2S \rightarrow MoS_2$
   $Re + 2S \rightarrow ReS_2$
2) $(1-x)MoS_2 + (x)\,ReS_2 \rightarrow Mo_{1-x}Re_xS_2$

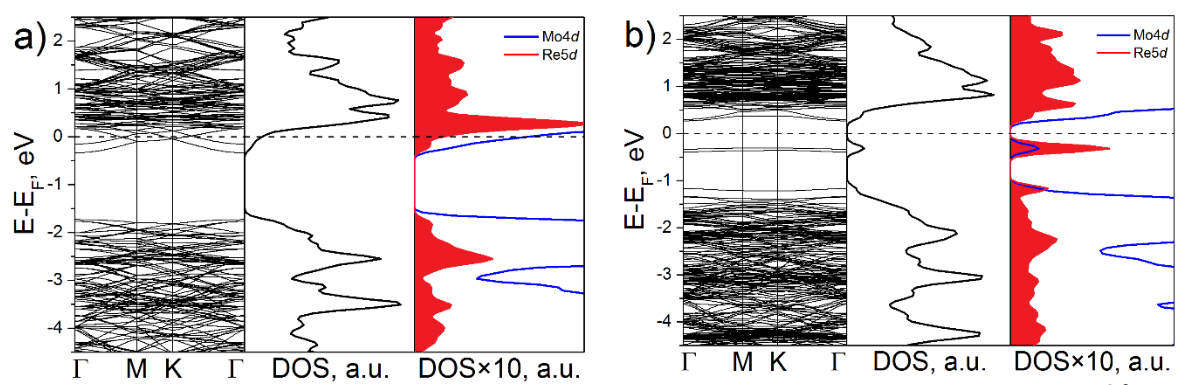
DFTB DFT GGA	ΔH_{mix}	
Re atoms	+ 0.38 эВ/Re	
«Re_2» dimers	+ 0.08 эВ/Re	Very low
«Re_n» clusters	— 0.06 эВ/Re	0.3 eV/Re atom



Dalmatova S.A., Fedorenko A.D., Mazalov L.N., Asanov I.P., Ledneva A.Yu., Tarasenko M.S., Enyashin A.N., Zaikovskii V.I., Fedorov V.E. , *Nanoscale* **2018**

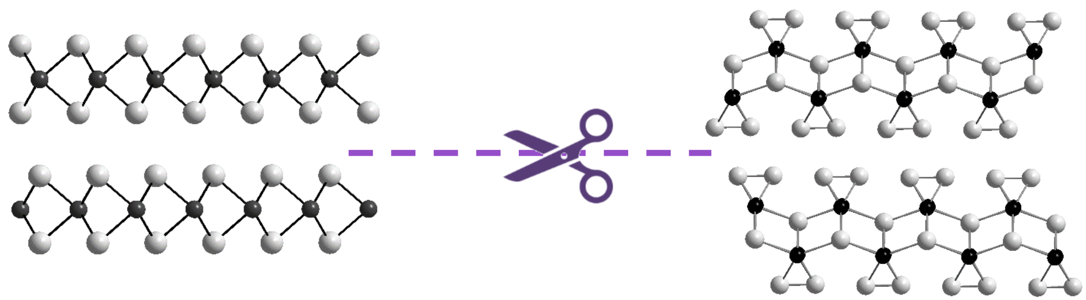
$Mo_{0.90}Re_{0.10}S_2$: Single Re atoms

clusters "Re_4"



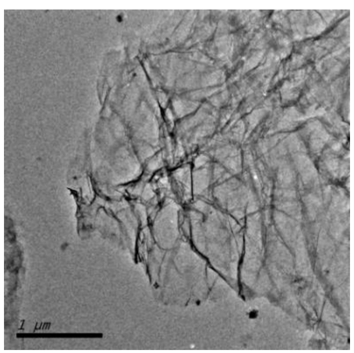
Liquid phase dispersion of layered compounds

Weak van der Waals interactions between layers → **The possibility of obtaining nanoscale 2D compounds using dispersion approaches**



MoS_2, WS_2, $MoSe_2$…

NbS_3, ZrS_3…

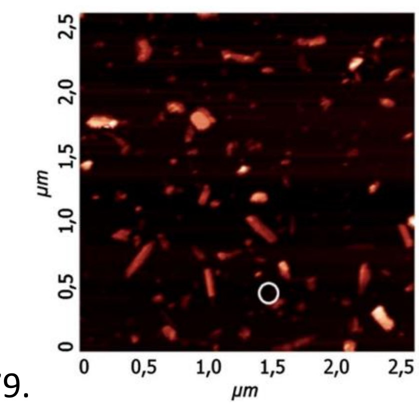


MoS_2 (TEM)

Science 2011, 331, 568– 571

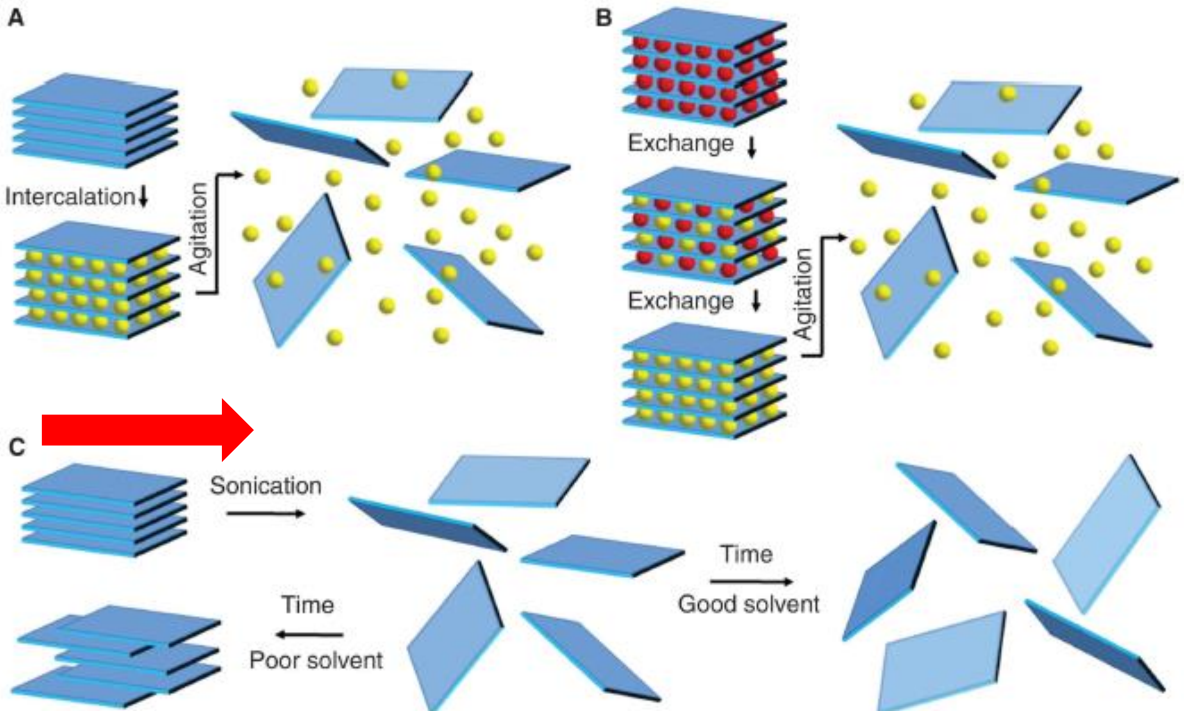
…

NIIC: J. Mater. Chem. C, 2014, 2, 5479.



NbS_3 (AFM)

Liquid phase exfoliation scheme for layered compounds (3 options – A, B, C)



Nicolosi V., Chhowalla M., Kanatzidis M.G., Strano M.S., Coleman J.N.,
Liquid Exfoliation of Layered Materials,
Science, 2013, V. 340, N 6139, pp. 1226419.

"Top-down" process) – ultrasonic processing of bulk materials.

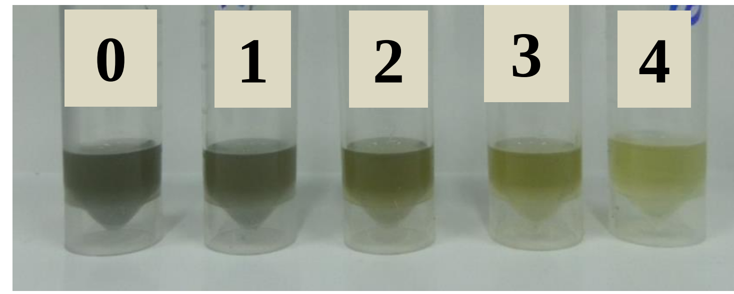
Colloidal dispersions of MoS2: the selection of a narrow fraction of NPs

Синтез
800ºС, 4 дня
$Mo + 2S = MoS_2$
X-Ray, EDS, Raman

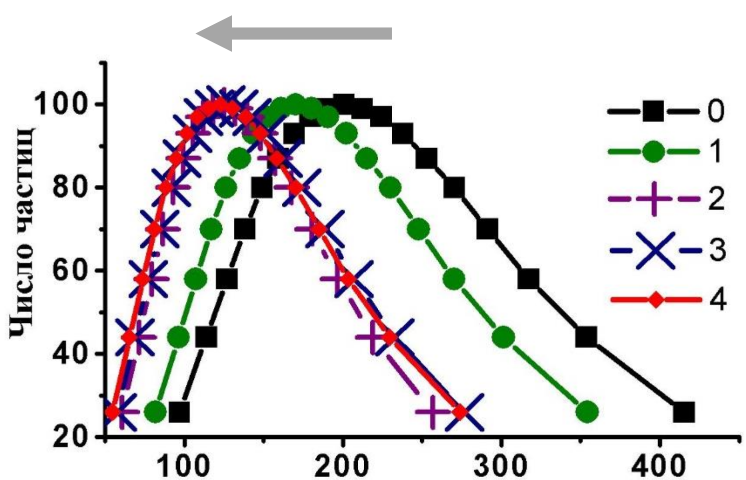
УЗ обработка в ДМФА (4 ч)

Отстаивание (20 h)

Коллоидные дисперсии MoS_2



Sequential centrifugation (30 minutes at each stage)



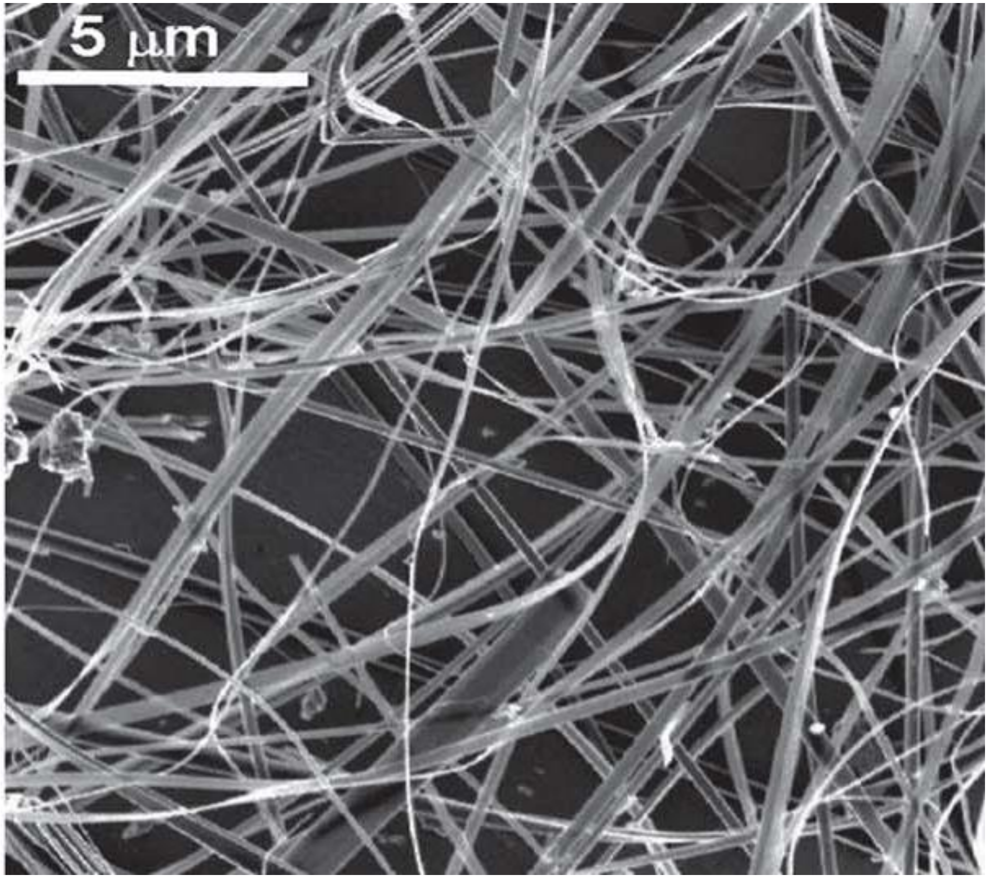
Average hydrodynamic diameters, nm

Данные ФКС (D_{hz})

<table>
<tr><th>№</th><th>Acceleration, g</th><th>D_{hz} (ФКС), nm</th><th>d (ФКС), nm</th><th>Thickness (X-Ray , WinFit), nm</th></tr>
<tr><td>«0»</td><td>-</td><td>200</td><td>250</td><td>35</td></tr>
<tr><td>«1»</td><td>126</td><td>170</td><td>220</td><td>18</td></tr>
<tr><td>«2»</td><td>504</td><td>130</td><td rowspan="3">160</td><td>11</td></tr>
<tr><td>«3»</td><td>1134</td><td>130</td><td>9</td></tr>
<tr><td>«4»</td><td>2016</td><td>120</td><td>8</td></tr>
</table>

The data is consistent with AFM

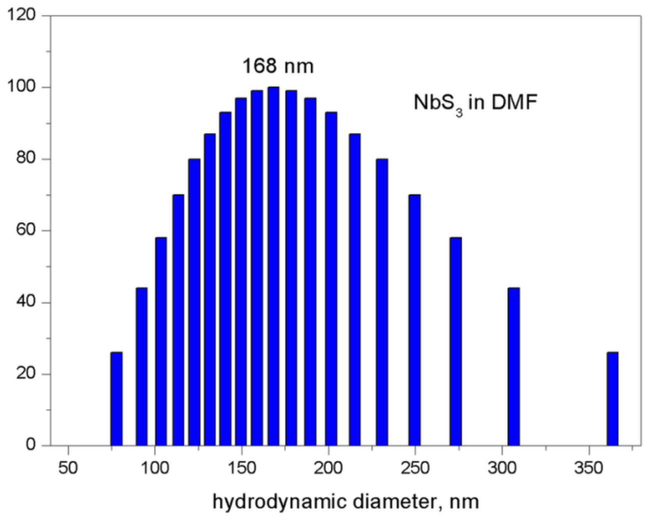
Monocrystals MoS2 and TaS3 synthesized by high-temperature reactions of elements in a sealed quartz ampoule



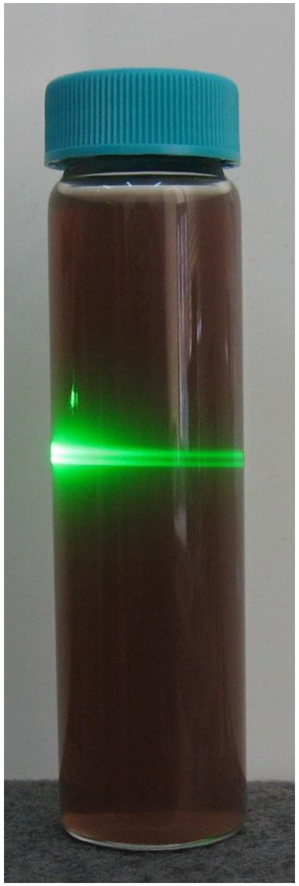
MoS_2 TaS_3

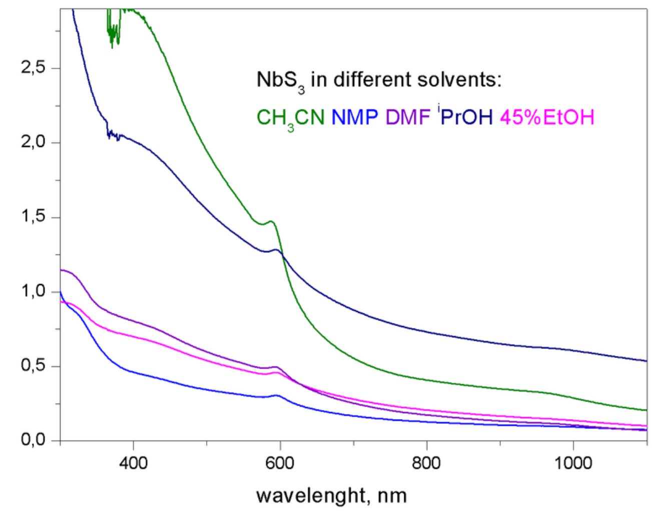
Various habit of MoS2 and TaS3 crystals determines the methods of their exfoliation

Characterization of colloidal dispersions NbS_3

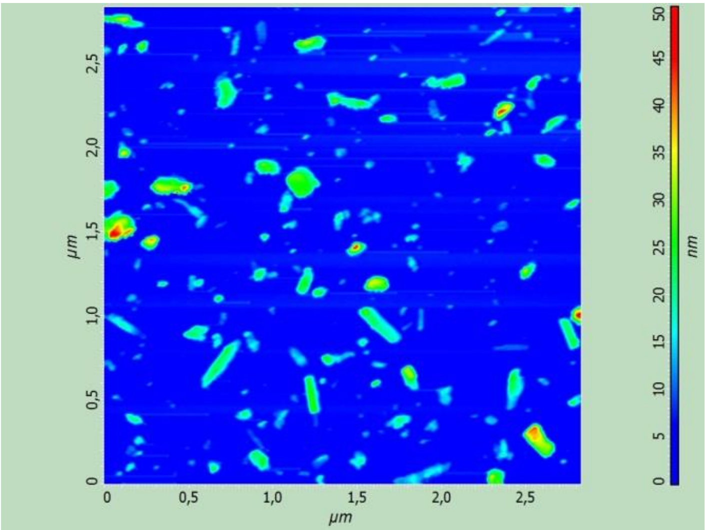


Photon correlation spectroscopy

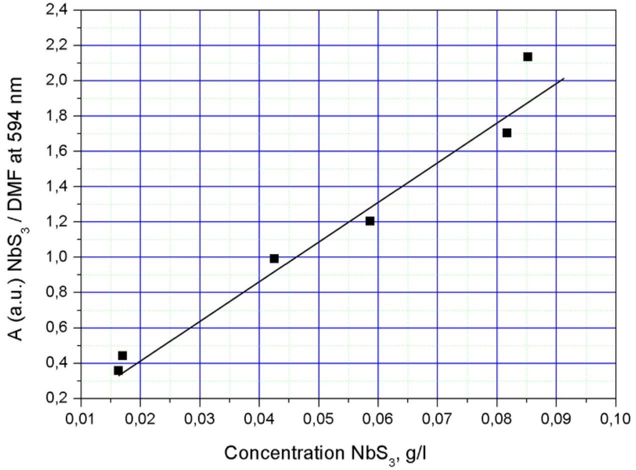




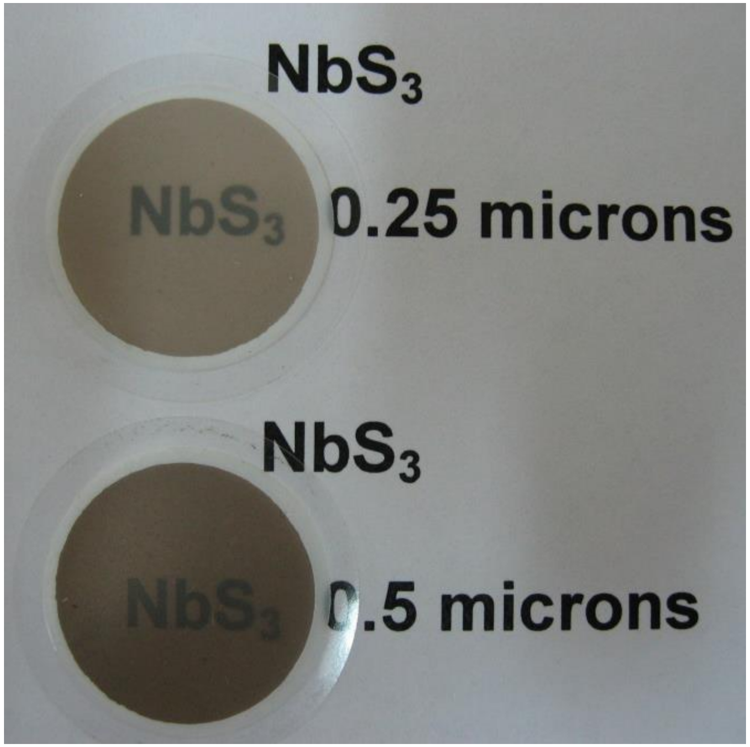
Electron spectroscopy

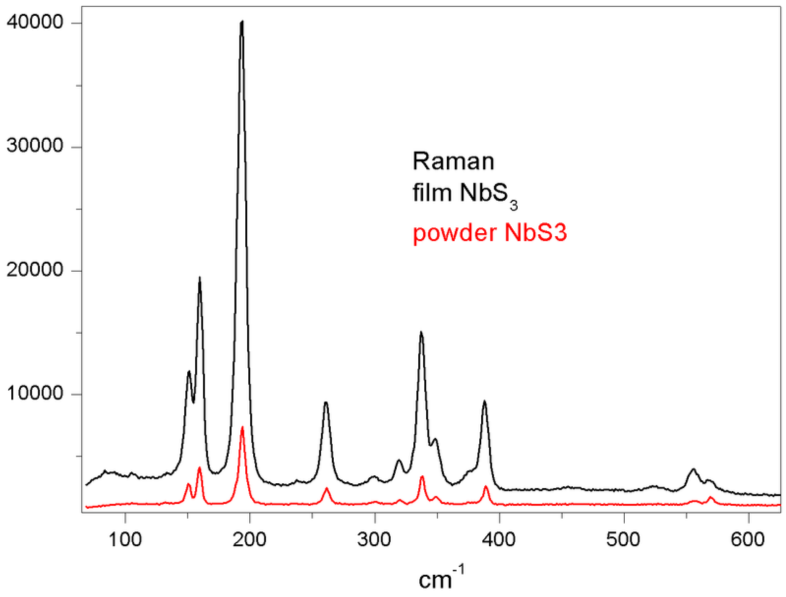


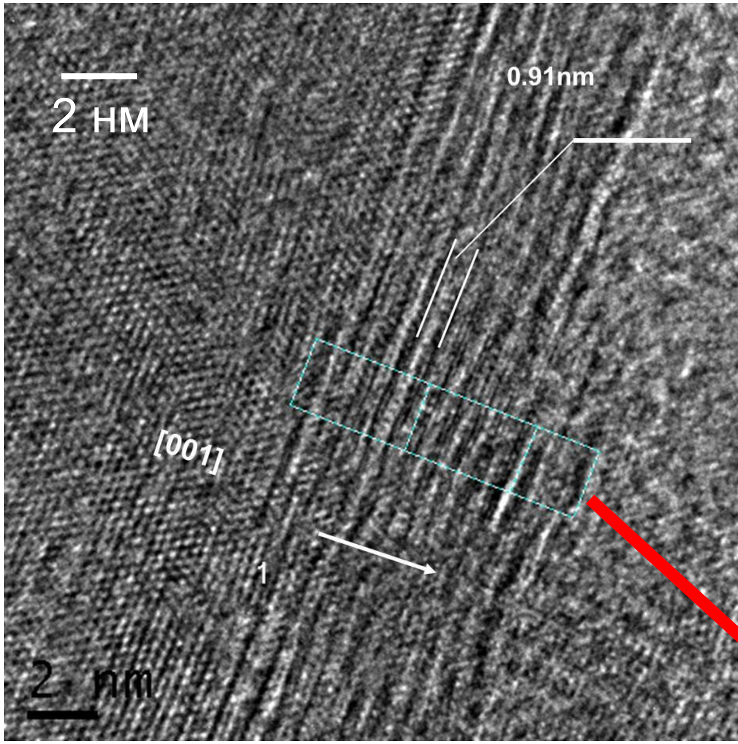
Atomic force microscopy

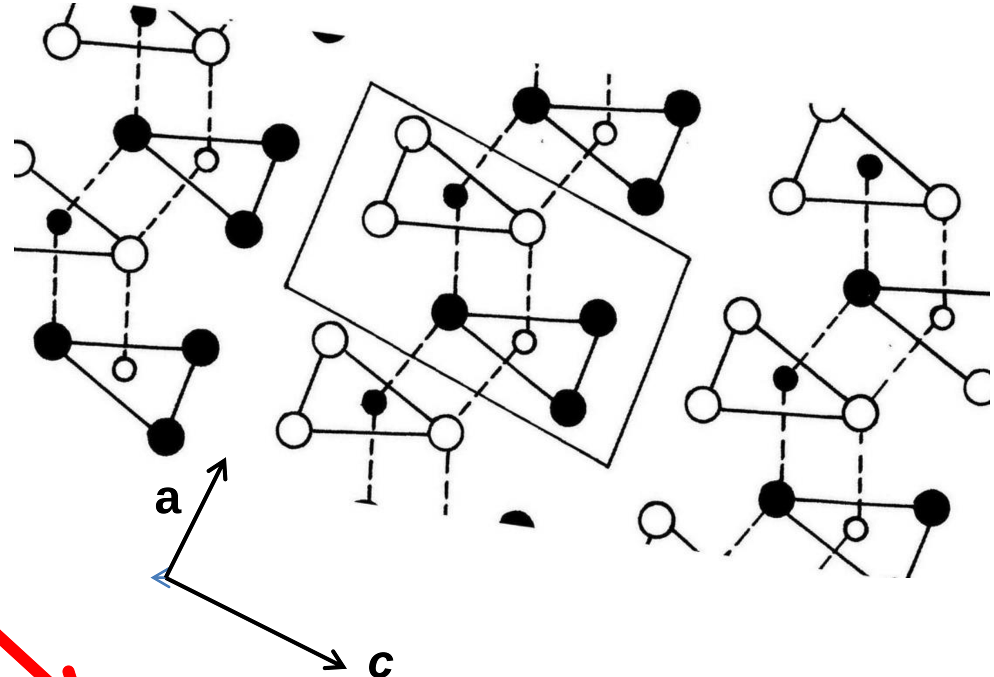


Photographs and Raman spectra of NbS3 films obtained by vacuum filtration of a colloidal dispersion of NbS3 / DMF through a membrane filter (pore diameter of 0.02 µm) and spray coating (spray-method) on a heated substrate.



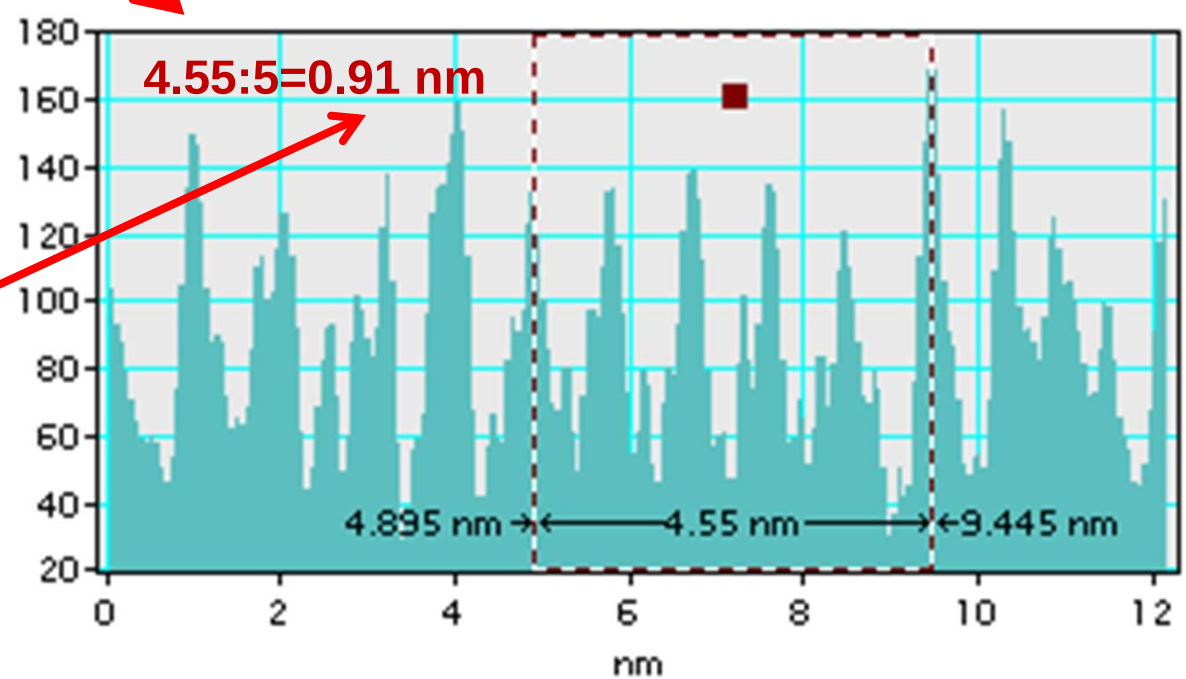




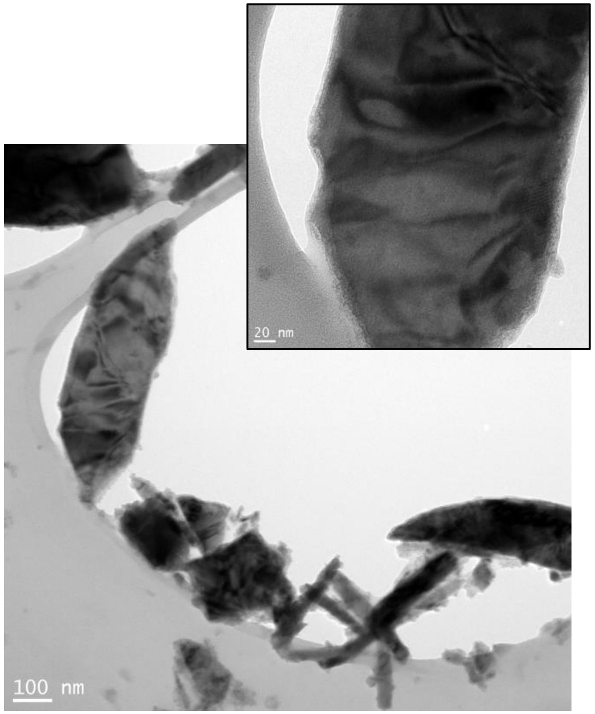


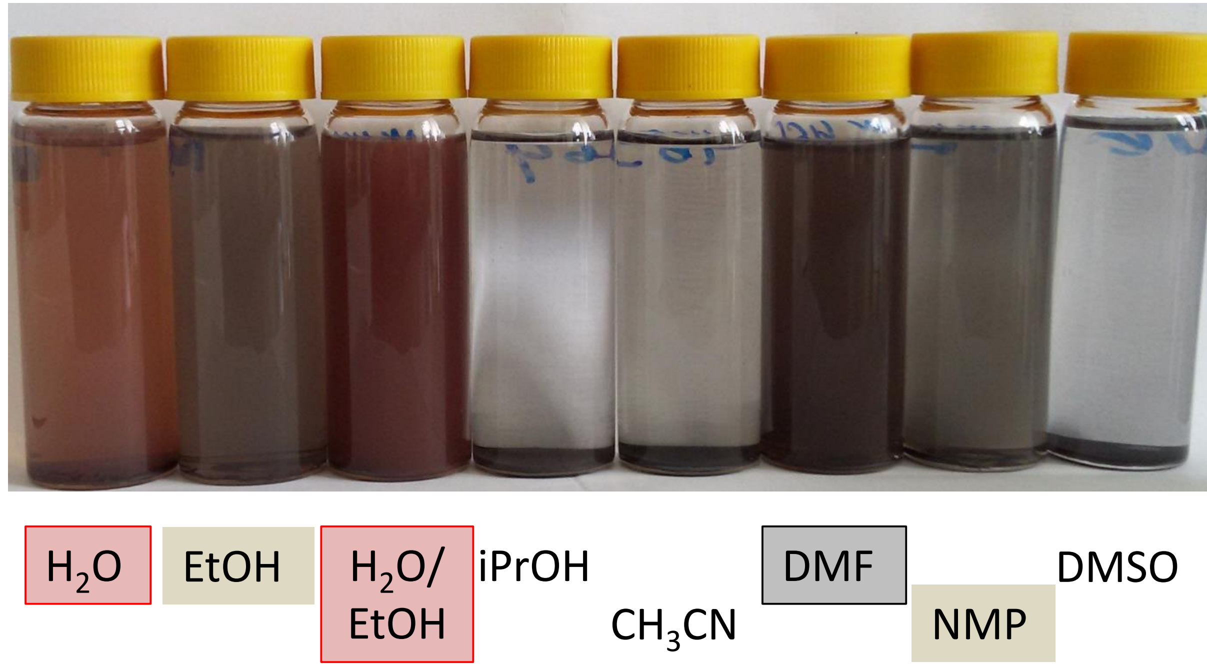
Unit cell parameters NbS_3

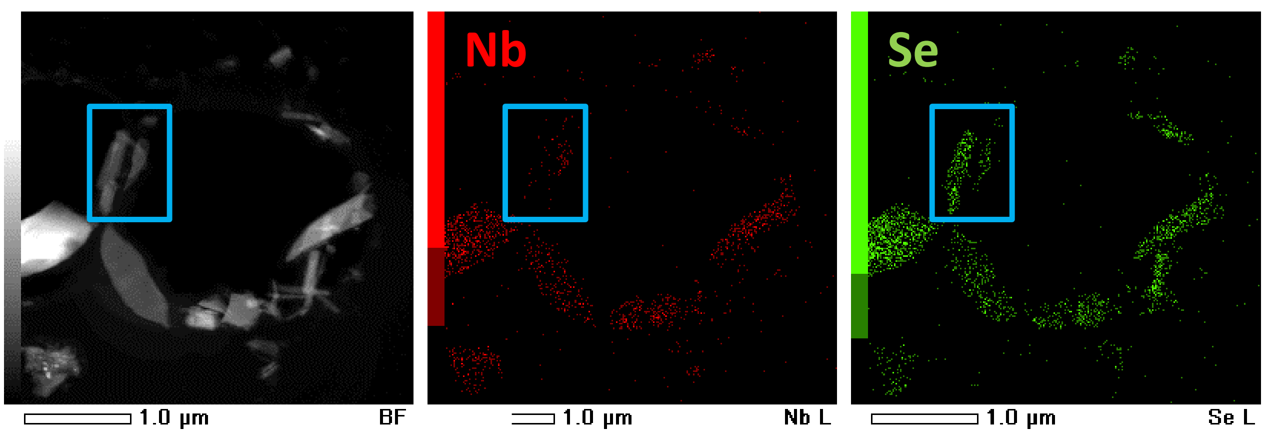
Triclinic P-1
a = 0.4963 nm
b = 0.6730 nm
c = 0.9144 nm
β = 97.17 deg.
Z=4



Exfoliation of Nb_2Se_3





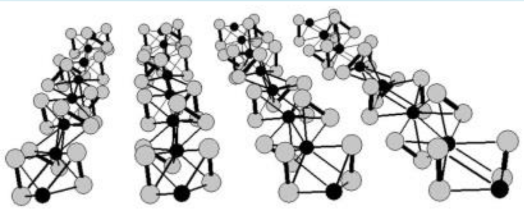


Synthesis of colloidal dispersions VS_4

Synthesis VS_4

400ºC, 10 days

$V + 4\,S = VS_4$



Synthesis of colloidal dispersions

ultrasound 3 h,
Settling 15-20 h.

Дисперсия VS_4 в i-PrOH. Луч лазера демонстрирует эффект Тиндаля.

Solvent	Concentration, mg/l
H_2O	-
EtOH	174
EtOH – H_2O (1:1)	219
i-PrOH	**316**
MeCN	78
ДМФА	187
ДМСО	37
NMP	-

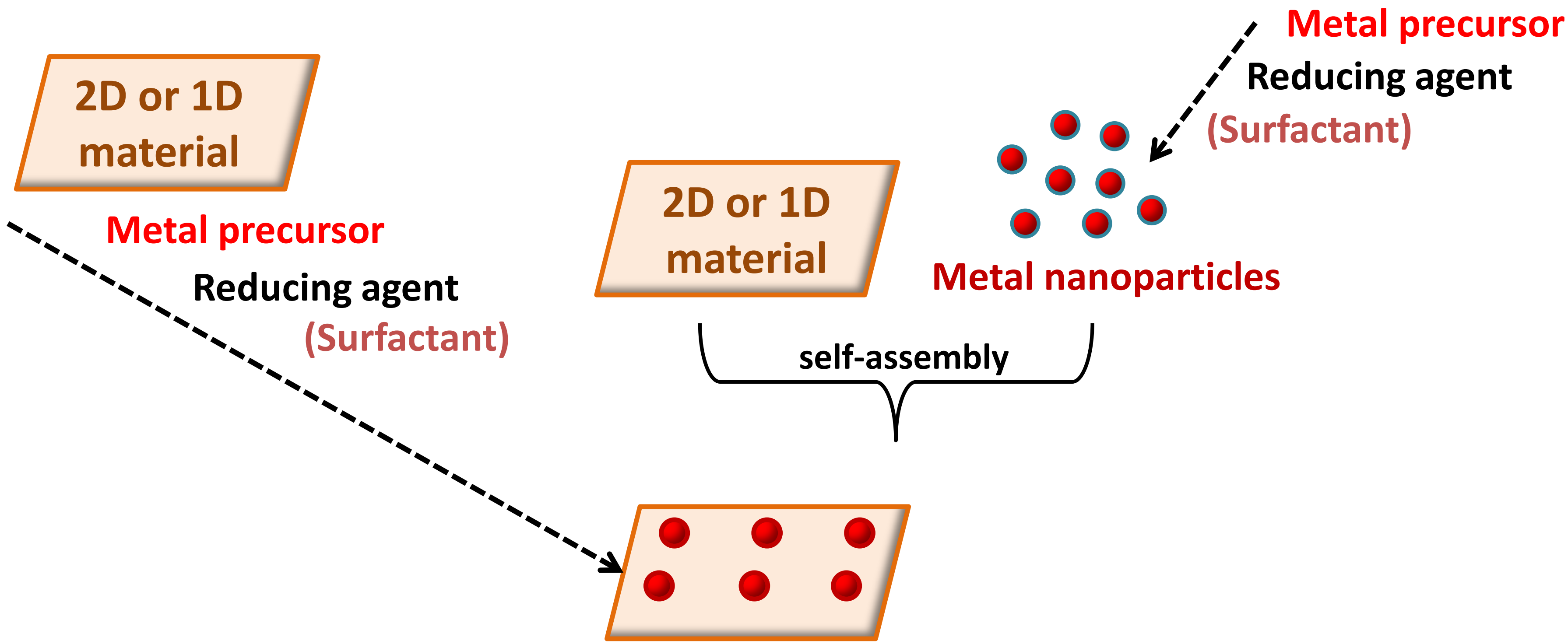
Two ways of preparation of composites with metal nanoparticles

In situ

Metal nanoparticles are formed in the presence of 2D (1D) material.

Ex situ (self-assembly)

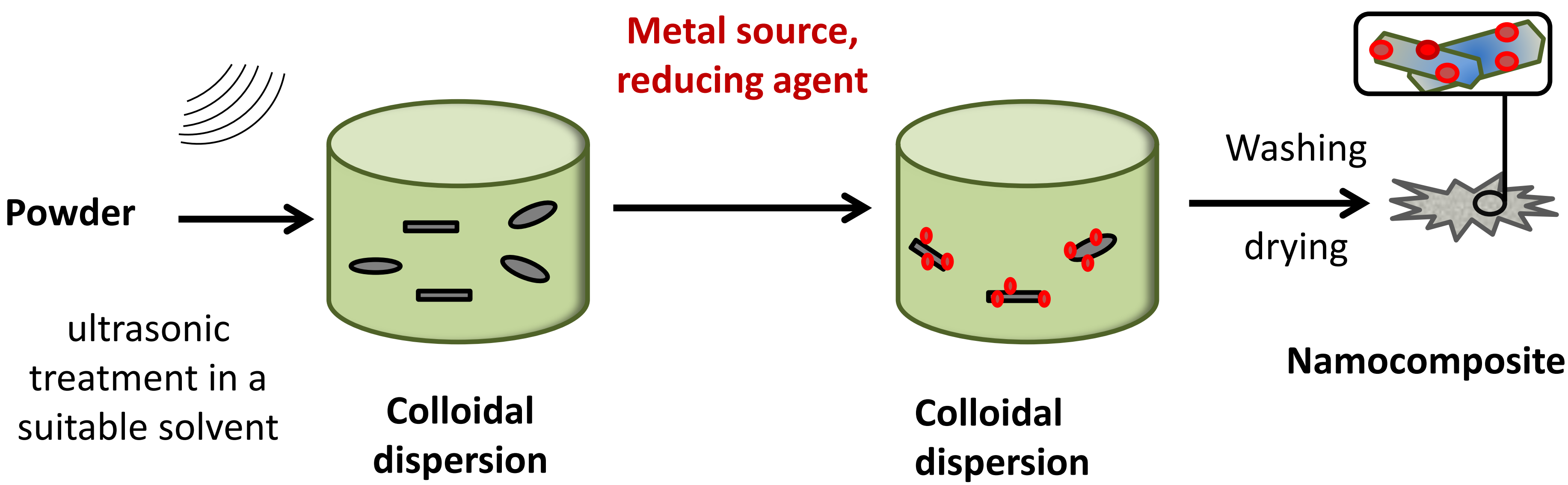
Mixing of 2D (1D) material and pre-synthesized nanoparticles.
Surface modification are often used.



Composite 2D (1D) material-metal nanoparticles

Universal strategy of applying nanoparticles of noble metals

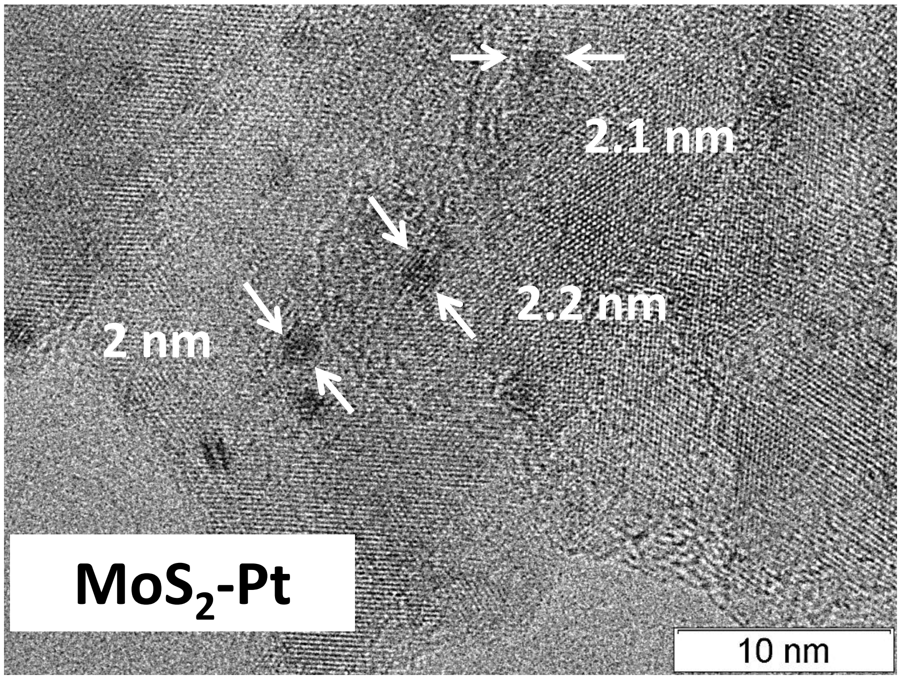
In situ iquid-phase method for the formation of metal nanoparticles in the presence of a colloidal dispersion

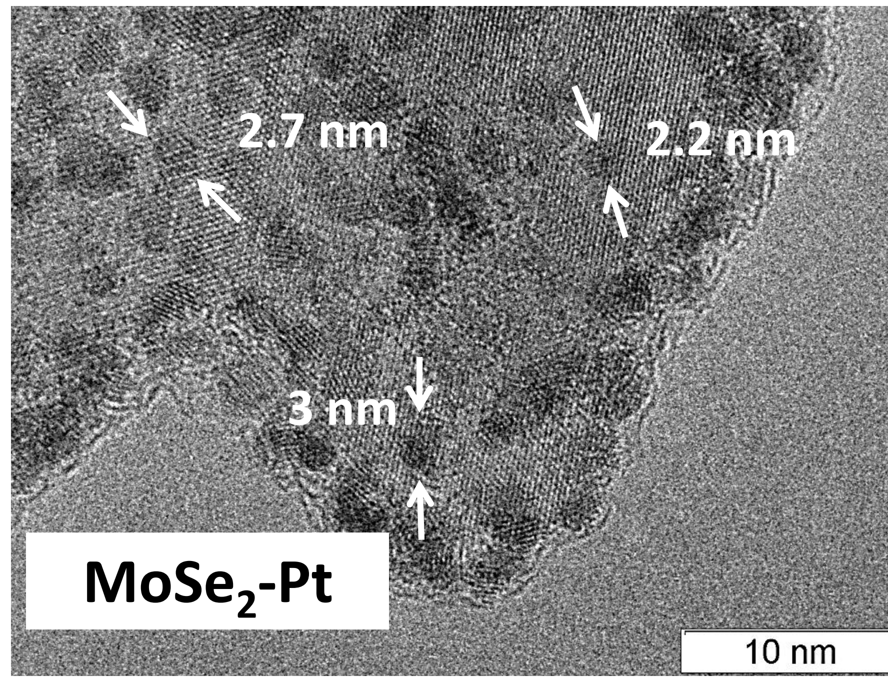


Can be applied for graphene, *h*-BN, MoS_2, $MoSe_2$, VS_4, NbS_3, Mo_2S_3

Metals: Ag, Au, Pt, Pd, Co, Cu, Fe, Ni…

2D composite MoS_2 ($MoSe_2$) - Pt

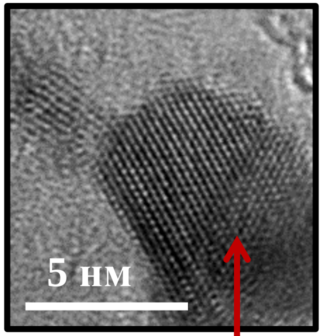




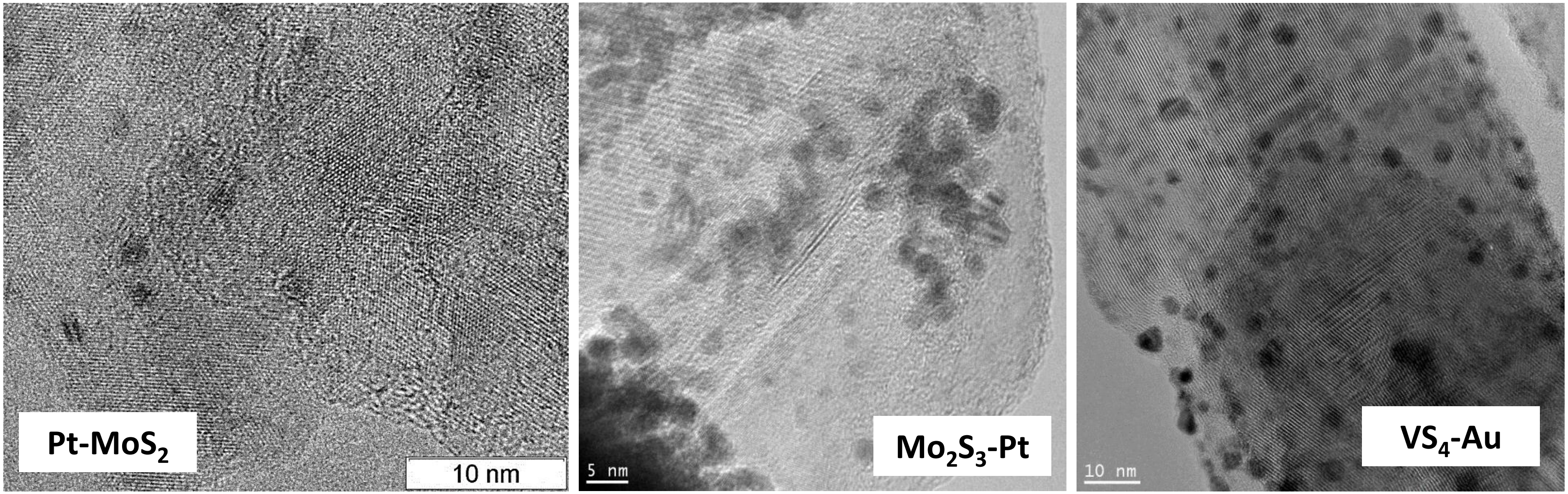
HRTEM images of composites

Deposition of nanoparticles Au, Pt, Pd

In the case of deposition of nanoparticles Au, Pt, Pd in the presence of colloidal dispersions of MoS2, Mo2S3 and VS4 on the surface of the carriers are stabilized nanoparticles of noble metals



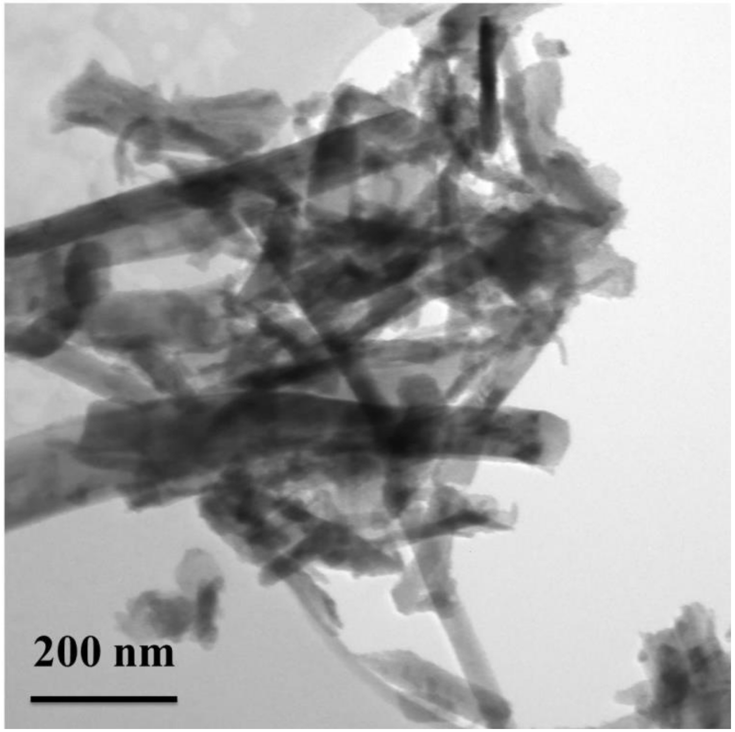
Interplanar distances 2,4 Å - (1 1 1) Au



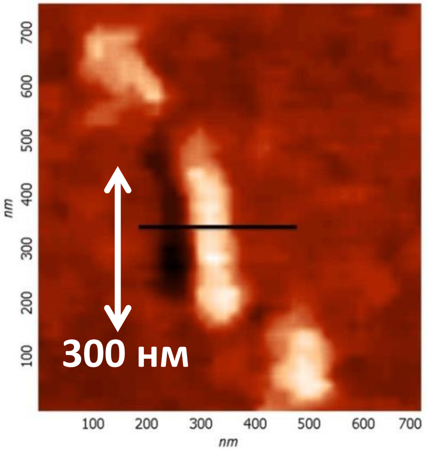
HRTEM images of composites

VS_4 colloidal dispersions

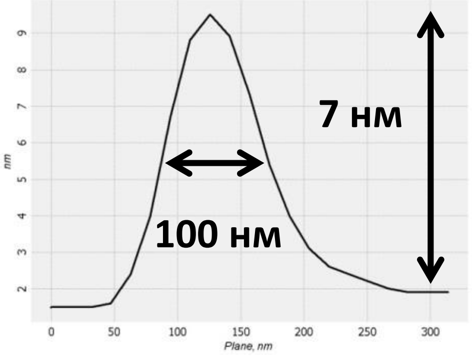
TEM data



AFM data

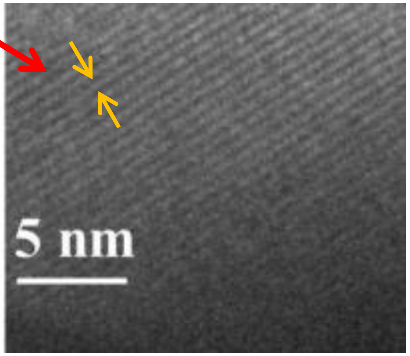


Profile



The interplanar spacing of 5.6 Å is close to 5.58 Å for (-1 1 1) VS_4

HRTEM image

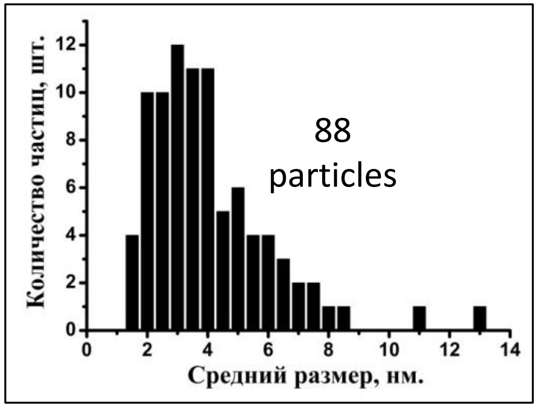


Particle shape: rods

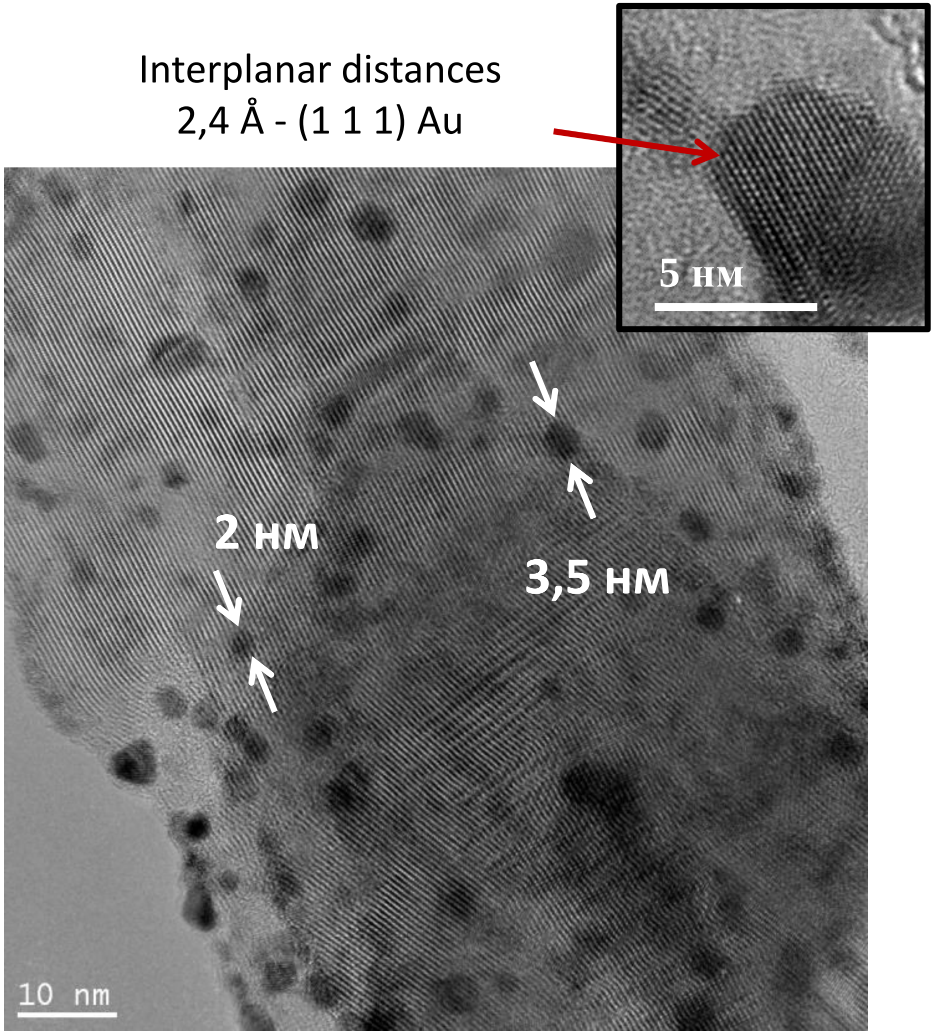
The length is 200 - 600 nm. Thickness 10 - 100 nm.

Composites with metal nanoparticles
VS_4 - Au

Gold Precursor: $AuCl_3$
The reducing agent is sodium citrate



Interplanar distances
2,4 Å - (1 1 1) Au



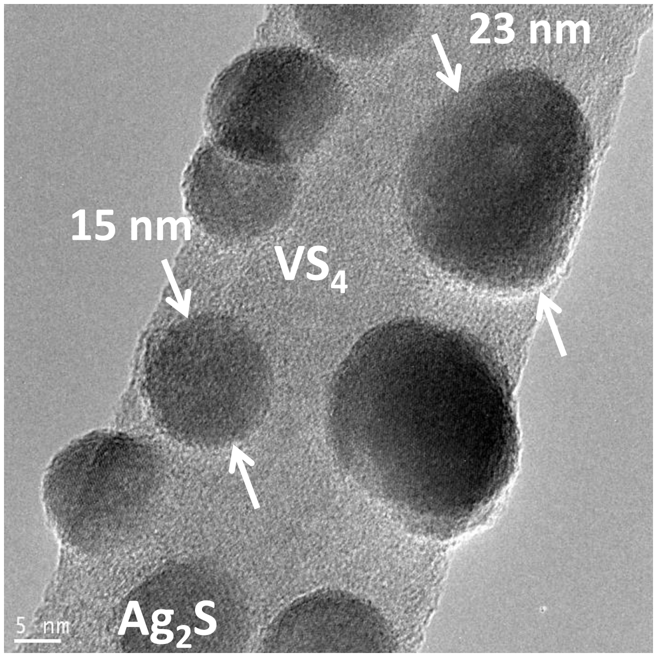
HRTEM image **VS_4-Au (10% from EDS)**

Ox-red properties of transition metal polysulfides

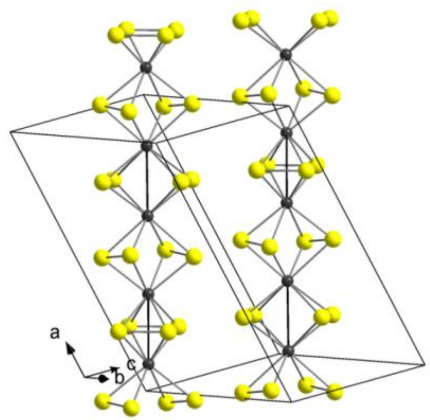
$$S_2^{2-}\ (VS_4\ NP) + Ag\ (NP) \rightarrow Ag_2S\ (NP)$$

$$S_2^{2-} + 2e \rightarrow 2S^{2-}$$

Ag_2S / VS_4

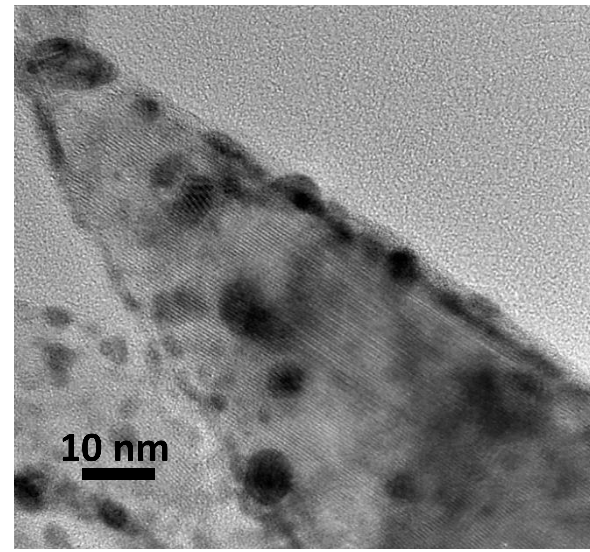


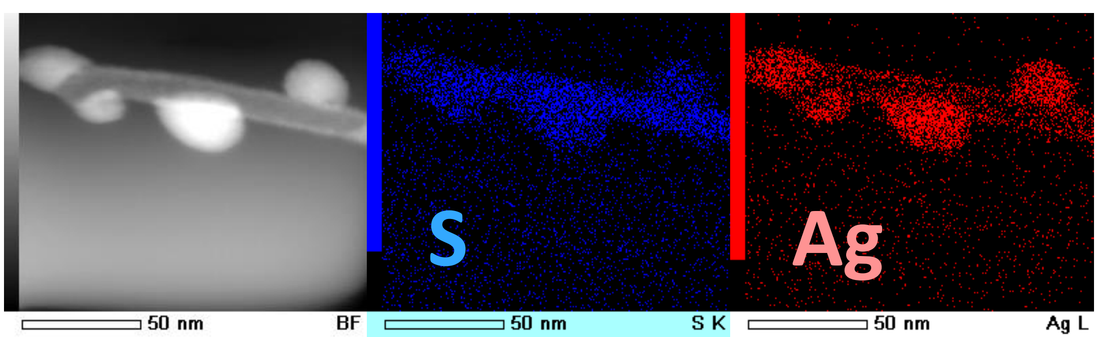
Interlayer distances
2,8 Å for (-1 1 2)
2,4 Å for (0 1 3) Ag_2S



VS_4

Au / VS_4





M.Kozlova, E.Grayfer, P. Poltarak, S. Artemkina, A. Cherkov, L. Kibis, A. Boronin, V. Fedorov, *Adv. Mater. Interfaces.* **2017**

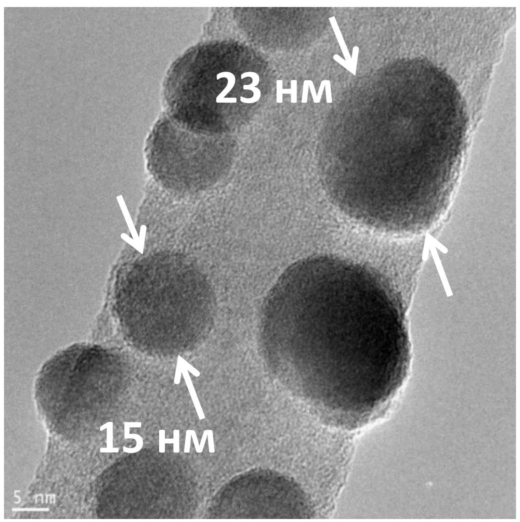
Composite $VS_4 – Ag_2S$

In situ

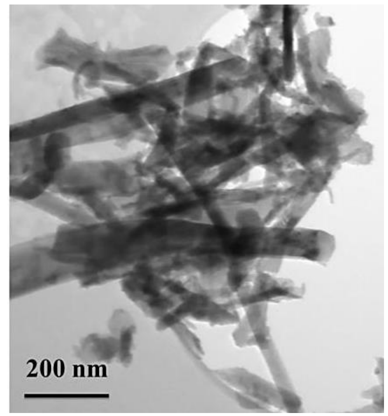
Metal nanoparticles are formed in the presence of a dispersion VS_4

Sodium citrate

$AgNO_3$



$VS_4 – Ag_2S$

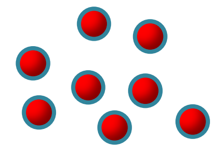


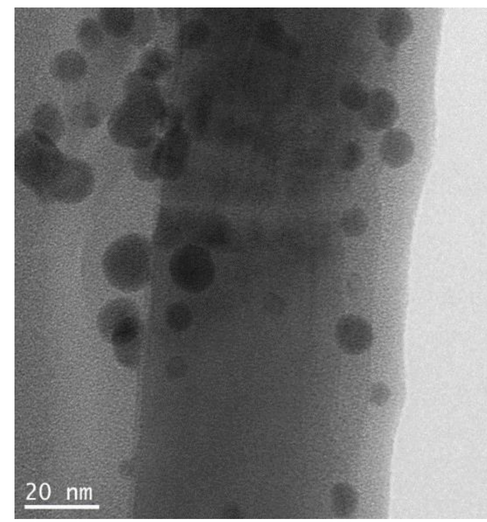
VS4 particles in i-PrOH

Ex situ

Self-assembly of the matrix and pre-synthesized metal nanoparticles.

Ag NP



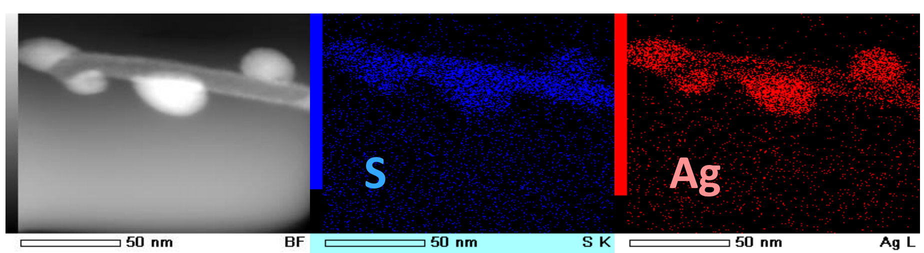


$VS_4 – Ag_2S$

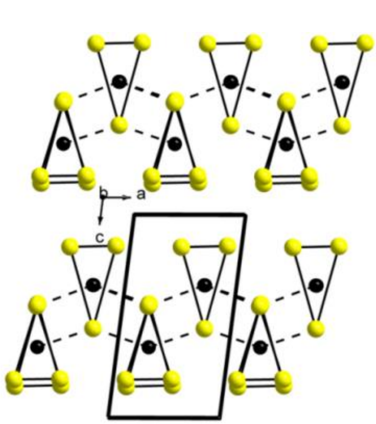
X-ray powder: Ag_2S

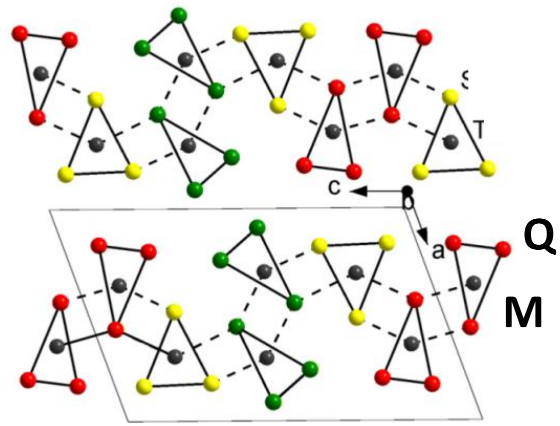
ВРПЭМ: Межплоскостные расстояния 2,8 Å (-1 1 2) и 2,4 Å (0 1 3) Ag_2S

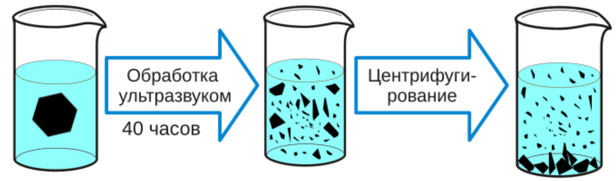
Данные РФЭС: $Ag^{\delta+}$



Colloidal solutions of transition metal trichalcogenides MQ_3

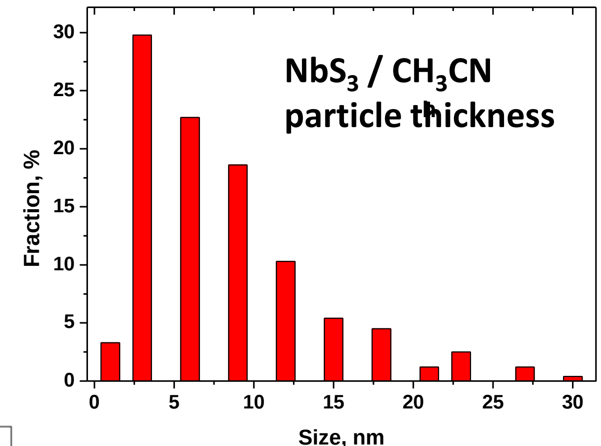




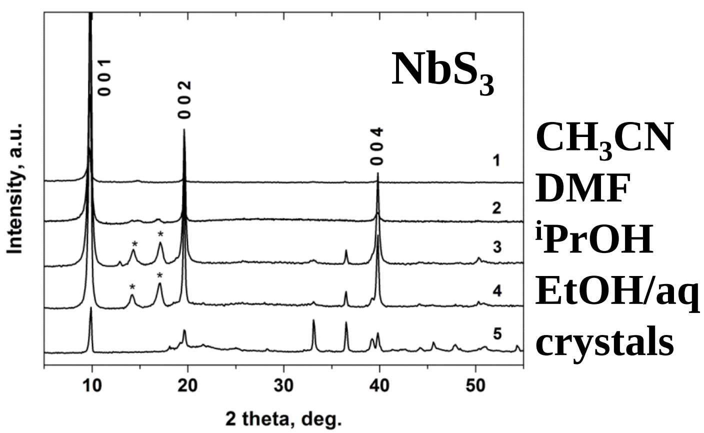


TiS_3, ZrS_3, NbS_3 **$NbSe_3$, TaS_3**

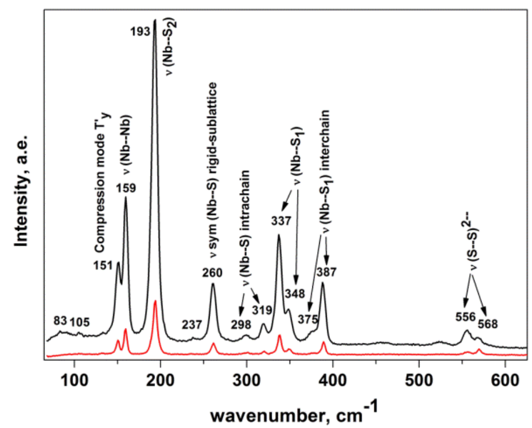
EtOH/H_2O, CH_3CN, DMF, $^{i}PrOH$, NMP

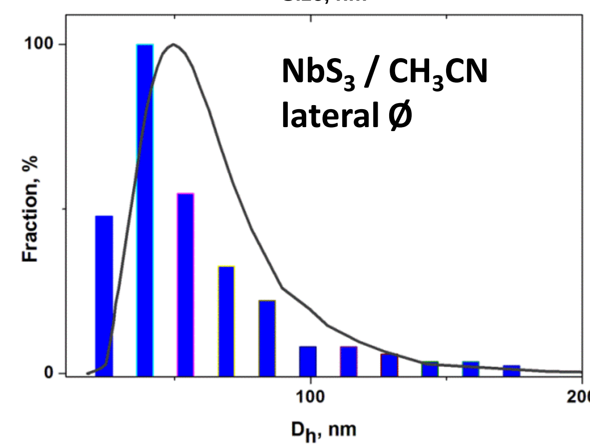


Powder diffraction



Raman

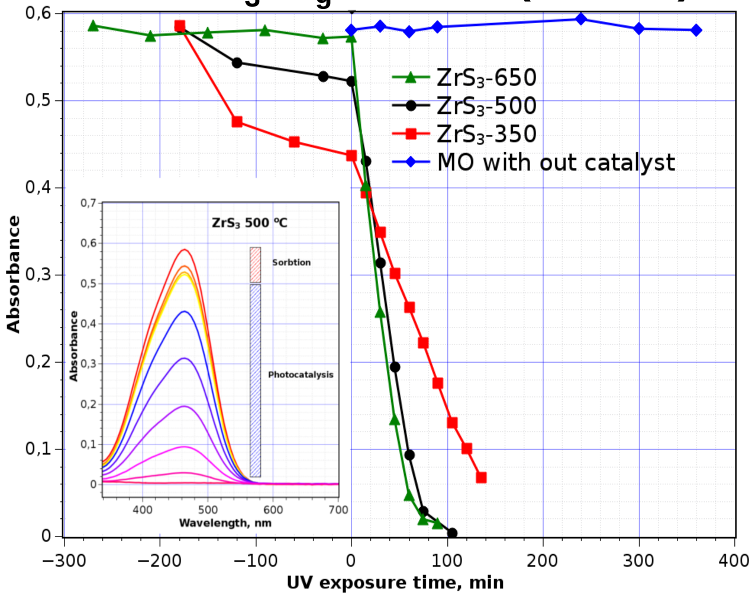




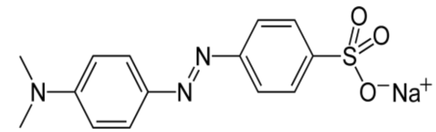
M.N. Kozlova, Yu.V. Mironov, E.D. Grayfer, A.I. Smolemtsev, V.I. Zaykovskii, et al. *Chem. Eur. J.* **2015**

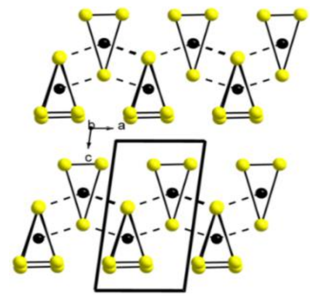
Photocatalytic activity ZrS_3

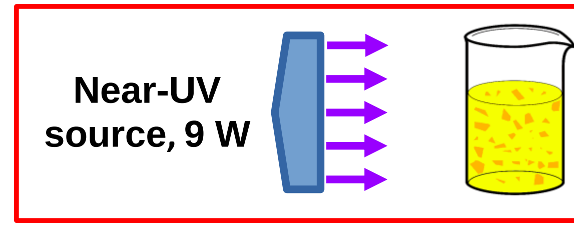
ZrS_3: E_g = 2.8 eV (443 nm)

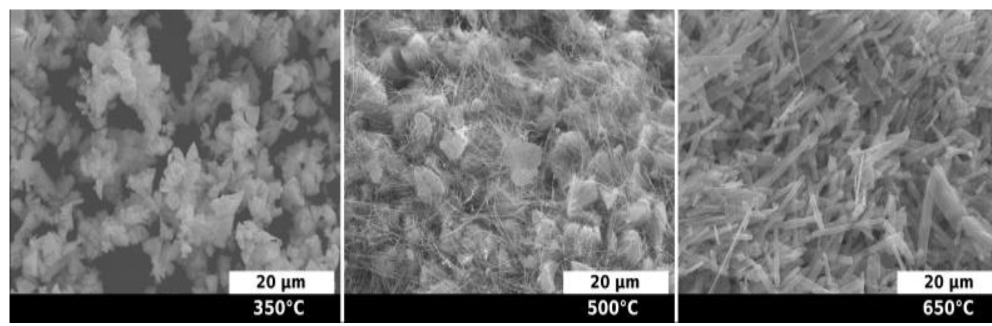


methyl orange







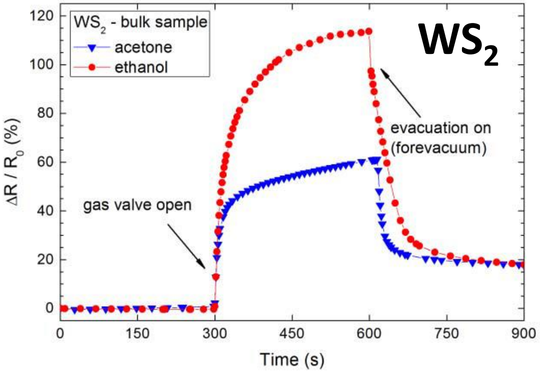


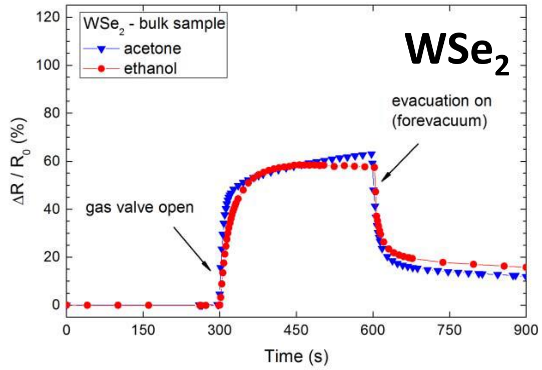
S. Artemkina, A. Poltarak, P. Poltarak, I. Asanov, V. Fedorov, *Adv. Sci. Technol. Eng. Syst. J.* **2019**

	TiO_2 Degussa P25	ZrS_3-350	ZrS_3-500	ZrS_3-650
BET, м²/г		49	24	9
MO (-50%)	138 min	48 min	36 min	27 min
MO (-90%)		144 min	71 min	59 min

Metal chalcogenide crystals as sensors for gases at room T

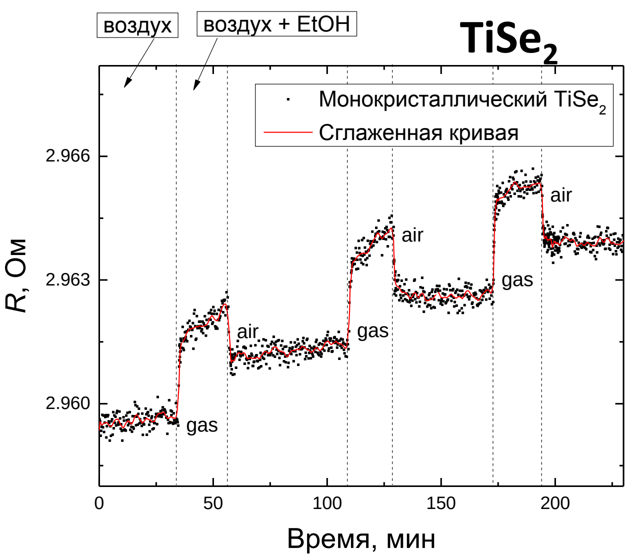
Pressed samples of WS2 and WSe2 - p-type semiconductor materials

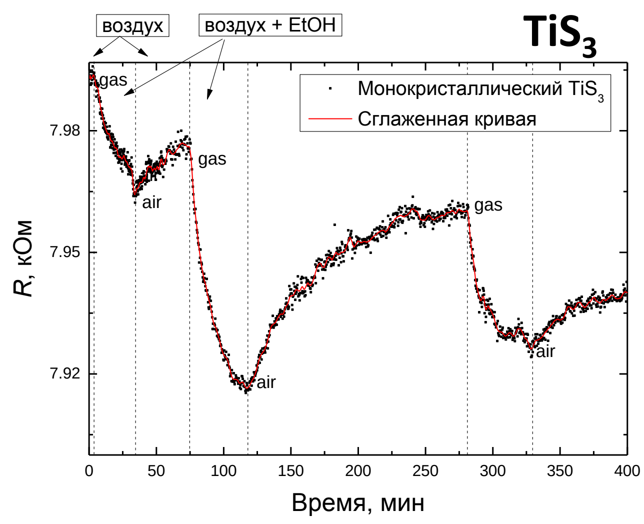


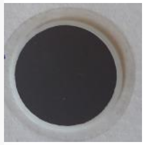


Gases - "reducing agents" acetone and ethanol

TiSe2 and TiS3 crystals are p- and n-type semiconductor materials

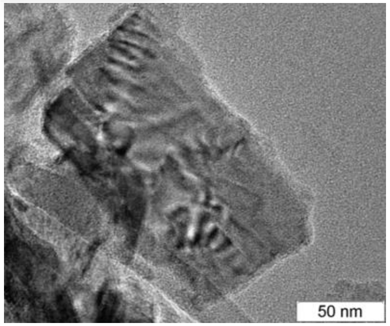


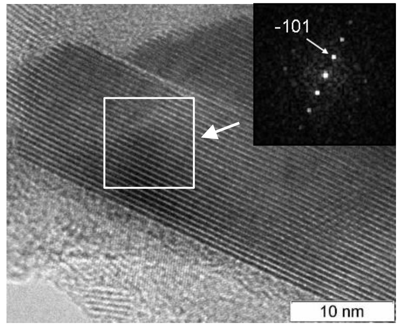




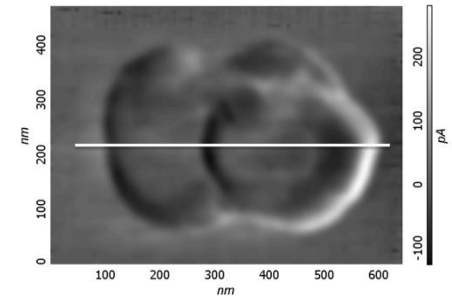
Sensitivity of Mo2S3 films to the gaseous medium

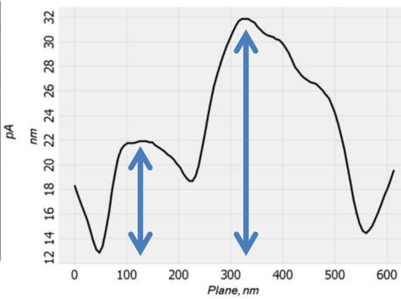
H_2O, DMSO, acetone, EtOH

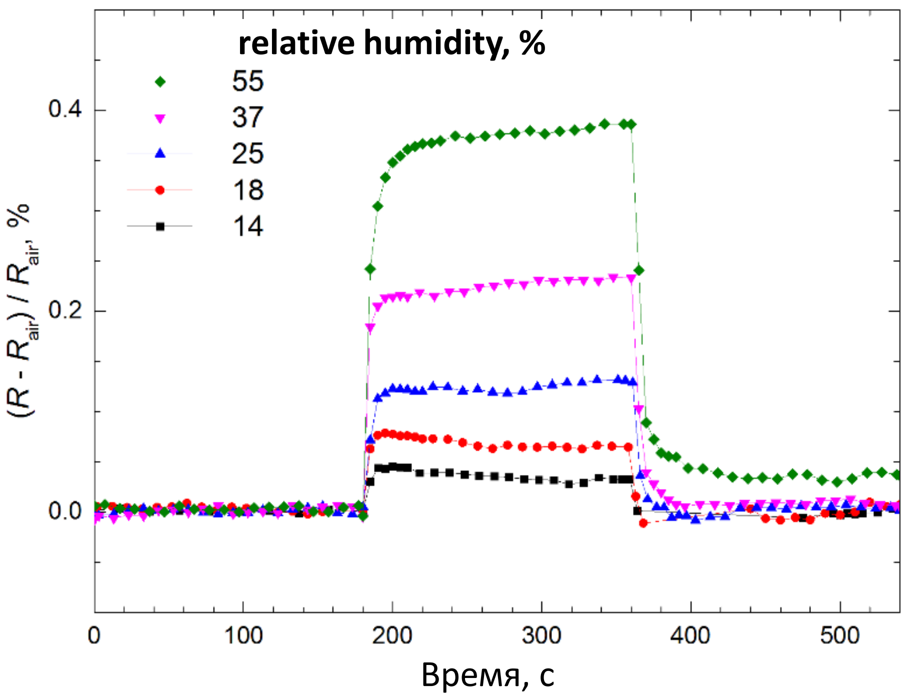


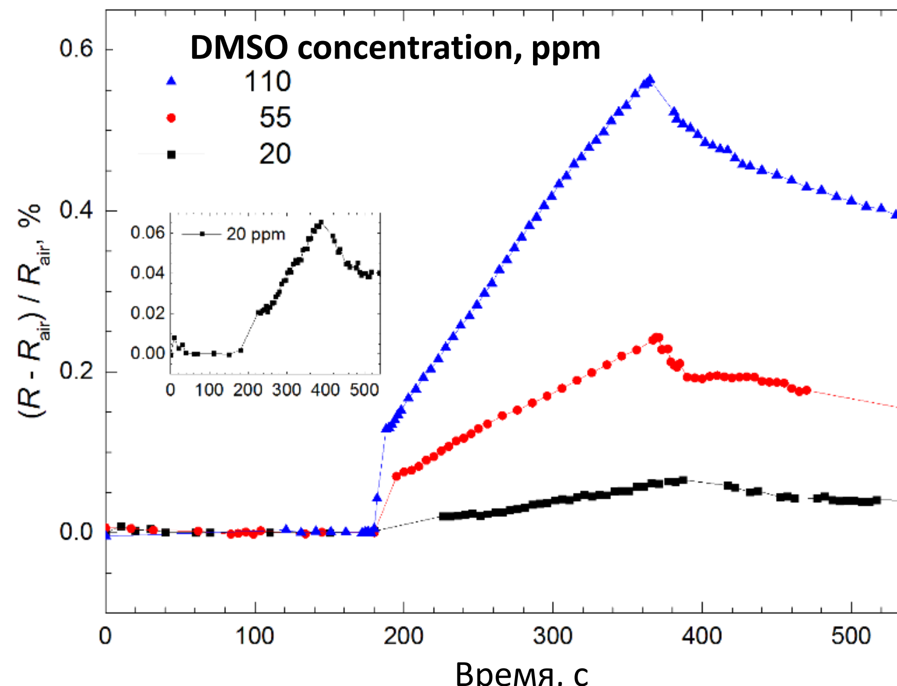


5 nm, 9 nm

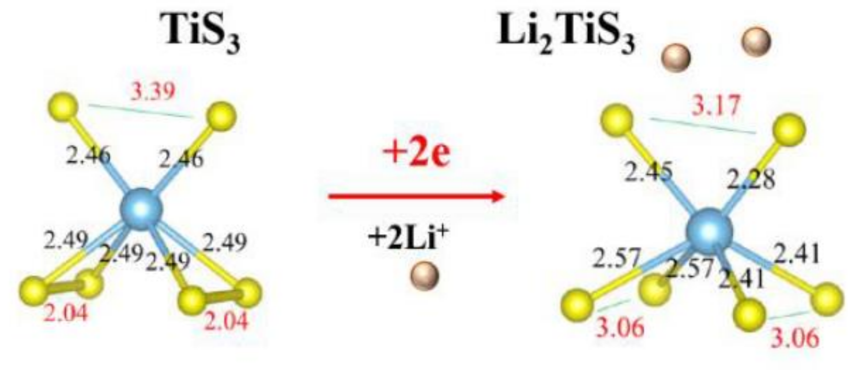




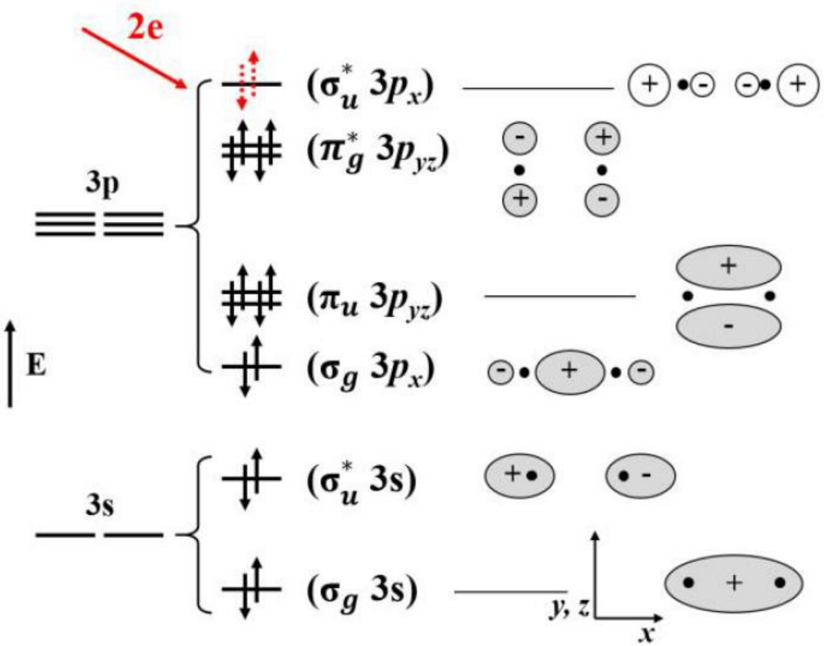




S_2^{2-} in polysulfides MS_n



J. Wu, D. Wang, H. Liu, *RSC Advances* 2015



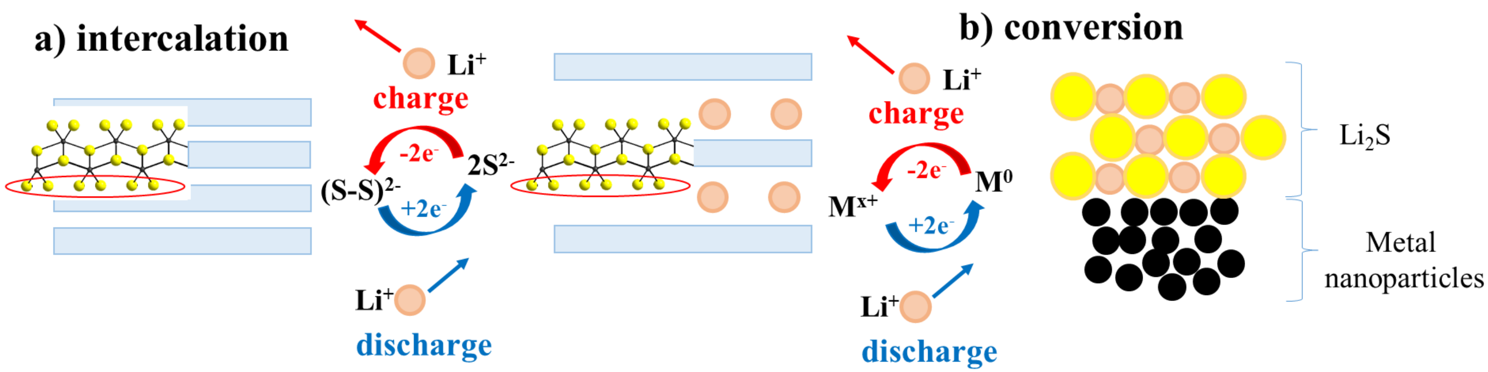
TiS_3 + BuLi / hexane

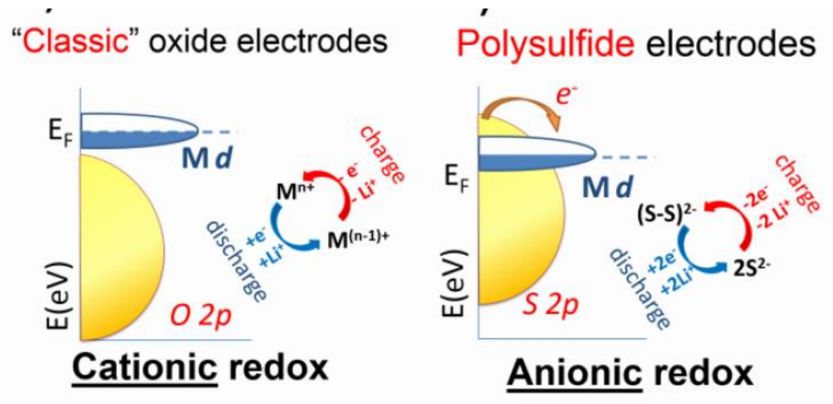
+ 2e ↓ ↑ − 2e

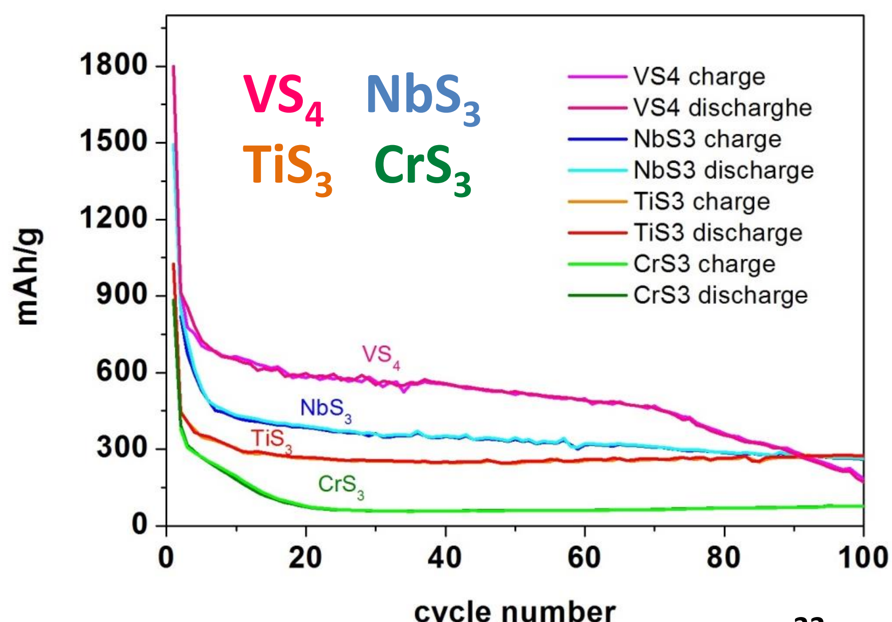
Li_2TiS_3 + C_8H_{18}

$$S_2^{2-} \underset{-\,2e}{\overset{+\,2e}{\rightleftarrows}} 2S^{2-}$$

Transition Metal Polysulfides in chemical current sources

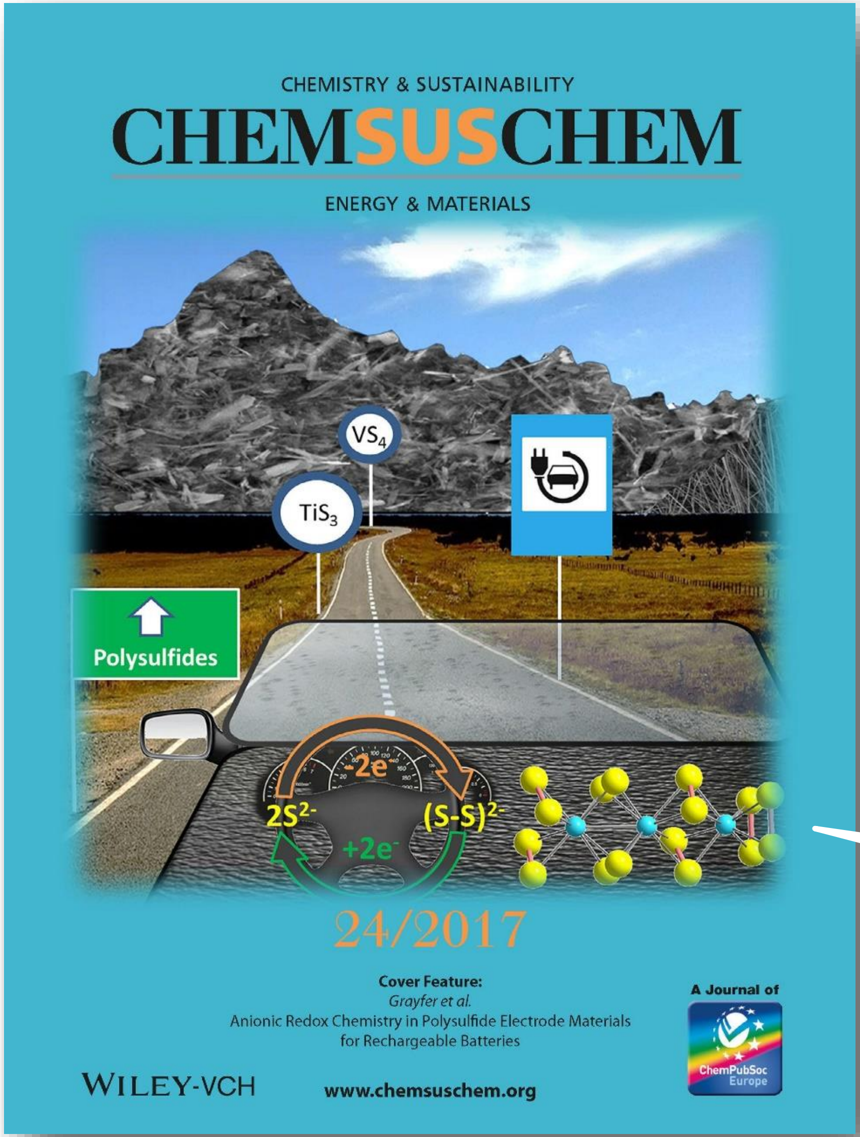






E. D. Grayfer, E. M. Pazhetnov, M. N. Kozlova, S. B. Artemkina
V. E. Fedorov, *ChemSusChem* **2017**

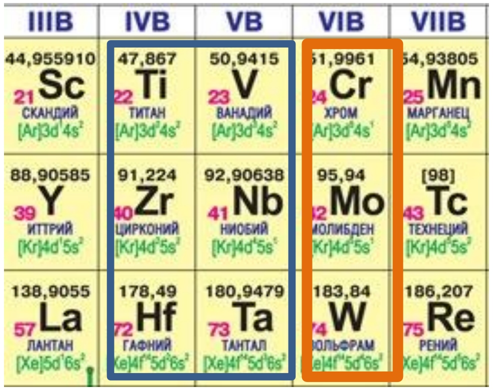
Anionic Redox Chemistry in Polysulfide Electrode Materials for Rechargeable Batteries

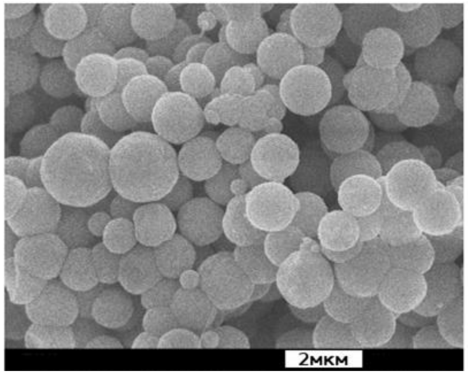


Grayfer E. D., Pazhetnov E. M., Kozlova M. N., Artemkina S. B. and Fedorov V. E. «Anionic Redox Chemistry in Polysulfide Electrode Materials for Rechargeable Batteries» // **ChemSusChem**; 2017, 10(24):4805-4811

Electric car of the future,
powered by Li-ion batteries
based on transition metal polysulfides

Simulation of the structure of amorphous MoS_5

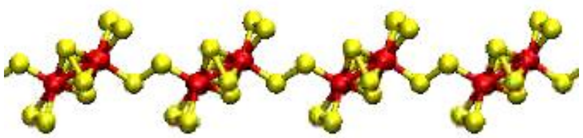


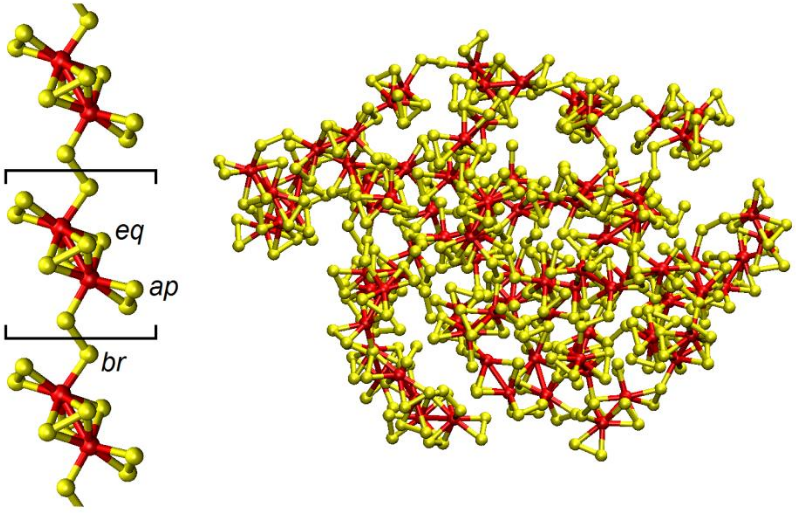


1) $M(CO)_6$ + 10~15 S → MS_n↓ 1,2-dichlorobenzene, 170°C (MoS_5, WS_5)

2) $(NH_4)MS_4$ + H^+ / aq. → MS_3↓ (MoS_3, WS_3)

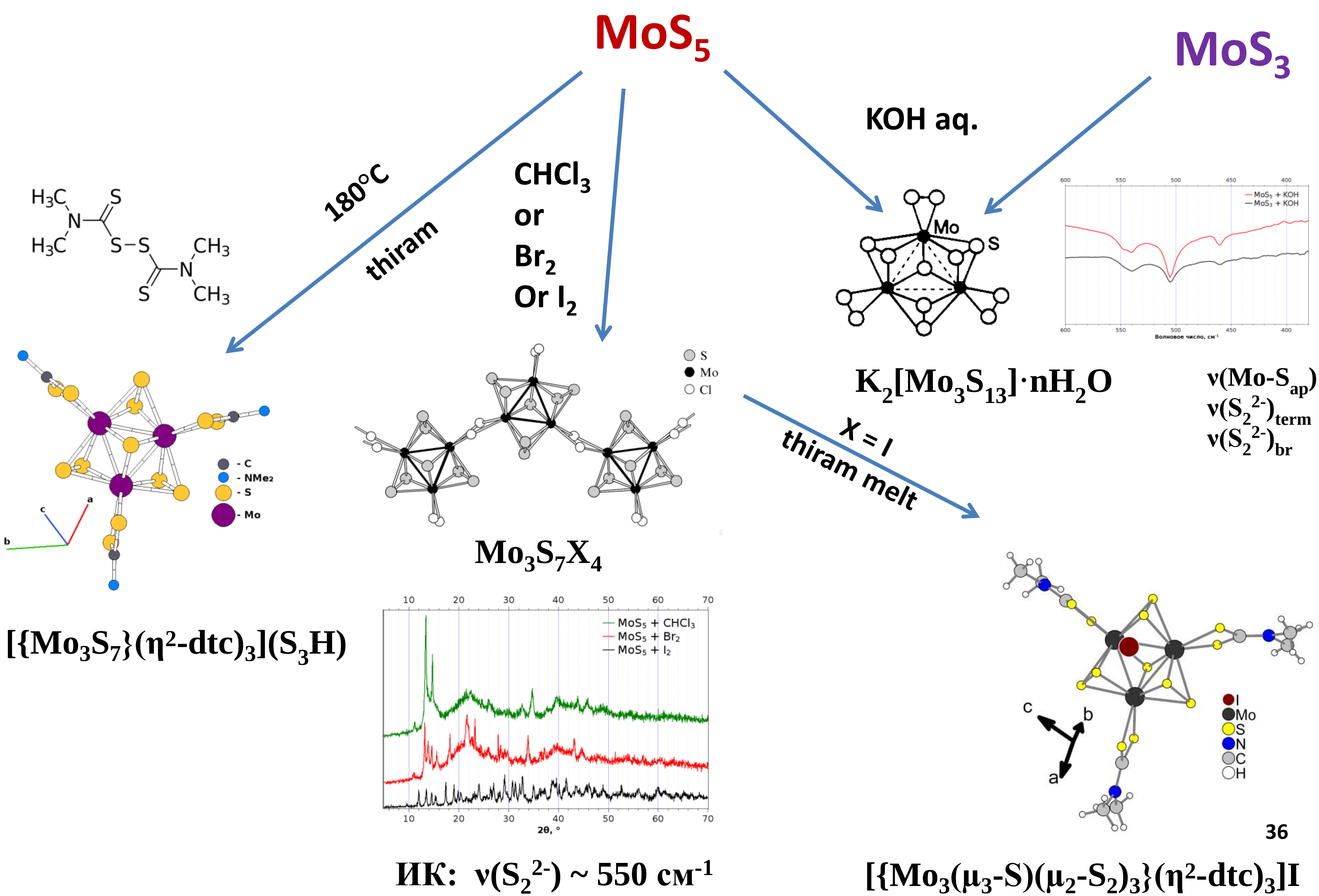
3) $[Mo_2S_{12}]^{2-}{}_{solv}$ + I_2 → $2MoS_6$↓ + $2I^-{}_{solv}$



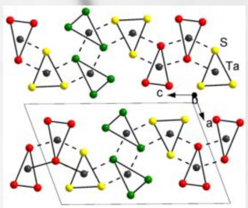


a) b)

Chemical properties of Mo and W polysulfides



Further Perspectives



exfoliation

preparation of nanocomposites

photosensitivity

Photocatalysis:
oxidation of organic molecules
CO, H2 or O2 release

MQ_n

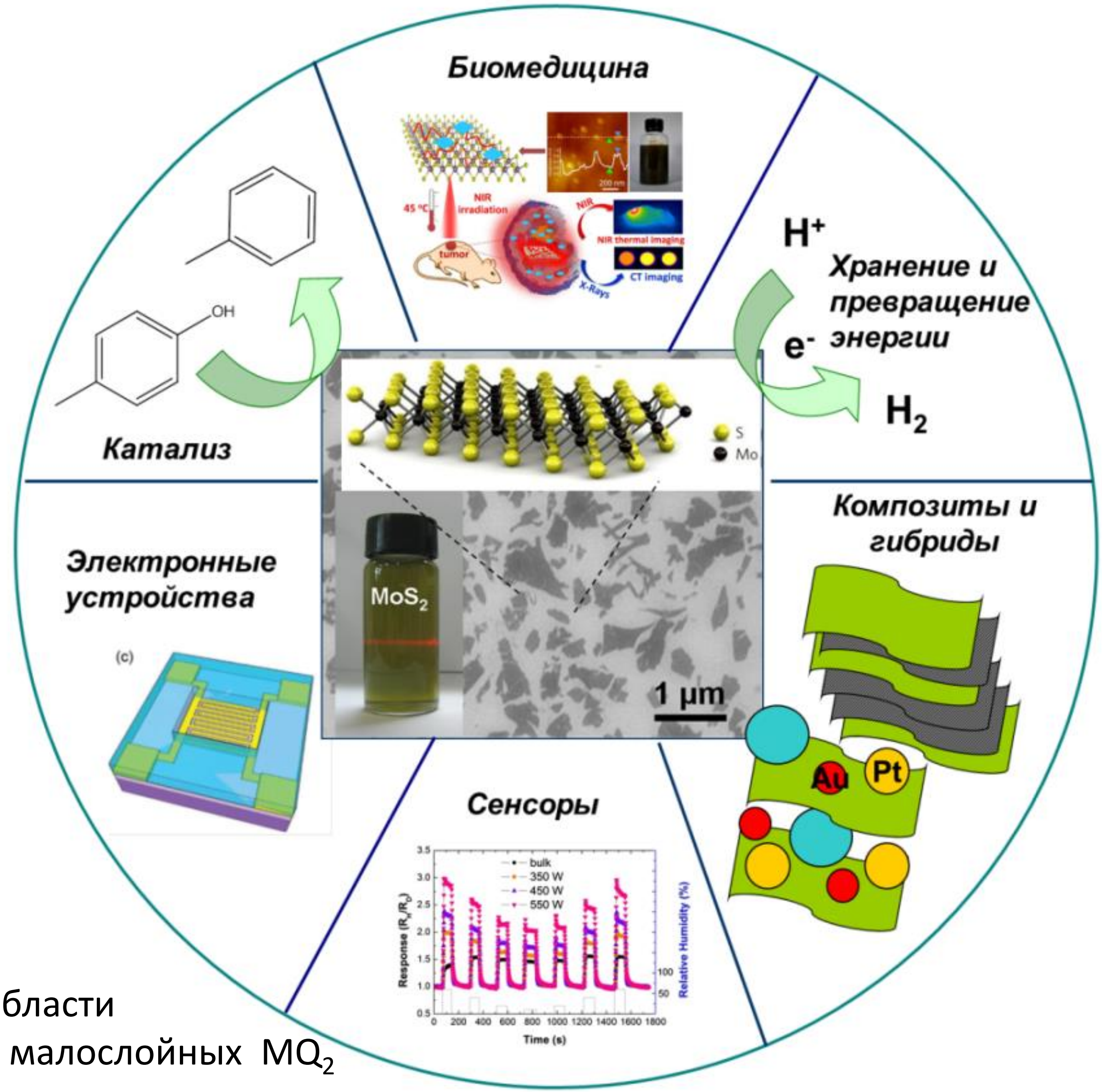
sernsors

strain gauge

Ox-red $Q_2^{2-} \leftrightarrow 2Q^{2-}$
$M^{n+} \leftrightarrow M^0$

Electrochemical cells

Low Layer Chalcogenides of Transition Metals



Различные области применения малослойных MQ_2

Thank you for attention!

Bird's-eye view of Akademgorodok - Novosibirsk, Russia