Novel experimental technique of synthesis two-dimensional nanoparticles of autointercalated Niobium Diselenide

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Introduction

Two-dimensional inorganic nanostructures as two-dimensional or graphene-like nanoparticles of d-transition metals dichalcogenides (“inorganic graphene-like nanostructures”; “2D nano-structures”; “ultrathin nanolayers”) including 2H–MCh_2 nanostructures (M = Nb, Ta; Ch = S, Se; 2H–TaS_2 structural type; metallic type of conductivity) and their intercalated nanophases have been receiving great attention in recent years because they show unusual physical properties which are the result of a quantum size effect associated to their ultra-thin structure. These 2D nanosheets are now considered to be excellent candidates for future electronic applications. As demonstrated by groundbreaking advances such as superconductors and magnetic superlattices, 2D nanostructures play a pivotal role to realizing electronic, magnetic and optical properties.

The family of layered 2D dichalcogenides represents an interesting system in which charge-density-wave (CDW) order coexists with superconductivity. The CDW transition temperature decreases, while the superconducting critical temperature (Tc) increases from 2H–TaS_2 and 2H–$NbSe_2$ to 2H–NbS_2, suggesting that these two parameters compete. Indeed, as became known, in 2H–TaS_2 and 2H–$NbSe_2$, T*c* increases under pressure while T*CDW* decreases. After CDW order disappears, T*c* remains approximately constant. All of anomalies, including an apparent anisotropy of the superconducting gap, is very important in physical research two-dimentional nanostructured systems.

Experimental part and results

The nanosynthesis was carried out by “top-down” with use of activated processes of intercalation/delamination (Li^+/H_2O) of autointercalated 2H–$Nb_{1.02(1)\div1.29(1)}Se_2$ micron particles. The timing data of galvanostatic processes of intercalation/delamination were learned by use of potentiostat (PI-50-1, reference electrode – AgCl). The structural properties of dispersed powders were investigated by XRD, SEM.

It was determined that activated processes of intercalation (Li^+/H_2O) lead to substantial dispersion of 2H–$Nb_{1.02(1)}Se_2$ micron particles along cleavage plane where weak Van der Waals forces act (Fig. 1). It has been found that under certain conditions of process intercalation/delaminating micron particles 2H–$Nb_{1.02(1)}Se_2$ was prepared the homogeneous, anisotropic graphene-like 2H-$Nb_{1.02(1)}Se_2$ nanoparticles (2H-TaS_2 structural type) with average sizes (XRD) of 22.7(7)–46.4(1.4) nm for [013] crystallographic direction, 61.9(1.7)–144(7) nm for [110] direction. The nanoparticles sizes are control efficiently by kinetic parameters of intercalation processes. The level of autointercalation under dispersion of micron particles is practically stable and is equal 0.02(1). Unit cell parameters (*a*, *c*) of 2H-$Nb_{1.02(1)}Se_2$ nanostructures correlate with average sizes of nanoparticles (Tabl.; fig. 2). It was shown for different values of pH aqueous solutions realize processes of self-assembly of dispersed nanoparticles 2H–$Nb_{1.02(1)}Se_2$ into larger particles and ascertained disordering and partial (concentration-dependent) structural transition 2H–TaS_2→2H–MoS_2 (average size of particles >200 nm). It was established that the management of the value pH considerably affects the stabilization of colloidal solutions of dispersed nanoparticles 2H-$Nb_{1.02(1)\div1.29(1)}Se_2$. This allows to control the processes of self-assembly of graphene-like nanoparticles 2H-$Nb_{1.02(1)\div1.04(1)}Se_2$, their dimensions and characteristics of real nanostructures and, therefore, structure-sensitive physical properties (Fig. 2–7).

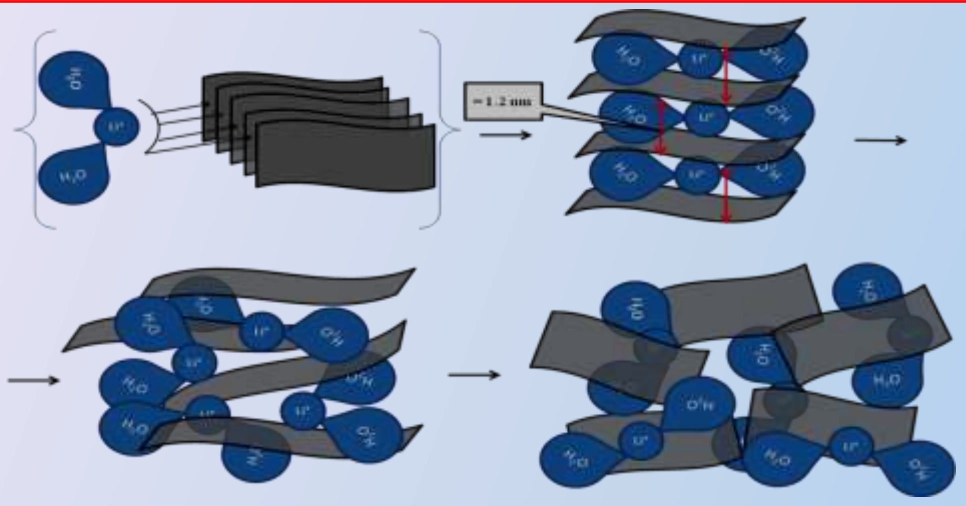

Fig. 1 The electrochemical lithium intercalation/delamination processes to produce 2D nanosheets of 2H-$Nb_{1+y}Se_2$ from the layered micron particles

Crystallographic parameters	Phase			
	2H-$Nb_{1,02}Se_2$(10мA)	2H-$Nb_{1,02}Se_2$(30 мA)	2H-$Nb_{1,04}Se_2$(10 мA)	2H-$Nb_{1,04}Se_2$(30 мA)
Parameters of unit cells, nm: *a*	0.34449(2)	0.34441(2)	0.344187(5)	0.344332(6)
c	1.25432(7)	1.25414(9)	1.25408(3)	1.25434(3)
Cell volume, nm^3	0.12891(2)	0.12883(3)	0.128660(6)	0.128795(7)
Calculated density ($g*cm^{-3}$)	6.462(1)	6.465(2)	6.4741(3)	6.4673(4)
2θ, sin θ/λ (max)	43.52; 0.689	44.04; 0.697	100.31; 0.498	100.31; 0.498
Factor of discrepancy, $R_{(intensity)}$	0.1143; 0.2905	0,1167; 0.3019	0.0851; 0.1240	0.0679; 0.1856
Contents atoms: Atomic %: Nb; Se; Li*	33.33; 66.67	33.33; 66.67	33.33; 66.67	33.33; 66.67
Weight %: Nb; Se; Li*	37.04; 62.96	37.04; 62.96	37.04; 62.96	37.04; 62.96
Coordinates of the atoms, (x, y, z)	Nb_1 – (0; 0; 1/4); Nb_2 – (2/3; 1/3; 1/4); Se – (1/3; 2/3; 0.1180(2))	Nb – (0; 0; 1/4); Se – (1/3; 2/3; 0.1175(3))	Nb_1 – (0; 0; 1/4); Nb_2 – (2/3; 1/3; 1/4); Se – (1/3; 2/3; 0.11652(4))	Nb – (0; 0; 1/4); Nb_2 – (2/3; 1/3; 1/4); Se – (1/3; 2/3; 0.11682(6))
Occupations (Nb_1, Nb_2)	Nb_1 – 0.953(5); Nb_2 – 0.047(5)	-	Nb_1 – 0.948(1); Nb_2 – 0.052(1)	Nb_1 – 0.961; Nb_2 – 0.039
Space group, structural type	$P6_3/mmc$, 2H-TaS_2, 2H-MoS_2	$P6_3/mmc$, 2H-TaS_2	$P6_3/mmc$, 2H-TaS_2, 2H-MoS_2	$P6_3/mmc$, 2H-TaS_2, 2H-MoS_2

Tables – Results of XRD 2H–$Nb_{1.02(1)}Se_2$ after electrochemical intercalation/delamination (Li^+/H_2O)

Compound	Parameters of unit cells of initial particles, nm		Data for the powders after electrochemical processing					
			Parameters of unit cells, nm		Average size of particles, nm, in the crystallographic directions [013] and [110]		Amount nanolayers,	Relation
	a	*c*	*a*	*c*	$d_{[013]}$	$d_{[110]}$	n	$d_{[110]}/d_{[013]}$
2H-$Nb_{1,02(1)}Se_2$	0,34449(2)	1,2554(1)	0,3447(2)	1,2597(9)	27,4(9)	75,0(1,9)	43	2,74
			0,3447(2)	1,2550(9)	41,6(1,4)	143,5(7,0)≈144(7)	66	3,46
			0,3447(2)	1,2558(8)	46,4(1,6)	183,4(9,6)≈180(10)	73	3,95
			0,3446(2)	1,2607(9)	25,4(8)	61,9(1,7)	40	2,44
			0,3444(2)	1,2563(9)	49,7(1,4)	164,8(7,4)≈165(7)	79	3,32
			0,3447(2)	1,2550(9)	28,1(8)	135,0(6,4)≈135(6)	44	4,80
			0,3448(2)	1,2551(9)	22,7(7)	132,4(4,2)≈132(4)	36	5,81

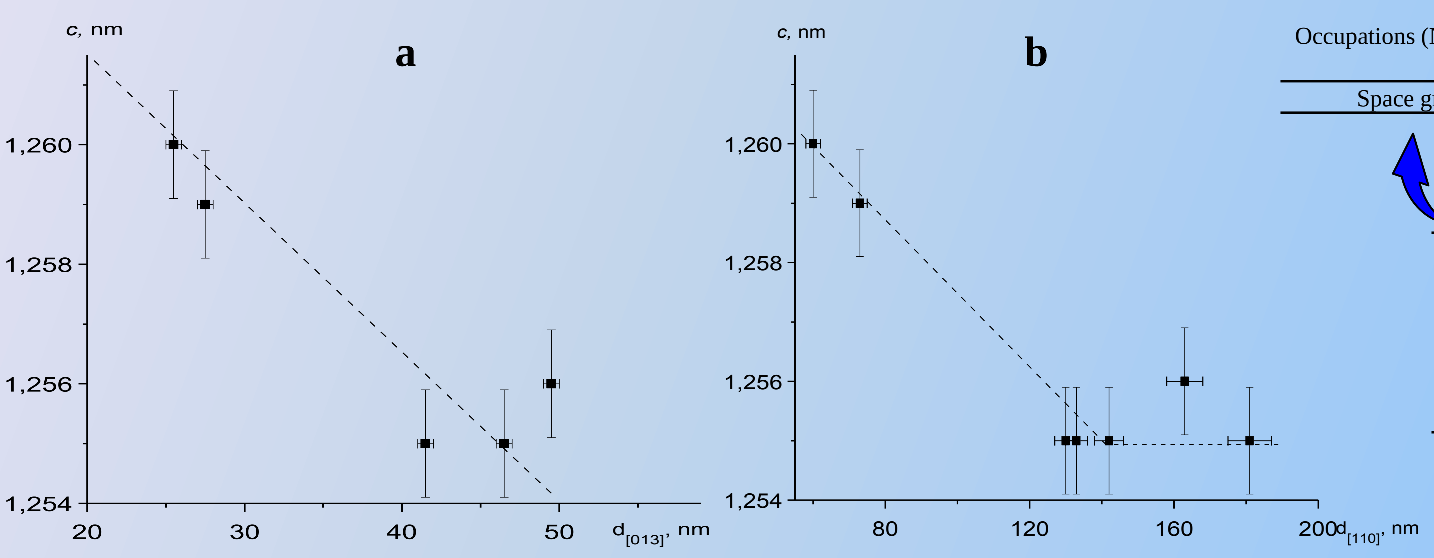

Fig. 2 Dependences of unit cell parameter *c* graphene-like nanoparticles 2H-$Nb_{1.02(1)}Se_2$ from average size of nanoparticles, d, in the crystallographic directions [013] (a) and [110] (b).

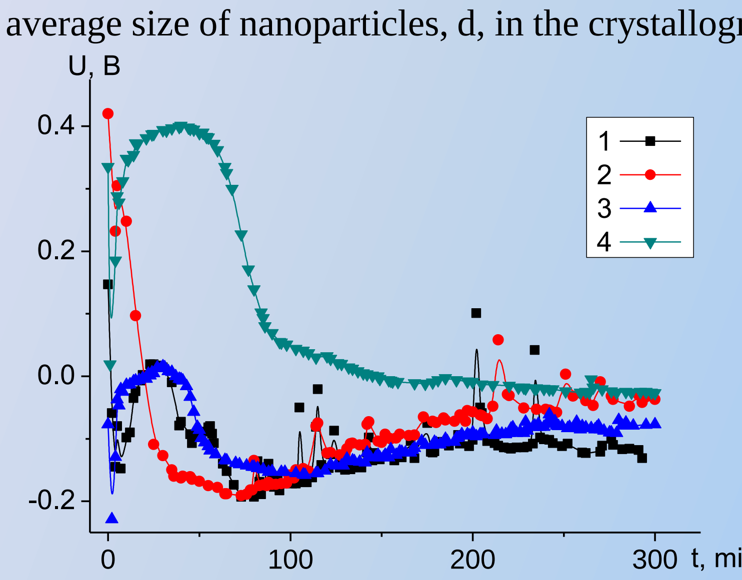

Fig. 3 Dependences of potential for 2H-$Nb_{1+y}Se_2$ particles, U, vs. time, t: 1 – 2H-$Nb_{1.02(1)}Se_2$, 2 – 2H-$Nb_{1.04(1)}Se_2$, 3 – 2H-$Nb_{1.09(1)}Se_2$, 4 – 2H-$Nb_{1.12(1)}Se_2$ (I=10 mA; m=2 g).

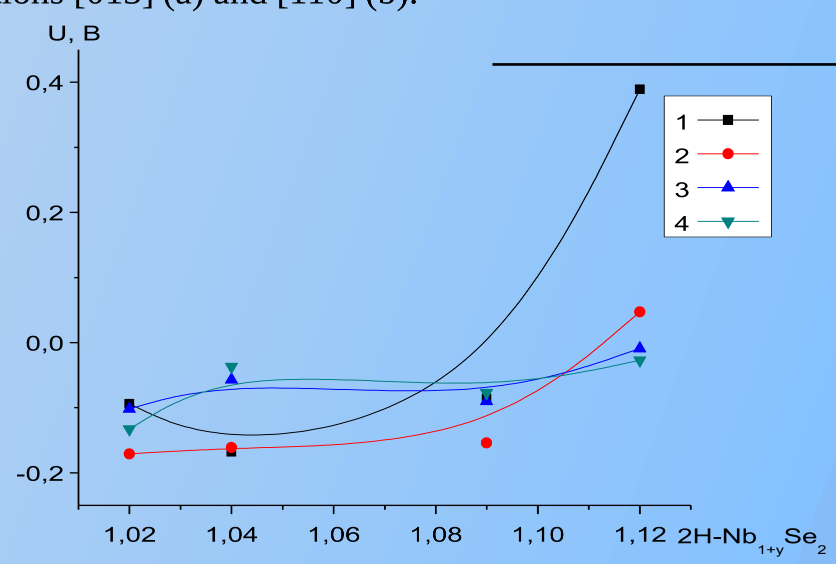

Fig. 4 Dependences of potential for 2H-$Nb_{1+y}Se_2$ particles, U, vs. composition of autointercalated at constant time, t: 1 – 50 min, 2 – 100 min, 3 – 200 min, 4 – 300 min (I=10 mA).

Graphene-like (2D) 2H-$Nb_{1.02(1)\div1,29(1)}Se_2$ nanoparticles have correct hexagonal form with considerable anisotropy sizes of length and thickness (scanning electron microscopy, ***Fig. 7***). It forms conglomerates, that can be explained considerably change value of pH during the passage of activated electrochemical intercalation (Li^+/H_2O) processes.

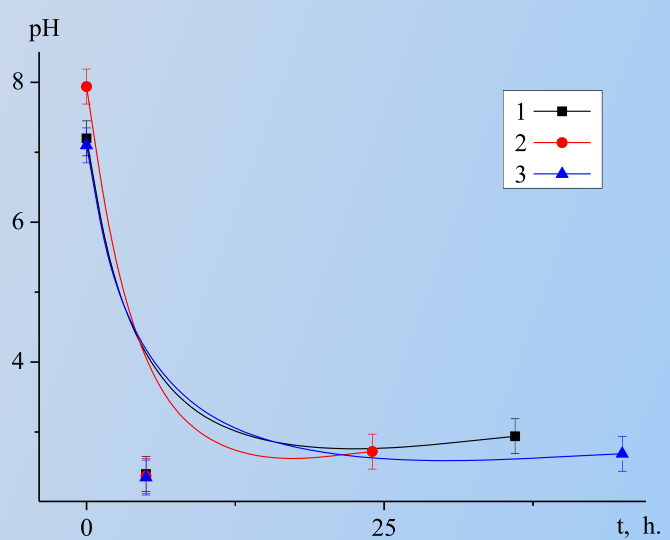

Fig. 5 Dependences of PH solution for 2H-$Nb_{1.02(1)}Se_2$ after electrochemical intercalation/delamination vs. time, t; the values of current, I: 1 – 10 mA, 2 – 30 mA, 3 – 50 mA.

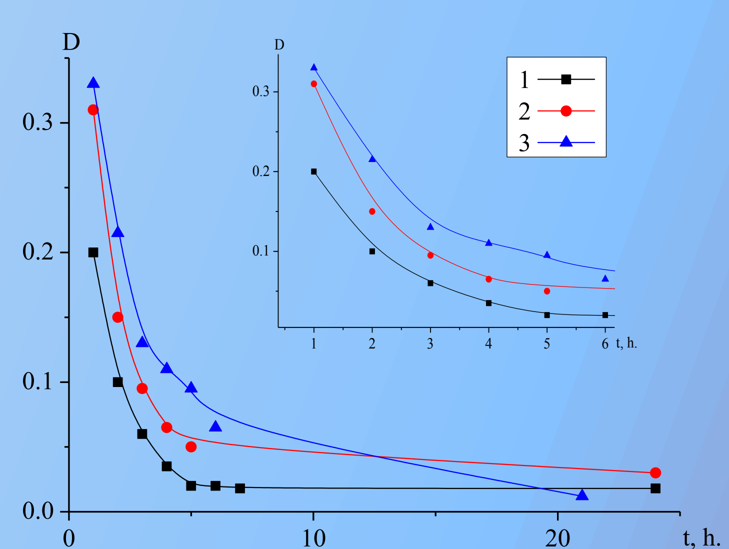

Fig. 6 Dependences of optical density, solution, D, for 2H-$Nb_{1.02(1)}Se_2$ after ultrasonic treatment (40 min) vs. settling time, t; the values of current, I: 1 – 10 mA, 2 – 30 mA, 3 – 50 mA.

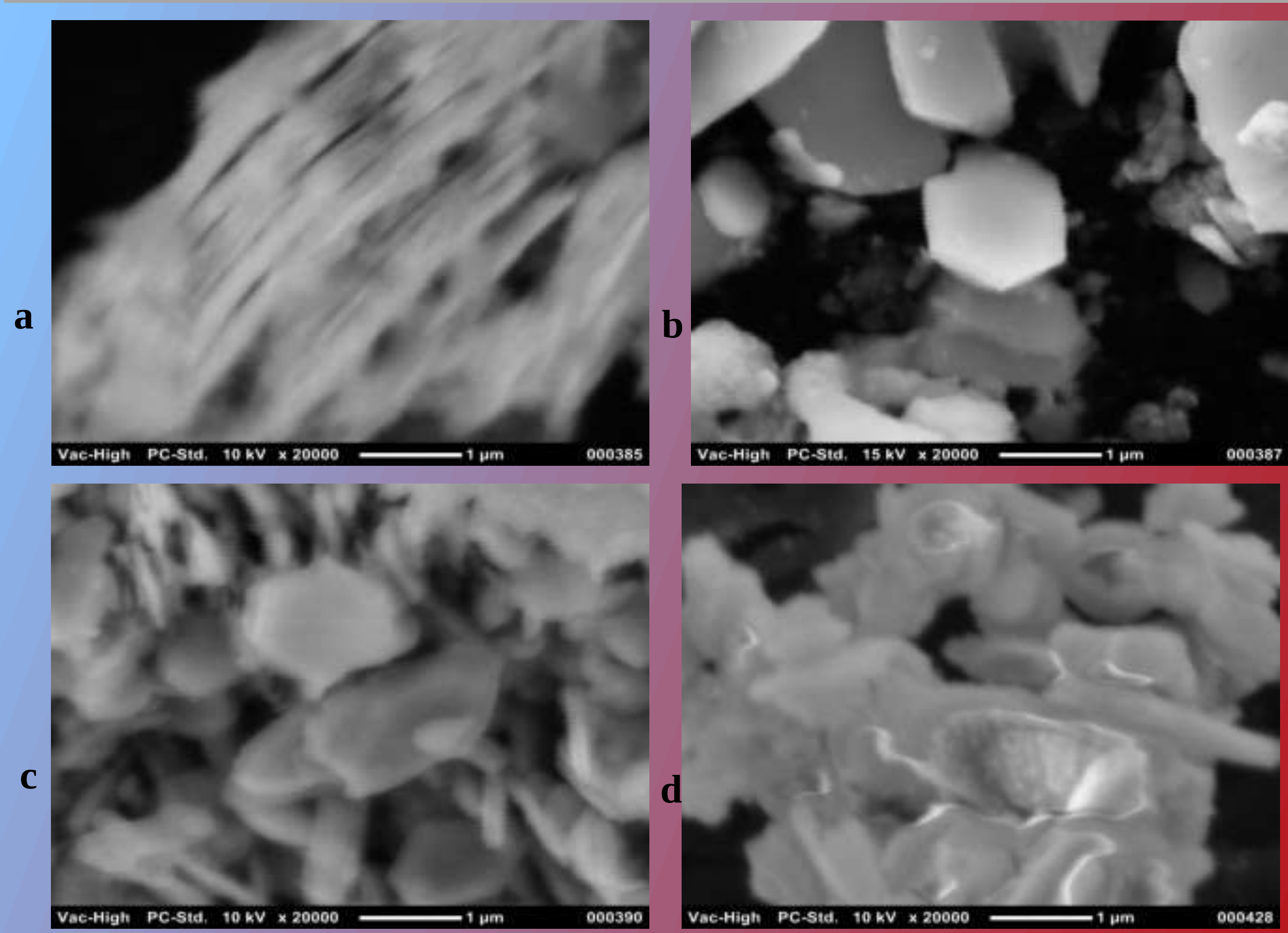

Fig. 7 The results of scanning electron microscopy of graphene-like nanoparticles 2H-$Nb_{1.02(1)\div1.29(1)}Se_2$, mass, m=1 g, the values of a current, I=30 mA (magnification: – x20000); a – 2H-$Nb_{1.02(1)}Se_2$, b – 2H-$Nb_{1.09(1)}Se_2$, c – 2H-$Nb_{1.12(1)}Se_2$, d – 2H-$Nb_{1.22(1)}Se_2$.

Conclusions

Graphene-like autointercalated 2H-$Nb_{1,02(1)\div1,29(1)}Se_2$ nanoparticles with wide structural-sensitive chemical, physical and physicochemical properties set are perspective for mentioned two-dimensional nanomaterials design.

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