

Review of nanoscale layered transition metal chalcogenide superconductors

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Abstract

Here we summarized the nanoscale layered transition metal chalcogenide superconductors, mainly based on the experimental results. In transition-metal chalcogenides the interplay between strong electron-electron and electron-phonon interactions produces a wide variety of instability ranging from charge density wave to superconducting state. The majority of bulk transition-metal dichalcogenides' T_c s are normally between 2 and 4 K. At present, superconducting transition-metal chalcogenides generally show low transition temperature ($T_c < 10$ K). Fe based transition-metal chalcogenides have certain higher T_c (in the range of 10 ~ 50 K). As have been reported, nano-transition-metal chalcogenides may be one of the routes to improve the superconducting transition temperature. In this review, we would like to give a brief introduction of superconductor development and crystal structure of transition-metal chalcogenides. Furthermore, we will describe major synthesis and physical properties of nano-transition-metal chalcogenides. Finally, recent status and outlook of superconductor based on nano-transition-metal chalcogenides are discussed. Copyright © 2019 VBRI Press.

Keywords: Superconductor, transition-metal chalcogenide, nanoscale.

Introduction

Superconductivity is a phenomenon of exactly zero electrical resistance and expulsion of magnetic flux fields occurring in certain materials, called superconductors, when cooled below a characteristic critical temperature. Generally, superconductors share the other major characteristic, magnetic flux quantum, except for zero electrical resistance and expulsion magnetic flux fields. Due to the aforementioned fancy characteristics, superconductors have potential applications in power station, superconducting sensors, single photon detectors and other technological fields, exhibiting indispensable function and significance.

Over nearly a century, scientists have been spared no efforts to develop superconducting materials. Before 1986, people focused on the low-temperature superconductors [1–3], mainly including alloy, oxide and organic materials. The critical temperature (T_c) of the most first generation superconductors is below 77 K (liquid nitrogen). In order to achieve more practical applications, scientists adverted to search superconducting materials with higher T_c . Cu-based superconductor system was then born after 1986. The first discovered Cu-based superconductor was BaLaCuO [4] system, one of the conductive ceramic, with T_c of 30 K. Subsequently, an amazing discovery of

YBa₂Cu₃O_{7-δ} [5] presented T_c of 93 K, making it possible that superconductor could work in temperature above liquid nitrogen. Subsequently, HgBa₂Ca₂Cu₃O_{9-δ} [6] was found to exhibit T_c of 130 K, whose T_c could arrive 164 K under high pressure. From then on, Cu-based superconductor system established domination for years. However, Cu-based superconductors are ceramic materials, such properties as brittleness and low mechanical strength making it difficult to be large produced on industries. Until 2008, Fe-based superconductor system started to break into our sight. F-doped LaFeAsO [7] system was firstly reported to present superconductivity in 26 K. In the same year, scientists pointed out that SmO_{1-x}F_xFeAs [8] and PrO_{1-x}F_xFeAs [9] could transform to superconductor in 43 K and 52 K, respectively. Moreover, the T_c of SmO_{1-x}F_xFeAs [10] could be improved to 55 K under high pressure. Although physician Macmillan [11] predicted a limitation of 40 K of superconductor according to traditional calculation, a numerous Fe-based superconductors with T_c above 40 K have been discovered, such as SmO_{1-x}F_xFeAs, PrO_{1-x}F_xFeAs, FeSe [12,13], LiFeAs [14], NaFeAs [15,16], (Ba, Sr, Ca) Fe₂As₂ [17–19], Sr₄V₂O₆Fe₂As₂ [20] and so on. Compared with Cu-based superconductors, Fe-based superconductors show metallic properties and easy processability. In spite of such advantages, Fe-based

superconductors indeed have barriers to be widely developed. The major reason is lack of theory base. Unlike the low temperature superconductor system, both Cu-based and Fe-based systems do not obey to the BSC theory, the traditional microscopic theory of superconductivity put forward by J. Bardeen, L.N. Cooper and J.R. Schrieffer. Due to the absence of theoretical explanation and prediction, scientists could hardly seek elements and design structures for more promising superconductors. In order to breakthrough this restriction, scientists have to pave another path.

Recently, layered transition metal chalcogenides (TMCs) have attracted large attention and become a new choice for superconducting materials. Overall, TMCs have the following features. Firstly, TMCs could present fancy properties via intercalation and substitution of both transition metals and chalcogenide elements. Besides, TMCs have abundant crystal structures (e.g. 1T, 2H, 3R, 4H *et al.*, see **Fig. 1**), which will be described in detail as below. Moreover, compared with As or La elements of Fe-based materials, TMCs component is nontoxic and costless. Additionally, the most important feature is that TMCs properties could be explained by the BSC theory, avoiding trying large quantity of materials without guideline. Last but not the least, TMCs may be easier synthesized compared with organic materials. Due to the above mentioned highlights, TMCs have been more widely studied and applied. According to the formula MX_n (M = transition metal, X = chalcogenide), we classified TMCs into three types, namely intercalated TMCs, M-substituted TMCs and X-substituted TMCs. For intercalated TMCs, the formula can be rewritten by IMX_n (I = intercalated atom, ion or molecule). FeX and MoX series are the two major intercalated TMCs, such as $K_{0.8}Fe_2Se_2$ [21], $NaFe_2Se_2$ [22], $KMoS_2$ [23], $(NH_3)_{0.4}Na_{0.5}MoSe_2$ [24], $(NH_3)_{0.4}Ca_{0.2}MoSe_2$ [25] and other series. Similarly, M-substituted and X-substituted TMCs can be marked as $M'_xM_{1-x}X_n$ and $MX_{n-x}X'_x$, respectively. Among them, 1T- $Fe_xTa_{1-x}S_2$ [26], 3R- $M_xTa_{1-x}Se_2$ [27], 1T- $Ta_{2-x}Se_x$ [28], $FeTe_{1-x}Se_x$ [29] and other materials are reported to show superconductivity. Although there exist many superconducting TMCs, most of them present low T_c (2 ~ 10 K). Only Fe-containing TMCs have certain higher T_c , such as $K_{0.8}Fe_2Se_2$ [21] (36 K), $NaFe_2Se_2$ [22] (46 K) and $FeTe_{1-x}Se_x$ [29] (15 K).

Nanostructure TMCs were firstly reported in 1979 [30] and found to have potential usages in solid-state lubricants [31], nano-electronics [32], hydrogen storage [33], catalysis [34], and other applications. Maybe superconductor is also possible. Some works were done by synthesizing nano-superconductors to improve their T_c . For instance, 2H- TaS_2 [35] is a superconductor with T_c of 0.6 ~ 0.8 K in bulk materials while 3.4 K in nanowires with diameter range from 100 ~ 600 nm. Another famous TMC superconducting material is FeSe. The T_c of bulk FeSe [36] is only 8 K, while its T_c could be twice as high when it was synthesized into nanorod array with the diameter of 100 nm and the

length of 600 nm of one nanorod [37]. Moreover, nanoparticle [38] and nanofilm [39] FeSe have been found to possess higher T_c of 33 K and 70 K, respectively. **Fig. 2** is the SEM image of the composite nanoparticles [38] containing FeSe nano islands entrapped within an ent- $FeSe-Pd_{16}Se_{15}$ -Au nanoparticle and sharing an interface with $Pd_{17}Se_{15}$. The inset graph shows the composite nanoparticle size distribution of 200 ~ 250 nm. From the above examples, we may reckon that minimizing grain size to nanoscale may improve the T_c of superconducting TMCs to some extent.

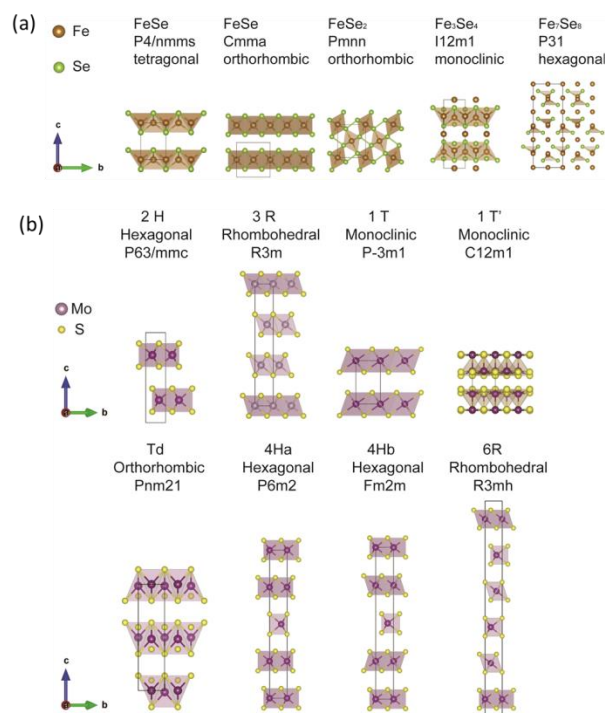


Fig. 1. Common phase illustration of (a) Fe-based TMCs and (b) MX_2 .

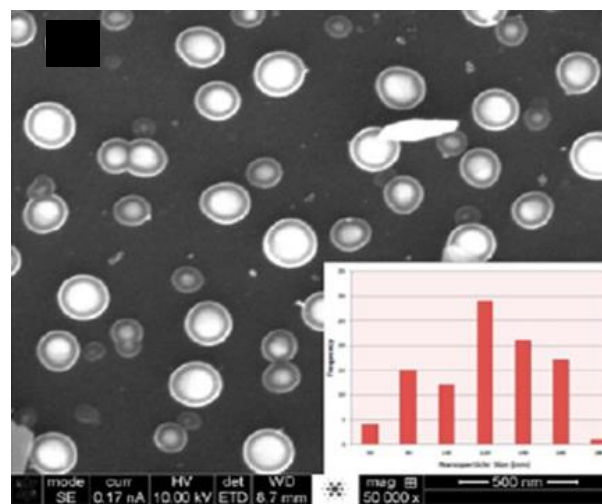


Fig. 2. Composite nanoparticles containing FeSe nanoislands entrapped within an ent- $FeSe-Pd_{16}Se_{15}$ -Au nanoparticle and sharing an interface with $Pd_{17}Se_{15}$ (inset shows the diameter distribution of the nanoparticles)³⁸. Reprinted from ref. 38. © 2014 American Chemical Society.

Crystal structure of TMCs

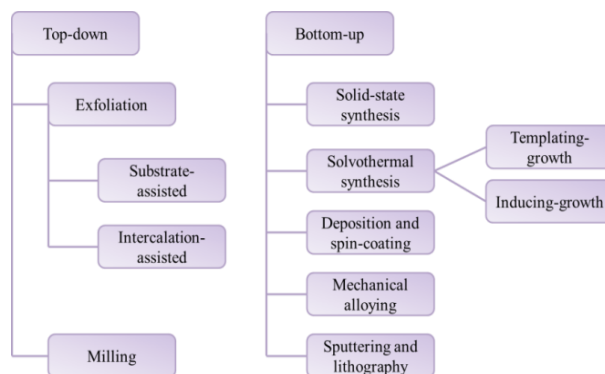
TMCs have abundant crystal structures and components, which will be leading to multifarious physical properties. For example, FeSe comes in several phases: (i) a tetragonal phase α -FeSe [40] with PbO-structure (P4/nmms, **Fig. 1a**), (ii) a NiAs-type β -phase (P63/mmc, **Fig. 1a**) with a wide range of homogeneity showing a transformation from hexagonal to monoclinic symmetry and (iii) an FeSe₂ phase that has the orthorhombic marcasite structure. The most studied of these compounds are the hexagonal Fe₇Se₈, which is a ferrimagnet with Curie temperature at ≈ 125 K, and monoclinic Fe₃Se₄. Moreover, similar structural materials possess widely different properties. For example, tetragonal FeSe (α -FeSe) is a superconductor with a transition temperature T_c of 8 K. Tetragonal FeTe [41] has a structure very analogous to superconducting FeSe, but does not show superconducting transition.

Layered transition-metal dichalcogenides (TMDCs) are studied widely due to their rich physical properties and crystal structures. TMDCs have a general formula MX₂, where M = Mo, W, V, Nb, Ta, Ti, Zr, Hf or Re, X = Se, S, or Te. Structurally, these compounds can be regarded as having strongly bonded (2D) X-M-X layers, with M in either trigonal prismatic or octahedral coordination with X, and weak inter-layer X-X bonding of the van der Waals type. **Fig. 1** shows 9 crystal structures for the common TMDs. The labels are easily recognized: the number indicates the number of layers per unit crystallographic cell, the letter the unit cell symmetry (T = trigonal, H = hexagonal, R = rhombohedral), and finally a third lower case letter is used when the first two do not uniquely identify the polytype [40]. In some of its forms, notably the 2H and 3R polytypes (**Fig. 1b**), Mo is found in trigonal prismatic coordination in S-Mo-S layers that are stacked along the c axis of the hexagonal (or rhombohedral) cell. The 2H and 3R polytypes [41-45] differ only in their stacking periodicity – the structure repeats after 2 layers in the 2H form (P63/mmc) and 3 layers in the 3R form (R3m). In one of the other polymorphs, the 1T type (P3m1) [42-47], Mo is found in octahedral coordination in the S-Mo-S layers, and the layer stacking along the c axis of the trigonal cell such that the structure repeats after only one layer. The T_d form (Pnm21) [48], with Mo in octahedral coordination, has an orthorhombic noncentrosymmetric structure. Monoclinic 1T' form (P121/m1) has a further distorted structure compared to T_d form but is centrosymmetric with the origin of the successive layers displaced with respect to what is seen in the T_d form. The layer structure is also preserved in the 1T'-form but the coordination around the metal atom is a slightly distorted octahedron of tellurium atoms, with the metal atoms displaced from the central position and making chains that run through the crystal in the crystallographic y direction. This increases the coordination number for the metal from six to eight. The 2Ha, 3R, 4Ha, 4Hc form possess purely trigonal

polymorphs whereas the 1T octahedral. The 4Hb and 6R forms are mixed octahedral–trigonal polymorphs. As with the 2Ha, the 2Hb and 3R consist only of trigonal prisms [49-53].

Synthesis methods of nano-TMCs

Generally speaking, there are top-down and bottom-up two methods for synthesis of nano-TMCs, as shown in **Scheme 1**.



Scheme 1. Classification of different methods for synthesis of nano-TMCs.

Top-down route

Top-down route is a synthesis method from bulk materials to nano-materials. To prepare nano-TMCs, exfoliation and ion milling are the two major methods.

Exfoliation

There exist various exfoliation approaches [54]. In this review, we classify them into two major kinds, substrate-assisted and intercalation-assisted exfoliation.

Substrate-assisted exfoliation

One of the substrate-assisted exfoliation is traditional mechanical exfoliation [55], which could produce multilayered and single-layered nanosheets, such as MoS₂, WSe₂, and other TMCs. In a typical mechanical exfoliation process, Scotch tape is acted as physical adhesive substrate to peel off thin films from bulk materials. Then plastic tweezers or other tools are used to rub the Scotch tape. Finally, multilayered and single-layered nanosheets were left. Additionally, nanosheets prepared by this layer-controlled method possess pristine, clean, and high-quality structures, which are suitable for the fundamental study and potential applications based on their intrinsic thickness-dependent properties.

Another substrate-assisted exfoliation use chemical adhesive gold substrate [56] (Au-S bond) instead of physical adhesive Scotch tape. The thickness of the as-prepared MoS₂ layer is 0.7 nm according to the scanning tunneling microscope (STM). This improved mechanical exfoliation is suitable for not only sulfides but also selenides and tellurides, such as MoS₂, WSe₂ and Bi₂Te₃. However, small yield and not large enough

lateral size for device fabrication are the major limitation of substrate-assisted exfoliation.

Intercalation-assisted exfoliation

Intercalation-assisted exfoliation is the other exfoliation route. Ion, atom, molecule, surfactant and even solvent itself could intercalate into the interval between layers. Then bulk materials will be exfoliated into nanosheets by means of extra force, such as electricity, pulsation and expansions.

Lithium intercalation by reacting with *n*-butyl lithium in hexane is the most popular method. After sonication, bulk powders could be exfoliated into nanosheets, such as TaS₂ [57], MoS₂ [58], MoSe₂ [58], WS₂ [58], Mo_{0.5}W_{0.5}S₂ [58] and MoSSe [58]. Further, T_c could be improved from 0.8 K (bulk materials) to 3 K [59] by restacking few layers of monolayer TaS₂, which is obtained by vacuum filtration. Another useful method is the electrochemical lithium intercalation [60]. As the authors described, electrochemical lithium intercalation was performed in a test cell using Li foil as anode, bulk materials (TiS₂ or TaS₂) as cathode and LiPF₆ dissolved in a mixture of ethyl carbonate and dimethyl carbonate as electrolyte. After the discharge process, the solid product was collected by sonication and centrifugation. As is reported, their thickness is 0.9 nm with lateral size from 0.5 to 1 μm. Lithium intercalation can also be achieved by solid-state synthesis of Li_xMX₂ [61, 62], using Li₂S as lithium source. Similarly, chemical vapor transport [63] with *n*-butyl lithium in hexane could also product Li_xMX₂. More conveniently, lithium intercalation in this method can avoid sonication subsequently. Instead, manual shaking in distilled water or acid, such H₂SO₄, is enough to produce single-layer MX₂. Lateral size of the obtained nanosheets is around 21.9 μm and the maximum can reach 100 μm [63] (Fig. 3).

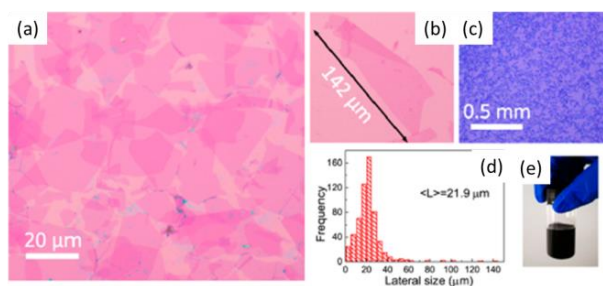


Fig. 3. (a-c) Typical optical images of the exfoliated TaS₂ monolayers on SiO₂/Si substrate; (d) Statistical analysis of the lateral sizes of the TaS₂ monolayers; (e) Photograph of the TaS₂ suspension [63]. Reprinted from ref. 63. © 2017 American Chemical Society.

Atom intercalation [64] could be illustrated by Se-doped Cu₂MoS₄. In a cosolvent system, bulk Cu₂MoS₄ and diphenyl diselenide were mixed and refluxed in inert atmosphere. After sonicate the precipitation, final nanosheets were obtained. The thickness of pristine material is 21 nm. After intercalated Se atom, it decreases to 1.5 nm. Final nanosheet deducing Se atom, the thickness could reach 1 nm.

Water molecule [65] could also be intercalated into the interval. Within a polypropylene tube, H₂O was transformed between liquid and solid with the alternative liquid nitrogen bath and oil bath. With the help of volume expansion, nanosheets were collected by centrifugation. Surfactant [66] could serve as hindered preventing aggregation of nanoparticles. In a suspension with bulk material, surfactant and solvent, probe sonication provides energy for breaking bulk into smaller one. Simultaneously, surfactant entre in the interval and absorb on the surface. Those with surfactant absorbed would not aggregate while those without surfactant absorbed would aggregate again and precipitate during centrifugation. The thickness of these nanoflakes is around 200 nm. Solvent [67] itself could also make function as surfactant. A successful solvent must fulfil two criteria. On the one head, it must be able to disperse / suspend the material for a reasonable amount of time. On the other head, the dispersed material must be highly exfoliated. Usually, these solvents tend to have surface tension within a well-defined range, which can minimize the energy of exfoliation, such as N-methyl pyrrolidone (NMP) and isopropanol (IPA). The typical thicknesses of NMP-dispersed MoS₂ and WS₂ individual flakes are 3 to 12 nm with lateral size from 50 to 1000 nm.

Redox exfoliation [68] has been reported recently. As shown in Fig. 4, bulk MX₂ powder is suspended in solvent (e.g., ethanol or acetonitrile) and treated with an oxidant (e.g., cumene hydroperoxide, CHP), resulting in partial dissolution of MX₂ and forming anionic peroxometalates (POMs) precursor, which adsorb to the surface of the TMD and result in exfoliation. After slow addition of NaBH₄, few-layer to monolayer TMD dispersions can be obtained. This method is demonstrated to be a universal method because it is suitable for various TMDs (Fig. 4).

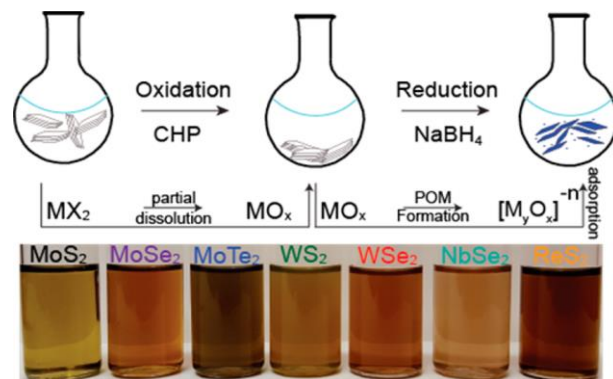


Fig. 4. General scheme for redox-based exfoliation of layered TMD powders [68]. Reprinted from ref. 68. © 2017 American Chemical Society.

Intercalation-assisted exfoliation usually performs in solution. This solution-based method could produce nano-TMCs on a larger scale than the substrate-assisted counterpart. However, irreversible chemical modification of nano-TMC structure and properties is inevitable.

Milling

High-speed ball milling can grind microcrystalline into nanocrystalline. The as-synthesized microcrystalline $\text{Pb}_2\text{P}_2\text{S}_6$ powders were treated with high-speed planetary ball milling technique. Pause was involved to prevent excessive heat to make nanoparticle aggregation. In this way, $\text{Pb}_2\text{P}_2\text{S}_6$ nanoparticles [69] (size of 60 nm) were obtained. Ion milling is conducted on as-exfoliated TMCs by Scotch tape. By tuning the parameters, nanosheet thickness would be controlled. A typical work is preparation of a serial of thick, thinner and ultrathin $\text{FeTe}_{1-x}\text{Se}_x$ nanoflake [70] (Fig. 5). However, in composite to the other nano superconducting materials, when the thickness of the $\text{Fe}(\text{Te}_{0.5}\text{Se}_{0.5})$ flake is reduced to less than the characteristic inhomogeneity length (around 12 nm), both the superconducting current path and the metallicity of the normal state in $\text{Fe}(\text{Te}_{0.5}\text{Se}_{0.5})$ atomic sheets are suppressed. With the aid of electron beam lithography, nanodevice was successfully fabricated though this method is energy-cost and high-demanding in apparatus.

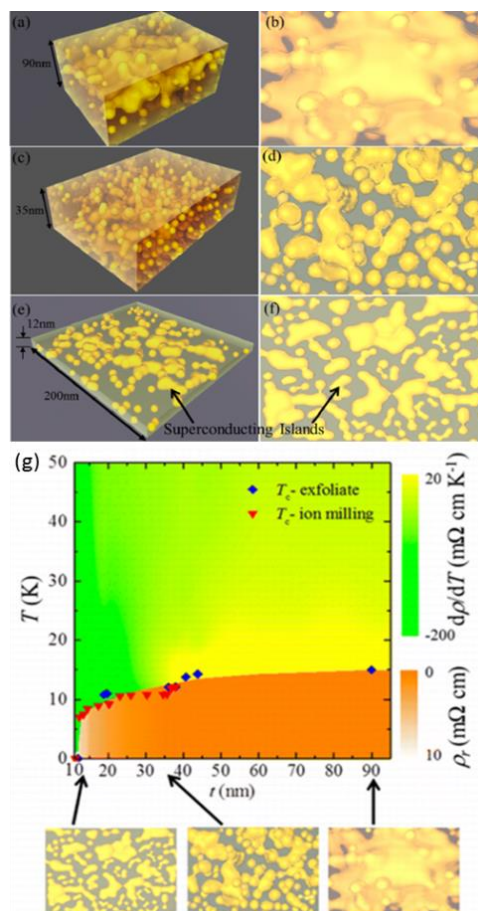


Fig. 5. (a, c, and e) 3D schematics for the development and connection of the superconducting islands in thick (a), thinner (b), and ultrathin (e) flakes; (b, d, and f) top view of the 3D schematics in (a), (c), and (e), respectively. (g) Phase diagram of the thickness dependence of superconducting and normal state properties. The contour plots illustrate the derivative of the normal state resistivity ρ and the residual resistivity ρ_r at 2 K [70]. Reprinted from ref. 70. © 2016 American Chemical Society.

Bottom-up route

Bottom-up route experiences nucleation and growth process. Nano-TMCs are built up from atoms, ions or molecules. Solid-state synthesis, solvothermal synthesis and sputtering are the three major methods of bottom-up route.

Solid-state synthesis

Solid-state synthesis usually takes place under high temperature ($> 500^\circ\text{C}$) and vacuum via chemical vapor deposition (CVD) or chemical vapor transport (CVT) for several days. For example, to synthesize TiS_3 , ZrS_3 and HfS_3 [71], in a typical CVD process, Ti, Zr, Hf elemental sheets and excess sulfur pellets are placed into one end of a quartz tube and vacuum-sealed then loaded into a two-zone furnace and heated up to 520°C for TiS_3 and 650°C for both ZrS_3 and HfS_3 in certain heating rate. After 5-days reaction, the quartz tube is cooled down to room temperature. The thickness of TiS_3 , ZrS_3 and HfS_3 nanosheets is in the range of 50 ~ 100 nm. Synthesis progress is similar to WSe_2 nanopowder [72] with diameter range from 3~5 nm, CuAlS_2 nanocrystallites [73] (about 5nm), Pd nanoparticle loaded TaS_2 composite [74] and other nano-TMCs.

Actually, some improved methods have been done. For instance, the mixture of Ta and S element powders are placed at one end of a fused-silica tube and a piece of Ta foil is placed at the opposite end [35]. As a result, a low-density fibrous material (LDFM), TaS_2 nanowires, is found perpendicular to the surface of Ta foil. Since the nanowires are bundles and filaments instead of individuals, their diameter is in the range of 100 ~ 600 nm and appropriately 1 mm length. In another case, ball-milling is conducted before solid-state synthesis to achieve micro-sized powders, which have larger surface and may be more active. The resulting Ti-doped WSe_2 nanoflakes [75] share the thickness of 30 ~ 50 nm and lateral size of 100 ~ 200 nm. Except for doped nano-TMCs, ternary one is also feasible. Such as TiCu_6S_4 [76], after the CVD reaction, grinding, pelletizing and annealing would be repeated several times to achieve pure phase. Additionally, H_2 reduction [77] is another way to prepare nano-TMCs. Trisulfide precursors, such as NbS_3 or TaS_3 , are heated in a sealed tube and reduced by H_2 in 1000°C to produce nanotubes. The diameter of the obtained NbS_3 nanotubes is 4 ~ 15 nm while the TaS_3 ones being 20 ~ 40 nm. Last but not the least, $\text{W}_{18}\text{O}_{49}$ nanowire could be reductive sulfurized to WS_2 nanotube [78] by reacted with H_2S at 850°C for 30 min.

Solvothermal synthesis

Solvothermal synthesis is conducted in a system of certain solvent with various sources and additives under relatively low temperature ($< 300^\circ\text{C}$) for several hours. According to growth mechanism, solvothermal synthesis includes templating-growth and inducing-growth.

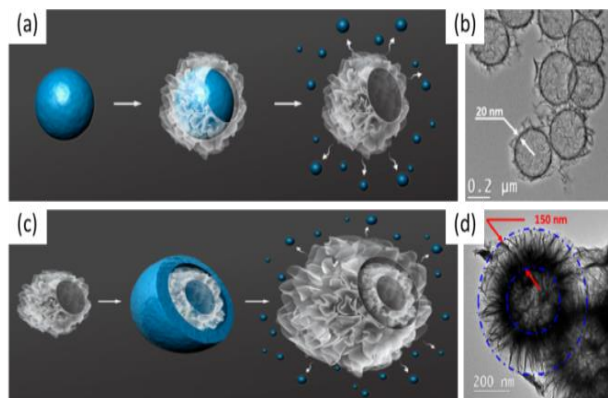


Fig. 6. Schematic of the synthesis of NiCo_2S_4 single-shell (a) and double-shell hollow sphere. TEM images of NiCo_2S_4 single-shell (b) and double-shell hollow sphere [79]. Reprinted from ref. 79. © 2015 American Chemical Society.

Templating-growth

With the help of template with certain nanostructure, ions or atoms would nucleate and then grow along the template to form nanostructures. The most popular template is Si nanoparticle. Different diameter Si nanoparticle would create counterpart nano-TMCs. NiCo_2S_4 nanoshell [79] is synthesized by templating-growth. **Fig. 6 (a)** shows the schematic process of the synthesis of NiCo_2S_4 single-shell hollow spheres. Firstly, Ni-Co hydrosilicate precursor with core-shell structure is prepared by urea, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution stirred for 12 h at 105°C . Next, Na_2S and the precursor are treated by hydrothermal reaction for 12 h at 160°C . At last, NiCo_2S_4 single-shell can be obtained after moving the Si template by NaOH . It is versatile to synthesize double-shell (**Fig. 6c**) just use the single-shell as template to grow silica and then use the silica to grow the other shell. The shell thickness of single-shell is appropriately 20 nm (**Fig. 6b**) while the double-shell is around 150 nm (**Fig. 6d**) and their diameters are both around 300 nm.

Surfactant is another kind of template. Cetyltrimethyl ammonium bromide (CTAB) is one of the common surfactant templates. Mesoporous WS_2 [80] is synthesized with this cationic surfactant. In the briefly process, $\text{Na}_2\text{O}_4\text{W} \cdot 2\text{H}_2\text{O}$, $\text{CH}_4\text{N}_2\text{S}$ and reductant HONH_3Cl are added into ethanol and deionized water co-solvent. Then CTAB is added in the suspension, which is stirred at 120°C for 2 h following by carried out at 180°C for 6 h. After centrifuged and washed the precipitant, mesoporous WS_2 is obtained. A proposal mechanism is that CTAB would form spherical micelles in the system and ranged orderly due to electrostatic repulsion. After wash or calcination, CTAB micelles would be removed and porous structures (30~60 nm) would be made. Polyvinylpyrrolidone (PVP) is another surfactant template, which acts as hindrance during nuclei. With the aid of PVP, $\text{Cu}_2\text{In}_2\text{ZnS}_5$ nanocrystals [81] and CuInS_2 nanopompons [82] are synthesized successfully.

Inducing-growth

Some organic ligands may induce certain planes and grow easier than others. This anisotropic grow resulting in dimension-limited nanostructures. In the case of synthesis of WSe_2 or MoSe_2 nanosheets [83], oleylamine, oleyl alcohol and oleic acid were examined for their influence to anisotropic growth. Their molecular formula are $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8\text{NH}_2$, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8\text{OH}$ and $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, respectively. As has been reported, alkyl amines tend to induce the formation of multiple layers of WS_2 and WSe_2 , such as oleylamine, in which case, WSe_2 shows 4 ~ 8 layers with a lateral size of 5 nm. When the ligand was changed to oleyl alcohol, layer number was decreased to 2 ~ 3 with a lateral size increased to 21 nm. Finally, single-layered (0.92 nm) WSe_2 was achieved when using oleic acid and its lateral size was sharply expanded to 200 ~ 400 nm. The increasingly obvious anisotropic growth of WSe_2 nanosheets indicates that $-\text{COOH}$ functional group is the most restrictive to the growth of c-axis and the most favorable to the other two axes (**Fig. 7**). MoSe_2 single-layer (thickness 0.98 nm, lateral size 200 ~ 500 nm) was also synthesized via the oleic acid-induced growth. The author found that ligands with different functional groups exhibit different binding energy with certain facet of metal, leading to anisotropic growth of metal chalcogenides. This binding energy difference is well-correlative with electron-donating ability of the ligands to the metal center in the order of amine, alcohol, and carboxylic acid.

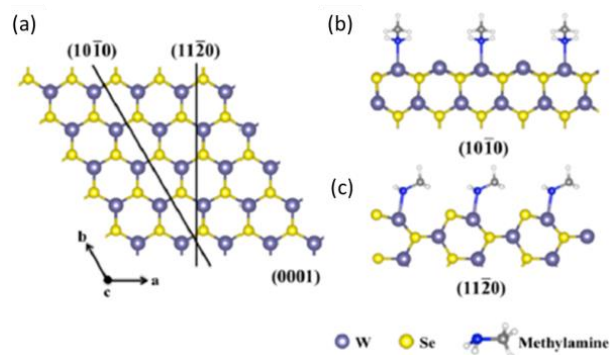


Fig. 7. Structure model of the WSe_2 basal plane viewed from the top. (a) The $(10\bar{1}0)$ and $(11\bar{2}0)$ cutting planes are shown with black lines. Ligand binding models for methylamine to the (b) $(10\bar{1}0)$ and (c) $(11\bar{2}0)$ WSe_2 edge facets, as viewed from the (0001) basal plane [83]. Reprinted from ref. 83. © 2015 American Chemical Society.

Furthermore, with the aid of oleylamine, solvent thermal reaction could synthesize ultrathin 2D nanosheets of layered intergrowth heterostructures which solid-state reaction could not do. For example, $\text{Sn}_m\text{Bi}_{2n}\text{Te}_{3n+m}$ homologous family [84] including SnBi_2Te_4 ($m = 1, n = 1$), SnBi_4Te_7 ($m = 1, n = 2$) and $\text{SnBi}_6\text{Te}_{10}$ ($m = 1, n = 3$). Due to incongruent melting of these intergrowth compounds, traditional solid-state synthesis with high temperature would produce bulk SnBi_2Te_4 with impure phase SnTe instead of phase pure

polycrystalline SnBi_2Te_4 . Actually, polycrystalline SnBi_2Te_4 and SnBi_4Te_7 samples have been synthesized earlier by subsequent heating of required elements above melting point followed by prolonged annealing via peritectic reaction (ca. at 770 K for 1000 h). However, this method could only produce bulk materials. Relative study also found that nanoparticles or nanopowders of SnBi_2Te_4 could be synthesized via solvothermal reaction for long duration (30 h). To successfully anisotropic grow nanosheets with pure phase, oleylamine was introduced into the solvothermal system and the thickness of the as-prepared SnBi_2Te_4 and SnBi_4Te_7 nanosheet was 1.13 and 2.35 nm, respectively. And their lateral size could reach $1 \sim 2 \mu\text{m}$.

Similarly, oleylamine together with hexamethyldisilazane (HMDS) could induce grow $1\text{T}'\text{-MoTe}_2$ nanoflowers [85] with diameter of 10 nm, whose edge thickness is only few layers. Last but not the least, oleylamine-induced $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ nanoflowers [86] were successfully synthesized with edge thickness of $2 \sim 5$ layers. The reported growth mechanism of the nanoflowers was described as a radial growth from a central crystalline core [87]. Primarily, in the nucleation process, center cores with randomly curled sheets form in the solution. Then, with different ODE-Se injection time (reaction time), the cores would not grow but the nanosheets grow. As can be seen from Fig. 8, longer reaction time would produce larger diameter nanoflowers.

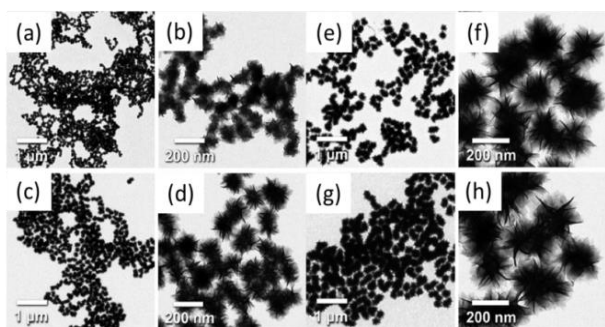


Fig. 8. TEM images of aliquots taken during the formation and growth of MoSe_2 nanoflowers, as described in the text: (a,b) 15 min, (c,d) 20 min, (e,f) 30 min, and (g,h) 40 min. [87]. Reprinted from ref. 87. © 2015 American Chemical Society.

Polymer surfactant has similar function as organic ligand. For example, PVP is easily absorbed on the (100) crystal face of $\beta\text{-FeSe}$ [88] and thereby reduces the growth rate along the [001] direction. With adjusting the concentration of NaOH in solution, iron selenides could be selectively synthesized. At low NaOH content, appropriately 10 mg in 10 mL ethylene glycol (EG), FeSe_2 dominates the product. With the increase of NaOH content, Fe_3Se_4 and $\beta\text{-FeSe}$ phases appear. Single-phased $\beta\text{-FeSe}$ could be eventually obtained by tuning NaOH content and Se source. Fig. 9 shows the temperature dependence of magnetic susceptibility of $\beta\text{-FeSe}$ nanosheets and the synthesis process. The thickness of single-phased $\beta\text{-FeSe}$ nanosheet was confirmed to be $10 \sim 150 \text{ nm}$.

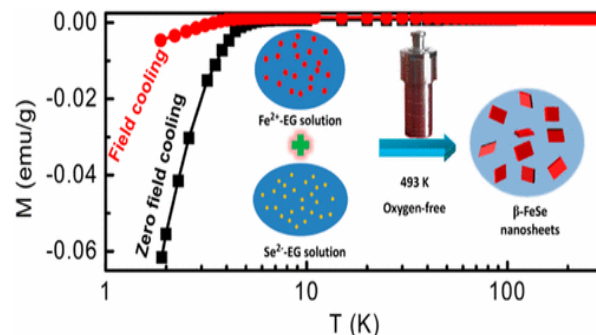


Fig. 9. Temperature dependence of magnetic susceptibility of $\beta\text{-FeSe}$ nanosheets, with zero-field-cooling curve (black) and field-cooling curve (red). The inset represents the synthesis process [88]. Reprinted from ref. 88. © 2017 American Chemical Society.

Aspartic acid (Asp), a simple, cheap, and commercially available amino acid, could induce Co anisotropic grow and forming Co-Asp ultralong nanowire, which would transform into CoS_2 or CoSe_2 mesoporous nanotube [89] by the sulfuration or selenylation in solution. Their average diameter is about 400 nm with length of several micrometers. The size of pore structures is appropriately 5.5 nm.

Seed layer can also induce subsequent formation of nanostructures. Take NiS nanorod array as an example. NiS nanoparticle firstly compact on the glass substrate and then inducing the growth of NiS nanorod array [90] (diameter of 50 nm and height of $1.29 \mu\text{m}$), whose mechanism is similar to CdS nanorod array [91] on ITO substrate. NiS nanoplatelet arrays (NPAs) [92] could be synthesized by sulfurizing the Ni(OH)_2 NPAs on fluorine-doped tin oxide (FTO) substrate similarly to the above process.

There still exist some nanostructures without clear mechanism. For example, KBiCu_2S_3 nanowires [93] are synthesized as a novel quaternary chalcogenide. FeS nanosheets [94] synthesized with Fe powder and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ are less air-sensitive compared to previous work using Fe^{2+} and S^{2-} , because its nucleation process is much slower and helpful to higher crystalline and fewer defects. $\text{Bi}_2\text{O}_2\text{S}$ nanocrystals [95] are directly formed via hydrothermal process, which could change into superconducting $\text{Bi}_4\text{O}_4\text{S}_3$ with T_c of 4.6 K by sintering at 500°C in vacuum for 6 h. As can be seen, not only 2D nanosheet and 3D nanoflower but also 1D nanotube could be synthesized via such inducing growth.

Deposition and spin-coating

Deposition and spin-coating could produce nanofilms on certain substrate. Solution and surface modification of substrate are prepared previously. In the case of fabricating CuS nanolayer or monolayer [96], thiourea and copper dichloride with chelating reagent NH_4OH and tetraethanolamine were mixed and glass substrate was treated with $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ solution, 3-trimethoxysilyl-1-propanethiol benzene solution, acetic acid and benzene, respectively. Tuning the deposition time and temperature, CuS thin films with

different thickness and even monolayer were obtained. ZnIn_2S_4 nanocrystalline thin film [97] is another example. The ZnIn_2S_4 thin films were deposited on FTO transparent conducting glass substrates via spin-coating method from the as-prepared precursor solution. Finally, ZnIn_2S_4 nanocrystalline thin films sulfuration in S vapor at 500°C for $0.5 \sim 2$ h. The crystalline sizes may range from 12.5 nm to 14.7 nm with different annealing times.

Mechanical alloying

Mechanical alloying (MA) has been developed as an industrial process in 1970s. This powder metallurgical process allows the preparation of many unique materials, including nanostructured alloys, amorphous compounds and unstable and metastable phases, which cannot be synthesized via conventional routes. MA technique can solve problems such as large difference in the melting points of source elements. As the authors point out, MA technique is low-temperature processing, easy control of composition, relatively inexpensive equipment, and the possibility of scaling up. $\beta\text{-FeSe}$ pure phase [98] (crystalline size of 60 nm) was synthesized with MA technique, showing a relatively high T_c of 8.41 K.

Sputtering and lithography

Sputtering could produce thickness-controlled nanolayer on certain substrate. Then combined with lithography technology, large area pattern TMC films would be synthesized. Additionally, sputtering and lithography could synthesize heterostructure [99]. For example, in the typical synthesis of MoS_2/WS_2 or WS_2/MoS_2 stacked heterostructures [100] (Fig. 10a), 1 nm thick Mo or W were firstly deposited on a Si/SiO_2 substrate by sequential magnetron sputtering and pattern by electron beam lithography. After reacting with sulfur, the stacked heterostructures of MoS_2 and WS_2 were successfully synthesized. The sulfuration process would not change the geometry and morphology of the lithography (Fig. 10b-f). As the authors point out, the average width of the square pattern is 199.0 ± 1.1 and 200.4 ± 1.0 micrometers before and after sulfuration. Although this method requires high-demanded equipment, it is facile to fabricate nanodevices directly.

Molten-salt-assisted chemical vapor deposition

In early 2018, a library of atomically thin TMCs was synthesized via molten-salt-assisted chemical vapor deposition [101]. The as-grow 47 samples include 32 binary compounds, 13 alloys and 2 heterostructure compounds. Salts in the reaction are NaCl or KI, which could reduce the melting point of metal precursors (metal oxide). In addition, some metal oxides will react with the salt to form metal oxychloride, which will evaporate under appropriate temperature and facilitate to the growth of TMC thin films.

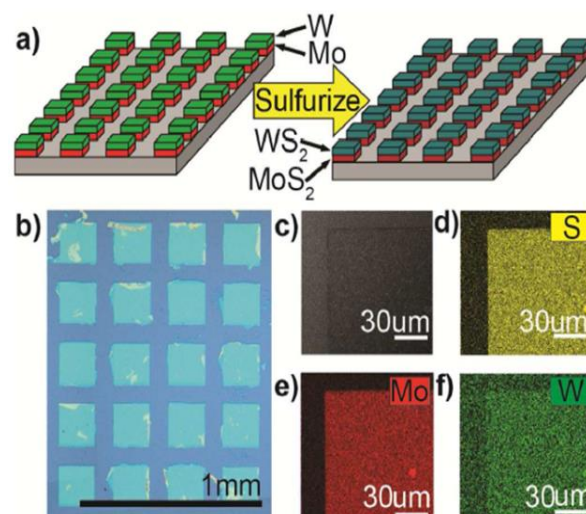


Fig. 10. Patterned growth of MoS_2 and WS_2 stacked heterostructures. (a) Schematic of TMDC growth from patterned metallic seed layers. (b) Optical image of patterned MoS_2 and WS_2 stacked heterostructure after sulfuration. (c) Top-down SEM image of the analyzed region. (d-f) Top-down SEM-EDS maps showing spatial distribution of (d) S, (e) Mo, and (f) W [100]. Reprinted from ref. 100. © 2016 American Chemical Society.

For comparison, different methods for synthesis of nano-TMCs are summarized in Table 1. Exfoliation, solid state and solvothermal methods usually produce large scale nano-TMCs samples, but take hours even some days to get the product. Ion milling and sputtering methods make smaller nano-TMCs samples, but take shorter preparing time.

Table 1. Comparison of different methods for synthesis of nano-TMCs.

Method	Material kind	Period	Energy-cost	Produce scale
Top- down				
Exfoliation	2D	Hours	Low (T_{room})	Large
Ion milling	2D		High (quality equipment)	Small
Bottom-up				
Solid-state	0, 1, 2, 3D	Hours to days	High ($300\sim 1000^\circ\text{C}$)	Large
Solvothermal	0, 1, 2, 3D	Hours	Low ($70\sim 300^\circ\text{C}$)	Large
Sputtering	0, 1, 2, 3D		High (quality equipment)	Small

Recent status of superconductor based on nano-TMCs

In 2015, Huang group [94] successfully synthesized superconducting tetragonal FeS via hydrothermal method. Most samples present microsheet morphology, which are aggregation of 50 nm nanosheets. In tradition method, tetragonal FeS was usually synthesized by iron

corrosion in aqueous H_2S or coprecipitation of Fe^{2+} and S^{2-} at room temperature and ambient pressure. Both the processes make FeS sample very reactive to oxygen and more likely to transform into other stable phases. However, tetragonal FeS synthesized via hydrothermal method from iron powder and sulfide solution is more stable and phase transform would not take place more than three months. Due to the high-quality tetragonal phase and well crystallinity, FeS sample exhibits a T_c of 5 K. **Fig. 11 (a)** [94] shows the temperature-dependent magnetic susceptibility measured under a magnetic field of 40 Oe. As can be seen, the as-prepared FeS sample is a Pauli paramagnet because the magnetic susceptibility is flat and temperature dependent in the high temperature range. The left inset graph indicates that the superconducting volume fraction is 84% at 2 K. The right inset graph shows the superconducting confirmation. **Fig. 11 (b)** [94] shows the temperature-dependent electrical resistivity, indicating the characteristic of metallic conductivity in the high temperature range. The resistivity suddenly decreases at 5 K and reaches zero at 4 K. With the increase of magnetic field, the superconducting transition temperature will become lower and lower, which can be seen from the left inset graph in **Fig. 11 (b)**. The right inset of **Fig. 11 (b)** shows the temperature dependence of the upper critical magnetic field. The estimated $H_{c2}(0)$ from BCS theory is 0.4 T, much smaller than that of FeSe superconductor (16.3 T) [103]. It is expectable that FeS-derived superconductors with higher T_c will come advent soon.

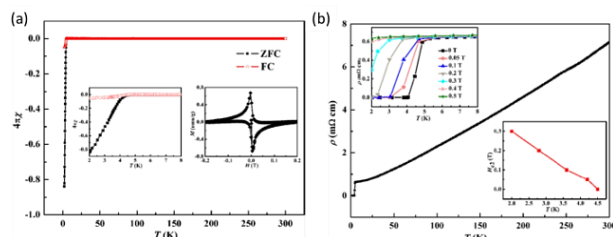


Fig. 11. (a) Temperature dependence of the direct-current magnetic susceptibility of tetragonal FeS measured under a magnetic field of 40 Oe, in both zero-field-cooling (ZFC) and field-cooling (FC) processes. The left inset shows the enlarged view of the temperature dependence of the magnetic susceptibility near the onset of superconducting transition. The right inset shows the magnetic hysteresis of the sample measured at 2 K. (b) Temperature dependence of the electrical resistivity of tetragonal FeS. The left inset shows the electrical resistivity measured under magnetic fields of 0, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 T below 8 K. The right inset displays the temperature dependence of the upper critical magnetic field [94]. Reprinted from ref. 94. © 2015 American Chemical Society.

Two years later, Huang group [59] subsequently reported a novel method to improve the T_c of TaS_2 , restacking nanosheets. Chemical exfoliation was the first step to break down the bulk materials. Then high-speed centrifugation was involved to select monolayer TaS_2 . Finally, the free-standing nanosheets were assembled layer-by-layer through vacuum filtration process. Compared with their bulk material ($T_c = 0.3$ K), the restacked TaS_2 nanosheet present a relatively high T_c of 8 K. Authors reckoned that it was the interface-

induced effect that enhance the superconducting of TaS_2 . In the bulk TaS_2 , layers were not twisted. But in the restacked TaS_2 nanosheet, layers were twisted inevitably by vacuum filtration and formed rich homogenous interfaces. This interface-induced superconducting system shows suppression of CDW transition and weaker diamagnetic susceptibility from freeze-dried sample. Density functional theory (DFT) calculations reveal the inner reason that there exist increase and more delocalization of electron states near the Fermi surface, which contributes the enhancement of superconducting in this twisted system. **Fig. 12a** [59] shows that the diamagnetic transition appeared at 2.9 K and the inset graph proves that the restacked TaS_2 is a type-II superconductor. **Fig. 12b** [59] shows that the nanosheet sample behaves as a metal in the entire temperature range and its resistance sharply decreases at 3 K and then become zero at 2.8 K. Compared with its bulk material, the restacked TaS_2 nanosheets do not appear CDW transition near 75 K. **Fig. 12c** [59] shows the magnetic dependence of T_c of the sample. With the increase of applied magnetic field, T_c will become lower and lower. **Fig. 12d** [59] shows the heat capacity undergoing sharp change around 3 K, which obviously confirms the superconductivity of restacked TaS_2 . But when applied 1 T magnetic field, superconducting transition will be suppressed.

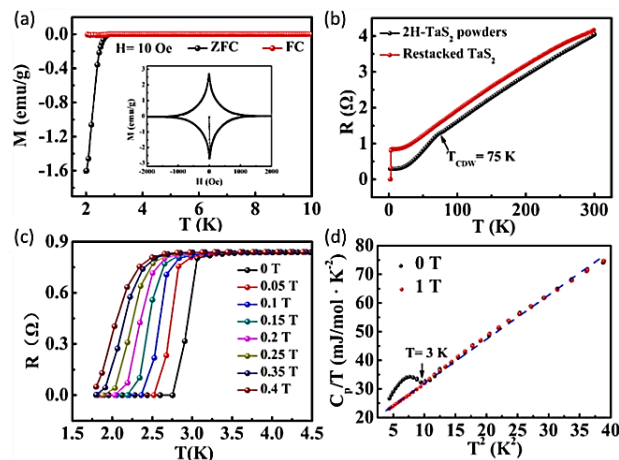


Fig. 12. (a) Temperature dependence of magnetic susceptibility of restacked TaS_2 nanosheets under the magnetic field of 10 Oe, with zero-field-cooling curve (black) and field-cooling curve (red). The inset represents magnetic hysteresis of the sheets at 2 K. (b) Temperature dependence of electrical resistivity of restacked TaS_2 nanosheets and 2H- TaS_2 powders. (c) Electrical resistivity of restacked TaS_2 nanosheets measured under magnetic fields of 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4 T below 4.5 K. (d) Low temperature specific heat of restacked TaS_2 nanosheets [59]. Reprinted from ref. 59. © 2017 American Chemical Society.

NbSe_2 is another famous superconducting TMC. Liu group [103] successfully prepared monolayer NbSe_2 via molten-salt-assisted chemical vapor deposition in 2017. By using chemical vapor deposited graphene as a protective capping layer, they achieved thickness-controlled NbSe_2 nanolayers. T_c was increased from 1 K to 5.46 K with layers from 1 to 10.

Take NbSe₂ nanosheet as research object, Xie group [104] investigated the coexistence of ferromagnetism and superconductivity in 2016. Generally, ferromagnetism and superconductivity are two competing electronic states and ferromagnetism often has negative impact on superconductor because it damages the singlet correlations responsible for pairing interaction. However, through surface-structure modulation, NbSe₂ nanosheet possessed coupled ferromagnetism and superconductivity, resulting in fascinating coupled effects of negative magnetoresistance and the Kondo effect. In the surface-structure modulation, exfoliation by n-BuLi firstly makes NbSe₂ nanosheets present negative charge. Then in the help of electrostatic interaction, the negative-charged nanosheet will absorb polar hydrazine molecules, which will trigger surface-structure distortion of Nb-Se bond and result in ferromagnetism ordering in superconducting NbSe₂ nanosheet. This surface-structure modulation strategy will provide versatile paths to prepare correlated systems with coexisting electronic.

Conclusion and future perspectives

In this review, we introduce several methods to synthesize nano-TMCs. Furthermore, the properties of the nano-TMCs are described briefly. The comparison of these methods can be seen in **Table 1**. Overall, the top-down route, not only exfoliation but also ion milling, majorly produce 2D materials. On the contrary, the bottom-up route could synthesize multiple nanostructures including 0D nanopowder, 1D nanotube, 2D nanosheet and 3D nanoflower. Within the top-down route, exfoliation takes place in solution with low temperature, which is possible to large production compared with ion milling. Besides, exfoliation usually uses sonicator and other relatively costless equipment. In contrast, ion milling has higher demand in equipment, resulting in energy costly to some extent. In despite of high cost, ion milling could control thickness more accurately and uniform. As for bottom-up route, solid-state synthesis tend to more energy-costly since it usually takes place at high temperature (300 ~ 1000°C) for long duration (hours to days). Solvothermal synthesis would not have this problem since it is low temperature (70~300°C) process and the reaction generally lasts for hours. Both solid-state and solvothermal synthesis are apt to large-scaled production. Sputtering and lithography is relatively small-scaled productive and costly because of the high-demanding equipment. Although each method has its disadvantages, it is believable that future nano-TMCs with various structures will come into being.

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Supporting information

Supporting informations are available from VBRI Press.

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