highest vanadium oxidation state. It has a layered structure and a positive cross-cell structure during crystallization [216]. The monolayer consists of a twisted triangular biconical polyhedron with O atoms around V atoms. The polyhedron forms a $(V_2O_4)_n$ zigzag double chain along the direction (001), sharing edges and cross-linking edges along the direction (100), forming a 2D layer. The layers are also stacked together by vdW force to form bulk crystals.

Among the currently known TMO materials, only a few have a layered structure, and most of them are nonlayered structures in which atoms are connected by chemical bonds in the 3D direction of the crystal [217]. Some common nonlayer structured TMOs are CeO_2, TiO_2, In_2O_3, HfO_2, and Fe_2O_3. Most of their crystal structures are different from each other, so there is no general formula [218]. CeO_2 is one example of nonlayer structured TMOs. CeO_2 has a fluorite structure and the space group is Fm3m (Figure 1.7c). Fluorite structure is formed on the basis of FCC unit cell, in which cations and anions occupy octahedral space. In the CeO_2 structure, each Ce^{4+} ion coordinates with eight equivalent O^{2-} nearest neighbors, while each O^{2-} ion coordinates with four nearest neighbors Ce^{4+} [78]. There is no obvious natural delamination inside the crystal of the material, so it cannot be separated by methods such as micromechanical exfoliation. However, if the vertical chemical bonds inside the crystal are broken, the thickness of the crystal is reduced to an atomic size and a 2D plane with a certain lateral size appears, then 2D TMOs different from the corresponding parent crystal can be obtained (Figure 1.7d).

Compared with layer structured TMOs, nonlayer structured TMOs combine the advantages of an atomically thin structure and a highly active surface and also produce many new characteristics. When the structure of the material changes from a 3D bulk to a 2D layer with an atomic thickness of only a few nanometers, the sharp decrease in the thickness causes the distortion of the material lattice structure, and finally a stable structure with a lower surface energy is formed. The reconstruction of crystal structure will also lead to the change of energy band structure and electronic state [219]. Due to the breaking of the chemical bonds in the vertical direction of the 3D matrix, a large number of unsaturated dangling bonds are generated on the newly formed surface. Together with the strong surface polarization, a highly active surface with many active sites and a large specific surface area is formed [218], making it expected to have high-efficiency catalytic ability and energy storage performance. In addition, the 2D planar structure makes 2D nonlayer structured TMOs compatible with microelectronic technology processing [220]. It can overcome the shortcomings of the high rigidity of traditional semiconductor materials such as silicon, making it expected to be widely used in the emerging flexible electronic fields such as wearable technology.

Different methods have been designed to synthesize 2D TMOs based on gas phase and liquid phase processes. It is still a challenging task to precisely synthesize inorganic planar crystals of one or more unit thickness during gas phase synthesis. Layer by layer epitaxy of two-dimensional films is classified as Frank van der Merwe growth [221]. For TMOs, the flux of adsorbed atoms and the lowest unfilled surface energy of the substrate on which the new material is deposited determine the occurrence of layer by layer oxide epitaxy [222]. For the physical deposition in the vapor phase, in a small period superlattice, one or more cell surfaces may grow independently or in combination. The most common 2D TMO vapor phase techniques include CVD, MBE, atomic layer deposition (ALD), and pulsed laser deposition (PLD). In order to successfully deposit atomic-scale thin oxide layer or superlattice, it is necessary to precisely adjust deposition parameters. Especially in MBE, 2D deposition needs to significantly reduce the flux of adsorbed atoms, so it usually needs ultrahigh vacuum environment, which increases the complexity of equipment and deposition cost. Another problem is the influence of the substrate on the perfect deposition of oxides. The lattice matching and surface energy factors should be considered at the same time.

Many current 2D TMO synthesis techniques rely on liquid phase environments. Oxide epitaxial layers can be solvothermally grown in liquid solutions (at elevated temperatures) with or without a guiding agent [218, 223]. The carrier solvent can be water based and depends on the evaporation temperature of the solution, which may be necessary to be carried out in a pressurized container. The purity of the analyte and solvent plays an important role in the final result. Solution-based technology can be performed in one step, forming a layer directly on the substrate. Similar to the vapor deposition technique, it is important to consider the registration of the unit cell and the substrate or the layers near it for the nonscattering displacement and exchange of free carriers. The crystal orientation should be controlled at the cell level in these cases, and other quasi liquid methods may also be applied. The precursor of the material can be obtained by secondary processes such as spin coating, dip coating, or drop casting, such as oxygen annealing.

If the products synthesized in liquid or gas phase are layered crystals, the number of layers can be reduced by using the exfoliation step. These layered crystals can form different material patterns between TMO planes. After the exfoliation is completed, the pattern can be left to stabilize the oxide layer or be removed [224].

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