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Ultrathin 2D nanosheets of transition metal (hydro)oxides as prospective materials for energy storage devices: A short review

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The ultrathin two-dimensional (2D) transition metal oxides and hydroxides (TMO and TMH) nanosheets are attractive for creating high-performance energy storage devices due to a set of unique physical and chemical properties. Flat 2D structure of such materials provides a sufficient number of active adsorption centers, and the ultra-small thickness, on the order of several nanometers, provides fast charge transfer, which significantly improves electronic conductivity. This brief review summarizes recent progress in the synthesis of materials based on ultrathin 2D nanosheets for energy storage applications, including pseudocapacitors, lithium-ion batteries, and other rechargeable devices. The review also presents examples of representative work on the synthesis of ultrathin 2D nanomaterials based on TMO and TMH for various power sources. In conclusion, the article discusses possible prospects and directions for further development of methods and routes for the synthesis of ultrathin two-dimensional transition metal oxides and hydroxides.

keywords: two-dimensional materials, transition metal oxides, layered double hydroxides, nanosheets, energy storage devices

1. Introduction

One of the relevant issues of materials chemistry is the creation of new highly efficient electrode materials for energy storage devices. In recent years, there has been an increasing need to develop and create new efficient energy sources that determine the development prospects for the production of industrial installations, autonomous devices, electric vehicles, automotive and aircraft, etc. A number of requirements are imposed on such power sources: high values of specific energy and capacity, stability of characteristics with multiple charge-discharge cycles, long service life, high operating voltage and power. In addition, these devices must be compact, resistant to environmental influences, environmentally friendly, and inexpensive to manufacture.

A key role in the development of such devices belongs to the creation of new electrode materials that allow one to increase specific energy and power to values close to theoretical ones. This explains the urgency of developing new routes and methods for the synthesis of electrode materials with improved electrochemical characteristics, which are inexpensive and environmentally friendly in production and disposal, and the possibility of developing such methods is largely determined by the solution of scientific problems of materials chemistry.

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From the point of view of application in energy storage devices, inorganic compounds of transition metals with a two-dimensional graphene-like morphology, the so-called "nanosheets", are the most promising due to their unique set of physical and chemical properties. Flat 2D structure of such materials provides a sufficient number of active centers and a high electroactive surface area. Another key characteristic of 2D materials is their ultra-thickness, on the order of several nanometers, due to which charge carriers can move over extremely short distances from the volume to the surface, while significantly improving electronic conductivity. However, the difficulty of obtaining such electrode materials by existing synthesis methods is the main problem at present.

Recently, many studies have been published on the synthesis of ultrathin two-dimensional nanocrystals of transition metal oxides and hydroxides for use as electrode materials, including for chemical current sources. However, there have been no systematic studies of the influence of various synthesis parameters on the formation of structural features, morphology, size of nanocrystals and their chemical composition, and, as a consequence, on the properties of synthesized compounds.

This review presents various synthesis techniques and the influence of the synthesis conditions on the formation of ultrathin 2D nanosheets of TMO and TMH, as well as on their electrochemical and capacitive characteristics.

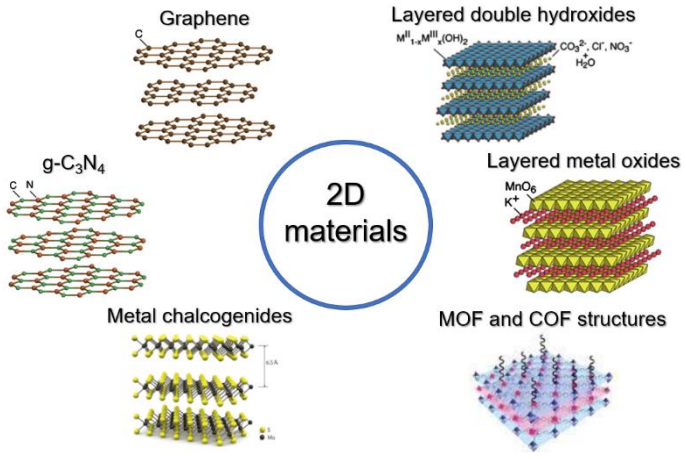

Figure 1 Examples of crystal structures of various 2D materials.

2. 2D materials based on inorganic compounds and their applications

Since the discovery of the method for producing graphene from graphite in 2004 [1], two-dimensional materials have been widely used due to their unique electrochemical, optoelectronic, and mechanical properties, ultra-high volume-to-surface ratio and high surface chemical activity compared to their three-dimensional counterparts [2]. Since then, a large number of two-dimensional materials have been obtained: from the original graphene to the later transition metal dichalcogenides (WS_2, MoS_2, WSe_2, $MoSe_2$, ReS_2, TaS_2, etc.) [3-5], noble metal dichalcogenides (PtS_2, PtSe, PdSe, etc.) [6], elementary two-dimensional materials (for example, black phosphorus (BP), tellurium, etc.) [7-9], double layered hydroxides (LDH) [10], graphitic carbon nitride (g-C_3N_4) [11], organometallic framework structures (MOF) [12], covalently organic frame structures (COF) [13], layered metal oxides [14], etc. (Fig. 1). 2D transition metal oxides and hydroxides have demonstrated excellent characteristics in electronics, optoelectronics, electrochemistry, various sensors, energy storage, catalysis, and other fields, which makes them attractive objects for research [15].

As a rule, 2D metal oxide nanocrystals can be divided into two categories based on their crystal structure: layered and non-layered. There are several layered compounds assembled from M-O octahedra (M:V, Mo or Mn) [16-20], in which the atoms in the plane are connected by a chemical bond, and the layers in the "stacks" are united by a weak Van der Waals interaction. Recently, a layered crystal structure with a unique planar hexagonal coordination has been discovered in the oxides of some metals (Ti, Mn, Fe, Co, Ni, Cu, Al, Gd and Ge). This crystal structure differs markedly from their usual unpolarized crystal structures at room temperature [21] and is similar to that of layered hexagonal transition metal chalcogenides. Researchers have also turned their attention to lamellar metal oxides with the inclusion of various ions between atomic layers [22, 23], a typical example of which are perovskites[24].

The functional properties of ultrathin two-dimensional metal oxides and hydroxides determine their value for possible applications. The unique 2D morphology and a thickness of a few nanometers affects the electrical, optical, mechanical and chemical properties of the materials. Typical functional properties of two-dimensional oxides and hydroxides include high specific

surface area, increased mobility of charge carriers, and high in-plane mechanical strength with out-of-plane flexibility. The trend towards minimizing devices while maintaining or even increasing performance challenges scientists to develop new materials. Thus, the use of 2D materials is a universal way of solving new complex technological problems.

3. Application of 2D nanosheets of transition metal oxides and hydroxides in electrochemical energy storage

The use of 2D nanocrystals of metal-oxygen compounds in rechargeable batteries and pseudocapacitors is a promising area of their application [25]. The most common type of such devices are lithium-ion batteries, in which the charge carriers are lithium ions. They are widely used as chemical current sources in modern devices, but they also have several disadvantages: high cost and complexity of processing lithium raw materials, relatively large mass, the possibility of overheating, and explosion hazard. Rechargeable batteries and pseudocapacitors can be a good alternative to lithium-ion batteries due to their low cost, improved safety, and better cyclic characteristics.

3.1. Pseudocapacitors

Supercapacitors can be divided into electrochemical double-layer capacitors (EDLC) and pseudocapacitors [26]. Electrochemical double-layer capacitors contain electrolyte ions, the adsorption of which on large specific surfaces of porous electrodes is necessary for charging the capacitor. Energy accumulation in pseudocapacitors occurs due to the rapid reversible redox reactions at the electrode-electrolyte interface. Pseudocapacitors combine two mechanisms of energy storage: a double electric layer mechanism and a mechanism of rapid redox reactions on the electrode surface. Consequently, pseudocapacitors are closer in functionality to batteries than EDLCs, however, their efficiency is limited by the ion diffusion rate. Typically, battery life is limited due to the formation of irreversible reaction products that slowly reduce the energy density after each recharge. Replacing or combining commonly used rechargeable batteries with pseudocapacitors can solve this problem. The choice of cell materials and the design of the electrodes are crucial for the performance of the pseudocapacitor. Transition metal oxides are one of the promising materials which can be used for the creation of pseudocapacitors. RuO2 is a well-known electroactive material with a very high capacity, however, the difficulty of extraction and high cost are major disadvantages. Cheaper alternatives with the same or slightly smaller capacity include transition metal oxides such as NiO, CuO, SnO_2, Co_3O_4, FeO_x, MoO_2, Cr_2O_3, MnO_2, V_2O_5, $NiCo_2O_4$, $ZnCo_2O_4$ and other [27-29].

3.2. Rechargeable metal-ion batteries

Rechargeable metal-ion (Na, K, Mg, Zn etc.) batteries are one of the most promising candidates for replacing lithium-ion batteries. They meet the requirements for advanced electrical energy storage devices due to the greater availability of raw materials, low cost, and high theoretical specific capacity (820 mAh/g) [30]. Recently, certain progress has been achieved in improving the electrochemical characteristics of electrode materials for such devices, but there are still problems associated with the lack of suitable cathode materials capable of withstanding multiple intercalation/deintercalation of metal ions [31]. The main function of a metal-ion battery cathode is to provide a stable structure in which Mn+ ions can be chemically bonded with low binding energy and fast kinetics. Thus, the cathode must have a crystal structure with suitable crystallographic sites for Mn+ accommodation, low-energy paths for ion diffusion, and high electronic conductivity for charge transfer. Layered and tunnel structured compounds with redox components are often chosen to meet these requirements. At the same time, the cathode must have sufficient porosity to ensure the penetration of the electrolyte solution, thereby increasing the number of active sites for the maximum charge transfer rate [32]. Among these materials, oxides of vanadium, manganese and cobalt are of the greatest interest in terms of their further commercialization, since they have a high specific capacity and a wide window of potential; moreover, they can be synthesized from relatively inexpensive and affordable precursors [33]. However, these cathode materials have low electronic conductivity, which does not allow them to approach the theoretical values of specific capacitance.

The solution to this problem may lie in obtaining 2D nanocrystals with graphene-like morphology of the nanosheets. Flat 2D structure of such materials provides a sufficient number of active adsorption centers. Another key characteristic of 2D materials is their ultra-thickness, on the order of several nanometers, so charge carriers can move over extremely short distances from the volume to the surface, while significantly improving electronic conductivity. As noted in the works

above, the main problem in creating cathode materials for hybrid batteries is the difficulty to use existing synthesis methods in order to obtain ultrathin oxide nanocrystals with nanosheets morphology, which would significantly reduce the degradation of the electroactive material and improve electronic conductivity (Fig. 2).

However, the authors also identify several currently existing problems that arise when obtaining this type of materials: difficulties in optimizing mass loading and obtaining materials with a developed morphology, difficulties in developing methods for uniform deposition of oxide material on the surface, creating a nanomaterial with a regular and stable structure.

In general, metal oxides prove to be indispensable materials for creating energy storage devices, and the use of materials with the morphology of 2D nanosheets demonstrates promising improvements in the values of specific capacity, energy density, and service life. Even though the group of 2D metal-oxygen compounds has many representatives, the development of a scalable, simple, efficient, and economical approach to their synthesis remains a serious problem.

4. Synthetic methods of ultrathin 2D transition metal oxides and hydroxides

As noted earlier, the choice of the optimal synthesis technique is the key factor in obtaining highly efficient capacitive materials. Approaches to the synthesis of ultrafine 2D transition metal oxides and hydroxides can be divided into two large groups: "top-down" (Fig. 3) and "bottom-up" (Fig. 4) methods. The top-down approach transforms three-dimensional layered crystals into many mono- and multilayer two-dimensional nanocrystals. This requires the use of external influences, such as: mechanical processing, ultrasound treatment, ion intercalation or the use of electrochemical processes. In the bottom-up approach, atoms or molecules are grown or assembled along one direction on a suitable substrate in a specific medium, eventually forming ultrathin 2D TMO and TMH. Some synthetic approaches of this type will be discussed in more detail below.

4.1. "Top-Down" routes

4.1.1. Mechanical exfoliation

Following the successful exfoliation of graphene from graphite, many metal oxides with nanosheet morphology have been obtained using a similar approach. This method is not only relatively simple and scalable, but also capable of maintaining a high degree of crystallinity. However, the thickness and transverse size of the nanosheets obtained by this method cannot be controlled. In addition, there are limitations associated with the number of types of delaminated 3D crystals, which greatly limits the scope of this method.

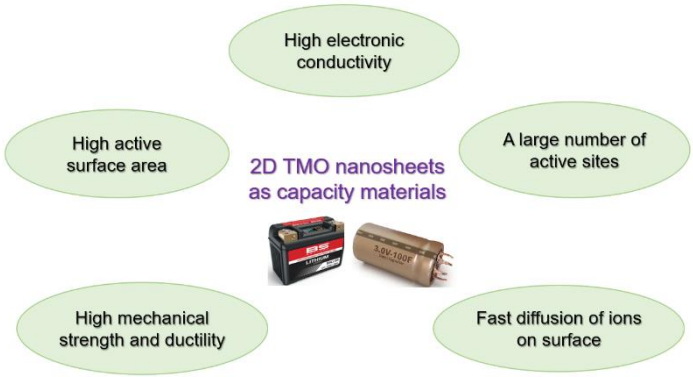

Figure 2 The main advantages of 2D TMO nanosheets, essential for the creation of high-performance capacitive materials.

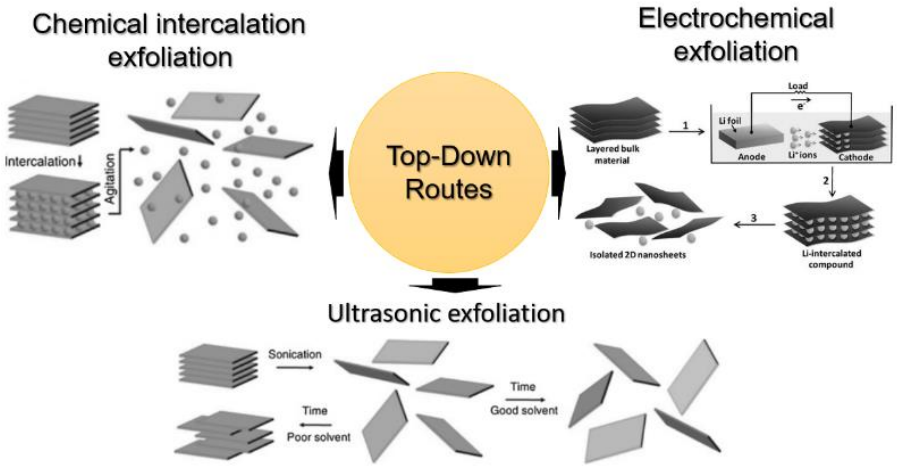

Figure 3 Schematic representation of various "top-down" routes.

Figure 4 Schematic representation of various "bottom-up" routes.

4.1.2. Ultrasonic exfoliation

Liquid-phase exfoliation is the treatment of layered crystals by ultrasound in certain stabilizing liquids. Ultrasonic waves destroy Van-der-Waals forces between layers without affecting covalent bonds in the plane of the layer. The mechanical energy of the ultrasonic wave creates a large number of cavitation bubbles around the bulk material. The waves generated during the bubble explosion increase the interlayer distance under the influence of uneven pressure, which contributes to interlayer separation, and, ultimately, to the production of a dispersion liquid containing two-dimensional nanosheets [34]. The choice of solvent is a key factor affecting the stability of stratified nanosheets [35]. Liquids may include certain solvents, surfactants, or polymer solutions. For surfactants or polymers, the repulsive forces between neighboring molecules and nanosheets are fairly stable. In addition, the strength of the Van der Waals interaction between solvents with the corresponding parameters of surface energy or solubility and two-dimensional nanosheets is similar to the bond strength between nanosheets, which prevents the aggregation of nanosheets [36].

4.1.3 Chemical intercalation exfoliation

The processes of "soft" chemical delamination are represented by two main methods: delamination by ion intercalation and exfoliation by ion exchange. Given the negatively charged nature of the TMO, an appropriate chemical force is required to overcome the strong electrostatic effect during delamination. The principle of ion intercalation is based on the transfer of molecules or ions into layers, which leads to the expansion of the layered structure, deformation, and an increase in the distance between the layers. When the interlayer interaction weakens, the base material finally forms a stratified dispersion in the corresponding medium.

Many layered oxides are mixed valence compounds containing a layer of exchangeable cationic counterions , therefore, the ion exchange method can be applied to them. For example, lamellar titanium oxide crystals tend to be negatively charged (due to the presence of Ti^{3+} and Ti^{4+} ions) and thus contain counterions, such as Cs^{+}, between the layers to ensure electroneutrality. During ion exchange in solutions, protons are exchanged for larger ions (for example, tetrabutylammonium cations), which leads to an increase in the space in the layer, and then stratification [37-39]. However, layered oxides such as MoO_3 occur naturally as monovalent compounds, which cannot be stratified by the ion exchange method [40]. Soft chemical delamination is often combined with ultrasound treatment, which significantly reduces the process time. The disadvantages of this method are high cost and relatively low efficiency.

4.1.4 Electrochemical exfoliation

Unlike traditional delamination methods, the electrochemical method uses an electric current as a driving force to transfer molecules or ions into the interlayer space, thereby increasing the distance between the layers. This method is environmentally friendly as the electrolyte is recyclable. In addition,

the reaction time usually varies from a few minutes to several hours with a very significant yield. However, a significant disadvantage of this method is poor scalability.

4.2. "Bottom-Up" routes

4.2.1. Hydrothermal and solvothermal synthesis

Hydrothermal and solvothermal synthesis is a typical method of "wet" chemical synthesis, which can be used to obtain a variety of two-dimensional TMO. Solvothermal synthesis is a chemical reaction in a liquid or supercritical liquid at high temperature. As a rule, the reaction is carried out in a closed system (autoclave or bomb) capable of withstanding high pressure. The final products are obtained after filtration and centrifugation [41,42]. Hydrothermal and solvothermal synthesis methods are simple, inexpensive and scalable approaches to the synthesis of ultrathin two-dimensional TMO, which is important in terms of successful commercialization. However, it is difficult to study the mechanism of these methods, since the reactions occur in a sealed autoclave. This complicates the development of experimental schemes for the synthesis of another two-dimensional TMO. In addition, synthesis by these methods is sensitive to the concentrations of precursors, the choice of solvents, surfactants, and temperature, which limits the ability to accurately control the structure, morphology and reproducibility. In addition, obtaining monolayers by this method is practically impossible.

4.2.2. Template self-assembly

The self-assembly process is often combined with hydrothermal solvothermal synthesis. In this method, surfactants are often used as agents limiting the growth of the compound in the selected directions. Metal oxide molecules self-assemble into lamellar structures with molecules of surfactants, then condense, polymerize and crystallize into atomically thin two-dimensional nanosheets. After that, the surfactant matrix is removed. Based on the self-assembly method using surfactants, two-dimensional oxides of some typical transition metals (TiO_2, ZnO, Co_3O_4, WO_3, $Fe3O_4$ and MnO_2) have been successfully obtained [43, 44]. Self-assembly is a common method of synthesis of many two-dimensional TMO; its main advantages are simplicity and efficiency. However, the lack of control over the thickness and transverse size of the nanosheets is a significant disadvantage of the method.

4.2.3. Chemical vapour deposition (CVD)

The method of chemical deposition from the gas phase or CVD (chemical vapour deposition) for the cultivation of two-dimensional nanomaterials includes three main stages: evaporation and thermal decomposition of precursors, transfer and migration of reagents, nucleation and growth of crystals on a substrate. By carefully selecting reagents, substrates, catalysts, temperature and gas atmosphere, it is possible to achieve controlled growth of two-dimensional nanomaterials with a controlled number of layers (or thickness) and degree of crystallinity [45]. The substrates used in the CVD method have a large number of defects randomly distributed over the surface, therefore, the process has a low mass transfer. Moreover, since the subsequent growth of two-dimensional nanocrystals after nucleation continues at fixed initial nucleation sites, self-assembly of grains grown on solid substrates is practically impossible. The resulting material usually has an inhomogeneous number of layers and consists of small domains and massive grain boundaries, which leads to large deviations from theoretical calculations [46].

4.2.4. Atomic layer deposition (ALD)

Compared to the CVD method, the ALD (Atomic layer deposition) method can produce highly homogeneous thin films [47, 48]. The ALD method is based on alternating deposition of layers in a controlled vacuum; reagents for the formation of each layer are supplied alternately. The substrate surface intended for film formation is functionalized in such a way that the chemical bond between the substrate and the reagents prevents possible peeling. Before the introduction of each subsequent reagent, the chamber is purged with an inert gas to remove any foreign or loosely attached molecules. The resulting surface usually consists of a monolayer of the required material, which can be converted into a multilayer film during further deposition cycles. For example, in [49], the ALD method was successfully used to obtain anode thin film materials for lithium-ion batteries based on nickel and cobalt oxides. Although ALD requires expensive and complex reaction chambers, carrier gases, and flow control systems, it has an unsurpassed ability to produce high-quality conformal thin films.

4.2.5. Chemical bath deposition (CBD)

The CBD (chemical bath deposition) method is a controlled chemical reaction during which a thin layer of material is formed by heterogeneous deposition. The coated substrate is immersed in an aqueous metal salt bath. Then, an anti-ion is added (for example, in the form of OH^- for

oxides/hydroxides or S^{2-} for sulfides) and, by adjusting the solubility of the target compound, a film is deposited on the surface of the substrate. It is assumed that the solution in the bath is thermodynamically unstable and is in a supersaturated state, which leads to precipitation.

4.2.6. Successive ionic layer adsorption and reaction (SILAR) or Successive ionic layer deposition (SILD)

The technique of successive ionic layer adsorption and reaction (SILAR) or successive ionic layer deposition (SILD) is based on the adsorption of a layer of ions on a surface, followed by a chemical reaction triggered by the sequential adsorption of other ionic substances. This reaction leads to the formation of an insoluble product, which consists of a thin-film coating. Then the process is repeated in order to increase the thickness of the applied layer. As a result of an exchange or redox chemical reaction, a layer of the target product is formed on the surface, which includes a secondary ionic precursor [50].

Compared to other techniques, the SILAR method has unique traits and advantages. For example, the ability to be applied on a planar surface without dimensional restrictions and the ability to easily adjust the film thickness over a wide range by controlling the concentration of particles and the number of depositions. Furthermore, by controlling the ionic reactions occurring at the solution substrate interface, the deposited films can be tuned to exhibit preferred crystallographic orientation and grain structure, crystal growth can be controlled, and deposited coatings can be annealed after deposition to trigger crystallization [50].

Over the past few years, several articles have been published on the topic of synthesis of ultrathin two-dimensional layered oxides and hydroxides by the SILAR method [51]. In particular, ultrathin (3-5 nm) nanosheets of layered double hydroxides were successfully synthesized via SILD technique in [52-54], which showed excellent electrochemical characteristics both in terms of specific capacity and electrochemical stability as materials for pseudocapacitors and alkaline batteries.

Moreover, in a number of studies have noted that factors such as the concentration and pH of solutions, the pH of washing liquids, the temperature of solutions, and the processing time of the substrate [55] directly affect the properties of the resulting thin films. Therefore, optimal deposition parameters can be determined for each system depending on the materials and solvents used.

The summary table (Table 1) shows the main advantages and disadvantages of the main synthesis techniques. It should be noted that in recent years, significant progress has been made in obtaining a variety of ultrathin two-dimensional TMO materials. However, there are several unresolved problems that prevent the widespread use of the developed synthesis techniques.

Table 1 – Possibilities and limitations of various methods of ultrathin 2D TMO and TMH synthesis

Method	Possibilities	Limitations
Mechanical exfoliation	Simplicity High quality	Low output Limited number of precursor materials
Ultrasonic exfoliation	Simplicity Low cost Scalability	Limited ability to control synthesis
Chemical intercalated exfoliation	Simplicity Modifiability	Low efficiency High cost
Electrochemical exfoliation	Environmental friendliness Effectiveness High output	Poor scalability
Hydrothermal (solvothermal) synthesis	Simplicity Low cost Scalability	Poor reproducibility Complexity of crystal growth control
Template self-assembly	Low cost Scalability	Inability to control the growth of film thickness High cost
CVD	A good opportunity to control the synthesis High quality	Inability to obtain a film of large thickness
ALD	Excellent synthesis control	High cost Large film thickness Inaccessibility
CBD	Simplicity Low cost	Poor film quality Poor reproducibility
SILAR (SILD)	Simplicity Good ability to control synthesis Low cost	Possibility of dissolution/peeling of the film during synthesis

5. Conclusions

The presented review briefly described recent achievements in the field of methods for the synthesis of electroactive materials based on ultrathin two-dimensional oxides and hydroxides of transition metals and noted the possibilities and limitations of each of

them. First of all, it should be noted that significant progress has been made in the research and development of these materials over the past decade. Many synthesis techniques have been proposed recently, including both "top-down" and "bottom-up" routes. However, as noted above, each of the methods, along with its advantages, has a number of limitations, which create certain problems for further commercialization and introduction into a wide industrial production. The review also noted the importance of the possibility of varying the conditions and parameters of synthesis and their influence on the formation of two-dimensional nanocrystals. From this point of view, bottom-up techniques seem to be the most promising, since they allow more precise control of the crystalline phase formation and the nanosheet size . The importance of thin-layer deposition methods, such as ALD, CVD and SILAR, for obtaining ultrathin nanosheets with specified parameters was also noted.

Possible directions for further successful development of the synthesis of high-performance electrode materials based on 2D TMO and TMH include:

1) Possible combination of several synthesis techniques in the production of electrode materials and the search for novel synthetic routes;

2) Possible further modification of the synthesized materials, in particular, the production of a 3D structure or a structure of perforated nanosheets;

3) Obtaining, along with TMO and TMH, nanocomposites with carbon materials, such as graphene and its derivatives (GO; RGO; N-doped graphene), multiwalled carbon nanotubes, MoS_2, g-C_3N_4, etc.

4) Solving the problems of scaling up to a wide industrial production without significantly increasing the cost of manufactured materials, which can be achieved by developing new efficient synthesis plants.

Undoubtedly, further research in the field of creating ultrathin two-dimensional transition metal oxides and hydroxides, as well as the improvement of synthesis techniques, will open up new prospects in the creation of not only highly efficient materials for energy storage devices, but also other areas of their application, such as electro- and photocatalyst, photochromic materials, magnetic materials, biosensors, etc.

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Author contributions

Artem Lobinsky: Conceptualization; Data curation; Writing – original draft.
Vadim Popkov: Supervision; Writing – review & editing.

Conflict of interest

The authors declare no conflict of interest.Additional information

Additional information

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Vadim Popkov is a specialist in the materials science, currently working as a leading researcher and the Head of the Hydrogen Energy Laboratory at the Ioffe Institute (St. Petersburg, Russia). He received his Ph.D. degree in chemistry in Lomonosov Moscow State University in 2017 and then completed a two-year postdoctoral fellowship at St. Petersburg State University. Now his research interests involve the physicochemical design of novel nanostructured materials, including photo-, electro-, and thermocatalysts, sorbents, magnetics, semiconductors, etc., as well as their in-depth structural investigation and functional performance exploration.

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