New Routes for the Synthesis of Nanocomposite Layers of Inorganic Compounds by the Layer-by-Layer Scheme

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Abstract—This short review is devoted to the presentation of new routes for the synthesis of nanocomposite layers at the solid-solution interface by the layer-by-layer scheme. A diversity of methodic approaches to the synthesis is divided into separate groups according to the nature of starting reagents. The methods of ion deposition, molecular, colloidal, ion-molecular, molecular-colloidal, and ion-colloidal deposition are set off from them. New routes of synthesis, which are based, in particular, on using soluble fluoride and oxalate metal complexes, polyoxometallates, and also colloidal solutions of layered double hydroxides, are discussed for the methods of ion, ion-colloidal, and colloidal deposition.

Methods of the layer-by-layer synthesis take an important place among methodical approaches to the synthesis of nanocomposite layers of inorganic substances with the use of reagent solutions. These methods are based on carrying out successive acts of adsorption of low-dimensional precursors on a support surface. The precursors include cations, anions, or colloidal particles, their unreacted excess being obligatory removed. Each act results in the formation of a nanolayer of the synthesized substance on the surface, i.e. the layer of units or fractions of nanometer in thickness. On multiple repetition of the adsorption the thickness of this layer increases proportionally to the number of treatment cycles.

Interest to such synthesis is supported by increasing number of publications. At the beginning of the 1990s only several papers a year were published, whereas in 1995, about 30, in 2000, more than 200, in 2003, about 400, and later by our data the number is on this level. The first reviews were published in the works [1–3], and partially, relative to the synthesis of polyelectrolytes, in [4, 5].

In our opinion the diverse reactions of layer-by-layer synthesis may be divided into separate groups according to the nature of starting substances used for the synthesis, i.e. to the groups including ions, molecules, or nanoparticles as precursors (those latter are mostly represented by colloidal particles in solutions) (Fig. 1). These procedures may be defined as molecular, ion, colloidal, ion-molecular, molecular-colloidal, and ion-colloidal depositions. The necessity of the suggested division is associated with the fact that each group of the noted procedures is characterized by its own regularities of the synthesis. As a rule, all these reactions are carried out on the surface of a support in a layer of chemically or physically adsorbed precursors. In the molecular deposition the polycondensation reactions between molecules are predominantly in use, in the ion deposition, the reactions of inner- and outer-sphere complexes formation on the surface, in the colloidal deposition, the reactions of adagulation, and in the ion-molecular, molecular-colloidal, and ion-colloidal de-positions, the corresponding combinations of these reactions. An essential moment in this classification is a more systematic presentation of the mentioned problems of synthesis, which is important for the teaching process.

Examination of the published data shows that the greatest attention in the synthesis of layers of inorganic substances using reagent solutions is given to the methods of ion, ion-colloidal, and colloidal depositions. One of the purposes of this work is the systematization of a number of experimental results obtained during the last five years and a more detailed presentation of new routes of the nanocomposite layers synthesis.
As the experiments show, it is rather difficult to determine conditions for the synthesis by the ion deposition method, since, in spite of the simplicity of the operations, with regard to the multiple stage character of the process, it is necessary to control ten and more synthesis conditions including, for example, the concentration and pH of several reagent solutions, pH of washing liquids, the treatment duration, etc.

The main problem of the synthesis of metal-oxygen layers by ion deposition using metal salt solutions consists in the complexity of achieving conditions of irreversible adsorption of metal cations on the support surface and after that, on the surface of the layer synthesized before. To obtain a layer of metal hydroxide on the support surface in the first stage, the adsorption of cations of this metal is carried out \[
\text{Surf.} + M^{n+} \rightarrow \text{Surf-M}^{+\text{\text{(d-1)}}} \], then the excess of salt is removed by washing the surface with the solvent, and the support is treated by a weak alkali solution \[
\text{Surf-M}^{+\text{\text{(d-1)}}} + \text{OH}^{-} \rightarrow \text{Surf-M(OH)}^{n-1} \]. The Surf-M(OH)\text{\text{(d-1)}} compound formed on the surface serves as the support for the synthesis of the next metal hydroxide layer. However on treating it with a metal salt solution in the second cycle of the ion deposition the deposited metal hydroxide layer is dissolved \[
\text{Surf-M(OH)}^{n-1} + \text{H}^{+} \rightarrow \text{Surf.} + M^{n+} \] and H\text{\text{+}} ions appear in the solution due to the hydrolysis of the salt of this metal.

To solve this problem for the synthesis of metal-oxygen layers containing cations having several oxidation states, we have proposed [6] a route based on successive and multiple treatment of the support with the salt solution containing the metal in the lowest oxidation state and on the oxidation of adsorbed cations in the stage of their hydrolysis. In this case the resulting layer of metal hydroxide with the highest oxidation state is not dissolved in the solution of the metal salt with the lowest oxidation state, as it is known that the pH of the precipitation beginning for metals in the lowest oxidation states lie in a more alkaline region.

For metals with a single oxidation state we have proposed [7] the route based on the conversion of metal hydroxide adsorbed layers to hydroxoperoxide layers, as the solubility of hydroxoperoxides, in particular, of Cu\text{\text{2+}}, Zn\text{\text{2+}}, Ln\text{\text{3+}}, is lower compared to hydroxides.

Fluoride and oxalate routes proposed in [8–11] open new possibilities for the synthesis. In these works the search for the conditions of the synthesis was carried out with the help of computer programs, Visual Minteq 2.40b and Hydra-Medusa in particular, which simulate hydrochemical equilibria in solutions, including also solutions of aqua, fluoride, oxalate et al. metal complexes.

With the help of calculations by these programs for each solution of “cation” and “anion” reagents a solution composition and its variation depending on pH were examined, the pH of the beginning of formation of a difficultly soluble compound layer and also the regions of the lowest solubility of the synthesized layer and of the support were determined. The composition (cation and anion), the concentration and pH of the reagent solutions corresponding to the conditions of the lowest solubility of the support and of the layer were also determined. Such sequence of calculations made up an algorithm, which was repeated on examining conditions of the synthesis of each of the layers.

When determining conditions of the synthesis of metal-oxygen compounds using solutions of metal fluorides, we calculated variations of the composition of solutions of metal fluoride complexes as a function of pH, of the reagent concentration, and of the relative content of fluoride ions. It this case the concentration of the reagents was varied within the range of 0.01–