Synthesis of metal–oxide, metal–hydroxide, and metal–peroxide nanolayers by successive ionic layer deposition method from solution

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Synthesis of metal–oxide, metal–hydroxide, and metal–peroxide nanolayers on surfaces of inorganic substrates is of interest from the viewpoint of tailoring novel catalysts, sorbents, pigments, anticorrosion coatings, electrochromic devices, etc.

We summarize our work devoted to synthesis of nano- and multinanolayers of metal–oxygen compounds by the method of successive ionic layer deposition (SILD) from solution. This method consists of implementation at room temperature of successive adsorption of the cations and anions that produce hard-to-dissolve compounds on a substrate surface. The procedure is conducted layer-by-layer, while the thickness control is on the order of fractions of one nanometer.

Six original, developed by the authors, routs of the synthesis of hard-to-dissolve hydrated metal–oxygen compounds are considered. Reagents in the synthesis were salts of metals and hydrogen peroxide or soluble peroxi-complexes of metals. The substrates were polished plates of fused quartz and Si(100). These routs are based on

1) reactions of adsorbed metal cations with H_2O_2 (OH^-), which was used to synthesize CuO_{1+x} [1], ZnO_{1+x} [2], and $La(OH)_x(OOH)_y$ [3];
2) oxidation of the adsorbed metal layer by a H_2O_2 solution, resulting in the subsequent formation of a layer of the metal peroxide (by example of the $Ce(OH)_x(OOH)_{4-x}$ layers [4]), metal oxides ($SnO_2{\cdot}nH_2O$ [5], $Tl_2O_3{\cdot}nH_2O$ [6], $PbO_2{\cdot}nH_2O$ [7]) or metal hydroxides (FeOOH [8]);
3) reactions of adsorbed metal cation (La_{aq}^{3+}) with peroxianion (NbO_8^{3-}) with formation of hard-to dissolve compound $La_xNbO_y{\cdot}nH_2O$ [9];
4) oxidation of adsorbed metal cation (Ce_{aq}^{3+}) by peroxianion (NbO_8^{3-}) with the following interaction and formation of $Ce_xNbO_y{\cdot}nH_2O$ [10];
5) reduction of adsorbed anions by cations (e.g., reduction of MnO_4^- by Mn^{2+} leads to formation of a $MnO_2{\cdot}nH_2O$ layer [11] and reduction of MoO_4^{2-} by a $SnCl_2$ solution results in formation of $Sn_xMoO_y{\cdot}nH_2O$ [12]);
6) reduction of adsorbed anions of heteropoly oxometalates (the $H_7PW_{12}O_{42}$ reduced by a $SnCl_2$ solution transforms into hybride isopoly (Sn-O)-heteropoly (H-P-W-O-) compound [13].

The nano- and multinanolayers obtained in this way were characterized using FTIR and UV/Vis spectroscopy, XPS, X-ray diffraction, electron microprobe, ellipsometry, chemical analysis and other methods. The results are discussed. Conclusions about the composition and structure of the multilayers are made.

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