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Successive ionic layer deposition. The use in nanotechnology

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Abstract. The problems related to the synthesis of nanolayers of various classes of substances (inorganic, organic and hybrid, *i.e.*, inorganic/organic) by successive ionic, ionic – molecular and ionic – colloidal layer deposition are discussed. The experimental data are systematised in terms of the type of reaction occurring on the surface during the synthesis. The use of successive ionic layer deposition in nanotechnology for the preparation of practically valuable nanolayers is considered. These nanolayers include the layers in SnO_2-based conductometric gas sensors, passivating protective coatings on the metal surface, semiconductor cells for solar energy conversion, photo-, electrochromic and magnetic materials, pervaporation membranes, electrocatalysts, light diodes, and so on. The bibliography includes 201 references.

I. Introduction

The development of nanotechnology brings about new challenges for the preparative chemistry, in particular, the precision synthesis of nano- and multinano-layers and 2D and 3D-nanostructues based on inorganic, organic and hybrid (inorganic/organic) substances.

Among the procedures of such synthesis, 'chemical assembly methods',[1,2] *i.e.*, layer-by-layer syntheses, occupy an important place. They are based on successive adsorption of low-dimensional precursors on the substrate surface with obligatory removal of an excess of non-consumed reagent. As a consequence, a layer of the substance being synthesised with a thickness of several nanometres or fractions of a nanometre (a nanolayer) is formed on the surface. Upon multiple repetition of the adsorption reactions, the layer thickness increases in proportion with the number of treatment cycles.

After the first publications by V B Aleskovskii and S I Kol'tsov,[3,4] as well as T Suntola,[5] the use of gaseous reagents for the thin-film synthesis began. This was believed to create conditions for the complete irreversibility of the reactions. However, the design of these structures is faced with the problem of low volatility of the precursors at the relatively low temperatures used for this purpose (as a rule, lower than 400 °C).

In recent years, solutions of salts containing ions that react on the sorbent surface to give poorly soluble compounds have been used more and more often as reagents in the preparation of nanolayers.

Most of reactions of inorganic compounds are carried out in solutions. In particular, metal complexes are synthesised in solution and then isolated by crystallisation, extraction or another method. Solutions are also used for the preparation of thin films of inorganic compounds by chemical metallisation, alkaline oxidation, phosphatation or chromatation, which have found wide use in mechanical engineering for the protection of the surface of metal articles.

The key feature of these methods is the use of so-called mixing regime in which the final product is formed from a mixture of reactants as the equilibrium shifts towards the least soluble compound.

The first syntheses by the 'layer-by-layer' procedure using colloidal solutions were carried out by Iler.[6] This procedure was further developed by using true solutions. The syntheses of ZnS and MnO_2 layers involving the cations and anions occurring in solutions were independently described in the patents by Nicolau [7] and Tolstoy *et al.*[8] The reaction conditions were found such that successive adsorption of cations and anions, which react to give the layer compound, takes place on the substrate surface in each stage of the synthesis.

This method of the synthesis has been called [9] Successive Ionic Layer Deposition (SILD).† An obligatory condition for the layer synthesis by this method is removal of excess reagents and products, for example, by washing with a solvent after each stage of adsorption. If the excess of reagents is not removed, the synthesis of the layer will take place under 'mixing' conditions and it will be impossible to control precisely the thickness of the growing layer. This distinguishing feature of SILD is illustrated by Fig. 1, which shows the variation of the reagent concentration at the substrate – solution interface during the synthesis.

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† Other names are Successive Ionic Layer Adsorption and Reaction (SILAR) or Layer-by-Layer (LbL) synthesis.

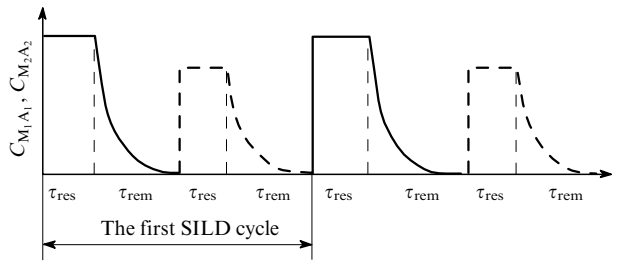


Figure 1. Variation of the reagent concentrations $C_{M_1A_1}$ and $C_{M_2A_2}$ in the layer at the solution–substrate interface during SILD synthesis (2 cycles).
τ_{res} is the residence time in solution of each reagent, τ_{rem} is the time of removal of excess reagent and reaction products by washing the substrate with the solvent.

The interest in these studies is increasing. Thus in the early 1990s several papers a year were published on this subject, in 2000 more than 200 papers appeared, while the number of publications in 2003 was ~ 400. Reviews [9, 10] and a collective monograph [11] devoted to the synthesis of polyelectrolyte layers were published.

This study describes systematically the results of investigations on the nanolayer synthesis carried out during the last 10 years and considers the most promising fields of its application in nanotechnology for the solution of practically valuable problems.

II. Conditions for successive ionic layer deposition reactions

The SILD reactions on the substrate surface are carried out using two types of special automated equipment. Devices of the first type are designed for the synthesis of layers on the surface of block substrates. They consist of beakers with reagents, an electromechanical drive with a cartridge for samples and a PC-based control unit. The synthesis is performed by successive immersion of the specimen into solutions of reagents. It is assumed that in the beaker containing a solution of the cationic reagent, for example $Pb(NO_3)_2$ (the simplest case), adsorption of the Pb^{2+} cations on the substrate surface takes place and then excess reagent and reaction products are removed. During treatment with an anion-containing solution, for example Na_2S, in the other beaker, adsorption of the S^{2-} or HS^- anions takes place in a similar way. A SILD cycle gives rise to a single nanolayer of the compound being synthesised (in this case, PbS). When the cycle is repeated many times, the layer thickness is increased.

Layers on the surface of disperse substrates are prepared using a flow-type setup. In this case, the substance to which the nanolayer is applied is fastened in a chemical reactor and reagent solutions and washing liquids are added in succession. The order of treatment is specified by the control unit by opening and closing the appropriate electromagnetic valves.

As shown by experience, tens, hundreds or more cycles of layer depositiont may give thin-layer structures according to a prespecified pattern.

After the SILD, a layer with a thickness of about several nanometres or fractions of a nanometre, *i.e.*, a nanolayer, is formed on the surface. This definition of the 'nanolayer' does not imply any information concerning its morphology. Indeed, the reactions on the surface can yield either the continuous layer of new structural units (monolayer) or a discontinuous layer. In some cases, due to incomplete coverage of the surface by a reagent or incomplete removal of the reagent during washing, one can expect an 'islet' mechanism of layer growth where the layer thickness in the growth area would exceed the monolayer thickness (but this would be still a 'nanolayer').

Even the fist experiments have shown that for most compositions, washing after the adsorption results in the removal of not only excess reagents and reaction products but also a part of the (or entire) adsorbed layer. Thus, determination of the conditions of a SILD synthesis is a complicated task, as more than 10 parameters are to be controlled (including the pH values and concentrations of several solutions of reagents, pH of wash liquids, residence times, and so on). The monographs [12, 13] devoted to studies of ion exchange on the surface cover the results of numerous papers. However, they do not clarify the point concerning the choice of optimal conditions of synthesis, because the studies were aimed at elucidating the conditions of adsorption of cations (or anions) by ion exchange resins and their subsequent desorption needed for regeneration of the ion exchanger. However, the conditions for irreversible adsorption for most ion exchangers have not been described systematically and, in some cases, they are presented only as oblique results. As a rule, these studies are devoted to adsorption on a sorbent or ion exchange resin, whereas the SILD method requires information on irreversible adsorption conditions in each cycle.

Nevertheless, the optimal conditions for the SILD synthesis of nanolayers of most classes of inorganic solid compounds, in particular, metal sulfides,[14–49] selenides,[50–52] oxides,[53–59] hydroxides,[60] peroxides [61–68] and fluorides,[69, 70] have now been elucidated. An important phase in the development of this subject would be systematisation of the accumulated experimental data and classification of the SILD reactions and the approaches used.

In our opinion, SILD procedures can be divided into groups according to the main types of reactions of cations with anions in solutions.[71] The major group comprises the surface reactions of an adsorbed cation (or anion) with an anion (or cation) situated in solution. The oxidation state of ions does not change. If the reaction gives a poorly soluble compound, a nanolayer is formed on the surface. The reaction of adsorbed Zn^{2+} aqua complexes with the HS^- anions to give a strong Zn–S bond is an example. Water molecules are 'squeezed out' of the coordination sphere of zinc cations. Drying affords a layer of anhydrous ZnS.

Yet another group comprises redox reactions. Two types of such reactions are distinguished. The first type includes reactions where the adsorbed cation is oxidised ($Sn^{2+} \rightarrow Sn^{4+}$) (see Ref. 55) or reduced ($Ag^+ \rightarrow Ag^0$) (see Ref. 72), or the adsorbed anion is reduced ($Cr_2O_7^{2-} \rightarrow Cr^{3+}$) (see Ref. 73), and so on. In this case, the dissolved molecules or ions of the oxidising or reducing agent involved in the process are not incorporated in the resulting layer.

The second type comprises redox reactions where the oxidising or reducing agent and probably the product of its chemical transformation are incorporated in the layer, giving rise to a multicomponent surface nanolayer (for example, $Sn^{2+} + MoO_4^{2-} \rightarrow Sn_xMoO_y$).[59]

There exists a group of 'conjugated' SILD processes in which the redox reaction of one of the types indicated above taking place on the surface is accompanied by adsorption of other cations or anions to give a poorly soluble compound. For example, treatment of an adsorbed Ce^{3+} layer with a solution containing H_2O_2 and OH^- results in the $Ce^{3+} \rightarrow Ce^{4+}$ oxidation, accompanied by adsorption of H_2O_2 and OH^- to give a $Ce(OH)_2OOH$ nanolayer.

Apart from the reactions of cations and anions, numerous processes involving reagents as molecules or colloidal nanoparticles can also be referred to as SILD reactions. The set of these reactions is schematically shown in Fig. 2; the methods of synthesis with these reagents are defined as ionic–molecular and ionic–colloidal layer deposition, respectively.

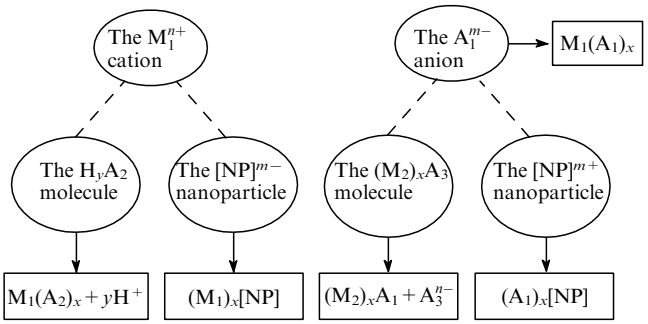


Figure 2. Main types of SILD reactions with solutions containing ions, colloidal particles and molecules in the liquid and gas phase as reagents.

III. Ionic layer deposition reactions without changes in the oxidation states of ions

1. Nanolayers of inorganic compounds

a. Synthesis of ZnS and CdS layers

The ZnS and CdS layers attract keen attention of researchers due to the attempts to create efficient electroluminescent and cathodoluminescent panels, windows for solid-state solar energy converters, photoconductors, *etc.*; therefore, the largest number of publications was devoted to this topic.[14–43]

A pioneering systematic study of the preparation of ZnS and CdS layers using solutions of metal chlorides and sulfates and a solution of Na_2S has been carried out by Nicolau.[14,15] The reagent concentrations were 0.005–5.0 mol litre^{-1}; the residence time in solutions and in water was 20 s; the substrates used were glass with indium and tin oxide (ITO) layers, Si, Ge, GaAs, InP, CaF_2, Al_2O_3 and $LiNbO_3$ single crystals, polycrystalline Ti, Mo, and Ta. The growth rate of the nanolayer depended on the solution concentration; the highest rates for ZnS and CdS, equal to 0.31 and 0.14 nm, respectively, were attained at $ZnCl_2$ and $CdCl_2$ concentrations of 5 mol litre^{-1} and a Na_2S concentration of 2.8 mol litre^{-1}. All other factors being the same, a higher growth rate was observed with chloride rather than sulfate solution. The effect of pH on the adsorption of the cations and anions on the surface of zinc and cadmium sulfides was judged from the data on the ξ-potential. These studies allowed one to determine more precisely the region of specific adsorption of ions and to construct adequate models of the processes taking place on the surface. The ZnS and CdS layers prepared under the optimal conditions were uniform and polycrystalline and had a mirror surface. The ZnS layers possessed a cubic structure and CdS layers were hexagonal, their predominant orientation being dependent on the substrate used.

In addition to layers of individual ZnS and CdS, solid solutions $Cd_xZn_{1-x}S$ were prepared.[23] Aqueous solutions (0.1 M) of $Cd(NO_3)_2$, $ZnSO_4$ and Na_2S were used as reagents and silicon and germanium plates were used as substrates. Solid solutions were obtained using a mixture of zinc and cadmium salts. The mole fraction of cadmium was varied from 0.0001 to 1.0. The thickness of the synthesised layers was estimated based on their interference colour. For CdS, the thickness was 0.32, while for ZnS, 0.29 nm per cycle. The ZnS layers synthesised on the silicon surface had a wurtzite type hexagonal lattice after the first 20 cycles and a sphalerite type cubic structure after 40 cycles. The subsequent cycles resulted in an increase in the crystallite size and gave rise to mosaic blocks whose $\langle 111 \rangle$ plane was oriented parallel to the substrate. The growth of CdS layers at the Ge $\langle 111 \rangle$ face started with the formation of a polycrystalline cubic phase, but as the layer thickness increased, some of the crystallites oriented themselves with the $\langle 111 \rangle$ plane. Solid solutions were formed if the mole fraction of cadmium was 0.0001–0.003, the most perfect ones were produced for a value of 0.0002. If the mole fraction of cadmium exceeded 0.003, layers with a CdS cubic structure were formed.

The ZnS/CdS multilayers on a glass surface coated with ITO or GaAs were prepared [39] by alternating treatment of the substrate with solutions of $ZnCl_2$ and $CdCl_2$ according to the SILD procedure. The thickness of each layer in the multilayer was 1–6 nm (and larger) and the overall thickness was 100–120 nm. The interfaces in the multilayer were not sharp and contained the $Cd_xZn_{1-x}S$ solid solution. The layer-by-layer identification was carried out by scanning electron microscopy (starting with 20 nm).

It has been shown [27] that ZnS layers on a poly(vinyl chloride) and polycarbonate surface can be synthesised under conditions similar to those used in the synthesis on the surface of inorganic solids. The difference lied in the special preparation of the polycarbonate surface. The poly(vinyl chloride) specimens were washed only with ethanol prior to the synthesis, while the polycarbonate specimens were treated with a 10% acidic solution of $KMnO_4$. The MnO_2 layer thus formed was etched with concentrated HCl to give surface carbonyl groups, which then participated in the sorption of reagents in SILD synthesis. The structure of these layers was polycrystalline in the case of poly(vinyl chloride) and amorphous in the case of polycarbonate. Apart from the zinc and sulfur atoms, the layers contained about 20% of oxygen [apparently, as a constituent of ZnO or $Zn(OH)_2$]. On the basis of these results, the researchers concluded that SILD can be used to obtain ZnS layers with good adhesion on a polymer surface.

The oxygen content in the ZnS layers synthesised on a glass surface with an ITO layer was determined by EXAFS.[28] Depending on the conditions of synthesis, this was 10%–30%. In non-heated samples, oxygen was incorporated in $Zn(OH)_2$, while in those heated at 500 °C, in ZnO. The crystal structure in the latter case was fully identical to the structure of the layers synthesised in the gas phase by molecular layer deposition at the same temperature.

The synthesis of ZnS layers was also performed on the polyether surface.[30] Prior to the synthesis, the polymer samples were kept for 12 h in a 0.1 M solution of $SnCl_2$ for the creation of the surface layer ensuring high adhesion. Then they were washed and dried in air. One SILD cycle gave, depending on the conditions, a 0.16–0.22-nm thick sulfide layer. The layers were amorphous, but at thicknesses of more than 250 nm, crystallite peaks were noted in the diffraction pattern.

b. Synthesis of Ag_7SbS_6 layers

The ways of synthesis of nanolayers containing two metals and an anion-forming element (S^{2-}, F^-, OH^-, *etc.*) have been considered.[19,20] The authors were the first to show that not only simple anions like S^{2-} but also complex thio salts such as SbS_4^{3-} can be used for SILD. The synthesis was carried out using solutions of S^{2-} and $AgNO_3$ or $Pb(NO_3)_2$.

The growth kinetics of Ag–Sb–S-containing nanolayers on a fused quartz surface was studied by spectrophotometry. From the dependence of absorbance on the concentration of the silver salt solution, it was found that an increase in the concentration above 0.01 mol litre^{-1} does not induce a substantial change in the absorbance. This indicates that the compound is formed in the layer of ions adsorbed on the substrate surface rather than in the solution. In 0.01 M solutions of $AgNO_3$ and Na_3SbS_4, the absorbance increased linearly upon an increase in the number of SILD cycles. This was indicative of a stepwise layer synthesis. The X-ray photoelectron spectrum of the layer showed electron binding energies of 368.0, 529.3 and 161.4 eV, which were assigned to the Ag^+, Sb^{5+} and S^{2-} ions, respectively. According to X-ray spectral microanalysis, the ratio of these elements in the layer prepared on silica gel over ten SILD cycles was Ag : Sb : S = 8.2 : 1.0 : 7.2. With allowance for the experimental error, this ratio corresponds most closely to Ag_7SbS_6. According to powder X-ray diffraction (CuK_a radiation), the layer was X-ray

Table 1. Synthesis of nanolayers of some metal chalcogenides and Cu(I) iodide and thiocyanate.

Layer	Substrate	Reagents	pH	τ_{res}/s	τ_{rem}/s	Note	Ref.
Ag_2S	SnO_2 layer	0.05 M $AgNO_3$,	–	10 – 12	–	Δd_1 = 14 nm	17
	on glass	0.4 M solution of thiourea	~6				
CuS	ITO-coated	(0.00625 – 0.05) M $Cu(OAc)_2$,	5.3 – 5.7	20	75 – 120	on a substrate with the CdS sublayer	45
	glass or CdS	(0.003 – 0.025) M Na_2S	11.0 – 12.0	–		a CuS layer (polycrystalline)	
	glass,	0.1 M $CuSO_4$,	~10	–	–	on glass, a CuS layer (amorphous),	46
	Si⟨111⟩	0.1 M solution of thiourea	~6	–	–	on Si, a CuS layer (polycrystalline)	
HgS	quartz glass	0.01 M $Hg(NO_3)_2$,	–	30	30		22
		0.01 M Na_2S	–	–	–		
PbS	Ge⟨111⟩	(0.01 – 1.0) M $Pb(NO_3)_2$,	–	40	10	single crystalline layer	37
		0.1 M Na_2S	–	–	–	with 0.1 μm blocks	
	Si,Na-silicate	0.2 M $PbAc_2$ with addition of TEA	7.7	20	70	Δd_1 = 0.08 – 0.12 nm. Polycrystalline	36,
	glass	0.4 M thioacetamide	4.6	–	–	layers with a cubic structure	38
PbSe	Si,Na-silicate	0.2 M $PbAc_2$ with addition of TEA	7.7	20	70	Δd_1 = 0.18 nm. Polycrystalline	51
	glass	sodium selenosulfite	–	–	–	layers with a cubic structure	
CdSe	glass	0.2 M solution of $CdSO_4$ and tartaric acid,	3.0	30	50	Δd_1 = 8 nm. Amorphous layer	44
		0.1 M Na_2SeSO_3	~10.5				
In_2S_3	quartz glass	0.01 M $In(NO_3)_3$, aqueous H_2S	–	30	30		18
	glass	0.05 M $InCl_3$	4.0	15 – 20	10	layers with cubic structure	44
		Na_2S	8.0	–	–		
Sb_2S_3	quartz glass,	$SbCl_3$ in acetic acid,	–	–	–	Δd_1 = 0.49 nm	21
	silica gel	aqueous Na_2S					
Sb_2Se_3	glass	0.2 M solution of the potassium salt of antimony tartrate,	–	–	–	layers with orthorhombic structure	50
		0.1 M Na_2SeSO_3	–	–	–		
As_2S_3	glass,	0.1 M As_2O_3 in HCl with EDTA,	1.0	15	10	t = 80 °C. Polycrystalline layer on Si	48
	Si ⟨111⟩	0.1 M $Na_2S_2O_3$	6.0	–	–		
Bi_2S_3	quartz glass	0.01 M $Bi(NO_3)_3$,	–	30	30		73
		solution of Na_2S	~8.5	–	–		
Bi_2Se_3	glass with	0.01 M $Bi(NO_3)_3$ with TEA additive	8.0	30	40	polycrystalline layers with hexagonal	50
	a SnO_2 layer	0.01 M Na_2SSeO_3	8.5	–	–	structure	
CuI	glass with	0.1 M $Cu(S_2O_3)^-$,	–	5 – 20	5	polycrystalline layers with a false	74
	a SnO_2 layer	0.0025 M KI	–	–	–	galena structure	
CuSCN	glass with	0.1 M $Cu(S_2O_3)^-$,	–	10 – 20	5	layers with orthorhombic structure	74
	a SnO_2 layer	0.00625 M KSCN					

Note. Here Δd_1 is the layer thickness per SILD cycle; TEA is triethylamine; EDTA is *N*,*N*,*N*′,*N*′-ethylenediaminetetraacetic acid.

amorphous; however, the X-ray diffraction pattern contained a small peak at $2\theta = 30.34°$, typical of Ag_7SbS_6.

The conditions and the results of syntheses of layers of other metal sulfides, selenides, iodides and thiocyanates are summarised in Table 1.

c. Synthesis of $LaF_3 \cdot n\,H_2O$ layers

The conditions of synthesis of $LaF_3 \cdot n\,H_2O$ nanolayers have been elucidated.[69, 70] Aqueous solutions of lanthanum chloride or nitrate and gaseous HF were used as reagents. First, the substrate was immersed into solutions of a lanthanum salt and then into water. Then the specimen was dried in an air flow and placed for 10 min into a flow reactor through which an air – HF gas mixture was passed. A concentrated solution of hydrofluoric acid through which air was passed at a flow rate of 0.2 – 0.3 $dm^3\ min^{-1}$ served as the source of hydrogen fluoride. This sequence formed one SILD cycle.

Solutions of NaF or NH_4F acidified with HF to pH ≈ 4.2 were other sources of fluoride ions used in the synthesis. These were used to obtain a sample of hydrofluoride complex in the solution and on the surface. The synthesis conditions were optimised by varying the concentration of metal salts, solution pH, residence times of the specimen in the liquid and gas phases and the number of SILD cycles. The change in the lanthanum salt concentration from 10^{-2} to 10^{-3} mol $litre^{-1}$ barely influenced the increment of the LaF_3 layer thickness (~0.45 nm) per SILD cycle. It was found by electron diffraction that the layer prepared using gaseous HF is polycrystalline and has a hexagonal LaF_3 structure with the unit cell parameters a = 0.716 and c = 0.732 Å.

d. Synthesis of $BiVO_4$ layers

In the synthesis of Bi – V – O-containing layers,[75, 76] 0.01 M aqueous solutions of $BiOClO_4$ and $NaVO_3$ were used as the reagents.

These layers were prepared at an equilibrium pH of the solution of $BiOClO_4$. The pH value of the solution of $NaVO_3$ varied, being 2.0, 3.0, 6.0 or 8.0. In a solution of $NaVO_3$ with pH 2, a light-yellow nanolayer with the ratio Bi : V = 1 : 0.79 was formed on the silica gel surface (according to X-ray spectral microanalysis of the specimen formed after ten SILD cycles). In a solution with pH 3.0, the layer was bright-yellow and the Bi : V ratio was 1 : 1. At pH 6.0 or 8.0, the colour was less bright, while the Bi : V ratio in the layer was 1 : 0.3.

These differences were attributed to different compositions of the vanadium(V) oxyhydroxide complexes in solutions at these pH values.[77]

The layers synthesised were amorphous (X-ray analysis) but the X-ray diffraction pattern of the specimen obtained from a solution of $NaVO_3$ at pH 3 showed a number of peaks typical of $BiVO_4$. On heating in air (300 °C), the intensity of these peaks increased.

e. Synthesis of metal hydroxyperoxide layers

A number of syntheses based on the formation of poorly soluble metal peroxide or hydroxyperoxide layers on the substrate surface

have been proposed. According to one of these, a layer can be obtained by successive adsorption of metal cations, H_2O_2 molecules and hydroxide ions. The adsorption irreversibility is attained due to lower solubility of hydroxyperoxides of some metals with respect to the solubility of hydroxides. First of all, this refers to the hydroxyperoxides $CuO_{1+x}\cdot n\,H_2O$,[63] $ZnO_{1+x}\cdot n\,H_2O$,[61,68] $NiO_{1+x}\cdot n\,H_2O$[62] and $La(OH)_{3-x}(OOH)_x$.[66] It is clear that after heating in air, metal hydroxyperoxides should be converted into hydroxides or oxides, although for some of them [in particular, for $La(OH)_{3-x}(OOH)_x$], the formation of relatively stable basic carbonates cannot be ruled out either.

In the synthesis of copper hydroxyperoxide $CuO_{1+x}\cdot n\,H_2O$, aqueous solutions of $Cu(NO_3)_2$, solutions of $Cu(OAc)_2$ in aqueous ethanol, aqueous and aqueous-ethanolic solutions of H_2O_2 and ammonia were used as the reagents. The substrate was successively treated with ammoniacal copper, wash solution, a weakly alkaline solution of H_2O_2 and again with the wash solution. The optimisation of the synthesis conditions demonstrated the necessity of using solutions of ammoniacal copper with pH $\approx 8-9$ and concentrations of $0.01-0.1$ mol litre^{-1} and $0.1\%-3.0\%$ of hydrogen peroxide. Under these conditions, an increase in the number of SILD cycles induces a regular increase in the absorbance of the layer in the UV transmission spectrum (*i.e.*, layer thickness). According to ellipsometry data, depending on the synthesis conditions, one SILD cycle gives a 0.3- to 1.5-nm thick layer.

It should be borne in mind that in weakly alkaline media, ammoniacal copper cations are adsorbed on the silica surface, the removal of their excess affording a $\equiv$SiOCuOH layer. When the specimen is put into a weakly alkaline solution of H_2O_2, the $\equiv$SiOCuOOH groups, which dissociate to give $CuOO^-$ and H^+ ions, appear on the surface.

The surface acquires again a negative charge and, hence, ammoniacal copper ions can again be adsorbed, thus forming the next copper peroxide layer.

Poorly soluble compounds are also formed when some metal cations react with soluble peroxo complexes. This synthetic protocol was tested experimentally to prepare $La_xNbO_y\cdot n\,H_2O$ layers using solutions of $La(OAc)_3$ and peroxoniobic acid.[64]

f. Synthesis of hybrid iso- and heteropoly oxometallates

The difficulty of preparing polyoxometallate layers on various substrate surfaces is due to their relatively low thermal stability; therefore, thin layers cannot be applied by, for example, vapour deposition. The preparation of heteropoly compound (HPC) layers from reagent solutions is also faced with difficulties, as due to the 'cluster' structure of HPC, the energy of their adsorption on most substrates is too low to produce a dense monolayer. In addition, the adsorbed HPC layer has no sites for sorption of the subsequent layer. However, some heteropolyacids (HPA), for example, $H_3PMo_{12}O_{40}\cdot n\,H_2O$, can be reduced rather readily to $[PMo_{12}O_{40}]^{n-}$ (in particular, with a solution of $SnCl_2$).[78] The resulting species may prove more reactive toward SILD synthesis. It is known[79] that the least soluble compound is formed in the reaction of the reduced form of phosphomolybdic acid with Zr^{4+} cations.

The use of aqueous solutions of $Zr(OAc)_4\cdot n\,H_2O$, $SnCl_2\cdot 2\,H_2O$ and $H_3PMo_{12}O_{40}\cdot n\,H_2O$ as reagents gave a $Zr_{2.6}(OH)_xPMo_{8.0}Sn_{1.9}O_y\cdot n\,H_2O$ layer on the surface.[80] It can be considered as a sort of 'hybrid' compound containing structural fragments of the initial HPA and zirconium polyhydroxy cations. Together with Sn^{4+} cations, the latter serve as a sort of bridges binding HPA anions to one another. Thus, a three-dimensional network of chemical bonds is formed on the surface.

2. Polyelectrolyte nanolayers

The first layer-by-layer synthesis of a polymer layer on a solid surface was reported by Nicolau *et al.*[81,82] This was done using solutions of pyrrole or aniline in ether, 3-methylthiophene in dichloromethane; and solutions of $FeCl_3$ in MeOH or MeCN were used as oxidants. Repeated successive adsorption of organic molecules and their oxidation on the substrate surface gave a layer of the corresponding polymer. In essence, this was a molecular layer deposition reaction.

Aqueous solutions of polyelectrolytes in the cationic or anionic form have been proposed[83–85] as reagents for precision synthesis of layers of organic compounds. Examples of such polyelectrolytes are poly(ethyleneimine) (PEI) with a molecular mass of 20 – 750 kDa (contains NH_2 groups and forms cations in the solution) and sodium poly(styrenesulfonate) (PSS) with a molecular mass of 70 – 500 kDa (contains SO_3^- groups and forms anions in solution). When the substrate whose surface has a charge opposite to the charge of the polyelectrolyte is immersed in the solution, the polyelectrolyte is adsorbed (Fig. 3). To produce a multilayer, the substrate is withdrawn from the solution, washed with water, placed into a polyelectrolyte solution (with the opposite charge of the macromolecule functional groups), kept in this solution, and once again withdrawn and washed with water (see Fig. 3). A distinctive feature of the process of synthesis of polyelectrolyte nanolayers compared to the synthesis of nanolayers of inorganic compounds is the necessity to dry the specimen in air after each cycle. This is required to remove water molecules from the layer and to enhance 'adhesion' of the long-chain polyelectrolyte molecules (to the substrate and to one another).

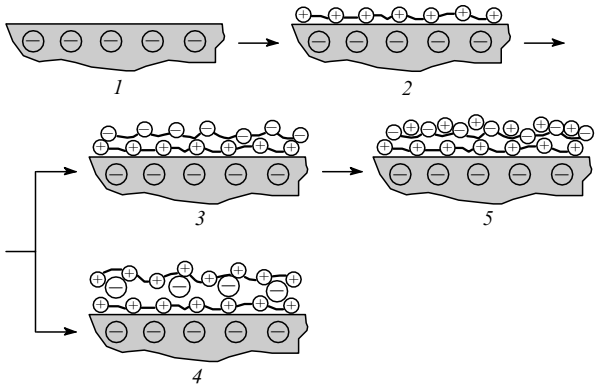


Figure 3. Schemes of SILD reactions involving polyelectrolyte solutions. (*1*) Initial substrate, (*2*) specimen with the layer of a cation-containing polyelectrolyte, (*3*) specimen with the layer of a cation- and anion-containing polyelectrolyte, (*4*) specimen after the adsorption of nanoparticles and a cationic polyelectrolyte layer, (*5*) specimen after the adsorption of metal cations.

The described method of synthesis has found a rather broad use.[86,87] The following compounds have now been studied as cationic polyelectrolytes: poly(diallyldimethylammonium chloride) (PDDA, 20 – 200 kDa), poly(allylamine hydrochloride) (PAH, 8 – 15 kDa), poly(L-lysine) (PLL) and poly(D-lysine) (PDL, 30 – 70 kDa), tetra(*p*-toluenesulfonate) 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin (TMPyP), diazo resin (DR), poly(amidoamine) (PAMAM), (4-vinylbenzyl)dodecyldimethylammonium chloride (VDAC), and 4,4′-bis(5-pyridylpentyloxy)biphenyl (4,4′-BPPOBp).

Among anionic polyelectrolytes, one can mention albumin, heparin, PSS (70 – 500 kDa), hyaluronic acid (HA), poly(L-Glu) (PGA, 50 – 100 kDa), polyacrylic acid (PAA, 90 kDa), polymethacrylic acid (PMA, 100 kDa), DNA, poly(aniline-*N*-butylsulfonate) (PANBUS, 3500 Da) and poly(vinyl sulfate) (PVS, 170 kDa).

These polyelectrolytes have been used to prepare PDDA/PSS, PVS/PAH, PLL/HA, PSS/PAH, heparin/PAH, PAA/PAH and other layers.

Detailed description of the reactions with polyelectrolyte solutions can be found in a collective monograph.[11] Some examples of the use of these nanolayers for solving practical problems are considered below.

3. Multinanolayers of hybrid (organic and inorganic) substances

The most significant studies deal with the synthesis of hybrid layers containing polyelectrolyte macromolecules in the cationic form and HPA anions. The use of polyelectrolytes allows one to overcome the above-noted (see Section II) problems which arise in the synthesis of HPA layers, because polyelectrolytes function as a peculiar transition layer, which glues together the HPA anions. Examples are provided by the layers containing PAH and $[Eu(P_2W_{17}O_{61})_2]^{17-}$ or $[Eu(SiW_{11}O_{39})_2]^{13-}$ (see Refs 88, 89), PAH and $[Eu(BW_{11}O_{39})_2]^{15-}$ (see Ref. 90), $[Eu(SiW_{10}VO_{39})_2]^{15-}$ and PEI,[91] $[Eu(SiW_{11}O_{39})_2]^{13-}$ and the poly(4-vinylpyridine)–Os(2,2′-bipy) complex,[92] PEI, $[PMo_{12}O_{40}]^{3-}$ and the $[Ru(bipy)_3]^{2+}$ complex,[93] $[W_{10}O_{32}]^{4-}$ or $[NaP_5W_{30}O_{110}]^{14-}$ and PEI,[94] PEI and $[NaP_5W_{30}O_{110}]^{14-}$ (see Ref. 95).

Anionic polyelectrolytes can form poorly soluble compounds and nanolayers with metal cations under the reaction conditions (see Fig. 3). The studies,[96–98] devoted to the synthesis of Tb^{3+}–PSS, Y^{3+}–PSS and Gd^{3+}, Eu^{3+} or Nd^{3+} and PSS layers, deserve attention.

IV. Successive ionic layer deposition with a change in the oxidation states of adsorbed ions

1. Reactions accompanied by the oxidation or reduction of cations

The preparation of layers of poorly soluble metal hydroxides using successive adsorption of metal cations and OH^- anions is faced with some complications. This is due to the fact that after adsorption of cations and anions, it is necessary to treat the substrate with a salt solution containing a metal cation. The hydroxide layer formed may react with the protons formed upon hydrolysis of the salt, this may result in hydroxide dissolution, and the synthesis of a thick layer may become impossible.

A solution of SnF_2 and a weakly alkaline solution of H_2O_2 have been chosen as the reagents in order to attain conditions for irreversible synthesis of SnO_2 nanolayers.[55] Under the action of hydrogen peroxide, the adsorbed Sn^{2+} cations are oxidised to Sn^{4+} [in an alkaline medium, the Sn^{2+} cations are converted into $Sn(OH)_4$]. The use of these reagents also appears justified based on the analysis of another publication,[77] which reports the precipitation conditions for Sn^{2+} and Sn^{4+} hydroxides from 0.001 M solutions. Complete precipitation of $Sn(OH)_2$ is known to occur at pH $\approx$ 6, and that of $Sn(OH)_4$, at pH $\approx$ 3, *i.e.*, the $SnO_2 \cdot H_2O$ layer synthesised by treatment of an alkaline solution with an oxidant is not dissolved in the next cycle.

In aqueous solutions at pH 2–3, adsorption of $SnOH^+$ ions takes place on the silica surface; after the removal of excess salt, a nanolayer of adsorbed Sn(II) hydroxide is formed. Then treatment with a weakly alkaline solution of H_2O_2 induces the Sn(II) $\rightarrow$ Sn(IV) transition.

In the second SILD cycle, the Sn(IV) hydroxide is not dissolved on treatment with SnF_2, and $SnOH^+$ ions are adsorbed on the surface. After SILD cycles repeated many times, a layer of the $Sn(OH)_4$ hydroxide is formed.

Similar redox reactions in the layer of adsorbed cations have been used in the synthesis of iron(III) hydroxide [60] and hydrated Tl(III) oxide layers.[54] A weakly alkaline solution of H_2O_2 is also an oxidant for the adsorbed Ce^{3+} cations. However, unlike SnO_2, apart from participating in the redox reaction, this reagent tends to form a stable peroxide compound by the reaction

$$\equiv SiOCe(OH)_{2,aq} + H_2O_2(OH^-) \longrightarrow \equiv SiOCe(OH)_{3-x}OOH_x .$$

The $\equiv SiOCe(OH)_{3-x}OOH_x$ fragment can dissociate to give the $\equiv CeOO^-$ groups, which function as adsorption sites for the Ce^{3+} ions in the subsequent SILD cycles.

For some cations, for example, Pb^{2+}, an alkaline solution of $KMnO_4$ is the most efficient oxidant.[56] On treatment of the substrate with a solution of $Pb(NO_3)_2$, the Pb^{2+} or $PbOH^+$ ions are adsorbed on the surface, while the subsequent treatment with a weakly alkaline solution of $KMnO_4$ results in $Pb^{2+} \rightarrow Pb^{4+}$ oxidation and reduction of Mn^{7+}, probably to Mn^{5+}. The latter reacts with excess solution of $KMnO_4$ to give MnO_4^{2-} ions. After washing, a $PbO_2 \cdot n\,H_2O$ layer is formed on the substrate surface. The layer has the structure of orthorhombic α-PbO_2 with the unit cell parameters: $a = 0.4038$, $b = 0.503$, $c = 0.5486$ nm; the c axis is perpendicular to the substrate surface.

The Ag^0 (see Ref. 72) and Cu^0 (see Ref. 99) nanolayers were synthesised by SILD by reduction of the cations adsorbed on the surface. The key problem of this synthesis (compared with the synthesis of, for example, metal sulfides or fluorides) is that the layer consists of only one sort of atoms and it is difficult to select conditions of irreversible layer-by-layer adsorption.

The reduction of Ag^+ in a weakly alkaline solution of H_2O_2 was chosen as a method for the synthesis of Ag^0 nanolayers. A metallic silver layer is formed in the mixing regime according to the following reaction

$$2\,Ag^+ + 2\,H_2O_2 \longrightarrow 2\,Ag^0 + 2\,H_2O + O_2 .$$

In the first cycle of SILD, the substrate was successively treated with a solution of $[Ag(NH_3)_2]NO_3$, washed with ammonia (pH 9) and with a weakly alkaline solution of H_2O_2, and then washed with distilled water. In the subsequent cycles, a solution of $AgNO_3$ was used for Ag^+ sorption, water was used for washing and the reduction of Ag^+ ions was performed by a weakly alkaline solution of H_2O_2. After treatment of the substrate with a solution of the silver ion and washing off the excess of the reagent with an ammonia solution, adsorption of ammoniacal silver takes place on the surface. Subsequently, after treatment with a solution of the reducing agent, only partial reduction of Ag^+ ions takes place to give known [100] compounds of the Ag_2^+ or Ag_4^{2+} type. They are characterised by a sharply lower intensity of the absorption bands of free and bound OH groups at 1370 and 1400 nm. Apparently, after treatment with a reducing agent, the Ag_2^+, Ag_4^{2+} and other clusters form peculiar complexes of the $\equiv Si-OAg_2$, $\equiv Si-OAg_4^+$ type on the surface. When the substrate is treated with a solution of $AgNO_3$, these complexes may function as adsorption sites for the Ag^+ ions, which are then (on treatment with a reducing agent) converted into Ag^0 to give a larger complex. As the number of SILD cycles increases, a layer of metallic silver is formed.

Layers of Cu^0 were prepared using solutions of Cu(II) salts and a highly alkaline (pH 13–14) solution of formaldehyde. Water served as the wash liquid. The nanolayers were characterised using scanning electron microscopy and atomic force microscopy (AFM). Unfortunately, the method used to check the completeness of reagent removal after reduction of the cations is not mentioned in the study cited.[99] Probably, alkali was not removed completely during washing, and treatment with a solution of the copper salt was accompanied by 'precipitation' of copper hydroxide, which was then reduced to the metal on multiple treatment with a solution of a reducing agent.

Metal cations can serve as oxidants for adsorbed cations. In the synthesis of $Ag_x^0 \cdot MnO_2$ layers,[101] Mn^{2+} cations function as reducing agents and Ag^+ cations are the oxidants. It is important that, for these cations, a pH region exists in which the reaction products formed on the surface, namely, MnO_2 and Ag^0, are poorly soluble. These underlay the choice of the reagents for the synthesis of so-called 'hybrid' metal–oxide layers.

For the synthesis of an Ag^0-Mn-O-containing nanolayer,[101] aqueous solutions of $Mn(OAc)_2$ and $AgNO_3$ were used as the reagents. The growth of the layer was observed when 0.01 M aqueous solutions of $Mn(OAc)_2$ (pH 7.5) and $AgNO_3$ (pH 8.5–9)

were used. To increase the pH in the solution of $Mn(OAc)_2$, a solution of sodium acetate was used; in the case of $AgNO_3$, this was attained by an ammonia solution. At the given pH values, the reagents were adsorbed on the surface, and irreversible Mn^{2+} oxidation and Ag^+ reduction took place. The X-ray photoelectron spectrum displayed a peak at 642.2 eV corresponding to Mn^{4+} ions ($2p_{3/2}$) in MnO_2 and a peak at 368.6 eV corresponding to Ag^0 ($3d_{5/2}$). The $Ag^0 : MnO_2$ ratio in the layer was determined from the peak intensities to be ~ 0.7. The diffuse reflectance spectra of the layers on the silica gel surface exhibited broad bands at 400 – 500 nm, *i.e.*, in the absorption region of metallic silver clusters. In a powder X-ray diffraction study, the metallic silver in the layer exhibited a peak at $2\theta = 64.48^\circ$. This confirms its crystalline structure.

2. Reactions involving the oxidation of cations and the reduction of anions

If the SILD makes use of reactions involving the oxidation of cations and the reduction of anions, the oxidant reacts with the adsorbed cationic layer, thus passing to a lower oxidation state and forming a poorly soluble compound with the layer of the oxidised cation.

This synthetic strategy was first tested in the preparation of $MnO_2 \cdot n\,H_2O$ nanolayers on the silica surface.[8,53] Solutions of $MnCl_2$, $MnSO_4$ and $Mn(OAc)_2$ served as the reducing agents and weakly alkaline solutions of $KMnO_4$ was used as the oxidant. When these compounds react in the mixing regime, a $MnO_2 \cdot n\,H_2O$ layer is produced on the surface, which is confirmed by X-ray fluorescence and IR spectroscopy. The layer is mechanically strong, its thickness being controlled by the number of SILD cycles.

If cations and anions of different elements are used in the redox reaction on the surface, the layer will be multicomponent, which was observed in the synthesis of layers containing Co(III) – Mn(IV) – O,[57] Ce(IV) – Mn(III) – O[58] and Fe(III) – Cr(III) – O.[102] The compositions of the prepared layers were described as $Co_3MnO_x \cdot n\,H_2O$, $Ce_4MnO_x \cdot n\,H_2O$ and $FeCr_{0.7}O_x \cdot n\,H_2O$, respectively.

The Ce_xNbO_y nanolayers were synthesised in a similar way.[103] The Ce^{3+} cations served as the reducing species, while the NbO_8^{3-} anions were the oxidants. The layer composition can be described as $Ce_{0.7}NbO_x \cdot n\,H_2O$.

A similar strategy has been used[59] to prepare nanolayers $Sn(IV)Mo(VI,V)_{0.6}O_y \cdot nH_2O$ using aqueous solutions of $SnCl_2$ and $(NH_4)_2MoO_4 \cdot 2\,H_2O$ or $(NH_4)_2Mo_7O_{24} \cdot 2\,H_2O$ as the reagents. Apart from the molybdate anions, heteropolyacid anions can also react with the reducing agent, a $SnCl_2$ solution. This was shown in a study[104] where $H_3PW_{12}O_{40} \cdot nH_2O$ was used to prepare the $Sn_{16}(OH)_xPW_{19}O_y \cdot n\,H_2O$ nanolayer.

V. Conjugated ionic layer deposition reactions including oxidation or reduction of ions and adsorption

Using the SILD method, it is possible to prepare not only one- but also multi-component layers, in particular, multilayers of different composition. A necessary condition for the synthesis of multilayers is the insolubility of the peroxide nanolayer already formed in the reagent solutions used to form the subsequent layers. The $CeO_{2+x} \cdot z\,H_2O$ and $LaO_{1.5+x} \cdot z\,H_2O$ multilayers have been obtained.[66] The synthesis was carried out on a silicon surface in the following way: one SILD cycle gave a $CeO_{2+x} \cdot z\,H_2O$ nanolayer; this was followed by the cycle giving a $LaO_{1.5+x} \cdot z\,H_2O$ layer; and then these cycles alternated many times (up to 60). The resulting multilayer was studied by X-ray photoelectron spectroscopy. The results showed the presence of both La(III) and Ce(IV). Their relative concentration equal to $\sim 1 : 1$ was determined based on the band intensities.

In the synthesis of multicomponent layers, metal ions can be introduced into the layer using mixtures of solutions of their salts. Thus for the synthesis of a two-component Ce- and La-containing layer, $La(NO_3)_3$ was added in different proportions to a solution of $Ce(OAc)_3$. The overall solution concentration was 0.01 mol litre^{-1}, while the mole fractions of lanthanum were 10%, 20% and 40%. However, the lanthanum concentrations in the resulting layer (according to X-ray photoelectron spectroscopy) were 9%, 15% and 22%, respectively. The decrease in the lanthanum content in the layer with respect to its concentration in the solution is due to lower sorbability of the La^{3+}_{aq} ions compared to that of Ce^{3+}_{aq}.

Yet another example of using conjugated SILD reactions is provided by the synthesis of nanolayers consisting of the double Fe(III) – Ni(II) hydroxide.[105] A freshly prepared solution of Mohr's salt $(NH_4)_2(FeSO_4)_2 \cdot 6\,H_2O$ and an ammoniacal solution of $NiSO_4$ (pH $\approx 8.0 - 8.5$) with concentrations of 0.01 mol litre^{-1} served as the reagents. The sequence of operations for the preparation of a Fe(III) hydroxide layer (this procedure has been reported[60]) is as follows: Fe^{2+} ions are adsorbed from a solution of Mohr's salt, the excess of the solution is removed, the sorbed ions are oxidised in an H_2O_2 solution, and the excess of hydrogen peroxide is removed by washing with water. For the synthesis of the double hydroxide layer, it has been proposed[105] to combine the oxidation of sorbed Fe(II) ions with sorption of Ni(II) ions and to synthesise a double hydroxide layer over a minimum number of surface treatment cycles. In an ammoniacal Ni(II) solution, the Fe(II) → Fe(III) catalytic oxidation with oxygen dissolved in water, the formation of a Fe(III) hydroxide layer on the surface and the adsorption of Ni(II) ions on this layer took place. The results of investigations of the layers showed that the Fe : Ni concentration ratio in the layer is 1 : 0.4, while the layer thickness increases by ~ 0.7 nm after every SILD cycle.

VI. Successive ionic layer deposition involving ions and molecules

The use of ionic reagents in one stage and molecular reagents (in the gas or liquid phase) in another stage of treatment allows one to markedly extend the range of obtained objects. This synthetic strategy can be referred to as ionic – molecular layer deposition. This method was first proposed by Tolstoy and Bogdanova[106] for the synthesis of a $BaHPO_4$ protective layer on the surface of carbon steel. The process was carried out in the following way: at a temperature of 280 °C, the steel surface was treated with P_4O_{10} vapour, the excess of the vapour being removed by evacuation; then the specimen was cooled and placed into a solution of a Ba^{2+} salt. After removal of excess salt by washing with water and drying, the sequence of operations was repeated. This gave a dense $BaHPO_4$ layer on the surface, which efficiently protects steel from corrosion.

To carry out alternating treatment with a reagent solution and vapour, the specimen has to be dried in between, which restricts the scope of the procedure. The use of this procedure is justified only if the layer cannot be prepared by SILD using reagent solutions. It has been shown[69] that this situation arises if the layer to be synthesised is dissolved in the solution of either of the reagents. For example, synthesis of the $ScF_3 \cdot n\,H_2O$ layer is accompanied by layer dissolution during treatment with aqueous NaF to give the $[ScF_6]^{3-}$ complex ion. Therefore, a procedure including surface treatment with a solution of the Sc^{3+} salt and with gaseous HF was used for the synthesis.

Yet another example of this sort is the synthesis of Ag_2S layers.[16] It was noted that with aqueous solutions of silver nitrate and sodium sulfid used as the reagents, no reproducible layer is produced, because of either the desorption of silver ions during washing of the specimen with water or the dissolution of the synthesised Ag_2S in excess Na_2S to give thio salts. Therefore, to attain the irreversibility of the surface reactions, a solution of ammoniacal silver with pH 8.8 – 9.2 and gaseous H_2S were used as

the reagents. After adsorption of $Ag(NH_3)_2^+$ cations, excess ammoniacal silver was removed from the substrate surface by washing with a solution of NH_4OH (pH 8.5). After that, the specimen was dried in an air flow at 70–80 °C. Apart from the removal of water, destruction of ammonia complexes took place during drying to give Ag–OH and Ag–O–Ag bonds on the surface. Treatment with gaseous H_2S followed by removal of its excess yielded a silver sulfide layer

$$[M]O-AgOH + H_2S \longrightarrow [M]OAgSH \cdot H_2S_{ads}.$$

The adsorbed hydrogen sulfide molecules and the S–H bonds on the surface served as the adsorption sites for the Ag^+ ions in the following SILD cycle and ensured a regular increase in the layer thickness.

VII. Successive ionic layer deposition involving ions and nanoparticles

The SILD reactions involving ions and nanoparticles were first accomplished by Iler,[6] who studied the conditions for synthesis of multilayers of cations, for example, $Al_2(OH)_5^+$, and nanoparticles from colloidal solutions of SiO_2 or boehmite on a silicate glass surface. Metal cations and negatively charged colloidal SiO_2 particles were successively adsorbed on the glass surface (Fig. 4).

The greatest number of publications is devoted to the synthesis of multilayers with participation of polyelectrolytes in the cationic or anionic form and nanoparticles in colloidal solutions (see Fig. 3). Pioneering studies in this field were published by Kotov *et al.*[107] and Fendler.[108] As an example, note the studies dealing with the syntheses of polyelectrolyte layers and nanoparticles of CdS,[109] CdSe,[110] CdTe,[111] ZnS,[112] PbS,[113] TiO_2,[114] ZrO_2,[115] Ag,[116] Au,[117] SiO_2,[118] MoO_2[119] and Fe_3O_4,[120] which have also been described in a monograph.[11]

Among the most recent studies, noteworthy is the synthesis of mesoporous layers consisting of TiO_2 nanoparticles ~6 nm in diameter on the surface of a gold crystal.[121] A specific feature of this study is that the researchers proposed to use, as the anion, the phytic acid multifunctional anion, which is adsorbed on the surface of TiO_2 nanoparticles through the PO_4^{2-} groups and simultaneously creates the adsorption sites for the next layer of nanoparticles.

VIII. Applications of nanolayers synthesised by successive ionic layer deposition

A highly important trend in the modern materials science is the design of devices with nanometre-range sizes of functional elements. The synthesis of 'hybrid' multilayers consisting of nanolayers of various classes of compounds is also topical, because in this case one can expect new practically valuable properties.

Among the methods used for the synthesis of nano- and multinano-layers, a special place is occupied by layer-by-layer methods, in particular, those using ion-containing solutions as precursors.

The scope of application of SILD reactions for the solution of practical problems is determined by features of the synthesis. In particular, the synthesis can be carried out under mild conditions at room temperature using automated devices with simple hardware; the layer can be applied on the surface of a series of articles of any complex shape, including disperse materials, rather than one article; dilute (10^{-1}–10^{-3} M) solutions with a broad pH range can be used; the thickness of the resulting layer can be precisely controlled, *etc*. These features make this method promising for the synthesis of new protective passivating coatings on metal surfaces, sensors, optical coatings for the devices used for solar energy conversion, electrochromic, photochromic and magnetic materials, biocompatible coatings on the metal surface, polymeric pervaporation membranes, quantum-sized structures for optoelectronics and so on.

Now we will consider several examples of the use of these nanolayers.

1. Synthesis of biochemical and gas sensors

New opportunities for the design of structures comprising an inorganic substrate, a polyelectrolyte multilayer and a biologically active macromolecule were implemented in the existing biochemical sensors.[122]

Several ways of immobilisation of biologically active molecules on the surface of a solid support can be distinguished: adsorption, adsorption in a matrix of a polymer layer fixed on the surface, positioning in space between the surface and a partially permeable membrane or in polymer capsules synthesised by SILD and fixed on a support surface. The last-mentioned version has been used to prepare glucose oxidase (GOx) encapsulated into the PSS/PAH layer and to study its sensory properties with respect to the glucose content in solutions. The sensor showed a linear response in the concentration range of 0–2 mmol litre^{-1} and a non-linear response up to 5 mmol litre^{-1}. Encapsulation results in a pronounced increase in the time of sensor operation.

For deposition of cholesterol oxidase (COx) or cholesterol esterase (CE) layers on the ITO, platinum, mica, quartz or silicon surface, the PSS/PEI multilayers were used as the sublayers.[123] This gave the PSS/PEI/COx, PSS/PEI/COx/PEI/CE, and PSS/PEI/COx–CE/PEI structures. Study of the voltammetric characteristics of these structures has shown that they can find application in flow-type electrochemical cells for detecting cholesterol molecules.

A new approach to addressing the problem of glucose determination in physiological solutions has been proposed.[124]

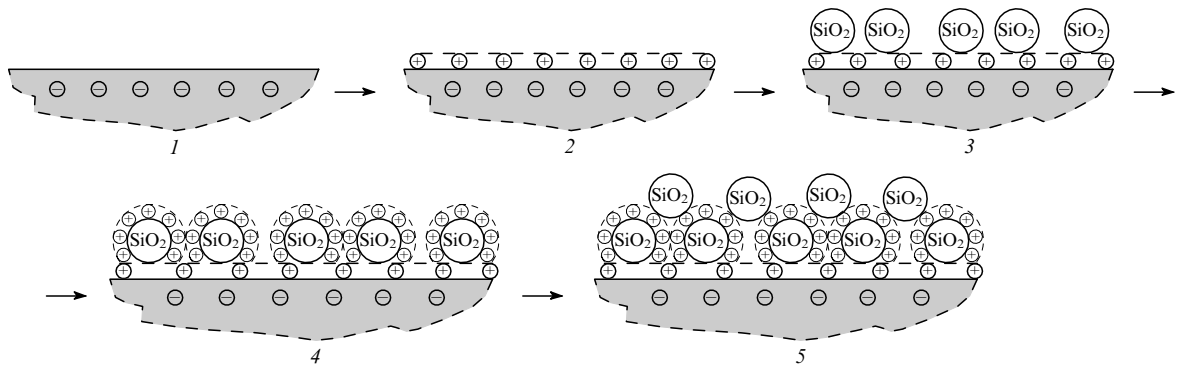


Figure 4. Schemes of SILD reactions involving SiO_2 colloidal particles and an Al(III) solution.
(*1*) Initial substrate, (*2*) after adsorption of Al(III) cations, (*3*) after treatment in a colloidal solution containing SiO_2 particles, (*4*) after adsorption of Al(III) cations, (*5*) after treatment in a colloidal solution containing SiO_2 particles.

According to this approach, the sensor is produced on the basis of the silicon cantilever of an atomic-force microscope coated with the pre-synthesised $(PEI/PSS)_3(PEI/GOx)_3$ layer. Study of the response of this sensor in various physiological solutions has shown that it is sensitive to the range of glucose concentrations of $1 \times 10^{-2} - 1 \times 10^{-3}$ mol litre^{-1}, which can be used for diabetes diagnosis.

If a PAH/PAA multilayer is synthesised on the surface of a quartz resonator (20 cycles),[125] this structure becomes sensitive to the adsorption of smoke particles from air. The adsorption of these particles in the multilayer is reversible: after heating in air or placing into hot water, the sensor restores its initial characteristics.

The ITO/PB/GOx – PAH structure (PB is the Prussian blue) was synthesised on the ITO surface on glass to design a sensor for determinining the glucose concentration in solution.[126] The efficiency of this sensor is due to not only high level of enzyme immobilisation but also to the minimisation of the diffusion problem in nanolayers. The biosensor exhibited high selectivity with respect to glucose in the presence of acetoaminophene, ascorbic and uric acids and proved to be stable for 20 days.

To determine the concentration of oxygen dissolved in water, a sensor based on the $[Ru(bipy)_3]^{2+}$ and PSS (or PDDA) multilayer has been proposed.[127] The layer shows a fluorescence maximum at 620 nm (λ_{excit} = 450 nm) whose intensity depends on the concentration of the dissolved oxygen (in the 0 – 12 mg litre^{-1} range).

In addition to the use as biochemical sensors, the layers synthesised by SILD proved to be efficient as parts of conductometric gas sensors based on SnO_2 films. It is known that modification of SnO_2 with transition metal oxides or noble metal clusters results in the change in adsorption and catalytic properties of the surface with respect to oxygen, water and gas molecules to be detected. This is accompanied by the change in the electrophysical properties of the sensor, and, hence, its response to a change in the concentration of the mixture under analysis. A series of studies devoted to this topic were carried out by Korotchenkov *et al.*[128 – 130] Both the SnO_2 layers synthesised by SILD on the quartz surface and SnO_2 films obtained on a glass-ceramic surface by spray pyrolysis and modified by oxide layers were used as investigation subjects. The SILD synthesis of SnO_2 layers was carried out by the procedure reported by Tolstoy[55] using solutions of SnF_2 and H_2O_2. After 40 SILD cycles, a nanostructured amorphous SnO_2 layer appeared on the substrate surface; after heating at 200 – 400 °C, the layer consisted of 6 – 7-nm particles. Testing of this layer as the conductive layer in sensors for ozone, CO and H_2 demonstrated its high sensitivity with respect to ozone. The sensor shows a fast (about 2 – 3 s) response to the change in the concentration of this gas.

The effect of the layer synthesised on the surface of a SnO_2 film obtained by spray pyrolysis on the properties of the conductometric sensor has been studied.[129] The experiments were carried out for Cu, Co, Mn and Fe metal–oxygen layers and Ag and P metal layers. Prior to testing, all specimens were heated at 300 °C. At this temperature, the initial peroxide or hydroxide layer synthesised by SILD decomposed to give the layer of the metal oxide. It was found that the sensitivity with respect to CO and ozone increases most sharply for the sensor containing Fe – O layers. The synthesis of the Fe – O-containing layers on a SnO_2 film surface results in enhanced 'gas response' of the sensor, whereas the synthesis of Cu – O layers sharply decreases the response in an ozone atmosphere. The Mn – O layers are sensitive to CO.

The synthesis of Pd and Ag layers on the SnO_2 surface increases the 'gas response' of the sensor in a reducing gas atmosphere more than 5 – 10-fold and sharply suppresses the sensitivity towards ozone. For example, after two SILD cycles, the 'gas response' decreases more than 20 – 40-fold for SnO_2 – Pd samples and more than 100-fold for SnO_2 – Ag.

Thus, it follows from the foregoing that the sensitivity and the selectivity of SnO_2-based sensors can be varied over a broad range by synthesising metal and metal oxide nanolayers on the surface.

2. Passivating protective coatings on the steel, zinc and silver surfaces

Nanolayers of inorganic compounds are widely used in the synthesis of passivating protective coatings on the metal surface. However, for some metals the corrosion resistance of this layer is limited due to its low thickness and porosity. Attempts to increase the corrosion stability by creating so-called 'conversion' passivating layers formed upon metal dissolution in a highly alkaline or acidic medium followed by deposition of a porous protective oxide layer on its surface have not provide the desired outcome.

Meanwhile, by using SILD, it is possible to synthesise protective layers under mild conditions using weakly alkaline or neutral solutions and to 'after-grow' the natural oxide layer on the metal. These experiments were carried out by Bogdanova and co-workers.[131 – 134] The layers were synthesised using the SILD method by multiple treatment of the metal pre-passivated in a solution of an oxidant (as a rule, $H_2Cr_2O_7$) with salt solutions containing ions that react to form a poorly soluble compound. In particular, the following processes were conducted successively on a zinc surface. The specimen was placed into a solution of $H_2Cr_2O_7$; as a result, a polymolecular layer of hydrated chromic acid was adsorbed on the surface. Then the specimen was withdrawn and dried in air at 120 – 180 °C, and the excess reagent was removed by water. The specimen was placed into a solution of a metal salt [for example, $Zn(OAc)_2$], dried and washed. This gave a surface layer of poorly soluble zinc chromate, which increased the corrosion resistance of zinc.

Apart from the above method, redox reactions have also been used to form a Cr(III) hydroxide layer.[133]

The effect of nanolayers on the corrosion resistance of metals has also been demonstrated for silver.[131] Corrosion tests were carried out by a drop method in a 0.18 M solution of Na_2S or by keeping the specimen in saturated vapour of a 0.1 M solution of Na_2S until a dark spot of Ag_2S appeared. The results of testing of Cr(III) – Cr(VI)-containing nanolayers showed that the corrosion resistance increases from 2 – 3 to 8 – 9 min as the number of SILD cycles increases from 1 to 6. Typically, the period of stability after six SILD cycles is 2 – 3 times longer than after other types of treatment.

3. Nanomaterials with magnetic properties

A nanomaterial synthesised using colloidal particles of Prussian blue, poly(ethyleneimine) and sodium poly(styrenesulfonate) can be a molecular ferromagnet.[135] The size of colloidal particles was 40 to 100 nm, the number of SILD cycles varied from 6 to 45. Fluorite, quartz, silicon and an ITO layer on glass were used as substrates. The synthesised layers were characterised by cyclic voltammetry, UV and IR spectroscopy, AFM and EPR. The researchers concluded that the concentration of, and the residence time in, the Prussian blue solution influence the content of colloidal particles in the synthesised layer; its magnetic properties at temperatures of 4 – 15 K were studied.

Multilayers of the PAH/PSS polyelectrolyte containing magnetite particles 20 – 30 nm in diameter were synthesised on the surface of melamine-formaldehyde (MF) grains 2.7 μm in diameter and human erythrocytes.[136] After dissolution of the MF matrix in an acidic medium, the polyelectrolyte capsule has nearly preserved its shape and still retained the magnetite particles. For capsules containing erythrocytes, the possibility of changing the orientation in space upon the change in the magnetic field was demonstrated. In view of these results, the researchers cited suggested that new nanomaterials with a unique set of physicochemical properties could be designed on the basis of polyelectrolytes.

Kim *et al.*[137] designed a new material exhibiting magnetic and electrically conductive properties. On a silicon surface, the [(PSS/

PPy)$_3$PSS/ferrite]$_2$ structure was synthesised (PPy is polypyrrole). The ferrite $Co_{0.67}Zn_{0.33}Fe_2O_4$ with 9 nm particles was taken as the nanomaterial with magnetic properties. The layers had a conductivity of 18 S cm^{-1} and exhibited a magnetic hysteresis.

Two procedures for the synthesis of Fe_3O_4 particles in PAH/PSS microcapsules 5.6 μm in diameter have been considered.[138] One is based on impregnation of the inner space of the microcapsule with a colloidal solution containing Fe_3O_4 particles 8 nm in diameter stabilised by citrate anions (pH 4.5). The other procedure involves the synthesis of nanoparticles inside the capsule. To this end, the capsules were kept in aqueous NaOH to create inside a solution with pH 10, which was treated with a solution containing 0.66 mol litre^{-1} of $FeSO_4$ and 0.62 mol litre^{-1} of $Fe_2(SO_4)_3$. This gave magnetite colloidal particles with an average size of 10 nm located inside the capsule.

A multilayer containing 10-nm Fe_3O_4 particles and PDDA macromolecules was prepared on the surface of SiO_2 nanoparticles.[139] It was shown by electron microscopy that one deposition cycle yields a 31 to 43-nm thick layer with a C : Fe ratio of ~ 2.3.

4. Luminophores, structures with a photochromic effect and photocatalysts

Europium-containing polyoxometallate layers exhibit photoluminescent properties. After UV excitation ($\lambda_{excit} = 276$ nm) of the PAH and $[Eu(P_2W_{17}O_{61})_2]^{17-}$ or $[Eu(SiW_{11}O_{39})_2]^{13-}$ layer, luminescence maxima are observed at 594 and 616–622 nm.[88,89] The intensity of the luminescence bands is directly proportional to the number of SILD cycles for layers synthesised in 1–12 cycles. The excitation of a PAH and $[Eu(BW_{11}O_{39})_2]^{15-}$ layer by the UV radiation of a xenon lamp gives rise to photoluminescence peaks at 591 and 613 nm,[90] while for $[Eu(SiW_{10}VO_{39})_2]^{15-}$ and PEI layers excited by the radiation with $\lambda = 310$ nm, the peaks are at 598 and 623 nm.[91] The maximum of the photoluminescence band ($\lambda_{excit} = 276$ nm) from a $[Eu(SiW_{11}O_{39})_2]^{13-}$ and poly(4-vinylpyridine) layer containing Os(2,2′-bipy), which was obtained over 1–9 SILD cycles, was at 617 nm.[92]

A layer containing PEI, $[PMo_{12}O_{40}]^{3-}$ and the $[Ru(bipy)_3]^{2+}$ complex has been synthesised.[93] Study of its photoluminescence showed that UV excitation with a xenon lamp results in an emission spectrum with a peak at 592 nm.

One of the polyanions can be represented by a molecule that gives a fluorescence spectrum. For example, it was shown [140] that a multilayer can be prepared from PVBC or PDDA polycations and fluorescein sodium salt anions. After nine SILD cycles, the PVBC/fluorescein layer exhibited an emission spectrum with peaks at 515 and 557 nm.

A luminescence spectrum was also observed for a multilayer consisting of $CdTe_xS_{1-x}$ nanoparticles 4 nm in diameter and PAH formed after four SILD cycles on the surface of polystyrene (PS) particles with a diameter of 0.6 μm. The emission maximum in the spectrum of this specimen was at 600 nm.[141] On the basis of these results, the researchers concluded that this method is suitable for preparing new coatings for photon crystals.

Layers of PAH and PSS polyelectrolytes with fluorescein isothiocyanate (FITC) on the surface of PS particles with a diameter of 640 nm have been proposed for the design of new class of particles with specified fluorescence and biofunctional properties.[142] Fluorescein isothiocyanate has been used previously as a label in immunochemical and biomedical assays. For the PS/(PAH–FITC/PSS)$_n$ specimen and $\lambda_{excit} = 492$ nm, the fluorescence peak was observed at 526 nm. It was shown that with allowance for the subsequent physical adsorption of proteins (immunoglobulin G), one can carry out biospecific recognition tests.

New multilayers of the hybrid compound $[W_{10}O_{32}]^{4-}$ or $[NaP_5W_{30}O_{110}]^{14-}$ and PEI exhibiting a photochromic effect have been reported.[94] Quartz and silicon served as substrates. The concentration of reagent solutions was 10^{-2} mol litre^{-1} and the residence time in each solution was 20 min. The number of bilayers applied varied from 1 to 12. After UV irradiation of the layers from a mercury lamp, light-blue colour was noted to appear; this was due to the W^{5+} ions resulting from the redox reaction of W^{6+} with the NH_2 groups of PEI. The colour disappears after a 5-min exposure in air, apparently, due to the oxidation of W^{5+} with the atmospheric oxygen.

The colour of the $[NaP_5W_{30}O_{110}]^{14-}$ and PEI layer can arise not only upon the UV irradiation but also on heating *in vacuo* to 120–180 °C.[95] In this case, a similar W^{6+} reduction takes place.

On the silica surface, a PEI/PSS layer and a multilayer composed of PDAC and colloidal particles $Zn_{1-x}Cu_xSe$ stabilised by mercaptopropionic acid were obtained.[143] Excitation of the layer ($\lambda_{excit} = 322$ nm) induced an intensive blue luminescence with a peak at 450 nm, the highest intensity being observed for specimens with 2% Cu^{2+}.

Photocatalysts for the oxidation of the iodide anion and decomposition of methyl orange based on TiO_2 nanoparticles and PAH with PAA have been developed.[144] Fused quartz, glass and silicon plates served as the substrates. The TiO_2 nanoparticles had a size of 4 nm and an anatase crystal structure. Photocatalytic reactions were induced by UV radiation of a xenon lamp (3 h). The specimens with different thickness of the TiO_2/PAH/PAA layer specified by the number of SILD cycles exhibited different activities. The final concentration of ions and molecules involved in the photocatalytic reaction in solution was lower for samples with thicker layers. Hence, no diffusion retardation for the reactants is present in the synthesised multilayer.

It has been shown [145] that polyelectrolyte multilayers on a glass surface may underlie the creation of a five-step photochemical structure having features of a natural photochemical structure analogous to plant leaves. The visible light is absorbed by so-called 'antennas', which represent PAH layers with coumarin (Coum) or fluorescein (Fl) additives and the porphyrin complex of divalent palladium ($PdTSPP^{4-}$) separated by inert $Zr(HPO_4)_2$ or $HTiNbO_5$ layers. Polyviologen molecules in poly(vinyltoluene) (PVT–MV) served as electron acceptors. The highest quantum yield was found for the Coum–PAH/$PdTSPP^{4-}$/Fl–PAH/$HTiNbO_5$/PVT–MV structure.

5. Electronic and optoelectronic devices and electrocatalysts

The synthesis of structures consisting of polyelectrolytes and semiconductor nanoparticles opens up the way for the development of a new class of electroluminescent devices, in particular, multicolour light-emitting diodes.[146–152] These diodes can consist of a polymer with *p*-type of conduction, *viz*., poly(*p*-phenylenevinylene) (PPV) and an *n*-type semiconductor (CdSe).

A brief review on the scope of the synthetic methods in question for the development of nanolayer-based diodes has been reported.[153] The following structures were considered: ITO/PPV/(HDT/CdSe)$_n$/Al layer (HDT is 1,6-hexanedithiol), ITO/PPy/(HDT/CdSe)$_3$/Al layer, ITO/(PDDA/TiO_2-nano)$_{10}$/PDDA/(GO)$_{30}$/PDDA/Au layer (GO is oxidised graphite), (*p*- or *n*-)Si–(Si-nano)PPy/Au layer. The CdSe nanoparticles in these structures had the size of 2–4 nm, TiO_2; 2.3 nm; Si, 5 nm.

Zener diodes have been produced.[154] To this end, a PPy layer and then (after several cycles), a PAH/CdSe layer were applied onto a gold substrate pre-treated with 2-mercaptoethylamine hydrochloride. The particle size of this compound was 2.0 nm. An aluminium layer sputtered onto the surface of a planar structure served as the second electrode. The synthesised nanolayers were studied by UV/Vis emission and absorption spectroscopy, AFM, X-Ray photoelectron spectroscopy and electrochemical methods.

Light-emitting diodes incorporating polyelectrolyte layers synthesised using SILD reactions have also been reported.[84,155,156]

The possibilities of the design of materials for optoelectronics have been considered [157–159] in relation to the layer-by-layer synthesis of a multilayer containing electron-conductive CdTe nanoparticles and hole-conductive polymers (for example, polyaniline and polypyrrole).

A new method for immobilisation of 5-nm CdS nanoparticles stabilised on the surface with 3-mercaptopropyltrimethoxysilane has been developed.[160] The method is based on nanoparticle adsorption on the substrate surface and hydrolysis of the Si–OMe groups of nanoparticles to give SiOH groups, which serve as the immobilisation sites in the next cycle of adsorption. The sequence of layer deposition cycles on the surface yields a multilayer of CdS nanoparticles non-uniformly coated by a SiO_2 layer. The photochemical reaction of CdS with atmospheric oxygen yields $CdSO_4$, which is water-soluble. The nanoparticle diameter decreases and they become enclosed in a SiO_2 nanocapsule.

In addition to semiconductor nanoparticles, an organic molecule giving an electroluminescence spectrum can be built-in into the multilayer of cationic and anionic polyelectrolytes. A light emitting diode was manufactured based on the PAH polycation, PAA polyanion and the Evans blue dye.[161] The multilayer consisting of five bilayers was applied onto ITO-supported glass, heated *in vacuo* for 3 h at 120 °C, and coated with an aluminium layer by sputtering. Study of the electroluminescence intensity showed that the structure synthesised in this way has 2–3 times better parameters than the structure based on an Evans blue layer obtained by solvent evaporation on a rotating substrate.

Recent years have seen the enhanced interest in the synthesis of conductive polymer layers transparent in the visible region, in particular, PEDOT/PSS [PEDOT is poly(3,4-ethylenedioxythiophene)]. These layers are used in electroluminescent cells as buffers between the layer of a transparent conductive ITO and a layer of organic molecules with hole conduction. These polymers were obtained by SILD.[162] To reduce the roughness on the layer surface, ultrasonic pre-treatment of the solution of PEDOT/PSS was carried out to destroy large colloidal particles. The resulting layers had a hole diffusion constant of 5×10^{-10} cm^2 s^{-1}, which is better than that for the layers synthesised by the mixing procedure.

The electrooptical properties of the layers obtained by SILD from high- and low-molecular-mass polyelectrolytes, PAH and PSS, have been studied.[163] It was found that stable layers are formed at pH 4.

A series of works on the synthesis and study of the nanowire exhibiting a diode effect was performed by Mallouk, Kovtyukhova, *et al.*[164–166] First, a silver layer was applied by the electrochemical method as one of the contacts into the 70–200 nm pores of the Al_2O_3 film obtained by anodic treatment of Al or into a polycarbonate membrane. Then TiO_2/PSS, ZnO/PSS or ZnO/PAH layers were formed in nine SILD cycles, and the second contact, *viz.*, a gold or platinum layer, was synthesised on the surface by an electrochemical procedure. The oxide or polycarbonate matrix was dissolved. The 'nanowire' thus formed showed voltammetric characteristics corresponding to the rectifying effect.

The structure metal–insulator–gold nanoparticles–insulator–metal, functioning as a one-electron tunnelling device, has been produced.[167] The size of gold nanoparticles was 2.5 nm and the insulator was represented by a multilayer containing α-$Zr(HPO_4)_2 \cdot H_2O$ and PAH nanoparticles. The 'upper' conductive layer which ensured the contact consisted of polypyrrole applied by polymerisation.

The properties of the Ag_2S,[17] $(CdS)_x(Bi_2S_3)_{1-x}$,[49] Bi_2Se_3[50] and $Bi_2Se_3 - Sb_2Se_3$[52] nanolayers synthesised by SILD have been studied within the solar cells. The photoelectrochemical characteristics were obtained for the cells comprising an electrode that included a fluorinated tin oxide layer coated with a sulfide or selenide layer synthesised on its surface, a carbon electrode and a polysulfide electrolyte layer ($Na_2S + NaOH + S$). For these cells, electrophysical characteristics in the light and in the dark, spectral and temporal response and other parameters were studied.

Photoelectrochemical characteristics were also measured for a cell consisting of an electrode represented by a thin layer of fluorinated SnO_2 on a glass surface and a TiO_2 layer applied thereon (from a TiF_4 solution).[168] To create internal porosity in this layer, prior to its deposition, a PAH/PAA layer was synthesised on the substrate in ten SILD cycles, and the resulting structure was heated in air at 650 °C to remove organic substances. A 0.3 M solution of LiI and a 0.03 M solution of I_2 in acetonitrile served as the electrolyte in this cell. Platinum was the counter electrode. The nanostructured TiO_2 layers showed a fourfold higher degree of light to electrical energy conversion than analogous continuous layers.

For the same purpose, SILD syntheses of polymer-based layers have been carried out.[169] Glass plates coated with an ITO layer were the substrates, and fullerene molecules positively or negatively charged by PPV and PSS polyelectrolytes and PAH served as the reagents. After 20–74 SILD cycles, the substrates were dried *in vacuo* at 270 °C and coated with a 200-nm thick Al layer. The voltammetric characteristics of the resulting structures were measured. A photoresponse whose magnitude depended on the 'architecture' of the resulting multilayer was found.

An important field of application of the SILD method is the development of new thin-layer structures exhibiting electrochromic effects. This was observed in relation to nanolayers of organic, inorganic and hybrid compounds. A polymer layer was obtained[170] on the ITO surface after successive treatments of the substrate in solutions of PANBUS, which is the anionic form of a polyelectrolyte, and VDAC, which is a polycation in solutions. The electrochemical cell contained ITO-coated glass with the PANBUS–VDAC bilayer applied by SILD as one electrode, an ITO layer on glass as the second electrode and the CF_3SO_3Li solid electrolyte in a photopolymerised polymer. Upon application of a potential from −3.0 to +3.0, the cell colour changed from yellow to dark-green. At 1–10 bilayers, the response time of the cell was ~10 s. If the number of bilayers exceeded 10, the response time sharply increased to be up to 24 s. Thus, the 'depth' of the colour of the active layer can be varied with high accuracy by specifying its thickness.

Electrochromic properties were found for layers of the hybrid compound consisting of tungstic acid and 4,4′-BPPOBp.[171]

A large number of publications report the synthesis of multilayers on the surface of electrodes and the study of their electrocatalytic activities. For example, it was found that the PDDA and cobalt tetrasulfophthalocyanine multilayer synthesised on a glass carbon surface[172] functions as an electrocatalyst in the oxidation of hydrazine; the multilayer comprising $[P_2W_{17}O_{61}]^{7-}$ and the complex obtained by the reaction of poly(4-vinylpyridine) with osmium bis(2,2′-bipy) chloride (*n*QPVP–Os)[173] reduces H_2O_2, NO_2^- and BrO_3^-; multilayers of PDDA and glucose oxidase involved in the redox reactions of enzymes were also studied. The properties of the layer of phosphomolybdic acid and PAMAM were studied on the surface of a gold electrode;[174] this layer was an efficient electrocatalyst in nitrite reduction and arsenite oxidation; an $H_5SiMo_{11}VO_{40}$ and *n*QPVP–Os layer[175] was studied in the electrocatalytic reduction of BrO_3^- and HNO_2; and the layer of tris(2,2′-bipyridyl)ruthenium and sodium decatungstate on the ITO surface[176] was found to function as an electrocatalyst in the reduction of iodate ions and oxidation of oxalate ions. New electrodes exhibiting unique redox properties were produced on the basis of multilayers containing PSS polyelectrolyte and Co(II) ions with a supramolecular ligand [for example, 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene[177]].

6. Biomaterials and polymer membranes

Using the layer-by-layer procedure and polyelectrolytes, it is possible to incorporate biologically active molecules into the layer being synthesised, to carry out immobilisation on various surfaces and encapsulation. A multilayer of this type has been prepared[178] on the surface of quartz in aqueous solutions of TMPyP and DNA using 2–20 cycles. The DNA/hexadecylamine multilayers were prepared[179] on the fluorite, quartz and silicon surfaces; the DNA/PDDA layer was formed on the glassy carbon and quartz surfaces;[180] DNA/PLL, on the quartz, silicon and mica

surfaces.[181] The PEI and DNA multilayer was produced on the surface of polylactic acid.[182]

This method provides the possibility of partial solution of the biocompatibility problem of different materials by the synthesis of multilayers on their surfaces. For example, the hydrophobic surface of the major material of contact lenses permeable for oxygen molecules can be made hydrophilic and compatible with eye tissues by coating it with a polyelectrolyte multilayer (6–20 cycles).[183]

For solving the biocompatibility problem for stainless steel and blood, it has been proposed [184] to use multilayers synthesised by multiple alternating treatment of steel surface in PEI and albumin solutions (in a citrate–phosphate buffer with pH 7.4). The morphology of these layers was studied by AFM. Investigations showed that 11 cycles of treatment of steel surface give a layer stable for 40 days which sharply increases the haemocompatibility. This synthesis was recommended for preparing biocompatible layers on the surfaces of other inorganic substrates.

Other researchers [185] increased the biocompatibility of stainless steel with blood by coating the steel surface with a PEI and heparin multilayer, which remained stable for 21 day after 13 cycles of SILD synthesis. The synthesis of such layers is possible on the surfaces of substrates having complicated shapes, in particular, on the inner surface of blood vessels.

The application of a polyelectrolyte layer on the surface with a complicated shape is used for encapsulation of various particles. The publications of Donat *et al.*,[186] Caruso *et al.*[187] and Radchenko *et al.*[188] should be considered among the first one along this line. First, a layer of macromolecules (in this case, a dextrin layer) is adsorbed on the surface of a matrix microparticle, for example, MF; subsequently, a PSS/PAH multilayer is deposited on its surface in four cycles. After dissolution of MF in 0.1 M HCl, dextrin becomes situated inside the PSS/PAH capsule (Fig. 5).

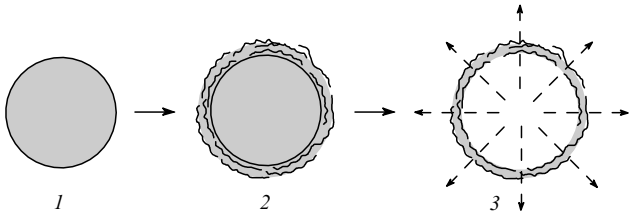


Figure 5. Scheme of SILD synthesis of a capsule on the surface of a solid particle.
(*1*) Initial particle; (*2*) after deposition of a multilayer consisting of cation- and anion-containing polyelectrolytes; (*3*) after dissolution of the initial particle.

The permeability of the PSS/PAH capsules for various compounds reversibly depends on pH.[189] When pH is low, defects and voids up to 100 nm in diameter appear on the walls due to the surface charge. This increases the permeability. In neutral and weakly alkaline media, the permeability disappears.

Apart from colloidal particles, biological blood cells or bacterial spores can be encapsulated into a polymer multilayer. In particular, the PDDA/PSS multilayers formed after two or four cycles [190] increased the adhesion of cells to the silicon surface (AFM study).

The multilayers of PEI/alginate or alginate/poly(L-lysine) polyelectrolytes on the surface of polylactic acid enhance its cytocompatibility with respect to chondrocyte cells, in particular, they are favourable for cell fastening on the surface, growth and activity.[191]

New systems for drug delivery in the form of microcapsules based on alginate/protamine multilayers have been proposed.[192] The encapsulation procedure of a biologically active compound (α-chymotrypsin) was based on its electrostatic interaction with alginate molecules inside the capsule. A $\sim$ 6.5 μm capsule accommodated up to 10^9 molecules, which is almost 1000 times larger than this value for the PSS/PHH capsule. For encapsulation of poorly soluble compounds, it has been proposed [97] to incorporate them into the multilayer of the capsule wall and then dissolve the matrix core; hence, the compound gets inside the capsule.

The possibility of increasing the time of action of drugs through encapsulation by polyelectrolyte layers has been considered.[193] Furosemide microcrystals with a size of 5 μm covered with 45- to 125-nm thick gelatin/PSS and gelatin/PDDA nanolayers served as the investigation subjects. The application of a layer formed in 2–6 SILD cycles on the single crystal surface increases the time of action of drugs 50– 300-fold. The effect of multilayers on the solubility of biologically active compounds was elucidated taking dissolution of the initial and modified naproxen crystals as an example.[194] The alginate/gelatin, dextran/gelatin, PAA/chitosan and dextran/chitosan layers were used.

Polyelectrolyte multilayers can serve as efficient membranes for the separation of liquid and gas mixtures. The important characteristics of such membranes are the selectivity and high permeability with respect to one of the components. The SILD method provides a unique opportunity for the design of high performance membranes for pervaporation of low-molecular-mass compounds. On the one hand, it allows one to form continuous polyelectrolyte layers, and on the other hand, it is possible to specify precisely the layer thickness and modify the composition (by various additives) thus changing the permeability. The properties of membranes based on multilayers of chitosan, PEI and PDDA polycations and PAA, alginic acid and PSS polyanions have been studied.[195, 196] The density of ionogenic chemical groups was found to be an important parameter of a PEI membrane that increases the selectivity in the separation of a mixture of low-molecular-mass alcohols. Water removal from ethanol and isopropyl alcohol with a separation factor of 10 000 for a PEI/PAA membrane was observed for the multilayer obtained over six SILD cycles. The number of these groups is also important for increasing the membrane stability and enhancing the interaction at the substrate–membrane interface. Examples of separation of water and alcohols have been reported.[197–199]

A membrane based on polyelectrolyte multilayers is also used for the separation of salt mixtures. The ion transport through ultrathin poly(vinylammonium)/poly(vinylsulfate) membranes, obtained by SILD using aqueous solutions of two polyelectrolytes, has been studied.[200] The spectroscopic study of the permeability showed that the transport of $CuCl_2$, $LaCl_3$, $BaCl_2$ and $K_4[Fe(CN)_6]$ is accompanied by simultaneous 'intercalation' of cations or anionic metal complexes into the membrane. In the case of Cu^{2+}, La^{3+} or $[Fe(CN)_6]^{4-}$ ions, intermolecular bonds are formed inside the membrane, thus decreasing its permeability with respect to other sals, for example, NaCl and KCl. Conversely, the Ba^{2+} ions induce a decrease in the number of bonds; hence, the membrane permeability with respect to NaCl and KCl increases.

On the basis of poly(ethylene glycol methacrylate) and linear poly(2-hydroxyethyl methacrylate) layer on the porous Al_2O_3 substrate, membranes for the separation of $O_2–N_2$ (with a selectivity of $\sim$ 2) and $CO_2–CH_4$ (with a selectivity of $\sim$ 20) gas mixtures were developed.[201] The porous structure of the substrate was not changed and the layer thickness was $\sim$ 50 nm.

Thus, different types of the SILD reactions are widely used to prepare nanostructures of inorganic and hybrid compounds on the substrate surfaces. Further development of studies along this line would apparently be related to variation of the layer composition by using diverse substrates and to the synthesis of new multilayers. This would extend the scope of practical application of nanolayers in nanotechnology.

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