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ORIGINAL CONTRIBUTIONS

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Layer-by-layer self-assembly preparation of layered double hydroxide/polyelectrolyte nanofilms monitored by surface plasmon resonance spectroscopy

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Abstract Layer-by-layer self-assembly was used to prepare nanofilms of (2:1) MgAl-layered double hydroxide (LDH) nanoparticles and polyacrylic acid or sodium polystyrene sulfonate. The multilayers were attached to ~50-nm thick gold films on microscopy glass slides prepared by vacuum evaporation. The contact between the gold film and the multilayered films was mediated via surface modification with thiols, adsorption of poly(diallyl dimethyl ammonium) chloride (PDDA) or direct binding of the LDH particles. Surface plasmon resonance (SPR) spectra of the multilayered films were analyzed by fitting the Fresnel equations. The shifts in the SPR angle ($\Delta\Theta_{SPR}$) due to the adsorption/deposition on the gold surface were used to evaluate the process of building up the multilayers. Strong surface/multilayer contact formed when electrostatic attraction and hydrophobic interaction were combined as in the case of mercaptopropanoic acid or PDDA sticking layers. The LDH suspension concentration strongly influenced the number of deposited layers. The multilayer films were investigated by reflection FT-IR spectroscopy.

Keywords Layered double hydroxide · Layer-by-layer self-assembly · Surface plasmon resonance spectroscopy · Polyelectrolytes · Nanofilms

Introduction

Polymer/solid composite structures organized in two dimensions, such as nanostructured multilayered films or nanocapsules, find application in industry and technology as materials with specifically designed properties [1, 2]. Their biological importance is due to the fact that inorganic/polymer compositions can be designed to imitate and/or simulate various biomineralization processes [3, 4]. The synthesis of such structures is based on supramolecular interactions ranging from Coulomb electrostatic attraction to hydrophobic interactions [5].

Layer-by-layer (L-B-L) self-assembly is a versatile tool to build supramolecular structures and nanostructures using various macromolecular and particulate building blocks [6, 7]. Although the first effort of R.K. Iler to build multilayers concerned alternate deposition of oppositely charged colloidal particles [8], posterior advances—presumably due to practical demands—showed up in applications of polyelectrolytes [9–11] and biopolymers or proteins [12–14] as layers, alternately deposited with colloidal solids. Alternate polyanions and polycations were also deposited alternately to give multilayered films [15, 16]. Anionic clay mineral particles with cationic polyelectrolytes were used to build sandwiched structures. Surface plasmon resonance (SPR) spectroscopy was established as an effective experimental method of the investigation [17, 18]. For SPR spectroscopic investigation, polyelectrolyte and inorganic particles are alternately deposited on a gold (or other metal) surface producing the surface plasmon electronic state. The deposition of the first layer is generally mediated by molecules chemically attached to the gold surface. Thiols (organic molecules with –SH end groups) are most frequently used for surface modification [19, 20].

The purpose of the L-B-L nanolayer deposition is to improve material properties such as electron transfer properties, antireflection, insulation, and mechanical or thermal properties. In addition, they find application in the ever-increasing field of sensors and biosensors [12].

We prepared L-B-L multilayers on the gold surface using the positively charged colloidal particles of (2:1) MgAl-layered double hydroxide (LDH) and anionic polyelectrolytes. LDH is an alternative choice of an ion-exchange material in addition to clay minerals [21]. The areas of application of the anion exchanger LDHs are being exploited at present.

Materials and methods

Materials

$Al(NO_3)_3{\cdot}H_2O$, $Mg(NO_3)_2{\cdot}6\ H_2O$, NaOH and $NaNO_3$ for LDH preparation were analytical grade reagents from Reanal, Hungary. Chromium plates (99.5% purity, Aldrich) and gold wires (99.9% purity, Aldrich) were evaporated on microscopy glass slides. To modify the gold surface, we used 2-mercaptoethanol (ME) (Fluka, purum) and 3-mercaptopropanoic acid (MA) (Fluka, purum). Polyacrylic acid (PAA, M_w ~$7.5{\times}10^5$), sodium polystyrene sulfonate (PSS, M_w ~10^6) and poly(diallyl dimethyl ammonium chloride) (PDDA, M_w ~4.0–$5.0{\times}10^5$) were Aldrich reagents.

LDH preparation

The LDH was prepared according to the standard co-precipitation method and crystallization. A mixture of 0.2 M of $Al(NO_3)_3{\cdot}H_2O$ and 0.2 M of $Mg(NO_3)_2{\cdot}6\ H_2O$ in 600 cm^3 boiled distilled water was added gradually (within 4 min) to a mixture of 0.35 M of NaOH and 0.12 M of $NaNO_3$ in 3,400 cm^3 boiled distilled water under continuous stirring. The precipitate was stirred at pH = 9 (adjusted using NaOH or HNO_3 solution), at 60–65 °C for 5 h in N_2 stream, then aged at room temperature for 1 week. During ageing, the supernatant was collected every second day, and the sediment diluted with distilled water. Finally, the suspension was centrifuged at 3,000 rpm for 12 min. After washing with distilled water several times, the sample was finally washed with ethanol. The LDH was dried at 100 °C and stored in a stoppered bottle, filled with N_2 gas to save the sample against atmospheric CO_2 [22].

Glass surface treatment for SPR experiments: coating with gold and functionalization

Microscopy glass slides were cleaned with chromic acid and thoroughly washed with distilled water, followed by drying in a N_2 stream. After cleaning, the plates were used immediately for preparation of the gold coating. First, a very thin chromium layer (~0.5 nm) was deposited to prevent the successive gold layer from detaching in a fluid flow. Onto the top of the chromium layer, a ~50-nm thick gold layer was deposited in high vacuum, evaproating gold wires at 120 A for 30 s.

The gold-coated glass plates were cleaned with ethanol and dried in N_2 flow before use. For the LDH/polyelectrolyte multilayer deposition, several substrate surfaces were applied:

1. Clean bare gold surface.
2. Gold surface modified with mercaptoethanol (ME): 10^{-4} M ethanolic solution of $HS–C_2H_4–OH$ was kept in contact with the gold-coated glass surface in the sample holder of the SPR spectrometer for 6 h [18]. After washing with ethanol, the layer was dried with N_2.
3. Gold surface modified with mercapto-propanoic acid (MA) followed by base addition to generate the negatively charged surface: 10^{-5} M ethanolic solution of $HS–C_2H_4–COOH$ was applied to the gold substrate in the SPR sample holder for 16 h, then the surface was washed with ethanol and dried in N_2. Next, the surface-modifying layer was treated with 10^{-2} M NaOH solution and subsequently dried.

Multilayer preparation

The LDH/polyelectrolyte multilayers were prepared in two ways, represented as procedure A and B in Fig. 1. In procedure A, the LDH layer was built directly on the bare or modified gold surface (1, 2 or 3), followed by the anionic polyelectrolyte layer (PAA or PSS). In procedure B, PDDA was attached to the bare gold surface, followed by the adsorption of PAA or PSS. LDH was deposited in the next adsorption step. The substrate was fixed in the SPR liquid cell sample holder (Fig. 2.) during all the sequential adsorption steps. The LDH suspension or the polyelectrolyte solutions were filled in the cell and left for half an hour. Next, the solutions were

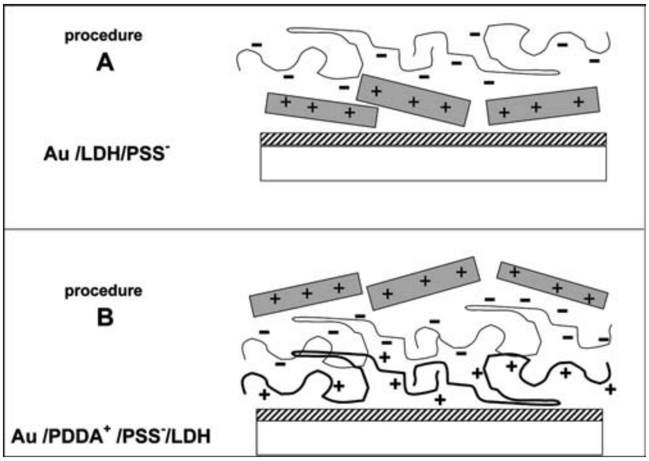


Fig. 1 Multilayer preparation. The first layer on gold or modified gold is a positively charged LDH particle (procedure A) or the cationic polyelectrolyte (PDDA) layer (procedure B). The second layer is the anionic (−) polymer layer (PAA or PSS). The LDH/polyanion sequence is then repeated several times

pumped off and the surface cleaned with 500 cm^3 distilled water and subsequently air dried before the addition of the next adsorbate solution. The LDH dispersions in distilled water were prepared in 0.1, 0.5, 1.5 and 5.0% concentration, and the pH was adjusted to 8.5. The polyelectrolytes were used as 0.01% (PAA), 0.1% (PSS) and 1.0% (PDDA) aqueous solutions. The pH of the solutions were ~4.5 (PAA) and ~6.8 (PSS).

LDH particle characterization

Potentiometric acid-base titration of the LDH sample in 0.01 M KNO_3 electrolyte medium was performed according to the procedure described in [23, 24]. We used a CO_2-free titration setup consisting of Dosimat 665 (Methrom) automatic burettes, and an OP 0808P combined glass electrode (Radelkis, Hungary). A homemade potentiometer/data converter/titration software system (GIMET) was applied.

The electrokinetic potential and the particle-size distribution were determined in a dynamic light-scattering apparatus (Malvern ZetaSizer 4 with a 5-mW power He–Ne, $\lambda = 633$ nm, laser source).

Multilayered nanofilm characterization: SPR, AFM and FT-IR methods

The stepwise construction of the multilayered LDH/polyelectrolyte sandwich structures was followed in SPR spectrometer by using the Kretschmann–Raether configuration, as represented in Fig. 2 [25, 26]. P-polarized He–Ne laser light was reflected from the sample, incident through a right-angle coupling prism. The refractive index of the prism corresponded with that of the glass substrate ($n = 1.518$). An index matching fluid was used between the prism and substrate. The angle of incidence was changed with an Oriel 13049-type goniometer.

The structure of the LDH/polyelectrolyte films was visualized in AFM (Multimode Scanning Probe Microscope, Digital Instruments, in contact mode).

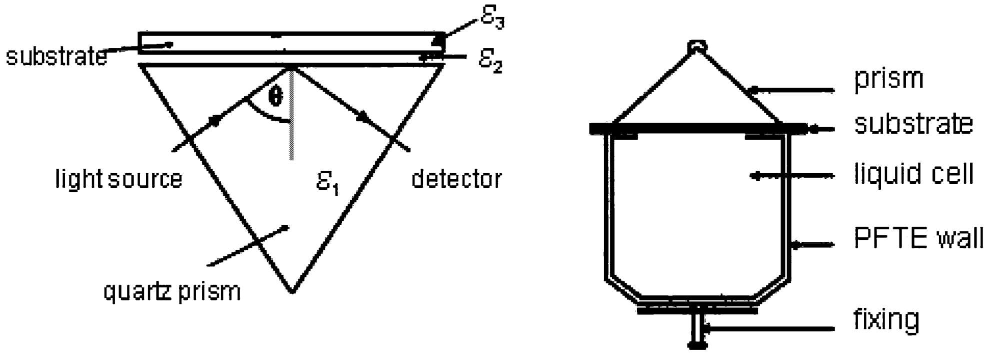
FT-IR reflection absorption spectra of the self-assembled multilayers were taken with a Bio-Rad Digilab Division FTS-65A/896 type spectrometer with a DTGS detector, at 4-cm^{-1} resolution, taking the average of 256 measured interferograms. The incidence angle was 30° and a gold mirror was used as the reference.

Results and discussion

LDH characterization

Potentiometric acid-base titration and electrokinetic measurement results for the LDH sample investigated are seen in Fig. 3. The net proton consumption in acid-base titrations results from all possible pH-sensitive processes. It can be equated to the surface-charge density only if several specific conditions are met [27, 28], ensuring that the change in pH is solely due to dissociation of surface groups. In the case of LDH, the net pH

Fig. 2 The sample holder of the SPR spectrometer. *Left* Connection of the light-coupling prism to the glass slide, by using an index-matching fluid. The upper side of the glass plate is gold-coated. *Right* Fluid-sample holder attached to the gold-coated side of the substrate



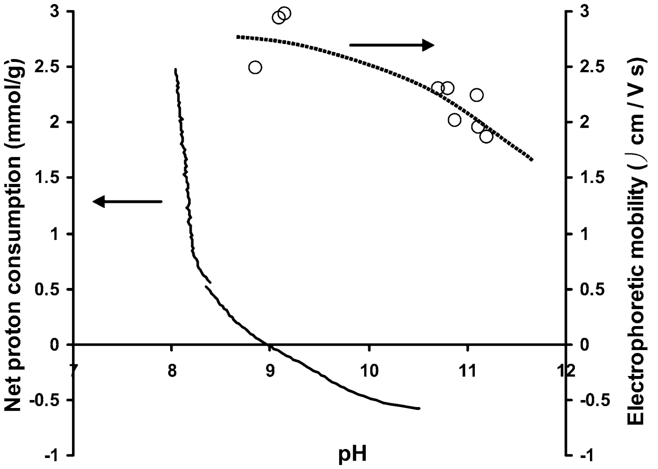


Fig. 3 Net proton consumption and electrophoretic mobility of LDH particles as a function of pH, determined in 0.01 M KNO_3

change results form at least three separate processes. First, with increasing pH, the hydroxide ions gradually replace the anions ($NO^{-}{}_{3}$ in our sample) by ion exchange. This process is expressed as a negative proton consumption (proton release). Second, surface Al oxide, hydroxide groups at the particle edge form negatively or positively charged sites depending on the pH of the medium, with a point of zero charge in the range of pH ~9. The proton consumption due to this process is positive at $pH < 9$, and negative at $pH > 9$. The third component in the total pH-change process is the large proton consumption due to the dissolution of LDH at $pH = 8$, seen in Fig. 3 as a steep rise in positive net-proton consumption. There is no solid LDH phase in equilibrium with the aqueous environment at $pH < 8$. The electrokinetic mobilities are large positive values in the entire measured pH range (from 9 to 11), as it is expected for an anion exchanger.

The *z*-average mean particle diameter in the aqueous LDH suspension (pH adjusted to 8.5 using KOH solution) was 400 nm as measured by dynamic light scattering. The range of the size distribution was relatively narrow (between 250 nm and 600 nm), suggesting that the suspension at this pH consisted of primary particles, and the presence of bigger aggregates can be excluded.

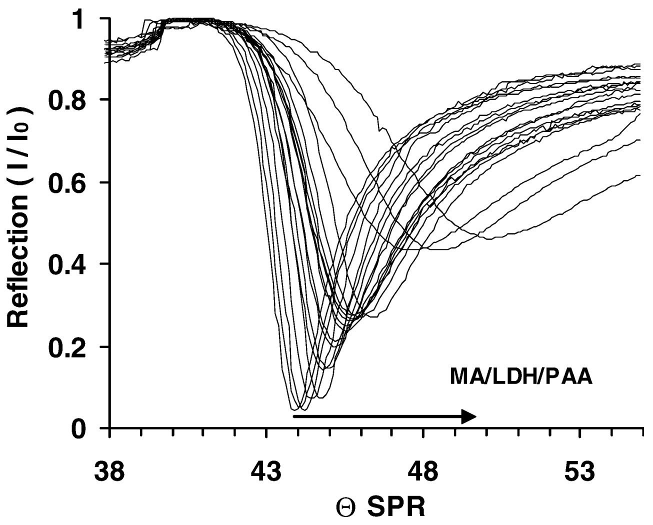


Fig. 4 SPR curves of the LDH/PAA multilayer films prepared on the 3-mercapto propanoate-modified gold surface. The *arrow* indicates the shifting of the SPR curves from that on the bare gold surface due to the successive multilayer buildup

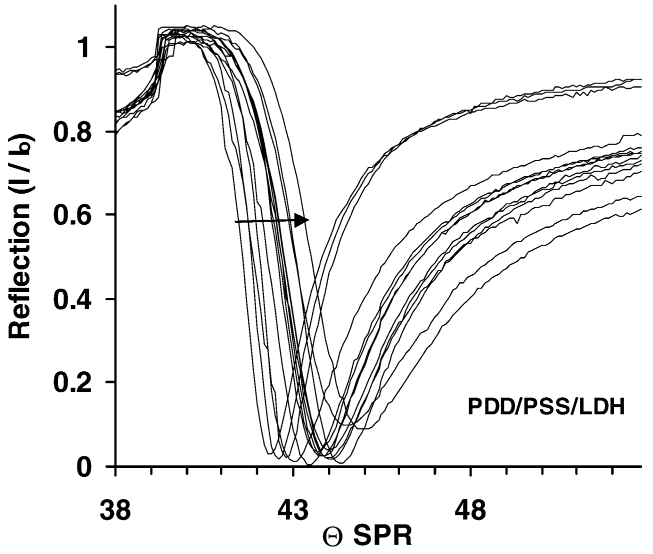


Fig. 5 SPR curves of the PSS/LDH multilayer films prepared on the PDDA-modified gold surface. The *arrow* indicates the shifting of the SPR curves from that on the bare gold surface due to the successive multilayer buildup

Film sturcutre characterization

Surface plasmon resonance spectroscopy and AFM

The SPR spectra of the LDH/polyelectrolyte multilayers (Figs. 4, 5) were analyzed on the basis of the Fresnel equations using the SPALL 4 curve fitting software [29, 30]. The dielectric constants (ε' and ε'', the real and imaginary part of the complex dielectric constant) and the thickness (*d*) of the individual layers are fitting parameters. The results of the sandwich structures prepared from the 0.1% LDH suspension following procedure A (with PAA) and B (with PSS) are collected in Table 1 and Table 2.

Using procedure A and gold/LDH attachment (1) 5 layers were formed in total. Only the SPR curves of the first 3 layers could be successfully fitted. In the attachment strategy (2), it was not possible to create multi-

Table 1 Fitting of the SPR curves for multilayer films prepared by procedure A

Method	Layer	ε′	*d* (nm)
Gold/LDH	Gold	−12.7	40.6
	LDH	4.99	2.5
	PAA	1.25	1.8
Gold/ME	Gold	−10.8	52.4
	ME[a]	1.45	0.8
Gold/MA	Gold	−10.8	48.5
	MA	1.99	0.7
	LDH	9.98	3.2
	PAA	1.32	2.3
	LDH	10.15	1.8
	PAA	1.32	1.6

[a] No attachement of LDH particles

Table 2 Fitting of the SPR curves of multilayer films prepared by procedure B

Layer	ε′	*d* (nm)
Gold	−10.8	52.4
PDDA	1.26	2.5
PSS	1.45	1.6
LDH	9.56	0.6
PSS	1.26	1.5
LDH	10.5	2.2

layered structures, because the LDH particles did not adsorb at the ME-modified gold surface. However, using the gold/MA attachment strategy (3) 18 layers formed in total, and the SPR curves (Fig. 4) of the first 6 layers were successfully fitted. The results of the three different attachment strategies show that the effect of charge density at the solid surface is of primary importance to the anchoring strength. The carboxylic groups at the MA-modified gold surface (3) are fully dissociated at the pH of the LDH suspension (pH = 8.5) from which the particles are deposited. LDH adsorbs via ion–ion electrostatic interaction, creating a stable basis for the consecutive polyelectrolyte/LDH adsorption layers. The bare gold surface (1) is polarized in the aqueous medium, also attracting the positively charged LDH particles. However, the latter ion-dipole electrostatic attraction is weaker and, consequently, the number of possible LDH/polyelectrolyte layers at the surface is smaller. The absence of LDH adsorption at the ME-modified gold surface (2) can be explained by the fact that the modifying alcohol molecules render the surface uncharged.

In procedure B, PDDA polycations were used as the sticking layer, followed by a PSS layer. Altogether 12 layers formed (Fig. 5), of which the first 6 curves were successfully fitted (Table 2).

Comparing the results from procedures A and B, it is apparent that both MA and PDDA very effectively bind the first layer of the multilayer stack by electrostatic attraction to the gold surface. However, a higher number of layers was built up by using PAA (3) than PSS (B). This difference is explained by the different degrees of dissociation of the polyelectrolytes. The dissociation

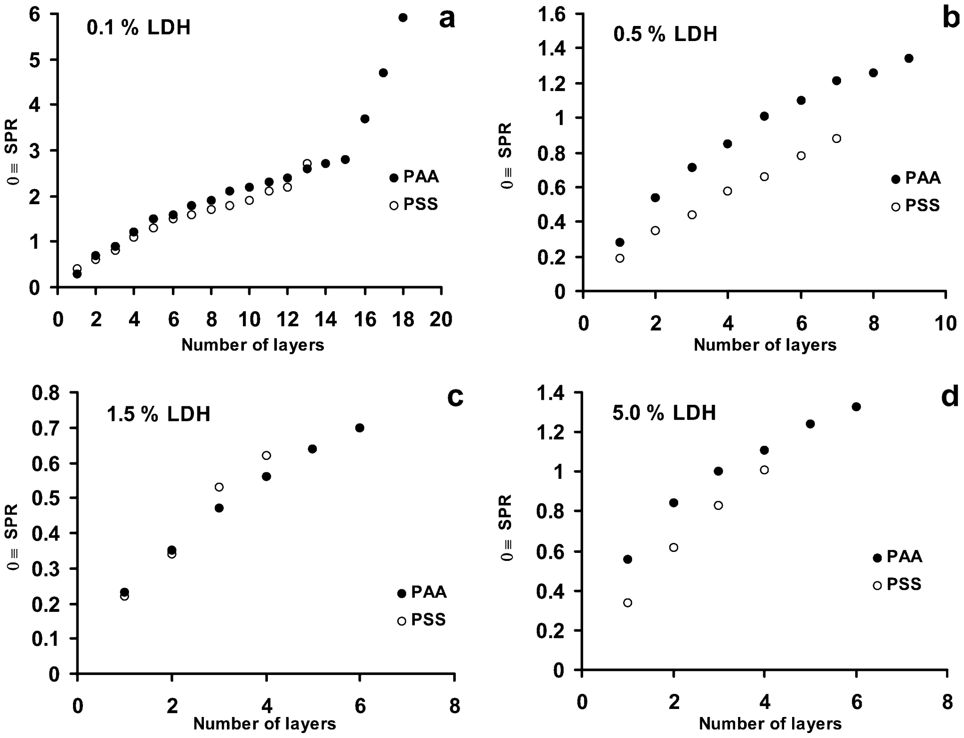


Fig. 6 Plots of the shifts of the SPR angle ($\Delta\Theta_{SPR}$) with increasing number of layers at different LDH suspension concentrations

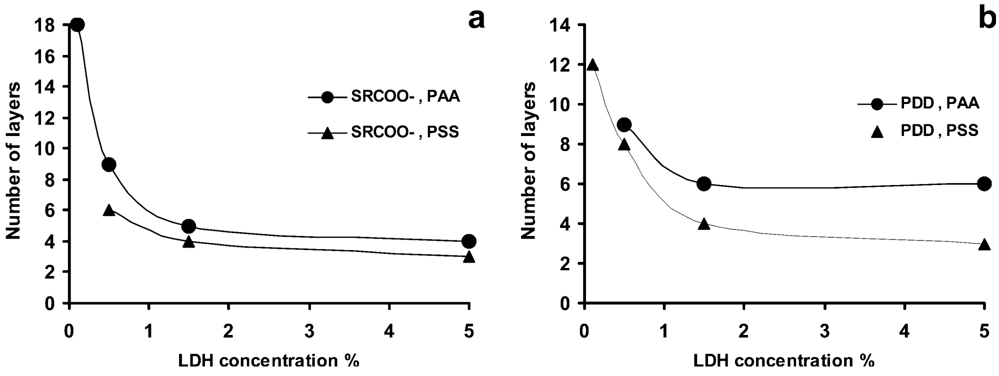


Fig. 7 The effect of the LDH suspension concentration on the maximum number of deposited layers (LDH and PAA or PSS) on 3-mercapto propanoate (**a**) and on the PDDA (**b**) modified gold surface

of the carboxyl groups of PAA is low (solution pH ~4.5, apparent $pK_a = 6.5$). The sulfonate groups of PSS were fully dissociated (solution pH ~6.8). The smaller the degree of dissociation, the stronger are the intramolecular/intermolecular attractive interactions between likely charged polyanions. The adsorbing polyelectrolyte molecules, besides the electrostatic attraction with the underlying LDH layer, are able to form nonelectrostatic bonds with other polyelectrolytes residing already in the surface, unless they are highly dissociated.

The effect of the LDH particle concentration was investigated by depositing the LDH layers from four different suspension concentrations (Fig. 6). Increasing the LDH suspension concentration decreased the maximum number of deposited layers (Fig. 7).

At a fixed LDH suspension concentration, more layers are built up with PAA than with PSS, as discussed above. According to AFM investigations, the particle density in the LDH layers depends on the LDH suspension concentration. Layers of densely packed particles were deposited from the more highly concentrated suspensions, and the surface coverage became very low at lower suspension concentrations. In Fig. 8, we show the AFM picture of the last LDH/PAA layer on the PDDA-coated gold surface, deposited from a 0.1% LDH suspension (the total number of layers was 18).

Analyzing the results of SPR and AFM measurements leads to the conclusion that besides the electrostatic attractive interactions, nonelectrostatic attraction forces must have great importance in directing the par-

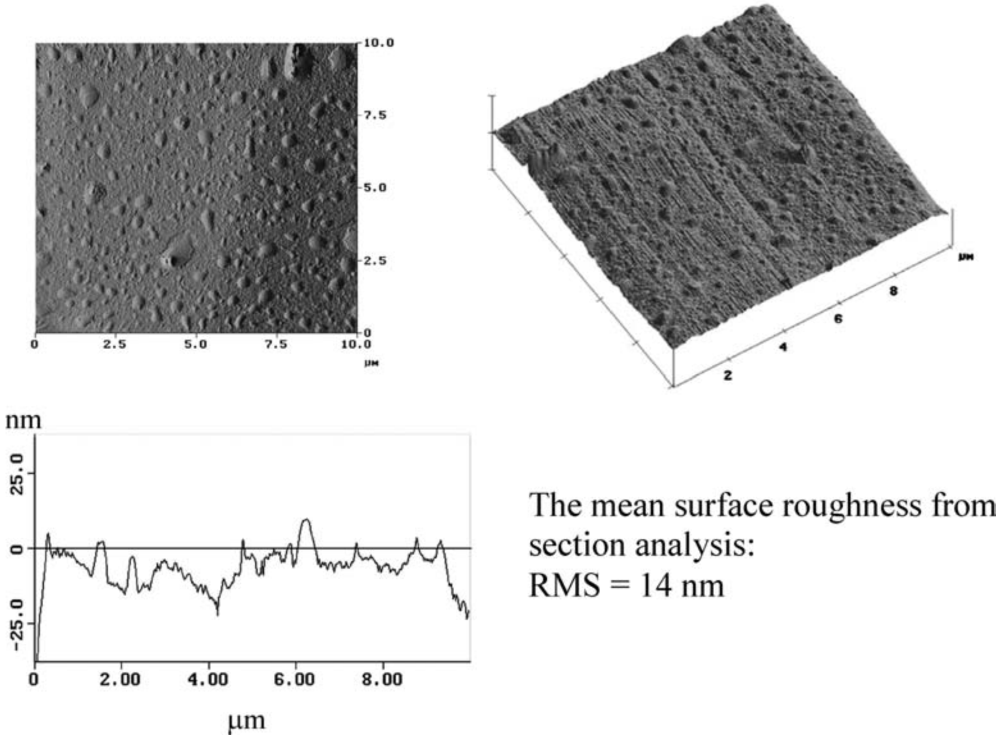


Fig. 8 AFM picture of the top PAA layer of the 18-layered PAA/LDH structure on PDDA-modified gold surface, deposited from 0.1% LDH suspension. The sample area is 10×10 µm, the average height of the PAA-coated LDH particles on the surface is ~14 nm

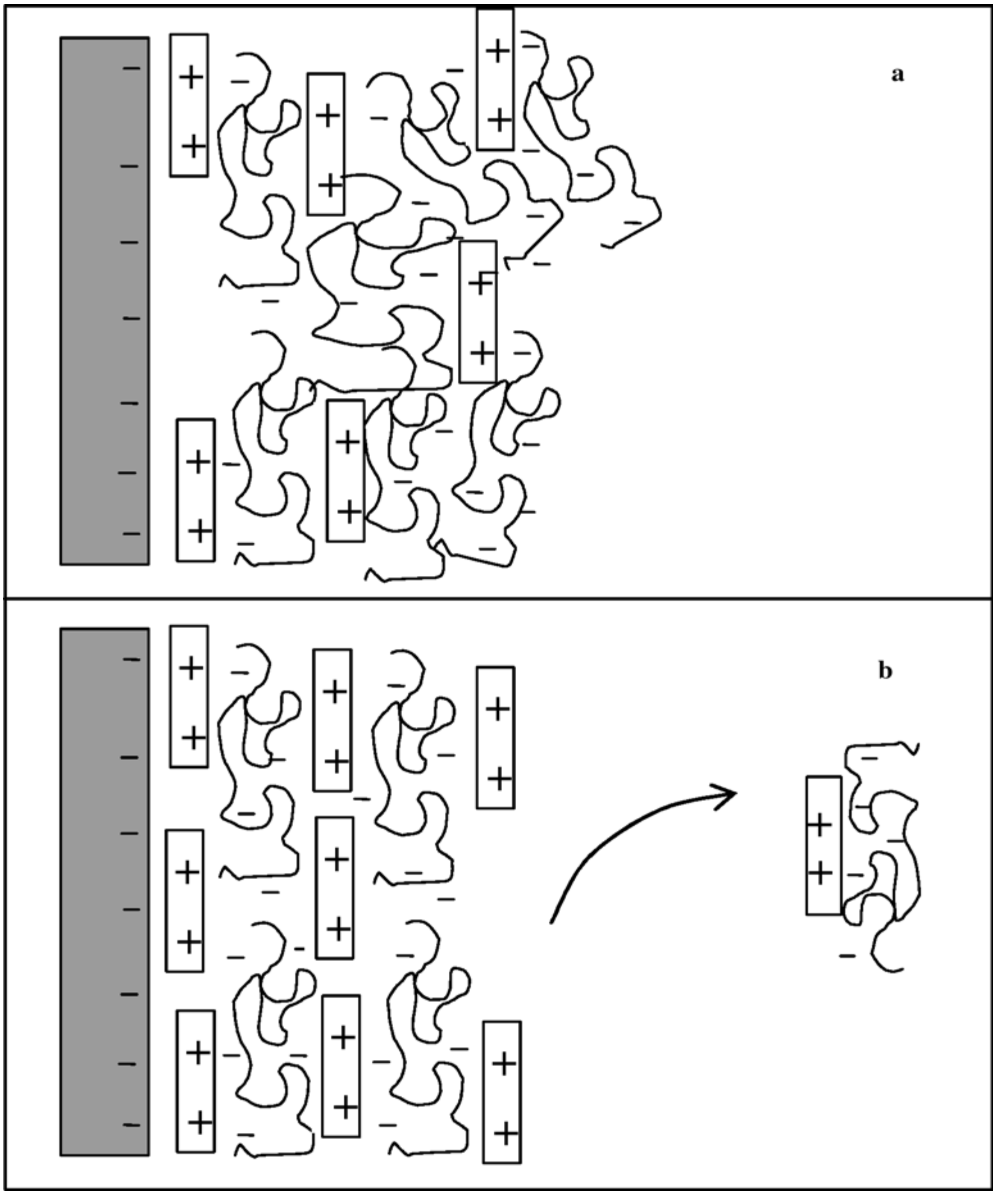


Fig. 9 The effect of particle density in the LDH layer. **a** Low particle density allows for attractive interactions between the successive polyelectrolyte layers. **b** High particle density restricts the attractive interlayer polyelectrolyte interactions

ticle/polyelectrolyte L-B-L deposition. This observation is in accordance with previous results [31]. The presence of nonelectrostatic attraction forces in addition to the electrostatic attraction allows a larger number of layers to be built up. It is apparent that the highly charged (fully dissociated) PSS is less effective in L-B-L deposition than the partially dissociated PAA. In addition, layers of densely packed particles in the film reduce the number of layers: 18 or 12 layers from dilute LDH suspensions, and 8, 6 or 4 layers from more highly concentrated LDH suspensions at otherwise identical conditions. In view of the above observations, we suppose that the interaction between two subsequent polyelectrolyte layers is of great importance in a L-B-L construction. A schematic representation of the structures in the case of loose and dense particle layers is shown in Fig. 9. At low layer density of LDH particles (Fig. 9a), the electrostatic attraction between loosely packed LDH particles and the polyanions is supplemented by nonelectrostatic attraction (hydrophobic or dipole interactions) between the two polyelectrolyte layers, one below and the other above the corresponding LDH layer. Attraction between the polyelectrolyte molecules decreases with increasing charge density. The latter effect is manifested in the noticeable difference in the number of sandwiched layers built with PSS and PAA. In contrast, densely packed LDH layers prevent the polyelectrolyte interaction (Fig. 9b). The adsorption of polyelectrolyte on the last-deposited LDH layer might remove particles from there, as the interaction strength

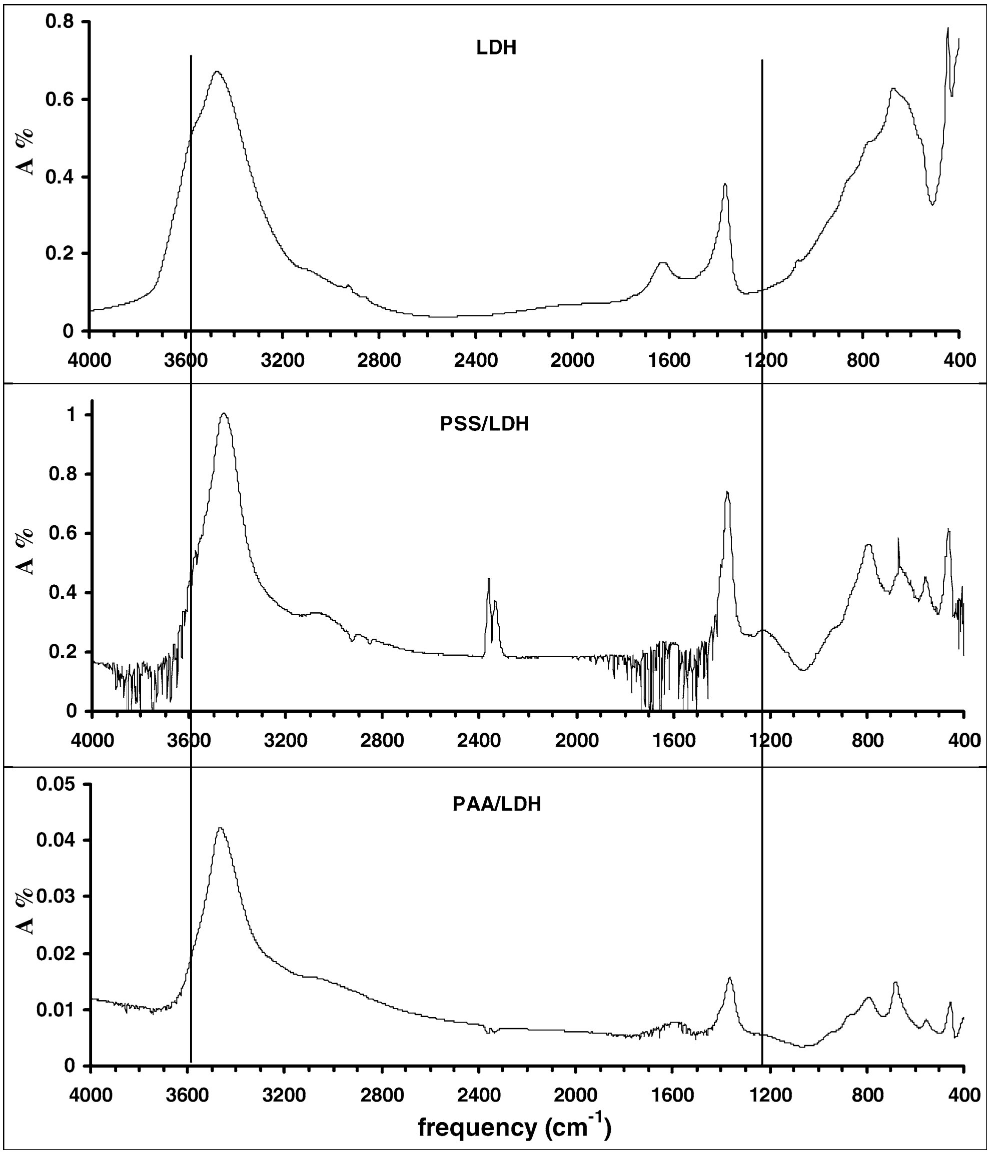


Fig. 10 FT-IR spectra of LDH (absorption spectrum, KBr pellet), 12-layered PSS/LDH on PDDA-modified gold surface and 18-layered LDH/PAA on MA-modified gold surface

between LDH and the two neighboring polyelectrolyte layers (below and above) is nearly equal.

Infrared spectroscopy

The FT-IR absorption spectra of LDH powder in KBr and reflection absorption spectra of two L-B-L multilayers (an 18-layered LDH/PAA and a 12-layered LDH/PSS structure) are presented in Fig. 10. Reference absorption spectra of PAA and PSS were also measured in KBr. The broad absorption bands around 3,450 cm^{-1} are due to the OH-stretching vibration. The shoulder at the high-energy side corresponds to the H–O–H deformation at ~3,600 cm^{-1} due to strong H-bonding [32]. The 3,600-cm^{-1} shoulder is absent in the L-B-L structures, both with PSS and PAA, suggesting that adsorption of the polyanions reduces the H-bonding. The absorption band at 1,650 cm^{-1} is attributed to the δ(HOH) bending mode of water [33]. The relative intensity of the latter band decreases by LDH/polyanion layering. The strong absorption band at 1,368 cm^{-1} seen in all spectra is attributed to the presence of NO_3^- in the ion-exchange positions on the LDH lamellae [34]. During L-B-L deposition, this band is not shifted, and the intensity is practically unchanged, revealing that the polyelectrolytes PAA and PSS do not penetrate into the interlayer space. Absorption in the region of 1,200 cm^{-1} is characteristic of both PAA and PSS, and is seen in the multilayer films as well. Discrete absorption bands appear in the fingerprint region (below 800 cm^{-1}) in both the PSS and PAA multilayer films, indicating the presence of organic molecules with specific IR-active groups.

Conclusions

Sandwiched multilayers (12–18 layers) were prepared from LDH particles and alternately deposited PAA or PSS on modified gold surfaces. The attachment of the first layer requires strong electrostatic attractive interaction with the surface. The gold surface can be coated with a charged layer either by chemical surface modification with small ions or adsorbing positively charged, fully dissociated polyelectrolytes. Modifying with 3-mercapto propanoate ions or PDDA was effective in anchoring the first layer to the gold surface.

After fixing the first layer, multilayer formation depends on the strength of attractive interactions between the layers which, in the first approximation, should be most effective using highly charged particles and polyelectrolytes. However, the polyelectrolyte charge must not be too high. More layers formed in the presence of partially than with fully dissociated polyelectrolyte (PAA at pH ~4.5 and PSS at pH ~8). It is apparent, that the two subsequent polyelectrolyte layers, which surround the particle layer below and above, interact with each other by attractive nonelectrostatic (van der Waals, H-bonding, etc.) forces to hold the multilayer structure together. Either a high charge on the two polyelectrolyte layers or a complete separation of them by an intervening layer of solid particles restricts the attraction between the polyelectrolyte layers, thus, reducing the number of layers deposited.

FT-IR spectra reveal that the polyions adsorb on the LDH surface: specific PSS and PAA bands appear in the spectra (800–600 cm^{-1}), and absorption bands due to H-bonds (3,600 cm^{-1}), characteristic of the original LDH sample, disappear in the course of multilayer formation.

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