Ultrathin hybrid films of clay minerals†

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Smectites or swelling clay minerals are naturally occurring nanomaterials that can be fully delaminated to elementary clay mineral platelets in dilute aqueous dispersion. This review article gives an overview of the recent progress on how the elementary clay mineral platelets can be reorganized in monolayered or multilayered hybrid nanofilms by layer-by-layer assembly or the Langmuir-Blodgett technique. In the latter case one hybrid layer consists of one layer of elementary clay mineral platelets with a theoretical thickness of 0.96 nm, covered on one side by amphiphilic cations. The organization of the elementary clay mineral platelets and that of the adsorbed amphiphilic cations in the nanofilms has been studied in great detail by ATR-FTIR, UV-Vis and fluorescence spectroscopy, XRD and AFM. The nanofilms carry functional properties, such as chirality, optical nonlinearity and magnetism, which are due to the nature of the amphiphilic cations and to the organization of both the amphiphilic molecules and the elementary clay mineral platelets.

Introduction

Nanoscience and nanotechnology are exponentially growing research areas. Nanomaterials can be synthesized (inorganic, organic, polymeric, biological), but nature offers also a large number of nanomaterials. Lipids and proteins in living organisms are the most prominent examples and a continuous source of inspiration.^{1,2} Also the inorganic world has a lot of nanomaterials to offer: oxides, such as silica; phyllosilicates, especially smectites or swelling clays. Both silica and smectites are industrially extremely important with a yearly production of millions of tonnes in very diverse areas of applications and technologies.^{3,4} Nanoscience and nanotechnology give the opportunity to open new research areas for these materials, which will eventually lead to new technologies and new industrial applications. The goal is to produce new functional nanomaterials with low cost and high added value.

Research on silica has accelerated strongly. We simply mention the ordering of silica spheres of uniform size into two- and three-dimensional structures, called colloidal crystals. These three-dimensional colloidal crystals are band gap materials that manipulate the propagation of light with potential use in waveguides, switches, optical filters and as biochemical sensors.^{5,6} The development of smectites into nanomaterials with specific functionalities is far less advanced. This development requires knowledge of (i) the organisation of the smectite nanoparticles in two and three dimensions; (ii) the organisation of molecules at the surface of these particles; (iii) the introduction of functionalities in the nanofilms either *via* the clay mineral particles or *via* the adsorbed molecules. Up to now functionalities (nonlinear optics, magnetism, chirality) have been introduced with a proper choice of the adsorbed molecules and their organisation. In any case, with such nanofilms one can study the fundamental properties of the elementary particles themselves at the level of the individual particle in the nanofilms and those of the adsorbed molecules with an unprecedented precision and depth.

In this review we discuss the state of the art synthesis and properties of monolayer and multilayer hybrid nanofilms, consisting of layers of smectite particles alternating with layers of functional molecules. It is divided into the following parts: (i) structure and properties of smectites; (ii) techniques for preparation of nanofilms; (iii) organisation of the smectite particles in the nanofilms; (iv) organisation of the adsorbed molecules; (v) functionalities of the films; (vi) other layered inorganic solids and (vii) conclusions.

Smectites

Smectites belong to the class of phyllosilicates and have swelling properties. The elementary sheet is composed of one layer of edge-shared octahedra of Al^{3+} or Mg^{2+} , sandwiched between two layers of corner-shared tetrahedra of Si^{4+} . The structure is shown in Fig. 1.

The thickness of such an elementary sheet, consisting of 4 layers of oxygen atoms, is 0.96 nm. We call this the elementary clay mineral platelet. With Al^{3+} in the octahedral layer 4 out of 6 octahedral sites are occupied and the mineral is called

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[†] The HTML version of this article has been enhanced with colour images.



dioctahedral; in the case of Mg^{2+} the six octahedral sites are occupied and the mineral is called trioctahedral. Isomorphous substitution occurs both in the tetrahedral and in the octahedral layers. The partial replacement of Si⁴⁺ by Al³⁺ in the tetrahedral layers and of Al³⁺ by Mg²⁺ or Mg²⁺ by Li⁺ in the octahedral layers creates a negative lattice charge, which is compensated by exchangeable cations. The latter are hydrated and located in the interlamellar space (Fig. 1). The idealized pseudo-unit cell formulae of the most common minerals are given in Table 1.

The negative charges of the structures are typically 0.5–1.2 electron charges per pseudo-unit cell. The corresponding cation exchange capacity (CEC) is 0.6–1.6 meq g^{-1} or 60–160 cmol_c kg⁻¹. The amount of isomorphous substitution in the octahedral and tetrahedral layers is variable. This is especially the case of the dioctahedral minerals where one has beidellite-montmorillonite series and beidellite-nontronite series, corresponding with various degrees of Al³⁺ and Fe³⁺ substitution, respectively.⁷ In reality small amounts of Fe³⁺ and Fe²⁺ are always present in the octahedral and tetrahedral layers of most smectites and might be associated with the clay minerals as oxidic impurities.

The length and width of the elementary sheets range from a few tens of nanometers to several micrometers. They are

Table 1 Most common smectites

Name	Idealized formula	Туре
Beidellite	(Si _{7.33} Al _{0.67}) ^{IV} (Al ₄) ^{VI} O ₂₀ (OH) ₄	Dioctahedral
Montmorillonite	$0.67 \text{Na}^+ \cdot n\text{H}_2\text{O}$ Sis ^{IV} (Al ₃ 33Mg _{0.67}) ^{VI} O ₂₀ (OH) ₄	Dioctahedral
	$0.67 \text{Na}^+ \cdot n \text{H}_2 \text{O}$	Diotunitari
Nontronite	$(Si_{7,33}Al_{0.67})^{IV}(Fe_4)^{VI}O_{20}(OH)_4$	Dioctahedral
Saponite	$(Si_{7,33}Al_{0,67})^{IV}Mg_{6}^{VI}O_{20}(OH)_{4}$	Trioctahedral
I	$0.67 \text{Na}^+ \cdot n \text{H}_2\text{O}$	
Hectorite	$(Si_8)^{IV}(Mg_{5.33}Li_{0.67})^{VI}O_{20}(OH)_4$	Trioctahedral
	$0.67 \mathrm{Na}^{-} \cdot n\mathrm{H}_2\mathrm{O}$	

organized face to face into aggregates, which occur in very different sizes and shapes. Some idealized examples are given in Fig. 2. The exchangeable cations are localized in the interlamellar space between two successive sheets of the aggregate. They are hydrated. One monolayer of water molecules in the interlamellar space corresponds to a d_{001} spacing of 1.25 nm; two layers of water molecules give 1.5–1.55 nm.

In aqueous dispersions large amounts of water can be adsorbed in the interlamellar space to such an extent that the aggregates disintegrate into elementary sheets, which are diffusing randomly in the water phase. This is the swelling of smectites. The extent of swelling depends on the size and charge of the cations and the CEC. Swelling is most pronounced for small univalent cations such as Li^+ and Na^+ . In the case of polyvalent cations such as Ca^{2+} , the lattice–cation attraction is in strong competition with the cation–water interaction and swelling is more difficult and often incomplete. In any case, the presence of water in the interlamellar space, even one layer, is sufficient for ion exchange. Almost every cation can be exchanged whatever its charge and size, including heavy metals, organic cations, dyes and cationic polymers.^{8–10}



Fig. 2 Shapes of clay mineral particles and aggregates.



Fig. 3 Representation of edge charges as a function of pH.

Finally, in aqueous dispersions the edges of the crystals are important. These edges are composed of oxygen atoms and hydroxyl groups that can accept or release a proton, depending on the pH of the medium. This is schematically shown in Fig. 3 for the edges of a dioctahedral clay mineral with Al in the octahedral layer. As a consequence smectites carry a pH independent charge, due to isomorphous substitution, and a small pH dependent charge at the edges. The total CEC has contributions of both, the pH dependent contributions being of the order of 10% of the total CEC.

Techniques of film preparation

Clay mineral films have been prepared by dropcasting, spincoating, layer-by-layer (L-b-L) assembly and the Langmuir– Blodgett (LB) technique. Dropcasting is applied to prepare films for infrared (IR) spectroscopy and spincoating for the preparation of clay-modified electrodes. Both techniques give rather well-defined thin films with thicknesses in the range of a few tens of nanometers (spincoating)^{11,12} to a few tens of micrometers (dropcasting).^{13–19} In this review we restrict our discussion to L-b-L assembly and the LB technique because they allow film construction with thicknesses down to elementary clay mineral platelets. The thickness of a clay monolayer without adsorbed molecules is then 0.96 nm.

Layer-by-layer assembly

Layer-by-layer (L-b-L) assembly is the alternating deposition of positively charged and negatively charged polyelectrolytes from dilute aqueous solutions or dispersions on a suitable substrate.²⁰ In the case of L-b-L assembled clay films, the negatively charged clay particles are combined with a positively charged polyelectrolyte, such as PDDA (poly(diallyldimethylammonium chloride)).²¹⁻³⁵ Each layer is deposited by alternating a dilute aqueous clay dispersion with a solution of PDDA. The film is washed before the next layer is deposited to remove excess material. The layers are formed by the electrostatic interactions between the negatively charged clay mineral particles and the positively charged PDDA molecules. In the case of smectites this electrostatic interaction can also be described as an ion exchange reaction, as the charge compensating Na⁺ cations (shown in Fig. 1) of the smectites are exchanged by the positively charged PDDA molecules in the next layer and washed away. Charge reversal occurs after each

deposition step. Thus, after deposition of one layer of PDDA on the substrate or on the clay layer, the film is positively charged and the next layer of elementary clay mineral platelets can be deposited. Besides cationic polymers other positively charged species such as proteins,^{36,37} the Al Keggin ion³⁸ and cationic dye molecules^{25,39,40} have been reported in L-b-L clay film formation.

Langmuir-Blodgett technique

In the Langmuir–Blodgett (LB) trough the subphase is a dilute aqueous dispersion of a smectite with Na⁺ or Li⁺ as exchangeable cations. The small univalent cations ensure maximal swelling and the presence of elementary clay mineral platelets of 0.96 nm thickness (not counting the hydration water). A solution of an amphiphilic cation in a volatile organic solvent is spread at the air-water interface of the LB trough. The solvent evaporates and a monolayer of molecules is formed. A rapid ion exchange reaction takes place between the smectite particles and the amphiphilic cations, leading to a hybrid monolayer at the air-water interface, consisting of one layer of amphiphilic cations and, ideally, one layer of elementary smectite sheets of 0.96 nm thickness (Fig. 4). This hybrid monolayer can be compressed and surface pressure-area isotherms are constructed. At a fixed surface pressure the hybrid clay-organic monolayer is transferred to a substrate either by vertical deposition in upstroke or by horizontal deposition. In the case of vertical deposition the substrate has to be hydrophilic and the layer of smectite particles is in immediate contact with the substrate. In the case of horizontal deposition, the substrate has to be hydrophobic and the layer of amphiphilic cations is in immediate contact with the surface of the substrate.

The LB technique leads to a higher degree of organisation than the L-b-L assembly. The higher degree of organisation is related to a fundamental difference between both methods: the LB film is formed at the gas-liquid interface, whereas the L-b-L assembled film is formed at the solid-liquid interface. At the gas-liquid interface the hybrid monolayer can be compressed and this leads to additional control on the lateral distribution of clay mineral particles and molecules.

The first experiments of constructing hybrid clay mineral films with the LB technique were performed by spreading organo-clay complexes dispersed in a volatile organic solvent



Fig. 4 The hybrid film deposition process of the Langmuir-Blodgett technique (vertical deposition in upstroke).

on the water surface.^{41,42} The organo-clay films were continuous and several clay lamellae thick. The spreading of cationic surfactants at the air–water interface of a dilute dispersion of clay minerals is a more elegant approach, as explained above. Surfactants for Langmuir–Blodgett clay films include alkylammonium cations, organic dyes and metal ion complexes.^{43–65}

Organisation of the clay mineral particles

The structure and surface roughness of L-b-L assembled films depend on several parameters including adsorption time, concentration of cationic polymer, amount of clay in the dispersion and pH. Lvov et al. studied the kinetics of adsorption of clay mineral particles and polymers by quartz crystal microbalance (QCM) measurements.³⁰ They observed that the adsorption of montmorillonite clay was saturated in 5-6 min with formation of a monolayer. This means that at shorter adsorption times submonolayer coverage with clay mineral particles is expected. For longer adsorption times the monolayer coverage is maintained, as excess adsorbed material is washed away after the deposition step. Fig. 5 shows an AFM picture of an L-b-L monolayer of saponite that was assembled using a short (5 s) deposition time.²⁴ This film is characterized by two features: (i) submonolayer coverage of the clay particles and (ii) randomly oriented, partially overlapping clay particles. The submonolayer coverage is not surprising in view of the short deposition time.

An important parameter that directly affects the organisation of deposited clay mineral platelets is the concentration of cationic polymers. van Duffel et al. observed that the surface roughness of clay-polymer L-b-L multilayers increases with cationic polymer concentration in solution.²⁴ This observation was explained as follows. At low polymer concentration the polymer chains can bind effectively with the clay mineral layer, resulting in a monomolecular polymer layer consisting of stretched chains and a small number of unbound polymer units. The film is characterized by a low surface roughness. At high polymer concentration multiple polymer chains are only partially bonded to the substrate and sticking out of the surface. Regions of high ionic strength are created, which adsorb bundles of elementary clay mineral platelets, more or less stacked on top of each other. The result is a rough film surface. Based on these observations, van Duffel et al. developed a simplified model for multilayer formation of clay minerals and PDDA.²⁴ In case of laponite, surface coverages of 90-98% were obtained while for hectorite and saponite the surface coverage was only in the range 60-72%. This difference is due to differences in particle size.

A clay–organic hybrid LB film comprises one layer of a cationic surfactant molecule in contact with one layer of elementary clay mineral platelets.⁵² These hybrid clay–organic LB films can be visualized with AFM. AFM images of LB films comprising saponite and 3,3'-dioctadecyl oxacarbocyanine (OXA) are shown in Fig. 6. One observes platelets of irregularly shaped clay mineral particles with lateral dimensions of several tens to more than 500 nm. Thicknesses in the range 1.5–3.4 nm were measured with AFM, corresponding roughly to one layer of elementary clay mineral platelets (0.96 nm) and one layer of surfactant molecules. Some particles



Fig. 5 AFM picture of a saponite monolayer, obtained by L-b-L assembly. (left: cantilever deflection signal image; right: topographical image; image size: 1995×1995 nm); Reprinted in part from *Langmuir*, vol. 15, pp. 7526, Fig. 2; copyright 1999 American Chemical Society.



Fig. 6 Atomic force microscopy topography images (left) and cantilever deflection images (right) of 3,3'-dioctadecyl oxacarbocyanine—saponite LB monolayers prepared on a saponite dispersion with a clay concentration of (a) 10 mg dm⁻³, (b) 50 mg dm⁻³ and (c) 250 mg dm⁻³. Reprinted from *Phys. Chem. Chem. Phys.*, vol. 6, pp. 4179, Fig. 5; copyright 2004 Royal Society of Chemistry.

are stacks of elementary clay mineral platelets (white areas in AFM picture of Fig. 6). The number of clay particles in the film obviously depends on the clay concentration of the subphase. At 10 mg dm⁻³ only few clay mineral platelets are adsorbed in the film, whereas at 50 mg dm⁻³ the film is nearly fully covered with clay with some empty spaces left between the particles. At still higher concentration, the clay particles are tightly packed in a monolayer, but the amount of stacks or aggregates of elementary clay mineral platelets increases. Thus, a fairly uniform and continuous hybrid monolayer of elementary clay mineral platelets can be obtained, which is an ideal material for detailed spectroscopic investigation.

Polarized attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is a commonly used tool for probing the orientation of chemical bonds in thin films. Fig. 7 and 8 give, respectively, the polarized ATR-FTIR spectra of hybrid monolayers of saponite and Wyoming montmorillonite.⁵² The FTIR band assignments are summarized in Table 2. The intensities of the in-plane and out-of-plane ν (Si–O) vibrations, respectively, at 996 cm⁻¹ and 1063 cm⁻¹ for saponite (Fig. 7B) and at 1022–1047 cm⁻¹ and 1085 cm⁻¹ for Wyoming montmorillonite (Fig. 8B), were used to determine the orientation of the clay particles in the hybrid



Fig. 7 Polarised ATR-FTIR spectra of a hybrid LB film of saponite with 3,3'-dioctadecyl thiacyanine prepared on a 50 mg dm⁻³ clay suspension, deposited on ZnSe at a surface pressure of 5 mN m⁻¹: (A) ν (OH) region, (B) ν (Si–O) region. Reprinted from *Langmuir* vol. 19, pp. 4295–4302, Fig. 3; copyright 2003 American Chemical Society.

clay–organic LB films based on polarized FTIR spectroscopy. Polarization analysis of the ν (Si–O) bands showed that the elementary clay mineral platelets are deposited with their plane strictly parallel to the surface of the substrate, in this case a ZnSe crystal. The three additional bands in Fig. 8B at 919, 885 and 846 cm⁻¹ are due to the bending vibrations of structural OH groups in the octahedral layer of Wyoming montmorillonite. The exact positions of these bands depend on the nature of the cations in the octahedral sites, which share this OH group (Fig. 1). For saponite this OH bending is below 800 cm⁻¹ and therefore not seen in Fig. 7B.

The orientation of the elementary clay mineral platelets was also confirmed by the polarization dependence of the structural O–H stretching vibrations, which is significant in the case of saponite and only weak in the case of Wyoming montmorillonite. Saponite is a trioctahedral phyllosilicate and the structural O–H groups are oriented perpendicular to the 001 plane; in the case of Wyoming montomorillonite, a dioctahedral 2:1 phyllosilicate, the OH groups are oriented nearly in



Fig. 8 Polarised ATR-FTIR spectra of a hybrid LB film of Wyoming montmorillonite with 3,3'-dioctadecyl thiacyanine prepared on a 50 mg dm⁻³ clay suspension, deposited on ZnSe at a surface pressure of 5 mN m⁻¹: (A) ν (OH) region, (B) ν (Si–O) + δ (OH) regions. Reprinted in part from *Langmuir* vol. 19, pp. 4295–4302, Fig. 4; copyright 2003 American Chemical Society.

Table 2 Si–O stretching, OH bending and OH stretching bands of saponite and Wyoming montmorillonite: position, dichroic ratio, experimental and calculated intensities⁵⁵

			Intensities		
Saponite	$\begin{array}{c} Position / \\ cm^{-1} \end{array}$	Dichroic ratio $A_{\rm s}/A_{\rm p}$	Observed	Calculated	
in-plane Si–O out-of-plane Si–O OH stretching	996 1063 3680	1.11 0.23 0.33	0.10-0.14	0.103	

			Intensities	3
Wyoming montmorillonite	Position/ cm ⁻¹	Dichroic ratio $A_{\rm s}/A_{\rm p}$	Observed	Calculated
in-plane Si–O	1047	1.22	0.082	0.097
	1024	1.11		
Out-of-plane Si-O	1085	0.12		
-	1116	0.95		
(Al-Al)-OH bending	919	1.18		
(Al-Fe)-OH bending	885			
(Al-Mg)-OH bending	846			
OH stretching	3628	1.08		

the 001 plane. In Fig. 7, the ν (OH) bands of saponite have maximum intensity in the A_p spectrum (out-of-plane) and very little intensity in A_s spectrum (in-plane). In contrast, very little difference is observed in the ν (OH) bands of Wyoming montmorillonite (Fig. 8A).

The intensities of the in-plane Si–O vibrations in the ATR-FTIR spectra depend mainly on the film thickness. It is then possible to calculate a theoretical intensity corresponding to one monolayer of elementary clay mineral platelets of 0.96 nm thickness. This has been done in the thin film approximation with absorption coefficients of 3.5×10^4 cm⁻¹ and 3.6×10^4 cm⁻¹ for the ν (Si–O) bands of saponite and of Wyoming montmorillonite, respectively. The data in Table 2 show that the observed absorbance values for the ν (Si–O) bands agree with the predicted absorbance value for a monolayer of clay. This provides additional confirmation that the hybrid clay–organic LB films are comprised mainly of a monolayer of elementary clay mineral platelets.

With infrared reflection absorption spectroscopy (IRRAS) it is possible to study the hybrid monolayers at the air-water interface directly (*i.e.* without requiring the transfer of the film to a solid substrate).⁵³ The spectra of Fig. 9A confirm the presence of both the cationic surfactant (3,3'-dioctadecyl-oxacarbocyanine) with characteristic bands at 1194, 1117 and 1087 cm⁻¹ and of saponite with its Si–O stretching at 996 cm⁻¹. Based on these data, it would be interesting to examine hybrid clay–organic LB films at the air–water interface and after deposition to a ZnSe or Ge substrate in order to detect differences, indicative of organizational changes between both systems.

On a gold surface only the out-of-plane Si–O stretch (1063 cm^{-1}) is active and the in-plane stretch (996 cm^{-1}) is suppressed (Fig. 9B).⁵³ The suppression of the in-plane Si–O stretching vibration results from the so-called "metal surface selection rule", which states that only vibrational transition dipole moments oriented normal to the surface will absorb light. This gives us an additional tool to study the hybrid monolayers.

Both specular X-ray reflectivity (SXR) and in-plane XRD measurements have been performed on hybrid monolayers of a synthetic montmorillonite (Kunipia P) and octadecylammonium (ODA) cations deposited on a Si plate with a SiO₂ surface.⁶⁴ The modelling of the SXR data resulted in a monolayer consisting of one layer of ODA with a thickness of 1.67 nm and one layer of elementary clay particles with a thickness of 1.56 nm. The latter value suggests that the elementary clay mineral platelets with a thickness of 0.96 nm carry hydrated Na⁺ cations on the surface, compensating the negative charge of the clav structure. If this is the case, the ODA cations are not ion-exchanged on the clay surface. Another problem is that the modelling gave 0.92 g cm⁻³ ODA and 1.37 g cm⁻³ clay in the hybrid monolayer. These numbers indicate that the amount of ODA exceeds the CEC of the clay, estimated to be 1 mmol g^{-1} , by a factor of almost 3. These results do not agree with the data of Ras et al.⁵² These authors showed that the lift-off area of surfactant dve cations in the LB trough are equal to the average area per charge of the clay minerals, thus confirming an ion exchange mechanism. Clearly, a systematic study of LB film formation and deposition is necessary for the hybrid films under discussion.



Fig. 9 (A) IRRAS spectra of a monolayer of saponite with 3,3'-dioctadecyl oxacarbocyanine at the water surface and on the surface of a clay suspension and (B) a monolayer of saponite with octadecylrhodamine B on gold. Reprinted from *Thin Solid Films* vol. 466 pp. 291–294, Fig. 2 + 3; copyright 2004 Elsevier.

Organisation of adsorbed molecules

Organisation of molecules is the core of nanofilm research. Molecules must be manipulated in such a way that the organised molecular system or nanofilm has specific properties, which are absent in materials with randomly organised molecules. Clay particles provide a host medium to assemble and organise guest molecules. It has been known for a long time that molecules can adopt specific organisational structures in the interlamellar space of smectites, depending on the size, shape and charge of the molecules and on the charge density of the clay mineral particles.^{66,67} In the case of the hybrid nanofilms under discussion we consider the organization of both elementary clay mineral platelets and molecules in two dimensions. In multilayer films these hybrid monolayers are stacked on top of each other and the organisation of the layers has to be taken into consideration as well.

Layer-by-layer assembly

Molecular organisation in L-b-L films has not been studied in a systematic way and only some general observations can be given. L-b-L assembled multilayer films involving clay minerals are sometimes described as nanocomposites with preferential orientation of the elementary clay mineral platelets rather than multilayers or stratified assemblies.²⁸ Efficient fluorescence resonance energy transfer is observed when a monolayer of acceptor dye molecules is deposited on top of a multilayer stack involving donor dye-polymers and elementary clay mineral platelets. This shows that donor and acceptor molecules are in close proximity. In other words the acceptor molecules from the final deposition step are not confined to the top laver but diffuse into the inner lavers of the multilayer assembly.³⁹ Molecules within the layer of a L-b-L assembled film are generally weakly organized. Polarized UV-Vis spectroscopy of a clay/PDDA/dye multilayer film shows that the dye molecules have a homogeneous distribution of angles relative to the surface normal.²⁵ Interestingly, the same study showed that the dye molecules are non-centrosymmetrically organized, as they have a second harmonic (SHG) response. The effect is due to the preferential adsorption of dye molecules on top of the clay layer. The clay surface can be seen as a platform onto which oriented polymer-dye complexes can be formed.

Langmuir-Blodgett

Hybrid mono- and multilayers, involving elementary clay mineral platelets and a range of amphiphilic molecules (= surfactants) have been constructed with the LB technique: alkylammonium cations, cationic dyes, zwitter-ions and transition metal ion complexes. In the process of film formation at the air-water interface three competing mechanisms come into play: (i) domain formation of surfactants at the air-water interface; (ii) ion exchange of Na⁺, associated with the elementary clay mineral platelets, by the amphiphilic cations at the air-water interface resulting in a hybrid film at the air-water interface (*i.e.* hybridization); (iii) the solubilization of the amphiphilic cations in water. The rate of hybridization is determined by the concentration of clay particles in suspension.



Fig. 10 Lift-off areas of alkylammonium cations as a function of alkyl chain length on a 100 ppm clay suspension (bottom axis, squares, solid line) and lift-off areas of octadecylammonium cations as a function of clay concentration (top axis, triangles, dashed line).

Alkylammonium cations. The role of these three mechanisms is clearly illustrated with experiments involving C_4 - C_{18} alkylammonium cations.^{56–59} First, we restrict the discussion to domain formation and hybridization by using octadecylammonium, a cationic surfactant which is nearly insoluble in water. Hybrid monolayers are formed at the air-water interface and the lift-off area per molecule increases (or the surfactant density decreases) with increasing amount of clay in the subphase, as illustrated in Fig. 10. This behaviour is explained as follows (see also Fig. 11). From monolayer studies on water it is known that after spreading of surfactants, the surfactant molecules have initially little interaction and the surfactant density is low. With time, surfactant molecules interact and they form monolayer domains of high surfactant density. When clay mineral particles are present in the subphase, hybridization occurs. In case of fast hybridization (at high clay concentration), clay minerals are adsorbed before surfactant domains have formed and the resulting



Fig. 11 Schematic illustration of the two most important phenomena occurring when water insoluble cationic surfactants are spread on the surface of a dilute clay dispersion: (i) formation of surfactant domains and (ii) hybridization of the surfactant monolayer with elementary clay mineral platelets.

surfactant density is low. In case of slow hybridization (at low clay concentration), clay minerals adsorb onto the formed surfactant domains.

A minimum lift-off area (or maximum surfactant density) is found at 2 ppm clay. This minimum of 0.16 nm² is smaller than the lift-off area of octadecylammonium in the absence of clay (0.20 nm²). This indicates that electrostatic repulsion between the octadecylammonium cations is decreased due to hybridization with the clay mineral platelets in the film, or it may reflect partial dissolution of hybridized ODA/clay platelets. This dependence of the lift-off area with clay concentration is a general observation for all LB films involving clay mineral platelets, independent of the nature of the amphiphilic cations.

We continue the discussion on the film formation mechanism by also taking the water solubility into account. When the chain length of the alkylammonium cations decreases (from C_{18} to C_4), their water solubility increases. Alkylammonium ions with alkyl chains shorter than C_{12} do not form stable floating monolayers on a pure water subphase. The observed lift-off areas on clay suspensions at constant clay concentration decrease with decreasing alkyl chain length (Fig. 10), but hybrid films can still be deposited. Thus, the hybridization through ion exchange is a fast process, competing successfully with the solubilization of the alkylammonium cations. The limit is butylammonium with a lift-off area of 0.08 nm^2 in the presence of 100 ppm clay. Such a small lift-off area is indicative of solubilization of most of the butylammonium cations before hybridization with clay minerals platelets has taken place. However, film formation with linear alkylammonium cations can suffer from side reactions. When chloroform, stabilized with methanol, is used, the alkylammonium cations react with solubilized CO_2 in the form of HCO_3^- to carbamate esters:68

$$C_{18}H_{37}NH_3^+ + HCO_3^- + CH_3OH \rightarrow C_{18}H_{37}NHCOOCH_3 + 2 H_2O$$

Secondly, alkylammonium cations are equilibrated at the air–water interface with the corresponding alkylamines. So, cations are partially transformed into neutral molecules and this may influence the film formation process significantly. One would expect it to be less efficient, because neutral molecules are not adsorbed so strongly and quickly as cations. One can avoid this by using quaternary ammonium ions such as the trimethyloctadecylammonium ion.

Umemura and Shinohara⁵⁶ studied the hybrid films of saponite and trimethyloctadecylammonium (TMODA). They found—as explained before—that the lift-off area per molecule increases with increasing saponite concentration, whatever the concentration of TMODA in the spreading solution. In addition the lift-off area decreases with increasing TMODA concentration at constant clay concentration. Table 3 compares these lift-off areas with the molecular areas obtained by spectroscopy. These molecular areas are determined from the intensity of the antisymmetric CH₂ stretching band at 2925 cm⁻¹, obtained on the films deposited on a glass plate by horizontal deposition at 20 mN m⁻¹. Again the molecular area increases with increasing amount of saponite in the subphase,

Amount of clay ppm	Lift-off $area^{a}/nm^{2}$ molecule ⁻¹	IR-area nm ² /molecule	XRD-d ₀₀₁ spacing/nm
10	0.50	$0.96 - 0.97^{b}$	$0.71 \rightarrow 0.84^{b}$
20	0.75	1.25-1.29	$0.59 \rightarrow 0.65 \rightarrow 0.56$
30	1.21	1.40-1.50	$0.49 \rightarrow 0.51 \rightarrow 0.49$
^a Deposition	at 20 mN m^{-1} .	^b The range indica	ites a slight dependence

on concentration in the spreading solution.

but there are two differences with the lift-off areas: (i) the molecular areas determined spectroscopically are systematically larger than the lift-off areas; (ii) they are within experimental accuracy independent of the concentration of TMODA in the spreading solution. For multilayered films the spacing between successive layers, as expressed by the d_{001} spacing of the clay mineral (Table 3), decreases with increasing clay concentration in the subphase. This is also an indication of increased randomness in the TMODA organisation in the interlamellar space of multilayered films.

The orientation of the molecules in the films depends on several parameters. In the case of horizontal deposition, as used for TMODA, the molecules are sandwiched between the hydrophobic substrate and the clay mineral platelets for the first layer and between clay mineral platelets in the successive layers (Fig. 12). In the case of vertical deposition the substrate is hydrophilic. The elementary clay mineral platelets are deposited on the substrate and the amphiphilic molecules make the top layer in direct contact with the air in a monolayer film and sandwiched between the clay mineral platelets in the subsequent layers (Fig. 12).

Thus, for monolayers vertical and horizontal deposition might lead to different orientations of the molecules under otherwise identical conditions.

Ras et al.⁶⁹ studied hybrid monolayers of octadecylammonium cations and saponite obtained by vertical deposition. At low saponite concentration in the subphase the antisymmetric stretch of the CH_2 group was found at 2917 cm⁻¹. It shifted to 2926 cm^{-1} upon increasing the clay concentration. The former frequency is characteristic of an all-trans configuration of the alkyl chain; the latter of a random configuration. The picture that emerges is as follows: at low clav concentration in the subphase hybrid monolayers are obtained, consisting of organic domains with amphiphilic cations only and hybrid domains, consisting of clay mineral platelets, hybridized with the amphiphilic cations. The former are dominant and the C_{18} alkyl chains have crystalline all-trans ordering. The characteristic frequency of the CH_2 antisymmetric stretch is 2917 cm⁻¹. As the clay concentration in the subphase increases, the hybrid domains expand. On the clay surface the alkylammonium molecules adopt a more randomized orientation and the frequency shifts to 2926 cm⁻¹. The randomized orientation is the preferred orientation in multilayers. The decrease of the d₀₀₁ spacing of multilayered films obtained by horizontal deposition, with increasing amount of clay in the subphase confirms this interpretation (Table 3).58



Fig. 12 Possible orientation of alkyl chains of alkylammonium cations in hybrid monolayer films obtained by (a) vertical deposition (b) horizontal deposition.

Cationic dyes. Cationic dyes have characteristic absorption bands in the visible and many of them also exhibit fluorescence. This gives two additional spectroscopic techniques to study the orientation and organisation of these dyes in the hybrid monolayers with elementary clay mineral particles. The octadecylester of rhodamine B (RhB18) has been the standard molecule in our studies of hybrid monolayers. Many other dyes can be envisaged and have been used in spectroscopy of dilute clay mineral dispersions. The subject has been reviewed by Yariv and Cross.⁹ Scheme 1 gives the most frequently used dyes.

In dilute clay mineral dispersions cationic dyes are instantaneously ion exchanged on the clay mineral particles. This leads locally to very high concentrations and H-dimers and H-type aggregates are immediately formed. This instantaneous process is followed by a slower redistribution of the cationic dye molecules over the available surface. A "pseudoequilibrium" state is reached in which dye monomers and several types of dye aggregates (H-dimers, H-aggregates and J-dimers) are formed. In some cases such as Methylene blue also protonation of the adsorbed cationic dye occurs. The relative abundance of each species depends on the type of clay mineral and the amount of dye adsorbed. At very low loadings the absorbance spectra are fingerprints of the type of clay mineral in the aqueous dispersion and this is illustrated in Fig. 13.⁷⁰

When water is removed *e.g.* by freeze-drying, desaggregation occurs and monomers become the dominant species. Presumably, in the absence of water the interaction between the cationic dye and the clay surface is dominant. One dye molecule neutralizes one negative charge of the clay mineral. The cationic dyes are distributed over the surface as monomers to neutralize the negative charge of the elementary clay mineral platelets as efficiently as possible. In water the clay–dye interaction is screened by the water molecules and dye–dye interactions are dominant, leading to H-type aggregates.

In the case of LB monolayers the following characteristics determine the organisation of the dye molecules: (i) the surface of the elementary clay mineral particles is fully covered by the dye molecules and (ii) the monolayer is hydrophobic, as there is no evidence of water.⁵² In view of our reasoning of the previous paragraph this means that monomers are expected to be the dominant species. Fig. 14 shows the absorbance and



Scheme 1 Cationic dyes frequently used in clay mineral research.



Fig. 13 Influence of the clay structure on the spectra of Methylene blue (MB) absorbed on clay mineral in dilute aqueous suspension.⁷⁰ 762 nm: protonated MB; 670 nm and 653 nm: monomeric MB; 610–575 nm: H-dimers and H-aggregates. Reprinted from Handbook of Clay Science, chapter 3, Fig. 3.8; copyright 2006 Elsevier.

fluorescence spectra of RhB18-saponite monolayers, prepared with different amounts of saponite in the subphase. The main feature in the absorption spectrum is the band at 563 nm, shifting to 583 nm with increasing amount of saponite in the subphase. The first maximum corresponds to that of the monomer; the second to that of the J-dimer. Thus, as the hybrid monolayer is formed, more and more J-dimers are present. We conclude that J-dimers are the preferred form of organisation of RhB18 molecules in the hybrid monolayers involving elementary clay mineral particles.

Also the conformation of dye molecules is affected by adsorption on the clay mineral surface. The fluorescence



Fig. 15 Structure of RhB18 showing the rotation of the phenyl ring with respect to the xanthene plane. The rotation of the phenyl ring causes a distribution in the energy level of RhB18 monomers. Resonance energy transfer occurs from monomer to monomer to populate the lower energy monomers. Reprinted from *Phys. Chem. Chem. Phys.*, vol. 6, pp. 5347–5352, Fig. 8; copyright 2004 Royal Society of Chemistry.

spectra are characteristic of the monomers. One observes in Fig. 14 (right) a shift from 595 to 585 nm for this monomer fluorescence, as the amount of saponite increases in the subphase. This can be ascribed to a change in the orientation of the phenyl ring with respect to the xanthene plane (see Fig. 15).

The hybrid monolayers, discussed so far, are prepared by vertical deposition and are characterized by a substrate/clay/ surfactant arrangement as depicted in Fig. 12a with RhB18 cations instead of alkylammonium cations. For such a situation Čapkova et al.71 have calculated the most stable organization of rhodamine B at the clay mineral surface. They found monomers with the xanthene plane parallel to the clay mineral surface at low loadings and J-dimers at high loadings, in qualitative agreement with the findings described above. Interestingly, in the interlamellar space, i.e. with rhodamine B cations between two elementary clay mineral platelets, both H- and strongly tilted J-dimers are found at the highest loadings or full coverage. This is exactly as found by Arbeloa et al.^{72,73} for the orientation of rhodamine 6G (see Scheme 1) in spin-coated laponite films with a thickness of about 250 nm. As the loading increases, they observe with polarized absorption and fluorescence spectroscopies a shift from monomers at small loading to J-dimers at intermediate loading and H-dimers at high loadings.

Transition metal ion complexes. There are two methods to introduce cationic metal complexes into hybrid LB films with elementary clay mineral platelets. Firstly, one can simply use an amphiphilic cationic complex in the spreading solution and



Fig. 14 UV-Vis absorption spectra (left) and fluorescence spectra (right; excitation wavelength = 550 nm) of RhB18-saponite LB films deposited on saponite in suspensions with varying clay concentration at a surface pressure of 2 mN m⁻¹. Reprinted from *Phys. Chem. Chem. Phys.*, vol. 6, pp. 5347–5352, Fig. 5 and 6; copyright 2004 Royal Society of Chemistry.



Fig. 16 Preparation of a hybrid multilayer according to method II. J: octadecylamminium; (a): trisphenanthrolineiron(II); -: elementary clay mineral platelets. Adapted from J. Phys. Chem. B, 2002, 106, 11168–11171, Scheme 1; copyright 2002 American Chemical Society.⁶³

a dilute aqueous clay dispersion as subphase (method I).^{45–46,48,51,65,74,75} The second method (method II) makes use of the ion exchange capacity of the hybrid monolayer.⁶³ This method is illustrated in Fig. 16. A hybrid monolayer of octadecylammonium cations and elementary clay mineral platelets is deposited by horizontal deposition on a hydrophobic substrate. The layer of elementary clay mineral platelets is the outer layer. When this hybrid monolayer is



Fig. 17 (a) Electronic spectra for hybrid films of octadecylammonium, clay platelets, and $[Fe(phen)3]^{2+}$ prepared from a clay suspension of 50 ppm. (b) Relation between absorbance at 523 nm and the hybrid layer number for hybrid films prepared from clay suspensions at 10, 25, and 50 ppm.⁶³ Reprinted from *J. Phys. Chem. B*, vol. 106, pp. 11168–11171, Fig. 2a and b; copyright 2002 American Chemical Society.

immersed in a solution of a cationic transition metal complex, the latter will be ion exchanged on the elementary clay mineral platelets. The procedure can be repeated for multilayers. In method I the hybrid layers have two components, elementary clay mineral platelets and amphiphilic transition metal cations. With method II it contains three components: elementary clay mineral platelets, cationic transition metal complexes and amphiphilic cations, such as octadecylammonium cations. This difference might influence the orientation and organisation of the transition metal ion complexes.

With both procedures a linear increase of the characteristic LMCT bands of $Fe(phen)_3^{2+}$ and $[Ru(phen)_2(dC_{12}bpy)]^{2+}$, respectively, at 523 and 492 nm with the number of layers was found.^{47,63} An example is shown in Fig. 17. This is indicative of a layer-by-layer deposition with identical average compositions of the layers. The number of cationic complexes per unit area in each layer is, on average, constant. If the extinction coefficients of the LMCT bands in aqueous solution are used, one can calculate the area per complex. These areas are shown in Table 4.

One finds that for Fe(phen)²⁺₃ the area per complex decreases from 1.38 to 0.92 nm² with increasing amount of clay in the subphase. 0.92 nm² is the cross-sectional area of the molecules. Thus, at 50 ppm we have a closely packed layer of Fe(phen)²⁺₃ complexes. For the Ru complex areas of 2.5 and 2.0 nm² are calculated for the Λ form and racemic mixture, respectively. There are two main reasons for the larger areas of the Ru complex: (i) the bpy ligand contains two C_{12} alkyl chains; (ii) the Fe(phen)²⁺₃ complex is deposited with a

Table 4 Areas per transition metal ion complex in hybrid multi-
layers a

		$[Ru(phen)_2(dC_{12}bpy)]^{2+}$	
Clay in subphase/ppm	$Fe(phen)_3^{2+}/nm^2$	Λ/nm^2	Racemic mixture/nm ²
10	1.38		
25	1.04		
50	0.92		
100	—	2.5	2.0
^{<i>a</i>} Log $\varepsilon = 4.05$ for Fe(phen) ₃ ²⁺ and 4.22 for [Ru(phen) ₂ (dC ₁₂ bpy)] ²⁺ .			

Functionality	Clay mineral	Other components	Reference
Humidity sensor	Laponite	PDDA	Kleinfeld et al.23
Organic light emitting diode	Montmorillonite	PMA and PPV	Eckle et al. ⁷⁹
Second harmonic generation	Saponite	PDDA and dye molecules	van Duffel et al.25
Magnetic properties	Montmorillonite	PDDA and Fe_3O_4 nanoparticles	Kotov <i>et al.</i> ³²
Artificial nacre; mechanical properties	Montmorillonite	PDDA	Kotov <i>et al.</i> ³⁵
Antimicrobial activity	Montmorillonite	PDDA and Ag nanoparticles	Kotov et al. ³⁴
PMA: poly(methacrylic acid); PPV: poly(p-p	henylenevinylene).		

Table 5 Functionalities of L-b-L clay mineral nanofilms

synthetic montmorillonite with a CEC of 107 cmol kg⁻¹; the Ru complex on a natural saponite with a CEC of 73 cmol kg⁻¹. If ion exchange is the main interaction mechanism, then a higher density of the complexes and thus a lower area per molecule is expected on the synthetic montmorillonite, as observed. Finally, the orientation of bpy and phen complexes is with their threefold axes tilted by about 45° from the normal to the surface, as observed by polarized light absorption spectroscopy on $Os(bpy)_{3}^{2+}$ and $Os(phen)_{3}^{2+}$ complexes.⁴⁷

Functionalities

Clays and clay minerals have a wide range of industrial applications, some of them with a huge tonnage.⁷⁶ In the field of nanotechnology the clay–polymer nanocomposites have found their way in industry and are subject to intense research by several groups worldwide.⁷⁷ In the framework of this review we limit ourselves to nanofilms, prepared by L-b-L and LB techniques. We will not discuss the clay modified electrodes, because they have been reviewed recently.¹² L-b-L films have been discussed by Kotov.⁷⁸ Tables 5 and 6 summarize the functionalities for, respectively, L-b-L and LB films containing clay minerals. The role of the clay minerals is fourfold: stratification; mechanical strength; electrical insulation of the layers; support for a specific organization of molecules or nanoparticles.

Some of the functionalities for LB films are described in more detail in the following paragraphs.

An area with a more systematic research effort is that of chirality and chiral recognition. In the case of layered inorganic materials, such as the swelling clay minerals under discussion in this review, a variety of polymorphs are created by stacking the elementary clay mineral platelets. Some of them are chiral. An example is kaolinite.⁸² Chiral materials can also be obtained by adsorption of chiral molecules. Thus, when the pure enantiomers of $Ru(phen)_3^{2+}$ are adsorbed on mica, they form a monolayer, as schematically drawn in Fig. 18. With the racemic mixture the amount adsorbed is 30%

more than in the case of the pure enantiomers. The picture that emerges is that in the case of the racemic mixture a double molecular layer is adsorbed, whereas the pure enantiomers adsorb in a monolayer, which is only partially covered with a second layer of $Ru(phen)_3^{2+}$ cations. In the latter case the surface roughness is higher and this was confirmed by AFM measurements.⁸³ When the same complex is ion exchanged on smectites, the amount of pure enantiomer adsorbed is equal to the CEC, while for the racemic mixture it is twice the CEC.⁸⁴ The charge density of smectites is smaller than that of mica and in both cases a monolayer of cationic complexes is deposited on the clay mineral surface. However, in the case of the racemic mixture the Δ and Λ forms make up a closely packed pair, while this is not possible with the pure enantiomers (Fig. 19).⁸⁵ Thus, the organisation of these chiral transition metal ion complexes can be controlled to a large extent with the charge density of the clay mineral and the adsorption of pure enantiomers or racemic mixtures.

This has been exploited by first adsorbing Δ -Ni(phen)₃²⁺ on a smectite surface, followed by Fe(terp)²⁺ (terp = 2,2',2"terpyridyl).⁸⁶ The Ni complex forms a monolayer similar to that of Fig. 19. There is enough space between these complexes on the surface to accommodate the Fe(terp)²⁺ cations. The interaction between both induces a typical CD spectrum of Fe(terp)²⁺, which can not be obtained with a mixture of the complexes in solution. This induction of a CD spectrum is evidence of the adsorption of Fe(terp)²⁺ in the holes between the Δ -Ni(phen)₃²⁺ complexes on the surface of a smectite clay, in this case montmorillonite.

Amphiphilic chiral transition metal complexes can also be incorporated in the hybrid monolayers and multilayers with the LB technique, either by methods I or II, as described in the previous section. These hybrid layers generate a SHG signal when illuminated with a Nd:YAG laser.⁴⁵ This is illustrated in Fig. 20, which gives the SHG intensities as a function of the number of layers in the hybrid LB films.

With method I Λ -[Ru(phen)₂(dC₁₂bpy)]²⁺ and rac-[Ru(phen)₂(dC₁₂bpy)]²⁺ are sandwiched between the elementary

Table 6 Functionalities of Langmuir-Blodgett clay mineral films

Functionality	Clay mineral	Other components	Reference
Chiral sensing	Montmorillonite	Chiral Os-complex	Umemura et al. ⁸⁰
Second harmonic generation	Saponite	Ru-complex + alkylammonium	Umemura <i>et al.</i> ⁴⁵
Photo-induced magnetization	Montmorillonite	Prussian blue	Umemura et al. ^{61,62,81}
Barrier for electron transfer	Saponite	Ru-complexes	Yamagishi et al.65
Light-driven electron transfer	Montmorillonite	Ru-complex	Umemura et al.44



Fig. 18 Schematic drawing of adsorption and organization of chiral metal ion complexes.

clay mineral platelets in the hybrid multilayers. A weak SHG signal is detected, the intensity of which is independent of the number of layers. With method II the complexes are sandwiched between a layer of octadecylammonium (ODA) cations and a layer of elementary clay mineral platelets. It is expected that the complexes are oriented with their C_{12} alkyl chains towards the hydrophobic ODA layer and the Ru center towards the hydrophilic clay surface. In that way a SHG signal is generated, the intensity of which increases quadratically with the number of layers. The intensity is also significantly higher for the Λ enantiomer than for the racemic mixture. In the case of the racemic mixture the complexes form a densely packed monolayer, consisting of pairs of Λ - and Δ -molecules. The pure enantiomers are adsorbed as isolated molecules. This difference in packing and the anisotropy of the environment (hydrophobic side and hydrophilic side) are at the origin of the generation of the SHG signal. It is also known that the clay surface electronically interacts in a subtle way with adsorbed molecules. Indeed, when extremely small amount of Methylene blue is ion exchanged on the elementary clay mineral particles in dilute aqueous suspension, a SHG signal is generated. The corresponding hyperpolarisability of the Methylene blue molecules is 10-11 times higher than their hyperpolarisability in solution in the absence of clay mineral particles.87

The same idea of adsorption of cationic inorganic complexes on the surface of elementary clay mineral platelets, modified with a layer of amphiphilic organic cations has been applied in the case of Prussian blue.^{60–62,81} The clay surface is covered with a monolayer of amphiphilic azobenzene cations and then dipped in a solution of FeCl₂ and K₃[Fe(CN)₆] to



Fig. 19 The adsorption structure of a pair of $Ru(phen)_3^{3^+}$ complexes as theoretically predicted.⁸⁵ Reprinted from *J. Am. Chem. Soc.*, vol. 114, pp. 10933–10940, Fig. 8; copyright 1992 American Chemical Society.



Fig. 20 SHG intensities for hybrid multilayers of $[Ru(phen)_2 (dcC12bpy)]^{2+}$ and a clay as a function of layer number: (a) multilayers of Λ - $[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method I, (b) multilayers of rac- $[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method I, (c) multilayers of Λ - $[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method II, and (d) multilayers of rac- $[Ru(phen)_2(dcC12bpy)]^{2+}$ and a clay prepared by Method II.⁴⁵ Reprinted from *J. Am. Chem. Soc.*, vol. 124, pp. 992–997, Fig. 7; copyright 2002 American Chemical Society.

form the Prussian blue layer with a thickness of 0.60 nm. The photo-induced magnetization of these films is shown in Fig. 21. A reversible switch of 11% in the magnetization is observed upon switching from UV to visible light illumination in an external magnetic field. In the case of Co–Fe Prussian blue the magnetic anisotropy was observed with respect to the direction of the applied magnetic field before and after illumination and a charge transfer from Fe(II) to Co(III) through the bridging CN group.⁶¹

There is still a long way to go to fully understand the properties of the hybrid mono- and multilayer films. But at least, they have shown potential in a number of areas.

Fig. 21 Changes in the magnetization for a 24-layer hybrid film, induced by UV and visible light illumination at 2 K with an external magnetic field of 10 G.⁶¹ Reprinted from *Chem. Mater.*, vol. 16, pp. 1195–1201, Fig. 9; copyright 2004 American Chemical Society.

Other layered inorganics

There are other types of layered inorganic nanoparticles, besides clay minerals, that can be used for synthesis of hybrid organic-inorganic thin films. LB and L-b-L films have been reported containing e.g., layered titanium dioxide, 88-93 dichalcogenides (MoS₂, MoS₂, WS₂),^{94,95} layered double hydroxide,^{96–98} niobate^{99–101} and zirconium phosphate.^{99,102} Film construction is, similar as for clay minerals, also based on electrostatic interactions. Among the listed types of lavered nanoparticles are semiconductors, which significantly broaden the range of potential functionalities for the films. For example, films have been made that exhibit high conductivity,94,95 photoconductivity,^{100,101} photocatalytic properties⁹³ and photoelectrochemical properties.⁹⁰ These film properties originate purely from the inorganic layer itself. Recently LB multilavers containing layered titania and europium-complexes have been reported to exhibit red luminescence as a result of efficient energy transfer upon UV excitation.⁹² In the latter case the interplay between the organic and inorganic components is essential to achieve the functionality.

Conclusions

Layered inorganics are suitable and versatile materials for preparation of nanofilms. Among them swelling clay minerals or smectites take a unique position. They are natural materials, but can also be synthesized in the laboratory. They swell in water and can be exfoliated to obtain almost exclusively elementary clay mineral platelets with a thickness of 0.96 nm, not counting exchangeable cations and adsorbed water layers. They have a characteristic ion exchange capacity. The disadvantage of being found in nature is that they occur in various sizes and shapes and that they might contain small amounts of impurities, even after thorough washing procedures.

Spincoating, L-b-L assembly and the LB technique have been used for nanofilm preparation. In the latter case the elementary clay mineral platelets are hybridized with amphiphilic cations such as alkylammonium cations, cationic dyes and transition metal ion complexes. The deposition of these hybrid monolayers on a suitable substrate allows the study of both the elementary clay mineral particles and of the adsorbed molecules.

The elementary clay mineral particles are found to be organized in monolayers of elementary clay mineral platelets, but in these monolayers they are randomly oriented. Surface coverages of 80-85% have been reached. One of the challenges is to organize the particles all in the same direction as reported for, *e.g.*, BaCrO₄ nanorods.¹⁰³

There are several parameters to control the organization of the amphiphilic molecules: the charge density of the clay mineral platelets, the size and shape of the molecules and the match between average area per charge of the clay mineral and the size, shape and charge of the molecules. This molecular organisation is a key parameter for obtaining functional films. This is because the molecules must contain the functionality that one wants to incorporate in the nanofilms. The elementary clay mineral platelets induce mechanical strength, are insulating and organize the molecules. If however, one could use synthetic clays in which transition metal ions substitute for Al^{3+} or Mg^{2+} in the lattice, one could prepare hybrid films in which the clay particles actively participate in the functionality, envisaged by the interaction between the transition metal ion in the clay lattice with the adsorbed amphiphilic cation.

Other layered inorganic compounds are under study in nanofilm configuration. One research avenue is to combine two types of layered inorganic compounds into one nanofilm. One can envisage nanofilms consisting of layers of negatively charged clay mineral platelets and layers of positively charged platelets such as layered double hydroxides (LDH). There is plenty of room for innovative research on the hybrid nanofilms, involving smectite-type clay minerals.

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