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Research paper

Functional hybrid clay mineral films

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ABSTRACT

Clay minerals are layered materials that lend themselves naturally to film formation. In these films the clay mineral layers are oriented horizontally on the substrate. There are four techniques for film formation: (1) casting; (2) spin coating; (3) layer-by-layer assemblage; and (4) the Langmuir–Blodgett technique. The principles of each technique are described. When molecules are organized in the interlayer space of the clay minerals, the films carry a functionality and are called functional hybrid clay mineral films. These functionalities may be (1) sensing of adsorbed molecules; (2) nonlinear optical properties; (3) energy transfer; (4) electron transfer; and (5) magnetism. The expression of functionality depends on the functionality of a molecule, on the degree of organization of these molecules in the interlayer space and on the degree of organization of the clay mineral layers in the films. This is illustrated with examples from the literature for each of the 4 methods of film formation.

1. Introduction

Clay minerals form a group of phyllosilicates or layered silicates. In nature they occur as assemblies of aggregates of particles (Bergaya and Lagaly, 2006), a particle being a group of more or less ordered layers. This is schematically shown in Fig. 1. A layer is the elementary building block of clay minerals. It consists of sheets of SiO_4^{4-} tetrahedra and Al^{3+} or Mg^{2+} octahedra. Smectites are a group of 2:1 clay minerals, consisting of an Al^{3+}, Mg^{2+} or $Fe^{2+/3+}$ octahedral sheet, sandwiched between two Si tetrahedral sheets. Isomorphous substitution occurs in the octahedral sheets or in the tetrahedral sheets, thus giving the layers a negative charge, which is compensated by exchangeable cations located in the interlayer space. Due to the hydration of these exchangeable cations, or more generally their solvation, the interlayer distance increases. The clay mineral is said to swell. In the limit of complete delamination the layers of smectites diffuse individually and randomly in liquid water. If the charge due to isomorphous substitution is too high, the Coulombic interaction between the layer and the exchangeable cations is strong and swelling by solvation of the exchangeable cations in the interlayer space is only partially possible or simply impossible. The formula unit of smectites is given by $[(Si_{4-x}Al_x)^{IV}(Al_{2-y}M_y)^{VI}O_{10}(OH)_2]M^+_{(x+y)}$ or$[(Si_{4-x}Al_x)^{IV}(Mg_{3-y}M_y)^{VI}O_{10}(OH)_2]M^+_{(x+y)}$ for Al and Mg octahedral sheets respectively. The former are called dioctahedral; the latter trioctahedral. Smectites or swelling clay minerals have a charge $(x + y)$ in the range 0.2–0.6. Vermiculites have a charge of 0.6–0.9 and micas have a charge above 0.9.

1:1 clay minerals consist of layers of a Si tetrahedral sheet and an Al octahedral sheet (kaolin group) or a Mg octahedral sheet (serpentin group). They have no isomorphous substitution and therefore no layer charge. There is a fundamental difference between 1:1 and 2:1 layers, that can be shown by their structures in Figs. 2 and 3. Kaolinite has a hydroxyl surface at the top of the Al octahedral sheet and a siloxane surface at the bottom of the Si tetrahedral sheet. The layer is dipolar and does not have a plane of symmetry. Particles of kaolinite can in principle be used to generate optical materials for e.g. second harmonic generation. The top and the bottom of the smectite layer consist of a siloxane sheet. The smectite layer does not carry a dipole moment and has a symmetry plane (Fig. 3). A functionality or a specific property can be given to a smectite layer by ion exchange of cations or by adsorption of molecules, that carry this specific property, in the interlayer space. If the cations and molecules are organized in a specific way in the interlayer space and if, in addition, one can organize the layers, a functional material, more specifically, a functional film is obtained. It is called a functional hybrid clay mineral or functional hybrid smectite film. The word hybrid means that the film consists of functional molecules and smectite layers. This is illustrated for the organization of dipolar molecules in the interlayer space in Fig. 4. The molecules can be organized with their dipole moments parallel or opposite. The smectite layers and the adsorbed molecules can be organized in films by combining one or several of the monolayer organizations in Fig. 3a–e.

There are 4 methods to prepare such functional hybrid films: casting, spin coating (SC), layer-by-layer assemblage (LbL) and the Langmuir–Blodgett (LB) technique. All four will be described, discussed and illustrated with examples from the literature. Special attention will be given to the functionality of the films. But observations on aqueous

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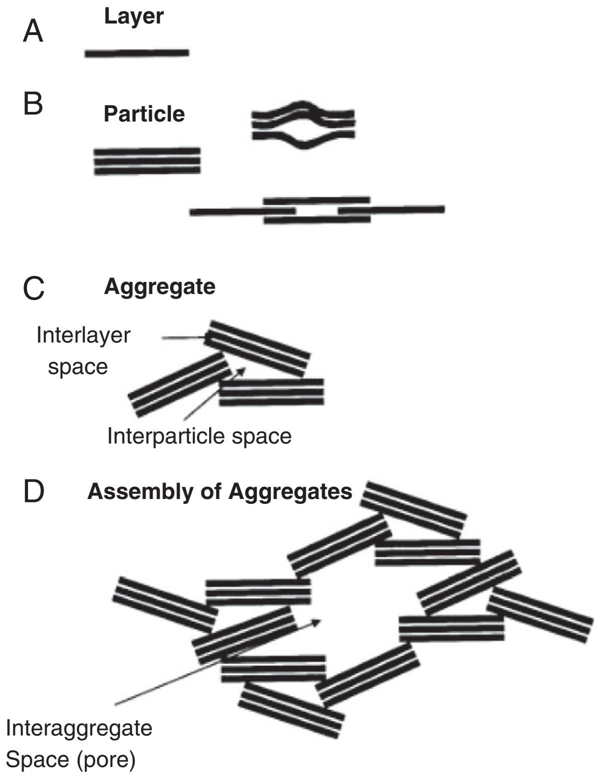

Fig. 1. Assembly of clay mineral layers into particles and aggregates of particles and definition of the corresponding spaces and pores.
Reproduced from Bergaya and Lagaly (2006) with permission of Elsevier.

dispersions give already a glimpse on what can be achieved with films. This is illustrated in Fig. 5, showing the hyperpolarizability of adsorbed methylene blue cations as a function of the loading in dilute aqueous dispersions of smectites. At extremely low loadings (10 nmol/g) the hyperpolarizability is 10–15 times higher than in aqueous solution (Boutton et al., 1997). However, it decreases quickly with increasing loading. This was tentatively ascribed to the organization of the MB molecules at the surface. Dimers can be formed with opposite direction of the dipole moments of the individual molecules and are indeed observed in aqueous dispersions at loadings below 1% of the cation exchange capacity (Bujdak, 2006; Cenens and Schoonheydt, 1988). This observation points to the importance of control on the organization of functional molecules at clay mineral surfaces.

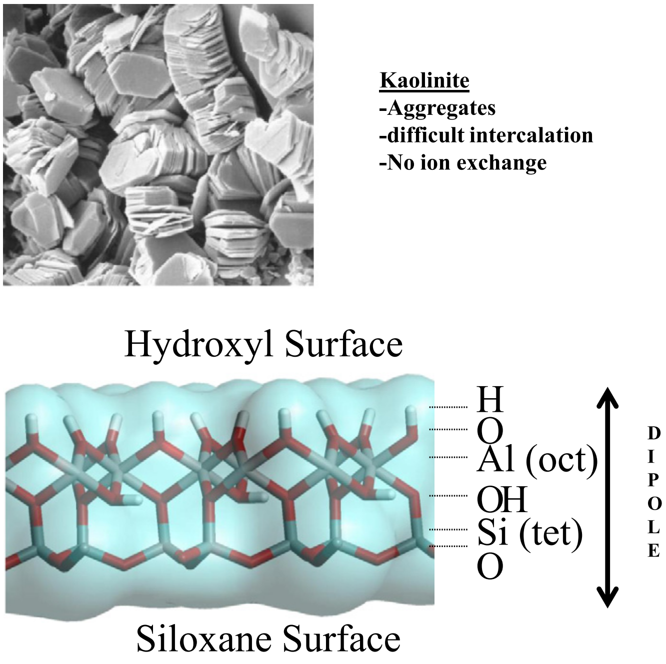

Fig. 2. Upper part: aggregates of hexagonal particles of kaolinite; lower part: the structure of a kaolinite layer with indication of the surfaces and the atoms.

2. Casting

A few drops of a dilute aqueous dispersion of a smectite are deposited on a hydrophobic surface, be it a hydrophobic glass surface or a polymer sheet e.g. mylar. The solvent water is allowed to evaporate slowly overnight in air at room temperature (Fig. 6). The clay mineral layers settle on the hydrophobic surface due to gravitational forces and form a continuous film without cracks. The film can be peeled off from the hydrophobic surface for further investigation. The film thickness depends on the concentration of clay mineral in the dispersion. However, dilute dispersions are preferred in order to maximize the number of individual layers in the dispersion. Aggregates and assemblies of aggregates of smectite layers must be minimized. They settle first, induce surface roughness in the film and disorder in the orientation of the clay mineral layers. Typical thicknesses of the films are in the range 0.1–2 mm. They have been and are used as self-standing films in FTIR spectroscopy in transmission mode (FTIR = Fourier Transform Infrared) and in EPR spectroscopy (EPR = Electron Paramagnetic Resonance). In principle they can be used in UV–VIS–NIR spectroscopy in transmission mode (UV–VIS–NIR = Ultraviolet–visible–Near Infrared). However, as the size of the clay mineral layers is of the order of the wavelength of the incoming light beam, light scattering poses serious problems, especially in the UV range. It can be minimized by using the thinnest films possible. In that case light absorption by the adsorbed molecules is only observed when they have a high extinction coefficient. This is the case for dye molecules, not for d–d transitions of transition metal ions.

The orientation of the adsorbed molecules and – indirectly – of the clay mineral layers in the films can be studied by FTIR using polarized light perpendicular to the film surface or by orienting the film in different directions with respect to the incoming unpolarized light beam. Pioneering IR spectroscopic studies of clay minerals and adsorbed molecules have been performed by such eminent clay mineral scientists as Mortland and Fripiat (1962) and Serratosa (1966). In the case of EPR spectra can be recorded with the magnetic field perpendicular to the film surface or perpendicular to the edge of the film. This is illustrated in Fig. 6 for the low spin, planar complex $[Co(en)_2]^{2+}$ (en = ethylenediamine) on hectorite (Schoonheydt and Pelgrims, 1982). This complex has one unpaired electron on Co^{2+}, which gives rise to an axially symmetric spectrum with two components, each characterized by two parameters, the g-factor and the hyperfine coupling constant A. The parallel component has $g_{zz} = g_{||} = 1.964$ and $A_{||} = 0.0149\ cm^{-1}$. The perpendicular component has $g_{xx} = g_{yy} = g| = 2.579$ and $A_{|} = 0.0174\ cm^{-1}$. When recording the spectrum with the magnetic field perpendicular to the film surface the parallel component is resolved. When the magnetic field is parallel with the film surface the perpendicular component of the spectrum is resolved. This shows that the clay mineral layers are oriented by-and-large with their surfaces parallel with the film surface and the planes of the complexes formed by the two en ligands and Co^{2+} are parallel with the clay mineral surface and with the surface of the film (Fig. 6). With such an orientation the complex maximizes the Coulombic attraction between the positive charge on cobalt and the negative layer charge and the dispersive interactions between the oxygen atoms of the siloxane surface and the ligand atoms, in this case H and N. This is energetically a favorable situation. One concludes that planar complexes prefer planar surfaces.