Synthesis, functionalization, and properties of intercalation compounds

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Abstract

Layered compounds are nanostructured, intrinsically anisotropic materials which often undergo intercalation reactions producing host–guest complexes. In this work examples from the molybdenum disulfide chemistry are used for discussing how the properties of the products may be regulated by appropriate selection of the guests species used for functionalizing the pristine sulfide. Special attention is given to new intercalates based in the intercalation of surfactants, which under special conditions may act as template promoting the conversion of the layered products into micro and nanotubes. The form how this kind of surfactants may be used for obtaining laminar derivatives of cadmium disulfide with the sulfide in a confined state is also described.
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1. Layered solids

Layered compounds are solids formed by pilling up planar or near planar layers. The layers extended along distances far away than the typical bond distances lead to characteristic nanostructured arrangements [1]. While the layers in these solids are constituted by relatively strong ionic–covalent interatomic interactions (150–300 kJ/mol), showing electronic structures which may be described by typical electronic bands schemes, interactions between the layers are much weaker, frequently in the range 40–150 kJ/mol. Depending on the chemical nature of the compounds, interlaminar interaction are van der Waals, hydrogen bonding, ionic, or Lewis acid–base interactions. Furthermore, layered compounds are intrinsically anisotropic. Starting from crystalline powders, it is often possible to induce macroscopically observable anisotropy by physical methods. For example, by pressing microcrystalline samples of MoS_2 conductivities with an anisotropy degree of about 10 are observed [2]. The self-assembling capacity of the layers in these solids may also be used for obtaining relatively ordered films and surfaces. In addition to all these intrinsic properties, layered solids may be chemically modified by altering the nature of the interlaminar phase. By this way new-layered host–guest compounds are obtained thus opening the possibility of regulating the properties of the products by an appropriate selection of the components. Such properties make layered solids interesting as materials for a variety of applications in fields like electrochemistry, electronic and optics.

In this article, we describe examples from the chemistry of the molybdenum disulfide [3] which illustrate how the properties of layered compounds may be changed and/or regulated by altering the nature of the interlaminar spaces. Attention is specially focused on the functionalization of the solids by intercalation of surfactants as well as on its use as templates for obtaining other layered or tubular species.

2. Intercalation compounds

Layered solids may be functionalized by the insertion of chemical species in the interlaminar spaces leading to host–guest compounds. A typical and widely known example of this kind of processes is the intercalation of electron donors like alkali metals [4,5]. Indeed, special attention has deserved the intercalation of lithium because the potentiality of these compounds as electrode materials in lithium batteries [6]. Intercalation may be performed by chemical as well as by electrochemical reactions

$$MoS_2 \xrightarrow[\text{or BuLi (hexane), 24 h, r.t.}]{\text{Au/Li/Li}^+\text{(solv)/MoS}_2\text{/Au}} Li_xMoS_2$$
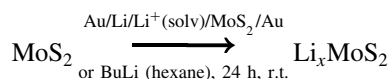
The intercalation energetics is mainly governed by the interaction between intercalated lithium and the layered

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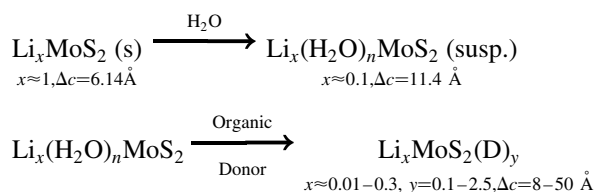*E-mail address:* ggonzale@uchile.cl

host [7]. Main contributions are due to host–guest charge transfer which in turn is determined by the nature of the host, particularly, by the capability of the latter for acting as electron acceptor; i.e. by the relative position of the valence and conduction bands of the layers. In lithium intercalation compounds, the extension of the charge transfer may be detected by observing the activity or the chemical potential of the lithium ion in the solid, which is directly determined from the potential of the couple Li/Li (intercalated) in an appropriate electrochemical cell. How far and how easily the transfer occurs, depends on both the electronic nature of the guest and the stabilization of the lithium ions in the interlaminar space.

Although intercalation processes are generally considered to be topotactic, because not important structural changes but alterations of the interlaminar distances occurs, there are cases like that of the MoS_2 where also subtle but significant structural changes are observed [3]. Indeed the coordination of molybdenum by sulfur atoms changes from trigonal prismatic in the pristine MoS_2 to an octahedral modification when it is intercalated. An important consequence of this structural change is a modification of the band structure, which implies the product being converted in an electronic conductor. This kind of functionalization of MoS_2 not only changes the conductive properties of the materials but also activates it for undergoing further intercalation processes.

3. Co-intercalation of lithium and organic species

The functionalization of laminar solids may be further accomplished by co-intercalation of lithium and organic electron pair donors [8]. The synthesis of these intercalates requires of the activation step mentioned above before the addition of the organic species. In the case of many semiconductors like MoS_2 that may be performed by a rapid hydrolysis of the host previously intercalated with lithium. The intercalation of organic species causes important changes of the interlaminar spaces. These changes may be clearly followed by powder X-ray diffraction analysis by observing the 001 reflections which—due to a partial orientation of the samples, a typical feature of layered systems— are normally enhanced. Purity degree of obtained phases is also apparent in the diffractograms

$$Li_xMoS_2 \text{ (s)} \xrightarrow{H_2O} Li_x(H_2O)_nMoS_2 \text{ (susp.)}$$
$$\begin{array}{cc} x\approx1,\Delta c=6.14\text{Å} & x\approx0.1,\Delta c=11.4\text{ Å} \end{array}$$

$$Li_x(H_2O)_nMoS_2 \xrightarrow[\text{Donor}]{\text{Organic}} Li_xMoS_2(D)_y$$
$$x\approx0.01-0.3,\ y=0.1-2.5,\Delta c=8-50\text{ Å}$$

The chemical potential of lithium is clearly altered by the intercalation of donors. As observed in Table 1, the potential increases with the electron pair donor capability of the neighborhood of lithium.

Table 1
Average open circuit, quasi-equilibrium potentials for MoS_2 derivatives

Compound	Average potential (V vs Li/Li$^+$)
MoS_2 (pure)	1.60
Li_xMoS_2 (exfoliated)	1.64
Li_xMoS_2 (PEO)$_{1.0}$	2.61
Li_xMoS_2 (DEA)$_{0.2}$	2.80

The intercalation of semiconductors generally leads to mixed ionic–electronic conductors. While electronic conductivity depends essentially on the electron structure of the host and the magnitude of the host–guest charge transfer, the ion transport is determined by the structure of the interlaminar phase. In general, the presence of donors enhances the lithium mobility. However, other factors are also involved. Thus, for instance, the lithium diffusion coefficients are notoriously higher for the compounds $Li_{0.2}MoS_2(DEA)_{0.2}$ [9] than for $Li_{0.1}MoS_2(PEO)_{1.0}$ [10]. Considering the structures of the interlaminar phases of these two products—homogeneously distributed in the interlaminar phase, tetrahedrically coordinated by the oxygen atoms of the polyether [11] in the PEO compound and forming trinuclear lithium cluster Li_3 in the amine derivative [12]—the lower energetic barrier to lithium mobility observed for the amine derivatives appears to be related to the presence of clusters with strong Li-Li interactions.

4. Intercalation of surfactants into MoS_2

The intercalation of long chain amines or of the corresponding alkyl ammonium salts leads to the expected intercalation compounds. As evidenced by the X-ray diffraction patterns of the products which, as seen in the example reproduced in Fig. 1, show well resolved 001 reflections, the compounds are formed by a bilayer of the surfactant intercalated in the MoS_2 interlaminar spaces [8,13].

These compounds are specially attractive among others because: (i) they define hydrocarbon-like interlaminar spaces; (ii) they potentially have coating properties similar
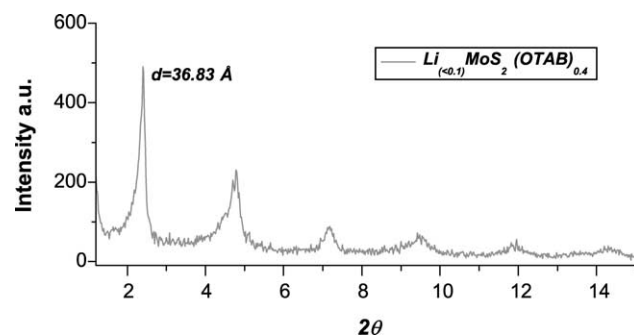

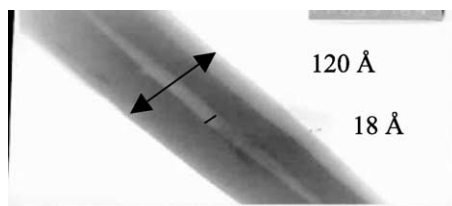Fig. 1. X-ray diffraction pattern of a MoS_2–octadecylamonium bromide nanocomposite.

Fig. 2. Transmission electron micrography of a nanotube obtained by hydrothermal treatment of a MoS_2–amine nanocomposite.

to those of typical long-chain bipolar species; and (iii) the stability and simultaneous flexibility of intercalated surfactants permits to use them, as discussed below, in template assisted transformations of the products or in the development of new laminar systems (Fig. 2).

5. Surfactant-templated formation of MoS_2 nanotubes

Laminar structures often lead to nanostructured materials [14–16]. However, reaction conditions are in general drastic and the yields frequently poor. The use of templates has proved to be favorable in order to produce nanostructures under milder conditions [17]. The treatment under hydrothermal conditions of surfactant–semiconductor nanocomposites like those discussed above leads indeed to micro and nanostructured products.

The distribution of the components in obtained mixtures may be often regulated by properly selecting the reaction conditions.

6. Surfactant–cadmium disulfide layered compounds

Although cadmium disulfide normally crystallizes with a wurtzite or zinc blende structure, the synthesis scheme described in Fig. 3 leads to laminar phases like those described for the MoS_2 intercalate described above.

X-ray diffraction patterns of the products like the typical one illustrated in Fig. 4 indicate that they may be described as surfactant bilayers intercalated in a layered CdS network.

The presence of the surfactant results in the formation of an ordered solid whose diffraction pattern does not permit to
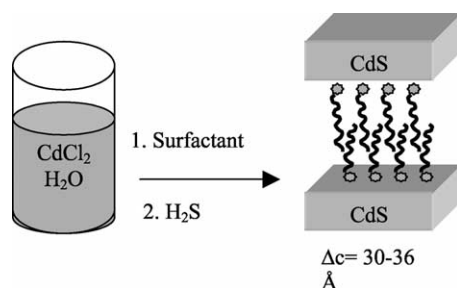

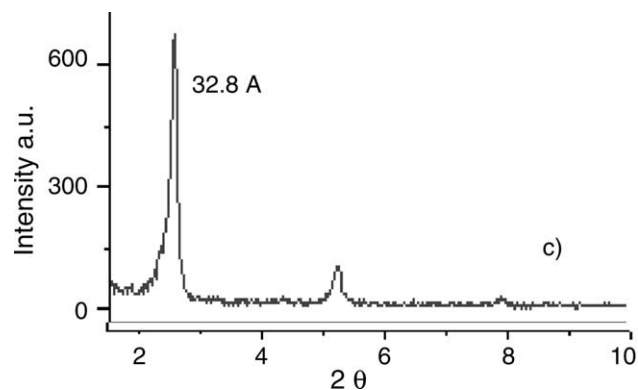Fig. 3. Scheme of synthesis of layered CdS–octadecylamonium bromide nanocomposites.

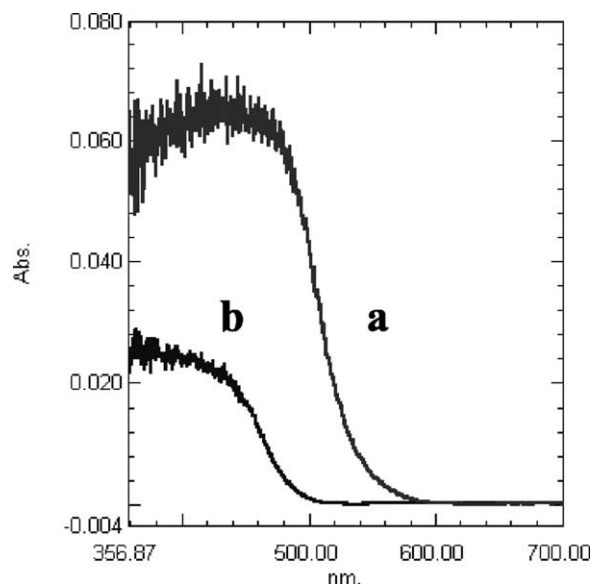Fig. 4. X-ray diffraction pattern of the compound $(CdS)_{0.5}CdCl_2$ (octadecilamonium bromide)$_{2.4}$.

Fig. 5. UV–visible absorption spectra of solid samples of bulk CdS (a) and of the compound $(CdS)_{1.2}CdCl_2$ (OTAB)$_{1.8}$ (b) at room temperature.

detect the structure of pure CdS; the phase appears to be a pure one. That not withstanding, studies in order to confirm the real structure and bonding in the cadmium sulfide in these compounds are in progress. Interestingly, the UV–visible absorption and luminescence spectra agree with the layered structure proposed above. Indeed, in this compound CdS appears to be in a confined state. As observed in Fig. 5, the absorption edge of the intercalation compound is shifted towards higher energies respect to that of bulk CdS. The same effect is observed in the luminescence spectra.

7. Conclusions

Layered solids are intrinsically bidimensional nanostructured materials constituted by self-assembled phases. Microscopic order in this compounds leads to a peculiar nanoheterogeneity and anisotropic properties which may be suitable for the development of new materials useful in a variety of applications, among them in the fields of

the electronic and the optics. Since the properties of layered solids are strongly influenced by the nature of the interlaminar spaces, the intercalation processes permit the regulation of properties, thus giving the systems great versatility. The intercalation of organic species, in particular surfactants, improves the application of these materials as thin films. Template ability of surfactants also permit the conversion under adequate conditions of layered into tubular structures. Furthermore, the use of surfactants, able to undergo self-assembling in layered structures under proper conditions, may be used as templates for the preparation of new layered solids. Properties like those described for CdS which under these conditions behaves as confined substance make this kind of products promissory for optoelectronic applications.

Acknowledgements

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