A modified Langmuir Schaefer method for the creation of functional thin films
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2010

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 6

Insertion of Nickel (II) Oxamate in clay template

6.1 Introduction

The controlled synthesis of inorganic materials with specific morphology is an important aspect in the development of new materials in many fields such as catalysis, electronics, nanocomposites, etc. The morphosynthesis of these novel materials into suitable ordered host systems capable of incorporating molecules with interesting physical and chemical properties is a major challenge in current materials science and nanotechnology. Our focus here is to use a new approach involving templating and self-assembly of nanoscale building blocks to prepare novel layered molecular magnet-based materials.\textsuperscript{1-3} Among the potential magnetic guest molecules, transition metal polynuclear coordination compounds have attracted much attention since the discovery, in 1993,\textsuperscript{4,5} of the first single-molecule magnet (SMM) with the formula Mn\textsubscript{12}O\textsubscript{12}(O\textsubscript{2}CMe)\textsubscript{16}(H\textsubscript{2}O)\textsubscript{4}(Mn\textsubscript{12}), which exhibits slow relaxation of the magnetization below a blocking temperature ($T_B$) of 4.0 K. Nevertheless, the integration of such materials into actual functional devices will require morphosynthesis strategies to achieve spontaneous multilevel organization. To this purpose, heterogeneous self-assembly approaches using both inorganic and organic materials as support host systems have been used.\textsuperscript{6} Here we present a simple synthetic strategy to prepare new magnetic thin films of preformed polynuclear building blocks through the use of single clay platelets as host template. As already discussed previously, Montmorillonite clay is a class of layered aluminosilicate minerals with a unique combination of swelling, intercalation, and ion exchange properties. Its structure consists of two tetrahedral silica layers sandwiching a central octahedral alumina sheet. The 0.96 nm thick layers are negatively charged and neutrality is obtained, for example when hydrated cations are present in the galleries. With the addition of water, the hydration shell around these cations can increase to such an extent that the clay aggregates not only swell but disintegrate into elementary clay mineral platelets.
This exfoliation that is an important part of our approach to build magnetic thin films; using the montmorillonite clay minerals as template in a combined Langmuir-Schaefer (LS) and self-assembly (SA) technique.

### 6.2 Method

As in the previous chapter, the type of montmorillonite we employed was a gift from Kuninine industries-Japan with the same formula as mentioned earlier. As magnetic guest molecule, we chose the octanuclear nickel(II) oxamate complex with the formula \([\text{[Ni}_2\text{(mpba)}_3\text{[Ni(dpt)(H}_2\text{O)}]_6}\text{(ClO}_4\text{)}_4\text{12.5 H}_2\text{O}}, where mpba is the bridging ligand m-phenylenedioxamate and dpt the terminal ligand dipropylenetriamine. The Ni₈ cations have a dimer-of-tetramers structure with a double-propeller topology. Importantly, one coordination position of each of the six peripheral octahedral metal ions, partially blocked with the dipropylenetriamine ligand, is occupied by a labile water molecule that can be readily exchanged by anchoring and/or bridging deprotonated silanol groups from the host matrix during the ion-exchange process.

To fabricate our films, we first prepared a diluted dispersion of negatively charged single clay nanosheets in water in a Langmuir-Blodgett (LB) trough. Then we spread cationic amphiphilic molecules, namely Dimethyldioctadecylammonium bromide \([\text{CH}_3\text{(CH}_2\text{)}_{17}\text{][CH}_3\text{N}^+\text{Br}^-}\) dissolved in \(\text{CHCl}_3\text{-C}_2\text{H}_5\text{OH (9:1)}}\), a non-aqueous volatile solvent, onto this dispersion. In contrast to a classical LB experiment, where the surfactant spreads and floats on a pure water surface, in our modified method some of the clay sheets in the subphase are electrostatically adsorbed onto the floating surfactant monolayer and hybrid floating DODA-clay platelet units are formed at the air-dispersion interface. Compressing the barriers of the LB trough a hybrid DODA-clay monolayer is formed. Figure 1 shows the surface pressure-area (\(\Pi-a\)) isotherm of DODA spread onto pure water and onto a Montmorillonite containing subphase (clay concentration of 10 ppm). The \(\Pi-a\) curve for the DODA/clay monolayer is steeper and shifted towards smaller areas per molecules than the corresponding curve for DODA on pure water. This effect can be explained by the adsorption of the negatively charged clay platelets on the positively charged surfactant monolayer, which partly compensates the electrostatic repulsion between DODA head groups, allowing for a higher molecular density at a given surface pressure. The molecular area of DODA in the presence of 10 ppm clay dispersion was estimate to be 82
Å²/molecule by extrapolating to zero pressure linear part of the isotherm where a condensed phase is formed.

6.3 Results and discussion

6.3.1 Isotherms and microscopy
The LS hybrid DODA/clay films, prepared with a clay concentration of 10 ppm in the subphase, were successfully deposited by horizontal lifting at a constant surface pressure of 10 mN m⁻¹. The AFM micrograph of one hybrid layer deposited onto hydrophobic glass plates shown as insert in figure 6-1, confirms the formation of a compact hybrid monolayer at the air-dispersion interface. The transferred film is covered on the outside with a clay layer, and some exchangeable cations (Na⁺) remain on the outer clay surface. By dipping this clay-terminated film in a solution containing a cationic compound (in our case Ni₈), the later will naturally be adsorbed on the surface by an ion-exchange reaction and form a 2D cation layer on top of the clay surface. As sketched in the scheme in figure 6-2, this deposition sequence can be repeated as desired to create multilayered systems.

![Figure 6-1. Π-a isotherms of DODA on pure water (dotted line) and on aqueous subphase of clay (10 ppm, solid line). The inset shows the AFM image of the hybrid monolayer DODA/clay transferred onto glass plates at the surface pressure of 10 mN m⁻¹.](image-url)
**Spectroscopic characterisation.** Infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), magnetic measurements and X-ray diffraction (XRD) all testify to the successful grafting of the Ni₈ species. The infrared (IR) spectrum of a 40 layer thick Ni₈-DODA-clay film is shown in figure 6-3. It presents characteristic bands at low wavenumber 1800-200 cm⁻¹ corresponding to the ν(CO) and ν(ClO) stretching vibrations from the oxamato groups and the perchlorate anions, respectively. For pure Ni₈ we should see only ν(CO) = 1600 cm⁻¹ and ν(CO) = 1100 cm⁻¹ hence both Ni₈ cations and some residual counterbalancing ClO₄⁻ anions are present in our films. XPS data were collected on 40 layer thick films of Ni₈-DODA-clay on mylar in order to identify the presence of the Ni₈ inside the hybrid structure. Figure 6-3 shows a survey spectrum of the synthesised compound, one can clearly identify Si, Al, C, N, O, and Ni photoemission line which confirm the presence of expected components, the Ni cluster, the surfactant and the clay. A detailed scan of Ni2p core level region is displayed in insert of the figure 6-3, and found to display the multiplet splitting typical¹⁰,¹¹,¹² of Ni²⁺ – as expected for Ni₈. Furthermore, the investigation of the nitrogen 1s core level spectra led to the same conclusion. Comparing three N1s spectra namely those of a clay-DODA multilayer film synthesized by LB and self assembly⁹ without the Ni₈ adsorption step, of pure Ni₈ layer produced by dropcasting and of the Ni₈-DODA-clay films, one observes that the N1s signal in of latter is a weighted superposition of the former two. This confirms the successful integration in the layered clay structure of the Ni₈ compound and its integrity.

Figure 6-2. Schematic the preparation method and model of layered structures of the hybrid multilayer prepared from clay dispersion.
Figure 6-3. Infrared spectra of hybrid Ni$_8$-DODA-montmorillonite film (green line) and hybrid DODA-montmorillonite film (red line) transferred onto CaF$_2$ plates at a surface pressure of 10 mN m$^{-1}$ and for a clay concentration in the subphase of 10 mg l$^{-1}$ and Ni$_8$(ClO$_4$)$_4$, powder (black line). Wide scan by X-ray photoemission spectra of the Ni$_8$-DODA-montmorillonite film (red line) and high resolution scan in the Ni 2p region (insert) 40-layer film on mylar.

### 6.3.2 XRD Patterns of Hybrid Multilayers.

XRD data for a 40-layer Ni$_8$-clay-DODA film (prepared with a 10 ppm clay concentration in the subphase) are shown in Figure 6-4. One can distinguish three broad peaks at $2\theta \sim 2.1\pm0.2$, $\sim4.8\pm0.2$ and $\sim6.7\pm0.2$. Using the Bragg formula, one
can deduce the corresponding d(00l) spacing of ~42±3 Å. This is a much larger spacing than what is observed for a pure a clay-DODA multilayer 9, where a clay – DODA repeating unit thickness of 25 Å was found. Hence also XRD confirms the presence of the guest SMM in the clay stack (42Å-25Å=17Å).

6.3.3 Magnetic Properties

The direct current (dc) magnetic properties of a 110-layer Ni₈-DODA-clay film in the form of the \( \chi T \) versus \( T \) plot, \( \chi \) being the dc magnetic susceptibility (in arbitrary units) and \( T \) the temperature, are qualitatively similar to those of pure Ni₈ complex (data not shown). \( \chi_M T \) for Ni₈-DODA-clay exhibits a characteristic minimum at 22 K (\( T_{\text{min}} = 45 \) K for pure Ni₈) which is typical of two strong antiferromagnetically coupled, oxamate-bridged Ni₄ propeller units (\( J = -26.6 \) cm\(^{-1}\) for pure Ni₈) that are weakly ferromagnetically coupled through the meta-substituted phenylenediamidate bridges (\( J' = +3.1 \) cm\(^{-1}\) for pure Ni₈). Upon further cooling, \( \chi_M T \) for Ni₈-DODA-clay shows a maximum at 7 K (\( T_{\text{max}} = 3 \) K for pure Ni₈) which is likely due to the zero field splitting (ZFS) of the moderately anisotropic \( S = 4 \) ground spin state (\( D = -0.23 \) cm\(^{-1}\) for pure Ni₈) and/or antiferromagnetic intermolecular interactions.

The alternating current (ac) magnetic properties of Ni₈-DODA-clay in the form of the \( \chi' \) and \( \chi'' \) versus \( T \) plot, \( \chi' \) and \( \chi'' \) being the in-phase and out-of-phase ac magnetic susceptibilities respectively, show no evidence of slow magnetic relaxation effects above 2.0 K (data not shown). This situation contrasts that of the pure Ni₈ complex which shows a slow relaxation of the magnetization below \( T_B = \)
3.0 K that is reminiscent of SMMs. The distinct magnetic properties of Ni\textsubscript{8}-DODA-clay suggest that the Ni\textsubscript{8} molecules are not isolated but are interacting with each other and with their surrounding; this could trigger the loss of the SMM behaviour. It is likely that the aggregation of the Ni\textsubscript{8} molecules on the surface of the tetrahedral silica layers is due to the mediating effect of the deprotonated silanolate groups. The intermolecular antiferromagnetic interactions are then propagated by the Si–O\textsuperscript{-} acting as bridges between the peripheral high-spin Ni\textsuperscript{II} ions of neighbouring Ni\textsubscript{8} molecules. Along this line, there has been an earlier reported on the incorporation and further aggregation of Ni\textsubscript{8} molecules in ordered mesoporous silica.\textsuperscript{6} In that case, the silica-mediated surface aggregation of Ni\textsubscript{8} molecules leads to ferromagnetically coupled oligomeric [Ni\textsuperscript{II}\textsubscript{8}]\textsubscript{n} aggregates with higher blocking temperatures (\(T_B = 4.5–10.5\) K) than those of the crystalline material. In fact, it is well-known that the nature of the magnetic coupling in related \(\mu\)-hydroxo, \(\mu\)-alkoxo, and \(\mu\)-phenoxo nickel(II) complexes depends critically on the Ni–O–Ni bridge angle (\(\gamma\)), passing from ferromagnetic to antiferromagnetic when increasing the \(\gamma\) value (for \(\gamma\) values close to 90°).\textsuperscript{13-18}

In summery we have described a new method to incorporate Ni\textsubscript{8} SMM in a hybrid organic-inorganic nanostructure. The combination of LS deposition with SA allows a control the film growth at the molecular level. Spectroscopic, crystallographic and magnetic data have proven the successful insertion of the guest cationic molecule within the clay template while preserving part of its interesting properties. Those results open a new route toward the highly controlled fabrication of tailored functional organic-inorganic nano-materials.

### 6.4 References

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