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New Magnetic Thin Film Hybrid Materials Built by the Incorporation of Octanickel(II)-oxamato Clusters Between Clay Mineral Platelets

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Materials

Clay

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The clay used for the preparation of the hybrid films was a natural sodium-saturated Montmorillonite Kunipia F (KUN) provided by Kunimine Industries Co. (Japan) with the structural formula $\text{Ca}_{0.11}\text{Na}_{0.891}(\text{Si}_{7.63}\text{Al}_{0.37})(\text{Al}_{3.053}\text{Mg}_{0.65}\text{Fe}_{0.245}\text{Ti}_{0.015})\text{O}_{20}(\text{OH})_4$ and cation-exchange capacity (CEC) 1.18 meq g⁻¹ of clay. The stock dispersion of the clay was prepared by stirring 1 g of clay for 12 hours in 1 litre of Millipore ultrapure water. The dispersion was diluted to a given concentration with pure water before being used as subphase in the LS deposition.

Surfactant

Dimethyldioctadecylammonium (DODA) bromide (purity 99+ %, Sigma-Aldrich) was used as received. DODA was dissolved in a mixture of HPLC-grade chloroform and methanol (9:1 in volume) to prepare a spreading solution of 0.1 mg ml⁻¹.

Ni₈ molecules

The octanuclear nickel(II) oxamate complex with the formula $\{[\text{Ni}_2(\text{mpba})_3][\text{Ni}(\text{dpt})(\text{H}_2\text{O})]_6\}(\text{ClO}_4)_4 \cdot 12.5 \text{ H}_2\text{O}$, where mpba is the bridging ligand *m*-phenylenedioxamato and dpt the terminal ligand dipropylenetriamine was prepared as detailed in references 1 and 2.

Preparation of the hybrid layers

All films were prepared by means of a Nima Technology thermostated 612D LB trough at a temperature of $21 \pm 0.5^\circ\text{C}$. The pressure sensor employs a Wilhelmy plate (small length of chromatography paper) to measure surface pressure (reduction in surface tension). Pure water and clay dispersions in Millipore Q-grade water were used as subphase. A clay concentration in the dispersion of

10 ppm was chosen as the optimal value.³ Depending on the requirements of the characterization method, samples were deposited either on glass for AFM, Mylar substrates for XRD, SQUID and XPS, or on CaF₂ plates for IR. First 200-300 μ l of CHCl₃-C₂H₅OH (9:1)-DODA mixture (0.1 mg ml⁻¹) were injected at the air water interface. After a waiting time of 20-30 min to allow for hybridization to occur, the hybrid DODA-clay layer at the air water interface was compressed at a rate of 30 cm²min⁻¹ until the chosen stabilization pressure of 13 mNm⁻¹ was reached. This pressure was maintained throughout the deposition process. We employed a Mitsubishi 6 axes robotic arm for the movement of the substrate during the whole deposition procedure. Films were deposited by horizontal lift onto one of the above mentioned substrates, with downward and lifting speeds of 10 and 2 mm min⁻¹, respectively. Samples were allowed to touch the water (very gentle dip of max 0.5 mm below the water level) and rinsed directly after dipping in 18 M Ω MilliQ water to eliminate possible weakly attached cations remaining from the hybridization process. The substrate was then dipped in a solution of Ni₈ for hybridization.

Characterization Techniques

Atomic Force Microscopy

Hydrophobic glass plates (modified with dodecyltrichlorosilane from ABCR GmbH & Co), were used as substrates for the AFM measurements. AFM images of the hybrid films were obtained using a Scientec 5100 equipped with Si n-type cantilever with a tip radius <10 nm and ~25-75 N/m of force constant. Images were recorded in tapping mode.

Infrared Spectroscopy (IR)

Calcium fluoride (CaF₂) plates, rendered hydrophobic by rubbing with molten ferric stearate, were used as substrates for FTIR measurements. Infrared spectra of the multilayer films on hydrophobic CaF₂

plates (15 mm x 10 mm x 1 mm) were measured in transmission mode with a Bruker IFS 66v/S vacuum FTIR spectrometer operating at 10^{-2} mbar. The FTIR spectrometer was equipped with a liquid nitrogen cooled MCT detector and a KBr beam splitter. Each spectrum was the average of 150 scans collected with 2 cm^{-1} resolution.

X-Ray Diffraction (XRD)

XRD patterns were collected using a Philips PANalytical X'Pert MRD diffractometer with a $\text{Cu K}\alpha$ radiation source ($\lambda=1.5418\text{\AA}$) operated at 40kV, 40mA, a 0.25° divergent slit and a 0.125° antiscattering slit. The reflectivity patterns were recorded in the 2-Theta (2θ) range from 0.5 to 10° with a 0.02° step and counting time of 10 s per step.

X-ray Photoelectron Spectroscopy (XPS)

Photoemission spectra were collected with a SSX-100 (Surface Science Instruments) spectrometer equipped with a monochromatic $\text{Al K}\alpha$ X-ray source ($h\nu$ 1486.6 eV) and operating in a base pressure of 3×10^{-10} mbar. The energy resolution was set to 1.3 eV and the photoelectron take-off angle was 37° . A flood gun providing 0.1 eV kinetic energy electrons in combination with a Mo grid placed above the sample were used to compensate for sample charging. All binding energies were referenced to the Si $2p$ peak^{4,5} of clay at 102.9 eV. Spectral analysis included a Shirley background subtraction⁶ and peak deconvolution using a linear combination of Gaussian and Lorentzian functions with a mixing ratio of 0.9 (90% Gaussian) in a least squares curve fitting program (WinSpec) developed at the LISE, University of Namur, Belgium.

Magnetic Characterization

Variable temperature (2–300 K) dc magnetic measurements of a 110 layer DODA-clay-Ni₈ film on Mylar were carried out with a Quantum Design SQUID magnetometer. Variable-temperature (2–6 K) ac magnetic measurements were performed under zero applied static field and at 1 G oscillating field in the frequency range 3–900 Hz.

XPS Spectra

The figure 1 shows the comparison between the N1s core level photoemission signal of a DODA-clay multilayer film synthesized by LS and self-assembly (see Toma *et al.*³) without the Ni₈ insertion step (A), a pure Ni₈ layer produced by dropcasting (B) and the DODA-clay-Ni₈ films (C) fits and raw data. One can clearly see a drastic difference in the line shape. The N1s signal of pure clay DODA is mainly composed by two peaks at 397.6eV and 399.8eV which are attributed to the C-N-C and C-N⁺-C nitrogen components within the surfactant molecule when attached to the clays. The N1s photoemission line of the pure Ni₈ compound was fitted with 1 asymmetric Gaussian component to account for the Ni-C=N, Ni-C-N at binding energies 399.0eV and 400.1eV, and an extra component, which we indicate as Ni-C-N*, at 401.9eV. In the DODA-Montmorillonite-Ni₈ case fitting of the N1s spectrum reveals 4 main contributions. A slight shift in binding energy position observed for the various N1s components of the Ni₈ compound when present in the inter-lamellar space could indicate some hybridization, a slight electron delocalization or some deformation of the bond due to the strong electrostatic interaction arising from the clay's natural charge imbalance. These spectra confirm the presence of the Ni₈ compound inside the clay layered structure and therefore testify to successful insertion.

Figure 1 X-ray photoemission spectra of the N1s region and fit of: a 40-layer DODA–Montmorillonite hybrid film on Mylar (A); of a pure Ni₈ layer produced by dropcasting (B), of a 40-layer DODA–Montmorillonite–Ni₈ hybrid film on Mylar.

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