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Magnetic-field-assisted assembly of CoFe layered double hydroxide ultrathin films with enhanced electrochemical behavior and magnetic anisotropy†

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Magnetic films based on CoFe LDH nanoplatelets and porphyrin anions were fabricated by the layer-by-layer assembly technique with an assistance of an external magnetic field, which show enhanced electrochemical behavior and magnetic anisotropy.

Self-assembly or directed assembly of discrete nanostructures into organized patterns provides a new route to the formation of functional materials. The use of external fields has attracted great interest as a powerful method to direct the assembly of colloidal nanocrystals and nanoparticles for tailoring the mechanical, optical and electronic properties of materials.¹ Controlled self-assembly of nanoparticles with field-assistance has offered a convenient tool for the fabrication of multifunctional materials or devices with asymmetric, anisometric or anisotropic properties, particularly when used with particles that are tailored to be intrinsically responsive. Recently, magnetic-field-assisted thin films have been achieved by the drop-auxiliary layer-by-layer (LBL) method utilizing the L1₀-FePt alloy,² which exhibited magnetic anisotropy and phototunable ferromagnetic properties. This inspires us to further challenge the goal of precisely-controlled film assembly based on the nanometre scale, which is seriously essential for the fine-tuning of highly ordered magnetic nanostructures. Moreover, the approach of magnetic-field-assisted assembly is extraordinarily important for the purpose of understanding the formation of magnetic anisotropy as well as fabricating various application-tailored devices.

Layered double hydroxides (LDHs) are a large class of typical inorganic layered materials which can be described by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{z+}(A^{n-})_{z/n} \cdot yH_2O$ (M^{II} and M^{III} are divalent and trivalent metals, respectively; A^{n-} is the interlayer anion compensating for the positive charge of the brucite-like layers).³ These materials have received considerable attention for their potential application

in the fields of catalysis,⁴ functional materials,⁵ biology and medicine.⁶ In addition, LDH materials containing magnetic transition metals (Fe, Ni, *etc.*) were also synthesized, which can be potentially used as sustainable and recycled catalysts and supports, adsorbents and ion exchangers with easy manipulation by an external magnetic field.⁷ Compared with other magnetic particles (Co, Fe, Fe₃O₄, Fe₂O₃, *etc.*), LDHs exhibit a specific layered 2D structure, which gives us impetus to explore the fabrication of anisotropic film materials with the assistance of an external magnetic field. It can be expected that such films possess the advantage of a single-domain structure where all spins align in one direction and flip simultaneously, thereby largely improving the magnetic anisotropy.

Herein, we demonstrate the fabrication of ultrathin films based on CoFe LDH nanoplatelets and porphyrin anions *via* the magnetic-field-assisted (MFA) layer-by-layer (LBL) method, which show largely enhanced electrochemical behavior and magnetic anisotropy. This is attributed to the dense packing and high orientation of building blocks (CoFe LDH nanoplatelets) with the coupling of simultaneous electrostatic field and magnetic field. Therefore, the MFA LBL technique applied in this work provides a promising approach for the fabrication of fine-tuning magnetic films with anisotropy which can be potentially used in magnetic-electric devices.

In this work, CoFe LDH (chemical composition: Co_{0.74}Fe_{0.26}(OH)₂(NO₃)_{0.25}·0.71H₂O; Co/Fe = 3 : 1) with high crystallinity was synthesized by a modified coprecipitation method (see ESI† for more details). Fig. 1a shows the XRD pattern of the CoFe LDH sample, which can be indexed as a rhombohedral structure with 2θ 11.4° ($d_{003} = 7.72$ Å). No other crystalline phase was detected, indicating the high purity of the product. Moreover, the FT-IR spectrum (Fig. 1b) provides evidence for the presence of NO₃⁻ existing in the LDH gallery (band at 1382 cm⁻¹); no absorption at 1356 cm⁻¹ was observed, indicating the absence of carbonate. The SEM image reveals that the individual CoFe LDH hexagonal nanoplatelets with a particle size of 80–100 nm and an aspect ratio of 5–7 crystallized with a narrow size distribution (Fig. 1c). The colloidal CoFe LDH suspension was obtained by thoroughly washing with deionized water and then filtering using a membrane filter (0.2 μm, Millipore). A clear Tyndall light scattering was observed (Fig. 1d), and the well-dispersed colloidal suspension was transparent and stable without any

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† Electronic supplementary information (ESI) available: Preparation of CoFe-LDH and (LDH/TPPS)_n ultrathin films. SEM images of (LDH/TPPS)_n, electrochemistry of the film, UV-vis absorption spectra and hysteresis loops of the WMFA and MFA (0.3 T) films. See DOI: 10.1039/c0cc04859c

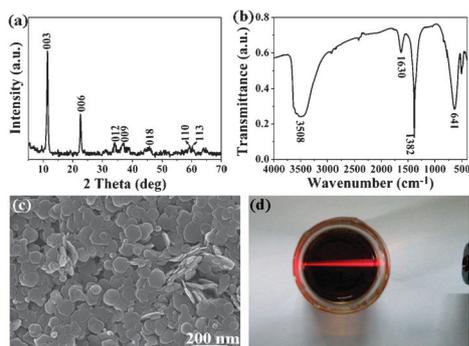


Fig. 1 Characterization of the CoFe LDH: (a) XRD pattern, (b) FT-IR spectrum, (c) SEM image, and (d) photograph of a colloidal suspension of CoFe LDH nanoplatelets. The red beam was incident from the side to demonstrate the Tyndall effect.

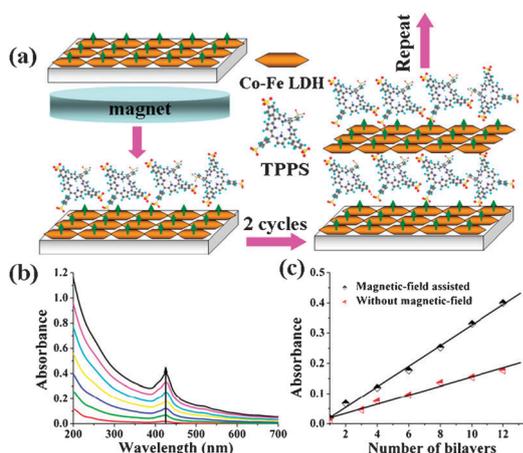


Fig. 2 (a) Schematic representation for the MFA LBL assembly of the (CoFe LDH/TPPS)_n film; (b) UV-vis absorption spectra of the MFA (CoFe LDH/TPPS)_n ($n = 1-12$) films; and (c) absorbance of the MFA and WMFA films at 421 nm as a function of n .

precipitation when stored in an N₂ atmosphere for more than one month.

Ultrathin films were fabricated by alternate assembly of LDH nanoplatelets with the porphyrin anion, 4,4',4'',4'''-(porphine-5,10,15,20-tetrayl)tetrakis(benzenesulfonic acid) tetrasodium salt hydrate (TPPS), by a magnetic-field-assisted (MFA) LBL method (schematically shown in Fig. 2a). The MFA and without-magnetic-field-assisted (WMFA) (CoFe LDH/TPPS)_n ($n = 1-12$) ultrathin films deposited on quartz substrates were, respectively, monitored by UV-visible absorption spectroscopy (Fig. 2b and Fig. S1, ESI[†]). The MFA (LDH/TPPS)_n films exhibit a strong absorption band at 421 nm attributed to the characteristic Soret band of TPPS, and its intensity correlates linearly with the increase of bilayer number n (Fig. 2c), indicative of a stepwise and regular deposition procedure with almost equal amounts of TPPS incorporated in each cycle. The UV-vis absorption spectra of the WMFA (LDH/TPPS)_n films display a similar increase at 421 nm along with the increase of n (Fig. S1, ESI[†]). However, the slope of the plot (absorbance at 421 nm vs. n) is much less than that of the MFA films (Fig. 2c). This indicates that a more dense packing of building blocks in a bilayer cycle

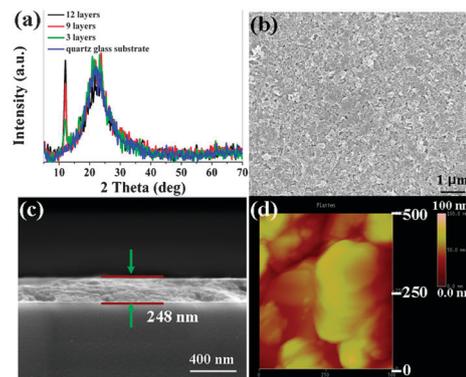


Fig. 3 (a) XRD patterns of the MFA (CoFe LDH/TPPS)_n films ($n = 3, 9, 12$), (b) top view of SEM, (c) side view of SEM and (d) AFM image for the (CoFe LDH/TPPS)₁₂ film.

deposition was obtained for the MFA (LDH/TPPS)_n films, as a result of the enhancement of the driving force including electrostatic interaction and magnetic attraction in the assembly process.

The XRD patterns (Fig. 3a) for the obtained MFA (CoFe LDH/TPPS)_n ($n = 3, 9, 12$) ultrathin films exhibit the characteristic reflection of the LDH structure with a (003) peak appearing as narrow, symmetric, strong lines at $2\theta = 11.4^\circ$, and both its intensity and symmetry increase successively upon increasing the deposition cycle. Moreover, the absence of any non-basal reflections ($h, k \neq 0$) at high angles is as expected for extremely well c-oriented assembly of LDH nanoplatelets.⁸ The surface morphology and thickness of MFA (CoFe LDH/TPPS)_n films were further investigated by SEM and AFM. The top view of an SEM image (Fig. 3b) shows that the film has a homogeneous surface and a high degree of c-orientation of the LDH platelets, consistent with the XRD results (Fig. 3a). The film thickness with varying bilayer number can be estimated from side view of SEM images (Fig. 3c and Fig. S2, ESI[†]). The approximately linear increase in the thickness with n confirms that the MFA films possess a uniform and periodic layered structure perpendicular to the substrates. The AFM image (500 nm × 500 nm) of the MFA (CoFe LDH/TPPS)₁₂ film is shown in Fig. 3d, from which the value of root-mean-square (rms) roughness was found to be ~ 13.9 nm, indicating a relatively smooth surface.

Subsequently, we focused on the electrochemistry of CoFe LDH/TPPS hybrid films, taking into account the multiple redox behavior of Co and Fe. Fig. 4a shows the cyclic voltammograms (CVs) of different electrodes in 0.1 M NaOH solution at a scan rate of 0.1 V s⁻¹. No electrochemical response was observed for the bare ITO (green curve). Both the MFA (black curve) and WMFA (red curve) (CoFe LDH/TPPS)₆ film modified ITO electrodes display two pairs of redox peaks, corresponding to the redox processes of cobalt (0.52 V and 0.56 V) and iron (0.15 V and 0.27 V), respectively. However, the redox current is significantly enhanced for the MFA film modified electrode compared with the WMFA film. This is related to the higher concentration of LDH nanoplatelets in the case of the MFA film. In order to further understand the redox process, CVs of MFA CoFe LDH/TPPS/ITO were carried out in NaOH solution with various concentrations (Fig. S3, ESI[†]). Negative

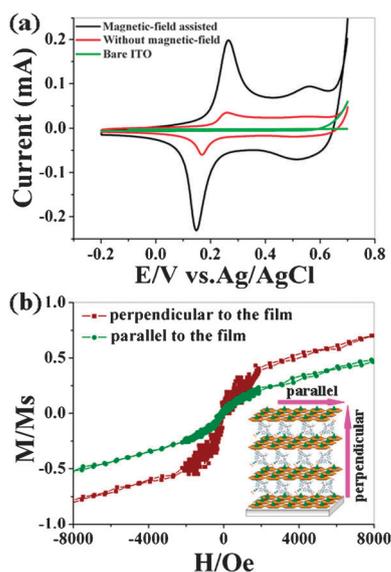


Fig. 4 (a) CVs of bare ITO (green), WMFA (red) and MFA (black) (CoFe LDH/TPPS)₆ the modified ITO electrode in 0.1 M NaOH at a scan rate of 0.1 V s⁻¹; (b) room temperature (300 K) hysteresis loops (0.5 T) at both orientations for the MFA (CoFe LDH/TPPS)₁₂ film. Magnetization values were normalized based on the corresponding saturation ones.

shifts in both anodic and cathodic peak potentials were observed upon increasing the concentration of OH⁻, indicating that OH⁻ plays a key role in the redox process of cobalt and iron. The effect of scan rate on the electrochemical response of the MFA (CoFe LDH/TPPS)₆ film is shown in Fig. S4 (ESI†). It was found that a linear relationship between the anodic (or cathodic) peak current and the potential sweep rate was obtained, indicating a surface-controlled process.⁹

To further investigate the effect of the external field on the assembly and property of the CoFe LDH/TPPS films, the hysteresis loops were employed to measure the magnetic anisotropy. The hysteresis loops (0.5 T) of the MFA (CoFe LDH/TPPS)₁₂ film measured at room temperature show that the coercive field and normalized remanence are much higher in the perpendicular direction than in the parallel direction (Fig. 4b). Moreover, the room temperature superparamagnetic behavior maintains simultaneously, similar to the synthesized CoFe LDH nanocrystals (Fig. S5, ESI†). The magnetic anisotropy of the MFA film decreased as the magnetic density used in the assembly process decreased to 0.3 T (Fig. S6, ESI†). In contrast, the hysteresis loops recorded with the WMFA (CoFe LDH/TPPS)₁₂ film both in the perpendicular and parallel directions of the substrate are identical (Fig. S7, ESI†). This demonstrates that the external magnetic field is crucial to the magnetic anisotropy of the MFA CoFe LDH/TPPS films, which can be attributed to the alignment of the magnetic domain for LDH nanoplatelets along the direction of the deposition field. In addition, dipolar interactions between LDH nanoplatelets in the magnetic field can be another contribution for the anisotropy property.^{1a,10}

In summary, CoFe LDH nanoplatelets with high dispersion and purity were prepared by a modified coprecipitation method. The MFA LBL assembly was employed to fabricate (CoFe LDH/TPPS)_n films by using LDH nanoplatelets and porphyrin anions as building blocks. The structural and morphological studies show that the MFA film is continuous and uniform with long range stacking order in the normal direction of the substrate. The coupling effect of interfacial electrostatic interactions and the external magnetic field gives rise to dense packing of LDH nanoplatelets compared with single electrostatic assembly. In addition, the assistance of external magnetic field induces the alignment of the LDH domain. As a result, enhancement of both electrochemical response and magnetic anisotropy was successfully achieved for the MFA (CoFe LDH/TPPS)_n films. Therefore, the novel strategy in this work can be effectively applied for the fabrication of magnetic anisotropic films and electronic devices with prospective application in magnetic information storage and sensors.

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