Hierarchical films of layered double hydroxides by using a sol–gel process and their high adaptability in water treatment†

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Layered double hydroxides (LDHs) films with hierarchical morphologies have been fabricated on different templates *via* the sol–gel nanocopying and *in situ* growth process, which exhibit desirable mechanical properties and high adaptability in water treatment.

Layered double hydroxides (LDHs), also well-known as hydrotalcite-like compounds or anionic clays, are inorganic layered materials which have attracted much attention because of their potential applications in catalysis, adsorption, separation, sensors, electrochemistry and bionanotechnology.[1] Their general formula is expressed by $[M^{II}_{1-x}M^{III}_{x}(OH)_2](A^{n-})_{x/n}{\cdot}mH_2O$ (M^{II} divalent and M^{III} trivalent metals respectively, A^{n-} *n*-valent anion). Recently, the preparation of nanostructured LDH films with rich morphologies is becoming the inevitable trend for the development of LDH materials.[2] Much effort has been focused on multifunctional LDHs films with micro- and nano-features for the propose of their applications in photonics, optoelectronics, full-color displays and as structured catalysts. To achieve the goals, many approaches have been reported, such as solvent evaporation,[3] hydrolysis of alkoxide,[4] ultrasonication,[5] coprecipitation,[6] layer-by-layer assembly[7] and *in situ* growth on aluminium.[8] Recently, a method of atomic layered deposition followed by *in situ* growth was reported by our group, for the purpose of fabricating hierarchical LDH films.[9] However, most of the techniques require rigorous experimental conditions, and the substrates are strictly limited to glass or metal wafers.[10] This is not suitable for easy preparation as well as practical application, and thus largely restricts the development of functional LDH films and remains a stimulating challenge. Therefore, it is highly desirable to achieve a new approach for the fabrication of LDH films with simple manipulation, low-cost, less equipment, large area production and applicability for various substrates.

Recently, much interest has been focused on the sol–gel synthesis of materials based on the hydrolysis and condensation of molecular precursors, for the preparation of a wide range of inorganic materials. Sol–gel chemistry applied to three-dimensional (3D) materials allows to develop simple but efficient routes to introduce some of the superb properties of biological structures into man-made materials all the way down to nanometre scale.[11] Huang *et al.* prepared metal oxide tubes maintaining stability on the macroscale by using the sol–gel process to replicate the templates that are abundant in nature, low cost and environmentally benign.[12] Sandhage and co-workers reported a continuous nanocrystalline rutile TiO_2-based coating on butterfly templates by the sol–gel technique, and the replica retains both the macro- and micro-structure of the organic tissue.[13] Therefore, the preparation principle through sol–gel synthesis of inorganic materials inspires and enlightens us to challenge the goal of construction of LDH films.

We report here the fabrication of hierarchical LDH films through a combination procedure of sol–gel process and *in situ* growth method, and demonstrate their application in water treatment. Three kinds of man-made supports (paper, cloth and sponge) were chosen as the template in this work (see ESI† for more details), and LDH films with 3D architectures composed of submicron features were obtained by a sol–gel process followed by an *in situ* growth technique. Moreover, the LDH films show high ability to remove dye molecules and heavy metal ions in water treatment. Compared with the corresponding powder samples, the LDH films provide desirable adaptability and mechanical properties, easy regeneration for water treatment and membrane separation technology. By virtue of the facile sol–gel replication and *in situ* growth technique, it is anticipated that LDH films can be fabricated on the surface of various substrates with specific potential applications.

In this work, the boehmite (Al(OOH)) primer sol was first prepared through hydrolysis of the precursor $Al(OPr)_3$, as described in ESI,† and its X-ray diffraction (XRD) pattern (Fig. S1†) can be indexed to orthorhombic AlOOH (JCPDS Card No. 21-1307). The substrates were washed thoroughly with water and ethanol, and immersed into the sol followed by a withdrawal velocity of 0.05 cm min^{-1} to ensure the deposition of a AlOOH coating. The substrates were then dried at room temperature in air. The continuous and uniform AlOOH coating was deposited on substrates with 40 cycles of surface sol–gel deposition.

As shown in Fig. 1A and B, disordered cellulose fibers can be observed on the surface of the filter paper, which possess hydroxyl groups and thus provide a suitable vehicle for the surface sol–gel process.[12a] The as-prepared AlOOH/paper (Fig. 1C and D) was found to replicate the morphology of the original filter paper. The process was an environmentally benign route and did not affect the surface architecture of the

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† Electronic supplementary information (ESI) available: Preparation and characterization of M(II)Al–LDH films, XRD pattern of the AlOOH sample, SEM images of ZnAl–LDH/cloth and ZnAl–LDH/sponge, XRD pattern and SEM image of ZnAl–LDH powder sample, adsorption rate curves of $K_2Cr_2O_7$ on the as-obtained ZnAl–LDH/paper film. See DOI: 10.1039/b926906a

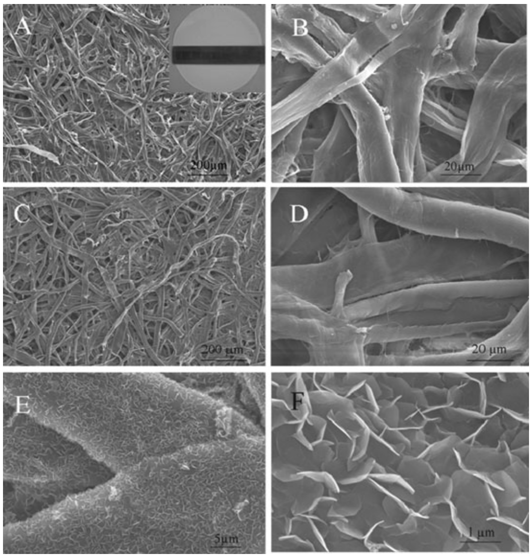

Fig. 1 SEM images of the original paper at (A) low magnification (an optical photograph of the paper is shown in the inset) and (B) high magnification; the paper with 40 deposition cycles of boehmite coating at (C) low magnification and (D) high magnification; the resulting ZnAl–LDH/paper film at (E) low magnification and (F) high magnification.

substrate. Subsequently, the ZnAl–LDH film was constructed based on the AlOOH/paper by an *in situ* growth technique reported by our group (ESI†), with the AlOOH coating serving as both substrate and source of aluminium. The resultant LDH/paper shows morphological characteristics of the original paper fibers (Fig. 1E), with numerous microcrystalline platelets (diameter of $\sim$1 μm) perpendicular to the surface of substrate as revealed by the high magnification (Fig. 1F). In order to verify the universality of the sol–gel *in situ* growth procedure, NiAl– and MgAl–LDH films were also prepared on the paper substrate with good crystallinity (Fig. 2). The different size of the NiAl– and MgAl–LDH microcrystallites is related to their respective crystallization process. Similar replication and growth processes were readily applied to other substrates such as cloth and sponge, resulting in ZnAl–LDH/cloth (Fig. S2†) and ZnAl–LDH/sponge film (Fig. S3†). The results above indicate that the as-grown LDH film mimics the original macroarchitecture of the supports.

The XRD patterns of the substrate and LDH films are shown in Fig. 3. The XRD pattern of the AlOOH/paper (Fig. 3(b)) is very similar to that of the pristine paper (Fig. 3(a)), with the reflections observed at 2θ 16° and 23°, indicating that the boehmite coating was amorphous. The XRD patterns of the synthesized M(II)Al–LDH (M = Zn, Ni, Mg) film on paper substrates after the *in situ* growth are displayed in Fig. 3(c), (d) and (e), respectively. In each case, the reflections can be indexed to a hexagonal lattice with $R3m$ rhombohedral symmetry, commonly used for the description of LDH structures.[14] The basal spacings of ZnAl, NiAl and MgAl–LDH are 0.877, 0.837 and 0.754 nm, respectively, close to the values reported for LDHs with NO_3^- (the former two) and CO_3^{2-} (the latter one).[8,15] Fig. 3(f) and (g) display the XRD patterns of ZnAl–LDH films grown on the cloth and sponge substrates respectively, also indicating the formation of

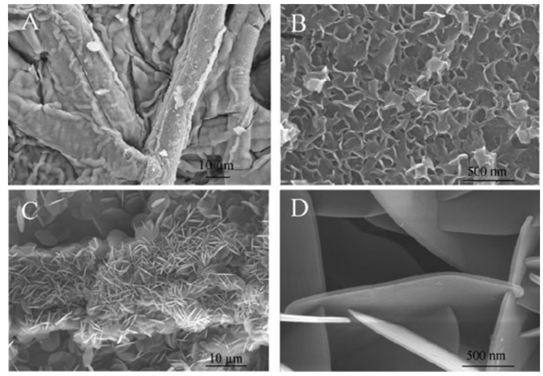

Fig. 2 SEM images of the NiAl–LDH/paper film at (A) low magnification and (B) high magnification; the MgAl–LDH/paper film at (C) low magnification and (D) high magnification.

a well-crystallized hydrotalcite-like LDH phase. The differences in intensity of LDH reflections may account for the different evolution and growth mechanism of the M(II)Al–LDH (M = Zn, Ni, Mg) films, respectively.[16] Based on the results above, it can be concluded that various LDH films with different morphologies which mimic the surface architecture of substrates can be prepared *via* the combined sol–gel–*in situ* growth procedure.

In recent years, many efforts have been devoted to study the adsorption and separation of pollutants in water by the use of LDH materials, owing to their low cost and excellent capability.[17] However, the regeneration and recycling of powder adsorbents remain a challenge for practical manipulation and application.[18] Through the general and reliable synthesis route in this work, the obtained ZnAl–LDH films with various morphologies and hierarchical structures show strong adsorption capability for dye molecules (sulforhodamine B and Congo red) and Cr^{VI} ion in water. Fig. 4 shows the adsorption rate curves of sulforhodamine B (RB) and Congo red on the as-obtained ZnAl–LDH/paper film, respectively, with the powder ZnAl–LDH as a reference sample (Fig. S4 and S5†). The absorption spectra of the solution as a function of time were recorded by using a UV-vis spectrometer. It was found

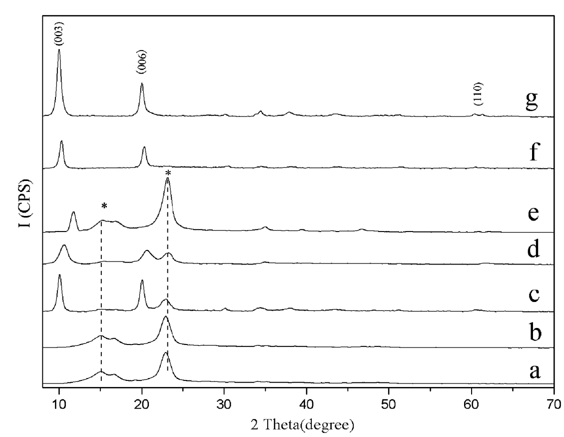

Fig. 3 XRD patterns of (a) paper, (b) AlOOH/paper, (c) ZnAl–LDH/paper, (d) NiAl–LDH/paper, (e) MgAl–LDH/paper, (f) ZnAl–LDH/cloth and (g) ZnAl–LDH/sponge (asterisks denote the reflections of paper substrate).

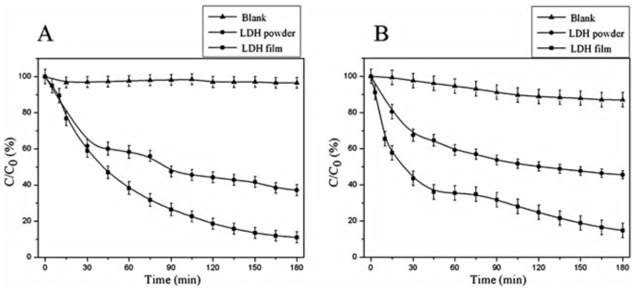

Fig. 4 Adsorption rate curves of (A) RB and (B) Congo red on the as-prepared ZnAl–LDH/paper film and the comparative powder sample.

that a rather slow self-adsorption of both RB and Congo red on the pristine paper was observed; while the ZnAl–LDH powder sample shows adsorption ability for the two dyes, with removal of ~63% (RB) and ~55% (Congo red) after 180 min. Compared with the powder sample, the ZnAl–LDH/paper film exhibits faster adsorption rate and higher removal capability. After 180 min, removal of ~89% (RB) and ~86% (Congo red) were achieved. Moreover, the adsorption capacity of the film sample reaches 2.0 mg g^{-1} (RB) and 20 mg g^{-1} (Congo red), much larger than that of the powder sample (1.3 mg g^{-1} (RB) and 11 mg g^{-1} (Congo red)). The poor adsorption behavior of the LDH powder sample is possibly due to its aggregation, which is generally inevitable for nano-scale materials. However, the well dispersed nano-crystals of LDH on the paper substrate without aggregation provide large specific surface area as well as good accessibility, accounting for the superior adsorption performances of the film sample. In addition, the ZnAl–LDH film was also demonstrated to serve as a water adsorbent to remove Cr^{VI} (10 ppm), considered as a primary highly toxic pollutant in water. Fig. S6† shows adsorption rate curves of $K_2Cr_2O_7$ on the as-prepared ZnAl–LDH/paper film, in which a removal of ~84% Cr^{VI} was obtained in 2 h. The results thus indicate that the templated-LDH film can be used as an excellent maneuverable adsorbent with faster elimination and higher adsorption capacity, compared with LDH powder samples.

In summary, various M(II)Al–LDH films on different substrates were obtained by sol–gel deposition and subsequent *in situ* growth procedure, which replicate the morphological properties of the templates with advantages of easy manipulation, low-cost, and large surface area. The obtained films show higher adsorption capacity and excellent ability to remove RB, Congo red and Cr^{VI} ion in water treatment, compared with the corresponding powder samples. By virtue of the facile sol–gel replication and *in situ* growth technique, it is expected that a wide variety of LDH films with complicated morphologies can be fabricated in a similar way. Therefore, this work provides new possibilities for the rational design and fabrication of hierarchical LDH films, which can be potentially applied in the fields of catalysts, adsorbents and membrane separation.

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