Journal of Membrane Science 567 (2018) 89–103

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Recent advances in layered double hydroxides (LDHs) as two-dimensional membrane materials for gas and liquid separations

Peng Lu[a], Yi Liu[b,*], Tuantuan Zhou[c], Qiang Wang[c], Yanshuo Li[a,*]

[a] School of Materials Science and Chemical Engineering, Ningbo University, 818 Fenghua Road, Ningbo 315211, PR China
[b] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, PR China
[c] College of Environmental Science and Engineering, Beijing Forestry University, 35 Qinghua East Road, Haidian District, Beijing 100083, PR China

ARTICLE INFO

Keywords:
2D-materials separation membranes
Gas separation
Liquid separation
Layered double hydroxides

ABSTRACT

Membrane-based technology represents an emerging strategy for energy-efficient gas/liquid separation. Among various factors, dimensionality and microstructure of membrane materials played a dominant role in determining their separation performance. Recently, unique structural properties of two-dimensional (2D) nanomaterials with atomic size thickness are rapidly emerging as desirable building blocks for the design of high performance membranes. Among them, layered double hydroxides (LDHs), a representative of anionic clays, have attracted extensive interest and exhibited promising prospects for membrane applications due to their uniform interlayer galleries, which may permit precise molecular sieving in case the gallery height was comparable with kinetic diameters of guest molecules. Moreover, highly tunable chemical compositions and gallery height as well as the rich surface functionality of LDH building blocks further endowed them with unprecedented opportunities for efficient gas/liquid separation. This paper summarizes recent breakthrough in LDH-based separation membranes with particular emphasis on the opportunities and challenges facing their commercial applications.

1. Introduction of two-dimensional membrane materials

Recently, unique physicochemical properties of two-dimensional (2D) nanomaterials with atomic layer thickness are rapidly emerging as superb building blocks for designing molecular sieve membranes surpassing the Robeson upper-bound [1–4]. The integration of 2D nanomaterials enables the formation of an ultrathin separation layer which promises unprecedented permeability and selective diffusion paths (interlayer galleries & in-plane pores) [5]. In addition, further incorporating 2D nanosheets into the polymer matrix, resulting in the formation of mixed matrix membranes (MMMs), is considered as a promising strategy for simultaneous improvement of both permeability and selectivity of polymer membranes [6,7]; moreover, their mechanical strength is anticipated to be improved either. At present, studies on 2D layered membranes are mainly focused on zeolites (e.g., exfoliated MFI nanosheets) [3,8–11], graphene-based materials [12–15], transition metal dichalcogenides (TMDCs) [16], metal-organic frameworks (MOFs) [17–19], covalent organic frameworks (COFs) [20–23], ionic clays (e.g. Montmorillonite [24,25] and anionic layered double hydroxides (LDHs) [26]). LDHs, also commonly called hydrotalcite-like compounds, are representative of anionic layered materials composed of positively charged brucite-like 2D sheets, charge compensating anions and solvation molecules located in interlayer galleries [27,28]. Compositional flexibility and gallery height adjustability of LDHs give rise to a functional diversity. Furthermore, microstructures of LDHs can be easily tuned by changing the synthetic strategy [29]. At present, LDHs have shown widespread applications in CO_2 adsorption [30–33], catalysts [34–37], polymeric modification [28,38,39], electrochemistry [40] and controlled drug delivery [41].

1.1. Chemical composition and structure of LDHs

Hydrotalcite, which was first discovered in Sweden and subsequently gave its name to a large mineral group of naturally occurring LDHs [42], could be expressed by the formula $[Mg_6Al_2(OH)_{16}]CO_3{\cdot}4H_2O$ [43]. Framework structures of naturally occurring LDHs, which could be expressed in rhombohedral and hexagonal forms, respectively, were indicated in Fig. 1(a) and (b). LDHs are made of layers of metal cations (M^{2+} and M^{3+}) with similar ionic radii. These metal cations occupy the centers of edge sharing octahedra, whose vertexes contain hydroxide ions that connect to form infinite 2D sheets [27]. A general molecular formula of LDHs can be expressed as

---

* Corresponding authors.
E-mail addresses: diligenliu@dlut.edu.cn (Y. Liu), liyanshuo@nbu.edu.cn (Y. Li).

https://doi.org/10.1016/j.memsci.2018.09.041
Received 29 June 2018; Received in revised form 15 August 2018; Accepted 14 September 2018

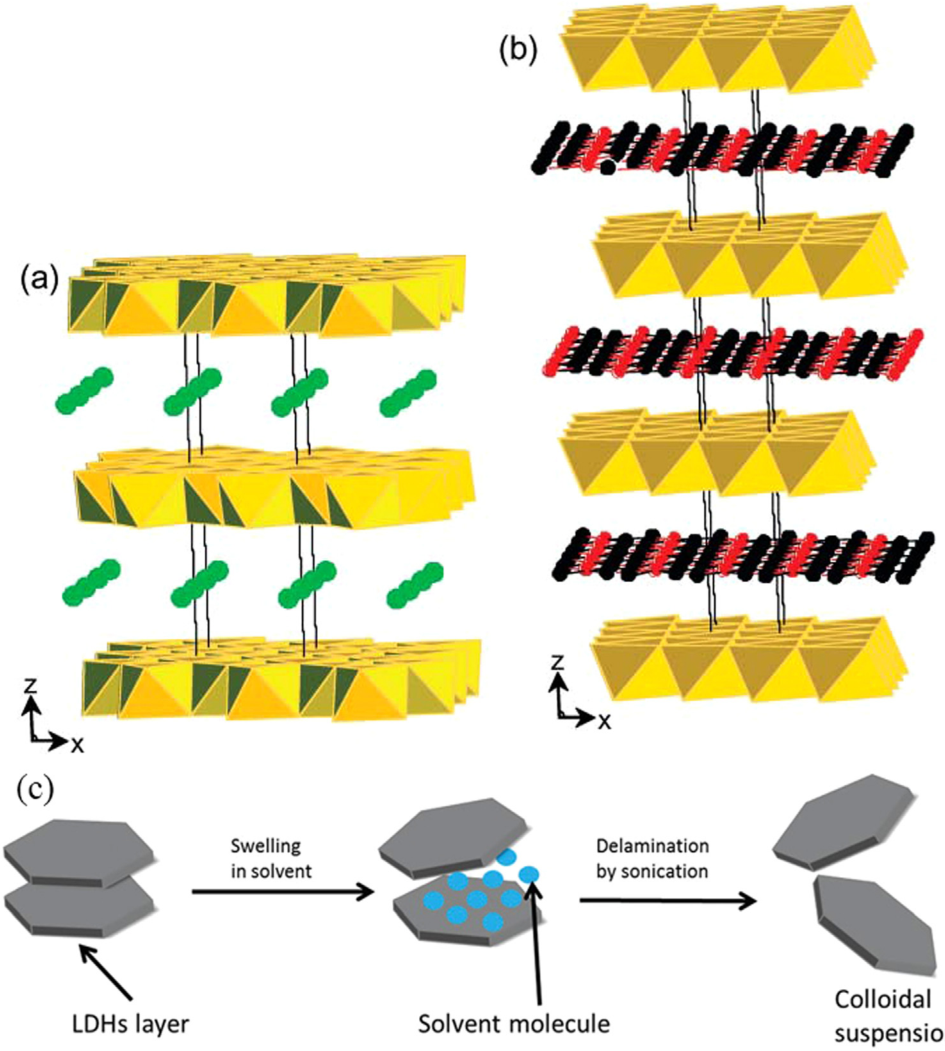


Fig. 1. Schematic structure of LDHs showing the polymorphic stacking patterns: (a) hexagonal, (b) rhomohedral. Reproduced with permission from Ref. [42]. Copyright © 2002, Royal Society of Chemistry. And (c) a generalized procedure for exfoliation of bulk LDHs. Reproduced with permission from Ref. [50]. Copyright © 2017, Royal Society of Chemistry.

$[M_{1-x}^{2+}M_x^{3+}(OH)_2][A^{n-}]_{x/n}\cdot mH_2O$, where M^{2+} represents divalent metal ions (such as Mg^{2+}, Zn^{2+}, Cu^{2+} or Ni^{2+}), M^{3+} represents trivalent metal ions (such as Al^{3+}, Fe^{3+}, Ga^{3+}, or Mn^{3+}) and A^{n-} represents charge compensating anions (such as CO_3^{2-}, NO_3^-, SO_4^{2-}, and stearate). Normally the x value is confined between 0.2 and 0.4 [26,28,30,31,39,44–47]. Compared with other layered materials, LDHs displays unique structural and physicochemical properties such as (1) multiple alternative metal cations allowing chemical compositions of host layers to be controlled precisely; (2) substitutable interlayer anions contributing to adjustable gallery height and surface functionality; (3) the unique memory effect endowing LDHs with the restorability to their original layered structures [48,49]. To summarize, the rich intercalation chemistry, surface functionality and unique memory effect of LDHs make them superb candidates for high performance membranes.

1.2. Preparation of delaminated LDHs and post-treatment of LDHs

In the past few years, diverse methods, including co-precipitation, hydrothermal synthesis, ion-exchange and calcination-reconstruction [50], have been developed for the preparation of LDHs with controllable microstructures. Among them, the co-precipitation method generally produces uniform LDHs with a wide grain-size range (10 nm to 1 μm) and lower crystallinity, which was more favorable for selective anion-exchange intercalation and exfoliation [51]. In contrast, the urea hydrolysis method normally led to the formation of carbonate-intercalated LDHs with larger size (microns in diameter), higher crystallinity and purity [52].

Conventionally synthesized LDHs are composed of uniformly stacked brucite-like nanosheets with a thickness of 0.48 nm [53]. Exfoliation of bulk LDHs into single-layer nanosheets enabled to maximize the surface area and re-adjust the gallery height during drying-reconstruction process [54,55], which was favorable for their utilization as high performance separation membranes [56–58]. Normally LDHs could be exfoliated by using formamide as the solvent [54] or organic anions as charge-compensating anions (e.g. anionic surfactants [59]) under ultrasonication (as shown in Fig. 1(c)) [50]. Particularly, it was noted that Wang [55] reported that the delamination degree of LDHs in formamide could be determined by simply analyzing formed LDH dispersion gels with XRD (Fig. 2), which was quite facile and convenient.

Furthermore, in order to maximize their separation performances, it is critical to prepare LDH-polymer MMMs in which LDH sheets/particles were well-dispersed. However, owing to the intrinsic hydrophilic nature of LDHs, they generally could not be well dispersed in nonpolar solvents. Therefore, post-treatment of LDHs with solvent has become a simple and cost-effective method for preparation of stable and transparent dispersion of the hydrophilic LDHs (Fig. 3(a) and (b)) [46]. For

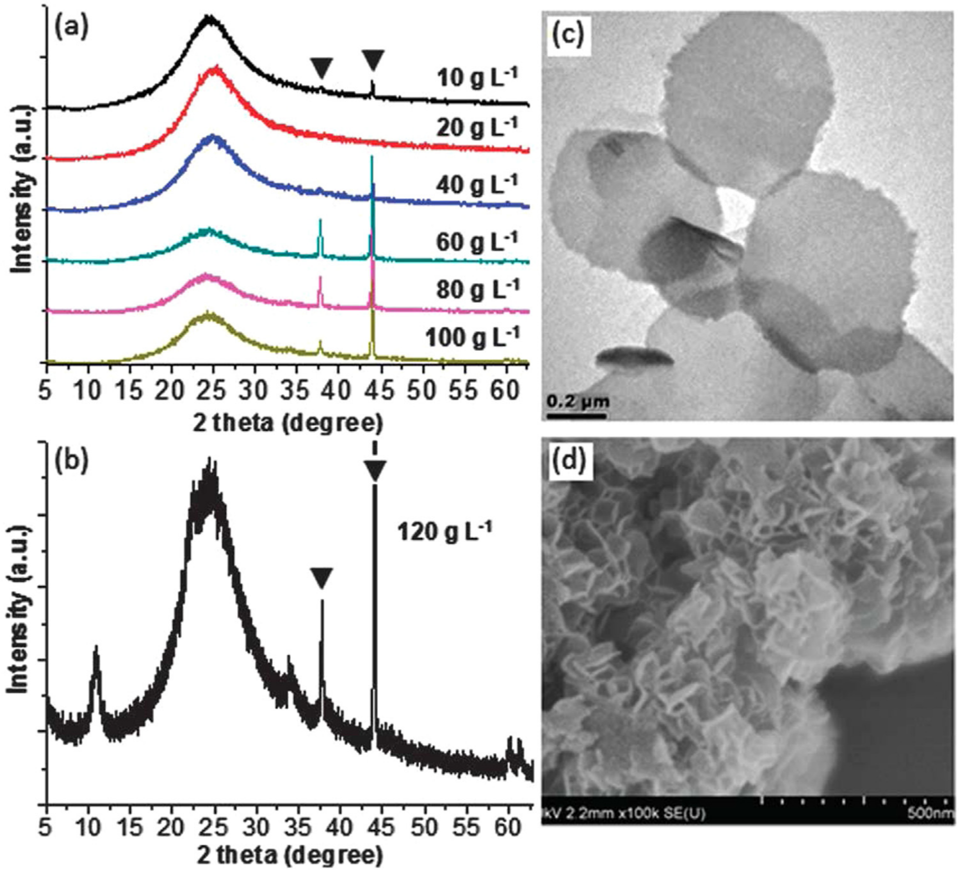


Fig. 2. (a, b) XRD patterns of delaminated Mg–Al–NO_3 LDH dispersion gels with concentrations from 10 to 120 g L^{-1}; (c) the HR-TEM image and (d) SEM image of MgAl–NO_3 LDHs. (▼) sample holder. Reproduced with permission from Ref. [55]. Copyright © 2014, Royal Society of Chemistry.

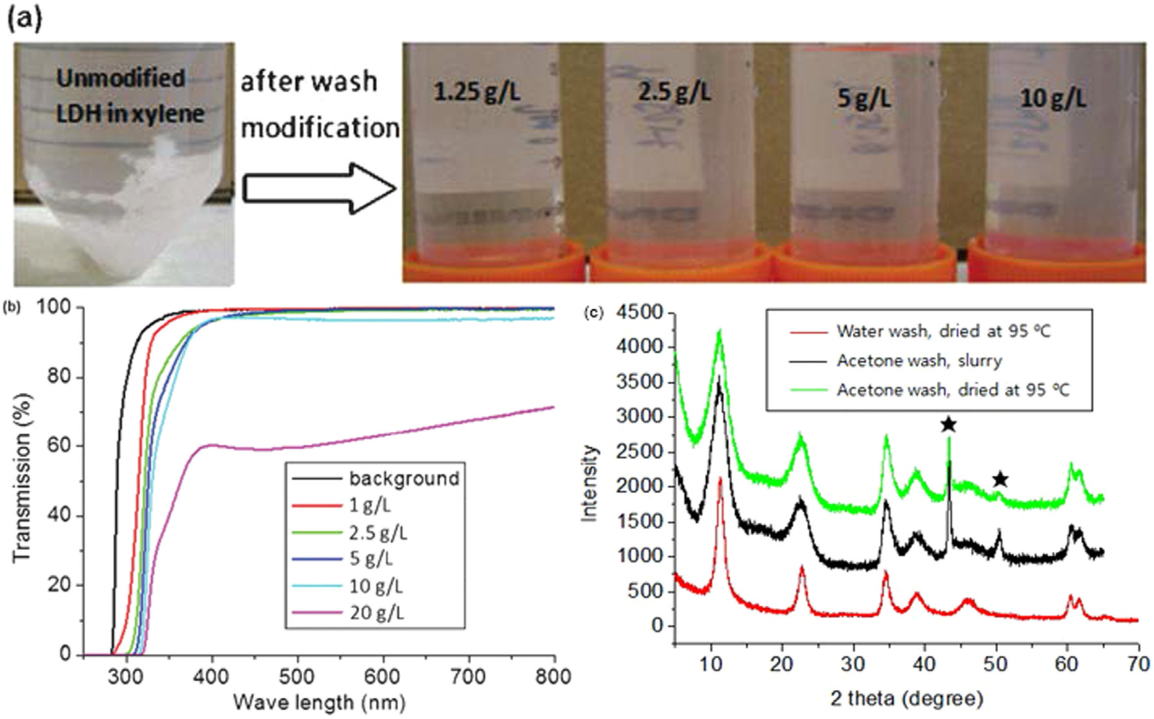


Fig. 3. Illustration of the effect of solvent post-treatment on hydrophobicity of MgAl-LDH nanoparticles. (a) Normally unmodified LDHs could not be dispersed in xylene; in contrast, LDHs nanoparticles could be well dispersed in xylene by washing modification; (b) UV–visible spectra of solvent-modified MgAl-LDHs in xylene; (c) XRD patterns of MgAl-CO_3 LDHs after washing with water or acetone, (★) sample holder. Reproduced with permission from Ref. [46]. Copyright © 2012, Royal Society of Chemistry.

instance, obtained LDH slurry was sequentially washed with equimolecular water/ethanol three times and acetone three times which did not change their composition, structure or particles size (see Fig. 3(c)). Afterwards, solvent-modified LDH nanoparticles could be well dispersed in xylene giving rise to formation of a stable suspension. It seems very promising that this procedure could be further extended to diverse LDH-polymer MMMs.

Potential applications of LDHs as high-performance separation membranes, which has become a hot research topic in recent years [57,60–62], have not been systematically summarized yet. This review summarized recent progress made in LDH-based separation membranes with particular focus on their unique adsorption, diffusion and molecular sieving behaviors essential for high-efficiency membrane separation. To the best of our knowledge, this represented the first review article focusing on potential applications of LDH-based separation membranes. In the following sections, we emphasize on the application of LDH-based membranes in gas and liquid separations, respectively.

2. LDH-based membranes for gas separation

2.1. LDHs as separation layers

LDHs as a representative of anionic 2D materials, not only exhibited high-affinity interaction with specific guest molecules [63], but also enabled to accurately tune the gallery height from nanometer to subnanometer scale. Recent progress made in the development of asymmetric LDH membranes has confirmed its great potential for efficient gas separation. Tsotsis [64] first employed a vacuum-suction approach for the preparation of MgAl-CO_3 LDH asymmetric membranes. Prepared LDH membranes showed an ideal CO_2/N_2 separation factor (SF) as high as 35 after repair of cracks and defects within LDH membranes by silicone coating. In the next step, electrophoretic deposition (EPD) technique was further employed to deposit LDH membranes on macroporous α-Al_2O_3 substrates. Prepared LDH membranes showed preferred selectivity towards CO_2, which was consistent with previous studies demonstrating their great potential as superb CO_2 adsorbents [65]. Caro's group was committed to extending the utilization of LDH membranes in H_2 purification. Well-intergrown NiAl-CO_3 LDH membranes were successfully prepared on mesoporous γ-Al_2O_3 substrates by in situ hydrothermal growth [66]. XRD pattern indicated a uniform gallery height of 0.31 nm, which was smaller than kinetic diameters of most gas molecules except H_2 (0.29 nm) (Fig. 4). Correspondingly, the SF of activated LDH membranes reached ~80 for H_2/CH_4, making them particularly attractive for H_2 purification (Fig. 4c). Furthermore, it was further found that the concentration of CO_2 dissolved in the precursor solution played an important role in controlling the preferred orientation of LDH membranes [67]. Trace amount of CO_2 induced formation of *ab*-oriented 0.6 μm-thick LDH membranes (Fig. 4(d)), whereas oversaturated CO_2 resulted in formation of randomly oriented 5 μm-thick LDH membranes (Fig. 4(e)). Experimental results demonstrated that both *ab*- & randomly oriented LDH membranes showed clear size-based selectivity. However, randomly oriented LDH membranes showed much higher H_2 selectivity possibly due to decreased mesoscopic defects. It should be emphasized that compared with the manufacturing process of graphene oxide (GO) or other 2D membranes, nucleation of LDH crystallites, their attachment to substrates and final formation of defect-free LDH membranes could be completed in one step [67].

2.2. LDHs as precursor layers

LDH membranes also enabled to significantly enhance the separation performance of MOF membranes. Caro successfully prepared ZIF-8-ZnAl-NO_3 LDH composite membrane in one step by partial conversion of 2.5 μm-thick ZnAl-NO_3 LDH precursor membranes (Fig. 5) [68]. Partial dissolution of ZnAl-NO_3 LDH precursor membranes led to reduced framework density and thickness (~ 1.3 μm), leading to significantly enhanced H_2 permeance. Moreover, since there existed two gas selective layers, prepared ZIF-8@ZnAl-NO_3 LDH composite membranes showed significantly enhanced gas selectivity (H_2/CH_4 and CO_2/CH_4 SF reached 54.1 and 12.9, respectively), which was significantly higher than former ZIF-8 and ZnAl-NO_3 LDH separation membranes [5].

2.3. LDHs as complementary buffer layers

LDHs could also serve as modifier for preparation of high performance ZIF membranes. Liu [69] prepared preferentially vertically aligned MgAl-CO_3 LDH layers on α-Al_2O_3 substrates by facile in situ hydrothermal growth. ~ 1.7 μm-sized LDH crystals showed typical plate-like morphology with mutual distances of ~ 1 μm. LDH layer-modified substrates were then covered with uniform zeolitic imidazolate frameworks (ZIF-8) seed layers by dip-coating. Owing to the hindrance from adjacent LDH walls, trapped ZIF-8 seeds were firmly attached to substrates. After secondary growth, well-intergrown ZIF-8 membranes were formed. The single gas permeability results demonstrated the SF of H_2/CO_2, H_2/N_2, and H_2/CH_4 gas pairs reached 4.2, 9.4, and 12.9, respectively, and related H_2 permeance reached 1.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. In addition, the use of "LDH buffer layer" represented a new concept for facile in situ synthesis of well-intergrown ZIF-8 membranes. For instance, Liu further in situ prepared the vertically aligned ZnAl-CO_3 LDH buffer layers on γ-Al_2O_3 substrates (Fig. 6) [70]. The high length-to-width of LDH grains greatly facilitated nucleation and growth of ZIF-8 crystals. After in situ solvothermal growth, well-intergrown ZIF-8 membranes with the thickness ~ 20 μm were prepared (Fig. 6(d)). Gas permeation results showed the SF of prepared ZIF-8 membrane reached 4.2, 10.0, and 12.5 for H_2/CO_2, H_2/N_2, and H_2/CH_4, respectively.

To enhance the gas selectivity of ZIF-8 membranes further, ZnAl-NO_3 LDH modified layers were calcined at 350 °C prior to solvothermal treatment with the ligand 2-methylimidazole. H_2/CH_4 gas selectivity of prepared ZIF-8 membranes reached ~83.1, which was by far the highest value ever reported for pure ZIF-8 membranes possibly due to the framework rigidization caused by neighboring ZnO nanocrystals [71]. To sum up, LDH complementary buffer layers not only enabled to guarantee the formation of well-intergrown ZIF membranes, but also facilitated their performance enhancement.

2.4. LDHs as transport channels for CO_2

Recently construction of facilitated transport membranes by establishing high-speed facilitated transport channels has been intensively investigated [72,73]. LDHs with specific interlayer spacing permit the rapid transport of smaller molecules (like CO_2). Wang proposed a calcination-reconstruction method to prepare MgAl-CO_3 LDH/PEIE (polyethyleneimine copolymerized with epichlorohydrin) facilitated transport membranes by designing high-speed CO_2 facilitated transport channels [74], which was schematically illustrated in Fig. 7. The active layer of prepared LDH/PEIE membrane was only 263 ± 15 nm. Prepared LDH/PEIE membrane displayed excellent CO_2 permselectivity by in situ reconstruction of calcined MgAl-CO_3 LDH fillers as high-speed facilitated transport channels. The CO_2 permeance reached 1.9×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with a CO_2/N_2 selectivity of 268 at the feed pressure of 0.11 MPa. To improve selectivity further, polyvinylamine (PVAm), a linear polymer containing abundant primary amine groups, was used as fixed-site-carrier membranes. The effect of divalent metal ions (Zn^{2+}, Ni^{2+}) in LDH nanofillers on the gas separation performance was further examined [75]. In addition, ZnAl-CO_3 LDH and NiAl-CO_3 LDH fillers also improved the CO_2/N_2 separation performance to a certain extent.

A summary of gas separation performance of LDH-based membranes was shown in Table 1. It was noted that LDH-based membranes with sub-nanometer sized gallery height exhibited accurate molecular sieving effect. In particular, in situ prepared ZIF-8@ZnAl-CO_3 LDH

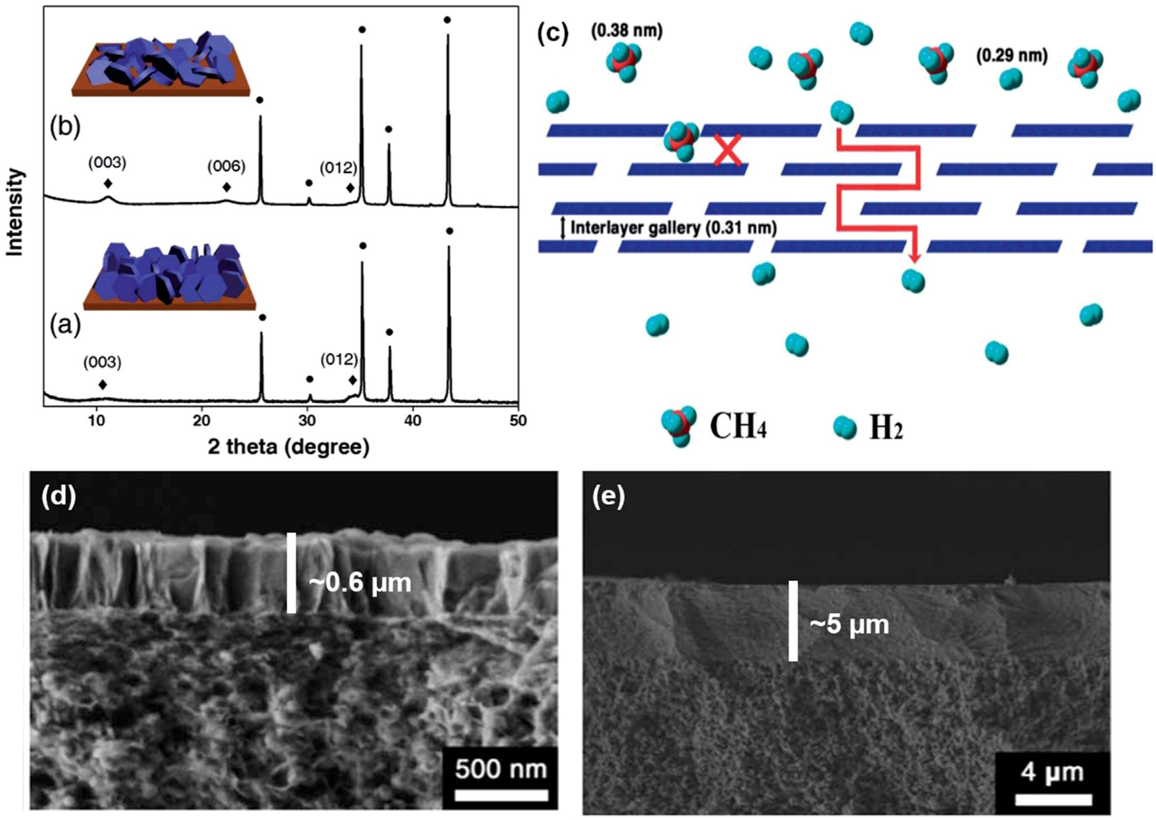


Fig. 4. XRD patterns of NiAl–CO_3 LDH membranes prepared with (a) DI-water and (b) CO_2-saturated water as solvents, respectively; (c) illustration of the concept of interlayer gallery-based separation and SEM images of NiAl–CO_3 LDH membranes prepared with (d) DI-water and (e) CO_2-saturated water as solvents, respectively. Reproduced with permission from Ref. [66]. Copyright © 2014, Royal Society of Chemistry.

composite membranes showed the gas selectivity significantly higher than single ZIF-8 or ZnAl-NO_3 LDH membranes. In addition, interlayer galleries of LDHs could serve as high-speed CO_2 facilitated transport channels within polymeric membranes for efficient CO_2 purification. It is therefore believed that LDHs may pave a brand-new avenue for designing and fabricating high-performance gas separation membranes.

3. LDH-based membranes for liquid separation

Recent decades witnessed significant progress made in membrane-based liquid separation technology, e.g. wastewater treatment [76,77], desalination [78,79], water recovery [80] and oil/water separation [81]. LDHs as a representative of clay materials had been employed in fabrication of LDHs/polymer nanocomposite membranes [82]. Several physicochemical properties of membranes (such as wettability [81], mechanical strength [62], thermostability [47], electroconductivity [83], flammability [39] and barrier properties [84]) have been proved to exert significant influence on the liquid separation performance of LDHs/polymer nanocomposite membranes.

3.1. *LDHs as nanofiller for nanocomposite membranes*

3.1.1. *Ultrafiltration (UF) membranes*

Versatile nanofillers have been added into the polymer matrix to improve the separation performance of UF membranes [85–87]. Among them, LDHs have been considered as a promising nanofiller for improving hydrophilicity, fouling resistance, mechanical strength, thermal stability and separation performance of UF membranes. Zhao [88] prepared ZnAl-LDH incorporated poly(ether sulfone) (PES) membranes with the phase inversion method and systematically investigated the effect of LDH doping content (0–3 wt%) on the separation performance of PES membranes. LDH incorporated PES UF membranes achieved higher water permeability, superior protein removal efficiency as well as better antifouling properties. Oskoui [60] employed nano-layered MgAl-LDHs (Fig. 8(a)) as the hydrophilic nanofiller of polyvinylidene fluoride (PVDF) UF membranes. Results showed that nano-layered LDHs could significantly improve the separation performance of PVDF membranes in case N-methyl-2-pyrrolidone (NMP) was utilized as the solvent. Moreover, the pore shape varied from sponge-like to finger-like in the presence of LDHs nanofiller (Fig. 8). Nevertheless, water flux was decreased at high doping concentration (4.0 wt%) due to the unavoidable aggregation of LDH nanolayers. To minimize the aggregation, Zhang [56] proposed the use of exfoliated MgAl-LDHs as the nanofiller for preparation of positively charged hybrid PES UF membranes via phase inversion method. This membrane showed higher rejection rate (above 85%) for PEG 20000 and lower adsorption amount for positively charged proteins. Furthermore, novel charged mosaic PES membranes were prepared by incorporating positively charged MgAl-LDHs surface-grafted with sulfobetaine methacrylate [89]. It was found that charged mosaic PES UF membranes showed excellent dyes rejection rate (86.7% for Reactive Red 49), low salt rejection rate (9.3%, 7.6% and 0.53% for $MgCl_2$, Na_2SO_4 and NaCl, respectively) and high pure water flux (80.2 $L\,m^{-2}\,h^{-1}$) under 0.4 MPa.

3.1.2. *Nanofiltration (NF) membranes*

NF membranes have been widely employed in wastewater treatment and desalination [90]. Zhang [56] utilized exfoliated MgAl-LDHs as inorganic additives for fabrication of PES NF membranes. Prepared NF membranes showed considerably high rejection rate for PEG400 but much lower rejection rate for $MgSO_4$. In response to this issue, exfoliated hydrotalcite/graphene oxide (EHT/GO) hybrid nanosheets were synthesized via flocculation deposition (schematically shown in

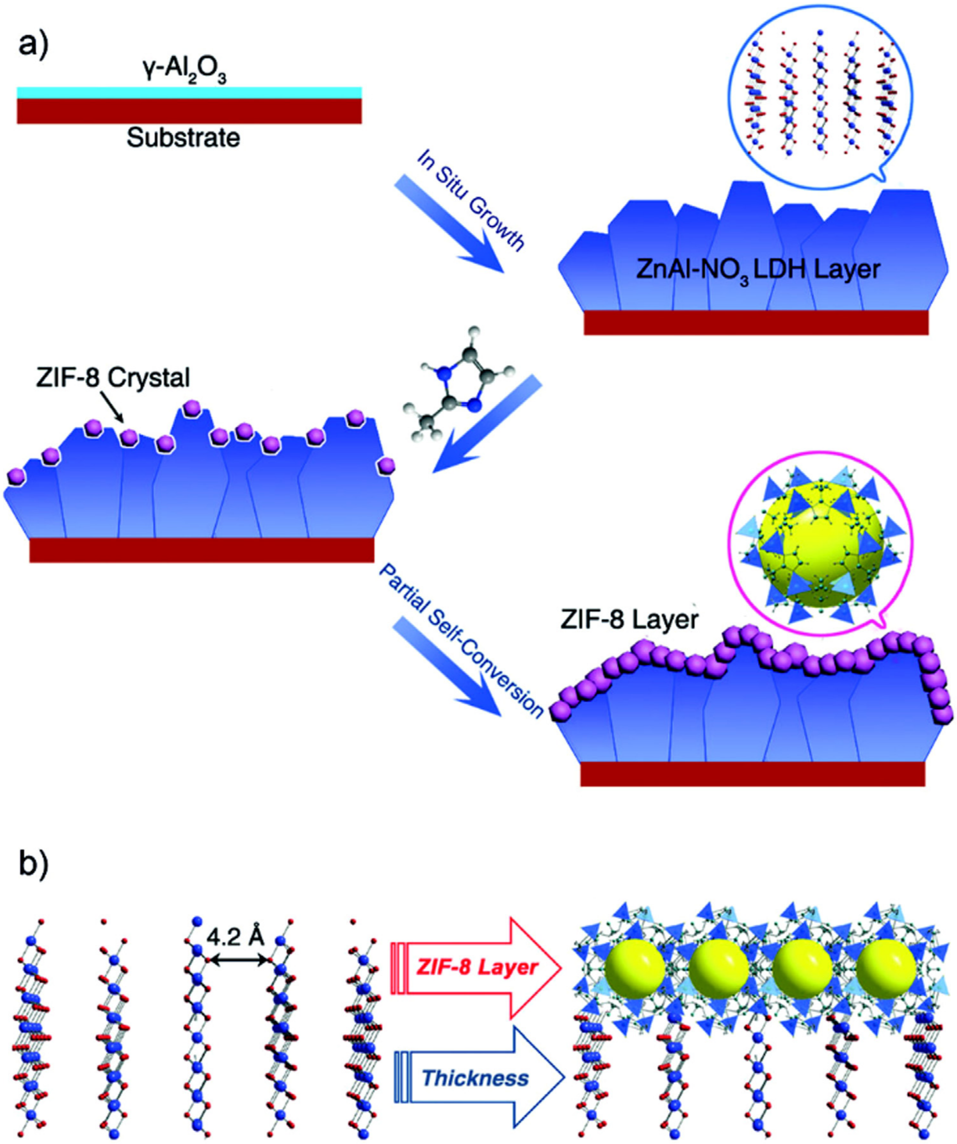


Fig. 5. a) Illustration of preparation of the ZIF-8@ZnAl-NO_3 composite membrane on a γ-Al_2O_3-modified α-Al_2O_3 substrate via partial self-conversion method of the ZnAl-NO_3 LDH precursor layer; b) structural change of the ZnAl-NO_3 LDH membrane after the solvothermal treatment with 2-methylimidazole. Reproduced with permission from Ref. [68]. Copyright © 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 9(a)) [57]. After being uniformly dispersed in polyethyleneimine (PEI) aqueous solution, compact NF thin-film nanocomposite (TFN) membranes (Fig. 9(e)) constructed by EHT/GO hybrid nanosheets were fabricated via interfacial polymerization (IP). Desalination experiment illustrated that incorporation of EHT/GO hybrid nanosheets into PA layer of TFN membranes effectively increased water flux to 26 $L\,m^{-2}\,h^{-1}$ at 0.8 MPa. Simultaneously, the $MgCl_2$ rejection ratio of EHT/GO membranes maintained at 97.0%.

3.1.3. Forward osmosis (FO) membranes

Past decades witnessed increasing attention paid to FO process due to low hydraulic pressure during operation, high rejection to a wide range of contaminants and enhanced anti-fouling properties [91,92]. Nevertheless, fabrication of high performance FO membranes remained a great challenge facing their practical applications [62]. Recent studies indicated that LDHs could serve as excellent nanofiller for FO thin-film composite (TFC) membranes. For instance, LDH nanoparticles were uniformly blended in the polysulfone (PSf) substrate of TFN membrane to increase the porosity, hydrophilicity, mechanical strength and thermal stability, which in turn were favorable for reducing internal concentration polarization (ICP) and enhancing water permeability [62]. After doping with 2 wt% LDHs, a ~ 42.5% increase in water flux of TFN membranes was achieved without compromise in reverse salt flux. Furthermore, Wang [93] prepared LDH modified-graphene oxide (LDH/GO) hybrid nanoparticles as the nanofiller of PSf substrates. Owing to omission of an additional drying step, dispersion condition of GO nanosheets was remarkably improved, resulting in significant improvement of salt rejection.

Cussler [94] proposed that layered materials could serve as effective additive for enhancing anti-corrosion and anti-fouling properties of original FO membranes. For instance, to further enhance chlorine and fouling resistance, LDH nanoparticles were directly bound on the surface of TFC membranes via polydopamine-induced immobilization process [84]. Excellent chlorine-resistant performance (~ 96 times high than bare TFC membranes) was then confirmed by the accelerated chlorination experiment (Fig. 10(c)). Simultaneously, LDH-modified TFN membranes exhibited superior anti-fouling capability (Fig. 10(b)). In addition, Pardeshi [61] investigated the influence of LDH content on the separation performance polyvinyl chloride (PVC) TFN membranes. It was observed that increasing LDH contents within PVC substrate

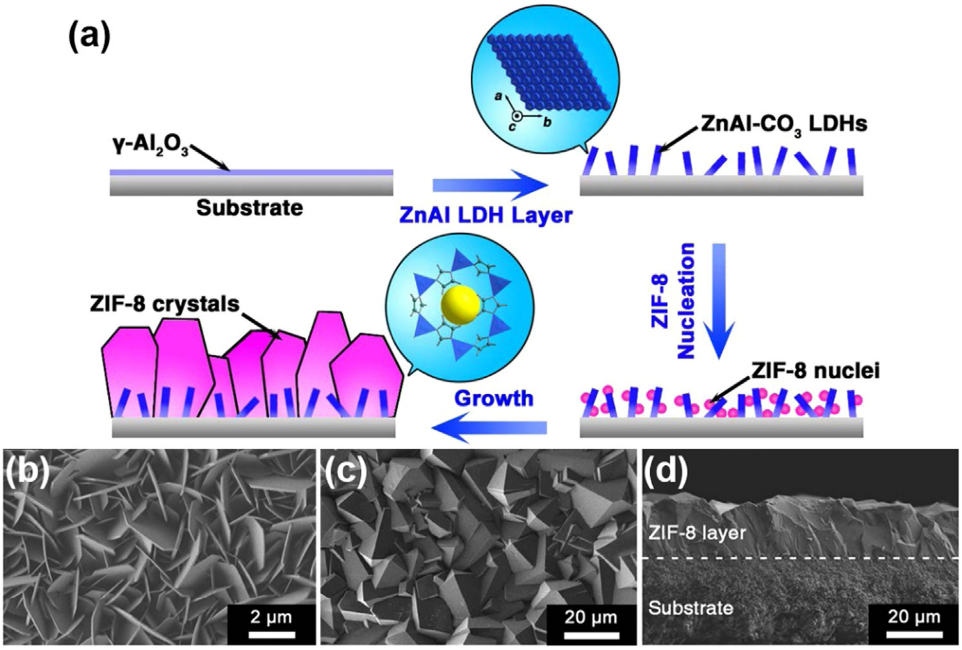
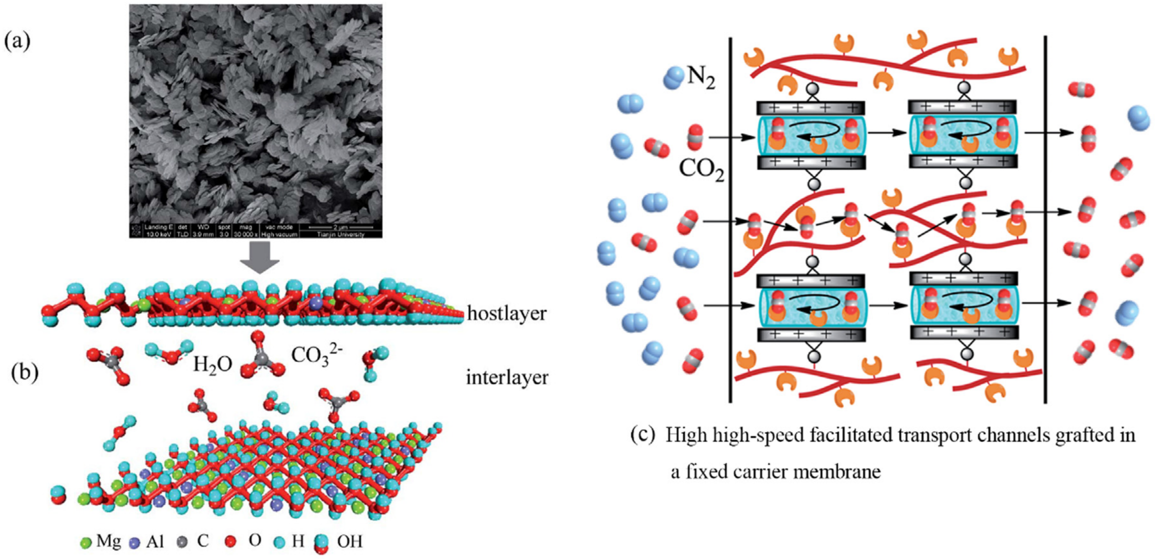


Fig. 6. (a) Illustration of ZIF-8 membrane growth on the ZnAl-LDH buffer layer-modified γ-Al_2O_3 substrate by in situ solvothermal growth; (b) the SEM image of the ZnAl-CO_3 LDH buffer layer, and SEM images of the (c) top and (d) cross-section of prepared ZIF-8 membrane. Reproduced with permission from Ref. [70]. Copyright © 2014, American Chemical Society.

induced an increase in water flux of TFN membranes. To sum up, above-mentioned studies demonstrated that incorporation of LDHs as nanofillers played an important role for performance improvement of TFN membranes.

3.2. LDHs as adsorbents for membrane adsorption

Early attempts evidenced that LDHs excellent adsorbents for removal of harmful diverse cations and anions (such as Pb^{2+}, Cd^{2+}, Cu^{2+}, arsenate, chromate and phosphate) from aqueous solutions relying on both surface adsorption and anion exchange of charge compensating anions located in interlayer galleries [95–101]. In addition, the unique "memory effect" of calcined LDHs, also known as layered double oxides (LDOs) [102], could be also utilized as cost-effective and energy-efficient adsorbents [48]. Membrane adsorption represents an emerging adsorption technology for wastewater treatment [103]. LDHs have attracted considerable attention for potential applications in membrane adsorption processes. Duan [104] prepared LDH/eggshell membranes (ESM) for Cr(VI) removal with an in situ hydrothermal crystallization method. Results indicated that prepared MgAl-Cl LDH/ESM composite membranes (Fig. 11) could be efficient adsorbents for Cr(VI) (adsorption capacity was 27.9 mg/g) removal even under the condition that pH values were adjusted by addition of acid. A removal efficiency higher than 90% was obtained after an elapse of only 30 min (Fig. 11(f)). Visvanathan [105] was devoted to developing high performance adsorption-based hybrid membranes for continuous removal of high concentration perfluorooctanoic acid (PFOA), one of the major perfluorinated compounds contaminating global water sources. A removal efficiency as high as 95% could be achieved by incorporating MgAl-LDHs into NF membranes without any adverse effect on flux as compared with direct membrane filtration. A 30% increase in rejection rate for LDH-based hybrid NF membranes was attributed to the



(c) High high-speed facilitated transport channels grafted in a fixed carrier membrane

Fig. 7. Structural demonstration of LDHs and LDH-modified polymer membranes: (a) SEM image of carbonate-intercalated LDHs with about 110 nm size; (b) schematic drawing of carbonate-intercalated LDHs; and (c) carbonate-intercalated LDHs grafted fixed carrier membrane with the high-speed facilitated transport channels. Reproduced with permission from Ref. [74]. Copyright © 2014, Royal Society of Chemistry.

Table 1
Gas separation performance of LDH-based membranes.

Membranes	Function of LDHs	Performance of gas separation	References
MgAl-CO_3 LDH on α-Al_2O_3 substrate	As separating layers	$SF_{CO2/N2}$ = 35 P_{CO2} = 2.07 × 10^{-7} mol m^{-2} s^{-1} Pa^{-1} (Single-gas, 25 °C, 0.21 MPa)	[64,65]
NiAl-CO_3 LDH on α-Al_2O_3 substrate	As separating layers	$SF_{H2/CH4}$ = 78.7 P_{H2} = 4.6 × 10^{-8} mol m^{-2} s^{-1} Pa^{-1} (1:1 mixture (H_2-CH_4), 180 °C, 0.1 MPa) P_{H2} = 5.2 × 10^{-8} mol m^{-2} s^{-1} Pa^{-1} (1:1 mixture (H_2-CH_4), 210 °C, 0.1 MPa)	[66,67]
ZnAl-CO_3 LDH on α-Al_2O_3 substrate	As separating layers	$SF_{H2/CH4}$ = 13.7 P_{H2} = 3.7 × 10^{-8} mol m^{-2} s^{-1} Pa^{-1} (1:1 mixture (H_2-CH_4), 180 °C, 0.1 MPa)	[67]
ZIF-8@MgAl-CO_3 LDH composite	As supporting layers	$SF_{H2/CH4}$ = 12.9 P_{H2} = 1.4 × 10^{-7} mol m^{-2} s^{-1} Pa^{-1} (1:1 mixture (H_2-CH_4), 25 °C, 0.1 MPa)	[69]
ZIF-8@ZnAl-NO_3 LDH composite	As supporting layers	$SF_{H2/CH4}$ = 12.5 P_{H2} = 1.4 × 10^{-7} mol m^{-2} s^{-1} Pa^{-1} (1:1 mixture (H_2-CH_4), 25 °C, 0.1 MPa)	[70]
ZIF-8 @ZnAl-NO_3 LDH composite	As supporting precursor layers	$SF_{H2/CH4}$ = 83.1 P_{H2} = 1.9 × 10^{-8} mol m^{-2} s^{-1} Pa^{-1} (1:1 mixture (H_2-CH_4), 30 °C, 0.1 MPa)	[71]
MgAl-CO_3 LDH/PEIE composite	As transport channels	$SF_{CO2/N2}$ = 268 P_{CO2} = 1.9 × 10^{-6} mol m^{-2} s^{-1} Pa^{-1} (15:85 mixture (CO_2-N_2), 25 °C, 0.11 MPa)	[74]
MgAl-CO_3 LDH/PVAm composite	As transport channels	$SF_{CO2/N2}$ = 296 P_{CO2} = 1.1 × 10^{-6} mol m^{-2} s^{-1} Pa^{-1} (15:85 mixture (CO_2-N_2), 25 °C, 0.11 MPa)	[75]

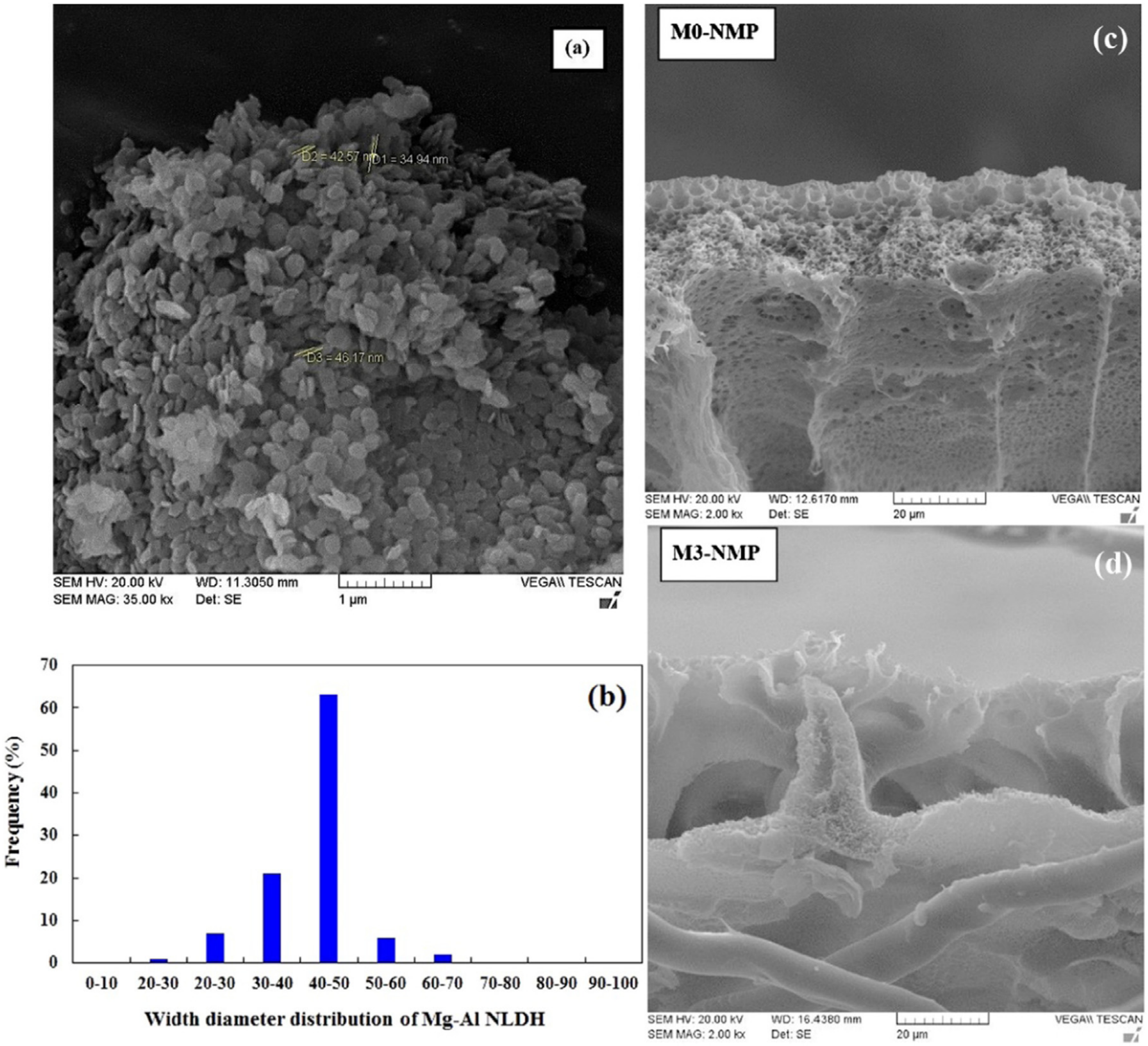


Fig. 8. (a) SEM image of nano-layered MgAl-LDHs; (b) width diameter distribution of the LDHs, and cross-sectional SEM images of (c) pure PVDF membranes and (d) LDHs/PVDF nanocomposite membranes (LDHs loading: 3 wt%). Reproduced with permission from Ref. [60]. Copyright © 2017, Elsevier.

formation of dense MgAl-LDH layers on membrane surfaces. Recently, Jia [58] incorporated exfoliated Mg-Al-Fe LDH nanosheets in PES membranes for efficient removal of phosphate and fluoride. Prepared composite membranes displayed higher adsorption capacity for phosphate (5.61 mg/g) and fluorides (1.61 mg/g) than un-exfoliated materials.

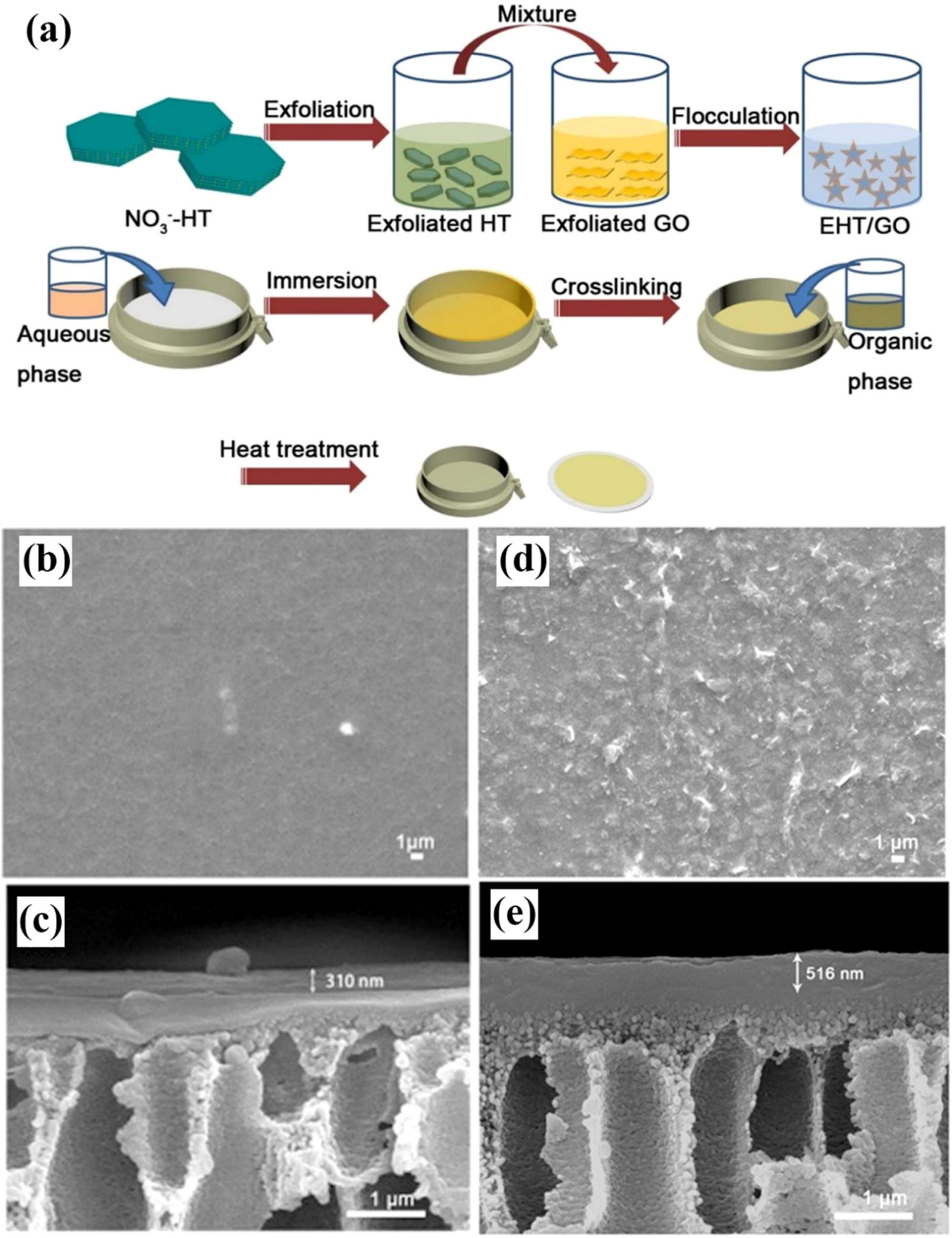


Fig. 9. (a) Illustration of the synthesis of EHT/GO hybrid nanosheets and the preparation of EHT/GO TFN nanofiltration membranes; SEM images of the top layer of TFN membranes with (b) 0 wt% and (d) 0.24 wt% EHT/GO loadings; and SEM images of the cross-section of TFN membranes with (c) 0 wt% and (d) 0.24 wt% EHT/GO loadings. Reproduced with permission from Ref. [57]. Copyright © 2017, Elsevier.

3.3. LDHs as hydrophobic layer for oil/water separation

Efficient oil/water separation represents the major environmental challenge due to the ever-increasing oil-containing wastewater discharge as well as increasingly frequent accidents of oil spill [106,107]. Membrane technology represents an effective approach for efficient oil-water separation [108]. Several studies have been carried out for developing LDH nanosheet-based oil/water separation membranes. For instance, Liu reported the fabrication of commercial textiles functionalized with LDH microcrystals as well as low-surface-energy molecules (schematically shown in Fig. 12(I)) [109]. Results showed that prepared textiles could be employed as not only high-performance oil/water separation membranes (separation efficiency > 97%), but also "bags" for selective oil recovery from aqueous suspension (Fig. 12(a)-(h)).

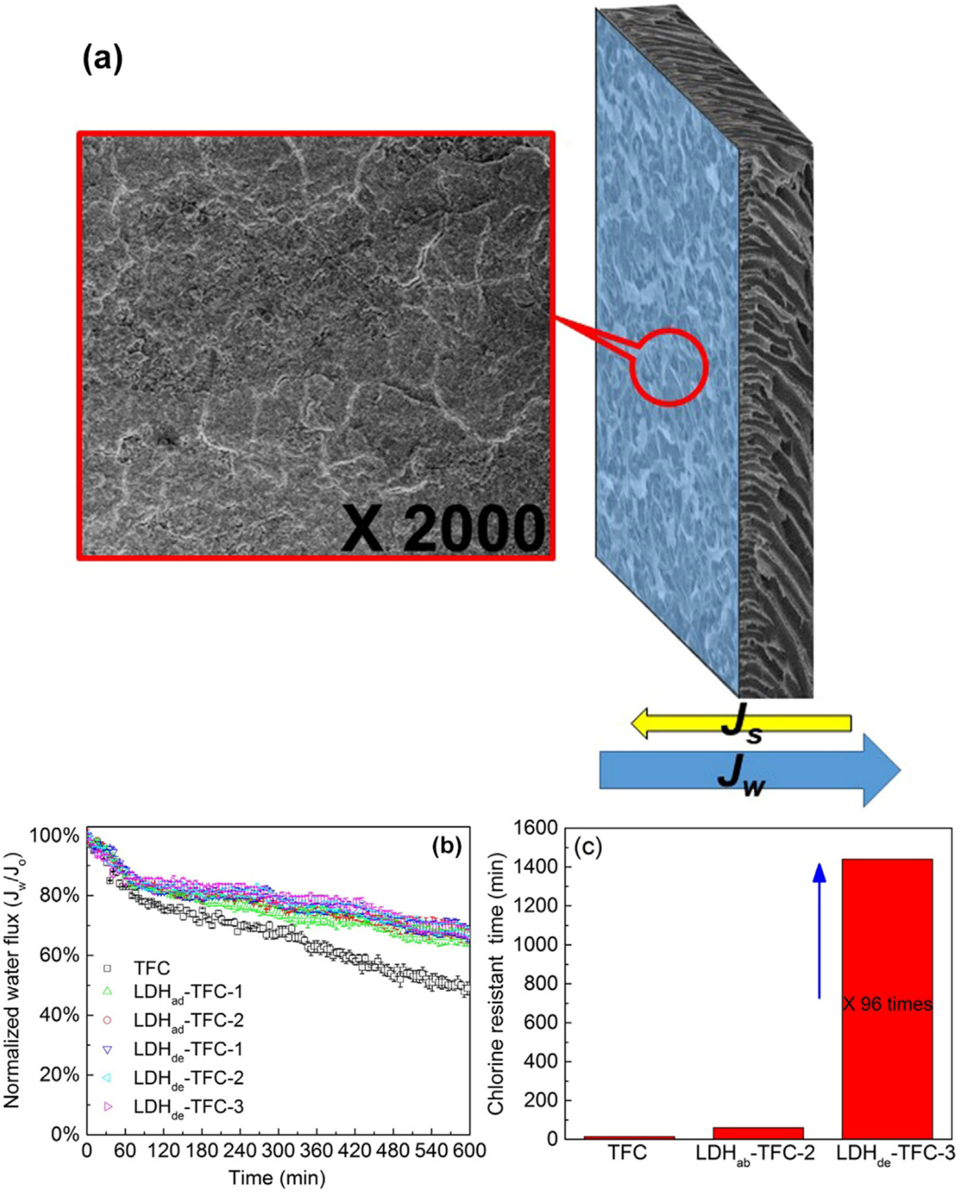


Fig. 10. (a) The schematic diagram of the LDHs deposition modified TFC membranes; (b) the normalized water fluxes of the unmodified and modified membranes at alginate fouling tested in FO mode; and (c) the chlorine resistant time of TFC, LDH_{ab}-TFC-2 and LDH_{de}-TFC-3 membranes by immersion in 1000 ppm NaOCl solution. Reproduced with permission from Ref. [84]. Copyright © 2017, Elsevier.

With an electrospun-nanofiber-templated in situ hydrothermal method, Shami [110] successfully introduced vertically aligned MgAl-LDH arrays on nanofibrous poly(acrylonitrile) (PAN) membranes which subsequently were surface-modified with cyclohexanecarboxylic acid. Prepared superhydrophobic/superoleophilic nanofabrics not only were capable of repelling both drinkable hot water (~ 95 °C) and cool water (~ 25 °C) but also allowed preferential permeation of oils across the membrane. An excellent oil recovery efficiency (including chloroform, toluene, *n*-heptane, hexadecane and motor oil) was then demonstrated.

Wu [81] employed a facile layer-by-layer self-assembly method for constructing 3D hierarchical membranes on porous cellulose acetate substrates surface-modified with sepiolite-grafted LDHs. Prepared membranes exhibited high flux and excellent underwater superoleophobic behaviors relying on the hierarchical microstructure. Recently, a simple and effective method was developed to prepare superhydrophobic cellulose/LDH membranes in an open oil/water two-phase system [111]. Prepared membranes exhibited high separation efficiency (> 95.0%), excellent recyclability and stable superhydrophobicity under harsh conditions, making them superb candidate for remediation of oily waste water. To sum up, above-mentioned studies demonstrated that microstructure optimization of LDH modified layers played a critical role in enhancing the oil/water separation performance.

3.4. LDHs as ionic conductors for direct methanol fuel cells (DMFC)

In comparison with traditional batteries, direct methanol fuel cell (DMFC) has become the focus of people's interest. Nevertheless, unavoidable crossover of methanol fuel, which seriously degrades the cell performance, remains a major hindrance to DMFC's industrialization [83,112]. Recently great efforts have been made to develop new types of anion exchange membranes for solving the methanol crossover problem. As a representative of anionic clays, LDHs remained stable in an alkaline media. For instance, Lee proposed fabrication of LDH-modified Nafion membranes by incorporating LDH nanosheets with different Mg^{2+}/Al^{3+} ratios for DMFC [113]. Nano-sized LDH-modified

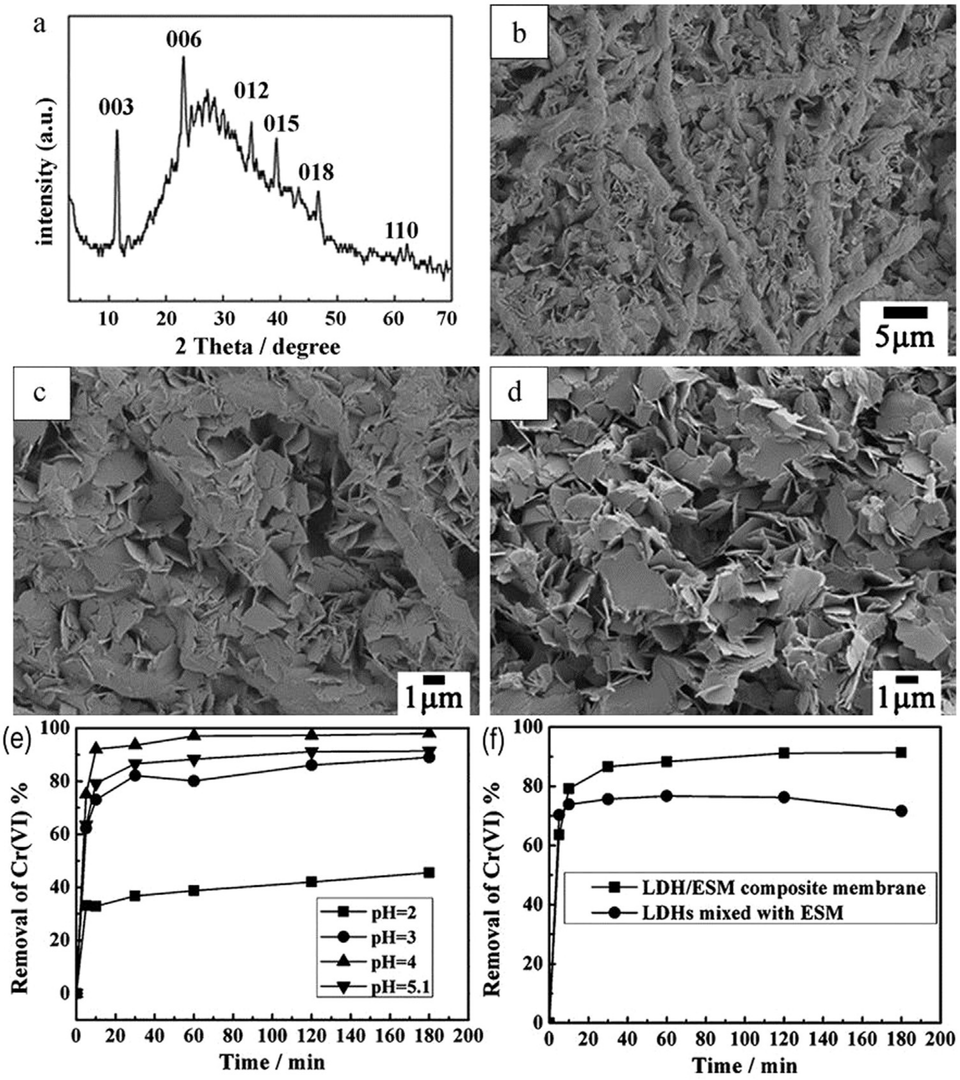


Fig. 11. (a) XRD pattern of the MgAl-Cl LDH/ESM composite membrane; SEM images of MgAl-Cl LDH/ESM composite membranes (b, c) top and (d) cross-section; (e) demonstration of the effect of pH values on Cr(VI) removal efficiency and (f) demonstration of the kinetics of Cr(VI) removal efficiency. Reproduced with permission from Ref. [104]. Copyright © 2014, American Chemical Society.

polyelectrolyte membranes reached a better balance between diffusion coefficient and ionic conductivity at high methanol feed concentrations (7 M). Nicotera [114] employed LDHs as nano-additives of Nafion-based membranes for H_2/air-fed fuel cells. Influences of Mg^{2+}/Al^{3+} metal ratio (2:1 and 3:1) and the type of interlayer anions (CO_3^{2-}, ClO_4^-, NO_3^-) on proton conductivity of LDH/Nafion nanocomposite membranes were systematic investigated. Tsotsis [115] prepared high performance LDH/poly(ether ether ketone) (SPEEK) nanocomposite membranes by in situ sulfonation of SPEEK and LDH films for DMFC. Prepared LDH/SPEEK nanocomposite membranes showed not only considerably high proton conductivity and low methanol diffusivity but also excellent performance comparable with commercial Nafion membranes. Lee [116] incorporated MgAl and NiTi LDHs into SPEEK membranes, respectively. Proton conductivity measurement indicated that MgAl-LDH/SPEEK nanocomposite membranes showed higher proton conductivities than that of NiTi-LDH/SPEEK membranes.

Zhao [117] synthesized crosslinked poly (vinyl alcohol)/MgAl-CO_3 (PVA/LDH) hybrid anion-exchange membranes for DMFC. It was found that incorporating 20 wt% LDHs into PVA matrix resulted in not only higher ionic conductivity but also lower ethanol permeability. The performance test of the DMFC using the PVA/LDH hybrid membrane demonstrated that the fuel cell yielded a power density of 82 mW cm^{-2} at 80 °C, which was much higher than that of the DMFC employing quaternary ammonium group functionalized PVA membranes. Similarly, Herrero [83] prepared sulfonated polysulfone (SPSU)/LDH composite proton exchange membranes for DMFC. Introduction of LDHs significantly affected water uptake amounts, electrical properties and transport behaviors of SPSU membranes. Impedance plots as a function of LDH addition amounts were then measured and shown in Fig. 13(a). It was observed that the diameter of the high frequency arcs decreased with the addition amount of LDHs, therefore indicating an enhanced proton conductivity by increasing LDH addition amounts. In addition, SPSU/LDH nanocomposite membranes exhibited superior electrical performance compared with pure SPSU membranes (Fig. 13(b)). Sun [118] fabricated novel charge-guided ion transport hybrid membranes consisting of anionic GO and cationic CoAl (or MgAl) LDH nanosheet superlattice units. Relative selectivity of prepared hybrid membranes towards monovalent and trivalent cations reached as high as 30 therefore indicating a synergistic effect originating from the molecular-scale cooperative hetero-assembly of GO and LDH nanosheets which played a dominant role in charge-guided ion filtration and separation.

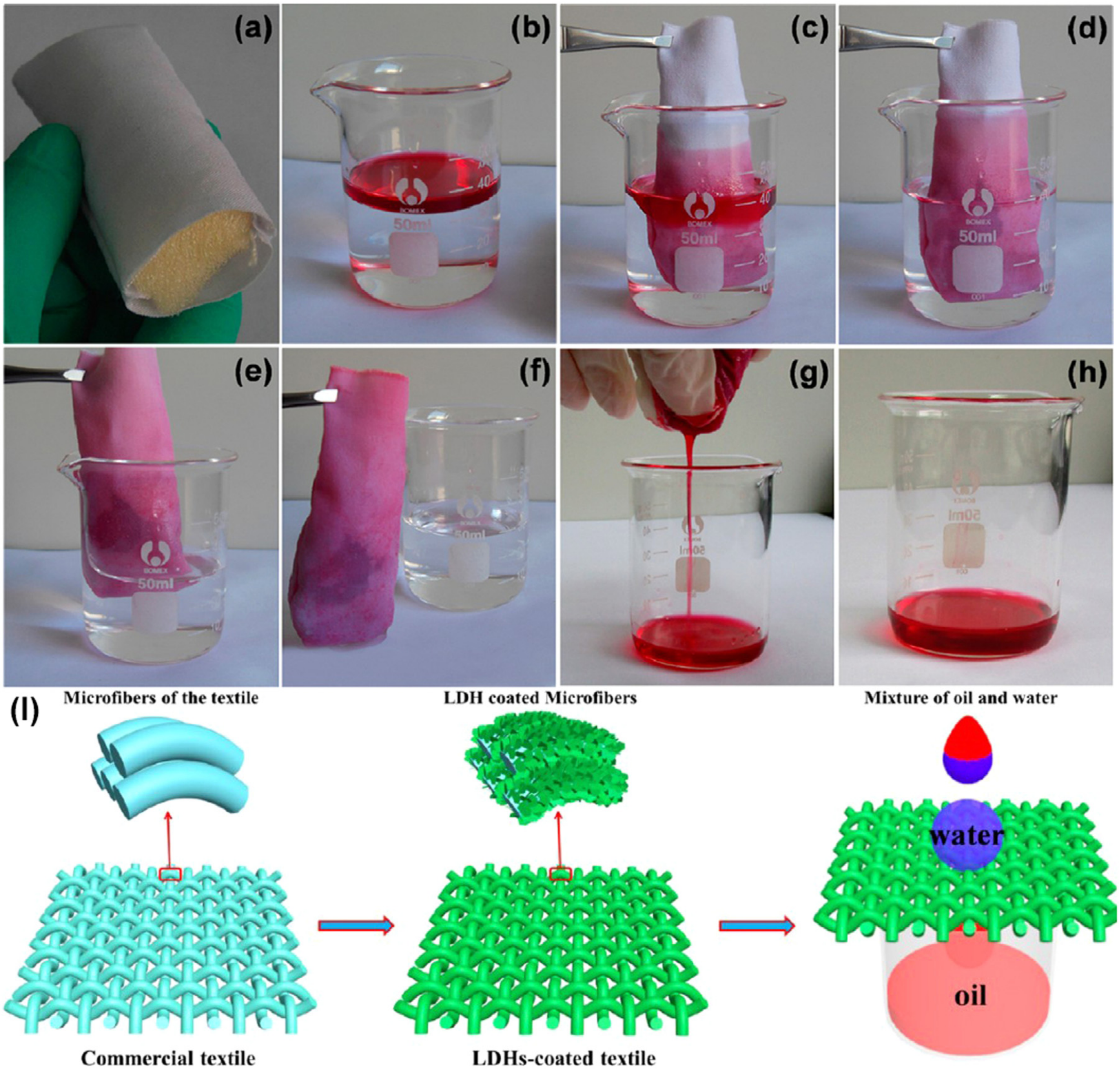


Fig. 12. Digital photographs of (a) the textile bag and (b – g) the oil adsorption and recycling process with the superhydrophobic textile bag; (I) schematic diagram of the modification of commercial textile with LDH and its application for oil/water separation. Reproduced with permission from Ref. [109]. Copyright © 2015, American Chemical Society.

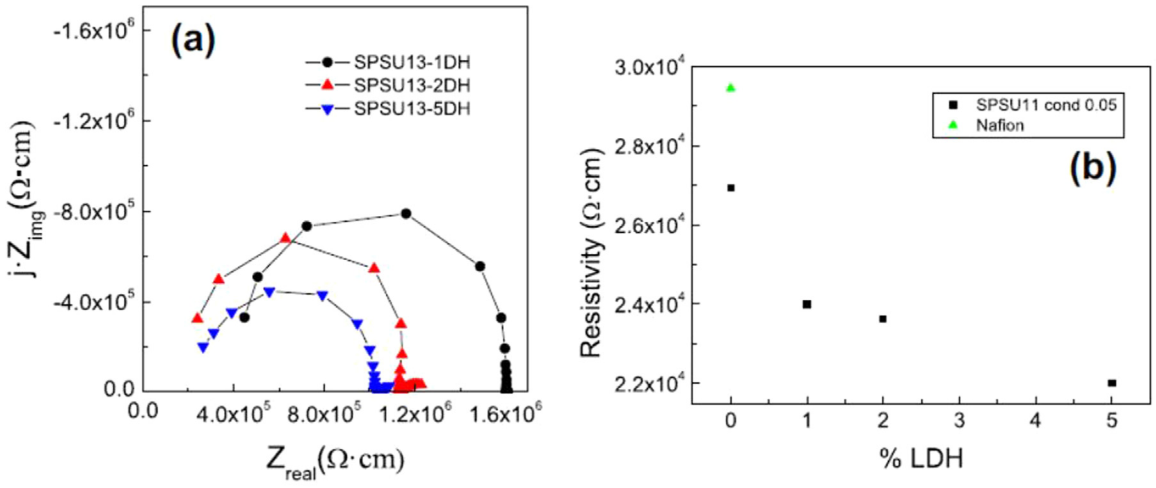


Fig. 13. (a) Nyquist plot of three composite membranes with different LDH (1%, 2% and 5%) loadings (c = 0.05 M HCl); (b) Resistivity of commercial Nafion membranes with different LDH loadings. Reproduced with permission from Ref. [83]. Copyright © 2013, Hydrogen Energy Publications, LLC. Publish by Elsevier.

4. Opportunities and challenges facing LDH-based separation membranes

LDHs as a representative of 2D materials have injected new vitality into membrane-based separation process. Compared with other 2D membrane materials, LDHs are unique in terms of 1) simple preparation process and low manufacturing cost; 2) uniform and tailorable gallery height; 3) rich surface functionality; 4) unique memory effect and regenerability; 5) excellent exfoliation capability; 6) excellent anti-fouling capacity; 7) easy scale-up and 8) considerable stability. These features have provided an avenue to design high-performance separation membranes. For instance, 1) compared with the relatively complicated manufacturing process of other 2D (like GO, 2D MOF, 2D COF, 2D zeolite, TMDC, MXene and g-C_3N_4) molecular sieve membranes, defect-free LDH membranes could be prepared in one step [66,67]; 2) relying on the uniform and tailorable interlayer gallery, LDH membranes have exhibited pronounced molecular sieving property for gas separation; in contrast, it remained a challenging task to maintain a uniform gallery height for most other 2D separation membrane, although some progress has been made in recent days [119,120]; 3) specific memory effect of LDHs has made it possible to construct high-speed facilitated transport channels for effective CO_2 purification [74,75] and effective removal of harmful diverse cations/anions [104,105]; 4) LDHs could be further exfoliated and serve as nanofillers for preparation of MMMs showing lower adsorption amount for positively charged pollutants, relying on unique electrostatic repulsive forces [56]. Combine with the functional diversity, commercial availability, low cost, stability and anti-fouling capacity, LDH-based membranes have shown excellent separation performance in diverse fields.

Nevertheless, a major challenge facing high performance LDH-base membrane fabrication resides in an accurate control of the interlayer spacing for specific separation. Furthermore, since the separation performance of LDHs-based membranes strongly depends on their microstructures (like the preferred orientation, grain boundary defects and thickness), facile methods for deliberate control of their microstructures are yet to be developed.

5. Conclusion

Relying on the uniform interlayer gallery, pure LDHs membranes have exhibited pronounced molecular sieving property for gas separation. Moreover, carbonate-intercalated LDHs could be further employed as competent high-speed facilitated transport channels for efficient CO_2 separation. In addition, LDHs could serve as competent buffer layers guaranteeing the formation of high performance MOF membranes. Further incorporation of LDHs into polymeric matrices resulted in the formation of nanocomposite membranes with significantly improved wettability, mechanical strength, thermostability, electroconductivity, chlorine-resistant and anti-fouling capability for efficient liquid separation. Taking consideration of the fact that LDHs can be further exfoliated into monodispersed nanosheets or chemically modified for improving the affinity interaction with the polymer matrix, it is anticipated that employment of LDHs may provide an avenue to design the next generation of high-performance separation membranes.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21622607, 21176231, 21761132009), the Thousand Youth Talents Program and sponsored by K.C. Wong Magna Fund in Ningbo University.

References

[1] F. Moghadam, H.B. Park, Two-dimensional materials: an emerging platform for gas separation membranes, Curr. Opin. Chem. Eng. 20 (2018) 28–38.

[2] J. Zhu, J. Hou, A. Uliana, Y. Zhang, M. Tian, B. Van der Bruggen, The rapid emergence of two-dimensional nanomaterials for high-performance separation membranes, J. Mater. Chem. A 6 (2018) 3773–3792.

[3] G. Liu, W. Jin, N. Xu, Two-dimensional-material membranes: a new family of high-performance separation membranes, Angew. Chem. Int. Ed. 55 (2016) 13384–13397.

[4] D. Li, Y.S. Yan, H.T. Wang, Recent advances in polymer and polymer composite membranes for reverse and forward osmosis processes, Prog. Polym. Sci. 61 (2016) 104–155.

[5] S. Qiu, M. Xue, G. Zhu, Metal-organic framework membranes: from synthesis to separation application, Chem. Soc. Rev. 43 (2014) 6116–6140.

[6] J. Yin, B.L. Deng, Polymer-matrix nanocomposite membranes for water treatment, J. Membr. Sci. 479 (2015) 256–275.

[7] T.S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, Prog. Polym. Sci. 32 (2007) 483–507.

[8] N. Ma, J. Wei, R.H. Liao, C.Y.Y. Tang, Zeolite-polyamide thin film nanocomposite membranes: towards enhanced performance for forward osmosis, J. Membr. Sci. 405 (2012) 149–157.

[9] A. Galve, D. Sieffert, E. Vispe, C. Téllez, J. Coronas, C. Staudt, Copolyimide mixed matrix membranes with oriented microporous titanosilicate JDF-L1 sheet particles, J. Membr. Sci. 370 (2011) 131–140.

[10] S. Castarlenas, P. Gorgojo, C. Casado-Coterillo, S. Masheshwari, M. Tsapatsis, C. Téllez, J. Coronas, Melt compounding of swollen titanosilicate JDF-L1 with polysulfone to obtain mixed matrix membranes for H_2/CH_4 Separation, Ind. Eng. Chem. Res. 52 (2013) 1901–1907.

[11] M.Y. Jeon, D. Kim, P. Kumar, P.S. Lee, N. Rangnekar, P. Bai, M. Shete, B. Elyassi, H.S. Lee, K. Narasimharao, S.N. Basahel, S. Al-Thabaiti, W. Xu, H.J. Cho, E.O. Fetisov, R. Thyagarajan, R.F. DeJaco, W. Fan, K.A. Mkhoyan, J.I. Siepmann, M. Tsapatsis, Ultra-selective high-flux membranes from directly synthesized zeolite nanosheets, Nature 543 (2017) 690–694.

[12] Y. Zhang, S. Zhang, J. Gao, T.S. Chung, Layer-by-layer construction of graphene oxide (GO) framework composite membranes for highly efficient heavy metal removal, J. Membr. Sci. 515 (2016) 230–237.

[13] Y.P. Tang, J.X. Chan, T.S. Chung, M. Weber, C. Staudt, C. Maletzko, Simultaneously covalent and ionic bridging towards antifouling of GO-imbedded nanocomposite hollow fiber membranes, J. Mater. Chem. A 3 (2015) 10573–10584.

[14] A. Gugliuzza, A. Politano, E. Drioli, The advent of graphene and other two-dimensional materials in membrane science and technology, Curr. Opin. Chem. Eng. 16 (2017) 78–85.

[15] J.Y. Chong, B. Wang, K. Li, Graphene oxide membranes in fluid separations, Curr. Opin. Chem. Eng. 12 (2016) 98–105.

[16] S. Manzeli, D. Ovchinnikov, D. Pasquier, O.V. Yazyev, A. Kis, 2D transition metal dichalcogenides, Nat. Rev. Mater. 2 (2017) 17033–17048.

[17] H. Ang, L. Hong, Polycationic polymer-regulated assembling of 2D MOF nanosheets for high-performance nanofiltration, ACS Appl. Mater. Interface 9 (2017) 28079–28088.

[18] I.H. Aljundi, Desalination characteristics of TFN-RO membrane incorporated with ZIF-8 nanoparticles, Desalination 420 (2017) 12–20.

[19] Z. Lai, Development of ZIF-8 membranes: opportunities and challenges for commercial applications, Curr. Opin. Chem. Eng. 20 (2018) 78–85.

[20] X. Wu, Z. Tian, S. Wang, D. Peng, L. Yang, Y. Wu, Q. Xin, H. Wu, Z. Jiang, Mixed matrix membranes comprising polymers of intrinsic microporosity and covalent organic framework for gas separation, J. Membr. Sci. 528 (2017) 273–283.

[21] Y. Cheng, Y. Ying, S. Japip, S.D. Jiang, T.S. Chung, S. Zhang, D. Zhao, Advanced porous materials in mixed matrix membranes, Adv. Mater. (2018) 1802401–1802421.

[22] H. Fan, A. Mundstock, A. Feldhoff, A. Knebel, J. Gu, H. Meng, J. Caro, Covalent organic framework-covalent organic framework bilayer membranes for highly selective gas separation, J. Am. Chem. Soc. (2018), https://doi.org/10.1021/jacs.8b05136.

[23] H.S. Sasmal, H.B. Aiyappa, S.N. Bhange, S. Karak, A. Halder, S. Kurungot, R. Banerjee, Superprotonic conductivity in flexible porous covalent organic framework membranes, Angew. Chem. Int. Ed. 130 (2018), https://doi.org/10.1002/anie.201804753.

[24] J.-H. Chang, J.H. Park, G.-G. Park, C.-S. Kim, O.O. Park, Proton-conducting composite membranes derived from sulfonated hydrocarbon and inorganic materials, J. Power Sources 124 (2003) 18–25.

[25] J.P.G. Villaluenga, M. Khayet, M.A. López-Manchado, J.L. Valentin, B. Seoane, J.I. Mengual, Gas transport properties of polypropylene/clay composite membranes, Eur. Polym. J. 43 (2007) 1132–1143.

[26] X. Guo, F. Zhang, D.G. Evans, X. Duan, Layered double hydroxide films: synthesis, properties and applications, Chem. Commun. 46 (2010) 5197–5210.

[27] Q. Wang, D. O'Hare, Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets, Chem. Rev. 112 (2012) 4124–4155.

[28] Y. Gao, Q. Wang, J. Wang, L. Huang, X. Yan, X. Zhang, Q. He, Z. Xing, Z. Guo, Synthesis of highly efficient flame retardant high-density polyethylene nanocomposites with inorgano-layered double hydroxides as nanofiller using solvent mixing method, ACS Appl. Mater. Interface 6 (2014) 5094–5104.

[29] J.H. Choy, S.J. Choi, J.M. Oh, T. Park, Clay minerals and layered double hydroxides for novel biological applications, Appl. Clay Sci. 36 (2007) 122–132.

[30] Q. Wang, Z. Wu, H.H. Tay, L. Chen, Y. Liu, J. Chang, Z. Zhong, J. Luo, A. Borgna, High temperature adsorption of CO_2 on Mg–Al hydrotalcite: effect of the charge compensating anions and the synthesis pH, Catal. Today 164 (2011) 198–203.

[31] Q. Wang, H.H. Tay, Z.Y. Zhong, J.Z. Luo, A. Borgna, Synthesis of high-temperature

CO_2 adsorbents from organo-layered double hydroxides with markedly improved CO_2 capture capacity, Energ. Environ. Sci. 5 (2012) 7526–7530.

[32] L. Huang, J.Y. Wang, Y.S. Gao, Y.Q. Qiao, Q.W. Zheng, Z.H. Guo, Y.F. Zhao, D. O'Hare, Q. Wang, Synthesis of LiAl2-layered double hydroxides for CO_2 capture over a wide temperature range, J. Mater. Chem. A 2 (2014) 18454–18462.

[33] J.Y. Wang, X.Y. Mei, L. Huang, Q.W. Zheng, Y.Q. Qiao, K.T. Zang, S.C. Mao, R.Y. Yang, Z. Zhang, Y.S. Gao, Z.H. Guo, Z.G. Huang, Q. Wang, Synthesis of layered double hydroxides/graphene oxide nanocomposite as a novel high-temperature CO_2 adsorbent, J. Energy Chem. 24 (2015) 127–137.

[34] Y.F. Zhao, B. Li, Q. Wang, W. Gao, C.L.J. Wang, M. Wei, D.G. Evans, X. Duan, D. O'Hare, NiTi-Layered double hydroxides nanosheets as efficient photocatalysts for oxygen evolution from water using visible Light, Chem. Sci. 5 (2014) 951–958.

[35] X. Mei, J. Wang, R. Yang, Q. Yan, Q. Wang, Synthesis of Pt doped Mg–Al layered double oxide/graphene oxide hybrid as novel NOx storage–reduction catalyst, RSC Adv. 5 (2015) 78061–78070.

[36] X. Mei, Q. Yan, P. Lu, J. Wang, Y. Cui, Y. Nie, A. Umar, Q. Wang, Synthesis of Pt/K2CO3/MgAlOx-reduced graphene oxide hybrids as promising NOx storage-reduction catalysts with superior catalytic performance, Sci. Rep. 7 (2017) 42862–42875.

[37] F. Song, X. Hu, Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis, Nat. Commun. 5 (2014) 4477–4486.

[38] Q. Wang, J.P. Undrell, Y.S. Gao, G.P. Cai, J.C. Buffet, C.A. Wilkie, D. O'Hare, Synthesis of flame-retardant polypropylene/LDH-borate nanocomposites, Macromolecules 46 (2013) 6145–6150.

[39] Y.S. Gao, J.W. Wu, Q. Wang, C.A. Wilkie, D. O'Hare, Flame retardant polymer/layered double hydroxide nanocomposites, J. Mater. Chem. A 2 (2014) 10996–11016.

[40] H. Chen, L.F. Hu, M. Chen, Y. Yan, L.M. Wu, Nickel- cobalt layered double hydroxide nanosheets for high- performance supercapacitor electrode materials, Adv. Funct. Mater. 24 (2014) 934–942.

[41] A.C.S. Alcântara, P. Aranda, M. Darder, E. Ruiz-Hitzky, Bionanocomposites based on alginate–zein/layered double hydroxide materials as drug delivery systems, J. Mater. Chem. 20 (2010) 9495–9504.

[42] A.I. Khan, D. O'Hare, Intercalation chemistry of layered double hydroxides: recent developments and applications, J. Mater. Chem. 12 (2002) 3191–3198.

[43] E. Manasse, Atti Soc, Toscan-. Sci. Nat. 24 (1915) 92.

[44] Q. Wang, H.H. Tay, Z. Guo, L. Chen, Y. Liu, J. Chang, Z. Zhong, J. Luo, A. Borgna, Morphology and composition controllable synthesis of Mg–Al–CO_3 hydrotalcites by tuning the synthesis pH and the CO_2 capture capacity, Appl. Clay Sci. 55 (2012) 18–26.

[45] Q. Wang, X. Zhang, C.L.J. Wang, J.H. Zhu, Z.H. Guo, D. O'Hare, Polypropylene/layered double hydroxide nanocomposites, J. Mater. Chem. 22 (2012) 19113–19121.

[46] Q. Wang, X. Zhang, J. Zhu, Z. Guo, D. O'Hare, Preparation of stable dispersions of layered double hydroxides (LDHs) in nonpolar hydrocarbons: new routes to polyolefin/LDH nanocomposites, Chem. Commun. 48 (2012) 7450–7452.

[47] Y. Gao, J. Wu, Z. Zhang, R. Jin, X. Zhang, X. Yan, A. Umar, Z. Guo, Q. Wang, Synthesis of polypropylene/Mg3Al–X (X = CO_3^{2-}, NO_3^{-}, Cl^{-}, SO_4^{2-}) LDH nanocomposites using a solvent mixing method: thermal and melt rheological properties, J. Mater. Chem. A 1 (2013) 9928–9934.

[48] S.Y. Huang, S. Song, R. Zhang, T. Wen, X.X. Wang, S.J. Yu, W.C. Song, T. Hayat, A. Alsaedi, X.K. Wang, Construction of layered double hydroxides/hollow carbon microsphere composites and its applications for mutual removal of Pb(II) and humic acid from aqueous solutions, ACS Sustain. Chem. Eng. 5 (2017) 11268–11279.

[49] P. Gu, S. Zhang, X. Li, X. Wang, T. Wen, R. Jehan, A. Alsaedi, T. Hayat, X. Wang, Recent advances in layered double hydroxide-based nanomaterials for the removal of radionuclides from aqueous solution, Environ. Pollut. 240 (2018) 493–505.

[50] J. Yu, Q. Wang, D. O'Hare, L. Sun, Preparation of two dimensional layered double hydroxide nanosheets and their applications, Chem. Soc. Rev. 46 (2017) 5950–5974.

[51] L. Sun, W.J. Boo, R.L. Browning, H.-J. Sue, A. Clearfield, Effect of crystallinity on the intercalation of monoamine in α-zirconium phosphate layer structure, Chem. Mater. 17 (2005) 5606–5609.

[52] T. Hibino, H. Ohya, Synthesis of crystalline layered double hydroxides: precipitation by using urea hydrolysis and subsequent hydrothermal reactions in aqueous solutions, Appl. Clay Sci. 45 (2009) 123–132.

[53] Q. Wang, D. O'Hare, Large-scale synthesis of highly dispersed layered double hydroxide powders containing delaminated single layer nanosheets, Chem. Commun. 49 (2013) 6301–6303.

[54] R.Z. Ma, Z.P. Liu, L. Li, N. Iyi, T. Sasaki, Exfoliating layered double hydroxides in formamide: a method to obtain positively charged nanosheets, J. Mater. Chem. 16 (2006) 3809–3813.

[55] J. Wang, L. Huang, Y. Gao, R. Yang, Z. Zhang, Z. Guo, Q. Wang, A simple and reliable method for determining the delamination degree of nitrate and glycine intercalated LDHs in formamide, Chem. Commun. 50 (2014) 10130–10132.

[56] J. Liu, L. Yu, Y. Zhang, Fabrication and characterization of positively charged hybrid ultrafiltration and nanofiltration membranes via the in-situ exfoliation of Mg/Al hydrotalcite, Desalination 335 (2014) 78–86.

[57] X. Wang, H. Wang, Y. Wang, J. Gao, J. Liu, Y. Zhang, Hydrotalcite/graphene oxide hybrid nanosheets functionalized nanofiltration membrane for desalination, Desalination (2017), https://doi.org/10.1016/j.desal.2017.05.012.

[58] Z. Jia, S. Hao, X. Lu, Exfoliated Mg-Al-Fe layered double hydroxides/polyether sulfone mixed matrix membranes for adsorption of phosphate and fluoride from aqueous solutions, J. Environ. Sci. 70 (2018) 63–73.

[59] M. Adachi-Pagano, C. Forano, J.P. Besse, Delamination of layered double hydroxides by use of surfactants, Chem. Commun. 0 (2000) 91–92.

[60] S. Arefi-Oskoui, A. Khataee, V. Vatanpour, Effect of solvent type on the physico-chemical properties and performance of NLDH/PVDF nanocomposite ultrafiltration membranes, Sep. Purif. Technol. 184 (2017) 97–118.

[61] P.M. Pardeshi, A.K. Mungray, A.A. Mungray, Polyvinyl chloride and layered double hydroxide composite as a novel substrate material for the forward osmosis membrane, Desalination 421 (2017) 149–159.

[62] P. Lu, S. Liang, L. Qiu, Y.S. Gao, Q. Wang, Thin film nanocomposite forward osmosis membranes based on layered double hydroxide nanoparticles blended substrates, J. Membr. Sci. 504 (2016) 196–205.

[63] Y. Gao, Z. Zhang, J. Wu, X. Yi, A. Zheng, A. Umar, D. O'Hare, Q. Wang, Comprehensive investigation of CO_2 adsorption on Mg–Al–CO_3 LDH-derived mixed metal oxides, J. Mater. Chem. A 1 (2013) 12782–12790.

[64] T.W. Kim, M. Sahimi, T.T. Tsotsis, Gas transport properties of hydrotalcite membranes, in: Presented at the 2006 AIChE Annual Meeting, CA, San Francisco, 2006, pp. Paper No. 285e.

[65] T.W. Kim, M. Sahimi, T.T. Tsotsis, Preparation of hydrotalcite thin films using an electrophoretic technique, Ind. Eng. Chem. Res. 47 (2008) 9127–9132.

[66] Y. Liu, N.Y. Wang, Z.W. Cao, J. Caro, Molecular sieving through interlayer galleries, J. Mater. Chem. A 2 (2014) 1235–1238.

[67] Y. Liu, N.Y. Wang, J. Caro, In situ formation of LDH membranes of different microstructures with molecular sieve gas selectivity, J. Mater. Chem. A 2 (2014) 5716–5723.

[68] Y. Liu, J.H. Pan, N. Wang, F. Steinbach, X. Liu, J. Caro, Remarkably enhanced gas separation by partial self-conversion of a laminated membrane to metal-organic frameworks, Angew. Chem. Int. Ed. 54 (2015) 3028–3032.

[69] Y. Liu, N. Wang, L. Diestel, F. Steinbach, J. Caro, MOF membrane synthesis in the confined space of a vertically aligned LDH network, Chem. Commun. 50 (2014) 4225–4227.

[70] Y. Liu, N. Wang, J.H. Pan, F. Steinbach, J. Caro, In situ synthesis of MOF membranes on ZnAl-CO_3 LDH buffer layer-modified substrates, J. Am. Chem. Soc. 136 (2014) 14353–14356.

[71] Y. Liu, Y. Peng, N. Wang, Y. Li, J.H. Pan, W. Yang, J. Caro, Significantly enhanced separation using ZIF-8 membranes by partial conversion of calcined layered double hydroxide precursors, ChemSusChem 8 (2015) 3582–3586.

[72] H. Lee, D.B. Kim, S.H. Kim, H.S. Kim, S.J. Kim, D.K. Choi, Y.S. Kang, J. Won, Zwitterionic silver complexes as carriers for facilitated-transport composite membranes, Angew. Chem. Int. Ed. 43 (2004) 3053–3056.

[73] K. Ramasubramanian, Y. Zhao, W.S. Winston Ho, CO_2 capture and H_2 purification: prospects for CO_2-selective membrane processes, AIChE J. 59 (2013) 1033–1045.

[74] J.Y. Liao, Z. Wang, C.Y. Gao, S.C. Li, Z.H. Qiao, M. Wang, S. Zhao, X.M. Xie, J.X. Wang, S.C. Wang, Fabrication of high-performance facilitated transport membranes for CO_2 separation, Chem. Sci. 5 (2014) 2843–2849.

[75] J. Liao, Z. Wang, C. Gao, M. Wang, K. Yan, X. Xie, S. Zhao, J. Wang, S. Wang, A high performance PVAm–HT membrane containing high-speed facilitated transport channels for CO_2 separation, J. Mater. Chem. A 3 (2015) 16746–16761.

[76] T. Tong, M. Elimelech, The global rise of zero liquid discharge for wastewater management: drivers, technologies, and future directions, Environ. Sci. Technol. 50 (2016) 6846–6855.

[77] D.M. Stevens, J.Y. Shu, M. Reichert, A. Roy, Next-generation nanoporous materials: progress and prospects for reverse osmosis and nanofiltration, Ind. Eng. Chem. Res. 56 (2017) 10526–10551.

[78] T. Matsuura, Progress in membrane science and technology for seawater desalination - a review, Desalination 134 (2001) 47–54.

[79] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination-Development to date and future potential, J. Membr. Sci. 370 (2011) 1–22.

[80] M. Xie, H.K. Shon, S.R. Gray, M. Elimelech, Membrane-based processes for wastewater nutrient recovery: technology, challenges, and future direction, Water Res. 89 (2016) 210–221.

[81] F. Li, R. Gao, T. Wu, Y. Li, Role of layered materials in emulsified oil/water separation and anti-fouling performance of modified cellulose acetate membranes with hierarchical structure, J. Membr. Sci. 543 (2017) 163–171.

[82] P. Anadao, L.F. Sato, H. Wiebeck, F.R. Valenzuela-Diaz, Montmorillonite as a component of polysulfone nanocomposite membranes, Appl. Clay Sci. 48 (2010) 127–132.

[83] M. Herrero, A.M. Martos, A. Varez, J.C. Galvan, B. Levenfeld, Synthesis and characterization of polysulfone/layered double hydroxides nanocomposite membranes for fuel cell application, Int. J. Hydrog. Energ. 39 (2014) 4016–4022.

[84] P. Lu, S. Liang, T.T. Zhou, T.S. Xue, X.Y. Mei, Q. Wang, Layered double hydroxide nanoparticle modified forward osmosis membranes via polydopamine immobilization with significantly enhanced chlorine and fouling resistance, Desalination 421 (2017) 99–109.

[85] S. Liang, K. Xiao, Y.H. Mo, X. Huang, A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling, J. Membr. Sci. 394 (2012) 184–192.

[86] S. Liang, Y. Kang, A. Tiraferri, E.P. Giannelis, X. Huang, M. Elimelech, Highly hydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes via post-fabrication grafting of surface-tailored silica nanoparticles, ACS Appl. Mater. Interface 5 (2013) 6694–6703.

[87] S. Wang, S. Liang, P. Liang, X. Zhang, J. Sun, S. Wu, X. Huang, In-situ combined dual-layer CNT/PVDF membrane for electrically-enhanced fouling resistance, J. Membr. Sci. 491 (2015) 37–44.

[88] Y. Zhao, N.N. Li, F.Z. Yuan, H.D. Zhang, S.J. Xia, Preparation and characterization of hydrophilic and antifouling poly(ether sulfone) ultrafiltration membranes modified with Zn-Al layered double hydroxides, J. Appl. Polym. Sci. 133 (2016)

43988–43998.

[89] J. Wang, Y.T. Zhang, J.Y. Zhu, J.W. Hou, J.D. Liu, B. Van der Bruggen, Zwitterionic functionalized layered double hydroxides nanosheets for a novel charged mosaic membrane with high salt permeability, J. Membr. Sci. 510 (2016) 27–37.

[90] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: recent advances and future prospects, Desalination 356 (2015) 226–254.

[91] P. Lu, Y.S. Gao, A. Umar, T.T. Zhou, J.Y. Wang, Z. Zhang, L. Huang, Q. Wang, Recent advances in cellulose-based forward osmosis membrane, Sci. Adv. Mater. 7 (2015) 2182–2192.

[92] P. Lu, S. Liang, T.T. Zhou, X.Y. Mei, Y. Zhang, C. Zhang, A. Umar, H.J. Wang, Q. Wang, Typical thin-film composite (TFC) membranes modified with inorganic nanomaterials for forward osmosis: a review, Nanosci. Nanotechnol. Lett. 8 (2016) 906–916.

[93] P. Lu, S. Liang, T.T. Zhou, X.Y. Mei, Y. Zhang, C. Zhang, Q. Wang, Layered double hydroxide/graphene oxide hybrid incorporated polysulfone substrate for thin-film nanocomposite forward osmosis membranes, RSC Adv. 6 (2016) 56599–56609.

[94] C. Yang, W.H. Smyrl, E.L. Cussler, Flake alignment in composite coatings, J. Membr. Sci. 231 (2004) 1–12.

[95] Y. You, H. Zhao, G.F. Vance, Adsorption of dicamba (3,6-dichloro-2-methoxy benzoic acid) in aqueous solution by calcined–layered double hydroxide, Appl. Clay Sci. 21 (2002) 217–226.

[96] K.H. Goh, T.T. Lim, Z. Dong, Application of layered double hydroxides for removal of oxyanions: a review, Water Res. 42 (2008) 1343–1368.

[97] T.-H. Kim, I.-T. Hong, J.-Y. Lee, J.-H. Kang, J.-M. Oh, Layered nanomaterials for environmental remediation applications, Energy Environ. Focus 3 (2014) 23–36.

[98] F.L. Theiss, S.J. Couperthwaite, G.A. Ayoko, R.L. Frost, A review of the removal of anions and oxyanions of the halogen elements from aqueous solution by layered double hydroxides, J. Colloid Interface Sci. 417 (2014) 356–368.

[99] X.F. Liang, Y.B. Zang, Y.M. Xu, X. Tan, W.G. Hou, L. Wang, Y.B. Sun, Sorption of metal cations on layered double hydroxides, Colloid Surf. A 433 (2013) 122–131.

[100] T. Zhang, Q. Li, H. Xiao, H. Lu, Y. Zhou, Synthesis of Li–Al layered double hydroxides (LDHs) for efficient fluoride removal, Ind. Eng. Chem. Res. 51 (2012) 11490–11498.

[101] D.G. Evans, X. Duan, Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine, Chem. Commun. 0 (2006) 485–496.

[102] X.Y. Yu, T. Luo, Y. Jia, R.X. Xu, C. Gao, Y.X. Zhang, J.H. Liu, X.J. Huang, Three-dimensional hierarchical flower-like Mg-Al-layered double hydroxides: highly efficient adsorbents for As(V) and Cr(VI) removal, Nanoscale 4 (2012) 3466–3474.

[103] Y. Guo, Z. Jia, Novel sandwich structure adsorptive membranes for removal of 4-nitrotoluene from water, J. Hazard. Mater. 317 (2016) 295–302.

[104] X.X. Guo, F.Z. Zhang, Q. Peng, S.L. Xu, X.D. Lei, D.G. Evans, X. Duan, Layered double hydroxide/eggshell membrane: an inorganic biocomposite membrane as an efficient adsorbent for Cr(VI) removal, Chem. Eng. J. 166 (2011) 81–87.

[105] R. Rattanaoudom, C. Visvanathan, Removal of PFOA by hybrid membrane filtration using PAC and hydrotalcite, Desalin. Water Treat. 32 (2011) 262–270.

[106] Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, A novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for oil/water separation, Adv. Mater. 23 (2011) 4270–4273.

[107] F. Zhang, W.B. Zhang, Z. Shi, D. Wang, J. Jin, L. Jiang, Nanowire-haired inorganic membranes with superhydrophilicity and underwater ultralow adhesive superoleophobicity for high-efficiency oil/water separation, Adv. Mater. 25 (2013) 4192–4198.

[108] H.-J. Li, Y.-M. Cao, J.-J. Qin, X.-M. Jie, T.-H. Wang, J.-H. Liu, Q. Yuan, Development and characterization of anti-fouling cellulose hollow fiber UF membranes for oil–water separation, J. Membr. Sci. 279 (2006) 328–335.

[109] X. Liu, L. Ge, W. Li, X. Wang, F. Li, Layered double hydroxide functionalized textile for effective oil/water separation and selective oil adsorption, ACS Appl. Mater. Interface 7 (2015) 791–800.

[110] Z. Shami, S.M. Amininasab, P. Shakeri, Structure-property relationships of nanosheeted 3D hierarchical roughness MgAl-layered double hydroxide branched to an electrospun porous nanomembrane: a superior oil-removing nanofabric, ACS Appl. Mater. Interface 8 (2016) 28964–28973.

[111] X.J. Yue, J.X. Li, T. Zhang, F.X. Qiu, D.Y. Yang, M.W. Xue, In situ one-step fabrication of durable superhydrophobic-superoleophilic cellulose/LDH membrane with hierarchical structure for efficiency oil/water separation, Chem. Eng. J. 328 (2017) 117–123.

[112] P.-C. Lee, T.-H. Han, D.O. Kim, J.-H. Lee, S.-J. Kang, C.-H. Chung, Y. Lee, S.M. Cho, H.-G. Choi, T. Kim, E. Lee, J.-D. Nam, In situ formation of platinum nanoparticles in Nafion recast film for catalyst-incorporated ion-exchange membrane in fuel cell applications, J. Membr. Sci. 322 (2008) 441–445.

[113] K. Lee, J.D. Nam, Optimum ionic conductivity and diffusion coefficient of ion-exchange membranes at high methanol feed concentrations in a direct methanol fuel cell, J. Power Sources 157 (2006) 201–206.

[114] I. Nicotera, K. Angjeli, L. Coppola, A. Enotiadis, R. Pedicini, A. Carbone, D. Gournis, Composite polymer electrolyte membranes based on Mg–Al layered double hydroxide (LDH) platelets for H_2/air-fed fuel cells, Solid State Ion. 276 (2015) 40–46.

[115] T.W. Kim, M. Sahimi, T.T. Tsotsis, Hybrid hydrotalcite − sulfonated poly(ether ether ketone) cation-exchange membranes prepared by in situ sulfonation, Ind. Eng. Chem. Res. 50 (2011) 3880–3888.

[116] N.H. Kim, A.K. Mishra, D.Y. Kim, J.H. Lee, Synthesis of sulfonated poly(ether ether ketone)/layered double hydroxide nanocomposite membranes for fuel cell applications, Chem. Eng. J. 272 (2015) 119–127.

[117] L. Zeng, T.S. Zhao, Y.S. Li, Synthesis and characterization of crosslinked poly (vinyl alcohol)/layered double hydroxide composite polymer membranes for alkaline direct ethanol fuel cells, Int. J. Hydrog. Energy 37 (2012) 18425–18432.

[118] P.Z. Sun, R.Z. Ma, W. Ma, J.H. Wu, K.L. Wang, T. Sasaki, H.W. Zhu, Highly selective charge-guided ion transport through a hybrid membrane consisting of anionic graphene oxide and cationic hydroxide nanosheet superlattice units, NPG Asia Mater. 8 (2016) e259–e269.

[119] L. Ding, Y. Wei, L. Li, T. Zhang, H. Wang, J. Xue, L.X. Ding, S. Wang, J. Caro, Y. Gogotsi, MXene molecular sieving membranes for highly efficient gas separation, Nat. Commun. 9 (2018) 155–162.

[120] J. Shen, G. Liu, Y. Ji, Q. Liu, L. Cheng, K. Guan, M. Zhang, G. Liu, J. Xiong, J. Yang, W. Jin, 2D MXene nanofilms with tunable gas transport channels, Adv. Funct. Mater. 28 (2018) 1801511–1801524.