

Results and discussion 3.1. Fabrication and characterization of L-CNM As schematically shown in Scheme 1, the L-CNM with a sheet-like structure was one-step in situ constructed by employing a facile electrospinning method. The spinning dope was prepared by mixing  $\text{LaCl}_3$  with a cellulose solution, while a  $\text{NaOH}$  aqueous solution was used as the coagulating bath. The sheet-like  $\text{La}(\text{OH})_3$  was decorated on CNM through hydrogen bonding interaction and physical wrapping. Owing to the synergy of the abundant hydroxyl groups and the special electron-deficient orbital structure of  $\text{La}(\text{OH})_3$ , the L-CNM exhibited superhydrophilicity and high affinity toward CR having two amine groups and electron-rich sulfonic groups, which could be of great advantages in oil/water separation and selective removal of dyes. The micro morphologies of pure CNM and L-CNM were observed with SEM. As showed in Fig. 1a, the neat electrospun cellulose nano fibers had an average diameter of  $\sim 360$  nm (see the fiber diameter distribution in Fig. S1) and the interpenetrated nanofibers formed numerous macropores, which ensured a high water flux of the membrane. Fig. 1b displayed the SEM image of L-CNM surface, where quite a lot of nanosheets with a uniform square shape were clearly visible. These nanosheets with a thickness of  $\sim 400$  nm and a width of  $1\text{--}9\text{ }\mu\text{m}$  were evenly dispersed in the cellulose nanofiber scaffold without any large aggregates. Meanwhile, most of the pores were still preserved. Moreover, the average fiber diameter of L-CNM decreased to  $\sim 280$  nm (Fig. S1). This was possibly attributed to the increased conductivity of the spinning dope after the addition of  $\text{LaCl}_3$  [37]. From the high-resolution SEM image in Fig. 1c, the nanosheets were wrapped by the cellulose nanofibers and intimately attached to them with vague phase boundaries, which may benefit the immobilization of those nanosheets in the membranes. Besides, the surface roughness ( $R_a$ ) of CNM and L-CNM were measured using CLSM. As shown in Fig. S2, the  $R_a$  of pristine CNM was  $0.065\text{ }\mu\text{m}$ . After being modified with  $\text{La}(\text{OH})_3$ , the  $R_a$  apparently increased to  $0.306\text{ }\mu\text{m}$ . And this improved roughness could benefit the wetting behavior of L-CNM according to the Wenzel model [38]. The surface chemical composition of the membrane was estimated by energy-dispersive spectrometry (EDS). The EDS results of pure CNM and L-CNM were presented in Fig. 1g and h, respectively. The characteristic peaks assigned to La element were observable in the EDS spectrum of L-CNM, but hardly could be detected for pure CNM. Moreover, the EDS mapping images revealed the C, O and La elements were distributed homogeneously in the whole material matrix (Fig. 1d–f), indicating the uniform dispersion of as-synthesized  $\text{La}(\text{OH})_3$  nanosheets in the membrane. The chemical composition of the membrane was further investigated by ATR-FTIR and XRD. Fig. 2a gave the ATR-FTIR spectra of CNM and L-CNM. The bands at  $1437\text{ cm}^{-1}$  and  $860\text{ cm}^{-1}$  in both samples were assigned to symmetric  $\text{CH}_2$  bending and  $\text{CH}_2$  stretching vibration, respectively [39]. A new peak appeared at  $674\text{ cm}^{-1}$  in the L-CNM's spectrum, which was attributed to the bend vibration of  $\text{La-O-H}$  [40]. Fig. 1. Structure characterization of the membranes: SEM images of (a) pristine CNM and (b,c) L-CNM at different magnifications. (d–f) EDS mapping images of L-CNM. EDS analysis of (g) original CNM and (h) L-CNM surface. From the XRD diffraction pattern of CNM (Fig. 2b), the cellulose II diffraction peaks at around  $20.2^\circ$  and  $12.6^\circ$  were observed owing to reflection from the (1 1 0) and (1–10) crystal planes of cellulose II [41]. The diffraction peaks at  $27.3^\circ$  and  $43.7^\circ$  for L-CNM corresponded to the (1 0 1) and (2 1 0) crystal planes of  $\text{La}(\text{OH})_3$ , respectively [40,42]. These results consistently suggested the successful synthesis of  $\text{La}(\text{OH})_3$  with the hexagonal phase [43]. The porosity

features of CNM and L-CNM were investigated by N<sub>2</sub> adsorption-desorption isotherms. As depicted in Fig. 3a, these isotherms displayed the type-IV isotherm shape with a typical H<sub>2</sub> hysteresis loop, indicating the membranes possessed an interconnected pore structure with both micro- and meso-pores [44]. Additionally, the high relative pressure part ( $P/P_0 > 0.9$ ) of the N<sub>2</sub> adsorption isotherms increased significantly, implying the existence of macro-pores in the membranes [45]. Fig. 3b showed the distribution of incremental pore volume with the pore width. It further demonstrated that both CNM and L-CNM had multiscale pores. And the average pore size of L-CNM (20.2 nm) was larger than that of CNM (10.1 nm). Cumulative pore volume versus pore size was given in Fig. 3c. A remarkable increase in the total pore volume of L-CNM (0.134 mL/g) by more than seven times that of CNM (0.019 mL/g) was recorded. In addition, the BET specific surface area of L-CNM (21.15 m<sup>2</sup>/g) was much larger than that of CNM (5.96 m<sup>2</sup>/g). The above results confirmed that the total pore volume, pore width and specific surface area of L-CNM increased sharply as compared with CNM, providing more water transfer channels for a high water flux.

### 3.2. Possible formation mechanism of La(OH)<sub>3</sub> nanosheets

To investigate the formation mechanism of the La(OH)<sub>3</sub> nanosheets, the time-dependent growth of La(OH)<sub>3</sub> in the membrane was monitored. When the LaCl<sub>3</sub>-containing electrospun cellulose nanofibers were immersed in aqueous NaOH for a short time (10 min), a large number of small and irregularly shaped La(OH)<sub>3</sub> nanoparticles were observed at the surface of cellulose nanofibers (Fig. 4a), as a result of the reaction between La<sup>3+</sup> and OH<sup>-</sup>. When the immersion time extended to 90 min, the La(OH)<sub>3</sub> nanoparticles agglomerated to form thin nanosheets (Fig. 4b). The nanosheet formation could be presumably explained by the Ostwald ripening mechanism [46]. In brief, due to the intrinsic anisotropic property of La(OH)<sub>3</sub>, the La(OH)<sub>3</sub> nanoparticles prefer to grow into 2D nanosheets with the exposure of low-energy facets to reduce the surface energy [46,47]. When increasing the immersion time to 6 h, more and more regular La(OH)<sub>3</sub> nanosheets were formed owing to the mass diffusion and Ostwald ripening (Fig. 4c). Moreover, these La(OH)<sub>3</sub> nanosheets were uniformly distributed either on the surface of cellulose nanofibers or at the spacing between adjacent nanofibers. The porous electrospun cellulose nanofiber scaffold offered a unique 3D space for the in situ growth of La(OH)<sub>3</sub> nanosheets thereof. And the hydrogen bonding interaction between the hydroxyls of La(OH)<sub>3</sub> nanosheets and cellulose nanofibers, as well as the physical wrapping should be mainly responsible for the solid anchoring of La(OH)<sub>3</sub> in the membrane.

### 3.3. Wettability of L-CNM

The surface wettability was crucial for membranes in water treatment. To evaluate the wettability of L-CNM, the dynamic wetting behaviors of a water droplet on the membrane in air and a heavy oil (1, 2-dichloroethane as a representative oil) on the membrane underwater were recorded. As presented in Fig. 5a, a 4  $\mu$ L water droplet fleetly spread on L-CNM within 160 ms and gave a water contact angle of near 0° (Movie S1), indicating that L-CNM was superhydrophilic. Whereas 400 ms was needed for CNM (Fig. S3a), showing a faster water spreading rate of L-CNM. When a 4  $\mu$ L 1, 2-dichloroethane was placed onto the membrane underwater, the oil droplet still retained a spherical shape with a high value of oil contact angle (> 150°), showing underwater superoleophobicity. Furthermore, even if the oil droplet was forced against the membrane until obvious deformation, it could detach from the surface of L-CNM easily (Fig. 5b and Movie S2), indicative of the ultralow oil adhesion. By contrast, an oil droplet was found to attach directly to CNM (Fig. S3b).

We believe the super-wetting behavior of L-CNM should be attributed to the synergy effect of the abundant Fig. 5. (a) Photographs of a water droplet spreading on L-CNM in air. (b) Photographs of dynamic underwater oil-repelling on L-CNM. (c) Anti-oil-fouling properties of L-CNM and original CNM.

Crude oil was used in this demo. Digital image in the red frame presented the oil fouling of CNM. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) hydroxyl groups from  $\text{La}(\text{OH})_3$  nanosheets and cellulose nanofibers as well as the enhanced roughness from  $\text{La}(\text{OH})_3$  nanosheets (Fig. S2). The anti-oil-fouling properties of L-CNM and

CNM against crude oil were further evaluated. Fig. 5c demonstrated the whole procedure: the membrane was pre-wetted with water and then immersed in crude oil totally. After lifted out of crude oil, the membrane was fully enshrouded by the crude oil. Finally, this membrane was placed into a beaker containing clean water. When L-CNM covered by crude oil was immersed into water, all the crude oil was spontaneously levitated off the membrane and no trace was left. Whereas obvious oil-fouling was seen on CNM. These results further manifested the outstanding underwater anti-oil-fouling property of

L-CNM even for the crude oil with a high viscosity. To sum up, the L-CNM exhibited remarkable selective wetting ability and outstanding anti-oil-fouling properties, which was favorable for oily wastewater treatment [7].

**3.4. Oil/water separation performance** The L-CNM had excellent capability in separation of oil/water mixtures. As demonstrated in Fig. 6a, the hexane/water mixture (v/v: 1:1) was poured onto the membrane, which was pre-wetted by water. Only driven by gravity, water could rapidly permeate

through the membrane owing to the superhydrophilicity, whereas hexane was repelled above the membrane because of the underwater super oleophobicity. No visible oil residue was found in the

filtered water, suggesting the high separation efficiency of the membrane. In addition, the water flux was as high as  $5897.7 \text{ L m}^{-2} \text{ h}^{-1}$  for L-CNM, almost two times that of CNM at a similar thickness. Such a

high water flux could be attributed to the faster water wetting rate and more water transfer channels available in L-CNM as compared with CNM (Fig. S3 and Fig. 3). In order to imitate the real separation applications, different types of oil were tested, including cyclohexane, petroleum ether, liquid paraffin, pump oil and crude oil. From Fig. 6b, all these oil/water mixtures could be effectively separated with high fluxes (from  $6318.9$  to  $8586.1 \text{ L m}^{-2} \text{ h}^{-1}$ ). Moreover, the separation efficiencies were well above 98.8%

(hexane 98.8%, cyclohexane 98.9%, toluene 99.7%, pump oil 98.9%, petroleum ether 99.3% and crude oil 99.1%). In addition, the recycling performance of the membrane was also evaluated using the

hexane/water mixture as a representative. Note that the membrane was just simply rinsed with water prior to next separation. Surprisingly, after 60 separation cycles, the membrane still preserved a high separation efficiency above 98.2%, along with a high flux over  $5443 \text{ L m}^{-2} \text{ h}^{-1}$  (Fig. 6c), indicating its

excellent recyclability. In addition, the L-CNM could still maintain remarkable underwater superoleophobicity with ultralow oil adhesion after 60 separation cycles (Fig. S4). From Table 1, the flux, separation efficiency and recyclability of L-CNM were comparable to or even outperformed many early reported electrospun membranes [48–56]. Besides, the bearable oil height for L-CNM was very high, up to 100.5 cm as demonstrated in Fig. 6d. The intrusion pressure was calculated to be 6.95 kPa. It means

the oil (hexane) cannot pass through L-CNM under this pressure. This intrusion pressure was comparable to that of SSA-PAAS-g-PVDF composite membrane as reported by Zhang et al. [57],

demonstrating a good stability of the separating system. In order to further evaluate the emulsion separation performance of L-CNM, Tween 80-stabilized toluene-in-water emulsion was prepared by mixing toluene with a Tween 80 water solution in a ratio of 5:100 (v/v) under vigorous stirring for 2 h. This emulsion was used as the feed solution to permeate through L-CNM by gravity. After separation, the white milky emulsion became transparent and colorless. Under a polarizing microscope, the whole view was composed of numerous micro scale droplets in the feed solution, whereas no oil droplet was observed in the filtrate (Fig. 7), suggesting the successful separation of the emulsion. The emulsion separation efficiency was calculated to be 98.5% according to the absorbance changes on toluene's characteristic peak at 261 nm in the UV-vis spectra before and after separation [58]. Moreover, the water flux was determined to  $436.4 \text{ L m}^{-2} \text{ h}^{-1}$  during the emulsion separation process, which was comparable to or outperformed other electrospun membranes [49,53]. The effects of  $\text{La}(\text{OH})_3$  loading on the oil/water separation and the dye adsorption capacity of L-CNM were also investigated and discussed in detail in the Supporting Information (Fig. S5 and S6).

### 3.5. Selective adsorption of dyes

Considering that the organic dyes are another major contaminant in wastewater apart from oils, the dye adsorption capacities of L-CNM was further evaluated. Cationic MB as well as anionic MO and CR were employed in the adsorption tests, and the corresponding UV-Vis spectra were displayed in Fig. 8a-c. Once the membrane was immersed in the CR solution, the characteristic peak for CR at 498 nm decreased drastically (Fig. 8c), showing the fast adsorption capacities. However, when the membrane was immersed in either MB or MO solution, the resultant UV-Vis spectra almost unchanged even over a prolonged time period of 240 min (Fig. 8a and b), suggesting the negligible adsorption toward MB and MO. This intriguing phenomenon inspired the further exploration of the membrane in selective adsorption of different dye pollutants. Two different mixed dye solutions, namely, MB/CR and MO/CR (1:1 vol ratio), were prepared. When the membrane was put in the MB/CR solution, the absorption peak at 498 nm corresponding to CR decreased markedly, while the peak at 664 nm assigned to MB was barely changed (Fig. 8d), indicating that CR was selectively separated from the MB/CR mixture. And the separation efficiency was calculated to be 91.2%. For the MO/CR mixture (Fig. 8e), only one maximum characteristic peak appeared after mixing because the maximum absorption peaks of MO and CR overlapped with each other, like the dye mixture of neutral red (NR) and reactive blue (RB) as reported by Cai et al. [59]. Specially, the shoulder peaks of CR at 238 nm and 340 nm weakened evidently while the shoulder peak of MO at 270 nm just decreased slightly after adsorption (Fig. 8e and Fig. S7). Moreover, the color changed from orange red for the MO/CR solution to pure orange for MO (Fig. 8f and Movie S3), suggesting that CR was selectively adsorbed by the membrane while MO was still left in the solution. These results indicated that L-CNM was capable of not only separating dye mixture of opposite charges, but also efficiently separating dye mixture with the same charge.

Fig. 6. (a) Gravity-driven oil/water separation experiment on L-CNM. Oil (hexane as the representative oil) was dyed with Oil Red O to aid visualization. (b) Variations in water flux and separation efficiency of L-CNM for different types of oil/water mixtures. (c) Evolution of the permeation flux and the corresponding efficiency of L-CNM for hexane/water mixture over 60 cycles (hexane as the oil example). (d) Measurement of oil (hexane as the representative oil) intrusion pressure of L-CNM. (For interpretation of the references to colour in this

figure legend, the reader is referred to the web version of this article.) 3.6. Adsorption mechanisms To examine the nature of interaction between CR and the adsorbent, the Freundlich [60] and Langmuir isotherm [61] models were used to simulate the adsorption isotherm. Fig. S8 provided the Freundlich and Langmuir isotherms of L-CNM in the solutions with different CR concentrations. The experimental data could be better fitted by the Freundlich model ( $R^2 = 0.998$ ) as compared with the Langmuir model in term of the correlation coefficient ( $R^2 = 0.872$ ). This result indicated the multilayer adsorption of CR on the heterogeneous surface of L-CNM [60]. The dye adsorption capacity of L-CNM was calculated to be 624 mg/g, much higher than that of CNM (260 mg/g). Moreover, the CR removal efficiency as a function of time at 30 mg/L initial concentration was shown in Fig. S9. In the first 1 min, almost 65% of total CR was removed by L-CNM, while 120 min was needed for CNM to achieve the same result. These results manifested that L-CNM had a faster adsorption rate and a higher adsorption capacity toward CR, which should be ascribed to the tremendous active sites provided by La(OH)<sub>3</sub> nanosheets. ATR-FTIR spectra of L-CNM before and after CR adsorption were given in Fig. S10. After adsorption, the new peaks at 1022 cm<sup>-1</sup> (attributed to the stretching vibration of S=O) and 1163, 1378, 1469 cm<sup>-1</sup> (assigned to the framework vibration of benzene rings) appeared, which confirmed the adsorption of CR onto L-CNM [62]. Note that the peak at 3421 cm<sup>-1</sup>, corresponding to the stretching vibration of OeH, shifted to a lower wavenumber (3378 cm<sup>-1</sup>) after adsorption. In addition, the OeH stretching peak was also broadened. This suggested that hydrogen bonds were formed between the hydroxyl groups of L-CNM and the amine groups of CR molecules [63]. Considering the fact that the adsorption of anionic CR was significant while the adsorption of anionic MO was almost negligible, it was speculated that the hydrogen bonding interaction rather than the electrostatic attraction might play the main role in the adsorption process. In addition, the electron-deficient La 4f orbitals in La(OH)<sub>3</sub> could induce strong affinity toward electron-rich sulfonic groups in CR, leading to the high CR adsorption capacity. Fig. 7. Digital photographs and polarizing microscopy photographs of the Tween 80-stabilized toluene-in-water emulsion (a) before and (b) after separation.