

Supporting Information (SI)

Morphological Control of Poly(Vinylidene Fluoride)@Layered Double Hydroxide Composite Fibers by Metal Salt Anions and Their Enhanced Performance for Dye Removal

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SI1 Effect of processing parameters on the properties of PVDF electrospun nanofibers

Electrospinning is an efficient and simple method to fabricate fibers down to the micro- and nanometer scale, where the morphologies and properties could be facilely adjusted by numerous processing parameters. In this manuscript, solution of PVDF in mixed solvent (N, N-dimethyl Formamide / Acetone, DMF/ACE = 3/2, v/v) with the polymer concentration of 15 wt% was used to prepare electrospun fibers at 25 °C. The distance between the needle tip and the collecting aluminum foil were fixed at 13 cm. The influence of different processing parameters: applied voltage, needle diameter, and flow rate were explored, since they were the ones strongly influencing the properties of the electrospun fibers¹.

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(1) Applied voltage (needle diameter of 0.7 mm and flow rate of 0.5 ml/h)

Fig. S1 gives the average diameter (AD) of the fiber under different applied voltage. The AD decreased from 780 nm to 370 nm with an increase in applied voltage from 5 kV to 15 kV. With the voltage increased further to 20 kV, the AD was nearly the same as that of 15 kV, but the AD distribution became wider because high voltage might lead to spinning instability.

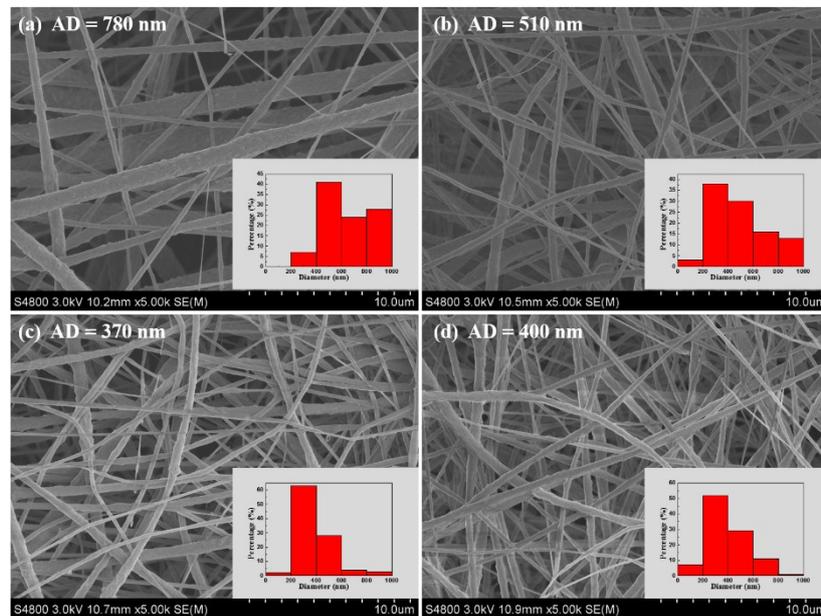


Fig. S1 FMSEM images of PVDF nanofibers obtained from the solution of 15/85 (15 % PVDF + 85 % mixed solvent by w/w) at a needle diameter of 0.7 mm and flow rate of 0.5 ml/h, with an applied voltage of (a) 5 kV; (b) 10 kV; (c) 15 kV; (d) 20 kV.

(2) Needle diameter (applied voltage of 15 kV and flow rate of 0.5 ml/h)

The needle diameter has a little influence on the AD of the electrospun fibers. As shown in Fig. S2, AD is about 370 nm for the needle diameter of 0.7mm, and 390 nm for the needle diameter of 1.2 mm respectively. Obviously, larger needle diameter led to a relatively larger AD and a wider AD distribution of the fiber diameters.

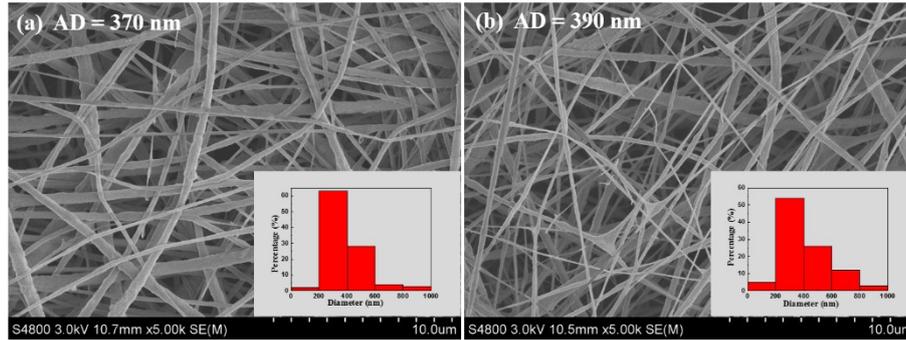


Fig. S2 FMSEM images of PVDF nanofibers obtained from the solution of 15/85 (15 % PVDF + 85 % mixed solvent by w/w) at an applied voltage of 15 kV and a flow rate of 0.5 ml/h, with a needle diameter of (a) 0.7 mm; (b) 1.2 mm.

(3) Flow rate (applied voltage of 15 kV and needle diameter of 0.7 mm)

The flow rate has significant effect on the fiber morphology as shown in Fig. S3. Faster flow rate would result in larger AD and wider AD distribution.

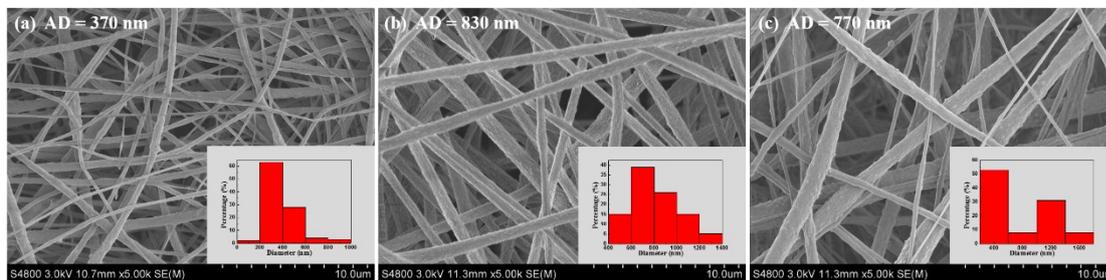


Fig. S3 FMSEM images of PVDF nanofibers obtained from the solution of 15/85 (15 % PVDF + 85 % mixed solvent by w/w) at a needle diameter of 0.7 mm and an applied voltage of 15 kV, with a flow rate of (a) 0.5 ml/h; (b) 1 ml/h; (c) 2 ml/h.

The effect of different parameters on the polymer phase, i.e. PVDF crystalline phase, could also be studied by means of the FTIR spectra (Fig. S4). Characteristic adsorption peaks for the α -phase (976, 795, 766 cm^{-1}) and β -phase (1279, 840 cm^{-1}) could be observed in all curves. But the signal strength of α -phase was much weaker than that of β -phase, indicating

β -phase are dominant in these as-obtained fibers. Adjusting the above parameters (applied voltage, needle diameter and flow rate) could not change remarkably the content of β -phase.

For better MO removal, a PVDF templet with higher specific surface area and more uniform morphology was needed, thus the PVDF electrospun fibers with smaller AD and narrower distribution seemed to be more suitable. In this manuscript, the optimal processing parameters were chosen as: needle diameter of 0.7 mm, applied voltage of 15 kV and flow rate of 0.5 ml/h.

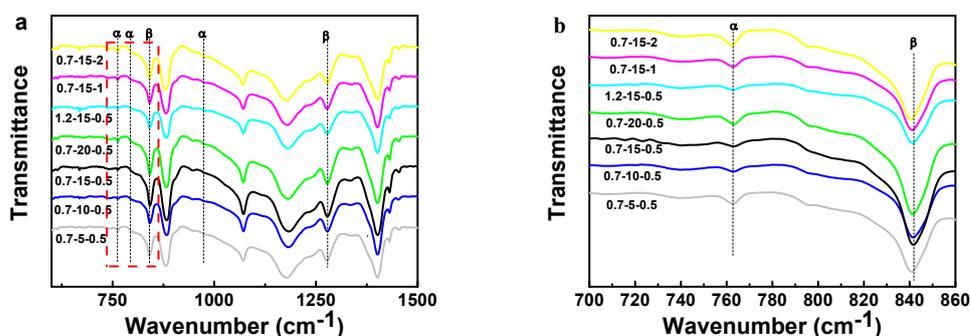


Fig. S4 (a) FTIR spectra of the PVDF electrospun nanofibers obtained at different processing parameters. (b)

Detail of FTIR spectra in the red dotted line frame enclosed area of (a). (Meaning of the symbol under the curve is: the first number is the needle diameter, the second number is the applied voltage and the third number is flow rate)

1. Ribeiro, C.; Sencadas, V.; Ribelles, J. L. G.; Lanceros-Méndez, S., Influence of Processing Conditions on Polymorphism and Nanofiber Morphology of Electroactive Poly(vinylidene fluoride) Electrospun Membranes. *Soft Materials* **2010**, *8* (3), 274-287.

SI2. Influence of polymer phase on the LDH growth process

PVDF usually present five distinct crystalline phases (α , β , γ , δ , ϵ) relating to different chain conformations, each of them possesses different polarity. The PVDF electrospun fibers obtained from the solution of 15/85 (15 % PVDF + 85 % mixed solvent (DMF/ACE = 3/2, v/v) by w/w, named solution A) consisted of a majority of β -phase (electrically active phase) and a small proportion of α -phase (non-polar phase). Adjusting the different processing parameters mentioned above only produced small difference in the content of β -phase. In order to obtain another PVDF electrospun fibers that have distinct polymer phase compositions, the initial polymer solution was varied. After some exploring experiments, the solution of 22/78 (22 % PVDF + 78 % DMF by w/w, named solution B) was selected with the other processing parameters kept constant.

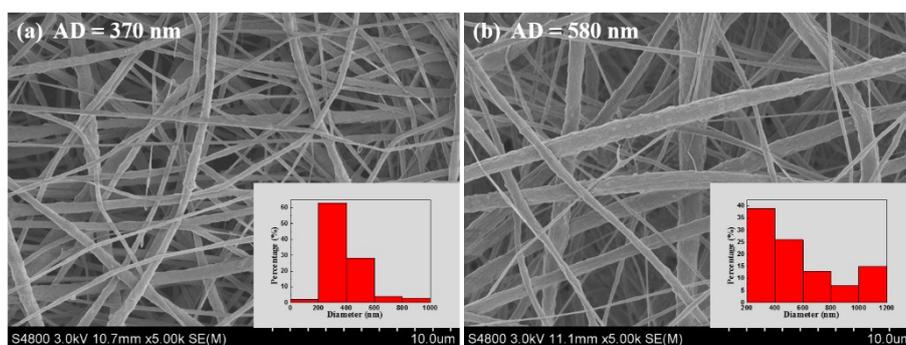


Fig. S5 FMSEM image of PVDF electrospun nanofibers obtained from the solution of (a) 15/85 (15 % PVDF + 85 % mixed solvent by w/w) and (b) 22/78 (22 % PVDF + 78 % DMF by w/w) at a needle diameter of 0.7 mm, a flow rate of 0.5 ml/h and applied voltage of 15 kV.

Properties of PVDF electrospun fibers obtained from solution A have discussed in detail (SI1). As shown in Fig. S5, the fibers obtained from solution B had an AD of 580 nm and a wider AD distribution. Furthermore, the FTIR spectra presented both obvious characteristic

adsorption peaks of α -phase and β -phase (Fig. S6), in which the signal strength of α -phase was much stronger than that of the fibers obtained from solution A.

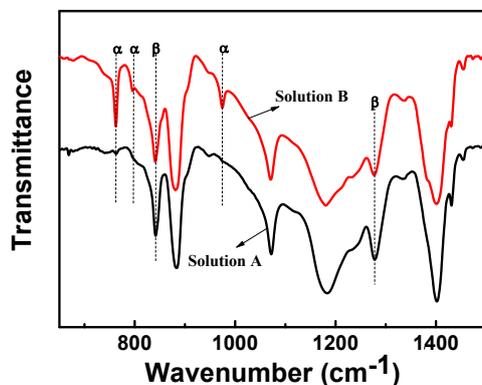


Fig. S6 FTIR spectra of the PVDF electrospun nanofibers obtained from different PVDF solutions.

These two kinds of PVDF electrospun fibers that had distinct polarity due to different β -phase content, were used as template for growing CoAl-LDH (sulfate system). As exhibited in Fig. S7(a, c), the morphology of these PVDF@LDH composite fibers was nearly the same. Numerous curly LDH nanosheets grew tightly on the surface of the PVDF nanofibers and well-defined core/sheath structure was obtained, indicating that the polarity of the fiber template has undiscerned influence on the composite fiber morphology. According to the reference², electrical interaction existed between the negative nanoparticle surfaces and the polymeric CH₂ groups that exhibited positive charge density when PVDF contained electrically active phase. In this manuscript, the LDH intermediates ([Al(OH)₆]³⁻) were negatively charged and the PVDF electrospun fibers mainly contained β -phase, the electrical interaction might exist between the LDH intermediates and the PVDF fibers. This interaction was expected to be influenced by the polarity arising from different polymer crystal phase

compositions. Nonetheless, since the interaction between LDH and PVDF nanofibers surface was really weak, the effect of polymer crystal phase compositions was limited, and therefore the morphology distinction could hardly be observed in the final obtained PVDF@LDH composite fibers.

Fig .S7(b, d) at a low magnification shows that the as-obtained membranes have a hierarchical core/sheath structure varied from nano- to microscales, but many big pores more than 10 μm existed in the latter obtained from the solution B, which might not be expected for the membrane filtration due to low adsorption amount.

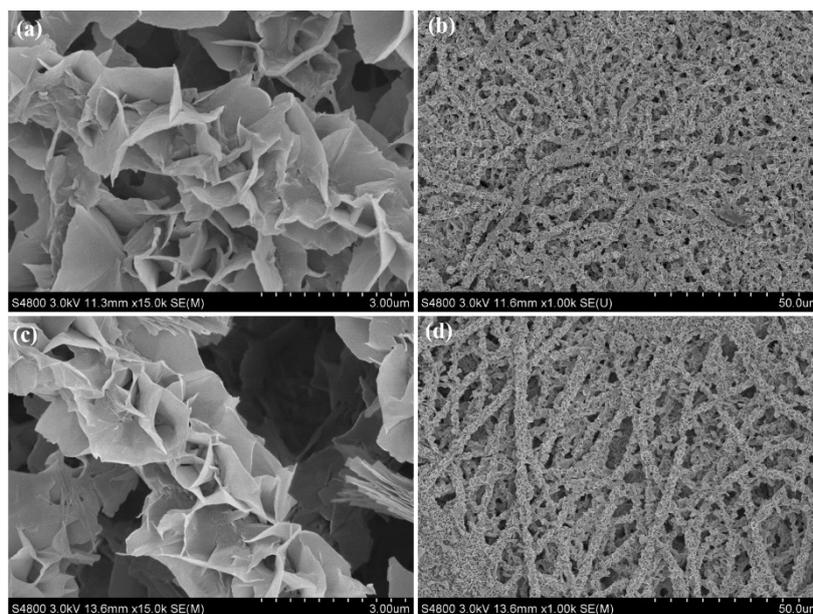


Fig. S7 FESEM images of PVDF@CoAl-LDH composite fibers obtained from different PVDF solutions of (a-b) 15/85 (15 % PVDF + 85 % mixed solvent by w/w) and (c-d) 22/78 (22 % PVDF + 78 % DMF by w/w) at different magnifications, with the total metal concentration = 60 mmol/L, reaction time = 12 h, temperature = 105°C.

Furthermore, the morphologies of the composite fibers by using the distinct PVDF electrospun fibers obtained from solution A and B respectively as templet in different metal

salt anions (SO_4^{2-} and NO_3^-) were observed. As shown in Fig. S8 (a, c) or (b, d), except tiny differences in the size of LDH nanosheets, no essential morphological distinction could be caught for the composite fibers obtained from different metal salt anions (SO_4^{2-} and NO_3^-). The XRD patterns of PVDF nanofibers and PVDF@MgAl-LDH core/sheath fibers synthesized in sulfate and nitrate system were also shown in Fig. S9. The results further confirmed the conclusion described above: the interaction between LDH and PVDF nanofibers surface was really weak, and the effect of polymer crystal phase compositions was limited.

To sum up, the different polymer phase of PVDF electrospun fibers have non-significant influence on the LDH growth process as well as the composite morphology.

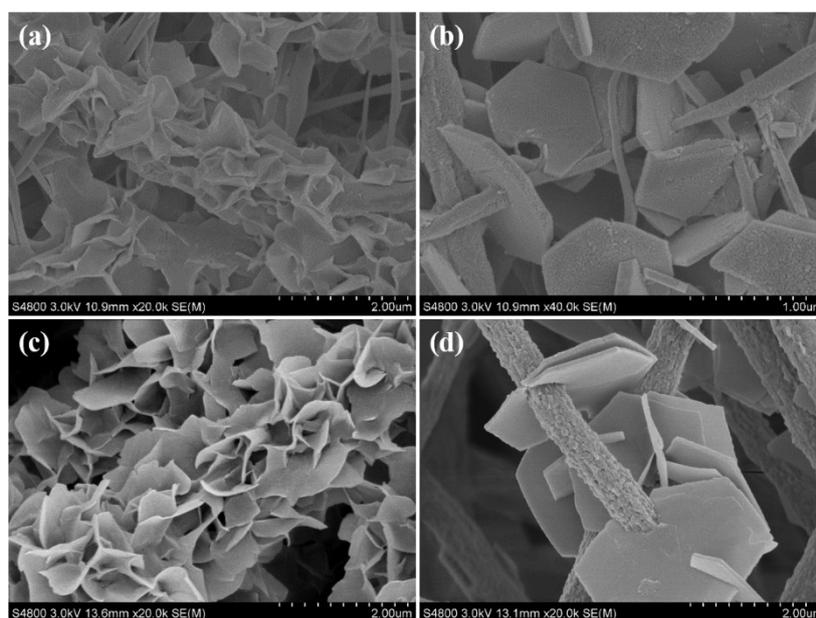


Fig. S8 FESEM images of PVDF@MgAl-LDH composite fibers obtained from different PVDF solutions of (a-b) 15/85 (15 % PVDF + 85 % mixed solvent by w/w) and (c-d) 22/78 (22 % PVDF + 78 % DMF by w/w) and different metal salts: (a, c) sulfates; (b, d) nitrates, with the total metal concentration = 60 mmol/L, reaction time = 24 h, temperature = 105°C.

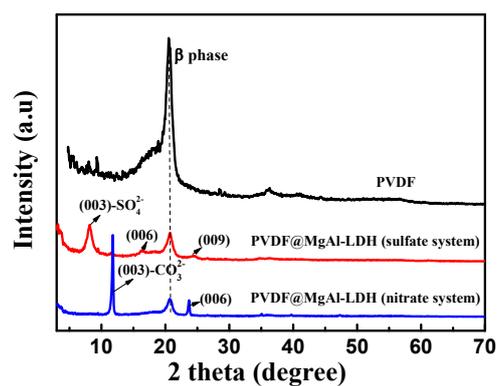


Fig. S9 (a) XRD patterns of PVDF nanofibers and PVDF@MgAl-LDH core/sheath fibers synthesized in sulfate and nitrate system.

2. Martins, P.; Caparros, C.; Gonçalves, R.; Martins, P. M.; Benelmekki, M.; Botelho, G.; Lanceros-Mendez, S., Role of Nanoparticle Surface Charge on the Nucleation of the Electroactive β -Poly(vinylidene fluoride) Nanocomposites for Sensor and Actuator Applications. *The Journal of Physical Chemistry C* **2012**, *116* (29), 15790-15794.