

Research article

Hydrophilic polyacrylonitrile nanofibrous membranes via Ritter reaction: Preparation, characterization and antibacterial properties (N-halamine)

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Abstract. Electrospun (e-spun) nanofiber materials have emerged as a prominent research focus owing to their extensive and promising potential applications across biomedical, energy, and environmental domains. Polyacrylonitrile (PAN) is a commonly used polymer for electrospinning (e-spinning). Due to insufficient hydrophilic properties of nitrile groups of PAN, its e-spun nonwoven membranes had low water absorption and moisture absorption, which limited application in medical and health fields. In this study, it was investigated that the hydrophilic modification of e-spun PAN nanofiber membrane (NFM) was conducted via Ritter reaction to convert nitrile groups into hydrophilic amide ones, thereby improving the hydrophilicity of PAN NFMs. The surface morphologies and structure of the modified e-spun fibers were characterized and verified by SEM, FTIR and XPS. After 60–90 min of Ritter reaction, the fiber diameter of the PAN NFM became thicker, transforming from a hydrophobic membrane to a hydrophilic one, and the water contact angle decreased from 124.2 to 40.7°. The amidated PAN obtained membrane was post-treatment with sodium hypochlorite to make some amide groups change to N-halamine, which took the PAN NFM antibacterial activity or bacteriostasis. This work suggested a strategy that the e-spun PAN NFMs modified would have a promising application in medical dressings, air filtration, *etc.*

Keywords: polyacrylonitrile, electrospinning, hydrophilicity, Ritter reaction, antibacterial

1. Introduction

Nanofiber membranes (NFM) have good properties, such as high specific surface area, high porosity, and fiber uniformity. As a new type of material, it is widely used in fields such as healthcare, environmental protection, energy, and smart textiles. Electrospinning (e-spinning) has been a fast and facile technique for preparing nanofiber membranes [1]. Polyacrylonitrile (PAN) is a commonly used raw material in electrospinning, and PAN NFM has been one of the most studied nanofibers due to their excellent properties,

such as good mechanical strength, chemical resistance, and good thermal stability. Due to the lack of sufficiently hydrophilic functional groups in PAN macromolecular chains and its tight structure, the material has poor hydrophilicity, which limits its applications in energy, healthcare, biomedical engineering, and environmental water treatment [2].

The hydrophilic modification of PAN NFM mainly focused on adding hydrophilic components to the e-spinning solution, mixing spinning with hydrophilic materials and finishing for hydrophilic modification.

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By incorporating hydrophilic polymers, such as polyvinyl alcohol (PVA) [3], polyvinyl pyrrolidone (PVP) [4, 5], cellulose acetate (CA) [6], hydroxypropyl methylcellulose (HPMC) [7], cellulose nanocrystals (CNC) [8], polyaniline [9] into the e-spinning solution, the hydrophilicity and wettability of the electrospun (e-spun) membranes were improved, thereby enhancing its application performance in energy and oil-water separation. The addition of sesbania gum and the loading of nanosilver onto hydrophilic e-spun fibers exhibited excellent antibacterial activity [10]. The nanofiber membrane prepared from highly dispersed and uniform silver nanoparticles (AgNP) e-spinning solution of agar/PAN improved the detection limit for determining the concentration of malachite green [11]. On the other hand, the addition of hydrophilic inorganic substances not only endowed PAN e-spun membranes with functionality, but also enhanced their hydrophilicity, such as fumed silica (SiO₂) [12], graphene or graphene oxide (GO) [13–15], AgBr/Ag [16], TiO₂ [17], etc.

The composite nanofiber membrane fabricated via mixed e-spinning with PAN can enhance the performance by incorporating hydrophilic fibers. The layered composite NFM with inner layer of hydrophobic PAN/PVDF and outer layer of highly hydrophilic cellulose acetate had good water transport and low friction properties [18], improving the comfort of the fabric. An alternately stack, durable and renewable cellulose/PAN composite nanofibers by e-spinning for water in oil separation processes, was prepared with a maximum separation efficiency of up to 97.31% [19]. Another e-spun thin PVA nanofiber layer with a thickness of several microns on the e-spun PAN nanofiber substrate was fabricated for oil-water emulsion separation, which the PAN/PVA composite membrane showed that the retention rate was 99.5% [20].

Surface finishing of membranes or fabrics is another common route to modify the hydrophilic properties. An e-spun polyvinylidene fluoride (PVDF)/polyacrylonitrile (PVDF/PAN) membrane was modified with different doses of electron beams [21]. The 13.56 MHz radio frequency inductively coupled plasma (RF-ICP) improved the surface of PAN fabric through oxygen treatment in plasma, making the surface of PAN fabric hydrophilic [22]. Hydrophilic e-spun PAN NFM modified by silica nanoparticles

was prepared by e-spinning/electrospraying technique, in which the membrane was used as an effective adsorbent for removing malachite green and methylene blue cationic dyes from aqueous solutions [23]. The parallel electrode method was used to prepare neatly arranged single-walled carbon nanotube/polyacrylonitrile (SWNTs/PAN) nanofiber membranes with good permeability, thermal properties, and wetting properties [24]. By the electrospinning/electrospray method, a special PAN/GO/SiO₂ microfiltration membrane sandwich structure was developed, which was used for efficient oil-water separation with a lower water contact angle [25]. An e-spun PAN NFM with TiO₂ spheres electrospay was sprayed, and then, *in situ*, polydopamine (PDA) growing was endowed with super hydrophilicity [17].

The nitrile groups in the chemical structure of PAN are also the active sites for its modification, such as partial hydrolysis [26], amination, reduction, and amidation [27, 28]. These reactions generate functional groups, such as amine, hydroxyl, carboxyl, imine, etc., on the surface of original PAN chains, making its surface active and hydrophilic. Surface-modified PAN NFM has been applied as a carrier for organic compounds, enzymes, and antibodies in biological research. They are also used to immobilize various organic ligands for adsorbing metal ions in water, serving as carriers for transition metal catalysts [26]. The Ritter reaction is a common reaction in organic synthesis that converts nitrile groups into hydrophilic amides with mild reaction conditions and high efficiency [29]. However, there is little research on Ritter reaction on the modification of PAN or its NFMs.

In this study, the primary investigation centered on the successful achievement of hydrophilic amidation modification of e-spun PAN nanofiber membranes. This was accomplished by utilizing the Ritter reaction of nitrile groups as the fundamental chemical procedure. Under relatively mild conditions, the nitrile groups of PAN would be converted to more hydrophilic amide ones, thereby improving the hydrophilicity of the e-spun PAN NFM. Then, the hydrophilic amidation-modified PAN NFM was post-treated by a sodium hypochlorite solution, which made some of the N–H bonds of amides convert into N–Cl ones. Antibacterial experiments showed that they had a good antibacterial effect.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN, M_w : 150 000) was obtained from Shanghai MackLin reagent Co. Ltd, China. *N,N*-dimethylformamide (DMF), *t*-butyl alcohol, acetic acid, sulfuric acid, isopropanol, ethanol and sodium hypochlorite were bought from China National Pharmaceutical Group (China), which were analytical reagents and used without further purification.

2.2. Preparation of e-spun PAN nanofiber membrane

0.8 g of PAN powder and 7.2 g of DMF were added into a 50 ml flask equipped with a magnetic stirrer. After stirring for 4 hours, the e-spinning precursor solution was successfully given. 5 ml of the e-spinning solution was taken out and added into a 10 ml syringe with an inner diameter of 0.62 mm needle.

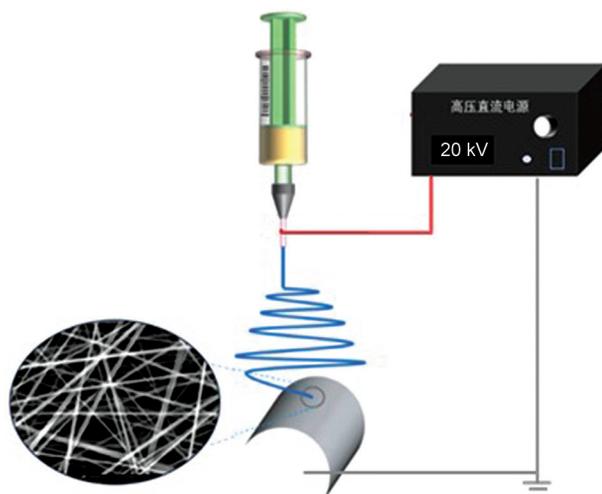


Figure 1. Illustration of e-spinning system.

As shown in Figure 1, the e-spinning parameters were as follows: the 20 cm distance of the tip-to-collector, the 0.5 ml/h speed of the propulsion pump, the 20 kV of DC voltage, and the 200 rpm rotating speed of the collector drum (diameter: 9 cm) grounded.

2.3. Hydrophilic modification of e-spun PAN NFM

The mechanism of *t*-butanol participating in the Ritter reaction is to generate a stable tertiary carbocation in a strongly acidic solution. This carbocation is subjected to nucleophilic attack by the nitrogen atom of nitrile, giving a nitrile onium ion, which then reacts with water and undergoes proton transfer to obtain hydrophilic *N*-substituted amides (Figure 2). 20 ml of *t*-butanol and 20 ml of acetic acid were added into a 100 ml beaker equipped with a magnetic stirrer. Slowly 2 ml of sulfuric acid was dropped into the beaker when stirring. The e-spun PAN NFM was cut strip (5×6 cm), and 4 strips were immersed into the aforementioned solution for Ritter reaction. Taking out a sample every half an hour, they were washed in turn four times with 20 ml of deionized water, and twice with 10 ml of ethanol. Then they were dried in an oven at 40 °C for 12 h, and stored in sealed bags, respectively.

2.4. N-halamine treatment of amidated PAN NFM

The sodium hypochlorite solution was used to carry out N-halamine treatment [30], and the N–H bond of the amidated e-spun PAN NFM was converted to

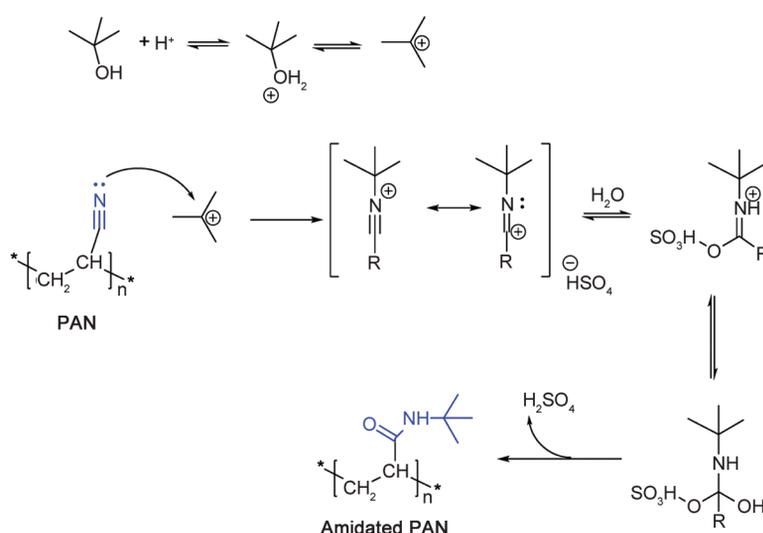


Figure 2. Ritter reaction mechanism.



Figure 3. N-halamine reaction mechanism.

N–Cl bond. 20 ml of sodium hypochlorite solution was added into a 100 ml beaker, and the amidated e-spun PAN NFM was cut into two pieces of 2×2 cm and placed in the beaker for 30 min. The obtained NFMs were washed three times with 10 ml of deionized water and then twice with 10 ml of ethanol. They were dried at room temperature for 12 h to obtain N-halamine PAN NFMs (Figure 3).

2.5. Characterization

The e-spun PAN NFM samples before and after Ritter reaction modification were observed using a scanning electron microscope (SEM, Phenomworld, The Netherlands) and the pore size was tested on a pore size analyzer (PSM-165, TOPAS, Germany). The structural changes of PAN NFMs were characterized by Fourier-transform infrared spectroscopy (FTIR, Nicolet iS5, Thermo Fisher Scientific, Waltham, MA, USA). The samples were placed under an infrared probe (ATR mode) for testing, with a cyclic scan of 32 and a wavelength range of 500–4000 cm^{-1} . Thermogravimetric analysis (TGA) of PAN NFMs before and after Ritter reaction modification was performed on a thermal analyzer (TGA/DSC 3+, Mettler Toledo, Columbus, OH, USA) with a nitrogen gas flow (20 ml/min) and a heating rate of 10 °C/min. The hydrophilicity or water wettability was indicated by a water contact angle measured on an instrument (JY-PHb, Chengde Jinhe Instrument Co., Ltd, China).

20 ml of nutrient broth was prepared (19.0 g/l), which was placed in two test tubes and sterilized in a portable pressure steam sterilizer (DSX-280B, Shanghai Shen'an Medical Equipment Factory) at a temperature of 121 °C for 15 min. A small quantity of bacteria was extracted and dissolved in sterilized nutrient broth, followed by incubation in a dual-function steam bath shaker for 24 h. The antibacterial tests were conducted using the agar diffusion plate method (GB/T-20944.1-2007). Firstly, the N-halamine-treated PAN NFM and blank control group were placed evenly on an agar diffusion plate sprayed with bacterial suspension (200 μl). Then, incubated

at 37 °C for 24 h, the inhibition zone was observed and calculated as a comparison.

3. Results and discussion

3.1. Morphologies of PAN NFMs

The morphologies of the PAN nanofiber membrane before and after the Ritter reaction were observed (Figure 2). The e-spun PAN fibers had smooth surfaces and were distributed uniformly in diameter (Figure 4a). After the Ritter reaction for 30 min, the fibers' average diameter gradually became thicker, ~286 nm and the morphologies more chaotic (Figure 4b). As the reaction progressed, every single fiber was uneven, and adhesion appeared obviously among the fibers, resulting in a greater increase in average diameter, ~306 nm (Figure 4c). After the reaction was carried out for 90 min, the e-spun fibers' surface showed cracks and became brittle. When the PAN NFM was dried for SEM characterization, shown in Figure 4d, the cracks were more likely to be caused by the dried hydrogel layer on the surface because of the hydrophilic amide produced and washed in water after the Ritter reaction finished. Correspondingly, the average diameter was up to ~397 nm. In fact, a pure PAN molecule chain has acid resistance and chemical resistance to a certain degree. Despite strong acid, the degree of acid hydrolysis within a few hours was still very low [31]. It was further observed that the Ritter reaction induced significant changes in the surface morphologies.

3.2. Structure analysis (XPS and FTIR)

XPS is an important method for characterizing surface chemical structures, especially for characterizing the composition structure within the thickness range of ~10 nm on the surface [32]. The changes in the chemical structure of the amidated PAN NFM were analyzed via XPS, and the high-resolution C1s and N1s spectra are shown in Figure 5. Compared with pure PAN, the peaks' shapes of the C1s and N1s of the amidated PAN NFM were different from that of pristine PAN NFM [33]. The C1s peak for the amidated PAN sample given by Ritter reaction for 60 min was broadened, and the C=O of newly generated amide via Ritter reaction was assigned. At the same time, the N1s spectrum of C≡N with one peak located at 399.18 eV, after amidation via Ritter reaction, C≡N was converted to O=C–N whose peak appeared at 400.08 eV, which coincided with the

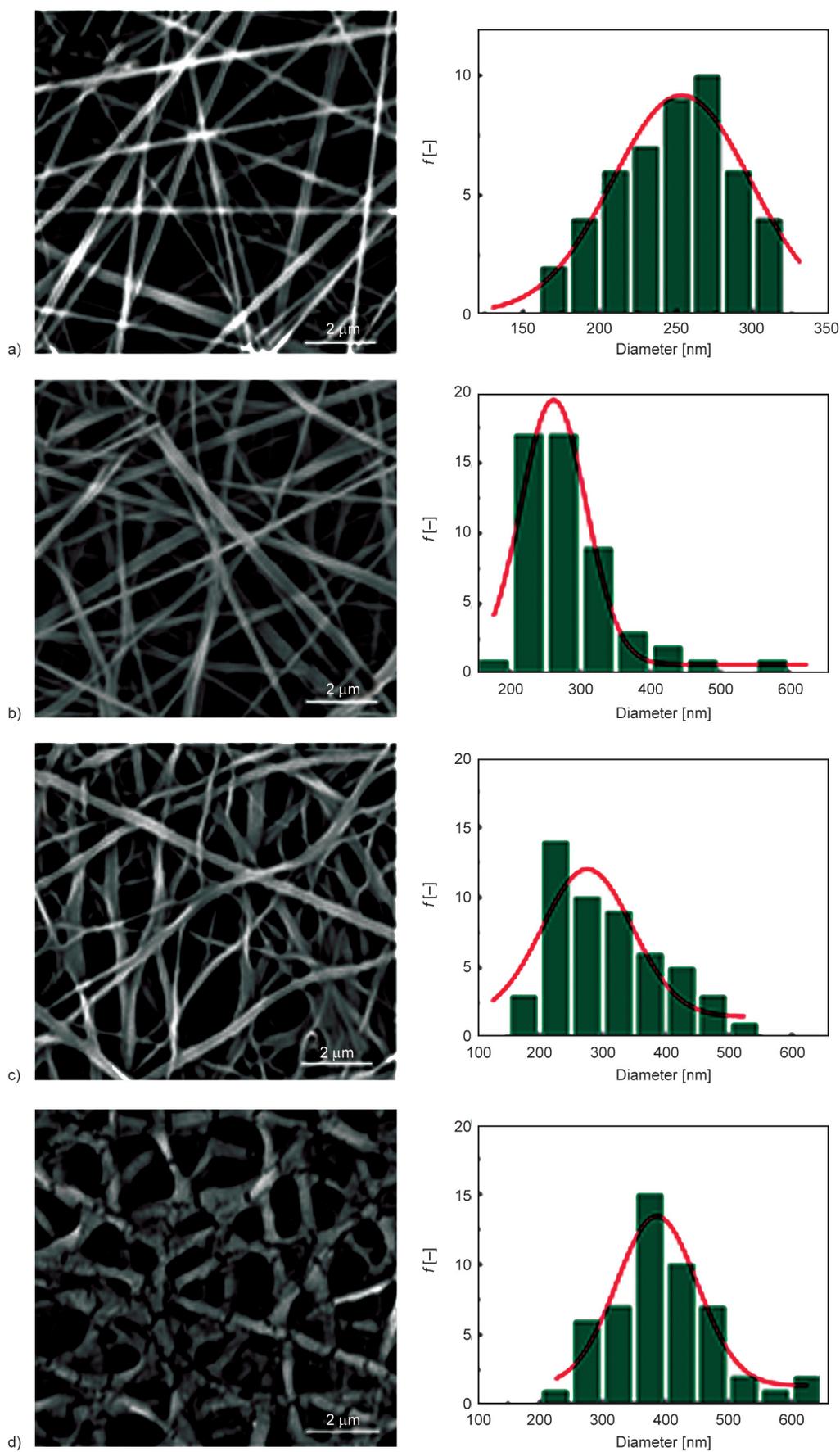


Figure 4. SEM images of PAN NFMs and their fiber average diameter distributions, a) pristine NFM, b)–d) ones after Ritter reaction conducted for 30, 60 and 90 min, respectively.

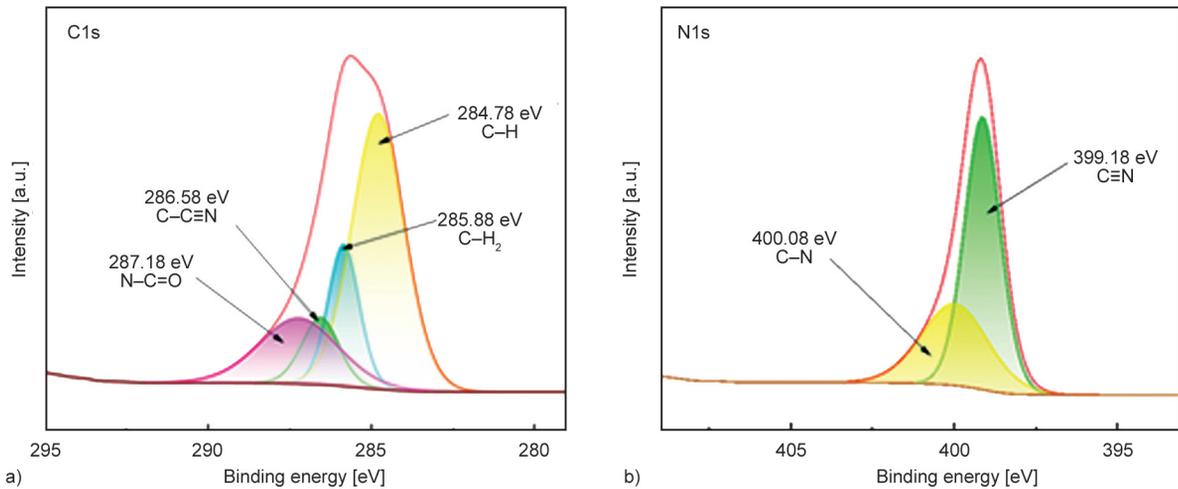


Figure 5. C1s (a) and N1s (b) XPS spectra of PAN NFM membranes after Ritter reaction carried out for 60 min.

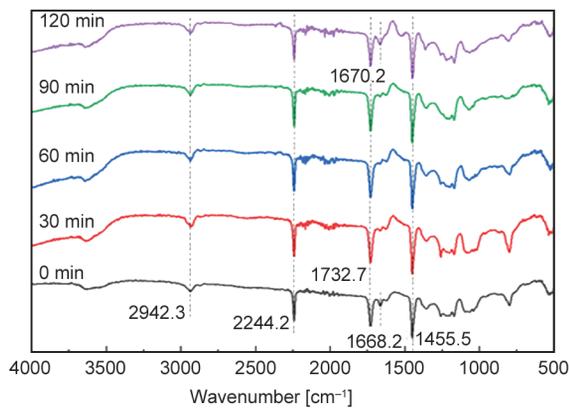


Figure 6. FTIR spectra of PAN NFMs before and after the Ritter reaction carried out for 0–120 min.

other kind of amidated PAN [28]. These results indicated that the amidated PAN NFM had considerable amounts of functional amide groups on the surface. As shown in Figure 6, FTIR spectra of e-spun PAN membrane showed that the peaks at 2942 cm^{-1} (related

to stretching vibration of CH_2), 2244 cm^{-1} (related to stretching vibration of CN), 1668 cm^{-1} (related to bending vibration of CN) and 1455 cm^{-1} (related to bending vibration of CH_2). After the Ritter reaction finished, some CN groups near the surface were converted to amide ($\text{O}=\text{C}-\text{N}$). The newly-produced amide groups and introduced $-\text{CH}_3$, whose characteristic absorption band should appear at 1650 and 1380 cm^{-1} , respectively, however, were not observed obviously in their IR spectra because IR presented the whole material and the content of amides only existing on the surface was much lower than others.

3.3. Thermal analysis (DSC/TG)

The DSC/TG curves of PAN NFM and amidated ones are shown in Figure 7. It could be observed that the TG curves of several samples were similar, and the main weight loss was between 300 and 450 $^{\circ}\text{C}$, which was due to the cyclization of PAN under

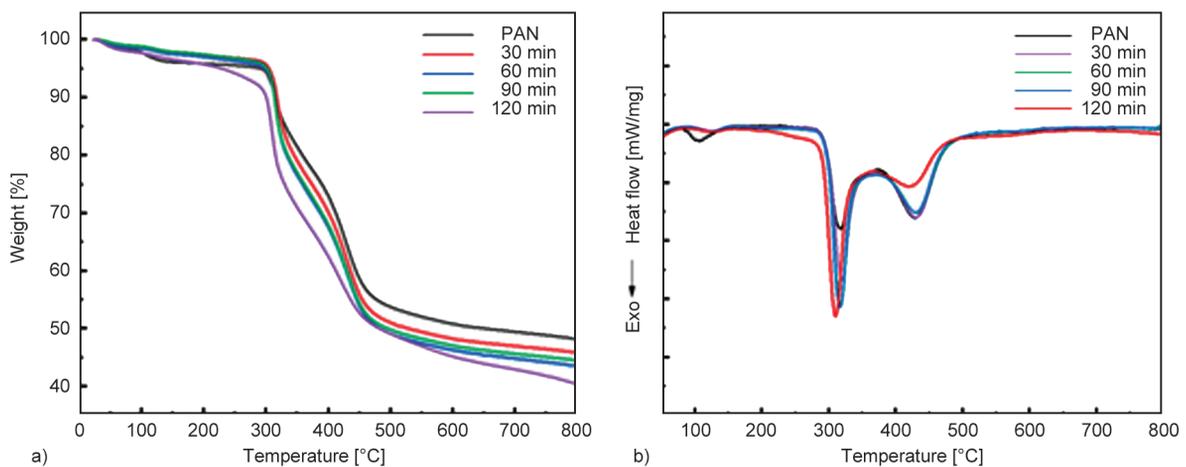


Figure 7. DSC/TG curves of PAN NFM and amidated ones, a) TG obtained synchronously with b) the DSC curves at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in N_2 .

nitrogen [34]. After amidated modification, especially the Ritter reaction, which only occurred on the surface of PAN fibers, the weight loss was not obvious except for that given after reaction for 120 min, which coincided with the result of FTIR. Moreover, the exothermic peak located at about 310°C grows significantly with the increase of amide group content due to longer Ritter reaction time. Thus, this peak may be assigned to the cyclization reaction which was initiated by the amides.

3.4. Water contact angle

The water contact angle (WCA) of the e-spun PAN NFMs was tested to show the changes in hydrophilic properties after modification. As shown in Figure 8, the WCA of the pure PAN e-spun NFM was 124.2°, which indicated that its surface was hydrophobic. After the Ritter reaction was carried out for 30, 60, 90 and 120 min, the WCA was 44.7, 42.8 and 40.7°, respectively, which demonstrated that the

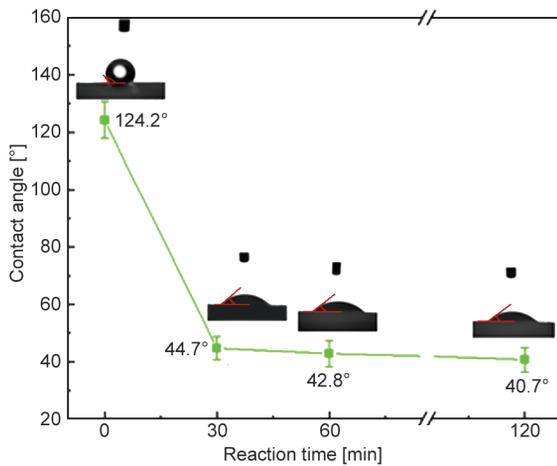
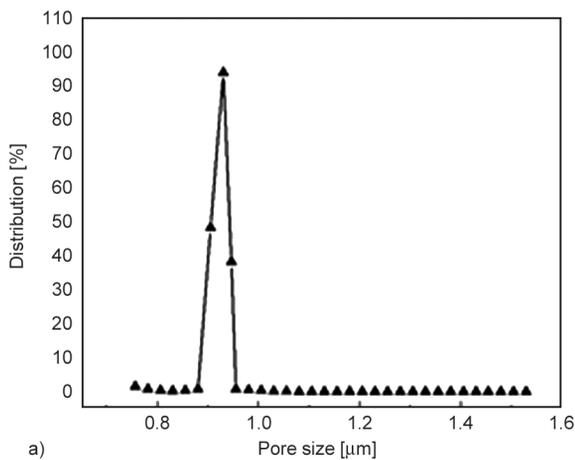


Figure 8. The water contact angle of PAN NFMs before and after modification via Ritter reaction



amidated PAN NFMs were obviously changed from hydrophobic to hydrophilic after Ritter reaction, and the hydrophilicity gradually increased with the increase of reaction time. Considering the changes in morphology and structure, a Ritter reaction time of 60–90 min was suitable.

3.5. Pore size analysis

E-spun fibers nonwoven membrane, as a type of non-woven breathable and moisture permeable ones, requires consideration of the pore size and pore distribution of the nonwovens in many applications, which were related mainly to the fibers' morphologies, diameter and diameter distribution. As shown in Figure 9, the mean pore size of pristine PAN NFM was 0.92 μm, and the pore distribution was relatively uniform. After being modified by the Ritter reaction, the pore size and distribution gradually decrease with the increase of the Ritter reaction time. However, the porosity was lower due to the thicker fibers with more chaotic surfaces.

3.6. Antibacterial activity after N-halamine treatment

Functionalized e-spun NFM with antibacterial activity has attracted more and more attention in various applications, such as tissue engineering, drug delivery, filtration, protective clothing, wound dressings, and sensor devices. The amide groups of polymer could be treated with NaClO solution and exhibited a good antibacterial effect [29]. After the Ritter reaction, the amidated PAN NFM was evaluated on antibacterial activity.

According to the national standard GB/T-20944.1-2007, after removing the sample from the agar plate,

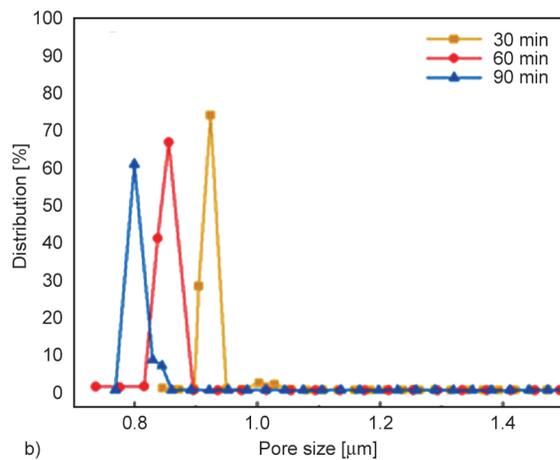


Figure 9. Pore distribution of PAN NFMs, a) before and b) after modification via Ritter reaction.

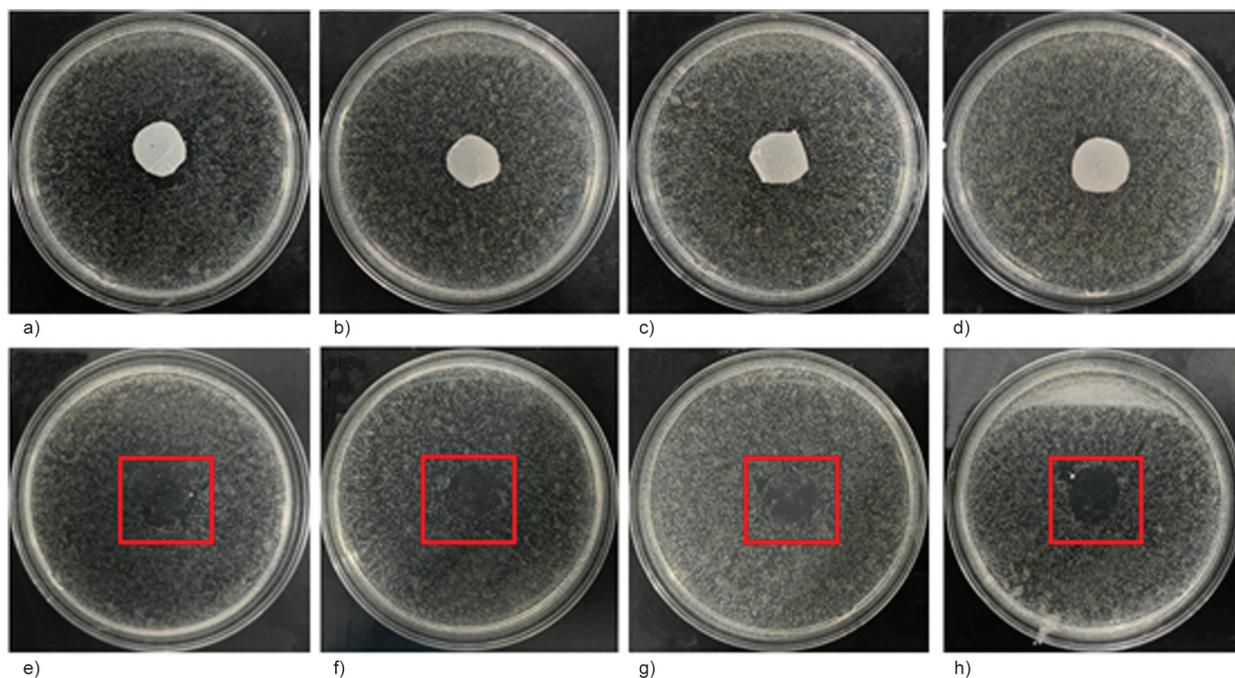


Figure 10. Antibacterial or bacteriostasis test for PAN NFMs (The diameter of the Petri dish is 90 mm), a) blank, control sample (*S. aureus*), b) after N-halamine (*S. aureus*); c) blank, control sample (*E. coli*), d) after N-halamine (*E. coli*); e)–h) corresponding to a)–d) where the PAN NFMs peeled off.

bacterial growth was observed, as shown in Figure 10. It can be seen that there were only a small number of colonies under the PAN nanofiber membrane after NaClO solution treatment for N-halamine, and bacteria growth was almost inhibited, especially *E. coli* (Figure 10h). This indicated that the treated PAN NFM has an antibacterial effect, which would be a potential application in biomedical engineering, such as medical dressings, etc.

4. Conclusions

In this study, the principle of the Ritter reaction was adopted to convert nitrile groups of PAN to hydrophilic amide ones, which was a hydrophilic modification on e-spun PAN NFMs. After 60–90 min reaction treatment, the morphologies and structure of the PAN NFM underwent significant changes. XPS showed the presence of amide groups on the fibers' surface, particularly with a water contact angle decreasing from 124.2 to 40.7°, achieving good hydrophilicity. The amidated PAN NFM was post treated further by NaClO solution to obtain N-halamine that had good antibacterial properties. This article provided a modification route to make e-spun PAN NFMs more suitable for applications, such as medical and filtration materials.

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References

- [1] Shi S., Si Y., Han Y., Wu T., Iqbal M. I., Fei B., R. K. Y. Li., Hu J., Qu J.: Recent progress in protective membranes fabricated *via* electrospinning: Advanced materials, biomimetic structures, and functional applications. *Advanced Materials*, **34**, 2107938 (2022). <https://doi.org/10.1002/adma.202107938>
- [2] Danagody B., Bose N., Rajappan K.: Electrospun polyacrylonitrile-based nanofibrous membrane for various biomedical applications. *Journal of Polymer Research*, **31**, 119 (2024). <https://doi.org/10.1007/s10965-024-03965-x>
- [3] Khodaverdi F., Vaziri A., Javanbakht M., Jahanfar M.: Improvement of PAN separator properties using PVA/malonic acid by electrospinning in lithium ion-batteries. *Journal of Applied Polymer Science*, **138**, 50088 (2021). <https://doi.org/10.1002/app.50088>
- [4] Chen H-M., Yang M., Wei B., Ren Z., Yu D-G.: Property improvement of electrospun drug-loaded nanofibers using composite PAN/PVP as filament-forming matrix (in '2010 4th International Conference on Bioinformatics and Biomedical Engineering', Chengdu, China), 1–4 (2010). <https://doi.org/10.1109/ICBBE.2010.5515462>

- [5] Meng H., Liang H., Xu T., Bai J., Li C.: Crosslinked electrospinning membranes with contamination resistant properties for highly efficient oil–water separation. *Journal of Polymer Research*, **28**, 347 (2021).
<https://doi.org/10.1007/s10965-021-02700-0>
- [6] Al-Rajabi M. M., Almanassra I. W., Khalil A. K., Atieh M. A., Laoui T., Khalil K. A.: Facile coaxial electrospinning synthesis of polyacrylonitrile/cellulose acetate nanofiber membrane for oil–water separations. *Polymers*, **15**, 4594 (2023).
<https://doi.org/10.3390/polym15234594>
- [7] Bigogno R. G., Dias M. L., Manhães M. B. N., Rodriguez R. J. S.: Integrated treatment of mining dam wastewater with quaternized chitosan and PAN/HPMC/AgNO₃ nanostructured hydrophilic membranes. *Journal of Polymers and the Environment*, **30**, 1228–1243 (2022).
<https://doi.org/10.1007/s10924-021-02273-5>
- [8] Paşaoğlu M. E., Koyuncu İ.: Fabrication, characterization and application of flat sheet PAN/CNC nanocomposite nanofiber pressure-retarded osmosis (PRO) membrane. *Desalination and Water Treatment*, **211**, 369–381 (2021).
<https://doi.org/10.5004/dwt.2021.26315>
- [9] Shakiba M., Nabavi S. R., Emadi H., Faraji M.: Development of a superhydrophilic nanofiber membrane for oil/water emulsion separation *via* modification of polyacrylonitrile/polyaniline composite. *Polymers for Advanced Technologies*, **32**, 1301–1316 (2021).
<https://doi.org/10.1002/pat.5178>
- [10] Lan S., Lu Y., Li C., Zhao S., Liu N., Sheng X.: Sesbania gum-supported hydrophilic electrospun fibers containing nanosilver with superior antibacterial activity. *Nanomaterials*, **9**, 592 (2019).
<https://doi.org/10.3390/nano9040592>
- [11] Yang T., Yang H., Zhen S. J., Huang C. Z.: Hydrogen-bond-mediated *in situ* fabrication of AgNPs/Agar/PAN electrospun nanofibers as reproducible SERS substrates. *ACS Applied Materials and Interfaces*, **7**, 1586–1594 (2015).
<https://doi.org/10.1021/am507010q>
- [12] Jung H-R., Ju D-H., Lee W-J., Zhang X., Kotek R.: Electrospun hydrophilic fumed silica/polyacrylonitrile nanofiber-based composite electrolyte membranes. *Electrochimica Acta*, **54**, 3630–3637 (2009).
<https://doi.org/10.1016/j.electacta.2009.01.039>
- [13] Khan T., Aslam M., Basit M., Raza Z. A.: Graphene-embedded electrospun polyacrylonitrile nanofibers with enhanced thermo-mechanical properties. *Journal of Nanoparticle Research*, **25**, 78 (2023).
<https://doi.org/10.1007/s11051-023-05728-z>
- [14] Lee J., Yoon J., Kim J-H., Lee T., Byun H.: Electrospun PAN–GO composite nanofibers as water purification membranes. *Journal of Applied Polymer Science*, **135**, 45858 (2018).
<https://doi.org/10.1002/app.45858>
- [15] Hou J., Yun J., Kim S., Byun H.: Highly controlled integration of graphene oxide into PAN nanofiber membranes. *Applied Sciences*, **9**, 962 (2019).
<https://doi.org/10.3390/app9050962>
- [16] Qayum A., Wei J., Li Q., Chen D., Jiao X., Xia Y.: Efficient decontamination of multi-component wastewater by hydrophilic electrospun PAN/AgBr/Ag fibrous membrane. *Chemical Engineering Journal*, **361**, 1255–1263 (2019).
<https://doi.org/10.1016/j.cej.2018.12.161>
- [17] Sun F., Li T-T., Ren H-T., Shiu B-C., Peng H-K., Lin J-H., Lou C-W.: Multi-scaled, hierarchical nanofibrous membrane for oil/water separation and photocatalysis: Preparation, characterization and properties evaluation. *Progress in Organic Coatings*, **152**, 106125 (2021).
<https://doi.org/10.1016/j.porgcoat.2020.106125>
- [18] Dong Y., Kong J., Mu C., Zhao C., Thomas N. L., Lu X.: Materials design towards sport textiles with low-friction and moisture-wicking dual functions. *Materials and Design*, **88**, 82–87 (2015).
<https://doi.org/10.1016/j.matdes.2015.08.107>
- [19] Karki H. P., Kafle L., Ojha D. P., Song J. H., Kim H. J.: Cellulose/polyacrylonitrile electrospun composite fiber for effective separation of the surfactant-free oil-in-water mixture under a versatile condition. *Separation and Purification Technology*, **210**, 913–919 (2019).
<https://doi.org/10.1016/j.seppur.2018.08.053>
- [20] Wang X., Zhang K., Yang Y., Wang L., Zhou Z., Zhu M., Hsiao B. S., Chu B.: Development of hydrophilic barrier layer on nanofibrous substrate as composite membrane *via* a facile route. *Journal of Membrane Science*, **356**, 110–116 (2010).
<https://doi.org/10.1016/j.memsci.2010.03.039>
- [21] Jia S., Huang K., Long J., Yang S., Liang Y., Yang N., Xiao J.: Electron beam irradiation modified electrospun polyvinylidene fluoride/polyacrylonitrile fibrous separators for safe lithium-ion batteries. *Journal of Applied Polymer Science*, **138**, 50359 (2021).
<https://doi.org/10.1002/app.50359>
- [22] Thongphud A., Visal-athaphand P., Supaphol P., Paosawatyanong B.: Improvement of hydrophilic properties on electrospun polyacrylonitrile fabrics surface by plasma treatment. *Advanced Materials Research*, **213**, 103–106 (2011).
<https://doi.org/10.4028/www.scientific.net/AMR.213.103>
- [23] Ebrahimi F., Nabavi S. R., Omrani A.: Fabrication of hydrophilic hierarchical PAN/SiO₂ nanofibers by electro-spray assisted electrospinning for efficient removal of cationic dyes. *Environmental Technology and Innovation*, **25**, 102258 (2022).
<https://doi.org/10.1016/j.eti.2021.102258>
- [24] Song Y., Xu L.: Permeability, thermal and wetting properties of aligned composite nanofiber membranes containing carbon nanotubes. *International Journal of Hydrogen Energy*, **42**, 19961–19966 (2017).
<https://doi.org/10.1016/j.ijhydene.2017.06.112>

- [25] Ebrahimi F., Nabavi S. R., Omrani A.: Fabrication of hydrophilic special sandwich structure of PAN/GO/SiO₂ electrospun membrane decorated with SiO₂ nanoparticles for oil/water separation. *Journal of Water Process Engineering*, **48**, 102926 (2022).
<https://doi.org/10.1016/j.jwpe.2022.102926>
- [26] Wang Z-G., Wan L-S., Xu Z-K.: Surface engineering of polyacrylonitrile-based asymmetric membranes towards biomedical applications: An overview. *Journal of Membrane Science*, **304**, 8–23 (2007).
<https://doi.org/10.1016/j.memsci.2007.05.012>
- [27] Bode-Aluko C. A., Perea O., Fatoba O., Petrik L.: Surface-modified polyacrylonitrile nanofibres as supports. *Polymer Bulletin*, **74**, 2431–2442 (2017).
<https://doi.org/10.1007/s00289-016-1830-0>
- [28] Zhang Q., Cai H., Liu X., Li Y., Wang M., Gao G., Meng Z., Sun H., Hao X.: Coordination-induced amidated modified polyacrylonitrile loaded ultrafine palladium nanoparticles for thermocatalytic hydrogen evolution. *Chemical Engineering Journal*, **493**, 152570 (2024).
<https://doi.org/10.1016/j.cej.2024.152570>
- [29] Ziarani G. M., Hasankiadeh F. S., Mohajer F.: Recent applications of Ritter reactions in organic syntheses. *ChemistrySelect*, **5**, 14349–14379 (2020).
<https://doi.org/10.1002/slct.202003470>
- [30] Wang R., Li Y., Si Y., Wang F., Liu Y., Ma Y., Yu J., Yin X., Ding B.: Rechargeable polyamide-based N-halamine nanofibrous membranes for renewable, high-efficiency, and antibacterial respirators. *Nanoscale Advances*, **1**, 1948–1956 (2019).
<https://doi.org/10.1039/C9NA00103D>
- [31] Krentsel L. B., Kudryavtsev Y. V., Rebrov A. I., Litmanovich A. D., Platé N. A.: Acidic hydrolysis of polyacrylonitrile: Effect of neighboring groups. *Macromolecules*, **34**, 5607–5610 (2001).
<https://doi.org/10.1021/ma010213o>
- [32] Krishna D. N. G., Philip J.: Review on surface-characterization applications of X-ray photoelectron spectroscopy (XPS): Recent developments and challenges. *Applied Surface Science Advances*, **12**, 100332 (2022).
<https://doi.org/10.1016/j.apsadv.2022.100332>
- [33] Zhang Y., Wang H., Li L., Zhang X., Dong X., Wang X., Pan Y., Wang T.: Effects of polyacrylonitrile carboxylation on pore structure and performance of thermally crosslinked organic solvent nanofiltration membrane. *Chemical Engineering Science*, **287**, 119731 (2024).
<https://doi.org/10.1016/j.ces.2024.119731>
- [34] Ouyang Q., Wang X., Wang X., Huang J., Huang X., Chen Y.: Simultaneous DSC/TG analysis on the thermal behavior of PAN polymers prepared by aqueous free-radical polymerization. *Polymer Degradation and Stability*, **130**, 320–327 (2016).
<https://doi.org/10.1016/j.polymdegradstab.2016.06.020>