Improvement of mechanical property for BNNSs/PAN composite films via electro-spinning with high filtration performance

Yingying Zhou¹, Runjun Sun² and Ruining Wang²

Abstract
People increasingly need air filters with ultra-high efficiency due to air pollution. In this work, BNNSs (boron nitride nanosheets) were prepared by chemical method using potassium permanganate and sulphuric acid. This functionalization induced the exfoliation of the layered structure of h-BN into monolayer or few-layer sheets. Infrared spectrum analysis shows that the oxidation functional group was introduced into hexagonal boron nitride. Further investigation of the crystallization property was accomplished by XRD analysis in conclusion that the crystal structure was not changed for the introduction of oxidation functional group. The polyacrylonitrile (PAN) and BNNSs/PAN nanofiber films were constructed by electrospinning. It is found that the electrospun nanofiber films had good filtration effect and could capture the most particles in the air because of electrostatic adsorption. The removal rate of particle by the filters reached 99.8% for BNNSs/PAN nanofiber films. Addition of BNNSs increased the mechanical property of the nanofiber films.

¹Introduction Technology Convergence Office, Xi’an Polytechnic University, Xi’an, China
²College of Textile Science and Engineering, Xi’an Polytechnic University, Xi’an, China

Corresponding author:
Yingying Zhou, Introduction Technology Convergence Office, Xi’an Polytechnic University, No. 19, Jinhua South Road, Beilin District, Xi’an 710048, China.
Email: 778118956@qq.com

Creative Commons Non Commercial CC BY-NC: This article is distributed under the terms of the Creative Commons Attribution-NonCommercial 4.0 License (https://creativecommons.org/licenses/by-nc/4.0/) which permits non-commercial use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (https://us.sagepub.com/en-us/nam/open-access-at-sage).
**Keywords**
electrospinning fabrication, nano fibers materials, polymer formation chemistry, synthesis chemistry, filtration fabrics

**Introduction**

In recent years, air pollution poses a serious risk to human health in Asia.\(^1\)\(^-\)\(^2\) Particle matter (PM) is very dangerous to human health, climate and ecosystems. Particularly, PM\(_{2.5}\) (particles with diameters less than 2.5 μm)\(^3\) has been classified as a first-level carcinogen by the World Health Organization (WHO) for it carry numerous bacterial or virus and then become an aerosol in the air which is very harmful to human lungs.\(^4\)\(^-\)\(^6\) It results in serious respiratory, cardiovascular diseases, cancers.\(^7\)\(^-\)\(^9\) Therefore, particle pollution control is widely concerned by the public and government.\(^10\)

Electrets filter is an important part of fabric filters used in particle control.\(^11\) Electrostatic electrets are dielectric materials that store space and dipole charges for a long time. At present, most electret materials are electrostatic electrets after fiber forming, but this method has the disadvantages of low charge and unstable charge. The surface charge of the electrets is space charge, such as surface charge or volume charge, or polarized charge arranged by dipole.\(^12\)\(^-\)\(^14\) At present, polypropylene (PP), nylon-11 (PA11), FEP and other materials are commonly used as electrets. These materials are good piezoelectric electrets (also known as ferroelectric electrets).\(^12\) If the space layer is too thin, the top and bottom electrets may contact each other under a small mechanical deformation, some researchers have made materials into fluffy or foam structures to achieve better electrostatic adsorption effect.

Electrospinning is an advanced technique to fabricate nanofibers and an effective way in-situ charge injection.\(^13\)\(^-\)\(^16\) The ability of charge retention depends on the dielectric properties and electric field strength of the polymer, especially the position where the charge is trapped in the material.\(^14\)

Gao and coworkers\(^6\) confirmed the volume charges trapped in deep energy levels and dipole charges formation during electrospinning. Compared with corona discharge filtration material, electrospun membrane has longer charge holding time and stronger filtration stability. The electrospun membrane composed of dielectric polymer showed enhanced charge stability and excellent filtration performance.\(^17\) It is a good material for disposable respirator and indoor air purifier. He and coworkers used polytetrafluoroethylene needle felt to prepare filter materials by corona discharge method.\(^18\) It was found that the filtration efficiency of filter materials after corona charging was significantly higher than that of uncharged filter materials, and the surface potential decreased with the deposition of particles on the filter membrane, resulting in the reduction of filtration efficiency of filter materials.\(^11,19,20\)

Nowadays, a variety of polymers are used to prepare nanofiber air filtration membrane by electrospinning technology, for example, polyacrylonitrile (PAN), polyamine ester (PU), polylactic acid (PA), polyvinyl alcohol (PVA), polyvinylidene fluoride (PVDF), etc.\(^21\)\(^-\)\(^22\) PAN is an amorphous vinyl-type polymer that contains a cyano group in each
repeat unit. It has smaller dielectric loss and higher thermal stability that allow it to be widely used as carbon fiber precursors.\textsuperscript{13,15} Boron nitride nanosheets (BNNSs) are 2D materials which can be exfoliated from hexagonal boron nitride (h-BN).\textsuperscript{23–24} The functional nanosheets could increase the storage modulus of the composites which improved the mechanical performance.\textsuperscript{25} The pristine PAN exhibits good flexibility but poor strength. The BNNSs/PAN nanofibrous membranes exhibit an excellent tensile strength. As the BNNSs loading increased, the tensile strength and Young’s modulus of BNNSs/PAN improved.\textsuperscript{26–27}

Herein, in this paper, BNNSs was exfoliated off by strong oxidant potassium permanganate and concentrated sulfuric acid. Nanofibrous membranes were prepared by adding BNNSs into a solution containing PAN. The as-prepared nanofibrous membranes were light in weight and possessed good mechanical and filtration performance. The addition of BNNSs enhanced the mechanical performance of PAN nanofiber film. The filtration efficiency performance of BNNSs/PAN nanofiber film remains an outstanding removal efficiency of 99.8%.

Experiment

Materials

Polyacrylonitrile (PAN) powder (Mw$\sim$150000) was purchased from sigma. N,N-Dimethylformamide (DMF) was purchased from Tian jin Fuyu Fine Chemical Co., Ltd. Boron nitride power was purchased from macklin.

Exfoliated of boron nitride

To preparation mono or few-layer h-BN, 1g of h-BN powder was mixed in 20 ml of concentrated sulfuric acid in a glass beaker stirring with magnetic stirrer at room temperature and cooling the beaker with running water. The potassium permanganate was slowly added to the beaker (1 g potassium permanganate added in 2 h). After the reaction was completed, the hydrazine hydrate was slowly added to neutralize the unreacted oxidant until the mixed solution turned white. BNNSs was obtained cleaned with water and dried in oven after centrifugation.

Preparation of electrospinning membrane PAN/BN composite

The prepared boron nitride nanosheets was put into a breaker with of 0.02g, 0.2g and 0.2g, the 18g DMF was added into the breaker, the mixed solution was heated to 60°C in a water bath for 30min. And then 2g of polyacrylonitrile fiber was added into the mixed solution until the fibers were completely dissolved. In the same way, polyacrylonitrile fiber (2g) was dissolved in 18g DMF solution. The electrospinning voltage is 20 kV, solution feed rate in the electrospinning process is 1 mL/h, the distance between the needle and the receiving plate is 15 cm and the humidity is 40%.
Material characterization

The morphology and microstructure of the samples were examined using a FEI Quanta 450 scanning electron microscope with the electron energy of 20 kV and EDS for element analysis. The molecular structure of samples was tested by Fourier transform infrared spectroscopy (FT-IR) in the wave number range from 4000 cm\(^{-1}\) to 650 cm\(^{-1}\) (PerkinElmer Spotlight 400). The strength was tested by single fiber strength tester. The filtration performance of the sample was tested by promo2000 with differential pressure 5 bar and the test time 300s. This test simulates the use of the masks to remove the particles in the air.

Results and discussion

Figure 1 is a schematic diagram of stripping of BN and electrospinning of BNNSs/PAN. After oxidation of boron nitride by strong oxidant, oxygen-containing functional groups were grafted, and the layers of boron nitride were separated from each other. This method is simple, low-cost, and the obtained few layers of boron nitride can exist stably. Figures

![Figure 1](image_url)

Figure 1. (a) Schematic diagram of boron nitride stripping, (b) Diagram of polyacrylonitrile and boron nitride nanosheets, (c) Diagram of electrospinning, (d) Schematic of BNNSs/PAN nanofiber film, (e) SEM of BNNSs/PAN nanofiber film.
1(d) and (e) is the suspension of BNNSs/PAN spinning solution just finished and 1 day later. The suspension of BNNSs/PAN spinning solution is stable after 1 day later because of hydroxyl (OH) groups of polyacrylonitrile interacts with BNNSs.

**Exfoliated and characterization of boron nitride**

The exfoliation process resulted in a uniform distribution of mono-layer or few-layer h-BN throughout the suspension, and the initial h-BN powder (before exfoliation) showed a large number of clusters with uneven thickness. After exfoliated, the boron nitride was peeled into a single layer or few layers which was observed under SEM.\(^{28}\) Compared with h-BN, the regular morphology of h-BN almost disappeared (Figure 2(a)), and the irregular shape of BNNSs after peeling was replaced. Figures 2(c) and (d) is the EDS analysis of BNNSs, The atomic percentage of elements B and N is about 1:1.

The crystallization behavior of stripped h-BN was studied by X-ray diffraction (Figure 3(a)). The X-ray diffraction data clearly show that most of the crystals are oriented in the (002) direction and the characteristic peaks are observed at 25.9°. The h-BN had characteristic hexagonal diffraction peaks at 25.9°, 40.9°, 43.1°, 49.5°, and 54.2°. These peaks are indexed to the (002), (100), (101), (102), and (004) planes, respectively, with the lattice constants of a = 0.2504 nm and c = 0.6661 nm. It can be seen from the figure that

![Figure 2. SEM of (a) BNNSs (b) h-BN, (c, d) EDS of BNNSs.](image)
the crystal form of boron nitride has not changed before and after stripping, which indicates that the exfoliation process of BNNSs without destroying its crystal structure.

The FT-IR spectra (Figure 3(b)) of the raw h-BN show that B-N stretching: in-plane ring vibration around 1343 cm$^{-1}$ and the B-N bending: out of plane vibration around 762 cm$^{-1}$. In addition, the BNNSs have an additional peak at 1015 cm$^{-1}$ different from the raw BN powder, which is the B-O deformation caused by the hydroxylation of the BNNSs.\textsuperscript{21}

Structure and mechanical properties of the BNNSs/PAN nanofiber film

The surface morphologies of the electrospun nanofiber with various BNNSs concentrations (0 wt.%, 1 wt.%, 5 wt.%, 10 wt.%) are shown in Figure 4 as well as the diameter distribution. It can be seen that the pristine PAN nanofibers have a smooth surface and an average diameter of 381 nm. The average diameter increased to 398 nm and 390 nm respectively when the addition of 1 wt.% and 5 wt.% BNNSs. When the concentration of BNNSs is 10wt.%, the composite BNNSs/PAN nanofiber can obtain a smaller diameter. The addition of BNNSs particle increased viscosity of spinning solution caused the nanofiber diameter increased. However, when a lot of BNNSs nanoparticle addition, the higher viscosity of electrospun precursor solutions provided electrospinning solution higher tensile force when exposed to an applied voltage. As shown in EDS mapping, BNNSs were uniformly distributed in PAN nanofibers.

Mechanical properties are the main indexes of nanofibrous membranes, which are usually studied by measuring their tensile strengths. Figure 5 shows the stress-strain curve of the PAN and different dosage of BNNSs/PAN nanofiber films. The BNNSs additive shows improved mechanical performance owing to interfacial interaction between the BNNSs particles and PAN. As shown in Figure 5, the strength of the nanofiber film is significantly increased with the addition of BNNSs. When the content of BNNSs increased to 5 wt.%, the tensile of the nanofiber film reached to maximum. And then the tensile strength decreased when the content of BNNSs increased to 10 wt.% owning to the
Figure 4. SEM of (a) PAN (b) BNNSs/PAN (1 wt.%) (c) BNNSs/PAN (5 wt.%) (d) BNNSs/PAN (10 wt.%), (e) SEM image of BNNSs/PAN corresponding EDS elemental maps of (f) C, (g) N, (f) B.

Figure 5. Strain-stress curves of PAN and BNNSs/PAN nanofiber films.
aggregation of BNNSs caused the uneven nanofiber. And an obvious decrease in elongation at break is observed indicating the nanofiber film becomes more brittle. The results indicate that the pristine PAN exhibits good flexibility but poor strength. Clearly, the BNNSs/PAN nanofiber films exhibit an excellent tensile strength as expected.

**Filtration performance of BNNSs/PAN nanofiber film**

The filtration performance of electrospun membrane is tested by light-scattering spectrometer. The whole test process simulates the use of the mask. The electrospun membrane is used as the filter. The theory of the measurement is test the number of tiny particles passing through the filter material and calculate the concentration of particles in a specific time using the laser. During the test, the instrument generates negative pressure of five ba, resulting the aerosol in the air was inhaled into the instrument passed the filter.

As shown in Table 1, there were 78.2 μg/m³ PM1 particles and 84.7 μg/m³ PM2.5 particles into the instrument in the air. However, there are only 0.2 μg/m³ and passed through PAN nanofiber film and 0.01 μg/m³ PM1 particles through BNNSs/PAN nanofiber film. Table 2 shown the particle concentration passed through the filter. There are 1153 p/cm³, 9.94p/cm³, 2.34p/cm³ particles for the control, PAN nanofiber film, BNNSs/PAN nanofiber film respectively. The experimental results show that the electrospun membrane has a good barrier effect on the micro particles in the air. The BNNSs/PAN composite membrane has a stronger barrier effect on the micro particles due to the role of boron nitride nano sheet. Calculation formula of filtration performance is:

$$R\% = \frac{C_t}{C_0} \times 100\%$$

Where $C_t$ is particles concentration in the air, and $C_0$ is particles concentration passed through the filters. By calculation, the removal rate of particle by the filters reached 99.8% BNNSs/PAN nanofiber film. Table 3 shows the filtration performance of BNNSs/PAN nanofiber film compared to other filters. The BNNSs/PAN nanofiber film exhibited a higher or equivalently filtration performance compared to reported previously, such as PAN/GO, PAN/GO/PI-6, TiO₂/PAN, AgNPs/PAN, PSA/PAN-B nanofiber film. This suggests that the obtained BNNSs/PAN nanofiber films viable candidates used for filter.

As seen from Fig.6(a), it has a lot of small particles passed through Non-woven fabric filter materials, and these particles will have an impact on human health. However, electrospun membrane can remove most of the tiny particles by electrostatic adsorption.

**Table 1.** Filtration performance of nanofiber films for PM₁ and PM₂.₅.

|                      | PM₁ (µg/m³) | PM₂.₅ (µg/m³) |
|----------------------|-------------|---------------|
| Control              | 78.2        | 84.7          |
| PAN nanofiber film   | 0.2         | 0.4           |
| BNNSs/PAN nanofiber film (5%) | 0.01  | 0.4           |
During the test period of 300s, there are 134069 particles in the air, only 251 particles passed through PAN nanofiber film and 65 particles passed through BNNSs/PAN nanofiber film. On the basis of the above analysis, it can be reasonably inferred that BNNSs/PAN nanofiber film has emerged as a good application prospect for the filtration of aerosols. The mechanism of the simultaneous effect of BNNSs/PAN nanofiber film on the aerosols filtration was shown in Fig.6(b). During the filtration process, aerosols were captured and tightly wrapped around the surface of nanofibers by electrostatic forces. The embedded BNNSs enhanced this filtration.

**Table 2.** Filtration performance of nanofiber films for particle concentration.

| Sample                  | Particle Concentration (p/cm³) | Filtration efficiency |
|-------------------------|-------------------------------|-----------------------|
| Control                 | 1153                          | —                     |
| PAN nanofiber film      | 9.94                          | 99.1%                 |
| BNNSs/PAN nanofiber film| 2.34                          | 99.8%                 |

**Table 3.** Filtration performance compared to reported works.

| Sample                          | Filtration efficiency |
|---------------------------------|-----------------------|
| PAN/GO nanofiber film           | 98.5%²⁹               |
| PAN/GO/PI-6 nanofiber film      | 99.5%²⁹               |
| TiO₂/PAN nanofiber film         | 97.9%⁷⁹               |
| AgNPs/PAN nanofiber film        | 99.8%⁹⁹               |
| PSA/PAN-B nanofiber film        | 99.52%⁹⁹             |
| BNNSs/PAN nanofiber film        | 99.8%                 |

**Figure 6.** (a) Particle number passed through the filter (b) Mechanism of the simultaneous effect of BNNSs/PAN nanofiber film on the aerosols filtration.
Conclusion

Boron nitride can be exfoliated by chemical method, which is simple, economical and efficient. Boron nitride nanosheets can be obtained when the ratio of boron nitride to potassium permanganate is 1:1 after 2 h reaction. Compared with the non-woven fabric, PAN nanofiber film, as well as BNNSs/PAN nanofiber film, the filtration performance of the electrospun membrane is significantly improved. Addition of BNNSs enhanced the filtration performance of the nanofiber film. The embedded BNNSs is one of the great important factors for enhancing mechanical property. For filtration performance, there are 134069 particles in the air, but only 65 particles passed through BNNSs/PAN nanofiber film indicating excellent filtration performance. The filtration efficiency of BNNSs/PAN nanofiber film could reach to 99.8% indicating that BNNSs/PAN nanofiber film had great potential as a cleaner use the treatment of smoke and dust pollutants.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by the Key Scientific Research Plan Projects of Shaanxi Education Department grant numbers 20JS049.

ORCID iD

Yingying Zhou  https://orcid.org/0000-0001-5774-2521

References

1. Zhu M, Cao Q, Liu B, et al. A novel cellulose acetate/poly (ionic liquid) composite air filter[J]. Cellulose 2020; 27(7): 3889–3902.
2. Fan X, Wang Y, Kong L, et al. A nanoprotein-functionalized hierarchical composite air filter[J]. ACS Sustain Chem Eng 2018; 6(9): 11606–11613.
3. Yang W, Lin L, Wang S, et al. Preparation of multifunctional AgNPs/PAN nanofiber membrane for air filtration by one-step process[J]. Pigment Resin Tech 2020; 49(5): 355–361.
4. Lu Z, Su Z, Song S, et al. Toward high-performance fibrillated cellulose-based air filter via constructing spider-web-like structure with the aid of TBA during freeze-drying process J. Cellulose 2018; 25(1): 619–629.
5. Li Y, Yang S, Ding B, et al. Semi-Interpenetrating Polymer Network Biomimetic Structure Enables Superelastic and Thermostable Nanofibrous Aerogels for Cascade Filtration of PM2.5 [J]. Adv Functional Materials 2020; 30(14): 1910426.
6. Gao H, He W, Zhao Y et al. Electret mechanisms and kinetics of electrospun nanofiber membranes and lifetime in filtration applications in comparison with corona-charged membranes[J]. J Membr Sci 2020; 600: 117879.
7. Su J, Yang G, Cheng C, et al. Hierarchically structured TiO$_2$/PAN nanofibrous membranes for high-efficiency air filtration and toluene degradation[J]. *J Colloid Interf Sci* 2017; 507: 386–396.

8. Gao H, Yang Y, akampumza A, et al. A low filtration resistance three-dimensional composite membrane fabricated via free surface electrospinning for effective PM2.5 capture[J]. *Environ Science-Nano* 2017; 4(4): 864–875.

9. Yang X, Pu Y, Li S, et al. Electrospun Polymer Composite Membrane with Superior Thermal Stability and Excellent Chemical Resistance for High-Efficiency PM2.5 Capture[J]. *ACS Appl Materials Interfaces* 2019; 11: 43188–43199.

10. Munyaneza J, Jia Q, Qaraah FA, et al. A review of atmospheric microplastics pollution: In-depth sighting of sources, analytical methods, physiognomies, transport and risks[J]. *Sci Total Environment* 2022; 822: 153339.

11. He W, Zhao Y, Jiang F, et al. Filtration performance and charge degradation during particle loading and reusability of charged PTFE needle felt filters[J]. *Sep Purif Tech* 2020; 233: 116003.

12. Zhong J, Yuan M, Song Y, et al. A Flexible Piezoelectret Actuator/Sensor Patch for Mechanical Human–Machine Interfaces[J]. *ACS Nano* 2019; 13(6): 7107–7116.

13. Yuan L, Fan W, Yang X, et al. Piezoelectric PAN/BaTiO$_3$ nanofiber membranes sensor for structural health monitoring of real-time damage detection in composite[J]. *Composites Commun* 2021; 25: 100680.

14. Cai R, Zhang L, Bao A, et al. PM collection performance of electret filters electrospun with different dielectric materials-a numerical modeling and experimental study[J]. *Building Environ* 2018; 131: 210–219.

15. Gao D, Guo S, Zhou Y, et al. Absorption-Dominant, Low-Reflection Multifunctional Electromagnetic Shielding Material Derived from Hydrolysate of Waste Leather Scraps[J]. *ACS Appl Mater Inter* 2022; 14: 38077–38089.

16. Liao Y, Loh C, Tian M, et al. Progress in electrospun polymeric nanofibrous membranes for water treatment: fabrication, modification and applications[J]. *Prog Polym Sci* 2018; 77: 69–94.

17. Bui TK and Seung Y. Ferroelectric PVDF nanofiber membrane for high-efficiency PM0.3 air filtration with low air flow resistance[J]. *Colloids Surfaces A-Physicochemical Engineering* 2022; 640: 128418.

18. He L, Lei W and Liu D. One-step facile fabrication of mechanical strong porous boron nitride nanosheets–polymer electrospun nanofibrous membranes for repeatable emulsified oil/water separation[J]. *Sep Purif Tech* 2021; 264: 118446.

19. Yin C, Ma Y, Liu Z, et al. Multifunctional boron nitride nanosheet/polymer composite nanofiber membranes[J]. *Polymer* 2019; 162: 100–107.

20. Lee G, Lee M, Park J, et al. Piezoelectric Energy Harvesting from Two-Dimensional Boron Nitride Nanoflakes[J]. *ACS Applied Materials Inter* 2019; 11(41): 37920–37926.

21. Yangsong Y, Dingxiang Y, Yue L, et al. Flexible Poly(vinylidene fluoride)-MXene/Silver Nanowire Electromagnetic Shielding Films with Joule Heating Performance[J]. *Industrial Eng Chem Res*, 2021, 60(27): 9824–9832.

22. Wang Y, Lu W, Wang Y, et al. Interpenetrating-Syncretic Micro-Nano Hierarchy Fibers for Effective Fine Particle Capture[J]. *Adv Eng Mater* 2019; 21(8): 1801361.
23. Xiao F, Naify S, Giberto G, et al. Edge-Hydroxylated Boron Nitride Nanosheets as an Effective Additive to Improve the Thermal Response of Hydrogels[J]. *Adv Mater* 2015; 27(44): 7196–7203.

24. Habib T, Devarajan Dinesh S, Khabaz F, et al. Co-solvents as Liquid Surfactants for Boron Nitride Nanosheet (BNNS) Dispersions[J]. *Langmuir* 2016; 32(44): 11591–11599.

25. Esfandiari A and Nazokdast H. Review of Polymer-Organoclay Nanocomposites[J]. *J Appl Sci* 2008; 8(3): 545–561.

26. Lee D, Lee B, Park KH, et al. Scalable Exfoliation Process for Highly Soluble Boron Nitride Nanoplatelets by Hydroxide-Assisted Ball Milling[J]. *Nano Lett* 2015; 15(2): 1238–1244.

27. Weng Q, Kvashnin DG, et al. Tuning of the Optical, Electronicand Magnetic Properties of Boron Nitride Nanosheets with Oxygen Doping and Functionalization[J]. *Adv Mater* 2017; 29(28): 1700695.

28. Le Y and Tran DNH. High-yield preparation of edgefunctionalized and water dispersible fewlayers of hexagonal boron nitride (hBN) by direct. *wet Chemical Exfoliation* 2021; 32: 405601.

29. Dai H, Liu X, Zhang C, et al. Electrospinning Polyacrylonitrile/Graphene Oxide/Polyimide nanofibrous membranes for High-efficiency PM2.5 filtration[J]. *Sep Purif Tech* 2021; 276: 119243.