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Immobilization of UiO-66-NH₂ into Bacterial Cellulose Aerogels for Efficient Particulate Matter Filtration

Qihang Dai ¹, Ju Liu ¹, Junjie Zheng ^{2,3,*} and Bo Fu ^{1,*} 

¹ Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

² School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

³ China National Quality Supervision Testing Center for Industrial Explosive Materials, Nanjing 210094, China

* Correspondence: junjiezhengnjust@163.com (J.Z.); fubo@njfu.edu.cn (B.F.)

Abstract: Metal–organic frameworks (MOFs) hold great potential for efficient removal of particulate matter (PM) due to their high porosity and tunable surface groups. In this work, sustainable bacterial cellulose (BC) was employed as a substrate for Zr-based MOF (i.e., UiO-66-NH₂) deposition. Specifically, the UiO-66-NH₂@BC aerogel exhibits a multi-level pore structure with a specific surface area of 103 m²/g. Pristine BC aerogels indicated a removal efficiency of 50.6% for PM_{2.5}, with a pressure drop of 22.8 Pa. While UiO-66-NH₂@BC aerogels showed a PM_{2.5} removal efficiency of 96.9%. The filtration mechanism can be assigned to the following reasons: (i) the interception/impaction of PM with the fibrous and porous aerogel network; and (ii) the presence of polar amine groups that boost electrostatic interactions between PM and MOFs. Moreover, as-prepared filters can be regenerated in a facile way with good reusability and long-term stability.

Keywords: UiO-66-NH₂; bacterial cellulose; air filter; particulate matter



Citation: Dai, Q.; Liu, J.; Zheng, J.; Fu, B. Immobilization of UiO-66-NH₂ into Bacterial Cellulose Aerogels for Efficient Particulate Matter Filtration. *Sustainability* **2023**, *15*, 13382. <https://doi.org/10.3390/su151813382>

Academic Editors: Xiongfei Zhang and Jianhao Qiu

Received: 6 August 2023

Revised: 26 August 2023

Accepted: 4 September 2023

Published: 7 September 2023



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1. Introduction

The rapid development of industry activities produces various pollutants including nitrate, sulfate, ammonium, and silicate in the air, and these pollutants can form hazardous particulate matter (PMs) [1]. Recently, atmospheric pollution caused by PMs constitutes a global challenge, as PMs seriously injure the environment and personal health [2]. In general, PM is classified by its size, for instance, PM_{2.5} refers to particle size less than 2.5 μm [3]. Owing to the devastating impacts of PM, considerable efforts have been devoted to the preparation of high-performance air filters for both industrial and residential applications [4]. Due to the small aerodynamic diameter, PM_{2.5} stably suspends in the air for weeks and spreads farther under atmospheric circulation [5]. Short-time exposure to ambient PM_{2.5} can cause threatening impacts to human health including coughing, bronchial asthma, lung irritation, etc. [6]. Thus, considerable strategies have been developed for the purification of PM-contaminated air. With the merits of low cost, simple operation, and high efficiency, mechanical filtration has been widely used to capture and eliminate harmful PMs [7]. To date, many kinds of polymers such as polypropylene, polyurethane, and alginate have been investigated as substrates for preparing air filtering systems [8]. In these filters, PMs are mainly captured by randomly stacking fibers through interception and impaction effects [9,10]. Nevertheless, there is a trade-off restraint between efficiency and pressure drop [11,12]. It is urgently needed to develop next-generation air filters with superior removal efficiency, good sustainability, high air transmission rate, low pressure drop, and long-term durability [7,13].

Metal–organic frameworks (MOFs), a promising group of porous inorganic–organic crystals, exhibit significant potential in air purification due to their remarkable inherent porosity, customizable pore size, easily adaptable structure, and modifiable functions [14,15]. The MOFs

with defects and unbalanced metal ions can provide positive charges to polarize the PM particle surface, achieving enhanced electrostatic adsorption of PM [16]. According to previous reports, the PM removal mechanisms can be summarized as: (i) electrostatic interaction effects between polar PM particles and positive MOF crystals (due to the unbalanced metal ions and defects of MOFs), (ii) interacting PM with highly polar functional groups (like $-NH_2$, $-SO_3H$) of MOFs, (iii) the binding of PM to the open metal sites of MOFs, and (iv) the creation of hierarchical pores [16]. Normally, MOFs exist in the form of rigid powders and there is a need to manufacture MOFs into easily handled and useful configurations for filtering applications [17–19]. Fortunately, MOFs exhibit diverse functional groups and they can be composed with polymer substrate easily [20,21]. Previously, Wang's group conducted significant pioneering research in the field of MOF-based air filters (MOFilters) [22,23]. They immobilized diverse MOFs (e.g., MOF-199, UiO-66, MOF-74, and ZIF-8) onto/into different substrates such as plastic mesh, glass cloth, metal mesh, nonwoven fabric, and melamine foam. For instance, they coated ZIF-8 on melamine foam via a hot pressing strategy and the filters had a $PM_{2.5}$ removal efficiency of over 95% for continuous 12 h [24]. Similarly, Jhung and Kyu deposited UiO-66 particles on cotton fabric and the interactions of filters' functional groups on PM removal efficiency were explored [25]. They discovered the preferential selective inhibition of PMs by $-SO_3H$ groups. The processability and flexibility of MOFs were greatly improved. However, most of the existing base media for air filters rely on petroleum-based polymers [26,27]. It is necessary to develop bio-based and sustainable air filters to reduce the overall carbon footprint [10].

Very recently, renewable and earth-abundant biomass has been viewed as appealing substitutes for synthetic polymers [28]. Cellulosic material has received extensive attention in PM filtration because of its good strength, superior flexibility, and high surface reactivity. Furthermore, cellulose is rich in surface hydroxyl groups, facilitating the hybridization with MOF materials. For example, bacterial cellulose (BC) usually exhibits an ultra-fine three-dimensional network, which holds great promise for air filters. BC-derived aerogels also present many outstanding advantages, such as interconnected porous structures and high specific surface areas. Wu et al. prepared a novel BC/AgNW composite filter by incorporating silver nanowires into a BC matrix [24]. Zhao et al. stringed Cu-BTC on cellulose fibers to fabricate composite membranes via a filtration-enabled gelation process [19]. The removal efficiency for $PM_{2.5}$ could keep over 95% even at a high initial PM concentration of $1000 \mu g/m^3$. Ma et al. [28] attributed this exceptional performance to the presence of a hierarchical porous structure and fibrous network. The cellulose aerogel was infused with a combination of double-component MOFs, which consisted of ZIF-8 and Ag-MOF. The filter showed a $PM_{2.5}$ removal efficiency of 94% and a low-pressure drop. In the porous filter, cellulose fibers construct a spider-web-like network to stabilize MOFs and intercept with PMs simultaneously. Hao et al. embedded Ti-based MOFs into bacterial cellulose (BC)/chitosan foam and created anisotropic channels through a directional freezing-drying method [29]. Such filters demonstrated a high efficiency in removing PM, while maintaining good long-term stability. Cellulose is an appropriate host for MOFs, and it proves huge promise for the preparation of efficient air filters [30,31].

The aim of this work is to develop sustainable and efficient air filters. Herein, Zr-based MOFs (UiO-66s) were anchored on BC aerogel to fabricate flexible air filters. Enabled by the porous structure of BC and the high surface area of MOFs, the composite aerogels are expected to have a superior PM removal performance. In particular, to enhance the air purification efficiency, amine-modified Zr-MOF (UiO-66- NH_2) was prepared and deposited into the aerogel matrix. With the aid of hydrogen bonding interactions, the MOF crystals strongly adhere to the cellulose fibers. The integration of MOFs leads to enhanced PM removal performance, and the optimal filtration efficiencies for $PM_{2.5}$ could reach 96.9%. Because of the highly porous structure, as-obtained filters presented a low-pressure drop. Additionally, the MOF-modified BC aerogels exhibit excellent durability and can be easily regenerated for repeated use. In the present work, the novelty mainly lies in three sides: (1) a more convenient and low-cost method for MOF@BC aerogel fabrication is proposed;

(2) amine-functionlized-UiO-66-NH₂ was incorporated into the BC matrix to investigate the effect of MOF addition on filter morphology and PM removal performance; (3) the MOF modified aerogels can be easily regenerated and superior reusability can be achieved. This work will shed light on the development of novel MOF-cellulose composites for air purification applications.

2. Materials and Methods

2.1. Materials

Powdered bacterial cellulose (BC, ≥99.0%) was purchased from Qihong Technology China. And BC was synthesized from the static fermentation of *Gluconacetobacter xylinus*. The BC sample was utilized in its original form without any additional purification. Zirconium chloride (ZrCl₄, ≥98%), 2-aminoterephthalic acid (ATA, 99%), and 1,4-benzendicarboxylic acid (BDC, 99%) were obtained from Aladdin Industrial Company, Shanghai, China. N,N-dimethylformamide (DMF, >99.5%), ethanol, and acetic acid (HAc) were supplied by Lingfeng Chemical Reagent, Shanghai, China. All chemicals were used without further purification. Mosquito coil incense (used for PM generation) was bought from Lanju Daily Chemical Industry, Zhongshan, China.

2.2. Preparation of UiO-66 and UiO-66-NH₂

The synthesis of UiO-66 and UiO-66-NH₂ crystals was modified from prior studies with a slight modification [32,33]. To synthesize UiO-66, 0.8 mmol of ZrCl₄ and 0.8 mmol of BDC were combined and then added to 82 mL of DMF. After stirring at 600 rpm for 30 min and undergoing 30 min of ultrasonic treatment, the solution was then transferred into a Teflon-lined autoclave with a volume of 200 mL and placed in an oven set at 120 °C for 24 h. The resulting products were subjected to centrifugation, then washing with DMF and methanol and then dried at 60 °C for 12 h. The UiO-66-NH₂ particles were prepared with the same procedures instead of ATA (0.15 g) was used as an organic precursor [34].

2.3. Preparation of UiO-66@BC Filters

By fixing the mass content of BC powders and changing the additional amount of MOF powders (0.1 to 0.4 g), composite materials with different MOF loadings were prepared. For comparison, a bare filter labeled as BC was also fabricated through the same method without the addition of MOF powders. The MOF particles were integrated into BC foams via a simple mixing and freeze-drying approach [35]. In a typical synthesis, 0.2 g of BC powders were dispersed into deionized water (20 mL) under stirring for 1 h to obtain a transparent suspension. Afterward, 0.2 g of as-prepared MOF powders were added into BC suspension under vigorous stirring and subjected to ultrasonic treatment for 1 h. The obtained mixed suspension was poured into a specific round mold with a diameter of 5 cm. The molds with suspension were then transferred into a freezer drier (−52 °C) for 24 h. The resulting samples were identified as UiO-66@BC and UiO-66-NH₂@BC, respectively.

2.4. Characterization

To acquire the information on crystalline patterns, X-ray diffraction (XRD) patterns of the MOF-deposited samples were carried out with a Rigaku Ultima IV using Cu Kα radiation from 5 to 40° at a scan speed of 5°/min and operated at 40 kV. Before XRD tests, the samples were coated with an Au layer. The Fourier transform infrared spectra (FT-IR) spectroscopy of the composite aerogels were acquired on an FT-IR spectrometer (Nicolet-360, Thermo Equipment, Waltham, MA, USA) with a typical KBr-pellet approach in the range of 400 to 4000 cm^{−1} for 32 scans at a resolution of 4 cm^{−1}. Microstructural images were recorded through the use of the Regulus SU8100 instrument for scanning electron microscopy (SEM) experiments. The compressive property was assessed using a dynamic mechanical analyzer (DMA, TA Q800) for 200 loading-unloading cycles. For zeta potential measurements, the aerogel specie suspension with a weight ratio of 0.01 wt% was ultrasonically treated for 10 min. The zeta potential values of the materials were analyzed

by ZETASIZER Nano-ZS (Malvern Instrument, Malvern, PA, USA) to investigate surface charges. An automatic instrument was used to perform nitrogen adsorption-desorption isotherms and specific surface areas were determined using the Brunauer–Emmett–Teller (BET) method.

2.5. Air Filtration Tests

The PM filtering capacity of the obtained composite aerogels were tested by a home-made experiment setup (Figure S1, Supporting Information). The wind velocity at the inlet of the device was tested by an anemometer (EMR, Oriental motor, Torrance, CA, USA). The simulated PM particles were produced by burning commercial incense and the generated smoke was diluted by air. To tune the wind velocity, a fan was used to accelerate the passage of air. Unless otherwise specified, the airflow velocity of 2 m/s was used to evaluate the air filter. We used an air detector (VSON WP6919S, Shenzhen, China) to measure the PM concentrations. The manometer used to estimate the pressure drop was SMART SENSOR AS510, manufactured in China. The following equations were used to obtain the PM filtration efficiency (η).

$$\eta = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

C_0 (ppm) and C_1 (ppm) represent the concentration of PM particles at the inlet and outlet, respectively.

Furthermore, the equation was used to determine the quality factor (Q_f).

$$Q_f = -\frac{\ln(1 - \eta)}{\Delta P} \quad (2)$$

where ΔP (Pa) is the pressure drop.

3. Results

3.1. Characterization of UiO-66s Deposited BC Filters

Bacterial cellulose (BC) is an excellent starting material for aerogel fabrication because of cellulose fibers can form highly entangled network with abundant pores. In this work, BC aerogel was used as a host for UiO-66 crystals. Pre-synthesized UiO-66 and UiO-66-NH₂ particles were introduced into BC suspension under stirring, subsequently the mixed suspension was subjected to freeze-drying treatment. After the process of ice sublimation, we were able to obtain aerogels that are lightweight and flexible. The density of UiO-66@BC and UiO-66-NH₂@BC was determined to be 9.2 and 13.7 mg/cm³, respectively. The aerogels display a network of interlinked pores in three dimensions. The presence of this permeable configuration is essential in minimizing gas diffusion hindrance.

XRD results are recorded in Figure 1a to explore the crystalline patterns of as-prepared aerogel filters. The original BC sample displays typical cellulose I topology, with a significant amorphous signal at 22.8°. The (002) crystal plane of cellulose is attributed to this peak. Meanwhile, UiO-66 and UiO-66-NH₂ demonstrate similar characteristic peaks with two sharp peaks at 7.2° and 8.3° (Figure S2, Supporting Information), which indexed well to the (111) and (200) crystal planes [35]. After the deposition of UiO-66s into BC matrix, the peaks attributed to both BC and UiO-66s are well preserved in the hybrid aerogels. This verifies the successful immobilization of MOF particles into the BC skeleton and the MOF patterns are maintained intact during processing [36,37].

FT-IR analysis was conducted to examine potential interactions between UiO-66s and BC. According to Figure 1b, the peaks located around 1600 cm^{−1} belong to stretching vibration of C=O groups. The band that stands out occurs at 1617 cm^{−1}, which corresponds to the stretching vibration of BC's C-O bonds. For the spectrum of pure UiO-66s, absorption peaks located at 1580 and 1395 cm^{−1} corresponded to the asymmetric and symmetrical stretching vibrations of the carboxyl groups in ligands. While the peaks between 600 and 800 cm^{−1} are associated with the existence of a Zr-O bond. By comparing the curves of UiO-66@BC and UiO-66-NH₂@BC, it can be inferred that the special absorption band of

amine groups is centered at 1657 cm^{-1} . When integrating UiO-66s into BC matrix, the bands associated with hydrogen bonding interactions (3415 cm^{-1}) became weakened, indicating the occurrence of group linkages. The presence of cross-linkages is beneficial for the enhancement of interface affinity and avoid the detachment of MOF particles [2,38]. XRD and FT-IR results reflected that UiO-66s are deposited into BC aerogel matrix.

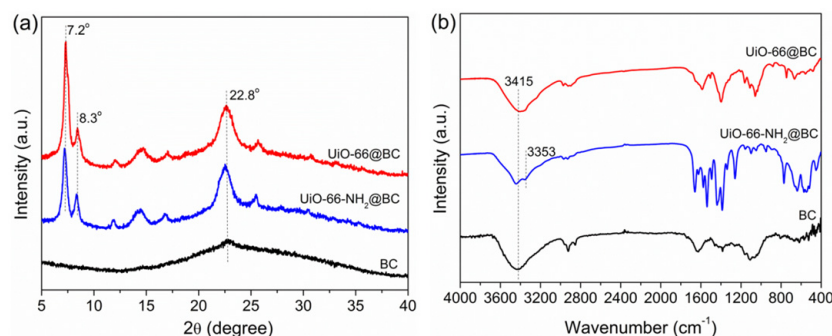


Figure 1. XRD patterns (a) and FT-IR spectra (b) of BC aerogel and UiO-66@BC composite aerogels.

The sizes of the obtained aerogels were determined by micrometer, as the diameter and thickness of the composite aerogels were ca. 4.8 cm and 0.5 cm, respectively. There is no obvious volume shrinkage during the lyophilization process. The density of bare BC was recorded at a low value of 8.3 mg/cm^3 in the absence of MOF deposition. The density of UiO-66@BC and UiO-66-NH₂@BC is increased to 13.1 and 13.4 mg/cm^3 , respectively, with the addition of UiO-66s. Figure 2a,c display the digital photos for bare BC and UiO-66-NH₂@BC aerogels, and there is no obvious appearance difference [39]. Figure 2b illustrates the micro-morphology of pristine BC sample, in which cellulose fibers are intricately intertwined to form spider-web-like structure. The micron-scale macropores in the BC matrix can be clearly identified. Figure 2d shows the aerogel that includes UiO-66-NH₂. No significant MOF aggregates appear in the composite aerogel, suggesting that MOF particles are highly dispersed. The identification of UiO-66-NH₂ particles occurs at higher resolutions, as shown in Figure S3b,c in the Supporting Information. Notably, the UiO-66-NH₂ particles with regular octahedral morphology are wrapped by the BC fibers rather than adhered to the aerogel surface. Furthermore, Zr and N were uniformly distributed throughout the entire plane according to the elemental mapping images (Figure S3a,b). This phenomenon is consistent with FT-IR observations, as there exist hydrogen bonding interactions between UiO-66-NH₂ and BC hydroxyl groups. In addition, physical entanglement and van der Waals forces also contribute to the superior MOF/BC interface compatibility [23,40].

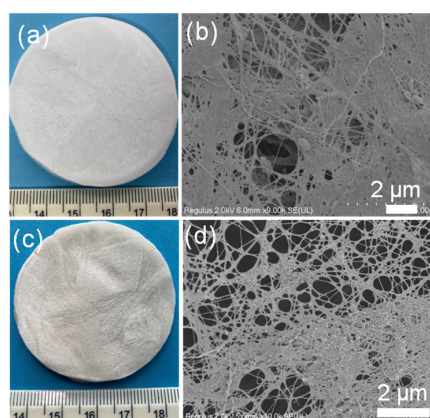


Figure 2. Digital photo (a) and SEM image (b) of bare BC. Digital photo (c) and SEM image (d) of UiO-66-NH₂@BC.

Nitrogen sorption isotherms were performed to acquire a comprehensive understanding of the pore structure of composite aerogels. The x-axis in Figure 3a represents relative vapor pressure, as P and P_0 refer to partial pressure of nitrogen and saturated vapor pressure of nitrogen at adsorption temperature, respectively. As anticipated, the initial BC aerogel exhibits a relatively small surface area of approximately $2.1 \text{ m}^2/\text{g}$ (Figure S4, Supporting Information). This is because BC aerogel primarily consists of macropores. As illustrated in Figure 3a, powdery UiO-66 and UiO-66-NH₂ have specific surface areas of 712 and $565 \text{ m}^2/\text{g}$, respectively. It is worth noting that the specific surface area of UiO-66-NH₂ is inferior to UiO-66 because of the existence of -NH₂ groups that occupy MOF channels. Mechanical properties of filters are significant to evaluate their structural stability to withstand high-pressure loadings in PM filtration process and thus the compressive stress-strain curves were correspondingly tested [41]. Upon the deposition of UiO-66s into BC network, the composite aerogels demonstrate a hierarchical pore structure with obvious hysteresis loops. The specific surface areas of UiO-66@BC and UiO-66-NH₂@BC are 135 and $103 \text{ m}^2/\text{g}$, respectively, which are 100 times higher than that of bare BC aerogel. This high surface area is attributed to the hierarchical pores, including inherent MOF micropores, aerogel micropores and mesopores generated by the cross-linking and compositing process. The prepared aerogels exhibit good mechanical strength and can withstand different types of deformations. Moreover, taking UiO-66-NH₂@BC aerogel as a sample, it can resist 100 compressive cycles (kept over 95% of its initial height) without cracks and MOF leaching (Figure 3b).

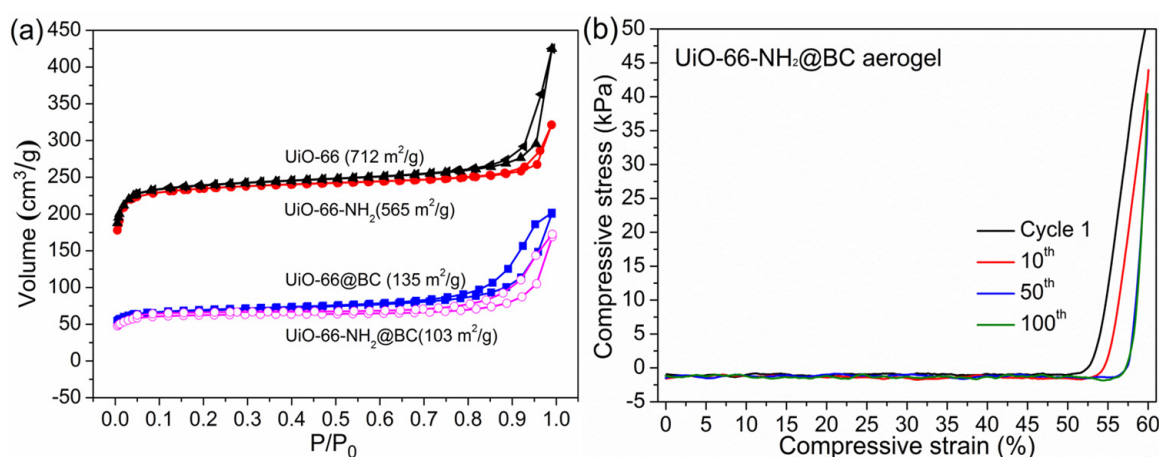


Figure 3. The nitrogen adsorption isotherms of UiO-66s and composite aerogels (a) and the compressive curves of UiO-66-NH₂@BC (b).

3.2. Air Purification Performance

We assess the PM filtration efficiency of MOF@BC filters by using a customized setup. Under the wind velocity of 2 m/s and initial PM concentration of $500 \mu\text{g}/\text{m}^3$, the determined filtration efficiencies, pressure drops, and quality factors are listed in Table 1. It should be noted that PM_{2.5} is employed as model pollutant during PM filtration tests. The filtration efficiency of PM_{2.5} for Pristine BC aerogel is relatively low at 50.6%. The pressure drop is determined to be 22.8 Pa. The filtration ability is mainly contributed by the fibrous network, which promotes the interception and impaction effects of PM with BC matrix. With the introduction of UiO-66s, there is an obvious enhancement for PM removal efficiency. As shown in Table 1, UiO-66@BC and UiO-66-NH₂@BC present filtration efficiencies of 91.1% and 96.9%, respectively. For UiO-66@BC aerogel, it can adsorb PM via electrostatic interactions as UiO-66 bears a Zeta potential of 38.3 mV. The pressure drop of UiO-66@BC is 27.3 Pa, which is slightly higher than that of bare BC aerogel. This indicates that the integration of UiO-66 particles provides a more tortuous gas pathway [42]. As a comparison, UiO-66-NH₂@BC aerogel has a pressure drop of 28.1 Pa, reflecting that the presence of amine groups presents a weak detrimental effect on gas permeation. Meanwhile,

the creation of hierarchal pores is important to reduce gas diffusion barriers. It is obvious that UiO-66-NH₂@BC has the optimal filtration performance based on the highest Q_f . A lower pressure drop represents less energy consumption and the pressure drop values of as-prepared aerogels are lower than other reported filters [2,22,28]. The optimal filtration performance is achieved by UiO-66-NH₂@BC, which is ascribed to amine groups. Quality factors are calculated and summarized in Table 1 and the UiO-66-NH₂@BC bears the highest quality factor of 0.124.

Table 1. The PM filtration performance of UiO-66s@BC filters.

Sample	Filtration Efficiency (%)	Pressure Drop (Pa)	Quality Factor
BC	50.6 ± 0.9	22.8 ± 0.5	0.031
UiO-66@BC	91.1 ± 1.1	27.3 ± 0.2	0.088
UiO-66-NH ₂ @BC	96.9 ± 0.7	28.1 ± 0.7	0.124

Please note that the filtration test was performed at a wind speed of 2 m/s and an initial concentration of PM of 500 µg/m³.

Figure 4a illustrates the impact of UiO-66-NH₂ loadings on filtration performance. By changing the UiO-66-NH₂ dosage from 0.1 to 0.2 g, the filtration efficiency displays an increase from 86.1% to 96.9%. This might be due to the higher MOF content offers sufficient active sites for PM capture. Nevertheless, when we increase the UiO-66-NH₂ loading from 0.2 to 0.3 or 0.4 g, there is a negligible variation on filtration efficiency. It suggests that the filtration efficiency is not positively related with MOF loadings [43]. On the contrary, excess UiO-66-NH₂ addition would block gas transport channels. The pressure drop increases notably with the increase in UiO-66-NH₂ loading. Figure 4b shows the influence of wind velocity on filtration performance. Filtration efficiencies exhibit a negative correlation with wind velocity. By varying the wind velocity from 2 to 6 m/s, the filtration efficiency of UiO-66-NH₂@BC aerogel presents an obvious decline from 96.9% to 93.1%. The reduced efficiency is assigned to the shorter residence time of PM in aerogel matrix. As the wind velocity increases, the pressure drop experiences a sharp increase, agreed with Darcy's law [7]. Furthermore, the humidity plays a crucial role for the filtration capacity of MOF-based filters. In practical PM filtration, the air commonly possesses a low humidity. We performed the filtration test in a relative humidity (RH) of 50%. The results demonstrated that the composite UiO-66-NH₂@BC filter has a good humidity tolerance and the removal efficiency just dropped by 0.4% after 12 h.

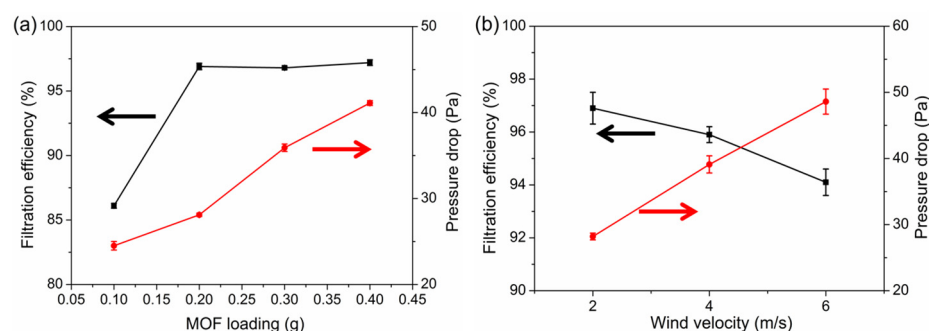


Figure 4. Effects of UiO-66-NH₂ loadings (a) and wind velocity (b) on the filtration performance of composite UiO-66-NH₂@BC aerogel.

The long-time stability of the aerogel filter is critical for its practical application. Figure 5a records the filtration efficiency variation of the UiO-66-NH₂@BC as a function of time. The composite aerogel proved an outstanding durability as the filtration efficiency kept at 96.1% after continuous 30 h test. The slight decline is caused by the adsorption of PM particles on UiO-66-NH₂ surface, thus weakening the electrostatic interactions. Another reason for the decrease in filtration efficiency is assigned to the block of pores, especially

for the micropores, and more PMs pass through the large pores with low selectivity. This causes the decrease of filtration efficiency and the increase of pressure drop. According to the wind velocity of the outlet is 2 m/s and the filtration area, the filtration volume is estimated to be ca. 1450 m³ during 30 h. The treatment capacity of the filter is 1.5 L s⁻¹. These results verified the huge, applied potential of as-prepared filters. Furthermore, the utilized filter can be conveniently revitalized through a simple process by flushing with water and ethanol (100 mL, with a molar ratio of 1:1). As demonstrated in Figure 5b, the PM removal efficiency maintained almost unchanged after 5 cycles (still higher than 96%). Such filter offers a novel material platform for PM removal, which might be extended to hazardous gas capture and volatile organic compound adsorption.

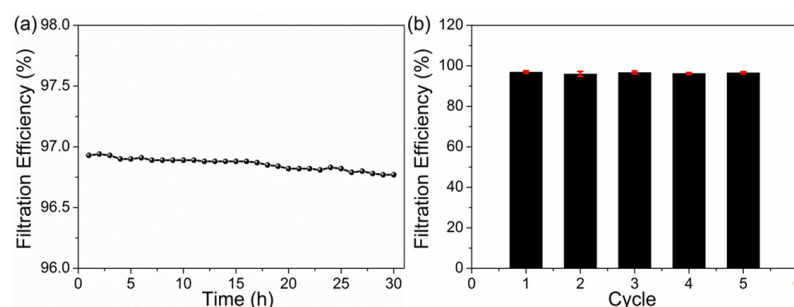


Figure 5. Long-time (30 h) test of UiO-66-NH₂@BC filter as a function of time (a), and cycling tests of UiO-66-NH₂@BC aerogel (b).

With respect to filtration mechanism, it is proposed that both pore structure and amine groups play combined roles. The channel size of pristine BC is much larger than the diameter of the PM particles, and PMs can easily pass through the BC pores. Bare BC aerogel demonstrated a low filtration performance. The filtering ability of bare BC sample is mainly derived from the porous matrix, which can intercept PM pollutants. Meanwhile, the nano-sized pores of crystalline UiO-66s are too tiny to adsorb and hold micro-sized PMs. Indeed, MOFs with abundant unsaturated metal sites are thought to be capable of removing highly polar PM through electrostatic interactions. The increase in surface area and micropores further facilitate the attachment of polar PMs to positively charged MOFs. In the UiO-66@BC filters, MOFs with positive zeta potential and unsaturated metal sites enable the effective removal of polar PM via electrostatic interactions, while the existence of abundant meso-/macropores ensure the sufficient air permeability. This synergy effect ensures the high-performance of composite filters. When the PM-containing air entered the aerogel filter, PM particles could interact with the cellulose fibers via physical interception and inertial impaction effects. The BC network is highly entangled and enhances the interception/impaction effects. The hierarchal pores can minimize diffusion barriers and allow the rapid passage of air. The addition of amine groups increased the electrostatic interaction, making it more effective for capturing PM particles.

4. Conclusions

The development of high-performance air filtering materials aiming at PM removal have attracted increasingly attention. MOFs hold great application prospects in PM capture because of their large surface areas, uniformly distributed metal centers, and tunable surface functionalities. However, MOF particles are usually difficult to be processed into easily-handled and application-specific forms. In this work, air filters were fabricated by encapsulating UiO-66s into BC aerogel matrix through a facile freeze-drying-induced self-assembly process. The presence of UiO-66s tuned the porosity and morphology of the aerogels, and UiO-66s@BC aerogels exhibited hierarchal porous structure. MOF particles were attached tightly to the cellulose surface groups, leading to a superior interface compatibility. Air filtration results demonstrated that the integration of UiO-66s leads to enhanced PM removal performance, and the optimal filtration efficiencies for PM_{2.5} could reach 96.9%

for UiO-66-NH₂@BC sample. A long-term durability and reusability can be achieved by the hybrid UiO-66-NH₂@BC aerogel. The PM filtration mechanism is the hierarchically pores and abundant amine groups. This study provides insights on the design of biomass-based materials for air quality protection and as-prepared materials are promising for catalysis and gas sensing applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su151813382/s1>, Figure S1: Illustration of the homemade setup for particulate matter filtration test; Figure S2: XRD patterns of powdery UiO-66 and UiO-66-NH₂ crystals; Figure S3: SEM image UiO-66-NH₂@BC (a) and energy dispersive spectrometer mapping of Zr (b) and N (c) elements. Figure S4: N₂ sorption isotherms of original BC aerogel.

Author Contributions: Conceptualization, Q.D.; methodology, J.L.; software, Q.D. and J.Z.; validation, J.L.; writing—original draft preparation, Q.D.; writing—review and editing, J.Z.; funding acquisition, J.Z. and B.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (21606133), and Jiangsu Provincial Natural Science Foundation of China (BK20160922). We also would like to acknowledge the support received from Advanced Analysis & Testing Center, Nanjing Forestry University for sample tests.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data will be available upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

Declaration of Competing Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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