

Article

Catalytic Performance of Flexible Polycationic Membrane Derived from Polyacrylonitrile for Advanced Applications

Yue Gao ^{1,*} , Xuan Qi ^{1,*} and Junfeng Zhang ²

¹ College of Chemical and Materials Engineering, Hainan Vocational University of Science and Technology, Haikou 571126, China

² School of Chemistry and Chemical Engineering, Hainan University, Haikou 570228, China; 992105@hainanu.edu.cn

* Correspondence: yueyuezs@163.com (Y.G.); 7duan@163.com (X.Q.)

Abstract

A novel polycationic membrane (PCM) was synthesized by the cyclization of polyacrylonitrile (PAN) with *m*-ethylene diamine, converting the nitrile groups into pyridine units, followed by quaternization with 1-bromobutane. The resulting PCM was further functionalized by loading the photocatalyst, phosphomolybdic acid (PMo), via anion exchange, forming a new type of photocatalytic material, PM-PCM. Under visible light irradiation, the PM-PCM photocatalyst achieved an impressive methylene blue degradation rate of 98%. Additionally, the nanofiber membrane morphology facilitates the efficient recovery of the catalyst, with 98% of the initial degradation efficiency maintained after five photocatalytic cycles. This robust, highly efficient, and recyclable material provides a new approach for catalyst support. To the best of our knowledge, PM-PCM is the first reported photocatalyst of this kind. This cost-effective, functionalized membrane material utilizes solar light as an economical and clean energy source, offering promising potential for sustainable environmental applications.

Keywords: polycationic membrane; polyacrylonitrile; nanofiber membrane; visible light photocatalyst

1. Introduction

Polyacrylonitrile (PAN) nanofiber membranes (PAN NFs) have gained significant attention due to their low density, excellent flexibility, and cost-effectiveness. These advantageous properties have led to their widespread use in industries such as textiles, construction materials, and as precursors for carbon fibers [1–4]. In addition, the chemical reactivity of the nitrile group in PAN allows for its functionalization into various groups, such as amino [5], carboxyl [6], and pyridine [7], which further expand its application scope, including metal ion adsorption, catalysis, and catalyst supports. These developments have provided valuable insights for the design of novel functional materials based on PAN NF membranes, particularly in the context of nitrile group functionalization [8].

Polycationic membranes (PCMs), which combine the properties of ionic liquids and traditional polyelectrolytes, have garnered considerable attention in recent years. They are particularly suitable as carriers for functional materials through simple anion exchange processes. Traditional methods of synthesizing PCMs often involve the free radical polymerization of ionic liquid monomers with vinyl groups [9]. This method is straightforward and holds broad application potential; however, the low polymerization degree of PCMs limits their range of



Academic Editors: Hui Ding and Sihui Zhan

Received: 13 December 2025

Revised: 23 January 2026

Accepted: 27 January 2026

Published: 18 February 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

applications [10]. An alternative approach is to modify the nitrogen-containing side groups (such as imidazole or pyridine) in synthetic polymers. Given that PAN can undergo cyclization with *m*-ethylene diamine to form poly-vinylpyridine, it is hypothesized that PAN-based PCM could be prepared by ionizing the pyridine groups while maintaining the high polymerization degree and nanofiber membrane morphology of PAN.

In recent years, the treatment of wastewater containing organic dyes has emerged as a key research area in environmental remediation [11]. While techniques such as membrane separation, adsorption, and biodegradation have made significant progress [12], challenges remain, including low pollutant removal efficiency, the generation of secondary pollution, and the formation of harmful intermediates [13–16]. As a result, these methods face practical limitations in real-world applications. Recently, photocatalytic degradation of organic dyes in wastewater, particularly under visible light irradiation, has attracted significant interest due to its effective use of renewable energy and environmentally friendly nature compared to other catalytic systems [17–19].

Polyoxometalates (POMs) are a class of stable transition metal oxide compounds with semiconductor properties [20,21]. However, the separation and recovery of water-soluble POMs present significant challenges. To address this issue, loading POMs onto carrier surfaces has proven to be an effective strategy [22–24]. Therefore, developing a low-cost, readily available, and highly immobilized stable carrier material is crucial.

Table 1 summarizes recent advancements in photocatalytic membrane materials. By comparing the characteristics of photocatalysts in terms of raw material selection, preparation methods, degradation substances, preparation costs, reusability, and visible light responsiveness, it is concluded that the development of a visible-light-responsive, low-cost, easily recyclable, flexible, and water-insoluble polymer catalyst is an effective approach for dye wastewater degradation.

Table 1. Comparison of photocatalytic membrane materials.

Photocatalytic Membrane	Preparation Method	Degradation Target	Value	Recyclability	Visible Light Responsiveness
PM-PCM	Independent	Methylene blue	Low	Easy	Yes
Al ₂ O ₃ /TiO ₂ [25]	Coating	Carbamazepine	High	Difficult	No
Ceramic/TiO ₂ [26]	Coating	Acid Red 4	High	Difficult	No
PVDF/TiO ₂ [27]	Mixing	Wastewater	High	Difficult	No
PU/ZnO [28]	Membrane Immersion	Methylene blue	High	Difficult	No
Carbon Nanotube/ZnO-TiO ₂ [29]	Membrane Immersion	Methylene blue	High	Difficult	No
PVDF/ZnO-TiO ₂ [30]	Membrane Immersion	Methylene blue	High	Difficult	No
PSF/Cu ₂ O [31]	Chemical Vapor Deposition on Membrane	IBP	High	Easy	Yes
GO/Fe ₂ O ₃ -TiO ₂ [32]	Hydrothermal Synthesis, Membrane Immersion	Humic Acid	High	Difficult	No
PVDF/ZnIn ₂ S ₄ [33]	Membrane Immersion	Water	High	Easy	Yes
RGO/Bi ₂ WO ₆ [34]	Membrane Immersion	Ciprofloxacin (CIP)	High	Difficult	Yes
RGO/PDA/Bi ₁₂ O ₁₇ Cl ₂ [35]	Membrane Immersion	Methylene blue	High	Easy	Yes
Steel/CeO ₂ [36]	Membrane Immersion	Methylene blue	High	Difficult	No
Ceramic/TiO ₂ [37]	Membrane Immersion	Humic Acid	High	Difficult	No
PVDF/TiO ₂ [38]	Electrospinning and Hydrothermal Reaction	CO ₂	High	Easy	No
PES/TiO ₂ [39]	Physical Deposition	Acid Red 1	High	Difficult	No

Polyacrylonitrile (PAN) nanofiber membranes (NF) are well-known for their low cost, excellent flexibility, and wide range of applications, including in textiles, construction materials, and carbon fiber precursors. However, their inherent properties can be further enhanced by functionalization, such as the conversion of nitrile groups into various functional groups, which broadens their applications in areas such as metal ion adsorption and catalysis. In recent years, polycationic membranes (PCMs) have attracted considerable attention due to their unique combination of ionic liquid and traditional polyelectrolyte properties, making them ideal candidates as functional material carriers via simple anion exchange processes. However, traditional methods for preparing PCMs often involve low polymerization degrees, limiting their application potential.

In this study, a novel approach is introduced wherein low-cost and flexible PAN NF membranes are modified into PCM and further functionalized with the photocatalytically active phosphomolybdc acid (PMo). The resulting PM-PCM composite membrane exhibits excellent photocatalytic performance for the degradation of methylene blue (MB) under visible light irradiation, demonstrating the potential of composite photocatalytic materials with high molecular weight and nanofiber membrane structures. This study highlights the excellent catalytic activity, reusability, and stability of PM-PCM as an efficient photocatalyst, providing a promising platform for sustainable environmental applications, particularly in the field of wastewater treatment. The structure of the polymer is shown in Figure 1.

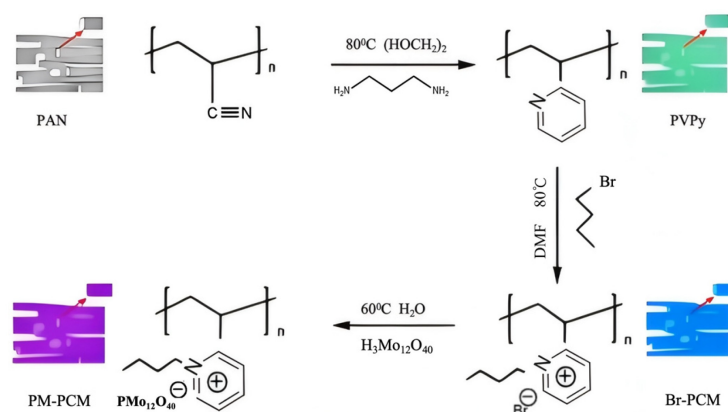


Figure 1. Schematic illustration of the synthetic routes for PVPy, Br-PCM, and PM-PCM, including the preparation of pyridine-functionalized polymer (PVPy), subsequent quaternization to obtain Br-PCM, and the final assembly/ion-exchange with PMo to form PM-PCM.

2. Results and Discussion

2.1. FTIR and SEM Analysis

The structural properties of the PAN, PVPy, Br-PCM, PM-PCM nanofiber (NF) membranes and PMo were characterized using Fourier transform infrared (FT-IR) spectroscopy, and the results are shown in Figure 2a. In the FT-IR spectrum of PAN, the absorption peak at 1451 cm^{-1} corresponds to the in-plane C-H vibration, while the peaks at 2246 cm^{-1} and 1074 cm^{-1} are attributed to the stretching and bending vibrations of the $\text{C}\equiv\text{N}$ group, respectively [40–42]. In the FT-IR spectrum of PVPy, the characteristic peak at 2246 cm^{-1} , associated with the $\text{C}\equiv\text{N}$ group, disappears, and new peaks at 1673 cm^{-1} and 1389 cm^{-1} are observed, corresponding to the $\text{C}=\text{N}$ and $\text{C}-\text{N}$ stretching vibrations in the pyridine ring. This confirms the successful transformation of the $\text{C}\equiv\text{N}$ group into pyridine units via cyclization with m-ethylene diamine [43,44].

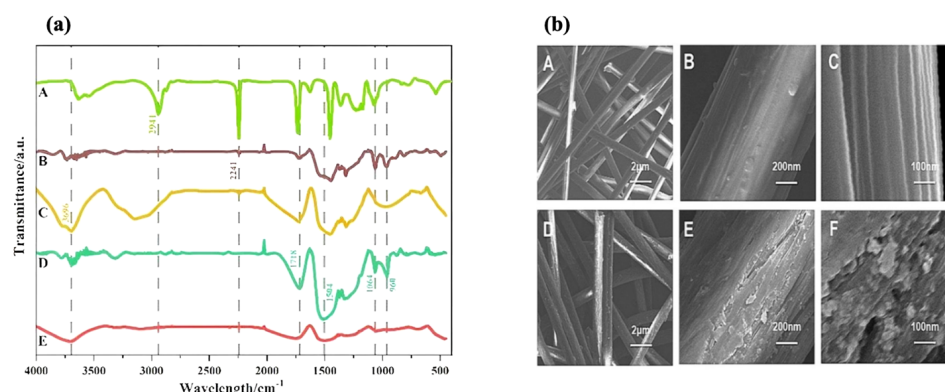


Figure 2. (a) FT-IR spectra of PAN (A), PM-PCM (B), Br-PVPy (C), PMo (D), and PVPy (E). (b) SEM images of the PAN NF membranes (A–C) at different magnifications; SEM images of the PM-PCM (D–F) at corresponding magnifications (scale bars: 2 μm, 200 nm, and 100 nm, respectively).

The FT-IR spectrum of PMo exhibits characteristic absorption peaks at 1074 cm⁻¹, 998 cm⁻¹, 892 cm⁻¹, and 813 cm⁻¹, corresponding to the P-O, Mo-O, Mo-O-Mo corner, and Mo-O-Mo edge vibrations, respectively. In the FT-IR spectrum of the PMo-PCM composite, the absorption peaks at 1074 cm⁻¹ and 998 cm⁻¹ are related to the P-O group vibrations and Mo-O resonance, while the peaks at 1673 cm⁻¹ and 1074 cm⁻¹ correspond to the vibrations of the pyridine structure [45] (The presence of pyridine still needs to be confirmed in combination with subsequent characterization methods. These results clearly indicate the successful preparation of the PMo-PCM composite).

Figure 2b presents the scanning electron microscopy (SEM) images of the PAN and PM-PCM NF membranes. Compared to the PAN membrane, the surface of the PM-PCM exhibits a rougher texture, which can be attributed to the uniform distribution of polyoxometalate (POM) on the surface of the PM-PCM. Additionally, a honeycomb-like cavity structure is observed on the surface of the PM-PCM. This unique morphology may enhance the specific surface area and adsorption capacity of the membrane [46], suggesting that the PM-PCM has the potential to serve as an ideal polymer support material for various applications (the nanofiber membrane offers a combination of flexibility, catalytic functionality, and easy modification through anion exchange).

The FT-IR and SEM analyses collectively confirm the successful fabrication of the PM-PCM and provide valuable insights into its structural characteristics. The incorporation of POM and the unique nanofiber morphology are expected to contribute to the enhanced photocatalytic performance and reusability of the PM-PCM, which is further investigated in the following sections.

2.2. AFM Analysis

The surface morphology and average roughness (Ra) of the composite nanofiber membranes were characterized by atomic force microscopy (AFM), and the corresponding three-dimensional topographical images are presented in Figure 3. As shown, the pristine PAN nanofiber membrane exhibits a relatively smooth surface with an Ra value of 0.32 μm. The surface features are dominated by gentle height variations along the fiber direction, indicating a uniform fiber distribution and limited surface irregularities.

After the introduction of PVPy, the average surface roughness slightly increases to 0.56 μm. However, this increase is not significant, and the AFM image reveals that the PVPy nanofiber membrane still maintains a relatively smooth surface without obvious protrusions or aggregated structures. This suggests that the incorporation of PVPy has a minimal impact on the surface topography, likely due to its good compatibility with the PAN matrix and homogeneous distribution within the nanofibers.

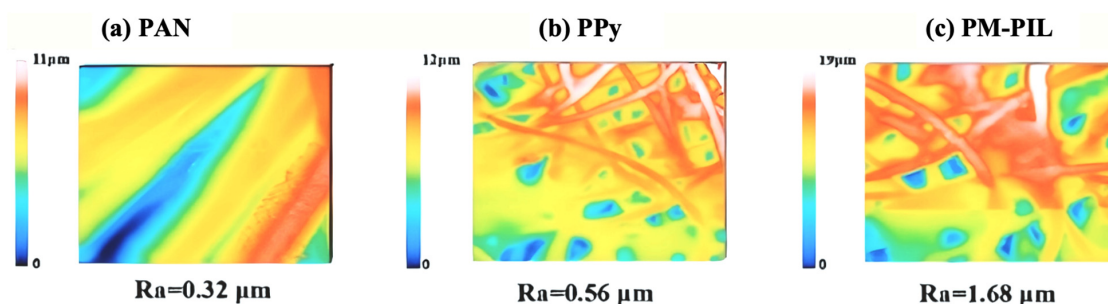


Figure 3. AFM topography images and corresponding average surface roughness (Ra) values of nanofiber membranes: (a) PAN, (b) PVPy, and (c) PM-PCM.

In contrast, a pronounced change in surface morphology is observed after the incorporation of phosphomolybdic acid (PM-PCM). The Ra value of the PM-PCM nanofiber membrane increases markedly to 1.68 μm , indicating a substantial enhancement in surface roughness. The corresponding AFM image displays more prominent height fluctuations and irregular surface features, which can be attributed to the successful incorporation of phosphomolybdic acid into the nanofiber matrix. These results confirm that the introduction of phosphomolybdic acid effectively promotes surface roughening, possibly due to the formation of micro–nano-scale surface heterogeneities and local aggregation effects.

The significant increase in surface roughness upon PM-PCM modification demonstrates that phosphomolybdic acid plays a critical role in tailoring the surface morphology of the nanofiber membranes. Enhanced surface roughness is generally beneficial for applications requiring increased surface area and improved interfacial interactions, such as adsorption, catalysis, or electrochemical processes. Therefore, the AFM results provide strong evidence that the composite strategy involving phosphomolybdic acid is effective in modulating the surface structure of nanofiber membranes.

2.3. XPS Analysis

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical composition and elemental valence states of the PM-PCM. As shown in Figure 4a, the survey XPS spectrum reveals the presence of C, O, N, P, and Mo elements on the membrane surface. The C and N signals originate from the PAN-derived polymer backbone, while the appearance of P and Mo elements can be attributed to the successful immobilization of phosphomolybdic acid (PMo) onto the PCM. Notably, the molybdenum content reaches 5.1 wt%, indicating that the anion exchange process proceeded efficiently and that PMo was effectively loaded onto the PCM framework.

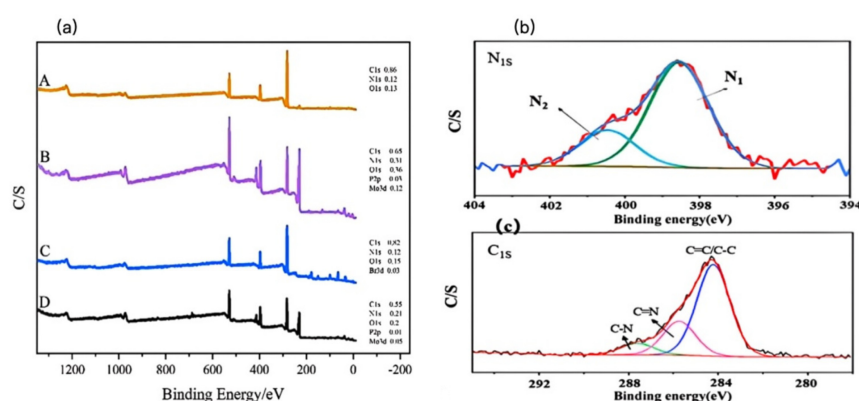


Figure 4. (a) XPS survey spectra of PAN (A), PMo (B), Br-PVPy (C), and PM-PCM (D). (b) High-resolution N 1s XPS spectrum of PM-PCM. (c) High-resolution C 1s XPS spectrum of PM-PCM.

To further elucidate the chemical states of nitrogen species, high-resolution N 1s XPS spectra were analyzed (Figure 4b). Two distinct peaks were observed at binding energies of 400.7 eV (N1) and 402.3 eV (N2), which are characteristic of nitrogen atoms in pyridine-like structures [47]. These results are consistent with the FTIR analysis and confirm the successful conversion of nitrile groups into nitrogen-containing heterocyclic units during the cyclization and ionization processes. The presence of positively charged nitrogen sites is crucial for stabilizing $\text{PMo}_{12}\text{O}_{40}^{3-}$ through electrostatic interactions, thereby enhancing the immobilization efficiency of the photocatalyst.

The high-resolution C 1s spectrum (Figure 4c) can be deconvoluted into three main components. The dominant peak corresponds to C–C/C–H bonds, indicating the polymer backbone structure. Two additional peaks with lower intensities are assigned to C–N and C=N bonds, respectively, further confirming the formation of pyridine-type structures and other nitrogen-containing functional groups on the membrane surface. These nitrogen-rich functionalities not only provide anchoring sites for PMo but may also facilitate charge transfer during the photocatalytic process. This process reduces recombination of electron-hole pairs, thereby improving the overall photocatalytic efficiency of the system during light-driven reactions.

Overall, the XPS results provide compelling evidence for the successful fabrication of the PM-PCM. Due to factors like steric hindrance, we employed a direct side-chain modification approach to create pyridine-containing polymers, which results in a significantly higher molecular weight and degree of polymerization compared to polymers generated by monomer polymerization. This increase in polymerization degree also leads to a substantial increase in catalytic sites on the surface, thereby enhancing the overall catalytic activity. The coexistence of PMo species and pyridine-based PCM structures on the nanofiber membrane surface is expected to play a synergistic role in enhancing visible-light-driven photocatalytic activity and structural stability during repeated catalytic cycles.

2.4. UV-Vis and XRD Analysis

To investigate the light absorption properties of the raw materials and their modified products, UV–visible diffuse reflectance spectroscopy (DRS) was conducted on polyacrylonitrile (PAN), PMo, PVPy, brominated polycationic membrane (Br-PCM), and PM-PCM nanofiber (NF) membranes. The corresponding spectra are shown in Figure 5a. As expected, pristine PAN exhibits negligible absorption in both the ultraviolet and visible light regions, indicating its photo-inactive nature. Similarly, pure PMo shows almost no absorption in the visible region (>400 nm), which significantly limits its photocatalytic performance under visible light irradiation.

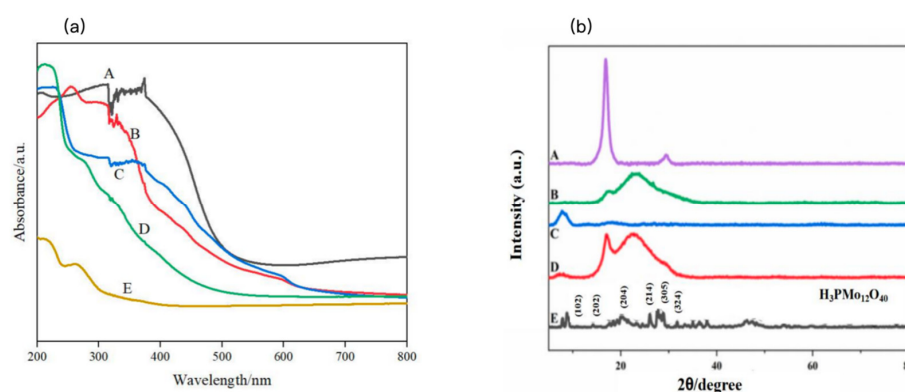


Figure 5. (a) UV–vis diffuse reflectance spectra (DRS) of PM–PCM (A), PMo (B), Br-PVPy (C), PVPy (D), and PAN (E). (b) X-ray diffraction (XRD) patterns of PAN (A), Br-PVPy (B), PM–PCM (C), PVPy (D), and PMo (E).

In contrast, the PM-PCM displays pronounced absorption across both the ultraviolet and visible regions. This enhanced light-harvesting capability can be attributed to the charge transfer characteristics of the polycationic membrane framework, which effectively extends the light response of PMo into the visible region [48]. These results suggest that the PCM matrix plays a crucial role in improving the visible-light utilization efficiency of the PMo photocatalyst. Based on the UV-vis DRS data calculated using the Kubelka–Munk function, the band gap energy of PM-PCM was determined to be 3.09 eV, which is favorable for visible-light-driven photocatalytic reactions.

X-ray diffraction (XRD) measurements were performed to examine the crystalline structures of PAN, PMo, PVPy, Br-PCM, and PM-PCM, and the results are presented in Figure 5b. The PAN NF membrane exhibits a diffraction peak in the 2θ range of $16\text{--}17^\circ$, which is attributed to the (100) plane of the hexagonal crystal system [49]. Additionally, a weaker diffraction peak observed at approximately $28\text{--}29^\circ$ corresponds to the (110) plane. In the XRD pattern of PVPy, the (100) diffraction peak at $2\theta = 17^\circ$ shows a noticeable shift, accompanied by other structural changes, which can be ascribed to the introduction of pyridine units and the resulting alteration of the polymer crystal structure.

For PMo, characteristic diffraction peaks are observed at 2θ values of approximately 10° , 20° , 23° , 25° , 28° , and 31° , corresponding to the (110), (200), (220), (310), (222), and (400) crystal planes, respectively. These diffraction features are in good agreement with the standard XRD pattern of PMo reported in the literature [50,51] and match well with the data from JCPDS card No. 50-0657, confirming the high crystallinity and phase purity of PMo.

The XRD pattern of Br-PCM shows a diffraction peak at $2\theta = 17^\circ$, similar to that of PVPy, while the signal at approximately 29° is significantly weakened [52]. A comparison between the Br-PCM and PVPy patterns indicates that the ionization process has a limited influence on the crystalline structure of PVPy. Notably, in the XRD pattern of PM-PCM, no impurity peaks are detected, demonstrating the high purity of the composite material. Compared with PAN, the diffraction peaks at $2\theta = 17^\circ$ and 29° disappear, while two new peaks emerge at 2θ values of approximately 8° and 23° , which can be assigned to the (200) and (001) crystal planes of PMo, respectively. These results further confirm the successful incorporation of PMo into the PCM and the formation of the PM-PCM composite.

Overall, the UV-vis DRS and XRD analyses collectively demonstrate that the introduction of the PCM framework not only significantly enhances the visible-light absorption capability of PMo but also enables its stable immobilization within the nanofiber membrane without generating impurity phases. This adsorption and interfacial interaction of optical and structural advantages is expected to play a key role in the excellent visible-light photocatalytic performance of the PM-PCM. We have clarified that the charge-transfer explanation is a plausible interpretation rather than conclusive proof.

2.5. TGA

Thermogravimetric analysis (TGA) was employed to investigate the thermal stability and structural composition of PAN and PM-PCM, and the corresponding TGA curves are presented in Figure 6. The mass loss behaviors of the two samples exhibit both similarities and distinct differences over the entire temperature range.

In the low-temperature region ($50\text{--}100^\circ\text{C}$), both PAN and PM-PCM show a slight mass loss, which can be attributed to the evaporation of physically adsorbed moisture. This initial weight loss is relatively small, indicating limited water content in both materials.

As the temperature increases to the range of $100\text{--}262^\circ\text{C}$, PAN begins to exhibit a gradual mass loss, suggesting the onset of thermal degradation processes. When the temperature exceeds 262°C , PAN undergoes rapid and substantial weight loss, which is

mainly associated with the decomposition of the polymer backbone and the breakdown of the polymer network structure.

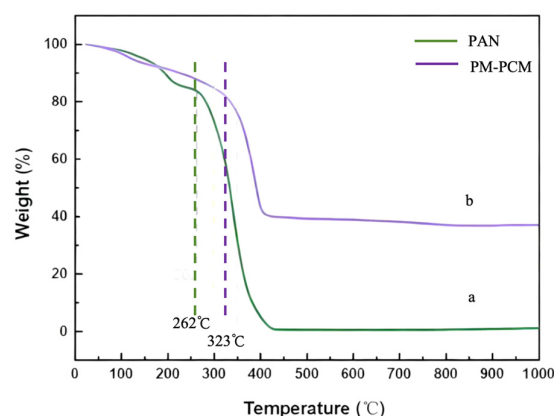


Figure 6. TGA curves recorded in air from 0 to 1000 °C: (a) PAN and (b) PM-PCM.

In contrast, PM-PCM demonstrates enhanced thermal stability compared with pristine PAN. The ionic liquid (IL) within the PM-PCM ionic gel exists in two forms: constrained (bound) ILs and free ILs. The bound ILs interact strongly with the PAN matrix and decompose concurrently with the polymer framework, while the free ILs remain thermally stable over a broader temperature range. As a result, the main thermal decomposition temperature of PM-PCM is shifted to higher values relative to that of PAN.

Furthermore, PM-PCM retains a significantly higher residual mass at elevated temperatures, which can be primarily attributed to the non-volatile nature of the ionic liquid. This behavior confirms that the incorporation of ionic liquids effectively suppresses mass loss during heating and enhances the overall thermal stability of the composite material.

Overall, the comparative TGA results clearly indicate that the introduction of polycationic membrane plays a crucial role in improving the thermal resistance of PM-PCM, making it more suitable for applications requiring enhanced thermal stability.

2.6. Visible-Light Photocatalytic Degradation Analysis

The photocatalytic performance of the PM-PCM was evaluated through the degradation of methylene blue (MB) in an aqueous solution under visible light irradiation. MB, a typical aromatic dye, contains reactive oxygen species (ROS)-induced oxidative degradation of methylene blue, which involves stepwise oxidation of the heterocyclic aromatic structure. In the presence of catalysts for oxidation such as polyoxometalates (POMs) or ozone, the photocatalytic degradation of methylene blue in this system primarily proceeds via highly reactive species such as $\bullet\text{OH}$ and $\text{O}_2\bullet^-$ generated under visible-light irradiation, which attack the conjugated aromatic framework of MB, leading to decolorization and mineralization. Therefore, MB was selected as a model pollutant to assess the visible-light-driven photocatalytic activity of the PM-PCM catalyst, and the corresponding degradation results are presented in Figure 7a [53].

To clarify the role of PM-PCM in the photocatalytic process, control experiments were conducted under identical conditions, including reactions without any catalyst and reactions using a simple physical mixture of polyacrylonitrile (PAN) and PMo. During the photocatalytic experiments, aliquots were withdrawn at regular intervals, and the concentration of MB was monitored by recording the UV-vis absorption spectra. As shown in Figure 7a, the degradation efficiency of MB under dark conditions was only approximately 1%, indicating negligible adsorption or self-degradation of MB in the absence of light irradiation.

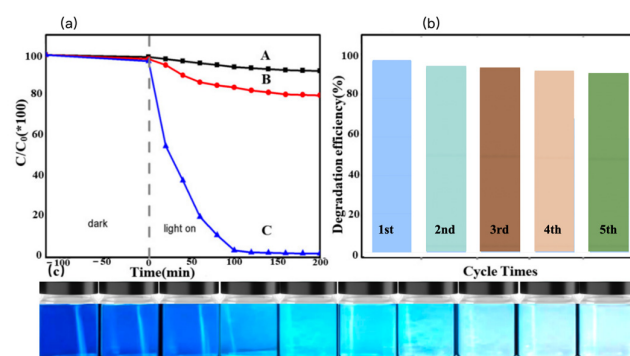


Figure 7. (a) UV-vis absorption evolution of methylene blue (MB) during the dark adsorption stage and the subsequent photocatalytic degradation under visible-light irradiation: (A) MB without photocatalyst, (B) MB in the presence of PAN/PMo blended sample, and (C) MB in the presence of PM-PCM under visible light. (b) Recyclability of the immobilized photocatalyst PM-PCM for MB photodegradation (catalyst loading: 1 mg mL^{-1} ; 20 mg catalyst dispersed in 20 mL aqueous solution; Mo concentration: 50 ppm). Aliquots were collected every 100 min for a total of five samples. (c) Digital photographs showing the macroscopic appearance changes in the MB aqueous solution recorded every 10 min during the photocatalytic degradation process.

In contrast, under visible light irradiation, the PM-PCM exhibited outstanding photocatalytic activity, achieving up to 98% degradation of MB within the same reaction time. The gradual color fading of the MB aqueous solution during the reaction process is clearly illustrated in Figure 7c, further confirming the efficient photocatalytic degradation capability of PM-PCM. These results demonstrate that PM-PCM acts as an effective visible-light photocatalyst for MB degradation, benefiting from the synergistic interaction between PMo and the polycationic membrane nanofiber matrix [54,55].

Moreover, as shown in Figure 7a,b, the photocatalytic degradation efficiency of MB reached only about 20% when a simple PAN/PMo mixture was used under the same experimental conditions. This significantly lower activity highlights the critical role of the PCM framework in enhancing photocatalytic performance. The immobilization of PMo within the PCM not only improves light absorption and charge separation efficiency but also promotes effective contact between the catalyst and the dye molecules. Consequently, the PM-PCM composite membrane exhibits superior photocatalytic efficiency compared to physically mixed systems.

Overall, these results clearly demonstrate that the rational design of PM-PCM enables efficient visible-light-driven degradation of MB, outperforming conventional polymer-supported or physically blended photocatalysts. This enhanced performance can be attributed to the improved light-harvesting capability, effective charge transfer, and stable immobilization of PMo within the PCM nanofiber network, making PM-PCM a promising candidate for practical wastewater treatment applications.

The recyclability of heterogeneous photocatalysts is a critical factor for their practical application. To evaluate the reusability of the PM-PCM, the catalyst was recovered from the photocatalytic reaction system after each cycle, thoroughly washed with deionized water and ethanol three times, and then dried in a vacuum oven at 60°C for 8 h. The regenerated PM-PCM was subsequently reused for the next photocatalytic degradation experiment under identical conditions.

As shown in Figure 7b, the PM-PCM exhibits excellent cycling stability. After five consecutive photocatalytic cycles, the degradation efficiency of methylene blue remained as high as 98% of the initial value, indicating negligible loss of photocatalytic activity. This outstanding reusability demonstrates that PM-PCM is not only an efficient visible-light photocatalyst but also a robust and durable material suitable for repeated use.

The superior recyclability of the PM-PCM can be attributed to its freestanding nanofiber membrane structure, which enables facile separation from the reaction system without the need for additional centrifugation or filtration steps typically required for powder-based catalysts. Moreover, the strong electrostatic (Coulombic) interactions between the negatively charged $\text{PMo}_{12}\text{O}_{40}^{3-}$ and the positively charged pyridinium groups within the PCM framework play a crucial role in stabilizing the immobilized photocatalyst. These interactions effectively suppress PMo leaching during the photocatalytic process, thereby maintaining high catalytic activity over multiple cycles.

Overall, the combination of structural integrity, strong electrostatic immobilization, and membrane-based morphology endows the PM-PCM with excellent reusability and operational stability. These advantages significantly enhance its potential for practical applications in wastewater treatment, offering a cost-effective, efficient, and recyclable solution for visible-light-driven photocatalytic degradation of organic pollutants.

2.7. Photocatalytic Mechanism Analysis

Based on the molecular energy levels and structural characteristics of the PM-PCM, a plausible visible-light-driven photocatalytic mechanism is proposed, illustrated in Figure 8 (conceptual mechanism diagram). According to the UV–vis diffuse reflectance spectroscopy (DRS) results, the PM-PCM composite exhibits a band gap energy of 3.09 eV, indicating its ability to absorb a broad range of ultraviolet and visible light. Further analysis using the Kubelka–Munk model suggests that the photogenerated electron migration energy of PM-PCM reaches approximately 0.09 eV, demonstrating efficient visible-light absorption and charge transfer capability within the composite material [56].

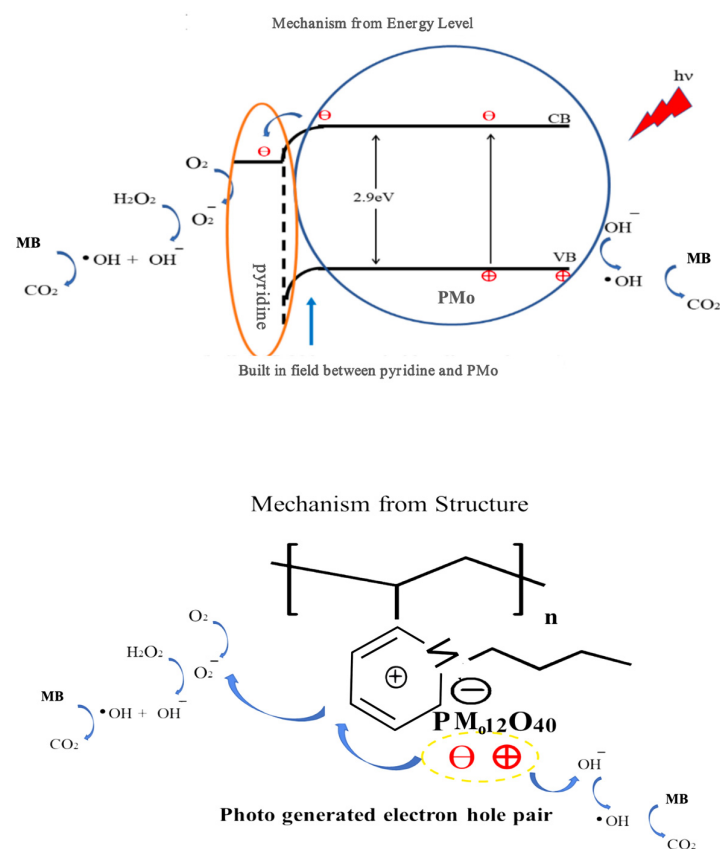


Figure 8. Conceptual mechanism diagram illustration of the band structure of PM-PCM and the photogenerated charge-carrier separation/transfer behavior under light irradiation, showing the excitation of electrons from the valence band to the conduction band and the corresponding hole formation, as well as the subsequent charge separation and migration processes.

The enhanced photocatalytic performance of PM-PCM can be attributed to the strong electrostatic interaction between the positively charged pyridinium groups in the polycationic membrane matrix and the negatively charged $\text{PMo}_{12}\text{O}_{40}^{3-}$. This Coulombic interaction induces the formation of an internal electric field at the PM-PCM interface, which effectively promotes the separation and directional migration of photogenerated charge carriers. As a result, the recombination of electron–hole pairs is significantly suppressed, thereby improving the overall photocatalytic efficiency.

Previous studies have shown that polyoxometalates (POMs) can be regarded as low-dimensional semiconductor-like materials with well-defined valence band (VB) and conduction band (CB) structures [57]. Under visible light irradiation, electrons in PMo are excited from the VB to the CB. The photogenerated electrons in the CB subsequently react with dissolved oxygen (O_2) adsorbed on the catalyst surface to generate superoxide radicals ($\text{O}_2\bullet^-$). Simultaneously, the photogenerated holes remaining in the VB interact with hydroxide ions (OH^-) or water molecules to produce highly reactive hydroxyl radicals ($\bullet\text{OH}$). These reactive oxygen species (ROS) play a dominant role in the oxidative degradation of methylene blue molecules adsorbed on the catalyst surface.

Furthermore, hydrogen peroxide (H_2O_2), employed as an initiator in the reaction system, serves as an effective electron acceptor and ROS promoter. H_2O_2 can react with both $\bullet\text{OH}$ and $\text{O}_2\bullet^-$ radicals to generate additional reactive oxygen species, thereby accelerating the photocatalytic degradation process and enhancing the overall reaction kinetics [58–60]. The synergistic effects of efficient light absorption, internal electric field-assisted charge separation, and abundant ROS generation collectively account for the outstanding visible-light photocatalytic activity of the PM-PCM.

In summary, the rational integration of PMo within the PCM nanofiber matrix not only improves light-harvesting capability but also facilitates charge carrier separation and transfer through electrostatic interactions. This synergistic mechanism under visible light irradiation endows the PM-PCM with superior photocatalytic performance, providing valuable insights for the design of advanced polymer-supported photocatalysts for environmental remediation.

3. Experiment

3.1. Materials and Methods

Polyacrylonitrile nanofiber (PAN NF, average molecular weight = 150,000) electrospun membranes were purchased from Fushun Petrochemical Company (Fushun, China). N,N-dimethylformamide (DMF), hydrogen peroxide (H_2O_2), propylenediamine, toluene, ethanol, phosphomolybdic acid (PMo), 1-bromobutane, methylene blue (MB), ethylene glycol, and acetone were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). All chemical reagents used in this study were of analytical grade and were used as received without further purification.

Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) to identify the chemical structures of the samples. The surface morphology and microstructure of the nanofiber membranes were observed using a scanning electron microscope (SEM, Hitachi S-4800, Hitachi Ltd., Tokyo, Japan). X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-2500 diffractometer (Rigaku Corporation, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) to analyze the crystalline structures of the materials.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI 5000 VersaProbe III system (Physical Electronics, Chanhassen, MN, USA) to determine the surface elemental composition and chemical states. UV–visible diffuse reflectance spectra (UV–vis DRS) were obtained on a UV–vis spectrophotometer (Shimadzu UV-2600,

Shimadzu Corporation, Kyoto, Japan) equipped with an integrating sphere, and BaSO₄ was used as the reflectance standard. Photocatalytic degradation experiments were conducted under visible light irradiation using a 300 W xenon lamp (CEL-HXF300, CEAULight, Beijing, China) with a 420 nm cutoff filter to eliminate ultraviolet light.

3.2. Sample Preparation

3.2.1. Sample Preparation for Pyridine-Containing Polymer Membrane (PVPy)

Polyacrylonitrile nanofiber (PAN NF) membranes (200 mg) were cut into small pieces and immersed in a mixed solution containing ethylene glycol (2 mL), propylenediamine (2 mL), N,N-dimethylformamide (DMF, 20 mL), and deionized water (20 mL). The reaction mixture was heated to 80 °C and maintained under a nitrogen atmosphere for 4 h to promote the cyclization reaction of the nitrile groups.

After completion of the reaction, the mixture was allowed to cool naturally to room temperature. The resulting modified membranes were thoroughly washed with deionized water and acetone three times to remove residual reagents and by-products. Finally, the membranes were dried in a vacuum oven at 60 °C for 8 h to obtain pyridine-functionalized poly(2-vinylpyridine) nanofiber membranes, denoted as PVPy.

3.2.2. Sample Preparation for Bromide-Based Polycationic Membrane (Br-PCM)

Pyridine-functionalized nanofiber membranes (PVPy NFs, 100 mg) were placed in a reaction flask containing N,N-dimethylformamide (DMF, 40 mL). Subsequently, 1 mL of 1-bromobutane was added to the system. The reaction mixture was heated to 80 °C and maintained at this temperature for 24 h to allow the quaternization reaction to proceed.

After completion of the reaction, the system was cooled naturally to room temperature. The resulting light-yellow membranes were collected and thoroughly washed with deionized water and ethanol three times to remove unreacted reagents and residual solvent. Finally, the membranes were dried in a vacuum oven at 60 °C for 8 h to obtain the bromide-containing polycationic membrane, denoted as Br-PCM.

3.2.3. Sample Preparation for PMo-Based Polycationic Membrane (PM-PCM)

Phosphomolybdic acid (PMo, 100 mg) and bromide-containing polycationic membrane (Br-PCM, 20 mg) were dispersed in deionized water (40 mL). The mixture was stirred at 60 °C for 4 h to complete the anion exchange process.

After the reaction, the resulting gray-green membranes were collected and washed thoroughly with deionized water three times to remove excess PMo and residual bromide ions. Subsequently, the membranes were dried in a vacuum oven at 60 °C for 8 h. The final product, a poly(1-butyl-2-vinylpyridinium) phosphomolybdate nanofiber membrane with PMo₁₂O₄₀^{3−} as the counter anion, was obtained and denoted as PM-PCM.

3.2.4. Sample Preparation for PM-PCM

The synthesis route of the PM-PCM is illustrated in Figure 1. Briefly, polyacrylonitrile (PAN) nanofiber membranes were first prepared by an electrospinning process. The nitrile groups in the PAN nanofibers were subsequently converted into pyridine functionalities through a cyclization reaction with propylenediamine, yielding pyridine-containing poly(2-vinylpyridine) nanofiber membranes, denoted as PVPy.

The obtained PVPy NF membranes were then subjected to a quaternization reaction with 1-bromobutane to generate bromide-based polycationic membrane (Br-PCM). Finally, an anion exchange reaction between Br-PCM and phosphomolybdic acid (PMo) was carried out to replace Br[−] with PMo₁₂O₄₀^{3−}, leading to the successful fabrication of PMo-based polycationic membrane, referred to as PM-PCM.

This stepwise modification strategy enables the retention of the nanofibrous membrane morphology while introducing ionic liquid functionalities and photocatalytically active PMo species, providing a robust platform for visible-light-driven photocatalytic applications.

3.3. Photocatalytic Degradation of Methylene Blue and Recycling Tests

The photocatalytic performance of the samples was evaluated by the visible-light-driven degradation of methylene blue (MB) in an aqueous solution. A 500 W xenon lamp (CHFXQ500W, Beijing Chengxin Technology Co., Ltd., Beijing, China) equipped with a 400 nm cutoff filter was used as the visible light source to eliminate ultraviolet irradiation. The light intensity was adjusted to 100 mW cm^{-2} .

The photocatalytic degradation experiments were carried out in an aqueous system. Typically, 20 mg of PM-PCM and 10 mL of hydrogen peroxide (H_2O_2) were added to 20 mL of MB aqueous solution with an initial concentration of 50 ppm. Prior to light irradiation, the suspension was magnetically stirred in the dark for 120 min to establish adsorption–desorption equilibrium. Subsequently, the reaction system was irradiated under visible light at room temperature for 2 h to initiate the photocatalytic degradation process.

For comparison, control experiments were performed under identical conditions without adding any photocatalyst or by using a physical mixture of PAN and PMo instead of PM-PCM. During the photocatalytic reaction, aliquots were withdrawn at regular intervals (every 20 min), and the residual concentration of MB was monitored by measuring the UV–vis absorption spectra of the solution.

In this study, the photocatalyst used is a freestanding nanofiber membrane rather than a powder catalyst. Therefore, for all photocatalytic degradation experiments, including the control tests, the same mass of catalyst material was used to ensure a fair comparison. Specifically, identical masses of the PM-PCM nanofiber membrane and the PAN/PMo control sample were employed in the visible-light-driven degradation experiments.

For the control experiment involving PAN/PMo, phosphomolybdic acid (PMo) was used as received in solid form and physically mixed with the PAN nanofiber membrane without chemical bonding or anion exchange. Under the experimental conditions, PMo is water-soluble and thus exists predominantly in the dissolved molecular/ionic state, rather than as a particulate suspension with a defined particle size. No deliberate control of PMo particle size or dispersion state was applied in the physical mixture, which reflects a simple, non-immobilized system.

The significantly lower photocatalytic activity observed for the PAN/PMo mixture, compared to the PM-PCM, demonstrates that the enhanced performance of PM-PCM does not arise merely from the presence of PMo, but from its effective immobilization and stabilization within the poly(ionic liquid) nanofiber matrix.

To investigate the recyclability of the supported photocatalyst, the PM-PCM was removed from the reaction system after each photocatalytic cycle, washed sequentially with deionized water and ethanol three times, and then dried in a vacuum oven at 60°C for 8 h. The regenerated membrane was reused for subsequent photocatalytic degradation experiments under the same conditions.

3.4. Characterization Methods

The surface morphology of the samples was examined using a scanning electron microscope (SEM, Hitachi S-4800, Hitachi Ltd., Tokyo, Japan) operated at an accelerating voltage of 15 kV. The UV–visible absorption spectra of liquid samples were recorded using a UV–vis spectrophotometer (TU-1901, Purkinje General Instrument Co., Ltd., Beijing, China).

The UV–vis diffuse reflectance spectra (DRS) of solid samples were obtained using a Shimadzu UV-2550 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) equipped with an integrating sphere, with BaSO₄ employed as the reflectance standard. The wavelength range for DRS measurements was set from 200 to 800 nm.

Fourier transform infrared (FT-IR) spectra were collected on a PerkinElmer Spectrum 1600 FT-IR spectrometer (PerkinElmer Inc., Waltham, MA, USA) to analyze the chemical structures of the samples. X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-2500 diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu K α radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 150 mA. The diffraction data were collected over a 2θ range of 5–90°.

The anion exchange degree and surface elemental composition of the samples were determined by X-ray photoelectron spectroscopy (XPS, ESCA MK II, Kratos Analytical Ltd., Manchester, UK). Photoluminescence (PL) spectra were recorded using a fluorescence spectrophotometer (FS5-TCSPC, Edinburgh Instruments Ltd., Livingston, UK) equipped with a 150 W ozone-free xenon lamp as the excitation source.

4. Conclusions

In summary, a robust, flexible, and recyclable PCM was successfully fabricated by sequential cyclization, quaternization, and anion exchange modification of low-cost polyacrylonitrile (PAN) nanofiber membranes. The resulting PM-PCM effectively immobilized polyoxometalate (POM) photocatalysts and was applied to visible-light-driven photocatalytic degradation reactions in aqueous systems.

The PM-PCM exhibited excellent photocatalytic performance, achieving a degradation efficiency of approximately 98% under visible light irradiation, while maintaining nearly unchanged catalytic activity after five consecutive recycling cycles. The outstanding stability and reusability of the membrane can be attributed to the strong electrostatic interactions between the negatively charged POM anions and the positively charged pyridinium groups within the PCM framework, as well as the freestanding nanofiber membrane structure that enables facile recovery without additional separation steps.

From an economic perspective, conventional PCMs are expensive, with market prices reaching approximately USD 150,000 per kilogram, whereas PAN is several orders of magnitude less costly. By using PAN as a precursor, the overall material cost is significantly reduced, making the proposed strategy economically attractive. Moreover, unlike powder-based photocatalysts that require energy-intensive centrifugation for recovery, the membrane-based photocatalyst offers a simple and efficient recycling process.

To the best of our knowledge, this work represents the first report on a PM-PCM photocatalyst. The low-cost, functionalized PCM developed in this study demonstrates strong potential for large-scale production and provides an economical and sustainable approach for visible-light-driven photocatalytic degradation. By utilizing solar energy as a clean and renewable light source, this photocatalytic membrane system offers a promising pathway toward environmentally friendly and sustainable processes. Future research will focus on the development of photocatalysts with enhanced visible-light activity and the expansion of their applications in environmental remediation and beyond.

Author Contributions: Material preparation, catalytic experiments and writing—original draft, Y.G.; writing—review and editing, X.Q. and J.Z. All authors have read and agreed to the published version of the manuscript.

Funding: The study was supported by the university-level team research project of Hainan Vocational University of Science and Technology in 2024, “Research on Polyionic Liquid Materials and Their Catalytic Properties (HKKY2024-TD-17)”; Hainan Province 2025 Higher Education Teaching Reform

Research Project: Research on the Ideological and Political Teaching Model of the “Principles of Chemical Engineering” Course Based on Target Problem-Oriented Approach (Hnjg2025ZC-127); Hainan Province 2025 Higher Education Scientific Research Project: Study on Polyionic Liquid Materials and Their Photocatalytic Performance (Hnky2025-66); and Research on Teaching Methods of Mechanical Manufacturing Courses under Informationization Conditions (HKJG2024-35). The Hainan University of Science and Technology Vocational College Innovation and Entrepreneurship Training Program for College Students also provided support (2025).

Data Availability Statement: The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

- Li, K.; Xu, L.; Bai, X.; Zhang, G.; Zhang, M.; Huang, Y. Potential environmental risks of field bio/non-degradable microplastic from mulching residues in farmland: Evidence from metagenomic analysis of plastisphere. *J. Hazard. Mater.* **2024**, *465*, 133428. [CrossRef] [PubMed]
- Wang, X.; Liu, H.; Chen, S.; Zhang, J.; Chen, S. In situ construction of covalent organic framework membranes on polyacrylonitrile nanofibers for carbon dioxide capture. *ACS Appl. Nano Mater.* **2024**, *7*, 10911–10920. [CrossRef]
- Töngüç Yalçinkaya, T.; Çay, A.; Akduman, Ç.; Kumbasar, E.P.A.; Yanık, J. Polyacrylonitrile and polyacrylonitrile/cellulose-based activated carbon nanofibers obtained from acrylic textile wastes for carbon dioxide capture. *J. Appl. Polym. Sci.* **2024**, *141*, e55475. [CrossRef]
- He, H.; Li, S.; Yang, X.; Xu, Y.; Du, W.; Ye, S.; Dong, H.; Zhao, X.; Yang, N.; Zhang, Y.; et al. Preparation of Cationic Polymer Nanofiber Adsorbents with Anionic Sites by Electrospinning for Efficient Recovery of Au (Iii): Adsorption Properties and Mechanism Studies. SSRN 5289786. Available online: <https://ssrn.com/abstract=5289786> (accessed on 26 January 2026).
- Mohammed, A.M.; Thalji, M.R.; Yasin, S.A.; Shim, J.-J.; Chong, K.F.; Guda, A.A.; Ali, G.A. Recent advances in electrospun fibrous membranes for effective chromium (VI) removal from water. *J. Mol. Liq.* **2023**, *383*, 122110. [CrossRef]
- Zhang, Y.; Niu, L.; Li, Z.; Yang, T.; Liu, Y.; Kang, Z. A recyclable ZnIn₂S₄/PAN photocatalytic nanofiber membrane for boosting visible light hydrogen evolution in seawater without cocatalyst. *Appl. Catal. B Environ. Energy* **2024**, *357*, 124300. [CrossRef]
- Singh, R.; Bhateria, R. Optimization and experimental design of the Pb²⁺ adsorption process on a nano-Fe₃O₄-based adsorbent using the response surface methodology. *ACS Omega* **2020**, *5*, 28305–28318. [CrossRef]
- Yang, S.-Y.; Lin, J.-Y.; Li, P.-R.; Hanh, N.T.D.; Srinophakun, P.; Liu, B.-L.; Chiu, C.-Y.; Ng, I.-S.; Chen, K.-H.; Chang, Y.-K. Functionalized polyacrylonitrile nanofiber membranes with carbonic anhydrase for enhanced carbon dioxide capture and conversion: A performance study. *Biochem. Eng. J.* **2025**, *213*, 109570. [CrossRef]
- Zhu, X.; Wu, Y.; Feng, S.; Zhao, X.; Xue, T.; Zhong, Z.; Zhong, J. Design and fabrication of gradient wettability PAN nanofiber membrane for enhanced liquid transport and efficient air purification. *Sep. Purif. Technol.* **2025**, *367*, 132938. [CrossRef]
- Wang, P.; Zheng, J.; Li, X.; Cui, W.; Liu, J.; Wan, Y.; Zhang, J.; Yamauchi, Y.; Wang, Z.; Niu, M.; et al. Carbon nanofiber catalysts containing high-entropy metal phosphides with low-content Ru for highly efficient hydrogen evolution reaction. *Rare Met.* **2025**, *44*, 324–335. [CrossRef]
- Qin, H.; Li, X.; Zhou, C.; Zhang, S.; Zhao, Y.; Zhang, M.; Guo, P.; Li, H.; Wang, R. Porous polyacrylonitrile nanofiber membranes modified with UiO-66-NH₂ nanosheets for excellent detoxification of nerve agent simulant. *Sep. Purif. Technol.* **2025**, *362*, 131721. [CrossRef]
- Wu, D.; Li, X.; Zhang, Y.; Alfred, M.; Yang, H.; Li, Z.; Huang, F.; Lv, P.; Feng, Q.; Wei, Q. Strong and robust cellulose-based enzymatic membrane with gradient porous structure in dynamically catalytic removal of sulfonamides antibiotics. *J. Hazard. Mater.* **2022**, *439*, 129676. [CrossRef]
- Ramalingam, G.; Arunkumar, P.; Alqahtani, M.D.; Elgarahy, A.M. Photocatalytic activity of microwave-assisted synthesized MoS₂/g-C₃N₄ composite for efficient decomposition of aniline green dye. *J. Clust. Sci.* **2025**, *36*, 171. [CrossRef]
- 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. *Polym. Adv. Technol.* **2021**, *32*, 1301–1316. [CrossRef]
- Hasanizadeh, M.; Aroujalian, A.; Raisi, A. Fabrication of PES/NaX nanocomposite nanofibrous adsorbent for the removal of Cu²⁺, Co²⁺ and Fe²⁺ from aqueous solutions. *Desalin. Water Treat.* **2017**, *78*, 221–230. [CrossRef]
- Koe, W.S.; Lee, J.W.; Chong, W.C.; Pang, Y.L.; Sim, L.C. An overview of photocatalytic degradation: Photocatalysts, mechanisms, and development of photocatalytic membrane. *Environ. Sci. Pollut. Res.* **2020**, *27*, 2522–2565. [CrossRef] [PubMed]

17. Porcu, S.; Secci, F.; Ricci, P.C. Advances in hybrid composites for photocatalytic applications: A review. *Molecules* **2022**, *27*, 6828. [[CrossRef](#)] [[PubMed](#)]
18. Chen, Q.; Li, S.; Xu, H.; Wang, G.; Qu, Y.; Zhu, P.; Wang, D. Co-MOF as an electron donor for promoting visible-light photoactivities of g-C₃N₄ nanosheets for CO₂ reduction. *Chin. J. Catal.* **2020**, *41*, 514–523. [[CrossRef](#)]
19. Xie, P.; Zhang, W.; Wu, W.; Shen, Z.; Wang, M.; Lai, Y.; Chen, Y.; Jia, Z. Phenoxyl mediators improve enzymatic degradation of organic pollutants: Effect and mechanism. *Int. J. Biol. Macromol.* **2022**, *215*, 606–614. [[CrossRef](#)] [[PubMed](#)]
20. Song, Y.-F.; Tsunashima, R. Recent advances on polyoxometalate-based molecular and composite materials. *Chem. Soc. Rev.* **2012**, *41*, 7384–7402. [[CrossRef](#)]
21. Shi, H.; Yu, Y.; Zhang, Y.; Feng, X.; Zhao, X.; Tan, H.; Khan, S.U.; Li, Y.; Wang, E. Polyoxometalate/TiO₂/Ag composite nanofibers with enhanced photocatalytic performance under visible light. *Appl. Catal. B Environ.* **2018**, *221*, 280–289. [[CrossRef](#)]
22. Wu, Y.; Wang, Y.; Chen, R.; Xu, J.; Zhang, H.; Ding, Y.; Li, B.; Dong, S.; Dou, S.; Zhang, X.; et al. On-site catalytic wastewater remediation by sustainably produced H₂O₂ via scalable single-atomic Fe-incorporated Janus membrane. *Appl. Catal. B Environ.* **2024**, *343*, 123533. [[CrossRef](#)]
23. Zhang, H.; Mane, A.U.; Yang, X.; Xia, Z.; Barry, E.F.; Luo, J.; Wan, Y.; Elam, J.W.; Darling, S.B. Visible-light-activated photocatalytic films toward self-cleaning membranes. *Adv. Funct. Mater.* **2020**, *30*, 2002847. [[CrossRef](#)]
24. Chakraborty, S.; Loutatidou, S.; Palmisano, G.; Kujawa, J.; Mavukkandy, M.O.; Al-Gharabli, S.; Curcio, E.; Arafat, H.A. Photocatalytic hollow fiber membranes for the degradation of pharmaceutical compounds in wastewater. *J. Environ. Chem. Eng.* **2017**, *5*, 5014–5024. [[CrossRef](#)]
25. Zhang, X.; Wang, D.K.; da Costa, J.C.D. Recent progresses on fabrication of photocatalytic membranes for water treatment. *Catal. Today* **2014**, *230*, 47–54. [[CrossRef](#)]
26. Kotobuki, M.; Gu, Q.; Zhang, L.; Wang, J. Ceramic-polymer composite membranes for water and wastewater treatment: Bridging the big gap between ceramics and polymers. *Molecules* **2021**, *26*, 3331. [[CrossRef](#)] [[PubMed](#)]
27. Ren, S.; Boo, C.; Guo, N.; Wang, S.-G.; Elimelech, M.; Wang, Y. Photocatalytic reactive ultrafiltration membrane for removal of antibiotic resistant bacteria and antibiotic resistance genes from wastewater effluent. *Environ. Sci. Technol.* **2018**, *52*, 8666–8673. [[CrossRef](#)]
28. Karimi, B.; Habibi, M.H.; Naghiha, R. *Synthesis, Characterization and Biological Properties of Fe₂Ti₃O₉ Nanoparticles: Antimicrobial Activity and DNA Cleavage Ability*; SSRN: Rochester, NY, USA, 2020.
29. Spoială, A.; Ilie, C.-I.; Dolete, G.; Petrișor, G.; Trușcă, R.-D.; Motelica, L.; Fica, D.; Fica, A.; Oprea, O.-C.; Dițu, M.-L. The development of alginate/Ag NPs/Caffeic acid composite membranes as adsorbents for water purification. *Membranes* **2023**, *13*, 591. [[CrossRef](#)]
30. Ren, S.; Guo, N.; Li, J.; Wang, Y. Integration of antibacterial and photocatalysis onto polyethersulfone membrane for fouling mitigation and contaminant degradation. *J. Environ. Chem. Eng.* **2023**, *11*, 110401. [[CrossRef](#)]
31. Song, Y.; Li, Y.; Chen, X.; Meng, C.; Ma, S.; Li, T.; Jiang, K.; Hu, C. Simultaneous degradation and separation of antibiotics in sewage effluent by photocatalytic nanofiltration membrane in a continuous dynamic process. *Water Res.* **2023**, *229*, 119460. [[CrossRef](#)]
32. Molinari, R.; Argurio, P.; Szymański, K.; Darowna, D.; Mozia, S. Photocatalytic membrane reactors for wastewater treatment. In *Current Trends and Future Developments on (Bio-) Membranes*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 83–116.
33. Kojabad, E. PEBA Mixed Matrix Membranes Containing 2D Macroporous FeTiO₂ Sheets for the Separation of CO₂. *Iran. Chem. Eng. J.* **2025**, *24*, 34–47.
34. Zhang, Q.; Chen, S.; Fan, X.; Zhang, H.; Yu, H.; Quan, X. A multifunctional graphene-based nanofiltration membrane under photo-assistance for enhanced water treatment based on layer-by-layer sieving. *Appl. Catal. B Environ.* **2018**, *224*, 204–213. [[CrossRef](#)]
35. Zhang, H.; Wan, Y.; Luo, J.; Darling, S.B. Drawing on membrane photocatalysis for fouling mitigation. *ACS Appl. Mater. Interfaces* **2021**, *13*, 14844–14865. [[CrossRef](#)] [[PubMed](#)]
36. Baig, U.; Matin, A.; Gondal, M.; Zubair, S. Facile fabrication of superhydrophobic, superoleophilic photocatalytic membrane for efficient oil-water separation and removal of hazardous organic pollutants. *J. Clean. Prod.* **2019**, *208*, 904–915. [[CrossRef](#)]
37. Li, C.; Sun, W.; Lu, Z.; Ao, X.; Li, S.; Wang, Z.; Qi, F.; Ismailova, O. Contribution of filtration and photocatalysis to DOM removal and fouling mechanism during in-situ UV-LED photocatalytic ceramic membrane process. *Water Res.* **2022**, *226*, 119298. [[CrossRef](#)] [[PubMed](#)]
38. Gao, Y.; Yan, N.; Jiang, C.; Xu, C.; Yu, S.; Liang, P.; Zhang, X.; Liang, S.; Huang, X. Filtration-enhanced highly efficient photocatalytic degradation with a novel electrospun rGO@TiO₂ nanofibrous membrane: Implication for improving photocatalytic efficiency. *Appl. Catal. B: Environ.* **2020**, *268*, 118737. [[CrossRef](#)]
39. Abdullah, N.; Ayodele, B.V.; Mansor, W.N.W.; Abdullah, S. Effect of incorporating TiO₂ photocatalyst in PVDF hollow fibre membrane for photo-assisted degradation of methylene blue. *Bull. Chem. React. Eng. Catal.* **2018**, *13*, 588–591. [[CrossRef](#)]

40. Chen, Q.; Yu, Z.; Li, F.; Yang, Y.; Pan, Y.; Peng, Y.; Yang, X.; Zeng, G. A novel photocatalytic membrane decorated with RGO-Ag-TiO₂ for dye degradation and oil–water emulsion separation. *J. Chem. Technol. Biotechnol.* **2018**, *93*, 761–775. [\[CrossRef\]](#)
41. Li, S.; Zhang, L.; Yin, X.; Wang, Y.; Guo, X.; He, Y. Efficient photocatalysis improves the self-cleaning property of the superwetting nanofibrous membrane toward emulsified oily wastewater. *J. Membr. Sci.* **2022**, *650*, 120440. [\[CrossRef\]](#)
42. Xu, Y.; Chiam, S.L.; Leo, C.P.; Hu, Z. Recent Advances in Photocatalytic TiO₂-based Membranes for Eliminating Water Pollutants. *Sep. Purif. Rev.* **2025**, 1–18. [\[CrossRef\]](#)
43. Guo, T.; Fan, X.; Jiang, X.; Qi, Y.; Du, J.; Zhang, A.; Wang, H. Engineering shape of BiOCl nanosheets with improved visible-light response for superior photocatalytic degradation of Rhodamine B. *J. Alloys Compd.* **2023**, *948*, 169586. [\[CrossRef\]](#)
44. Wang, X.; Li, S.; Chen, P.; Li, F.; Hu, X.; Hua, T. Photocatalytic and antifouling properties of TiO₂-based photocatalytic membranes. *Mater. Today Chem.* **2022**, *23*, 100650. [\[CrossRef\]](#)
45. Formo, E.; Yavuz, M.S.; Lee, E.P.; Lane, L.; Xia, Y. Functionalization of electrospun ceramic nanofibre membranes with noble-metal nanostructures for catalytic applications. *J. Mater. Chem.* **2009**, *19*, 3878–3882. [\[CrossRef\]](#)
46. Wang, X.; Huang, W.; Fu, L.; Sun, X.; Zhong, J.; Dong, S.; Zhu, J. Preparation of superhydrophilic/underwater superoleophobic membranes for separating oil-in-water emulsion: Mechanism, progress, and perspective. *J. Coat. Technol. Res.* **2021**, *18*, 285–310. [\[CrossRef\]](#)
47. Xue, G.; Dai, Q.; Jiang, S. Chemical Reactions of Imidazole with Metallic Silver Studied by the Use of SERS and XPS Techniques. *J. Am. Chem. Soc.* **1988**, *110*, 2393–2395. [\[CrossRef\]](#)
48. Shen, X.; Zhang, Y.; Shi, Z.; Shan, S.; Liu, J.; Zhang, L. Construction of C₃N₄/CdS nanojunctions on carbon fiber cloth as a filter-membrane-shaped photocatalyst for degrading flowing wastewater. *J. Alloys Compd.* **2021**, *851*, 156743. [\[CrossRef\]](#)
49. Samadi, M.; Moshfegh, A.Z. Recent developments of electrospinning-based photocatalysts in degradation of organic pollutants: Principles and strategies. *ACS Omega* **2022**, *7*, 45867–45881. [\[CrossRef\]](#)
50. Chen, C.; Fei, L.; Wang, B.; Xu, J.; Li, B.; Shen, L.; Lin, H. MOF-based photocatalytic membrane for water purification: A review. *Small* **2024**, *20*, 2305066. [\[CrossRef\]](#)
51. Keggin, J.F. The Structure and Formula of 12-Phosphotungstic Acid. *Proc. R. Soc. Lond. Ser. A* **1933**, *144*, 75–100. [\[CrossRef\]](#)
52. Matsumoto, H.; Tanioka, A. Functionality in electrospun nanofibrous membranes based on fiber's size, surface area, and molecular orientation. *Membranes* **2011**, *1*, 249–264. [\[CrossRef\]](#)
53. Gao, Y.; Meng, Q.-B.; Wang, B.-X.; Zhang, Y.; Mao, H.; Fang, D.-W.; Song, X.-M. Polyacrylonitrile Derived Robust and Flexible Poly(ionic liquid)s Nanofiber Membrane as Catalyst Supporter. *Catalysts* **2022**, *12*, 266. [\[CrossRef\]](#)
54. Cao, T.; Gao, Y.; Xia, W.; Qi, X. Preparation of Bi@Ho³⁺:TiO₂/Composite Fiber Photocatalytic Materials and Hydrogen Production via Visible Light Decomposition of Water. *Catalysts* **2024**, *14*, 588. [\[CrossRef\]](#)
55. Gao, Y.; Cao, T.; Du, J.; Qi, X.; Yan, H.; Xu, X. The Bi-Modified (BiO)₂CO₃/TiO₂ Heterojunction Enhances the Photocatalytic Degradation of Antibiotics. *Catalysts* **2025**, *15*, 56. [\[CrossRef\]](#)
56. Gao, Y.; Feng, T.; Qi, X.; Yan, H.; Du, J.; Zhang, Y.; Zhang, J. Vacuum-Treated Brown Mesoporous TiO₂ Nanospheres with Tailored Defect Structures for Enhanced Photoresponsive Properties. *Molecules* **2025**, *30*, 4746. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Wang, H.; Li, X.; Zhao, X.; Li, C.; Song, X.; Zhang, P.; Huo, P. A review on heterogeneous photocatalysis for environmental remediation: From semiconductors to modification strategies. *Chin. J. Catal.* **2022**, *43*, 178–214. [\[CrossRef\]](#)
58. Gao, Y.; Li, N.; Qi, X.; Zhou, F.; Yan, H.; He, D.; Xia, W.; Zhang, Y. A Dual Photoelectrode System for Solar-Driven Saltwater Electrolysis: Simultaneous Production of Chlorine and Hydrogen. *Crystals* **2025**, *15*, 233. [\[CrossRef\]](#)
59. Yu, K.; Yang, S.; He, H.; Sun, C.; Gu, C.; Ju, Y. Visible light-driven photocatalytic degradation of rhodamine B over NaBiO₃: Pathways and mechanism. *J. Phys. Chem. A* **2009**, *113*, 10024–10032. [\[CrossRef\]](#)
60. Lan, J.; Wang, Y.; Huang, B.; Xiao, Z.; Wu, P. Application of polyoxometalates in photocatalytic degradation of organic pollutants. *Nanoscale Adv.* **2021**, *3*, 4646–4658. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.