In-situ preparation of MIL-88A(Fe)/MIL-100(Fe)/PVA-Co-PE nanofiber membranes for efficient photocatalytic reduction of CO₂

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Abstract: In this paper, we tend to ready a polyvinyl alcohol-polyethylene (PVA-Co-PE) composite nanofiber membrane catalyst decorated by bimetallic organic framework MIL-100(Fe)/MIL-88A(Fe). The experimental results of the performance of photocatalytic reduction of CO₂ show that it exhibits glorious photocatalytic activity for the reduction of CO₂ underneath actinic ray irradiation, and also the best conversion rate of CO₂ is 8.3 mL/h. Through SEM, XRD, BET, DRS, FTIR, and alternative characterization ways, the factors touching the photocatalytic CO₂ reduction method of the composite nanofiber membrane were investigated. Studies have found that the bimetallic framework structure increases the photocurrent density and significantly reduces the photoluminescence intensity. The versatile composite nanofiber membrane has high photocatalytic activity and smart reusability and features a smart prospect within the photocatalytic reduction of CO₂ treatment.

1. Introduction
Using alternative energy to convert dioxide into the valuable organic product is one among the most effective solutions to the issues of worldwide warming and energy shortages¹. So far, numerous photocatalysts principally embody inorganic semiconductors², metal-bound zeolites³, and homogeneous transition metals⁴, and area units largely restricted to valuable catalysts. Therefore, it's of nice significance to develop effective photocatalysts composed of cheap transition metals. Metal-organic frameworks (MOFs) area units a kind of three-dimensional crystalline porous hybrid material composed of metal clusters interconnected by multiple clusters of organic linkers⁵. Their unique large surface area⁶, uniform⁷ but tunable cavity⁸, and adjustable chemical properties make them have unparalleled advantages and application scope in the field of photocatalytic CO₂ reduction⁹. though most inorganic catalysts exhibit high stability throughout the reaction, these materials area unit comparatively inert in terms of chemical reactivity and photogenerated charge carriers¹⁰⁻¹⁶. For molecular complexes, the situation will have higher activity¹⁷⁻¹⁹.

Nanofibers are often used to fix metal nanoparticles through chemical modification and have the advantage of being easily functionalized to support metal nanoparticles²⁰⁻²³. The combination of photocatalyst and nanofiber materials to form a hybrid membrane is a good way to recover photocatalysis. The advantages of nanoparticle immobilization on fiber support are as follows: (1) the expensive separation steps are avoided; (2) the self-cleaning performance of membrane substrate is given; (3) the synergistic effect of membrane separation and photocatalytic reaction²⁴⁻²⁶. Recently, our
cluster has developed a straightforward technique to arrange PVA-Co-PE nanofibers. Cellulose acetate butyrate (CAB) as an insoluble matrix can be used to prepare nanofiber materials on a large scale by co-rotating twin-screw extrusion equipment. The structure and properties of the support and also the interface between the nanoparticles and also the support material play an important role in promoting its chemical process performance. During this paper, through the mutual attraction of the electricity interaction between the metal-organic frameworks, MIL-100(Fe)/MIL-88A(Fe) was with success obtained and loaded on the active PVA-Co-PE film. Through the photocatalytic reduction of carbon dioxide performance experiment, the interface mechanism is explained.

2. Experiment section

2.1. Synthesis of MIL-88A(Fe), MIL-100(Fe), and MIL-100(Fe)/MIL-88A(Fe)

According to the literature, MIL-88A (Fe) and MIL-100 (Fe) were prepared. Disperse 0.5 g of MIL-88A (Fe) prepared in 100 mL of deionized water under ultrasonic conditions. The MIL-88A (Fe) suspension and 0.25 g of MIL-100 (Fe) were stirred for 48 hours under room temperature. The supernatant was removed by filtration, and also the residual product was washed with deionized water 3 times then dried at 60°C for eight hours to get a MIL-100 (Fe)/MIL-88A (Fe) powder.

2.2. Synthesis of PVA-Co-PE nanofiber suspension (PCP) and composite nanofiber membrane (MOFs/PCP)

PVA-Co-PE nanofibers were ready in keeping with the strategy within the literature. Then weigh 15 g of the nanofiber membrane and dissolve it in 500 mL of isopropanol and deionized aqueous solution with a volume ratio of 1:1, and the nanofibers were dispersed in the aqueous solution using a high-speed shear mixer to form a stable suspension.

Take 20 mL of the prepared PVA-Co-PE nanofiber suspension, mix three different mass doping ratios (1/5, 1/6, 1/7) of MIL-100(Fe)/MIL-88A(Fe) powders and disperse them in the fully dissolved solution to reach equilibrium, and perform ultrasonication for 30 min. The membrane obtained by suction filtration of the solution was dried in an oven at 40°C overnight to obtain a MIL-100(Fe)/MIL-88A(Fe)/PVA-Co-PE composite nanofiber membrane.

2.3. Characterization of the catalyst

The surface morphology was characterised by the Hitachi S-4800 scanning microscope (SEM) instrument (Hitachi Ltd., Japan). The X-ray powder diffraction (XRD) pattern was obtained on the Bruker D8 powder X-ray diffractometer (Cu Kα radiation, 40 kV, 40 mA, λ = 0.15406 nm). A Fourier rework infrared spectroscope (Nicolet 6700) was used for Fourier rework infrared (FT-IR) chemical analysis. The Brunauer-Emmett-Teller (BET) area was obtained by the N2 adsorption-desorption isotherm measured on the 3H-2000PM2 surface area analyzer at 77 K. The optical performance of the photocatalyst was tested by mensuration the ultraviolet radiation-visible diffuse reflection factor spectrum (Shimadzu UV 2700). Use Guangdong analytical instrument F-380 spectrophotometer to analyze the photoluminescence (PL) spectrum, the excitation wavelength is 500 nm.
3. Results and discussion

3.1. Photocatalytic performance experiment

![Photocatalytic CO₂ performance experiment of MOFs/PCP-x (x=1/5, 1/6, 1/7)](Figure 1)

Figure 1 shows the yield of CO₂ photoreduction of MIL-100/88A (Fe) nanofiber membranes doped in different proportions below light irradiation. When the added amount of MIL-100/88A (Fe) increases from 1/7wt% to 1/6wt%, the CO₂ conversion rate reaches the maximum. This shows that the appropriate amount of MIL-100/88A (Fe) is provided to fully couple with the nanofiber membrane, and the interface interaction is best at this time. When the amount of MIL-100/88A (Fe) added was further increased to 1/5wt%, the conversion rate dropped rapidly. Excessive MIL-100/88A (Fe) clogged the pores and hindered the CO₂ adsorption process.

3.2. SEM

![SEM images of MIL-100/88A (Fe) and MOFs/PCP (1:6)](Figure 2)

Figure 2. SEM images of MIL-100/88A (Fe) (a) and MOFs/PCP (1:6)

MIL-88A (Fe) has a good crystalline rod-like structure according to Figure 2a, MIL-100 (Fe) shows a granular morphology, and MIL-88A (Fe) particles are MIL-100 (Fe) surface support. MIL-88A (Fe) particles are fixed to the surface of MIL-100 (Fe) via a fixed layer. this is often in keeping with the results of the XRD pattern. From Figure 2b, we can see that the composite nanofiber membrane shows a network-like fiber morphology, the fibers are randomly distributed, and there is a porous structure inside. When MIL-100/88A (Fe) is fixed to the fiber matrix, the surface of the nanofibers appears to be wrinkled.
3.3. XRD

Figure 3. XRD patterns of MIL-100 (Fe), MIL-88A (Fe), and MIL-100/88A (Fe) (a), MIL-100 / 88A (Fe) and PCP and MOFs/PCP (b)

Figure 3a shows the XRD patterns of MIL-100(Fe), MIL-88A(Fe), and MIL-100/88A (Fe). The results show that MIL-88A (Fe) shows four major peaks at 2θ = 8.2 °, 10.4 °, 12.9 °, and 20.8 °. MIL-100 (Fe) shows seven main peaks at 2θ = 6.46 °, 11.1 °, 14.3 °, 18.3 °, 20.1 °, 24.2 °, and 27.7 °, which are consistent with those reported in the literature. During the preparation of MIL-100/88A (Fe), MIL-100/88A (Fe) retains the characteristic peaks of the two iron-based metal-organic frameworks. The electrostatic interaction between MIL-100 (Fe) and MIL-88A (Fe) reduces the intensity of the characteristic peaks to some extent. Figure 3b shows the XRD pattern of MIL-100/88A (Fe) and PVA-Co-PE nanofiber membranes and composite fiber membranes. Pure PVA-Co-PE has a characteristic diffraction peak at 2θ = 20.8 °, and the composite nanofiber membrane has five characteristic diffraction peaks at 2θ = 11.1 °, 14.3 °, 20.8 °, 24.2 °, 27.7 °. The intensity of the characteristic peak is reduced to a certain extent due to the interface effect between MIL-100/88A (Fe) and PVA-Co-PE.

3.4. FTIR

Figure 4. FTIR spectra of MIL-100 (Fe), MIL-88A (Fe), and MIL-100 / 88A (Fe) (a), MOFs/PCP-x (x=1/5, 1/6, 1/7) (b)

The FTIR spectrum in Figure 4a detects the vibration of the C=O cluster at the peaks of 1605 and 1399 cm⁻¹. The characteristic peaks at 1220 and 571 cm⁻¹ correspond to the tensile vibrations of C-C and Fe-O, respectively. The enhanced CO₂ reduction effect is mainly that Fe-O clusters will directly absorb actinic ray and transfer electrons. The direct excitation of Fe-O clusters in the iron-based metal-organic framework causes electrons to transfer from O²⁻ to Fe³⁺ to form Fe²⁺, that is the key to photocatalytic CO₂ reduction. Figure 4b tests the infrared analysis spectra of three composite nanofiber membranes doped at different ratios (1: 7, 1: 6, 1: 5), 3200 cm⁻¹ to 3500 cm⁻¹, and 2800 cm⁻¹ to 2900 cm⁻¹. The peak represents the hydroxyl association peak and the methylene expansion and contraction vibration peak, respectively. Compound ring oscillation peaks seem at 1505 cm⁻¹ and 1542 cm⁻¹. The results show that MIL-100/88(A)Fe was with success loaded onto the surface of the nanofiber membrane.
3.5. BET

Figure 5. N\textsubscript{2} adsorption−desorption isotherm of (a) 100Fe/88A; (b) PCP; and (c) MOFs/PCP(1:6) and corresponding BJH PSD curves (inset).

Table 1. Textural Properties of 100Fe/88A, PCP, and MOFs/PCP(1:6)

| sample               | \(S_{\text{BET}}\) (m\textsuperscript{2}g\textsuperscript{-1}) | \(V_{\text{total}}\) (cm\textsuperscript{3}g\textsuperscript{-1}) | \(D\) (nm) |
|----------------------|-------------------------------------------------|-------------------------------------------------|-------------|
| MIL-100/88A(Fe)      | 207.6                                           | 0.1388                                          | 2.6748      |
| PCP                  | 2.3                                            | 0.0234                                          | 40.1109     |
| MOFs/PCP             | 50.2                                           | 0.0558                                          | 4.4485      |

Figure 5 shows the N\textsubscript{2} adsorption and desorption isotherms of MIL-100/88A(Fe), nanofiber membranes, and composite nanofiber membranes. When combined with the pore size distribution map within the figure, the pore size of the nanofiber composite membrane changes significantly compared to the pure nanofiber membrane, exposing more surface active sites, which improves photocatalytic capacity. The table shows the test parameters such as MIL-100/88A(Fe), nanofiber membrane, specific surface area (\(S_{\text{BET}}\)) of composite nanofiber membrane, total pore volume (\(V_{\text{total}}\)), and average pore diameter (D). Increasing the adsorption capacity also helps to improve the conversion efficiency of photocatalytic CO\textsubscript{2} reduction. The large BET and high surface assimilation performance of this new catalyst area unit thanks to MIL-100/88A(Fe). The Fe\textsuperscript{3+} species in MIL-100/88A(Fe) can even be used as dioxide surface assimilation sites and photoexcited electron capture sites, and the improved CO\textsubscript{2} adsorption function can accelerate the photocatalytic process.

3.6. DRS

Figure 5 (a) and (b)
Figure 6. DRS spectra of 100Fe/88A, PCP, MOFs/PCP(1:6) and; (b-d) plots of $(\alpha h\nu)^{1/2}$ as a function of vs. photon energy of 100Fe/88A, PCP, MOFs/PCP(1:6)

Figure 6 shows that MIL-100/88A(Fe), PVA-Co-PE, and MOFs/PCP all have high visible light absorption. Compared to nanoparticle samples, the light absorption of composite nanofiber membranes is significantly increased. Besides, a redshift at the absorption edge was observed on the composite nanofiber membrane. These data further indicate that Fe, C, and O were successfully doped into the crystal structure of the nanofiber membrane, which is in step with the XRD data. The bandgap of the composite nanofiber membrane calculated by the Kubelka-Munk technique is 1.68 eV, that is under the bandgap of the nanoparticle sample (2.18 eV). This distinction is because of the surface interaction between the nanoparticles MIL-100/88A(Fe) and the nanofiber membrane, which affects the band structure of the new composite. The slim bandgap of the composite nanofiber membrane facilitates the light absorption process. Interfacial interactions between composite nanofiber membranes give effective channels for fast charge transfer throughout chemical science reactions, absorbing light and transferring electrons from organic linkers to Fe-O clusters.

3.7. PL

Figure 7. Photoluminescence spectra of 100Fe/88A, PCP and MOFs/PCP(1:5,1:6,1:7)

As shown in Figure 7, the PL spectra of the composite nanofiber membrane showed similar peaks at completely different intensities. The emission peak at 503 nm was determined by photoexcitation at 500 nm, demonstrating the recombination of light-excited electron-hole pairs. Compared to the nanoparticles MIL-100/88A(Fe) and nanofiber membrane samples, the emission peak intensity of the composite nanofiber membrane is weaker, and the interfacial interaction between the two is beneficial for improving photo separation efficiency. The PL results of different proportions of nanoparticles also show that an appropriate MIL-100/88A(Fe) content (1:6) can achieve the best ability to inhibit photo-generated carrier recombination, that is additionally in line with the results of the photocatalytic performance experiment consistent.
4. Conclusion
1) Iron-based organometallic framework composite nanofiber membrane photocatalysts were ready by unmoven chemical action. The MOFs/PCP (1:6) composite film showed the best photocatalytic performance, with a CO production rate of 8.3 mL/h. The CO production rate increased 4 to 8 times compared to the samples of other ratios. At the same time, it solves the difficult problems of photocatalyst recovery and secondary contamination.

2) According to the results of XRD, SEM, BET, DRS, PL, FTIR, after doping with MIL-100(Fe)/88A(Fe), the light absorption range of the pure nanofiber membrane becomes wider and the bandgap is significantly reduced, which indicates that the nanoparticle doping facilitates the separation of the sub-carriers.

3) Iron-based metal-organic framework film has high photocatalytic activity. The solvent-free approach can produce gas-solid interface reactions, which can increase the possibility of contact between the catalyst and the reaction gas. Interfacial interactions between composite nanofiber membranes also can absorb lightweight and transfer electrons from organic links to Fe-O clusters manufacture Fe^{2+} to reduce carbon dioxide.

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