Zeolitic Imidazole Framework/Graphene Oxide Hybrid Functionalized Poly(lactic acid) Electrospun Membranes: A Promising Environmentally Friendly Water Treatment Material

Xiu Dai, Xu Li, Mi Zhang, Jiong Xie, and Xinlong Wang

School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, China

ABSTRACT: Poly(lactic acid) (PLA) electrospun membranes immobilized with Zeolitic imidazole framework/graphene oxide hybrid (ZIF-8@GO) are fabricated via electrospinning. At first, ZIF-8@GO is synthesized by the in situ growth method. The UV-visible light (UV-vis) result demonstrates that ZIF-8@GO has a narrower band gap than ZIF-8. The performance of the obtained composite membrane is investigated by scanning electron microscope, Fourier transform IR spectroscopy, tensile test, water contact angle, and methylene blue (MB) removal test. The results demonstrate that the degradable PLA/ZIF-8@GO electrospun membrane shows enhanced tensile strength than neat PLA. The composite membrane also shows great MB removal ability by adsorption and photocatalytic degradation. The MB removal efficiency could reach over 90% at very low ZIF-8@GO concentration (0.06 mg/mL).

1. INTRODUCTION

Water pollution is always a serious international problem which needs much technological concern. The dyes comprising a great portion in those industrial contaminants in wastewater effluents are highly toxic, affecting human health. A variety of methodologies, such as ion exchange, physical adsorption, chemical precipitation, bioremoval, and photocatalytic degradation, have been developed to remove dyes from water.1-3 Among these methods, photocatalytic degradation is one of the most effective and environmentally friendly processes for the removal of dyes.6,7 Electrospinning is a simple, versatile, and low-cost technique. This technique enables the production of membranes with a high surface area to volume ratio, large porosity, and uniform fiber diameter.8,9 The electrospun membranes have been widely used in the water treatment because of their good adsorption ability as well as the easy immobilization of the nano photocatalysts onto them.10,11 Because the photocatalysts are the most critical factor in the photocatalytic degradation of dyes by the electrospun membranes, a lot of photocatalysts have been used to prepare the electrospun membranes with photocatalytic ability. Almeida et al. prepared the poly(vinylidene difluoride-co-trifluoroethylene) fibrous membranes decorated with TiO2/graphene oxide (GO).12 They found that the porous structure and the high specific surface area of the electrospun samples as well as the advantageous electrical and structural properties of GO promote the photocatalytic performance. Metal–organic frameworks (MOFs) have been studied for applications in photocatalysis, adsorption of organic pollutants, and water treatment owing to their ultrahigh porosity, surface area, and chemical functionalities.13-15 Many studies showed that the graphene (GR) and GO have positive effects on the photocatalytic activity of the catalyst.16-18 Song et al.19 constructed plasmonic Ag/Ag2CO3–rGO photocatalysts for the photocatalytic oxidation of pollutants. They found that graphitic structures reduced the recombination rate of photogenerated electrons and holes. The hybrids of nano-MOFs and GO hybrid nanocomposites combine the unique advantage of MOFs and GR or GO.20,21 It has been found that they showed good CO2 uptake, enhanced activity for the photo-reduction of CO2 and hydrogen selectivity, but their photocatalytic active property for dyes has not been reported. Among the utilized polymers in electrospun membranes, poly(lactic acid) (PLA) is more environmentally friendly because it is biodegradable and its raw materials are...
Zeolitic imidazole framework (ZIF-8) as a stable and easy prepared MOFs, has been used as a photocatalyst to decompose methylene blue (MB) under UV light irradiation. Therefore, we report an attempt for the fabrication of PLA/ZIF-8@GO composite nano fibers via a simple electrospinning technique based on the advantages of electrospun membrane, PLA, ZIF-8, and GO. The adsorption capacity and photocatalytic activity for MB of the prepared composite nanofibers were studied. The PLA/ZIF@GO membrane exhibited perfect adsorption capacity and photocatalytic efficacy for MB.

2. RESULTS AND DISCUSSION

2.1. Characterization of ZIF-8@GO. The transmission electron microscopy (TEM) images of ZIF-8@GO are shown in Figure 1a. It is obvious that a great number of ZIF-8 nanoparticles have grown on the surface of the exfoliated GO sheets to fabricate the ZIF-8@GO nanosheets. Figure 1b displays the C 1s X-ray photoelectron spectroscopy (XPS) spectra of ZIF-8@GO. The peaks at 292.2, 287.8, 285.8, and 284.5 eV belong to C═N bond, C═O bond, C═O/C═N bonds, and C–C bond, respectively. The C═O and C–O bonds are the characteristic bands of GO. The inset in Figure 1b demonstrates that the contents of C, O, N, and Zn in ZIF-8@GO are 63.5, 17.5, 14.8, and 4.4%, respectively. The XPS results further demonstrate that ZIF-8 nanoparticles have been effectively loaded on the GO sheets. Figure 1c shows the X-ray diffraction (XRD) patterns of ZIF-8, GO, and ZIF-8@GO. The XRD pattern of ZIF-8@GO shows the same diffraction peaks as ZIF-8. The (001) reflection of GO is absent because ZIF-8 has destroyed the regular stack of GO. The UV–vis spectra of ZIF-8 and ZIF-8@GO composite are displayed in Figure 1d. The absorption band at 215 nm for ZIF-8 shifts to 217 nm in the spectrum of ZIF-8@GO, which could be the result of energy or charge transfer interaction between ZIF-8 nanoparticles and GO sheets. This further indicates the existence of the interaction between ZIF-8 and GO. The absorption intensity of ZIF-8@GO is higher than that of ZIF-8. The increased intensity of ZIF-8@GO in the visible light region may due to the charge transfer from the valence band to the conduction band. The band gap energy of ZIF-8 and ZIF-8@GO can be determined by the following Eq

![Figure 1](image1.png)

![Figure 2](image2.png)
where $\alpha$, $h$, $\nu$, $A$, and $E_g$ represent absorbance, the Planck constant, light frequency, proportionality constant, and band gap energy, respectively. From the plot of $(ah\nu)^0.5$ versus $h\nu$ (Figure 1d inset), the band gaps of ZIF-8 and ZIF-8@GO are estimated to be 4.87 and 4.73 eV, respectively. ZIF-8@GO has a narrower band gap than ZIF-8.

Textural characterization was carried out by measuring the $N_2$ adsorption isotherms at 77.5 K. Figure S1 in the Supporting Information shows the $N_2$ adsorption—desorption isotherms of ZIF-8 and ZIF-8@GO and the pore size distribution from Barrett—Joyner—Halenda (BJH) calculation based on the adsorption branch of the corresponding isotherm. Table S1 in the Supporting Information lists the summary of textural properties (BET surface area, total pore volume, and average pore size). As calculated by the isothermals, the specific surface areas (BET method) of ZIF-8 and ZIF-8@GO are 1185.2 and 587.4 m$^2$/g, respectively. The decrease in the specific surface area results from the nonporous nature of GO. It can be seen in Figure S1b that ZIF-8 and ZIF-8@GO show similar pore size distribution. Table S1 shows that the total pore volume and pore size of ZIF-8@GO (0.38 cm$^3$/g and 13.4 nm) are lower than that of ZIF-8 (0.61 cm$^3$/g and 16.6 nm).

### 2.2. Morphology of PLA/ZIF-8@GO Electrospun Membranes

Figure 2 shows the scanning electron microscopy (SEM) images and element composition of the PLA/ZIF-8@GO electrospun membranes. In the presence of ZIF-8@GO or ZIF-8, the peaks at 1086, 1183, and 1453 cm$^{-1}$ corresponding to C–O stretching vibration, C–C stretching vibration, and C–H bending vibration, respectively, remain unchanged. Therefore, the presence of the filler did not influence the main chain structure of the PLA matrix. However, the peak of pure PLA at 1756 cm$^{-1}$ attributed to the C=O stretching vibration shifts to a lower wavenumber with the increasing content of nanoparticles. This confirms the presence of the interactions between nanoparticles and the PLA matrix. The main force should be the hydrogen bonds between the C=O in PLA and the N–H and O–H in ZIF-8@GO.

### 2.3. Interactions between ZIF-8@GO and the PLA Matrix

The Fourier infrared spectra (FT-IR) analysis is an effective analytical technique to investigate the interactions between ZIF-8@GO particles and the PLA matrix. Figure 3 shows the FT-IR spectra for PLA and its composite electrospun membranes. In the presence of ZIF-8@GO or ZIF-8, the peaks at 1086, 1183, and 1453 cm$^{-1}$ corresponding to C–O stretching vibration, C–C stretching vibration, and C–H bending vibration, respectively, remain unchanged. Therefore, the presence of the filler did not influence the main chain structure of the PLA matrix. However, the peak of pure PLA at 1756 cm$^{-1}$ attributed to the C=O stretching vibration shifts to a lower wavenumber with the increasing content of nanoparticles. This confirms the presence of the interactions between nanoparticles and the PLA matrix. The main force should be the hydrogen bonds between the C=O in PLA and the N–H and O–H in ZIF-8@GO.

### 2.4. Contact Angle of PLA/ZIF-8@GO Electrospun Membranes

As one of the vital properties of membranes, hydrophilicity significantly controls adsorption capabilities. The contact angle (CA) is an important parameter that quantifies wettability which is related to roughness, chemistry, and porosity of the surface. As shown in Figure 4, the static CA of PLA/ZIF-8@GO and PLA/ZIF-8 electrospun membranes.

![Figure 3. IR spectra of PLA/ZIF-8@GO electrospun membranes.](Image)

![Figure 4. CA of PLA/ZIF-8@GO and PLA/ZIF-8 electrospun membranes.](Image)
2.5. Mechanical Properties of PLA/ZIF-8@GO Electrospun Membranes. The stress–strain curves of the prepared composite electrospun membranes with different ZIF-8@GO loadings are shown in Figure 5. As shown in Figure 5, the incorporation of ZIF-8@GO nanoparticles leads to a significant increase in tensile strength. With the increasing loading of ZIF-8@GO, the tensile strength increases first and then decreases, reaching a maximum at the content of 1.0 wt %. A ZIF-8@GO loading of 1.0 wt % gives rise to the increase in average tensile strength from 2.77 to 6.17 MPa. In our previous work, ZIF-8 nanoparticles have been proved an efficiency reinforcement for the PLA matrix.34 To the contrary, Sahoo reported that the presence of GO and nano-sized MOFs (nMOF) could decrease the mechanical strength and Young’s modulus of the electrospun PLA composite membranes because of irregularity in the dispersion.35 It is apparent that the incorporation of ZIF-8@GO into the PLA matrix results in an improvement in tensile strength, indicating a strong interfacial interaction between ZIF-8@GO and PLA.37,38 The strain at break increased from 58% for pure PLA to 87% for PGZ1.0. However, the strain at break is dramatically decreased at 1.5 and 3.0 wt % loading, which may be attributed to the aggregation of ZIF-8@GO at higher filler content.

2.6. Photocatalytic Application of PLA/ZIF-8@GO Electrospun Membranes in the Adsorption and Degradation of MB. The adsorption property of the materials toward MB molecules is one of the important factors to affect the photocatalytic activity. In the current study, we measured the adsorption capacity for PLA, PGZ0.1, PGZ1.5, PGZ3.0, and PZ3.0 over MB in darkness. We also evaluated the influence of ZIF-8@GO content of the composite membranes on the degradation of MB under UV-light irradiation after 4 h darkness treatment. The MB removal efficiency is summarized in Figure 6. The adsorption efficiencies of MB depend significantly on the ZIF-8@GO content. The increased adsorption property could be partially attributed to the noncovalent intermolecular interactions between MB molecules and ZIF-8@GO as well as to the increased hydrophilicity.39,40 In addition, the large specific surface area and ultrahigh porosity of ZIF-8@GO providing available adsorption sites could also be a factor. In the case of pure PLA membrane, no clear photodegradation of MB is observed under UV irradiation. However, for PGZs, the absorbance of MB solution at 661 nm decreases rapidly with the increase of irradiation time, which is more obvious at high filler content. As shown in Figure 6, after 240 min of darkness treatment and 180 min of UV irradiation, 16.2, 53.5, 69.5, 93.2, and 42.13% of MB is removed by PLA, PGZ0.1, PGZ1.5, PGZ3.0, and PZ3.0, respectively. As can be seen more clearly in Figure 7a, both the adsorption efficiency and the photocatalytic activity of PGZ3.0 are higher than those of PZ3.0, indicating the more superior performance of ZIF-8@GO than ZIF-8. On the basis of the abovementioned analysis, there are two essential reasons why PGZ3.0 has a higher MB removal efficiency than PZ3.0. First, the enhanced hydrophilicity and wetting ability as discussed above make MB more accessible to the surface of composite fibers.41 Additionally, the narrow band gap of ZIF-8@GO as shown in Figure 1d is favorable for the utilization of the light radiation.42 The long-term stability of the composite membrane was also examined. After 240 min of darkness treatment and 180 min of UV irradiation, PGZ3.0 was centrifuged and put into the following MB solution. Figure 7b shows the MB removal efficiency of PGZ3.0 in three consecutive cycles. The MB removal efficiency of PGZ3.0 remain above 85% after three cycles, indicating the good stability of PGZ3.0 as water treatment materials.

The possible mechanism for MB removal by PLA/ZIF-8@GO electrospun membranes is proposed here as shown in Scheme 1. With the high specific surface area and increased hydrophilicity tailoring by ZIF-8@GO, the prepared electrospun fiber can absorb MB efficiently. Electrons, excited on organic ligands of ZIF-8, transfer from ZIF-8 to GO and react with O2 to produce O2•−. The resulted O2•− then reacts with H+ to form H2O2 which continues to react with electrons to form *OH during UV irradiation.43 At the meantime, the holes left behind also produce *OH by oxidizing H2O. These active species (O2•−, H2O2, *OH, etc.) lead to the MB degradation. In this MB removal system, the PLA matrix plays the role of an adsorbent and a carrier, while ZIF-8 produces electrons and holes which result in a series of reactions.43,44 Additionally, the electrons can transfer along the large GO sheets, which makes GO a suppressor of electron–hole pair recombination, increasing the photocatalytic efficiency.12,44 What needs to be emphasized is that the maximum of the ratio of photocatalyst to water is 0.06 mg/mL in our study, which is much lower than those reported in the literature (0.5 mg/mL as reported by Chen and 0.4 mg/mL as reported by Xu).45,46 Moreover, the solution mixing method we used to immobilize the photocatalyst into the PLA matrix is much simpler, more economical, and more suitable for mass production than the in situ growth method. In terms of environmental protection and practical application, the PLA/ZIF-8@GO electrospun membrane is a good candidate for wastewater treatment.

Figure 5. Stress–strain curves of PLA/ZIF-8@GO electrospun membranes.

Figure 6. Photocatalytic activities of PLA, PGZ0.1, PGZ1.5, and PGZ3.0 for MB degradation under UV-light irradiation.
3. CONCLUSIONS
The PLA membranes with the embedded ZIF@GO composite were prepared using a simple electrosprinning technique. The IR results demonstrated the strong interaction between ZIF@GO and the PLA matrix. With the increase of ZIF@GO content, the surface morphology of PLA fibers changed greatly, and the surface became more and more hydrophilic. The incorporation of ZIF@GO at low contents (≤1 wt %) enhanced the tensile stress and the strain at break. The PLA/ZIF@GO membrane exhibited enhanced adsorption capacity and photocatalytic efficacy for MB. These results indicate that PLA/ZIF-8@GO electrospun membranes are quite promising in dye wastewater treatment.

4. MATERIALS AND METHODS
4.1. Materials. PLA (290, Haizheng, China), graphite powder (1–44 μm, Sinopharm, China), Zn(NO₃)₂·6H₂O (Sinopharm, China), N,N’-dimethylformamide (DMF, 99.5%, Sinopharm, China), methanol (99.5%, Sinopharm, China), CH₂Cl₂ (99.5%, Sinopharm, China), and 2-methylimidazole (MeIm, 98%, Aladdin, USA) were used as received in this work.

4.2. Preparation of the ZIF-8@GO Nanohybrid. GO was prepared from natural graphite (1–44 μm) according to an improved Hummer’s method. The ZIF-8@GO nanohybrid was synthesized with a method similar to a previously reported procedure as shown in Scheme 1. Briefly, 163 mg of oven dried GO was dispersed in 200 mL methanol and sonicated for 5 h. The GO suspension was then divided into two equal parts. One was added with 1487 mg Zn(NO₃)₂·6H₂O and the other with 1602 mg MeIm. Subsequently, the two solutions were mixed and stirred for 1 h continuously. Finally, the white product was centrifuged and washed 3 times with fresh methanol before they are dried at 80 °C.

4.3. Preparation of PLA/ZIF-8@GO Electrospun Membranes. The preparation procedure of the PLA/ZIF-8@GO membrane is displayed in Scheme 2. First, PLA was dissolved in 8 mL CH₂Cl₂ at room temperature. Subsequently, different loadings of ZIF-8@GO nanoparticles were dispersed in 2 mL DMF by an ultrasonic bath. The ZIF-8@GO dispersion was added into the PLA solution with constant magnetic stirring. Uniform composite solution was achieved by stirring for 4 h. The concentration of the composite solution is 10 wt % based on the weight of the overall electrospinning solution. Prepared composite solution was loaded in the syringe that was connected to a metering pump. All membranes were prepared at 22 kV at the flow rate of 0.5 mL/h. The metal plate collector covered with a copper mesh was 15 cm from the tip of the syringe. The thickness of each PLA/ZIF-8@GO electrospun
membrane (measured by a digital display micrometer) is ~0.05 mm. The samples containing 0, 0.1, 0.5, 1, 1.5, and 3.0 wt % ZIF-8@GO are abbreviated as PLA, PGZ0.1, PGZ0.5, PGZ1 PGZ1.5, and PGZ3.0 in this paper. For comparison, PLA with 3 wt % ZIF-8 (PZ3.0) is also prepared in the same manner as PGZ3.0.

4.4. Characterization. The morphology of ZIF-8@GO was observed using TEM (JEM-2100, JEOL, Japan). XPS (PHI 5300, ULVAC-PHI, USA) was used to analyze the composition of ZIF-8@GO. The XRD measurements were recorded on a diffractometer (D8 ADVANCE, Bruker, Germany) using Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. N2 isotherm adsorption at 77.5 K is recorded on an ASAP 2020 BET surface analyzer (Micromeritics, America). Prior to the adsorption measurements, the samples were outgassed at 80 °C for 5 h. UV–vis spectra of ZIF-8 and the ZIF-8@GO hybrid were recorded on a spectrophotometer (UV-6100s, Mapada, China) in the range of 200–800 nm. The SEM (S-4800, Hitachi, Japan) was used to observe the surface morphology of the PLA/ZIF-8@GO fibrous membranes. The FT-IR spectra were obtained using a spectrometer in the range of 400 to 4000 cm−1 (FT-IR-8400S, Shimadzu, Japan). Tensile testing was carried out on a tensile tester (CMT, Sans, China) at a rate of 10 mm/min. The samples were cut into strips of 0.5 cm × 4 cm. The values were averaged over five measurements. The CAs were measured by a CA tester goniometer (SL200B, Kino, USA). The membrane samples were measured using the sessile drop method with water.

4.5. MB Removal Experiment. Photocatalytic properties of PLA/ZIF-8@GO electrospun membranes were determined by measuring degradation of MB under 100 W UV light at a wavelength of 254 nm. PLA/ZIF-8@GO electrospun membranes (100 mg) with different ZIF-8@GO content were immersed in 50 mL MB solution (2 mg/L) with stirring for 4 h to reach adsorption equilibrium in a dark room before exposure to UV light. The photocatalytic degradation of MB was measured by monitoring the changes of the dye absorbance at intervals of 30 min with the range of 200–800 nm using a UV-6100s spectrophotometer (Mapada, China). The concentration of MB was estimated by the intensity of the main adsorption peak at 661 nm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00792.

N2 adsorption–desorption isotherms of ZIF-8 and ZIF-8@GO; the pore size distribution from BJH calculation based on the adsorption branch of the corresponding isotherm; textural properties of ZIF-8 and ZIF-8@GO; SEM image of PZ3.0; and element composition of PLA, PGZ0.1, PGZ1.5, and PGZ3.0 (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: wxinlong323@163.com. Phone: +86 25 8431 5949 (X.W.).

ORCID

Xinlong Wang: 0000-0001-7910-2402

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Science and Technology Support Program (Social Development) of Jiangsu Province, China (BE 2013714) and Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

REFERENCES

(1) Wu, J.; Ma, L.; Chen, Y.; Cheng, Y.; Liu, Y.; Zha, X. Catalytic ozonation of organic pollutants from bio-treated dyeing and finishing wastewater using recycled waste iron shavings as a catalyst: removal and pathways. Water Res. 2016, 92, 140–148.

(2) Abidi, N.; Errais, E.; Duplay, J.; Berez, A.; Jrad, A.; Schäfer, G.; Ghazi, M.; Semhi, K.; Trabelsi-Ayadi, M. Treatment of dye-containing effluent by natural clay. J. Cleaner Prod. 2015, 86, 432–440.

(3) Zeng, X.; Sun, Z.; Wang, H.; Wang, Q.; Yang, Y. Supramolecular gel composites reinforced by using halloysite nanotubes loading with in-situ formed Fe3O4 nanoparticles and used for dye adsorption. Compos. Sci. Technol. 2016, 122, 149–154.

(4) Liu, D.; He, L.; Lei, W.; Li, K.; Dong, K.; Kong, L.; Chen, Y. Multifunctional Polymer/Porous Boron Nitride Nanosheet Membranes for Superior Trapping Emulsified Oils and Organic Molecules. Adv. Mater. Interfaces 2015, 2, 1500228.

(5) Sun, K.; Wang, L.; Wu, C.; Deng, J.; Pan, K. Fabrication of alpha-Fe2O3@rGO/PAN Nanofiber Composite Membrane for Photocatalytic Degradation of Organic Dyes. Adv. Mater. Interfaces 2017, 4, 1770132.

(6) Liu, Y.; Zhang, D. The preparation of reduced graphene oxide–TiO2 composite materials towards transparent, strain sensing and photocatalysis multifunctional films. Compos. Sci. Technol. 2016, 137, 102–108.

(7) Xu, Z.; Li, X.; Wang, W.; Shi, J.; Teng, K.; Qian, X.; Shan, M.; Li, C.; Yang, C.; Liu, L. Microstructure and photocatalytic activity of electrospun carbon nanofibers decorated by TiO2 nanoparticles from hydrothermal reaction/blended spinning. Ceram. Int. 2016, 42, 15012–15022.

(8) Li, X.; Teng, K.; Shi, J.; Wang, W.; Xu, Z.; Deng, H.; Lv, H.; Li, F. Electrospun preparation of polyacryl acid nanoporous fiber membranes via thermal-nonsolvent induced phase separation. J. Taiwan Inst. Chem. Eng. 2016, 60, 636–642.

(9) Xu, Z.; Wang, L.; Wang, W.; Li, N.; Chen, C.; Li, C.; Yang, C.; Fu, H.; Kuang, L. Migration behavior, oxidation state of iron and graphitization of carbon nanofibers for enhanced electrochemical performance of composite anodes. Electrochim. Acta 2016, 222, 385–392.

(10) Ramasundaram, S.; Son, A.; Seid, M. G.; Shim, S.; Lee, S. H.; Chung, Y. C.; Lee, C.; Lee, J.; Hong, S. W. Photocatalytic applications of paper-like poly(vinylidene fluoride)–titanium dioxide hybrids fabricated using a combination of electrospinning and electrospraying. J. Hazard. Mater. 2015, 285, 267–276.

(11) Chen, S.; Huang, X.; Xu, Z. Decoration of phthalocyanine on multiwalled carbon nanotubes/cellulose nanofibers nanocomposite for decoloration of dye wastewater. Compos. Sci. Technol. 2014, 101, 11–16.

(12) Almeida, N. A.; Martins, P. M.; Teixeira, S.; da Silva, J. A. L.; Sencadas, V.; Kühn, K.; Cuniberti, G.; Lancerос-Mendez, S.; Marques, P. A. A. P. TiO2/graphene oxide immobilized in P(VDF-TrFE) electrospun membranes with enhanced visible-light-induced photocatalytic performance. J. Mater. Sci. 2016, S1, 6974–6986.

(13) Oveisi, M.; Asli, M. A.; Mahmoodi, N. M. MIL-Ti metal-organic frameworks (MOFs) nanomaterials as superior adsorbents: Synthesis and ultrasound-aided dye adsorption from multicomponent wastewater systems. J. Hazard. Mater. 2018, 347, 123–140.

(14) Liu, S.; Xiang, Z.; Hu, Z.; Zheng, X.; Cao, D. Zeolitic imidazolate framework-8 as a luminescent material for the sensing of metal ions and small molecules. J. Mater. Chem. 2011, 21, 6649–6653.
(15) Kwon, H. T.; Jeong, H.-K. In situ synthesis of thin zeolitic–imidazolate framework ZIF-8 membranes exhibiting exceptionally high propylene/propane separation. J. Am. Chem. Soc. 2013, 135, 10763–10768.

(16) Neelgund, G. M.; Oki, A. Graphene-Coupled ZnO: A Robust NIR-Induced Catalyst for Rapid Photo-Oxidation of Cyanide. ACS Omega 2017, 2, 9095–9102.

(17) Mukherjee, M.; Ghoraie, U. K.; Samanta, M.; Santra, A.; Das, G. P.; Chattopadhyay, K. K. Graphene wrapped Copper Phthalocyanine nanotube: Enhanced photocatalytic activity for industrial waste water treatment. Appl. Surf. Sci. 2017, 418, 156–162.

(18) Xu, D.; Li, L.; He, R.; Qi, L.; Zhang, L.; Cheng, B. Noble metal-free RGO/TiO2 composite nanofiber with enhanced photocatalytic H 2 production performance. Appl. Surf. Sci. 2018, 434, 620–625.

(19) Song, S.; Cheng, B.; Wu, N.; Meng, A.; Cao, S.; Yu, J. Structure effect of graphene on the photocatalytic performance of plasmonic Ag/Ag2CO3-rGO for photocatalytic elimination of pollutants. Appl. Catal., B 2016, 181, 71–78.

(20) Kumar, R.; Jayaramulu, K.; Maji, T. K.; Rao, C. N. R. Hybrid nanocomposites of ZIF-8 with graphene oxide exhibiting tunable morphology, significant CO2 uptake and other novel properties. Chem. Commun. 2013, 49, 4947–4949.

(21) Wang, X.; Zhao, X.; Zhang, D.; Li, G.; Li, H. Microwave irradiation induced UIO-66-NH2 anchored on graphene with high activity for photocatalytic reduction of CO2. Appl. Catal., B 2018, 228, 47–53.

(22) Wu, X.; Ma, Y.; Zhang, G.; Chu, Y.; Du, J.; Zhang, Y.; Li, Z.; Duan, Y.; Fan, Z.; Huang, J. Thermally Stable, Biocompatible, and Flexible Organic Field-Effect Transistors and Their Application in Temperature Sensing Arrays for Artificial Skin. Adv. Funct. Mater. 2015, 25, 2138–2146.

(23) Sinha Ray, S. Polylactide-based bionanocomposites: a promising class of hybrid materials. Acc. Chem. Res. 2012, 45, 1710–1720.

(24) Shi, H.; Gan, Q.; Liu, X.; Ma, Y.; Hu, J.; Yuan, Y.; Liu, C. Poly(glycerol sebacate)-modified polyolatic acid scaffolds with improved hydrophilicity, mechanical strength and bioactivity for bone tissue regeneration. RSC Adv. 2015, 5, 79703–79714.

(25) Wang, J.; Wang, Y.; Zhang, Y.; Ulana, A.; Zhu, J.; Liu, J.; Van der Bruggen, B. Zeolitic Imidazolate Framework/Graphene Oxide Hybrid Nanosheets Functionalized Thin Film Nanocomposite Membrane for Enhanced Antimicrobial Performance. ACS Appl. Mater. Interfaces 2016, 8, 25508–25519.

(26) Yang, L.; Tang, B.; Wu, P. Metal−organic framework-graphene oxide composites: a facile method to highly improve the proton conductivity of PEMs operated under low humidity. J. Mater. Chem. A 2015, 3, 15838–15842.

(27) Wee, L. H.; Janssens, N.; Sree, S. P.; Wiktor, C.; Gobechiya, E.; Fischer, R. A.; Kirschhock, C. E. A.; Martens, J. A. Local transformation of ZIF-8 powders and coatings into ZnO nanorods for photocatalytic application. Nanoscale 2014, 6, 2056–2060.

(28) Chen, B.; Zhu, Y.; Xia, Y. Controlled in situ synthesis of graphene oxide/zeolitic imidazolate framework composites with enhanced CO2 uptake capacity. RSC Adv. 2015, 5, 30464–30471.

(29) Xu, W.-T.; Ma, L.; Ke, F.; Peng, F.-M.; Xu, G.-S.; Shen, Y.-H.; Zhu, J.-F.; Qiu, L.-G.; Yuan, Y.-P. Metal-organic frameworks MIL-88A hexagonal microrods as a new photocatalyst for efficient decolorization of methylene blue dye. Dalton Trans. 2014, 3792–3798.

(30) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. Poly (lactones). 9. Polymerization mechanism of metal alkoxide initiated polymerizations of lactide and various lactones. Macromolecules 1988, 21, 286–293.

(31) Chen, C.-C.; Chueh, J.-Y.; Tseng, H.; Huang, H.-M.; Lee, S.-Y. Preparation and characterization of biodegradable PLA polymeric blends. Biomaterials 2003, 24, 1167–1173.

(32) Jin, R.; Bian, Z.; Li, J.; Ding, M.; Gao, L. ZIF-8 crystal coatings on a polypyrrole substrate and their catalytic behaviours for the Knoevenagel reaction. Dalton Trans. 2013, 3936–3940.

(33) Feng, Y.; Zhang, X.; Shen, Y.; Yoshino, K.; Feng, W. A mechanically strong, flexible and conductive film based on bacterial cellulose/graphene nanocomposite. Carbohydr. Polym. 2012, 87, 644–649.

(34) Dai, X.; Cao, Y.; Shi, X.; Wang, X. The PLA/ZIF-8 Nanocomposite Membranes: The Diameter and Surface Roughness Adjustment by ZIF-8 Nanoparticles, High Wettability, Improved Mechanical Property, and Efficient Oil/Water Separation. Adv. Mater. Interfaces 2016, 3, 1600702.

(35) Chen, J.; Yao, B.; Li, C.; Shi, G. An improved Hummers method for eco-friendly synthesis of graphene oxide. Carbon 2013, 64, 225–229.

(36) Sahoo, P. C.; Sambudi, N. S.; Park, S. B.; Lee, J. H.; Han, J.-I. Immobilization of Carbonic Anhydrase on Modified Electrospun Poly (Lactic Acid) Membranes: Quest for Optimum Biocatalytic Performance. Catal. Lett. 2015, 145, 519–526.

(37) Khoshkava, V.; Kamal, M. R. Effect of surface energy on dispersion and mechanical properties of polymer/nanocrystalline cellulose nanocomposites. Biomacromolecules 2013, 14, 356–351.