Fabrication and Photocatalytic Properties of Bi$_2$O$_3$/SiO$_2$ Electrospun Nanofiber Membranes: Implication for Wastewater Degradation

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Abstract. The Bi$_2$O$_3$ nanostructures with narrow band gap and strong photoresponse to visible light were used to couple with SiO$_2$ by electrospinning method, to prepare Bi$_2$O$_3$/SiO$_2$ nanofiber membranes. Compared to pure Bi$_2$O$_3$ powder, the as-prepared photocatalytic membrane is more convenient to recycle. Moreover, Bi$_2$O$_3$ active components are evenly dispersed on the SiO$_2$ fiber membrane by electrostatic spinning. Furthermore, the Bi$_2$O$_3$/SiO$_2$ electrospun nanofiber membrane calcined at 340$^\circ$C can maintain a high purification rate of 84% in the test.

1. Introduction
Wastewater is one of the major pollutants, which usually emits from industrial production and building materials [1]. Due to its harmful effects on human health, it is necessary to find suitable method to reduce the pollutant concentration at sunshine. Bi$_2$O$_3$ nanostructures exhibited excellent performance to degrade many organic pollutants due to its narrow band gap and strong photo response to visible light [2, 3]. However, since catalyst powder is prone to aggregation in the application, it will be difficult to recycle and not conducive to industrial production.

Currently, photocatalytic is considered as one of the most effective and economical feasible methods to degradation pollutants [4, 5]. Especially the catalyst hybrid membranes by electrospinning method exhibit higher degradation activity for wastewater pollutants, because electrospun fibers are ideal supports to grow nanostructures [6-8]. And the catalysts can be used for infinitely many times in theory. In this study, Bi$_2$O$_3$ was as precursor solution mixed with SiO$_2$ fiber membrane by electrospinning method. And the Bi$_2$O$_3$/SiO$_2$ hybrid membrane exhibits good wastewater purification performance and recyclability.

2. Experimental
PVA solution was prepared by dissolving PVA powder into DI water heated on a hotplate with vigorous stirring. A silica gel was prepared by hydrolysis and polycondensation of TEOS assisted with H$_3$PO$_4$
with stirring. Besides, the bismuth-based precursor solution was prepared by dissolving L-asparagine into DI water ultrasounded. The bismuth nitrate was dropped into the above solution and stirred by ultrasounding. Finally, the solution was reacted in an oil bath to obtain a bismuth-based precursor solution.

Then the equal weight of silica gel was dropped slowly into PVA solution and stirred before electrospinning. Simultaneously, the bismuth-based precursor solution was added. After that, sonicating the solution for a period to obtain a white suspension. Finally, electrospinning with needleless spinning.

The Bi$_2$O$_3$/SiO$_2$ membrane structure was analyzed by scanning electron microscopy (SEM, Hitachi SU8010) with energy dispersive spectrometer (EDS), thermogravimetric analysis (TG-DSC).

Rhodamine B was used as a representative of wastewater pollutants to evaluate and optimize the photocatalytic performance. Visible light was illuminated by a Xe lamp with a 400 nm UV cut-off filter. 5 mg of Bi$_2$O$_3$/SiO$_2$ fiber samples were added into 10 mL of an RhB solution (10 mg/L). Then, the system was kept in the dark for 1 hour to achieve saturation adsorption. The absorption of the solution was measured at 15, 30, 60, 120 min by UV-Vis spectroscopy.

3. Results and Discussion

It can be found from Figure 1 that the Bi$_2$O$_3$/SiO$_2$ electrospun nanofiber membrane is more convenient to recycle than pure Bi$_2$O$_3$ powder. When degrading the RhB solution, the Bi$_2$O$_3$/SiO$_2$ membrane is not easily dissolved and broken, however, the Bi$_2$O$_3$ powder will be dispersed in the solution.

![Figure 1. Digital photo of Bi$_2$O$_3$/SiO$_2$ electrospun nanofiber membrane calcined at 340oC.](image)

The fabrication procedure of the Bi$_2$O$_3$/SiO$_2$ nanofiber structure is illustrated in Figure 2. Three samples were chosen from different operation conditions. It can be observed from Figure 2(a, b) that the surface of SiO$_2$ nanofibers was very smooth without calcination, on which there were no obvious Bi$_2$O$_3$ nanoparticles before calcination. After calcined at 340°C for 2 h, the peak of O, Si and Bi elements were observed from EDS image, it can prove the particles are more uniformly dispersed, as shown in Figure 2(c, d).

However, while the calcination temperature further increased to 550°C, the particles are agglomerated, as shown in Figure 2(e, f). The result indicates that too high calcination temperature is not conducive to catalyst loading on the membrane. It can also be seen from Figure 2 bismuth-based catalysts can be successfully supported on SiO$_2$ membranes by electrospinning method because of its surface modification treatment, which can effectively increase its surface area and mesopores content.

This study will use the 340°C calcined membrane as a sample to discuss its composition and degradation performance.

The chemical composition of the Bi$_2$O$_3$/SiO$_2$ was analyzed by energy dispersive spectrometer (EDS). Figure 3 shows the EDS value measured at a local position of a sample containing a bismuth-based catalyst at a size of 10µm, the peak of O, Si and Bi elements were observed in the spectrum, indicating the inclusion of elements in the formed compound.
Figure 2. SEM images of Bi$_2$O$_3$/SiO$_2$ electrospun nanofiber membrane without calcine (a, b), and calcined at 340 °C (c, d), 550 °C (e, f), respectively.

Figure 3. EDS pattern of Bi$_2$O$_3$/SiO$_2$ electrospun nanofiber membrane calcined at 340°C.

Taking the spun-free photocatalyst film and spun photocatalyst film for the TG-DSC test, the heating rate is 10 k/min, the air flow rate is 40 ml/min. The results are shown in Figure 4. As can be seen from Figure 4a, the weight loss of the inner film at 100-250°C is caused by the removal of water and the self-condensation of silanol groups. The weight loss within 250-350°C is due to the decomposition of the side chain of PVA. When the temperature reaches 400°C, the main chain of PVA starts to decompose, and when it reaches 600°C, the decomposition of PVA is basically complete, as shown in Figure 4b. In the range of 400-600°C, the rapid decomposition of most PVA polymer may result in the aggregation of Bi$_2$O$_3$ nanoparticles which were just deposited on the surface of PVA-SiO$_2$ nanofibers. This is in line with the results of SEM images.
Figure 4. TG-DSC curve of thermal decomposition of (a) SiO2 membrane. (b) Bi2O3/SiO2 electrospun nanofiber membrane.

The RhB purification test for the Bi2O3/SiO2 membrane calcined at 340℃ is shown in Figure 5. It can be found that with the light time increases, the strong absorption band around 450-600 nm gradually decreases, as shown in Figure 5a. The variations of RhB concentration C/C0 verse the irradiation time are presented in Figure 5b. It can be seen from the figure that with the increase of the irradiation time, the concentration of RhB shows a downward trend. When it reaches 120 minutes, the RhB decreases by about 84%, indicating the catalyst exhibits excellent degradation activity under visible light.

Figure 5. Electronic absorption spectra for RhB degradation at various times of Bi2O3/SiO2 (a), and degradation profiles of RhB catalyzed by Bi2O3/SiO2 under visible light irradiation(b).

4. Conclusion
Firstly, the Bi2O3/SiO2 electrospun nanofiber membrane is more convenient to recycle than pure Bi2O3 powder. Then it can be seen from the SEM images that Bi2O3 active components are evenly dispersed on the SiO2 fiber membrane by electrostatic spinning, EDS images prove the presence of components. Further, from SEM and TG-DSC images, we found the calcination temperature of the photocatalytic membranes will affect the loading of Bi2O3, of which 340℃ is the optimal temperature. At last, the as-prepared Bi2O3/SiO2 electrospun nanofiber membrane exhibits good wastewater purification performance at room temperature. The purification rate can always maintain as high as 84% in the test.

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