Preparation of flexible titanium dioxide nanofiber membrane and its degradation of malachite green dye

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Abstract. With the continuous development of science and technology, people begin to pay attention to environmental protection. At present, there are many fields causing environmental pollution, among which printing and dyeing wastewater has become the most difficult to degrade in our daily life due to the complexity and instability of organic substances in its water. The seriousness of printing and dyeing wastewater pollution has a great impact on our living ecological environment. As a typical material in semiconductors, titanium dioxide has the advantages of low price, strong compatibility, non-toxicity, self-cleaning and stable physical and chemical properties. These advantages determine that titanium dioxide has absolute advantages and deeper potential in the field of photocatalysis. There are a variety of types and forms of titanium dioxide, including titanium dioxide film, powder, particle, fiber and so on. The flexible titanium dioxide nanofiber membrane prepared by electrospinning has the characteristics of high specific surface, large pore size and high transmittance. Flexible titanium dioxide nanofiber membrane is more available and recyclable and can avoid secondary pollution as well. Therefore, the preparation and selection of reasonable photocatalytic materials is also a key step in the field of photocatalytic technology.

1. Introduction
In order to find a solution to the problem of printing and dyeing wastewater, scientists and researchers at home and abroad are making continuous efforts and have also developed many schemes for treating printing and dyeing wastewater\textsuperscript{[1]}. Among them, photocatalytic degradation becomes more and more noticeable. It has strong oxidation, uses light energy as well as complete purification but creates no pollution nor secondary pollution\textsuperscript{[2]}. Plus, it is efficient regarding the decomposition of nutrients in sewage and inhibition of microbial reproduction. Also, the costs involved are so acceptable\textsuperscript{[3]}. All of the abovementioned advantages make the photocatalytic technology the mainstream technology in the 21st century. Semiconductor materials have high activity and can produce strong redox reaction under light. Therefore, semiconductor materials are an important support of photocatalytic materials\textsuperscript{[4]}. There are many kinds of materials that can be used as photocatalytic materials on earth. Among them, titanium dioxide has strong oxidation ability, stable chemical properties, inactive and non-toxic\textsuperscript{[5]}. Therefore, titanium dioxide is the best choice for photocatalytic raw materials. It is also the material with the most use of photocatalytic technology in recent years. However, there are many methods to prepare titanium dioxide, including gas-phase method, liquid-phase method, electrospinning, etc. Electrospinning technology, as an emerging technology, has attracted much attention\textsuperscript{[6]}. The nanofiber membrane prepared by electrospinning technology can realize fixed-point and directional structural regulation, and
the internal regulation of the fibre can be carried out according to the required properties of the material, so as to achieve the desired effect.

### Table 1 Experimental materials

| Reagent name              | Molecular formula | Specifications | Manufacturer          |
|---------------------------|-------------------|----------------|-----------------------|
| Isopropyl titanate       | Ti(OCH₃)₂         | 95%            | Aladdin Co., Ltd      |
| Absolute ethanol          | EtOH              | 99.5%          | Aladdin Co., Ltd      |
| Glacial acetic acid       | CH₃COOH           | 99.7%          | Aladdin Co., Ltd      |
| Deionized water           | H₂O               | /              | YOUPU pure water      |
| Polyethylene oxide        | PEO (Mw=60k)      | Aladdin Co., Ltd|
| Polyvinylpyrrolidone      | PVP (Mw=130k)     | Aladdin Co., Ltd|
| Nano titanium dioxide     | P25               | Degussa, Germany|

This paper focuses on the preparation of a flexible titanium dioxide nanofiber membrane by electrospinning technology as a photocatalytic material, and explores the performance of titanium dioxide nanofiber membrane in the field of photocatalytic degradation of wastewater.

### Table 2 Experimental instrument

| Instrument name             | Model / specification | Manufacturer                                           |
|-----------------------------|-----------------------|--------------------------------------------------------|
| A magnetic stirrer          | HJ-6A                 | Gongyi Yuhua Instrument Co., Ltd                       |
| Precision electronic balance| AL-104-IC             | Mettler Toledo Instrument Co., Ltd                     |
| scanning electron microscope| S-4800                | Hitachi Japan                                          |
| Thermogravimetric analyzer  | SDT Q600              | American TA company                                    |
| Ultraviolet visible photometer | TU-1810              | Beijing puxie General Instrument Co., Ltd             |
| X-ray polycrystalline diffractometer | D8 Advance | Bruker, Germany                                       |

2. Preparation of nanofiber membrane materials

The process of preparing nanofiber membrane is mainly divided into three steps: the first is the preparation of spinning precursor solution; the second is the electrospinning technology to spin into nanofiber hybrid membrane, and the last is the high-temperature calcination of pure titanium dioxide nanofiber membrane in muffle furnace.

3. Experiment operation

First, experimenter turns on the UV-vis diffuse reflectance spectrum analyzer, places the deionized water in two cuvettes, tests and obtains the deionized baseline. After obtaining the baseline, experimenter takes out 100ml of prepared mg Malachite dye, pours it into the beaker, places it in the gout kitchen, and puts 20mg of titanium dioxide nanofiber membrane into the sample, and stands for 60 min in the dark for adsorption and desorption treatment. After dark treatment, experimenter turns on the installed UV lamp equipment as the UV light source, takes out 2ml of solution every 10min, puts it into the centrifuge tube for centrifugation, takes the supernatant solution, puts it into the cuvette to test the UV absorbance of the solution, and observes the degradation of malachite green concentration in the dye through origin mapping.

4. Results and analysis

(a) SEM of PEO (TiO₂) (b) Physical image of PEO (TiO₂) nanofiber film
Figure 1 shows the inorganic titanium dioxide nanofiber membrane prepared by electrospinning from PEO / PVP two different polymer templates, which is scanned and analyzed by SEM. It is the scanning pictures of electron microscope under different magnification after calcination in muffle furnace. We can clearly see that the diameter of titanium dioxide nanofiber membrane spun from different polymer templates is relatively uniform without obvious difference. After increasing the magnification, we can clearly find the difference. The fibers on titanium dioxide nanofiber membrane spun from PEO template have obvious smoothness and stronger softness. Moreover, the fiber has good continuity, smooth luster and strong sense of compactness. However, we spun the nanofiber film with PVP as the template. We can clearly see that the fiber on the titanium dioxide nanofiber film has obvious granular cracks, the fiber surface appears slightly rough and the fiber breaking rate is high, and the fiber does not have good smoothness and softness. It can also be seen from the real object in the figure 2 that PEO (TiO$_2$) can show good flexibility, TiO$_2$ nanofibers can also show strong flexibility after 800 °C high-temperature calcination, while PVP (TiO$_2$) shows strong brittleness. After 600 ° high-temperature calcination in muffle furnace, it shows very strong brittleness. The calcined PVP (TiO$_2$) nanofiber membrane does not have self-supporting mechanical properties and exists in the form of fragments.

Through XRD analysis and comparison of TiO$_2$ nanofiber films prepared with different templates and P25 (powdered titanium dioxide) available on the market after calcination in muffle furnace at high temperature, we can obviously find that the TiO$_2$ nanofiber films prepared by electrospinning have the same diffraction peaks as P25 samples. In XRD analysis, the three samples can clearly represent the crystalline phase planes of titanium dioxide (101), (004) and(200), (211), (204). This shows that after the titanium dioxide nanofiber membrane prepared by electrospinning technology is calcined in muffle furnace, the impurities of ethanol, acetic acid solvent and PEO / PVP organic template in the nanofiber membrane have been basically removed, and the component in the nanofiber membrane is pure TiO$_2$. 

Fig.2 Physical picture of PEO (TiO$_2$) nanofiber membrane XRD analysis comparison of titanium dioxide nanofiber membrane prepared by different template methods and P25
According to the XRD colorimetric cards of anatase and rutile, it can be analysed that the characteristic peaks of anatase of the three samples are obvious. At present, the anatase phase of the three samples is much larger than the rutile phase, so they all present anatase type.

The above figure shows the organic matter analysis in different infrared bands of Fourier infrared spectra of PVP (TiO$_2$), PEO(TiO$_2$) hybrid nanofiber films and calcined (PEO) TiO$_2$, PVP (TiO$_2$) and PEO (TiO$_2$) nanofiber films. From the fig.3, we can clearly see that there are several obvious peak differences before and after calcination of PEO(TiO$_2$). After referring to papers, it is known that there are 1028cm$^{-1}$ C-O characteristic peak, 1440cm$^{-1}$ - CH$_2$ characteristic peak and 1540cm$^{-1}$C (=O) O - characteristic peak in PEO polymer or acetic acid ethanol solvent in the calcined titanium dioxide nanofiber film, which indicates that there is no polymer and acetic acid ethanol solvent in the calcined titanium dioxide nanofiber film. The fig.4 shows the Fourier infrared analysis of titanium dioxide before and after calcination of PVP polymer template. We can also clearly see that there are five obvious characteristic peaks in the fig.4. After consulting the literature, the five characteristic peaks are 1028cm$^{-1}$ C-O characteristic peak, 1290cm$^{-1}$c-n characteristic peak, 1440cm$^{-1}$ - CH$_2$ characteristic peak, 1540cm$^{-1}$ - C (=O) O characteristic peak and 1654cm$^{-1}$ C = O characteristic peak. After high-temperature calcination in muffle furnace, the characteristic peaks disappear. Obviously, this shows that the organic components such as polymer PVP and acetic acid ethanol solvent in the calcined PVP (TiO$_2$) have basically eliminated volatilization. We obtained the titanium dioxide nanofiber membrane through calcination, which is a pure titanium dioxide nanofiber membrane.

Preliminary dye degradation experiments were carried out on the configured dyes under UV conditions, as shown in the figure above. Fig.5 shows the photodegradation data of titanium dioxide nanofiber membrane and P25 prepared by different templates under UV conditions. The samples of the three were pre-treated in the dark for the first 60 minutes in order to achieve the adsorption and desorption equilibrium. We can see that the concentration of malachite green dye was basically constant after 60 minutes of dark treatment, and after 60 minutes of UV irradiation, the malachite green content
in the three solutions basically tends to be zero, which shows that the malachite green dye can be removed under UV irradiation. Moreover, it can be clearly seen from the figure that the titanium dioxide nanofiber film prepared with PEO has a stronger degradation effect with P25 powder and titanium dioxide nanofiber film prepared with PVP.

In Fig. 6, after the sample is pre-treated in the dark, the degradation performance of titanium dioxide nanofiber films calcined at different temperatures is explored. It is obvious that these titanium dioxide nanofiber films can degrade malachite green dye under UV conditions after calcination at different temperatures in muffle furnace, but the degradation rate of malachite green dye is different after calcination at different temperatures. We can find that the degradation performance of titanium dioxide nanofiber membrane calcined at 700 °C and 800 °C is better, and the performance is slightly better than that of P25 powder samples on the market. The reason for this result may be that the titanium dioxide nanofiber membrane calcined at different temperatures has different crystal structures.

5. Conclusion
Based on electrospinning technology, two kinds of titanium dioxide nanofiber films were prepared by using PEO / PVP two different polymer templates. SEM characterization analysis, XRD crystal analysis and Fourier transform infrared functional group analysis were carried out for the two kinds of nanofiber films. After analysis, it was found that the titanium dioxide nanofiber prepared with PEO as template has certain flexibility. Then, the dye degradation experiment of the prepared titanium dioxide nanofiber membrane was carried out. Finally, it was found that the titanium dioxide nanofiber membrane could degrade malachite green dye under the action of ultraviolet light.

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