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Surface Morphology and Modulus, Wetting Behavior and Photocatalytic Activity of the TiO_2 Coated Materials Based on PMMA/O-MMT Composite Microfibers

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Abstract

Poly(Methyl Methacrylate) PMMA/Organically Modified Montmorillonite (O-MMT) composite microfibers membrane coated with TiO_2 has significant advantages in cationic dyes adsorption and can break down the adsorbed dyes under UV radiation, which is quite useful in water treatment. In this work, PMMA/O-MMT composite microfibers were firstly prepared by emulsion polymerization combined with electrospinning, and then coated by nanosize TiO_2 using RF magnetron sputtering. The effects of TiO_2 sputter coating on morphology and surface modulus was characterized by Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM), while the wetting behaviour was studied by drop shape analyzer. The photocatalytic degradation of methylene blue was tested under UV radiation and the properties of the treated and untreated samples were compared. It was observed from SEM images that TiO_2 was well dispersed and deposited on the surface of PMMA/O-MMT microfibers, while the AFM results showed increase in the surface modulus after TiO_2 coating. Besides, the wettability of the microfibers membrane coated with TiO_2 was altered, which facilitated water treatment in practical use. Furthermore, the PMMA/O-MMT microfibers membrane coated with TiO_2 performed well in photocatalytic degradation of methylene blue. In conclusion, PMMA/O-MMT composite microfibers membrane coated with TiO_2 was quite promising in water treatment.

Keywords: Electrospinning; RF (Ratio Frequency) Magnetron Sputtering; TiO_2; Microfibers; Water Treatment

1 Introduction

Comparing to the other conventional fibrous structures, Microfibers have interesting properties due to their extremely high surface to weight ratio and high porosity, which make microfibers ideal

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for use in such application areas as filtration, sensor, protective clothing and functional materials [1-4]. Poly(Methyl Methacrylate) (PMMA) is a common synthetic organic polymer traditionally used in various industrial applications [5]. Besides, clay particles have been shown to be easily electrospun with different polymers such as nylon 66, poly(viny alcohol) or poly(vinylidene fluoride) for various applications [6-10]. Addition of clays into polymer solutions increased the extensional viscosity, the extent of strain hardening and thus the electrospinnability of the resulting polymer/clay dispersions. The electrospun PMMA/O-MMT composite microfibers showed enhanced thermal stabilities at high temperature over the electrospun pristine polymeric microfibers. Composite microfibers electrospun from other polymer/clay dispersions were also shown to exhibit enhanced mechanical properties, such as shear modulus, and higher thermal properties, such as glass transition temperature [11, 12].

Nanoscale titanium dioxide (TiO_2) has a broad range of good properties, such as permanent effect, safe to use and no secondary pollution to the environment [13]. Because of these reasons, various techniques have been developed to produce fabrics with nanoscale titanium dioxide films for a wide range of applications. Magnetron sputtering coating is an ideal way to produce nanoscale titanium dioxide functional films due to the better adhesion between the substrate and the function films and it is an environmentally friendly process. The ability to deposit well-controlled coatings on microfibers would expand the application of microfibers, based on changes to both the physical and chemical properties of the microfibers.

In the present work, the electrospun PMMA/O-MMT composite microfibers were modified with nanosize TiO_2 by magnetron sputter coating. The effects of TiO_2 sputter coating on structure and surface morphology were observed by Scanning Electron Microscope (SEM). Besides, the surface modulus of the treated and untreated microfibers were analyzed and compared by Atomic Force Microscope (AFM). In addition, the wetting behavior and photocatalytic activity were also investigated.

2 Experimental

2.1 Materials Preparation

The Organically Modified Montmorillonite (O-MMT) by hexadecyl trimethyl ammonium bromide (cation exchange capacity, CEC, 97 mequiv./100g of clay) was purchased from Zhejiang Fenghong Clay Chemicals Co., Ltd. The average thickness of the particle was less than 25nm, and the ratio of diameter to thickness was about 200. PMMA and PMMA/O-MMT composite materials were synthesized in our laboratory by in situ emulsion polymerization. Chloroform and N, N-dimethylformamide (DMF) were used as received.

2.2 Preparation of Electrospun Composite Microfibers

PMMA/MMT dispersions were prepared by dispersing the nanocomposite at concentrations of 6 wt.% in chloroform. The solution was vigorously stirred for 8 hrs at room temperature. The polymer solution was electrospun at a positive voltage of 15kv with a working distance of 150 cm, and the flowrate was set as 0.5 mL/h.

2.3 Sputter Coating

A magnetron sputter coating system JZCK-420B (Shenyang, Juzhi Co., Ltd.) was used to deposit a nanolayer on the composite microfibers. A high purity Ti target (diameter: 50mm; purity: 99.99%) was placed below the substrate. The sputter power was set as 80 w, 100 w, 120 w, 140 w, respectively. The deposition thickness of the TiO_2 functional films on the surface of the fabrics is determined by the sputtering time, while the crystallographic form of TiO_2 is related to the voltage ratio of the oxygen gas to the argon gas. The sputtering parameters were chosen as Table 1, considering the ideal catalysis function [14, 15].

Table 1: Experimental parameters of sputter coating

Parameters	Value
Base pressure (Pa)	9.8×10^{-4}
Sputtering pressure(Pa)	3
Flow ratio of O_2 to Ar (sccm/sccm)	10/80
Distance between target and substrate(mm)	120
Substrate temperature	Room temperature
Sputtering time (min)	90

2.4 Characterization

Scanning Electron Microscope (SEM, Quanta 200, Holland FEI company) was used to examine the surface morphology of the composite microfibers. The samples were coated with a thin layer of gold by sputtering before the SEM imaging.

Force-distance curves of PMMA/MMT composite microfibers before and after treatment were analyzed by Atomic Force Microscope (AFM, CSPM 4000, Benyuan) to investigate their surface modulus.

Droplet Shape Analyzer (DSA100, Germany KrÜss company) was employed to investigate the wetting behaviour of the samples.

2.5 Photocatalytic Activity Evaluation of TiO_2 Films

The photocatalytic performance of the composite membranes sputter coated with TiO_2 under different sputter power was evaluated through degradation of MB under 100 w ultraviolet (UV) light at a wavelength of 254 nm. The samples weighed as 0.02 g were placed in beakers containing 20 ml MB solution for 12 hours' absorption equilibrium in darkroom before exposure to UV-light. The concentration of MB was 1.8 mg/L. The decolorization of MB was calculated using the formula,

$$\text{Decolorization} = (A_0 - A)/A_0$$

where A_0 and A are the absorbency of the initial and remaining MB, respectively. The absorbency was measured with a UV-vis spectrophotometer (UV-2100, China) at 664 nm (λ_{max} for MB).

3 Results and Discussion

3.1 Surface Morphology

The surface morphology of electrospun microfibers before and after sputter coating is investigated by SEM. The original sample is coarse on the surface with nanopores (Fig. 1(a)), which is caused by rapid phase separation during the electrospinning process.

After sputter coating with the sputter power set as 80 w and 100 w, the surface of the microfiber is becoming honeycomb and the TiO_2 particles are uniformly distributed inside the "honeycombs". According to the principle of nucleus growth of thin film [15], titanium atoms leave the surface of the target during the sputter process and react with oxygen atoms before they deposit on the surface of substrate with certain energy. When the sputter power is relatively low, only a few titanium atoms are sputtered with comparatively low energy. This kind of particles deposited lack the ability to inhibit the growth of large particles in defective areas. Hence, TiO_2 particles are likely to deposit and grow on the sunken areas of the fibers' surface, in consist with what Fig. 1(b) and Fig. 1(c) show, and the nanoparticles are more compact with the sputter power as 100 w.

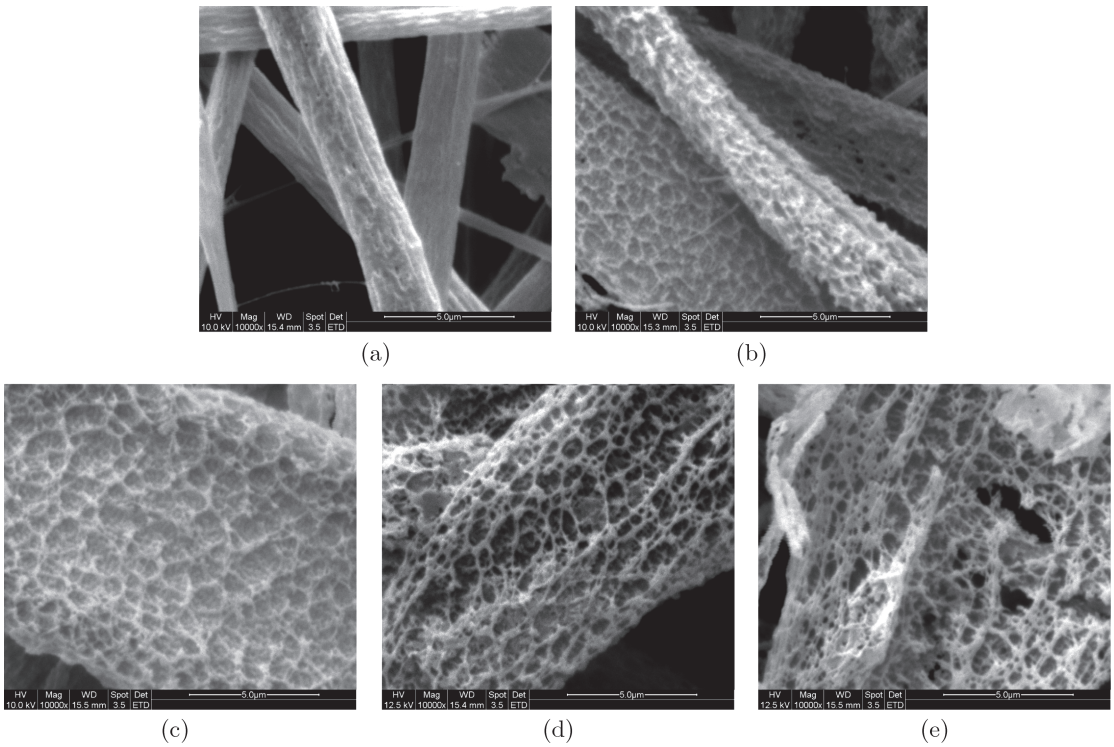

Fig. 1: SEM images of (a) original sample (b) treated by 80 w sputter coating (c) treated by 100 w sputter coating (d) treated by 120 w sputter coating (e) treated by 140 w sputter coating.

When the sputter power increased to 120 w, the TiO_2 particles crashed into the microfibers with high speed and surface temperature. As it is known, PMMA is poor in thermal and surface mechanical properties. So when the TiO_2 particles with high energy ran into the microfibers, they went inside the microfibers and the route the particles went through became hollow. When the sputter power further improved, the microfibers' surface is more porous and some regions are even penetrated by the TiO_2 particles.

3.2 Surface Elastic Modulus

After sputter coating, some of the areas on the microfiber's surface were replaced by nanosize TiO_2, which may change its surface mechanical properties. Force-distance curves showed by Fig. 2 are used to analyze the change of surface modulus of the composite microfibers before and after sputter coating.

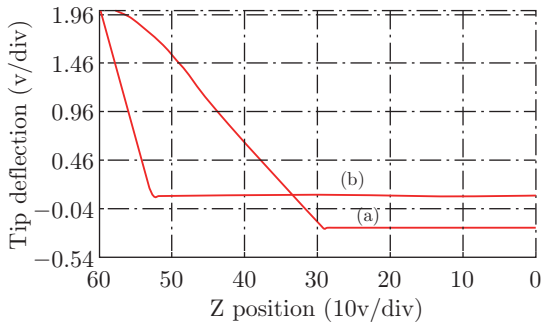

Fig. 2: Force-distance curves of (a) untreated, (b) treated PMMA/O-MMT composite microfibers.

From the curves, it can be inferred that after sputter coating, the surface modulus is greatly increased, which means that TiO_2 coated microfiber is stiffer than the uncoated. Table 2 showed the surface modulus of microfibers before and after sputter coating calculated by formula 1. The modulus of microfibers sputter coated is about 5 times the modulus of the original ones. So, TiO_2 coating dramatically improved PMMA microfibers' surface elastic modulus.

Young's modulus of a single microfiber is calculated by the formula as follows:

$$k = \frac{F}{|D|} = \frac{F}{Z - \delta} = \frac{F}{Z - F/k_c} = \frac{Fk_c}{Zk_c - F} \tag{1}$$

k—elastic modulus for a single microfiber, F—force on probe, D—deformation on the surface of microfiber, Z—the advance range of scanner, δ—the deformation value of probe, k_c—elastic modulus of the probe.

Table 2: Modulus of composite microfibers before and after sputter coating

samples	k_c(N/m)	Z(nm)	F(N)	K(N/m)
Before treatment	0.60	29	2.2	0.0868421
After treatment	0.60	7	1.7	0.408

3.3 Wetting Behaviour

The wetting behaviour is investigated by drop shape analyzer, as shown by Fig. 3, from which it can be seen that the water contact angle decreases with the increase of sputtering power.

With the increase of sputtering power, the surface of the microfibers became more porous, and so the wettability is improved correspondingly.

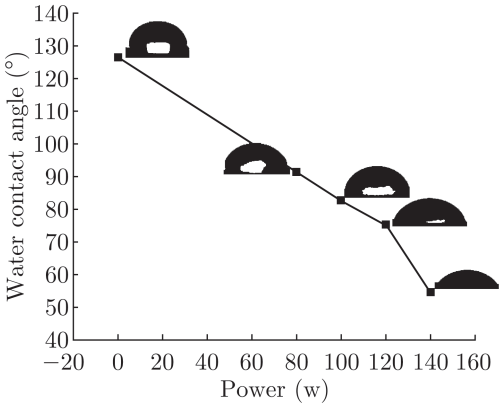

Fig. 3: Water contact angle of PMMA/MMT composite microfibers membrane sputter coated under different sputter power.

3.4 Photocatalytic Degradation of Methylene Blue

In Fig. 4, samples 0, 1, 2, 3, 4, 5 represent the test sample, original sample, membranes treated under 80 w, 100 w, 120 w, 140 w, respectively.

Fig. 4 shows that in the absence of composite membranes, the solution of MB had a light degree of degradation under UV light irradiation for 240 min, so we may rule out the effect of UV radiation itself on the degradation of MB.

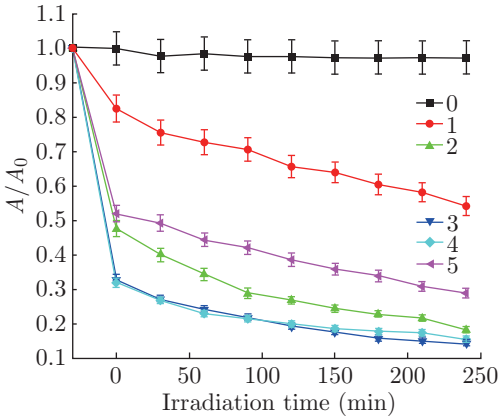

Fig. 4: Effect of sputter power on photodegradation rate.

After 12 hours' adsorption in the dark room, the adsorption rate of MB were 17.511%, 52.426%, 67.194%, 68.038%, 47.996% for sample 1, 2, 3, 4, 5, respectively. The samples sputter coated were better in MB adsorption than the original sample due to the porous structure and hydrophilcity. With the increase of sputter power, the adsorption rate increased first and decreased later. The surface of the composite microfibers became more porous and hydrophilic when the sputter power increased, and so the adsorption rate was improved initially. However, when the sputter power achieved 140 w, the microfibers were penetrated and so the effective area was reduced, which led to the decreased adsorption rate of MB.

After the adsorption process, the samples were exposed to UV illumination. During this period, the TiO_2 particles continuously hydrolyzed and produced a certain quantity of oxidative groups

such as ·OH, $\cdot O^{2-}$, ·OOH. These groups accelerated the catalytic activity of TiO_2 deposited composite membranes.

The degradation rate for sample 1, 2, 3, 4, 5 are 28.27%, 29.325%, 18.355%, 16.456%, 23.207%, respectively. In the case of sample 1, the membrane started to adsorb MB after it was exposured to UV illumination. This might attributed to the effect of UV illumination on the MMT. UV illumination enhanced the cation exchange reaction between MMT layer and MB known as a cationic dye, which facilitated MB adsorption. For samples 2, 3, 4, 5, the degradation rates are mainly related to the initial concentration of MB at 0min. If the initial concentration is too low, the photocatalytic property could not be fully revealed. The decrease of UV absorbance during UV illumination process could be caused by a combination effect of cation exchange reaction and TiO_2 photocatalytic degradation of MB.

To sum up, sample 3 and 4 performed best in MB adsorption and degradation.

4 Conclusions

The PMMA/O-MMT composite microfibers were prepared by emulsion polymerization combined with electrospinning. The surface functionalization of composite microfibers was achieved by depositing well-controlled TiO_2 nanoparticles using sputter coating. The influences of the sputter coating process and nanosize TiO_2 on surface morphology and modulus, were wettability and photocatalytic degradation of Methylene Blue were investigated. TiO_2 particles are well coated on the surface of the microfibers when the sputter power set as 80 w and 100 w. However, when the sputter power as 120 w and 140 w, the TiO_2 particles entered into the inside of the microfiber, making the microfibers multi-level structured. The force-distance curves showed that after sputter coating, the microfiber became stiff on the surface. The wettability is increased with the increase of sputter power. The photocatalysis showed that the sputter power at 100 w and 120 w performed better than the other samples.

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