Morphology and Properties of CNTs/La3+ Doped TiO2 Electrospinning Nanofibers

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***Abstract* — TiO2 nanofibers doped with carbon nanotubes(CNTs) and rare earth La3+ were prepared by electrospinning. And a research were carried on the relation between the relative molecular mass of PAN, the ratio of rare earth La3 and carbon nanotubes(CNTs) , carbonizing temperature and morphology and diameter. The morphology of the nanofibers were scanned by SEM, EDX and also the mechanical properties were tested. The results showed that the ratio of the carbon nanotubes and the rare earth had a great effect on the fiber morphology. The diameter of the nanofiber was influenced by the ratio of rare earth and the carbonization temperature. The conclusion of spinning condition was that the weight average molecular weight of PAN was 60000 and 0.05% La3+ doped TiO2 nanofibers. Meanwhile the degradation rate of the methylene blue could reach 98.87 %.**

Keywords - carbon nanotubes(CNTs); rare earth La3+; TiO2 nanofiber; electrospinning; morphology

I. INTRODUCTION

Since 1972 Fujishima and Hondafound that TiO2 photocatalytic performance since the combination of nanotechnology and photocatalytic material as the research focus has been in the field[1]. Electrospinning technology in recent years, more and more prepared to use photocatalysts materials technology, its advantages are easy operation, the process is adjustable and strong, simple equipment with easy operation[2-4]. Currently, a variety of polymer melt or solution system is used for electrostatic spinning, and successfully obtained titania nanofibers. But in the ongoing process of research, we found that titanium dioxide as light catalytic material science and there are still some technical problems in the actual use of the process, focused on two aspects: 1) TiO2 photocatalytic material as light absorption wavelength range limitations, usually only excited by ultraviolet light, visible light does not have the spectrum of use; 2) quantum yield is low. Numerous studies show that TiO2 can improve the range of visible light through the use of doping methods and reduce the light-generated electron - hole recombination probability, thereby improving the photocatalytic ability of titanium dioxide, Wherein the two-component or multicomponent preparation photocatalyst doped compared to the previous one-component catalyst having higher catalytic activity, becoming a research hotspot in recent years[5-11]. Rare earth metal ions having unsaturated 4f5d shielded by the external electronic configuration, the rare earth ions doped lattice is expanded and distorted, it can produce a large number of oxygen defects, trapping more electrons and reduce the electron - hole Compound chance to improve the catalytic efficiency purposes; and rare earth metal ions can also absorb infrared light, and after it is converted into visible light, which greatly increased the use of TiO2 spectrum of visible light. Kozlova et al[12] and in Jiang Wei et al[13], respectively, the use of rare earth elements of Ce3 + and Sm3 + doped TiO2, have achieved good catalytic effect. Photocatalysts materials are widely used in practice, but also the need to improve the efficiency of immobilized TiO2. A metal and semiconductor features of carbon nanotubes (CNTs) cooperation synergy can occur between TiO2, not only as a carrier photocatalytic material, but also on the electronic storage and transmission, expanding the scope of the use of visible light.

This chapter attempts to exploit electrostatic spinning prepared CNTs / La3 + co-doped titanium dioxide nano fibers. Electrospinning process is mainly carried out at ambient temperature and pressure, this experiment does not involve other more complex conditions of high temperature, high pressure or low pressure, can be obtained composite nanofibers in a relatively short period of time, during the experiment to CNTs and rare earth La3 + as preparing a source of inorganic material, and in order to increase the spinnability of the solution, was added to the mixed solution of polyacrylonitrile (PAN) mixed sol composition for electrostatic spinning.

II. EXPERIMENT

A. Reagents and Instruments

N-N dimethylformamide (DMF) AR, Sinopharm Chemical Reagent Co., Ltd.; tetrabutyl titanate (Ti (OC4H9) 4), AR, Wengjiang Chemicals Limited; lanthanum nitrate, 3N, Medicines Group of chemical reagents Limited; multi-walled carbon nanotubes (MWCNTs), an inner diameter 5-10nm, the outer diameter of 10-30nm, purity> 95%,

purchased from Suzhou Global Limited; polyacrylonitrile (PAN) powder, molecular weight of about 6.0 × 104, the British company Courtaulds.

Vacuum oven (DZF-6021), a constant Technology Co., Ltd. Shanghai; analytical balance (AR1530 / C), Wuxi Hongyuan Group Co., Ltd; temperature magnetic stirrer (H01-3), the Hai Mei Ying Pu Instrument Manufacturing Co. company; vacuum tube furnace (GSL 1600X), Hefei Branch Crystal materials Technology Co., Ltd.; laboratory electrospinning simple homemade device.

B. Purified Carbon Nanotubes

With 63% nitric acid at reflux nanotubes 2 h, the carbon nanotube purified by the method of centrifugal separation of the nitrate and carbon nanotube separation, repeatedly washed with deionized water and centrifuged, and finally washed until neutral, washed after drying in an oven using carbon nanotubes.

C. Sample Preparation

The purified carbon nanotubes 0.02 g dissolved in DMF, at 25 □, 24 hours ultrasonic dispersion. The 2 g PAN in a vacuum oven dried 2 h, and at 80 □ was dissolved in 25 ml DMF solvent. Then CNTs / DMF was slowly added to a mixed solution of PAN / DMF in, and ultrasound 10 h, to give CNT / PAN ratio was stirred by a vacuum method (1: 100) wt% spinning solution 25 ml [15] and then the nitrate according to a different ratio of lanthanum was added to a solution of 2 ml of glacial acetic acid and 2.5 ml tetrabutyl titanate (Ti (OC4H9) 4) mixed solution to form La3 + doped TiO (OAc) 2 solution, then under magnetic stirring was slowly added to the above CNT / PAN mixed solution, after the addition was complete, magnetic stirring continued 10 h, to give the final spinning solution and spun stoichiometric.

Spinning process, the spinning solution configured into homemade needle electrospinning apparatus, the distance between the spinning head and the receiving device is 15 cm, the DC voltage 15 kV, the discharge rate of the spinning solution 1.0 mL / h, the ambient temperature to 25 □, relative humidity electrostatic spinning at 65%, 10 h after spinning, to get different content La3 + doped carbon nanotubes doped TiO2 nanofibers. Then both ends of TiO2 nano-fibers obtained graphite sheet is fixed at both ends keep the distance 10 cm, after clamping with a clip placed 120 □ drafting, and pre-oxidation at 200 □ 1 h. Finally, the black pre-oxidized samples obtained La3 / CNTs co-doped TiO2 placed in a tube furnace to / h speed 100 □ temperature, and calcined at 500 □ insulation 2h, eventually get a different content of La3 + doped La3 / CNTs co-doped TiO2 (CLCT).

D. Mechanical Performance Test

Because the nanofibers CLCT small diameter, there is currently no uniform method of testing the mechanical properties of the nanofibers, commonly used test is the unit of measurement area by the mechanical properties of nano-fiber membranes. In this study, contact thickness measurement methods have been tested in accordance with test standard GB4456-84 were tested, were tested five different points TiO2 nanofiber membrane thickness. Powerful electronic multifunction machine (Shenzhen Rui Geer Instrument Co., Ltd.) measuring the tensile strength of nano fiber membrane.

In this experiment, a temperature of 25 □ and a humidity of 63% of the laboratory, first TiO2 nanofiber membrane and cut into a rectangular sample × width 50 mm × 10 mm, and adjust the upper and lower strength tester chuck interval 30 mm, then the sample is sandwiched between the upper and lower chuck powerful machine, under the load of 10 N to 10 mm / min speed of the sample is stretched. The mechanical properties of the above tests are in the same test conditions, measured after five averaged. According to collected data strength and elongation, according to formula (1) and (2) to calculate the stress nanofiber membrane, strain, (δ-ε).

$$\delta(\mathrm{MPa}) = \frac{f(N)}{w(mn)\times h(mm)} \quad (1)$$

$$\varepsilon = \frac{l(mm)}{g(mm)}\times 100\% \quad (2)$$

Wherein, f (N) represents the tensile breaking strength; w (mn) for the nanofiber membrane width; h (mm) thickness of nanofiber membrane; l (mm) elongation at break table nanofiber membrane; g (mm) is the distance between the grips of the tensile tester and down.

E. Photocatalytic Experiments

Methylene blue formulated into a solution of 0.2 g L /, take 100mL added quartz beaker, 0.1 g nanofibers (CLCT), with plastic wrap to seal the mouth of the reactor, ultrasonic dispersion under dark conditions 10 min, in the visible under catalytic reaction conditions. 30 min after sampling, after centrifugation test absorbance values and record data. Nanofibers CLCT methylene blue degradation rate using the following formula:

Degradation rate = (C0-C) / C0 (3)

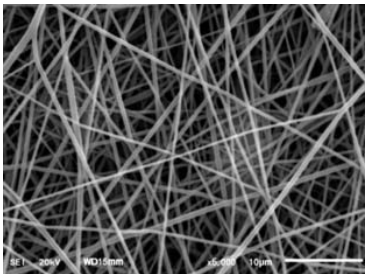
Where, C0, and C represent the initial absorbance of the solution and the remaining absorbance.

III. RESULTS AND DISCUSSION

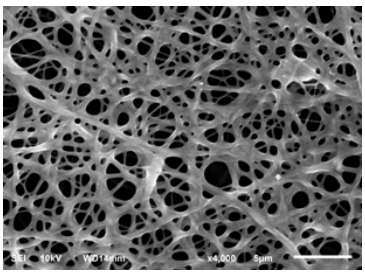
A. Lanthanum Nitrate Ratio on Fiber Morphology

Because of the rare earth lanthanum nitrate was added to increase the conversion efficiency of the titanium dioxide to visible light, so you can study different ratio of added amount of lanthanum nitrate effect on fiber morphology and catalytic properties. Increased body spinning sol of inorganic salts of lanthanum nitrate concentrations could theoretically increase the absorption from the photocatalytic ability of titanium dioxide. However, the concentration of lanthanum nitrate to be controlled within a reasonable range, as tetra-n-butyl and the PAN are all salts have a certain degree of tolerance. When the content of lanthanum nitrate is too low, TiO2 and after the formation of lanthanum ions are not binding enough electrons - the empty point, it will not produce the photocatalytic activity of great influence on the TiO2; when the content of lanthanum nitrate is too high, lanthanum nitrate will be coated on the surface of TiO2, the impact of TiO2 anatase crystal structure to change, not only can not achieve the purpose of improving the catalytic

performance, To a certain extent reduced its catalytic effect. Therefore, during the configuration of electrostatic spinning solution, we need a reasonable allocation of lanthanum nitrate ratio. In the undoped condition lanthanum nitrate, PAN / CNTs and (Ti (OC4H9) 4) formed in a smooth jet spinning solution, the spinning process smooth, uniform diameter of the obtained nanofiber. When La3 + Ti molar concentration equivalent to 0.01 to 2.0%, little effect on fiber morphology formed, fiber evenness, as shown in Figure 1 (a) below. When the amount of the rare earth lanthanum nitrate increased 2.0% to 2.5%, the resulting fiber adhesion to each other at this time, uneven thickness, such as 1 (b) shown in this phenomenon is mainly due to the electrostatic spinning solution of inorganic addition of lanthanum nitrate salt ingredient caused by excessive. According to the principle of electrostatic spinning, during electrostatic spinning, electrostatic spinning solution under an applied electric field strength and the solution itself the dual role of electric charge rapidly after ejected from the electrostatic spinning nozzle hole split, formed after evaporation of the solvent nanofibers, and when the addition amount of lanthanum nitrate increased from 2.0% to 2.5% resulting in a higher charge repulsion between the surface charge of the electrostatic spinning solution, electrostatic force becomes large, to enhance the degree of stretching, then spinning liquid injection process will split over the shunt, causing the jet unstable trajectory shifted in the injection process, on the receiving screen is difficult to collect, few received uneven fiber diameter, fiber thinner. Hence the need to control the amount of lanthanum rare earth nitrate in a certain range, having a diameter of nanofibers are more.



(a)



(b)

Figure 1. The SEM images of (a) La3+ adulterating content 0.04%; (a) La3+ adulterating content 2.0%

By EDX test, the doping amount of lanthanum nitrate molar ratio of 0.04%, the fiber surface of the element analyzed, as shown in Fig. As can be seen from the figure CNTs / La3 + spectra of co-doped TiO2 fibers in addition to the presence of foreign C, O and Ti element, there is a weak peak La may be formed after the La-doped La-O-Ti key, we need to be further and further determine the optimal doping amount of lanthanum nitrate with subsequent photocatalytic experiments.

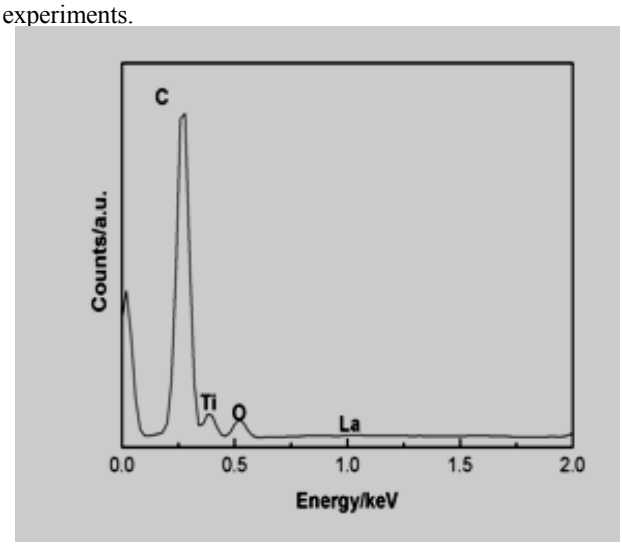


Figure 2. The EDX images of La3+ adulterating content 0.04%

B. High Temperature Carbonization of the Fiber Morphology

By scanning electron microscopy, respectively doping amount of lanthanum nitrate molar ratio of 0.04% of the fiber of CNTs / La3 + nanofibers morphology before and after firing co-doped scanning, as shown in FIG. From Figure 3 (a) can be seen, the nanofibers before and after calcination, uniform fiber diameter, the fiber has a good appearance, mainly due to the nanofibers before calcination presented as a homogeneous composition, distribution, and thus the fiber smooth surface. From Figure 3 (b) is found, the nanofibers after calcining at 500 □, the fiber diameter is significantly reduced, which is mainly due to the nano-fibers and organic phase separation occurs during calcination decomposition caused.

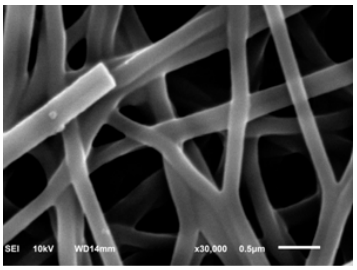


Figure 3. The SEM images of La3+ adulterating content 0.04% after calcine

C. Mechanical Performance Analysis

Figure 4 shows the mechanical properties of the test results nanofibers with different rare earth lanthanum nitrate doped. As it can be seen from the figure, with increasing rare earth content, CNTs / La3 + tensile strength co-doped TiO2 nanofibers declined. Because when only PAN and carbon nanotubes, tetra-n-butyl Total mixed, the molecule between two substances in hydrogen bonding interactions, has good compatibility. When the rare earth La3+ doping amount equivalent to the molar concentration of Ti is 0.01 to 1.0%, the mechanical properties of the fibers is almost unaffected. But with increase of the added amount of lanthanum nitrate is added, there has been a blend between nanofibers defects, resulting in declining tensile strength. This is mainly due to the rare earth lanthanum nitrate as a water-soluble charged ions, with an increase in the fiber content spinnability also decrease the adhesion between the fibers to each other, resulting in uneven thickness, thickness unevenness of the phenomenon. So choose Lanthanum nitrate ratio of 0.01 to 1.0 mol% of nanofibers catalytic experiments.

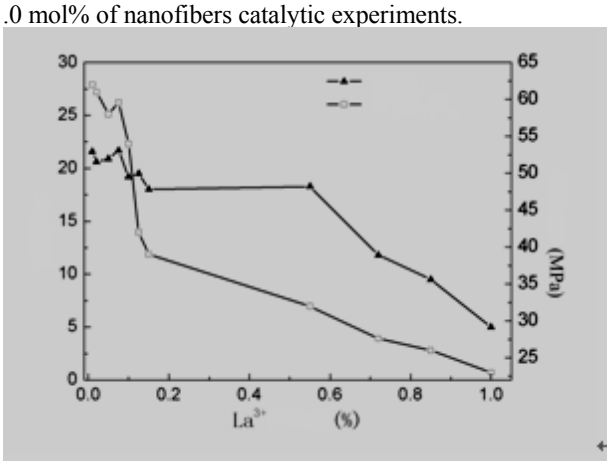


Figure 4. Mechanical properties of adulteration La3+ content (%) of CLCT

As shown in Figure 5, from 0.01 to 1.0% fiber (CLCT) photocatalytic degradation of methylene blue solution process. As it can be seen from the figure, after catalytic 3h, when the rare earth lanthanum nitrate molar ratio of 0.01%, the nano-fiber (CLCT) methylene blue degradation rate of 85.63%, the effect is significantly lower than that of the rare earth nitrate molar ratio of 0.05% when Victoria 98.87%; and when the content of lanthanum nitrate continued to increase to 0.07%, the catalytic effect but decreased to 92.32%, whereas when the content of lanthanum nitrate continued to increase to 0.15%, the catalytic effect but decreased to 78.65%, when lanthanum nitrate content continues to increase to 1.0%, the catalytic effect is reduced to 28.65%. This is mainly due to the cause when the La3+ may be added after the nanofibers (CLCT) uneven surface charge, forming a large number of oxygen defects, To compensate for this imbalance, rare earth La3+acts as in the process of electron trapping agent, continues to attract more electrons, thus the catalytic efficiency continues to improve, however, when the rare earth La3+ content continues to increase, due to the La3+ of radius much larger than Ti4 +, may no longer be part of La3 + doped into the lattice form but in the form of La2O3 inside cover surface of titanium dioxide, and in some way to reduce the junction to promote the formation of titania defect location, thus greatly reducing the activity of the center, causing the photocatalytic reduced activity

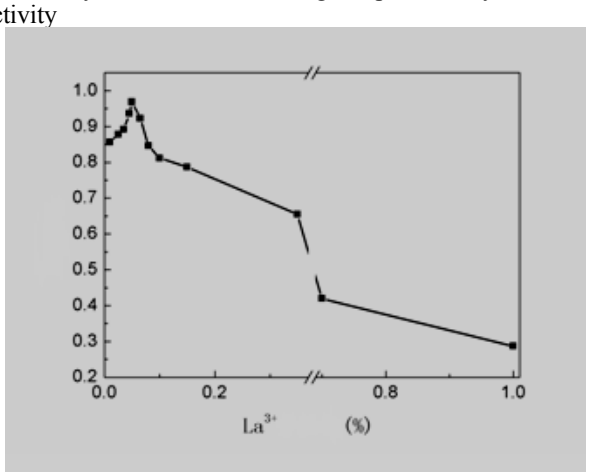


Figure 5. The degradation rate of adulteration La3+ content (%) of CLCT

IV. CONCLUSION

By electrospinning, prepare different content La3 + Doped La3 / CNTs of TiO2 (CLCT) nanofibers. And by SEM, EDX its morphology and mechanical properties observed. The study found that a molar ratio of 0.05% fiber evenness, good mechanical properties, while the water and methylene blue exhibit excellent catalytic performance. Rare earth lanthanum nitrate molar ratio of 0.05% of the fiber on the water methylene blue removal rate got 98.87 %.

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