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Preparation and Properties of Electro-Spun PVP / Silver Nanowire Composite Nanofibers

Shaowei Pang, Liyan Ding, Xiangyang Chen, Mingjie Xing*, Zhihao Sun, Jihao Tao

Collage of Textile and Apparel, Qingdao University, Qingdao, China

Email address:
qddxpsw@163.com (Shaowei Pang), xmjqdu@126.com (Mingjie Xing)

*Corresponding author

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Abstract: The silver nanowires were produced by the hydrothermal reaction, and the influences of different reaction conditions on morphologies of silver nanowires were researched. Then the PVP/silver nanowire composite nanofibers with different concentrations of silver nanowires were produced by the way of electrospinning in order to research the morphologies and performances. And the optimal solution was obtained when the solutions were stirred for 10 minutes and then stood for 30 minutes. When the hydrothermal reactor was heated at 180°C for 24 hours, the morphologies of silver nanowires were the best. Morphologies of silver nanowires and composite nanofibers with different proportions of silver nanowires were examined by scanning electron microscope. Finally the antibacterial property was tested by the inhibition zone method and the photocatalytic performance was measured by the degradation of methyl orange. The results show that when the proportion of silver nanowires in composite nanofibers exceeds 5%, the antibacterial property is significantly improved; when the ratio of silver nanowires is 10%, the antibacterial property remains stable; when the proportions of silver nanoparticles and silver nanowires are same, the antibacterial property of PVP/silver nanowire composite nanofiber is better; the photocatalytic performance is better when the proportion of silver nanowires is 8%.

Keywords: Electrospinning, Silver Nanowire, Antibacterial Property, Photocatalytic Performance

1. Introduction

Electrospinning is a process of producing nanofibers through the action of high-voltage electric field. There are three primary parts that include the appreciate high-voltage, the needle with small diameter and the collector. The polymer solution is put into the injector and it can be extruded by the pusher, then the high-voltage is added to the droplet. When the electrical force overcomes the surface tension of the droplet, a jet is ejected [1]. The polymer jet becomes very fine and long through the unsteady stretch process. At the same time, the solvent evaporates and the polymer fibers are collected into the collector. Compared with the traditional non-woven materials, electrospun nanofibers have many advantages such as small fiber diameter, large specific surface area and high porosity [2].

Electrospinning have wide applications and some of the possible commercial uses are listed below: as reinforcing fibers in composite materials [3]; as a non-wetting surface layer on ordinary textiles [4]; as a support for very thin polymeric separation membranes; for application of insecticide on plants [5]; as a route to the production of non-woven fabrics; as a wound dressing material [6]. For example, the diameter of nanofibers is smaller than that of cells, so it can imitate the structure and biological function of natural extracellular matrix in order to be applied in drug controlled release, wound repair, biological engineering and so on; the filtration efficiency of fiber filter material can increase with the decrease of fiber diameter, therefore, electrospinning is a good method to improve the filtration performance; electrospinning nanofibers have a high specific surface area and porosity which can increase the sensing area of the sensing material, and then it can improve the performance of the sensor.

In recent years, the technology of electrospinning to get pure polymer nanofibers is gradually mature. However, the pure polymer nanofibers have been unable to meet the needs in many aspects because of the increasing demand of nanofibers. Therefore the composite nanofibers by the carrier

of the electrospinning polymer have been the hotspot. The electrospinning composite nanofibers with metal nanoparticles have been popular and there are different metal nanoparticles such as gold, silver, tin, titanium, zinc and others. Actually, nano-silver materials with excellent antibacterial properties [7], electrical conductivity, good biocompatibility, thermal conductivity and catalysis [8] have been widely used in biological sciences, medical and health, optoelectronic materials [9] and other research fields.

Nano-silver means the size of silver is in nanometer. The physical form of nano-silver is powder and it is dark black. The size of nano-silver is about 100nm and most of the silver nanoparticles are generally between 25nm and 50nm. Metal silver has good electrical conductivity and it can be doubled to enhance when silver is in nanometer. Many electronic conductive products are doped with nano-silver material to improve their performances. Surface effects and quantum size effects also make nano-silver materials be used in many other areas, such as medical dressings and optical materials.

At present, there are many methods to prepare silver nanowires [10] such as the polyol reduction method [11], the solvothermal (hydrothermal) method [12], the electrochemical method, the light reduction method [13] and the chemical plating method. The factors that affect the growth of silver nanowires include chemical additives [14], reaction conditions [15] and others. (1) The polyol reduction method is the way that the certain types of reducing agents and dispersants are added to the silver compounds or salt solutions in order to restore the silver ions or to substitute silver by other more active metals. This method has short reaction time and good reproducibility, but the operation is more cumbersome and the reaction time and the solution flow requirements have to be strictly controlled. (2) The solvothermal method is also called the hydrothermal method. This method needs to prepare the reaction solution firstly and then the sizes and morphologies of silver nanoparticles can be changed by setting different concentrations and PH values in the hydrothermal treatment. (3) The electrochemical method is the way to get different morphologies of silver nanoparticles by changing some experimental conditions through the connection of the electrochemical workstations and the ultrasonic waves. (4) Of course the light reduction method makes use of the reduction effect of the visible light. Under the specific experimental conditions, some organic matters are reduced to get different morphologies of silver nanoparticles. This method requires precise operation and the controllability is poor. (5) After the silver gel solution is made by the experimental method, it can be electroplated by using ultrasonic technology to acquire the silver nanoparticles. It is the chemical plating method.

In this paper, silver nanowires were prepared by the hydrothermal method. The effects of hydrothermal reaction conditions on the growth of silver nanowires were studied. Then the PVP/silver nanowire composite nanofibers were prepared by electrospinning and the morphologies of composite nanofibers were characterized. Finally the antibacterial properties were tested by the inhibition zone and the photocatalytic properties were tested by the degradation of methyl orange under visible light.

2. Experimental

2.1. Composite Preparation

Firstly, three kinds of solutions were prepared. They were 50 mL 0.02 mol/L silver nitrate ($AgNO_3$) solution, 50 mL 0.2 mol/L sodium chloride (NaCl) solution and 100 mL 6.5 mol/L glucose solution. 7 mL NaCl solution was slowly dripped into 35ml $AgNO_3$ solution which was put in the magnetic stirrer with the rotary speed 120 r/min. Then it can be found the white silver chloride (AgCl) precipitate increased with the increasing of NaCl solution. The mixed solution was stirred for 10 min to obtain the solution A. Then the solution A was wholly put into the glucose solution and stirred for 10 min to make solution B. The solution B was transferred into the hydrothermal reactor with the liner of polytetrafluoroethylene and then the reactor was put into dryer to make the solution C. The solution C was transferred into the centrifuge tube and was centrifuged in distilled water for three times and in absolute ethyl alcohol for two times. After the centrifugal treatment, the centrifuge tube was dried at 60°C for 3 h and the furvous silver nanoparticles were obtained. In this procedure, the setting time of solution A and the hydrothermal temperature and the hydrothermal time of solution B were different in order to observe the growth characteristics of silver particles. Finally the best experimental conditions were selected to make the silver nanowires.

The polyvinylpyrrolidone (PVP) solutions with the concentration of 10% were prepared by dissolving PVP powder in absolute ethyl alcohol with intensive stirring for 3 h. When the PVP solution was divided into five equal samples after defoaming treatment, the silver nanowires with different concentrations (2%, 4%, 5%, 8% and 10%) were respectively added to them and the stable spinning solutions were obtained after stirring.

2.2. Electrospinning

The electrospinning apparatus includes high voltage power supply, metal collector, syringe pump, syringe and stainless steel needle. The polymer solution was injected into the syringe until the liquid surface reached the top line of the stainless steel needle. During electrospinning, the solution was charged with a high electric voltage and the solution flow speed was controlled by the syringe pump. The parameters for electrospinning process are listed in Table 1. Nanofiber productivity was collected in the metal collector.

Table 1. *Electrospinning conditions.*

Parameters	Values
Applied voltage	20 kV
Solution flow speed	0.005 mm/s
Spinning distance	15 cm
Humidity	60% RH
Environmental temperature	20°C

2.3. Structure and Performance Testing

2.3.1. Scanning Electron Microscopy Analysis

The microstructures of silver nanowires under different conditions were observed by scanning electron microscopy.

The microstructures of PVP/silver nanowire composite nanofibers with different silver nanowires were observed by scanning electron microscopy.

2.3.2. Analysis of Antibacterial Properties

There were PVP/silver nanowire composite nanofibers and PVP/silver nanoparticles nanofibers; two strains which were staphylococcus aureus (susceptible strains) ATCC25923 and escherichia coli ATCC25922 were provided by Qingdao University Medical College.

The inhibition zone method was used in this experiment. 1 mL of staphylococcus aureus (escherichia coli) was cultivated at 37°C in 25 ml sterile conical flask for 24 h, and then 20 ml physiological saline was poured. When it was shaken to be stable, 15 ml the solution was injected into the plate. Five kinds of prepared PVP/silver nanowire composite nanofibers were made into round test samples with the diameter of 1 cm which were denoted as A, B, C, D and E. A PVP/silver nanoparticle composite nanofibers with 10% of silver nanoparticles concentration was noted as F to be the comparative experiment. The samples were placed in culture plates and complete contacted with the bacteria to incubate at 37°C in an incubator. After 24 hours, the diameters of inhibition zone were measured.

2.3.3. Analysis of Photocatalytic Performance

In order to study the photocatalytic activities of PVP/silver nanowire composite nanofibers with different concentration of silver nanowires, two kinds of samples with the concentration of 5% and 8% of silver nanowires were measured by the degradation of methyl orange under visible light. The process was as follows.

Two samples with same weight were placed in a certain concentration of methyl orange solutions for catalytic decomposition reaction. The photocatalytic activities were determined by the change of dye absorbance. The degradation rate is calculated by Eq.1.

$$\eta=\frac{A_0\text{-}A}{A_0}\times 100\% \quad (1)$$

where A_0 is the peak of the initial absorbance curve of methyl orange. A is the peak of the absorbance curve after photocatalytic degradation.

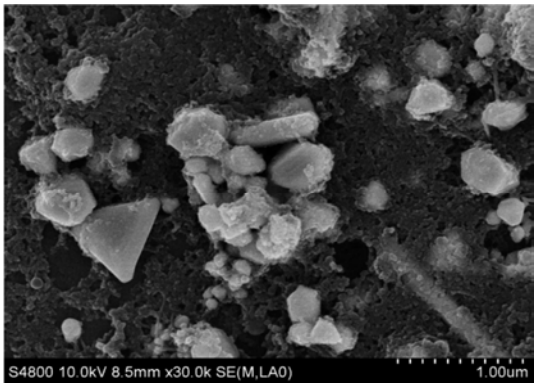
3. Results and Discussion

3.1. SEM Characterizations of Silver Nanowires

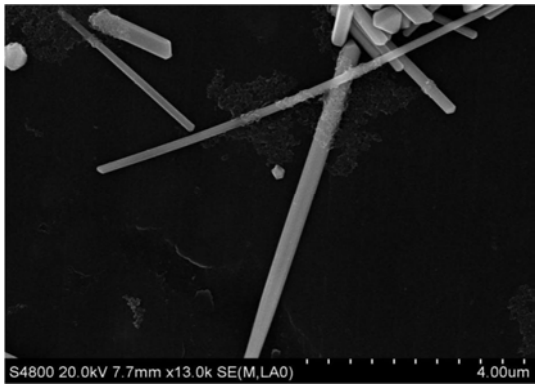
The linear morphology of silver nanowires can be affected by many factors such as the hydrothermal time, the hydrothermal temperature and the solution setting time. In the experiment, the silver nanoparticles with different morphological characteristics were prepared by controlling these different factors, and the influences of these factors were analyzed.

3.1.1. Effect of the Hydrothermal Temperature

The effects of the hydrothermal temperature on the morphologies of silver nanowires were obtained when other factors were same. In this experiment, four hydrothermal temperatures were selected which were 120°C, 140°C, 160°C and 180°C. After 24 hours of reaction, four groups of silver nanowires were scanned by scanning electron microscopy. The results are revealed in Figure 1.



(a)



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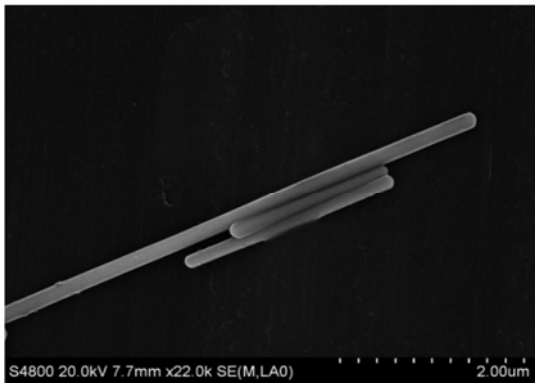

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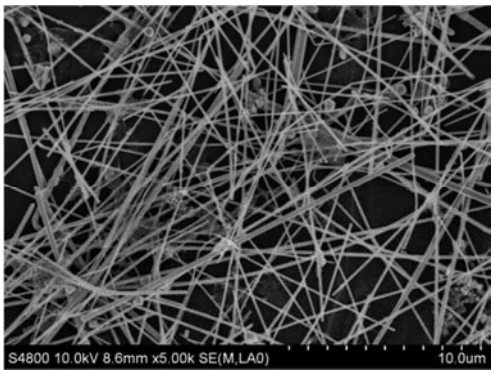


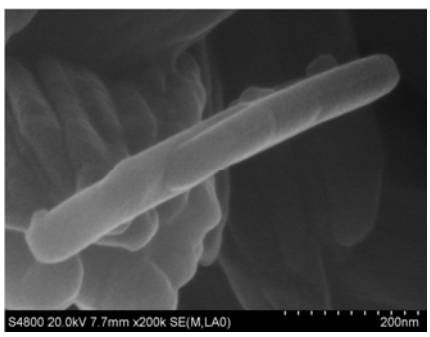
(d)

Figure 1. *SEM images: (a) Morphologies of silver nanoparticles in 120°C; (b) Morphologies of silver nanoparticles in 140℃; (c) Morphologies of silver nanoparticles in 160℃ and (d) Morphologies of silver nanoparticles in 180°C.*

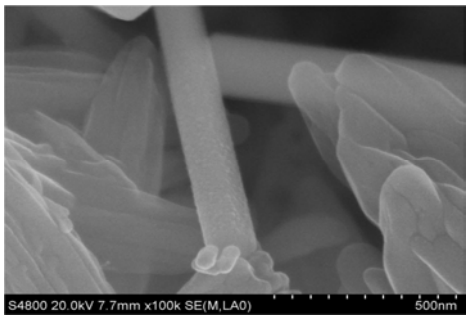
When the hydrothermal temperature is 120°C, the silver nanoparticles obtained after 24 hours are mostly polyhedrons in Figure 1 (a). The particles have smaller particle size and gradually grow from irregular shape to regular triangular prism. From Figure 1 (b), the hydrothermal temperature is raised to 140°C and parts of silver nanoparticles grow into silver nanorods. But there are still some silver nanoparticles, and the silver nanorods have different lengths and diameters. As shown in Figure 1(c), when the temperature is raised to 160°C, the silver nanoparticles have almost disappeared, and they are replaced by a large number of silver nanorods with uniform diameters. However, the lengths of silver nanorods are quite different, which is not the appearance of silver nanowires. After heating at 180°C for 24 h, the morphologies of silver nanoparticles are revealed in Figure 1(d). It can be found that the silver nanowires are smooth and defective, and the particle size is uniform and the length is basically same. In a word, the best hydrothermal temperature to make silver nanowires is at 180°C.

3.1.2. Effect of the Hydrothermal Time

When other conditions were consistent, the effect of hydrothermal time on the morphologies of silver nanowires was obtained by controlling different hydrothermal reaction time. When the hydrothermal temperature was 180°C, the three kinds of hydrothermal reaction time respectively were 16 h, 20 h and 28 h. The SEM images of the silver nanowires obtained in the three groups are shown in Figure 2.



(a)



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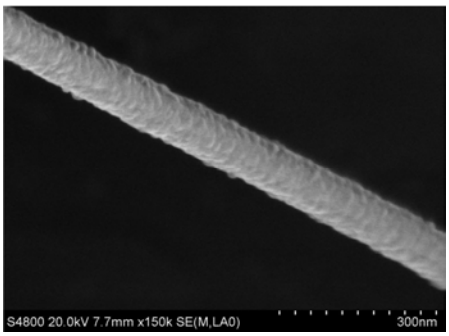

(c)

Figure 2. *SEM images: (a) Morphologies of silver nanoparticles after 16h; (b) Morphologies of silver nanoparticles after 24h and (c) Morphologies of silver nanoparticles after 28 h.*

It can be seen from the three groups of experiments, when the hydrothermal time is different, the morphologies of silver nanoparticles will have differences. As shown in Figure 2 (a), after 16 hours of the hydrothermal reaction, most of the silver ions are not reduced, they are still in the form of silver ions and only a very small number of silver nuclears grow into silver nanorods. The formations of silver nanorods are extremely short and the surface is protruding. When the heat conditions are shown in Figure 2 (b), some silver nuclears have developed and grow into rods with relatively uniform particle size and smooth surface, but the length is shorter and does not meet the spinning requirements. As revealed in Figure 2 (c), the final silver nanowires are uniform in size and medium in length, but the surface morphology of the silver nanowires is rough. Therefore, when the hydrothermal time is short, the silver nanoparticles can't produce silver nanowires which can meet the requirements. When the time is too long, the surface of the silver nanowires is rough and the morphology is not good.

3.1.3. Effect of the Solution Settin Time

In addition to the hydrothermal time and the hydrothermal temperature, the solution setting time is also an important factor affecting the morphology of silver nanowires. Three solutions that tabled as the solution A, the solution B and the solution C were respectively placed for 30 min, 1 h and 3 h, then the phenomenon were observed and analyzed. The results are as follows.

With the prolongation of the solution setting time, the mixed solution ($AgNO_3$ and NaCl) gradually changes from

milky to blue. The longer the setting time is, the darker the blue is. When the solution is setting for 3 h, the solution appears to have sediment. After the hydrothermal reaction, it can be found that the silver nanowires produced by the solution A are in good morphologies, and the solution B and the solution C didn't produce rod or linear nanoparticles. The reason to explain the phenomenon is that the free silver ions can be produced when $AgNO_3$ and NaCl are mixed and silver ions are restored to silver after adding glucose. If it can't reach the suitable hydrothermal temperature for a long time, silver nucleus will not grow and silver ions will continue to restore, and finally it can separate out the metallic silver.

3.2. Characterization of PVP/Silver Nanowire Composite Nanofibers

The PVP/ silver nanowire composite nanofibers were characterized by SEM, as revealed in Figure 3.

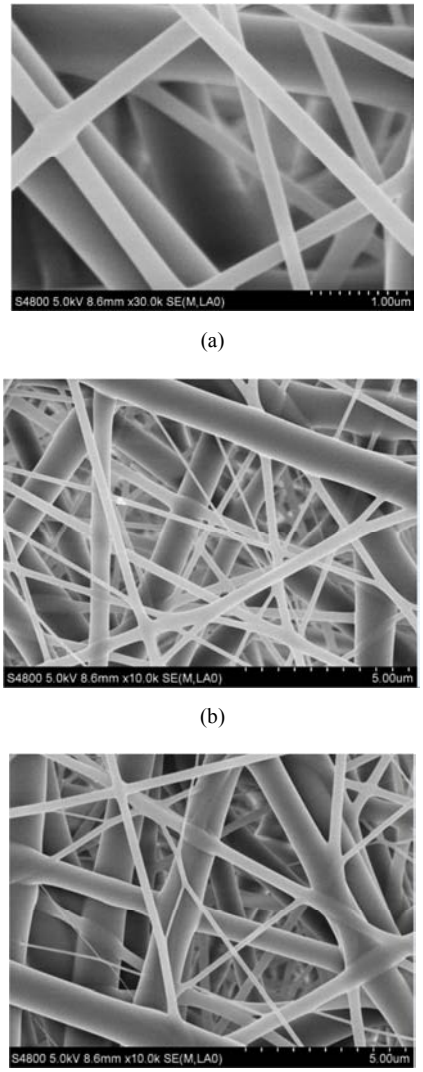

Figure 3. *SEM images: (a) PVP/ silver nanowire composite nanofibers when the proportion of silver nanowires is 5%; (b) PVP/ silver nanowire composite nanofibers when the proportion of silver nanowires is 8% and (c) PVP/ silver nanowire composite nanofibers when the proportion of silver nanowires is 10%.*

It can be seen that the distribution of silver nanowires on the surface of PVP/silver nanowire composite nanofibers is better when the concentration of silver nanowires is 5%. With the increase of the concentration of silver nanowires, the uniformity of silver nanowires on the surface is reduced. The distribution of silver nanowires will not be uniform when the concentration of silver nanowires increases. The phenomenon is owing to the agglomeration of silver nanowires. The excessive silver nanowires can't be broken up under high pressure conditions.

3.3. The Antibacterial Properties

There are five samples of PVP/silver nanowire composite nanofibers and they are tabled as sample A, sample B, sample C, sample D and sample E. The concentration of silver nanowires in sample A is 2%, the concentration in sample B is 4%, the concentration of silver nanowires in sample C is 5%, the concentration in sample D is 8% and in sample E the concentration is 10%. The compared sample tabled as sample F is the PVP/silver nanoparticles composite nanofibers and the concentrations of the silver nanoparticles is 10%. After the antibacterial tests of all the samples, the diameters of the inhibition zones are different, and the results are shown in Figure 4.

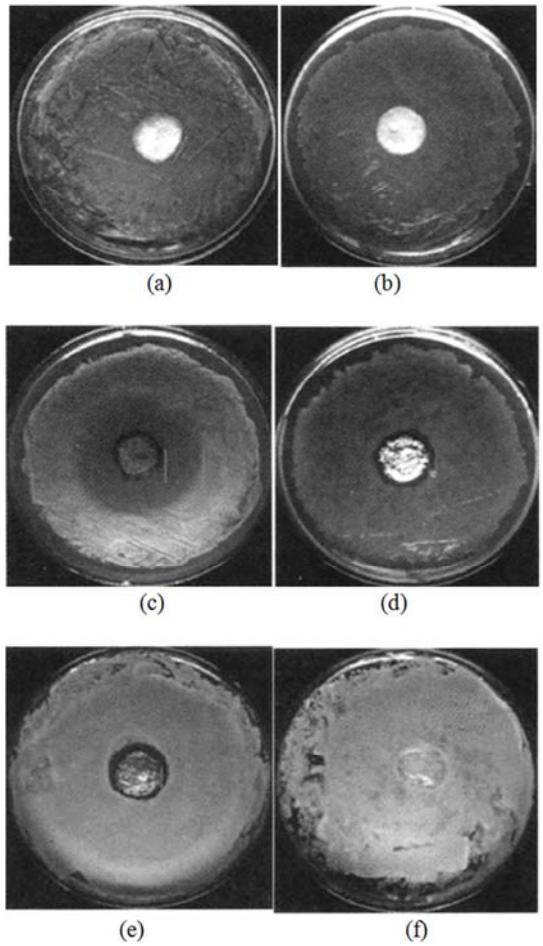

Figure 4. *Photos of inhibition zone: (a) the inhibition zone of sample A; (b) the inhibition zone of sample B; (c) the inhibition zone of sample C; (d) the inhibition zone of sample D; (e) the inhibition zone of sample E and (f) the inhibition zone of sample F.*

As shown in Figure 4, the inhibition zones are observed around all the samples and the sizes of inhibition zones can be measured. The diameters of the inhibition zone from sample A to sample F are respectively 10.1 mm, 13.6 mm, 24.5 mm, 27.0 mm, 29.8 mm, and 27.4 mm. The results show that PVP/silver nanowire composite nanofibers can inhibit the growth of staphylococcus aureus and escherichia coli, and PVP/silver nanowire composite nanofibers have excellent antibacterial properties when the concentration of silver nanowires is more than 5%. From the front five samples, the higher the concentration of silver nanowires are, the better the antibacterial property is.

By comparing with the sample F and the samples E, it can be found that even though the concentrations are same, the antibacterial effect also has a certain difference. By comparing the diameters of the inhibition zones of sample D and sample F, the antibacterial effects of silver nanowires with 8% concentration is basically consistent with that of silver nanoparticles with 10% concentration. Therefore, the silver nanowires have better antibacterial effect than the silver nanoparticles. Compared with silver nanoparticles, silver nanowires have a greater specific surface area and contact area, so the antibacterial property of silver nanowires is more superior than that of the silver nanoparticles.

3.4. Photocatalytic Performance

Two kinds of PVP/silver nanowire composite nanofibers that the concentrations of silver nanowires are 5% and 8% were tested by the experiments of photocatalytic degradation of methyl orange with visible light. The UV-visible absorption spectrum was obtained in Figure 5.

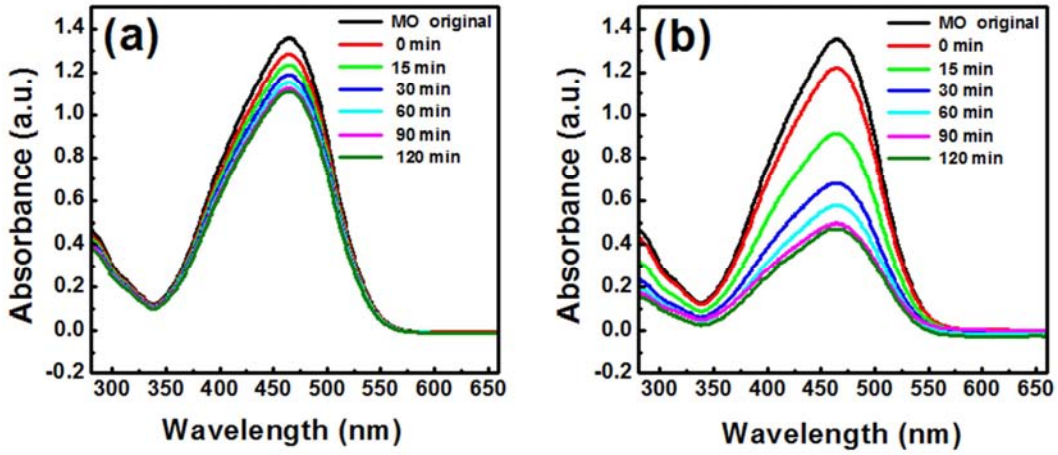

Figure 5. *Ultraviolet visible absorption spectrum of two kinds of composite nanofibers after photocatalysis.*

After the photocatalytic degradation experiments for 2 hours, as shown in Figure 5, the degradation efficiencies of the PVP/silver nanowire composite nanofibers with 5% silver nanowires is 95.2% and the degradation efficiencies is 99.1% when the concentration of silver nanowires is 8%. Therefore, the photocatalytic performance of PVP/silver nanowire composite nanofibers is better when the concentration of silver nanowires is 8%, and the degradation efficiency of PVP/silver nanowire composite nanofibers can reach more than 70% after 10 times of repeated use.

4. Conclusion

(1) The silver nanowires were prepared by the hydrothermal reaction method, and the optimal solution was obtained when the solutions were stirred for 10 minutes and then stood for 30 minutes. When the hydrothermal reactor was heated at 180 ℃ for 24 hours, the morphologies of silver nanowires were the best.

(2) By adjusting the concentration of silver nanowires and comparing the SEM characterization of PVP/silver nanowire composite nanofibers, it was found that when the concentration of silver nanowires was low, the distribution of PVP nanofibers was uniform and the uniformity of distribution would decrease when the concentration of the silver nanowires increased.

(3) The antibacterial properties of PVP/silver nanowire composite nanofibers with different concentrations of silver nanowires were tested by the inhibition zone method, and the compared group which was the PVP/silver nanoparticle composite nanofibers was set up. The results showed that the antibacterial ability of PVP/silver nanowire composite nanofibers was improved when the concentration of silver nanowires exceeded to 5%. When the concentration of silver nanowires reached to 10%, the antibacterial ability was gradually stable. When the concentration of silver nanoparticles and silver nanowires were same, the antibacterial properties of PVP/silver nanowire composite nanofibers were more excellent.

(4) The photocatalytic performance of PVP/silver nanowire composite nanofibers was tested by the experiments of photocatalytic degradation of methyl orange with visible light. The composite nanofibers with silver nanowires concentration of 8% had better photocatalytic performance and the degradation efficiency could slow down slowly after reused.

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