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Preparation and Properties of Nano-TiO_2 Photo-catalytic Silk Respirator Paper

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Abstract: In order to obtain paper respirator with dust resistance performance and antibacterial property, silk photo-catalytic respirator paper was made by loading nano-TiO_2 photo-catalyst on silk based respirator paper. The pore structure, surface topography and TiO_2 distribution, and the filtration performance of silk respirator paper were studied by using a pore size meter (PSM), a field emission scanning electron microscope (FESEM), and a filter tester, respectively. In addition, the antibacterial property of silk respirator paper was also investigated. The results showed that the pore structure and filtration performance of silk respirator paper could be controlled by changing the degree of beating of silk pulp and the basis weight of silk paper. Silk respirator paper of 45 g/m^2 made from silk pulp having beating degree of 85 ^{o}SR had high filtration efficiency and appropriate filtration resistance. Nano-TiO_2 particles were mainly attached to the surface of silk paper, and the loading of nano-TiO_2 photo-catalyst resulted in a slight decrease in filtration resistance and filtration efficiency of silk respirator paper. It, however, improved the antibacterial property of silk respirator paper effectively.

Keywords: Silk, Nano-TiO_2, Silk respirator paper, Filtration performance, Antibacterial property

Introduction

In recent years, Severe Acute Respiratory Syndromes (SARS), bird flu, pandemic influenza (H1N1), and other worldwide respiratory infections have caused serious threat to human health. These infectious germs infringe people's respiratory tract through air in the form of microbial aerosol. Respirator is the most commonly used protective appliances in people's daily life, but it usually has less antibacterial or bacteria-killing function, so there exists the defect of cross infection when bacteria is absorbed in the respirator. Therefore, giving the protective function to common respirator paper has become the hotspot in the research of health protection. Titanium dioxide (TiO_2) has been the focus of numerous investigations for innocuity, anti-bacteria, UV protection, super hydrophilicity, and high coloration in recent years [1-3]. Nano-TiO_2 is a semiconductive photo-catalyst [4-11] and can kill bacteria or inhibit bacterial growth [12,13]. Therefore, a photo-catalytic antibacterial respirator paper made by loading nano-TiO_2 on silk paper has a good application prospect in the field of respiratory disease prevention.

The removal efficiency of dust and microbe in the air depends on the filter characteristics of respirator materials [14]. High performance filter materials can meet the requirements of medical protective respirator. Silk, the "Queen of Fibers" for thousands of years, possesses many excellent features [15]. It is a kind of porous fiber with good air permeability [16], and its fiber diameter is only one tenth to one fifth of that of wood fiber, so it is suitable for making specialty paper having high air permeability and absorbability [17,18]. In addition, silk paper has good softness and comfortableness because of silk fiber's flexibility, and the pore structure of the silk paper can be controlled by changing the basis weight of silk paper and the beating degree of silk pulp, so it is a very promising functional material. In this paper, a kind of multi-function respirator material with filtering-photo-catalysis synergy effect was prepared through loading nano-TiO_2 on silk paper, and the influence of the manufacturing process on the pore structure, filtration performance, and antibacterial property of the silk respirator paper made from waste silk fiber was studied.

Experimental

Raw Materials

Nano-TiO_2 powder was provided by Hangzhou Wan Jing New Material Co., Ltd., and the physico-chemical characteristics of nano-TiO_2 is: white powder, molecular weight: 79.87, grain size: 6 nm, crystalline form: anatase, purity: 99.2 %, specific surface area: 200 m^2/g. Waste silk was derived from a filature of Zhejiang province, China. Polyethylene oxide (PEO) was provided by Shanghai Zhanhe industrial Co., Ltd., which is a kind of water soluble white powder, and is used as dispersant in paper industry to improve the uniformity of paper. Na_2CO_3 (analytically pure) was purchased from market and culture medium was provided by Hangzhou Cyanine Chemical Co., Ltd., which includes peptone (reagent pure grade), agar powder (reagent pure grade), beef extract (reagent pure grade), and sodium chloride (analytically pure). Strains applied in the experiment was bacillus subtilis and was provided by the Microbiology Laboratory of School of Biological and Chemical Engineering, Zhejiang University of Science & Technology.

Preparation of Silk Respirator Paper

Silk fiber was cut into 5 mm length and placed in a 1000 m*l*

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beaker, and 0.5 wt% Na_2CO_3 solution was used to process the silk in a constant temperature water bath at 100 °C for 60 min to remove silk glue [19,20]. After removing silk glue, silk was washed completely and was disintegrated and cut properly in a Valley beater at the concentration of 0.5 wt% and then were further refined in a PFI refiner at the concentration of 15 wt%. Finally, 0.1 wt% PEO solution was added to the prepared silk pulp to disperse silk fibers evenly, and silk paper was manufactured on a standard sheet former.

Nano-TiO_2 was dispersed into water to prepare nano-TiO_2 suspension of the concentration of 1 wt%, and then ultrasonic dispersion was further carried out for 15 min to obtain well dispersed suspension. Placing silk respirator paper in a Büchner funnel to filter the well dispersed nano-TiO_2 suspension. After filtering, dry the paper with flat dryer, and then the photo-catalytic silk respirator paper was manufactured.

Pore Structure and Surface Structure Analysis of Silk Respirator Paper

A Pore Size Meter PSM165 (TOPAS company, Germany) was used to determine the maximum and mean pore size of silk respirator paper. The test procedure is fully automated. Measurement results may be presented in customized reports using PSM Win software. The testing fluid used is Topor (perfluoro compound, Topas specific testing fluid), the pressure drop is 350 mbar, sample adapter is 11 mm, sample diameter is 30-40 mm, the test duration is 5~15 min. A Field Emission Scanning Electron Microscope (FESEM) - SIRION-100 (FEI company, USA) was used to characterize the surface structure of silk respirator paper and the distribution of nano-TiO_2 particles.

Filtration Performance Analysis of Silk Respirator Paper

A TSI-8130 Automated Filter Tester (USA) was used to determine the filtration resistance and aerosol penetration of silk respirator paper. The aerosol particles applied in the test were solid sodium chloride (NaCl), the mean particle size of NaCl aerosols is 0.3 μm and the geometric standard deviation is <1.83, the flow rate was 32 *l*/min, the flow velocity was 5.3 cm/s. Test area is 100 cm^2. Particles of 0.3 μm have the maximum penetrability, and are widely used as the test dust to test and evaluate the filtration efficiency of filters. The filtration efficiency (E) or penetration (P) is usually given in % and the relation between them is [21]:

$$E = 1 - P \quad (1)$$

Antibacterial Property Analysis of Silk Respirator Paper

Preparation of Culture Medium

2.0 g peptone (reagent pure grade), 4.0 g agar powder (reagent pure grade), 0.6 g beef extract (reagent pure grade), and 1.0 g NaCl (analytically pure) were put into distilled water, stirred, and heated to dissolve them. After pH was adjusted to 7.4~7.6, the mixture was put in a high temperature steam sterilizer and kept for 20 min to kill bacteria, then cooled it to 55-60 °C and 15 m*l* of it was poured into plate. Finally, it was covered with the lid and placed on the desktop.

Bacterination

Cant inoculation method was used. A few strains from test tube filled with microbes (bacillus subtilis) were picked and inoculated to a blank test tube with sterile cant culture medium. When the bacteria grew fully, the test tube was plugged with silica gel plug and stored in the refrigerator at 4 °C.

Antibacterial Experiment

Hole puncher was used to punch the silk respirator paper into small rounds with diameter of 6 mm. After high-pressure sterilization, these small rounds were then dried and stored in a drying oven for subsequent use. Strains were dispersed in 0.9 wt% physiological saline to prepare well mixed strains suspension of 10 mg/m*l*. 0.2 m*l* of strains suspension was pipetted and spread out on culture medium evenly. Small circular silk paper was picked up with small sterile tweezers and placed face up on the plating medium coated with strains, then the plating medium was placed in incubator and kept for 24 h at 37 °C. The condition of bacteria growth was observed and the diameter of inhibition zone was determined using transparent ruler. All the instruments used in this experiment were sterilized under the UV lamp for 20 min.

Results and Discussion

Effect of Beating on the Silk Fiber Morphology

The mechanical action of beating and refining crushes of the silk fibers make the fiber surface fluffy and increases the softness and flexibility of silk fibers. However, silk fibers are also cut short by the mechanical action. After being beaten and refined, the beating degree of silk pulp was measured by a Schopper-Riegler beating degree tester, and the fiber morphology was observed under a microscope (silk fibers were dyed by Herzberg's stain). Silk fiber morphology with different beating degrees was shown in Figure 1. From the Figure, it can be seen that the higher beating degree is, the more flexible the silk fibers are with more fibrils on the surface of silk fibers.

Effect of the Beating Degree and Basis Weight on the Filtration Performance of Silk Respirator Paper

The filtration efficiency and filtration resistance of silk respirator paper with different basis weight and made from silk pulp having different beating degrees were shown in Figure 2.

The filtration efficiency of porous filter material depends, to a large extent, on its void fraction and pore size. The smaller the void fraction and pore size are, the higher the filtration efficiency is [22]. It can be seen from Figure 2 that

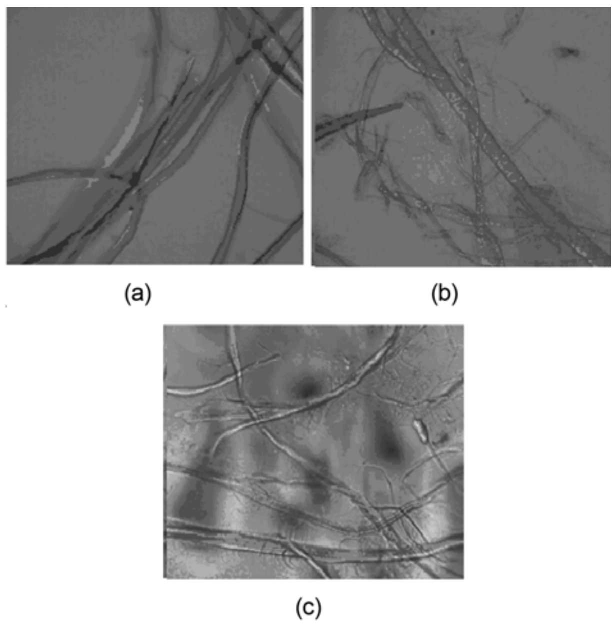

Figure 1. Effect of beating on the silk fiber morphology (×400): (a) 28 °SR, (b) 51 °SR, and (c) 85 °SR.

the filtration efficiency and filtration resistance of silk paper with the same basis weight increased with the increase of beating degree of silk pulp, and the filtration efficiency and filtration resistance of silk paper with different basis weight had the same trends. Because silk pulp having high beating degree is characterized by internal fibrillation and external fibrillation of fibers [23] and there are more fibrils and hydroxyl groups exposed on the surface of silk fibers, this increased fiber bonding strength, made silk paper more denser, and lowered porosity [24,25], thus increasing the filtration resistance and filtration efficiency of NaCl particles. The filtration resistance and filtration efficiency of silk paper with high basis weight were higher than those of silk paper with low basis weight, because paper with high basis weight has large thickness and low porosity.

Generally, filter materials with high filtration efficiency and low filtration resistance are suitable for making respirator [26,27]. As shown in Figure 2, self-made silk paper of 60 g/m^2 has high filtration efficiency, but its filtration resistance

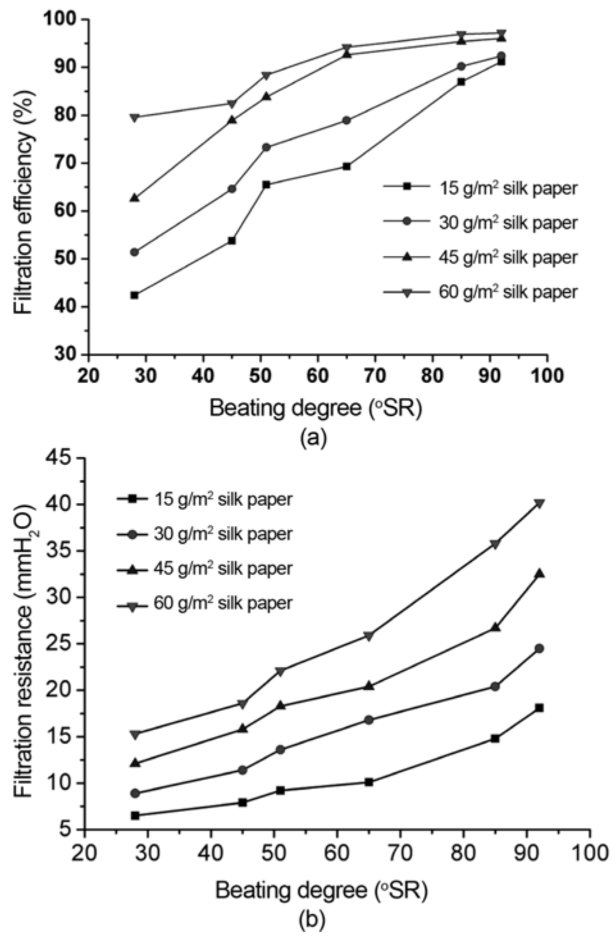

Figure 2. Effect of beating degree and basis weight on the filtration efficiency and filtration resistance of silk respirator paper: (a) filtration efficiency and (b) filtration resistance.

was also very high, which was unfavorable for breathing. Silk paper weighing 15 g/m^2 and 30 g/m^2 had low filtration resistance, but their filtration efficiency was also very low. Only the silk paper of 45 g/m^2 made from pulp having beating degree of 85 °SR has high filtration efficiency and appropriate filtration resistance, and is suitable for making respirator.

At present, the commercially available respirators in

Table 1. The filtration performance of commercially available respirators

Type of filters		Flow rate (*l*/min)	Penetration (%)	Filtration efficiency (%)	Resistance (mmH$_2$O)
Cotton cloth respirator	12-layers	32	50.3	49.7	25.8
	16-layers	32	31.6	68.4	27.6
Nonwoven respirator	2-layers	32	12.5	87.5	28.7
	3-layers	32	7.6	92.4	34.5
	4-layers	32	4.9	95.1	42.0
Self-made silk respirator paper (45 g/m^2)	Beating degree (85 °SR)	32	4.6	95.4	26.7

China mainly include cotton cloth respirator, nonwoven respirator, and so on. The filtration performance of the commercially available respirator materials and self-made silk paper of 45 g/m^2 are shown in Table 1.

It can be seen from Table 1 that the filtration efficiency of the cotton cloth respirators is very low, and the filtration efficiency of 4-layers nonwoven respirator is relatively high, but its filtration resistance is very high. Self-made silk paper is more suitable for making respirator than the commercially available filters.

Pore Structure of Silk Respirator Paper

The surface structure of silk respirator paper (45 g/m^2) and the distribution of nano-TiO_2 particles were shown in Figure 3. As shown in Figure 3(a) and Figure 3(b), silk paper made from silk pulp with higher beating degree has higher nano-TiO_2 particle density. In addition, most of the nano-TiO_2 particles were intercepted on the surface of silk paper, and there are less nano-TiO_2 particles inside the silk paper. Since nano-TiO_2 particles are polar particles with high specific surface and they were loaded on silk paper by surface filtration, nano-TiO_2 particles were strongly absorbed by the surface of silk paper which has more polar groups. However, it is difficult for nano-TiO_2 particles to reach the inside of silk paper along thickness direction due to the small and tortuous pore size in silk paper. The paper surface covered with nano-TiO_2 particles can be used as the outside of respirator. This will be beneficial for respirator to produce anti-bacteria action and self-cleaning effect due to the photo-catalysis action of nano-TiO_2.

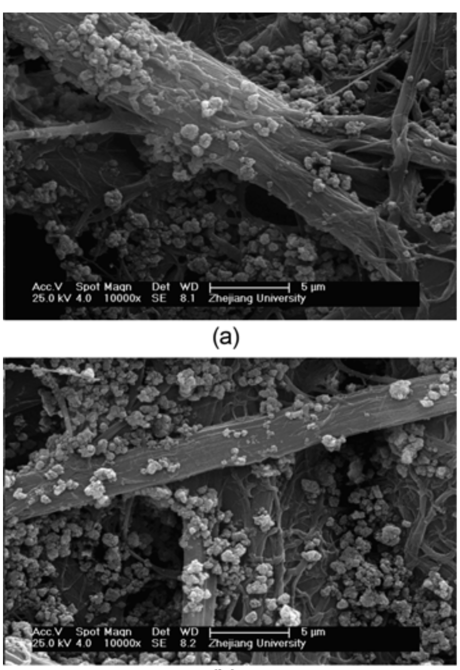

Figure 3. FESEM photographs of nano-TiO_2 distribution on silk paper. (a) 5 % nano-TiO_2 loading (51 ^{o}SR) and (b) 5 % nano-TiO_2 loading (85 ^{o}SR).

After loading nano-TiO_2 particles, the basis weight of silk papers increased. The changes in basis weight of silk papers and the retention rate of nano- TiO_2 were shown in Table 2.

It can be seen from Table 2 that the retention rate of nano-TiO_2 particles in silk paper made from silk pulp having beating degree of 85 ^{o}SR was higher than that in silk paper made from silk pulp having beating degree of 51 ^{o}SR, because silk paper made from silk pulp having high beating degree had compact structure and more nano-TiO_2 particles were intercepted by it.

Pore size distribution of silk respirator paper of 45 g/m^2 was shown in Figure 4. It showed that the maximum and average pore size of silk paper with same basis weight decreased with the increase of beating degree. When the beating degree of pulp increased from 28 ^{o}SR to 92 ^{o}SR, the average pore size of silk paper decreased from 5.01 μm to 0.41 μm, and the maximum pore size of silk paper decreased from 7.82 μm to 1.09 μm. The trap ability of the filter materials depends directly on the maximum pore size of filtration materials in the initial stage, so the decrease of the maximum and average pore size can improve the filtration precision of silk respirator paper.

Table 2. Retention rate of nano-TiO_2 particles in silk paper

Item	Beating degree 51 ^{o}SR	Beating degree 85 ^{o}SR
Basis weight of unloaded silk papers (g/m^2)	45.1	45.2
Added amount of nano-TiO_2 (g/m^2)	2.25	2.25
Basis weight of silk papers loading nano-TiO_2 (g/m^2)	47.0	47.3
Retention rate of nano-TiO_2 (%)	84.4	93.3

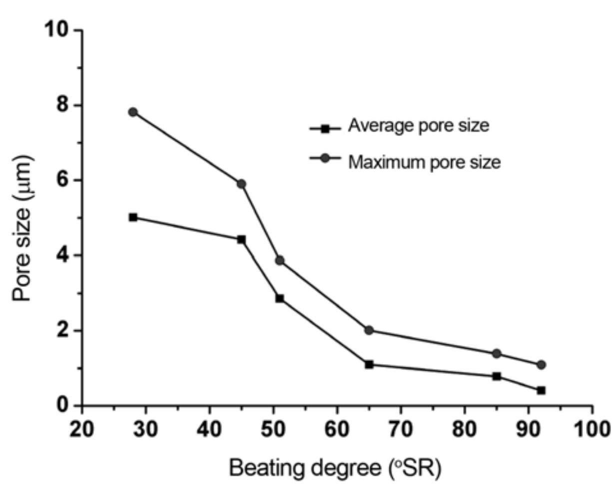

Figure 4. Effect of beating degree on the pore size of silk respirator paper.

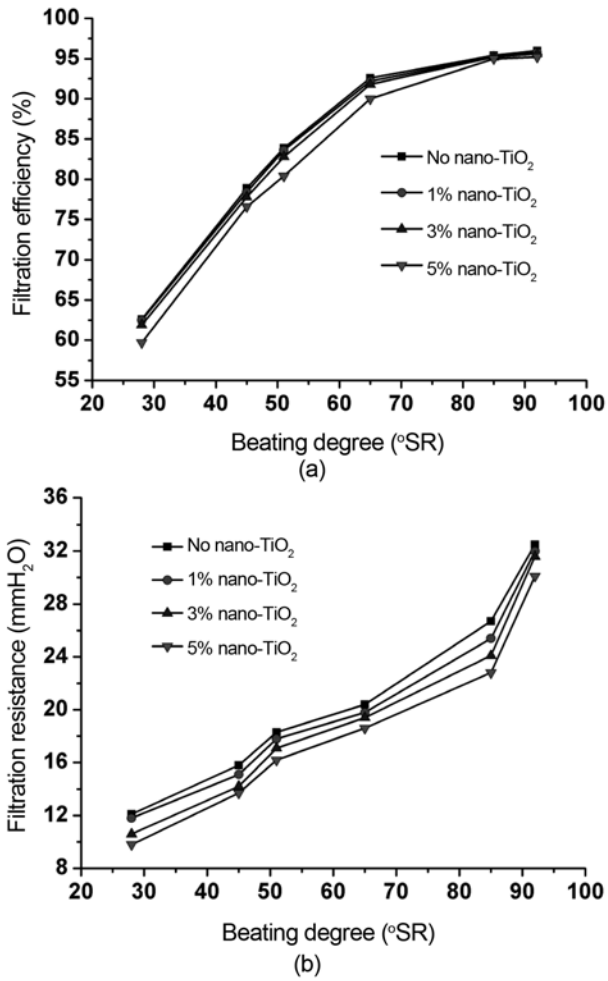

Figure 5. Filtration efficiency and filtration resistance of photo-catalytic silk respirator paper. (a) filtration efficiency and (b) filtration resistance.

Filtration Performance of Silk Respirator Paper

After loading nano-TiO_2, the filtration efficiency and filtration resistance of silk paper weighing 45 g/m^2 and made from silk pulp having different beating degree were shown in Figure 5. It can be seen from Figure 5 that the filtration efficiency and filtration resistance displayed the same trends before and after loading nano-TiO_2. The filtration efficiency and filtration resistance of silk paper loading nano-TiO_2 were a little lower than that of unloaded silk paper. The filtration efficiency and filtration resistance of silk paper varied with the amount of nano-TiO_2, but the change was not obvious. Nano-TiO_2 particle was intercepted by silk fibers, but there was no bonding between nano-TiO_2 and silk fibers, so the loading of nano-TiO_2 interfered with fiber bonding and increased the void fraction in silk paper, which resulted in decrease in filtration resistance filtration efficiency. However, since nano-TiO_2 particles were very small, its influence was very limited.

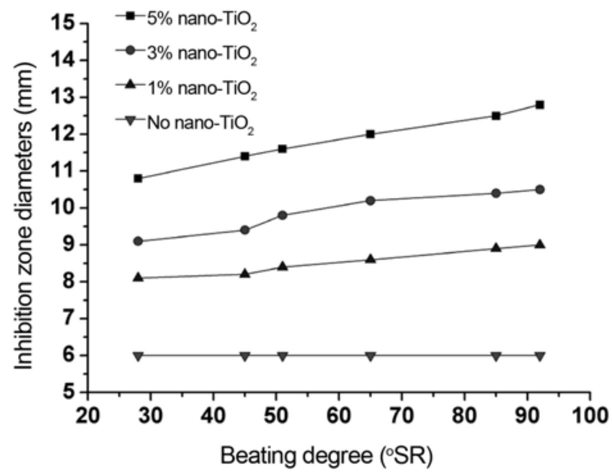

Figure 6. Antibacterial property of photo-catalytic silk respirator paper.

Photo-catalytic Antibacterial Property of Silk Respirator Paper

Antibacterial property of silk respirator paper of 45 g/m^2 was shown in Figure 6. Nano-TiO_2 is a semiconductive photo-catalyst with the properties of sterilization and decomposition of organic materials. After being excited by ultraviolet light, nano-TiO_2 can react with cell components directly or indirectly and kill bacteria [28]. Figure 6 showed that the diameters of inhibition zone increased with the increase of beating degree at the same amount of nano-TiO_2. The larger the diameter of inhibition zone means the better bacteriostatic effect. Silk paper made from pulp having high beating degree is dense, which is good for the retention of nano-TiO_2 in silk paper and the improvement the bacteriostatic effect. For silk paper with the same basis weight, the diameter of inhibition zone increased with the increase of the amount of nano-TiO_2. When the beating degree was 85 °SR, with the load of nano-TiO_2 increased from 1 % to 5 %, the diameter of inhibition zone increased from 8.9 mm to 12.5 mm. However, the diameter of inhibition zone is only 6 mm if no nano-TiO_2 was loaded.

Conclusion

The void fraction and pore size of silk paper decreased with the increase of the beating degree of silk pulp, and its filtration resistance and filtration efficiency increased with the increase of the beating degree of silk pulp. Therefore, it is possible to control the pore structure and dust removal performance of silk paper by adjusting the beating degree of silk pulp. Since silk paper with the basis weight of 45 g/m^2 made from silk pulp having the beating degree of 85 °SR has higher filtration efficiency and appropriate filtration resistance, it can fulfill the requirements of general medical respirator and dust respirator.

After loading nano-TiO_2, the filtration resistance and filtration efficiency of silk respirator paper decreased, but the change was not obvious. Nano-TiO_2 particles were mainly intercepted in fiber network, and the bacteriostatic efficiency of silk paper increased with the increase of the amount of nano-TiO_2 and also increased with the increase of the beating degree of silk pulp.

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