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Study on the Photocatalytic and Antibacterial Properties of TiO₂ Nanoparticles-Coated Cotton Fabrics

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Abstract: Herein, the amino-capped TiO₂ nanoparticles were synthesized using tetrabutyl titanate and amino polymers by a two-step sol-gel and hydrothermal method technique for the fabrication of functional cotton fabric. The prepared TiO₂ nanoparticles and the treated cotton fabric were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) photocatalytic and antibacterial measurement. The results indicate the typical characteristic anatase form of the amino-capped TiO₂ NPs with an average crystallite size of 14.9 nm. The treated cotton fabrics exhibit excellent antibacterial property and good photocatalytic degradation of methylene blue.

Keywords: amino-capped TiO₂ NPs; cotton fabric; photocatalytic degradation; antibacterial properties

1. Introduction

Cotton as an important natural renewable cellulose fiber has good hygroscopicity and breathability, which is widely used in clothing, home textiles, medical materials and other fields. Despite the excellent properties of cotton, some inherent features such as being poor persistence to ultraviolet (UV) radiation inhibited its wide application in advanced fields. In recent years, functional finishing of cotton has attracted the greatest attention. Nanomaterials can impart new functional properties to cotton fiber for its applications, such as antimicrobial properties [1], ultraviolet (UV) protection [2,3], superhydrophobicity [4], self-cleaning [5–7] and flame retardancy [8].

As one of the most important nano-inorganic material, titanium dioxide nanoparticles (TiO₂ NPs) possesses efficient photo catalyst activity and chemical stability [9]. It is widely used in antibacterial, anti-ultraviolet materials [10–12], self-cleaning glass [13], lithium batteries [14], photocatalysts and paints [15,16]. TiO₂ NPs prepared by sol-gel method have good uniformity, high purity, small particle size and simple preparation process, which can simultaneously improve the UV protection performance and photocatalytic efficiency of fabric. For instance, Dao and Xin reported the nucleation and successful growth of anatase crystallites on cotton fabrics. Cotton fabric coatings with TiO₂ exhibit good anti-UV, antibacterial and self-cleaning properties [17]. Li and Zhu prepared TiO₂/Ag through a two-step process. The functionalized cotton fabrics were imparted with UV protection and antibacterial properties [10]. However, TiO₂ NPs with small particle size and large specific surface area are easily adsorbed to form aggregates. TiO₂ nanoparticles (NPs) lack chemical bonds to link with fibers, which will bring

about unsatisfied durability. Therefore, some binders, such as citric acid (CA), polyurethane resin and polyacrylic esters (PALS), were required to fix the nanoparticles on fibers to provide durability of functional properties. Moreover, numerous chemicals used in preparation of nanoparticles and the finishing process may be associated with environmental toxicity or require complex processes as well as high-energy consumption and costs, making them unsuitable for large-scale production [18].

In our previous study, an amino-hyperbranched polymer (HSDA) was synthesized. It was utilized to control synthesis of Ag and ZnO nanoparticles, and also served as a binder to impart and fix the nanoparticles on cellulose fabric to provide antimicrobial properties [19–21]. In this paper, amino-capped TiO₂ NPs were attempted to be synthesized by the sol-gel and hydrothermal method, using a mixture of tetrabutyl titanate (TBT) and amino polymers as a raw material. In the process of sol-gel formation of TiO₂ NPs, hyperbranched polymer can control the particle size of TiO₂ NPs and improve the dispersion uniformity of nanoparticles to prevent its agglomeration. The prepared TiO₂ NPs were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD) and ultraviolet-visible spectra (UV-vis) measurement. Then, amino-capped TiO₂ NPs were coated on cotton fabric by the impregnation method. As cotton fiber contains a large amount of -OH, thus the amino-capped TiO₂ NPs can be firmly combined with the fiber through hydrogen bonding and van der Waals force. The antibacterial properties and photocatalytic efficiency of TiO₂ NPs-coated cotton fabric were investigated, the comparison of similar research is listed in Table S1.

2. Materials and Methods

2.1. Materials

Cotton fabric with a basic weight of 100 g/m² was obtained from Hua Fang Co., Ltd. (Suzhou, China). Tetrabutyl titanate (TBT, 98%) and ethanol (99.7%) were purchased from Guoyao Chemical Technology Co., Ltd. (Shanghai, China). Amino polymers were prepared as described in our previous paper [19].

2.2. Synthesis of Amino-Capped TiO₂ NPs

The amino polymer-modified nano-TiO₂ sol was prepared by a one-step sol-gel method at 25 °C under vigorous magnetic stirring, an ethanol solution containing 5 mL of TBT was added dropwise to 12 mL of ethanol solution containing amino polymers (0.5 g), deionized water (3 mL) and glacial acetic acid (pH 3 to 4). The mixed solution was continuously stirred to form a pale yellow three-dimensional network gel. Afterward, a mixture of absolute ethanol (10 mL) and deionized water (15 mL) were added dropwise. Stirring was continued until the mixture was homogeneous. The sol was transferred to a high-temperature hydrothermal Teflon reaction vessel, sealed in a steel cup and heated in an oven at 240 °C for 10 h. The obtained TiO₂ NPs were washed with deionized water, centrifuged and dried by grinding to obtain the amino-capped TiO₂ NPs fine powders.

2.3. Preparation of TiO₂ NPs-Coated Cotton Fabric

A cotton fabric weighing 5 g was immersed in a 20 g/L NaOH solution at a bath ratio of 1:50. The mixture was shaken in a water bath at 60 °C for 1 h. The cotton fabric was washed with deionized water and dried for use. The amino-capped TiO₂ NPs were dispersed in 100 mL water with a concentration of 2 g/L. The alkali-treated cotton fabric was immersed in the amino-capped TiO₂ NPs dispersion solution at a bath ratio of 1:30 and shaken in a water bath at 60 °C for 2 h. The TiO₂ NPs-coated cotton fabric was thermally pre-treated at 80 °C for 5 min and then at 150 °C for 3 min [22,23].

The amino polymer with a concentration of 0.5 g/L was prepared, and the cotton fabric was treated in the amino solution as contrast.

2.4. Characterization of the Amino-Capped TiO₂ NPs and Treated Cotton Fabric

The morphology and lattice characteristics of the amino-capped TiO₂ NPs were characterized by TEM (JEOL, Tokyo, Japan). The crystalline phase of TiO₂ NPs and the treated fabric were analyzed by XRD, (Philips, Amsterdam, The Netherlands) via a Cu K α X-ray light source at a voltage of 40 kV and a current of 30 mA. The light absorption properties of TiO₂ NPs were analyzed by UV-vis spectra (UV-3010 Hitachi spectrophotometer, Tokyo, Japan). The surface morphology of cotton fiber was characterized by field emission scanning electron microscopy (FE-SEM) (Scios Dual-Beam, Brno, Czech Republic) and energy dispersive spectrometer (EDS) (Carl Zeiss, EVO15, Oberkochen, Germany). The antibacterial activity of amino-treated fabric and TiO₂ NPs-coated fabric against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) was tested according to GB/T 20944.3-2008 (China) using the shake flask method. 0.75 g of the pristine fabric sample was cut into pieces of about 0.5 \times 0.5 cm² size, and immersed in a flask containing 70 mL of 0.3 mM phosphate buffer saline medium with a concentration of 1 \times 10⁵ CFU/mL–4 \times 10⁵ CFU/mL. The flask was then shaken on a rotary shaker at 150 rpm for 18 h at 24 °C. One mL of the solution was taken from each of the incubated samples, diluted and dispensed onto agar plates. All plates were incubated at 37 °C for 24 h and the formed colonies were counted. The photocatalytic of the amino-capped TiO₂ NPs were evaluated by degradation of methylene blue under ultraviolet irradiation, the light flux in this experiment was 300 mW/cm² and the reaction vessel was 10 cm. The amino-capped TiO₂ NPs-coated cotton fabric of 1 g and a 200 mL methylene blue solution (5 mg/L) were placed in the GHX-3 type photochemical reaction apparatus. The as-prepared samples were taken every 30 min. Under the same conditions, the amino- treated cotton fabric was evaluated as contrast. After the supernatant was taken and centrifuged, the absorbance of the methylene blue solution at 664 nm was measured by an UV-visible spectrophotometer. The photocatalytic degradation rate of methylene blue solution in the presence of amino-capped TiO₂ NPs-coated cotton fabric was calculated as:

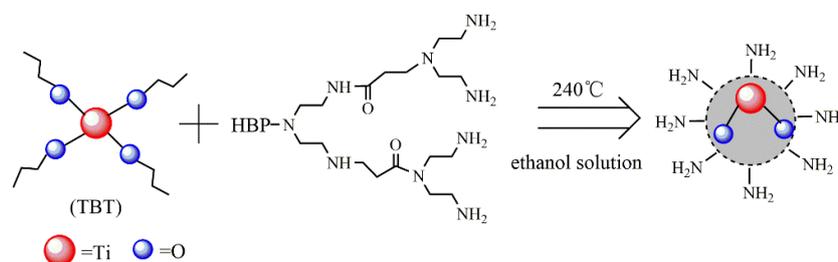
$$\eta(\%) = 1 - A_t/A_0 \quad (1)$$

where η is the photocatalytic degradation rate; A₀ and A_t are the absorbance of the methylene blue solution before and after degradation, respectively.

3. Results

3.1. Synthesis and Characterization of Amino-Capped TiO₂ NPs

The principle of synthesizing the amino-capped TiO₂ NPs is described in Scheme 1. The solution of amino polymer was added into the TBT/ethanol solution by hydrothermal reaction. The TiO₂ colloids prepared in acidic media were adsorbed strongly onto the TiO₂ surface. The amino served as a dispersing agent and stabilizer to prevent the agglomeration of TiO₂ NPs [24]. Upon hydrothermal dissolution-recrystallization reaction, the amino-capped TiO₂ NPs were obtained.



Scheme 1. Schematic illustration of synthesis of amino-capped TiO₂ nanoparticles (NPs).

The prepared TiO₂ NPs were observed by the TEM and XRD measurement. Figure 1a shows the TEM image of the amino-capped TiO₂, much more grains with tetragonal shape can be seen. The diameter of amino-capped TiO₂ NPs was found about 12 nm in Figure 1b. Series of diffraction

rings appeared in the selected area electron diffraction (SAED) pattern, as presented in Figure 1c, indicating the pure anatase crystalline phase in the amino-capped TiO₂ NPs.

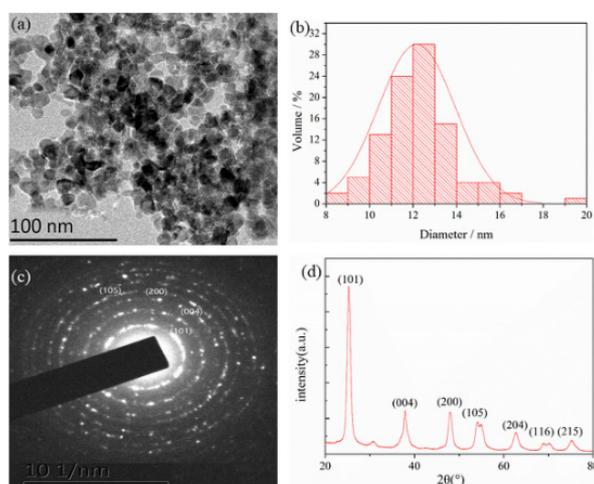


Figure 1. (a) TEM images, (b) size distribution, (c) selected area electron diffraction (SAED), (d) XRD of amino-capped TiO₂ NPs.

The crystalline phase of the amino-capped TiO₂ NPs was characterized by the powder XRD method shown in Figure 1d, with the XRD pattern similar to that of anatase TiO₂ (JCPDS No. 21-1272). After the hydrothermal process, the amino-capped TiO₂ NPs actively formed well crystalline TiO₂ NPs and completed phase change under the control of amino. Reflection peaks are observed at 2θ values of 25.26, 37.8, 47.96, 54.14, 54.94, 62.76, 68.94, 70.12, and 75.12, indexed to diffraction peaks from the (101), (004), (200), (105), (211), (204), (116), (220), and (215) planes of anatase crystalline phase of TiO₂ [24,25]. Obviously, the amino-capped TiO₂ NPs exhibit an anatase phase structure and extremely small particle sizes. The UV-vis absorption properties of TiO₂ NPs and amino-capped TiO₂ NPs were investigated by UV-Vis spectroscopy, with results shown in Figure 2. The absorption at 320 nm corresponds to the bandgap of the anatase TiO₂ (3.2 eV) [26], which requires UV radiation ($\lambda < 387$ nm) to transfer an electron from valence to conduction band. As TiO₂ NPs has poor solubility, it shows very faint shades in the aqueous solution. The TiO₂ NPs that were capped by amino can enhance the solubility, which exhibited a transparent blue color in the aqueous solution (inset of Figure 2). Compared with the pure TiO₂ (Figure 2a), the amino-capped TiO₂ NPs (Figure 2b) absorb more ultraviolet light in the region of 200 nm to 400 nm, which demonstrates that the amino-capped TiO₂ NPs possess good UV absorption intensity for UV light [27].

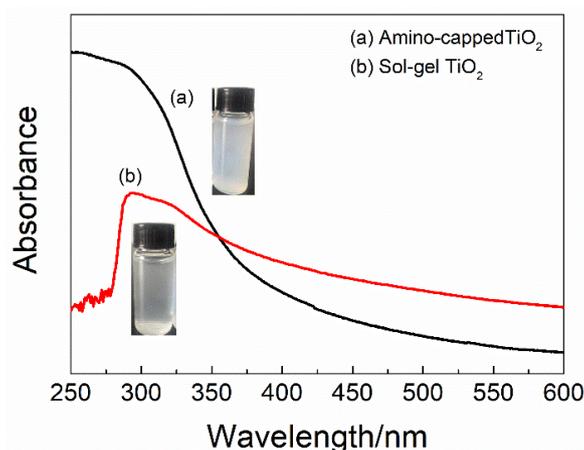


Figure 2. UV-vis spectra of (a) TiO₂ and (b) amino-capped TiO₂ colloidal solution.

3.2. Preparation and Characterization of the Cotton Fabric Coated by the Amino-Capped TiO₂ NPs

As TiO₂ has large surface energy it is difficult to disperse and combine it with cotton fibers. To provide the TiO₂ NPs-coated cotton fabric and impart the cotton fabric with photocatalytic activity and antibacterial properties, the cotton fabric was treated with the aqueous solution of amino-capped TiO₂ NPs by the impregnation method. The surface morphology of cotton fabric and TiO₂ NPs-treated cotton fabric was observed by FE-SEM, as displayed in Figure 3a, the pure cotton fiber has wrinkles and a smooth surface. The TiO₂ NPs-coated cotton fiber presenting obvious differences, which were covered with a large quantity of TiO₂ NPs and the nanoparticles were well-dispersed.

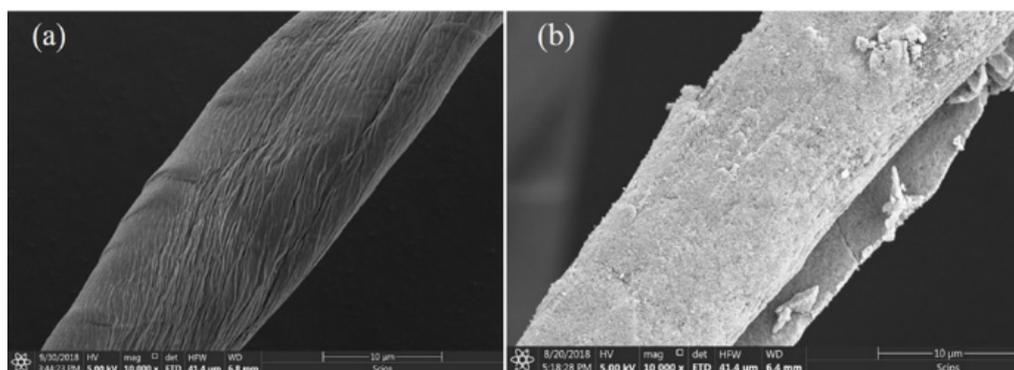
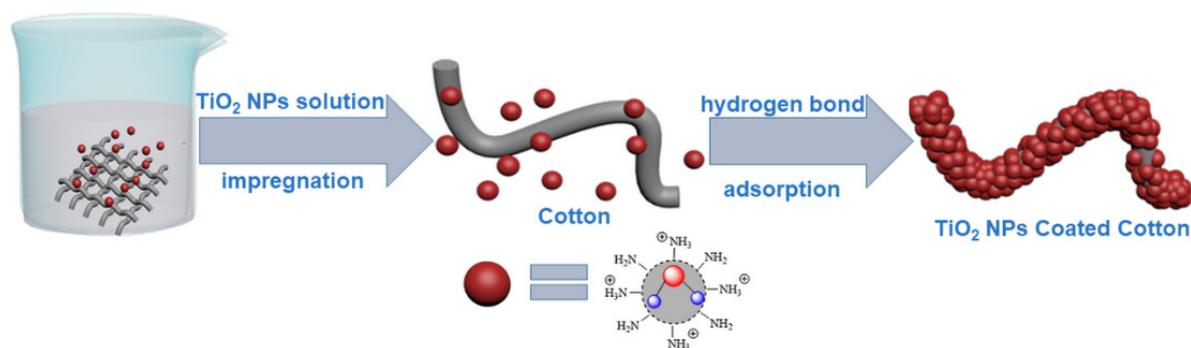


Figure 3. SEM images of (a) cotton fiber, (b) TiO₂ NPs-coated cotton fiber.

The mechanism of the evenly dispersed TiO₂ NPs on cotton fabric is provided in Scheme 2. TiO₂ NPs shows the positive charge as it was capped by the amino polymer shown in Figure S1. In the amino-capped TiO₂ NPs solution, TiO₂ NPs can be easily combined with cotton fabric through intermolecular hydrogen bonds between amino end groups and pendent hydroxyl groups on cellulose fiber. As the side-chain OH groups of cotton fiber can be typically ionized in the aqueous phase and the cotton fiber carries certain negative surface charges. Electrostatic bonding interactions between the negatively charged hydroxyl groups on cellulose fiber and positively charged amino end groups can enhance the stability of amino-capped TiO₂ NPs on the surface of cotton fabric [28].



Scheme 2. Schematic illustration of TiO₂ NPs-coated cotton fiber.

The elements of the treated cotton fabric were further investigated using the EDS mapping method. As shown in Figure 4a and Figure S1, additional Ti elements on the surface of the cotton fabric are observed. From Figure 4b–d, O and C elements of the cellulose fiber, as well as the even distribution of Ti on the fabric surface are found. The result is in good agreement with FE-SEM measurement. To determine the TiO₂ NPs-coated on cotton fabric, the XRD patterns of the control and treated cotton fabrics were tested, as shown in Figure 5. The diffraction peaks at 2θ values of 22.82 and 34.26 are shown in Figure 5a,b, which are assigned to the (002) and (040) planes of cellulose fiber. In contrast, the treated cotton fiber has reflection peaks at 2θ values of 25.28, 37.92, 47.92, which are indexed to

the (101), (004), (200) planes of the anatase phase shown in Figure 5c. The results confirm that the amino-capped TiO₂ NPs were coated on the cotton fiber effectively [10,24].

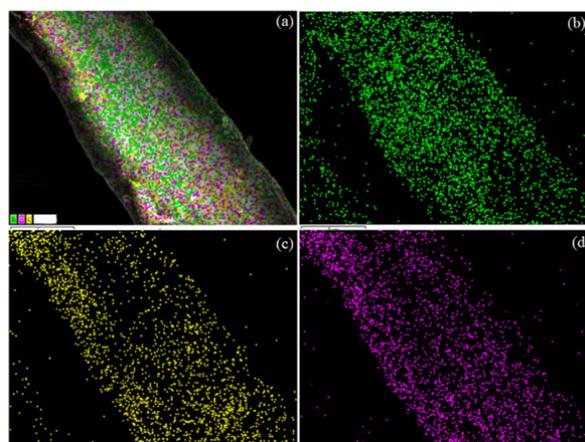


Figure 4. EDS (energy dispersive spectrometer) images of amino-capped TiO₂ NPs grafted cotton fabric: (a) cotton, (b) Ti, (c) O, (d) C.

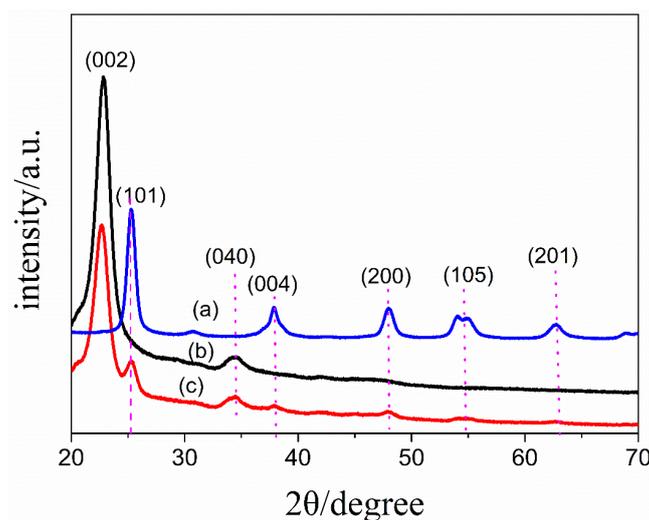


Figure 5. XRD patterns of (a) anatase TiO₂, (b) cotton fabric and (c) TiO₂ NPs-coated cotton fabric.

3.3. Photocatalytic Activity of the TiO₂ NPs-Coated Cotton Fabric

Photocatalytic experiments were implemented to investigate the photocatalytic activity of the amino-treated and TiO₂ NPs-coated cotton fabrics. The cotton fabrics were firstly dipped in methylene blue solution in dark condition to examine the adsorption property. Amino-treated and TiO₂ NPs-coated cotton fabrics have the similar adsorption capacity shown in Figure S3, they can absorb about 25% of the methylene blue in solution. Figure 6a shows the absorbance of methylene blue solution added with amino-treated cotton fabric with time under UV light irradiation. A medium change of absorbance value and a slight impact of the UV light on the degradation rate of methylene blue are observed. Figure 6b shows the gradual decrease in the absorbance of methylene blue solution added with amino-capped TiO₂ NPs-coated cotton fabric. It indicates that the TiO₂ NPs-coated cotton fabric degraded the methylene blue solution. Figure 6c shows the decrease rate of methylene blue solution under UV light irradiation. After 7 h, the decrease rate of methylene blue solution reached 53.14%, and that of TiO₂ NPs-coated cotton fabric was up to 92.03%.

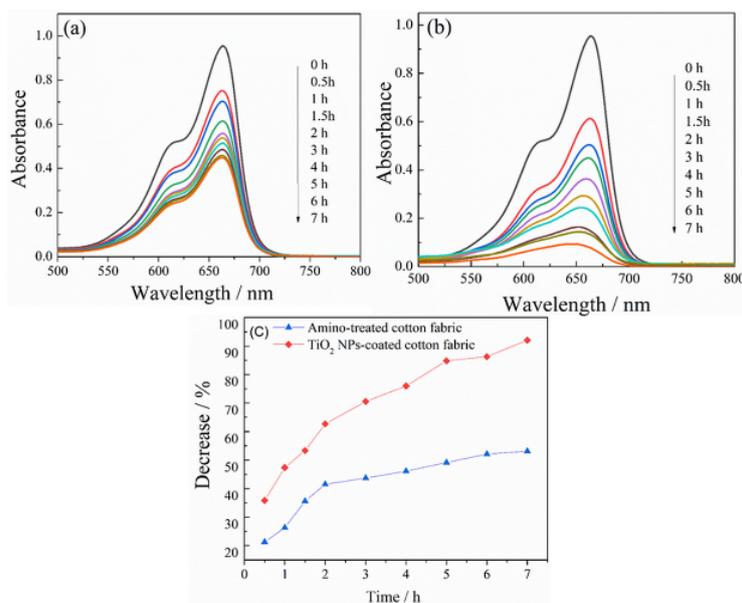
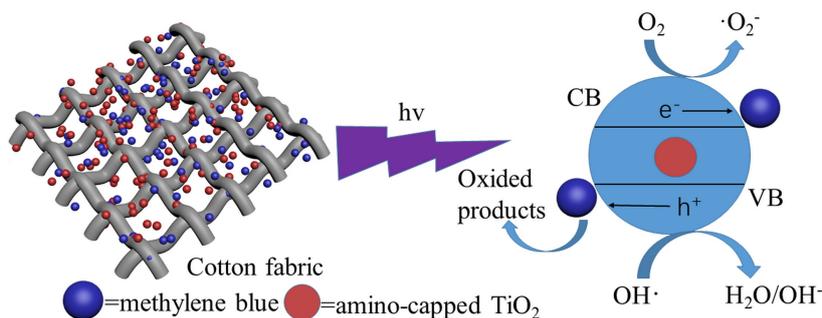


Figure 6. The absorbance of methylene blue by (a) amino-treated cotton fabric, (b) TiO₂ NPs-coated cotton fabric under UV-light, and (c) the decrease rate of methylene blue by amino-treated and TiO₂ NPs-coated cotton fabric.

The mechanism of photocatalytic activity and self-cleaning properties (Figure S4) of the TiO₂ NPs-coated cotton fabric was illustrated in Scheme 3. The amino-capped TiO₂ NPs on cotton fabric could adsorb the methylene blue molecules in the solution. When the light energy is equal to or greater than the band gap energy, a high concentration of conduction-band electrons (e^-) and valence-band holes (h^+) is generated in the density of TiO₂ nanoparticles on cotton fabric. Photogenic positive hole (h^+) reacts with hydroxyl group ($-OH$) and/or adsorbed water molecules produces hydroxyl radicals ($\bullet OH$), which act as strong oxidants during the photocatalytic reaction. Furthermore, photo generated electrons (e^-) react with an electron acceptor, such as O₂ and are adsorbed on the surface of the catalyst or dissolved in water to produce superoxide radical anions O₂ \bullet^- and $\bullet HO_2$. Free radicals react with each other, leading to formation of hydrogen peroxide and increasing gaseous oxygen in the photocatalytic reaction. [25,29–31] All this react with methylene blue molecules for their full degradation.



Scheme 3. Proposed mechanism of photocatalytic degradation of methylene blue by amino-capped TiO₂ NPs under UV illumination.

The antibacterial activity of cotton fabric was qualitatively evaluated by the shake-flask method under visible light. The comparison results between *E. coli* and *S. aureus* bacteria cells between amino-treated and TiO₂ NPs-coated cotton fabric were presented in Figure 7. As presented in Figure 7a,b, bacteria had grown all over the plate, meaning that amino-treated fabric did not show antibacterial activities against *S. aureus* and *E. coli* colonies. By contrast, TiO₂ NPs-coated cotton fabric exhibited excellent antibacterial activities because nearly no bacteria grew in the plate, as shown in

Figure 7b,d. The bacterial reduction rate of both *S. aureus* and *E. coli* can reach more than 99%. Both *S. aureus* and *E. coli* exhibits negative charge, the positively charged amino can adsorb the bacteria on the surface of TiO₂ by electrostatic adherence. As reported, TiO₂ has good photocatalytic property under ultraviolet conditions, it can generate OH radicals. Due to the electron mediator transports between cells and TiO₂, OH radicals destroyed bacterial cells caused by reduction of coenzyme cell content [32]. Moreover, TiO₂ NPs are known to inactivate bacteria by binding to electron-donating groups and cause little pores in bacterial cell walls, leading to increased permeability and cell death [33]. In this research, amino-capped TiO₂ NPs have good photocatalytic activity and adsorption property attributed to their high UV absorption intensity (Figure 2), this can endow that amino-capped TiO₂ has good antibacterial properties under visible light.

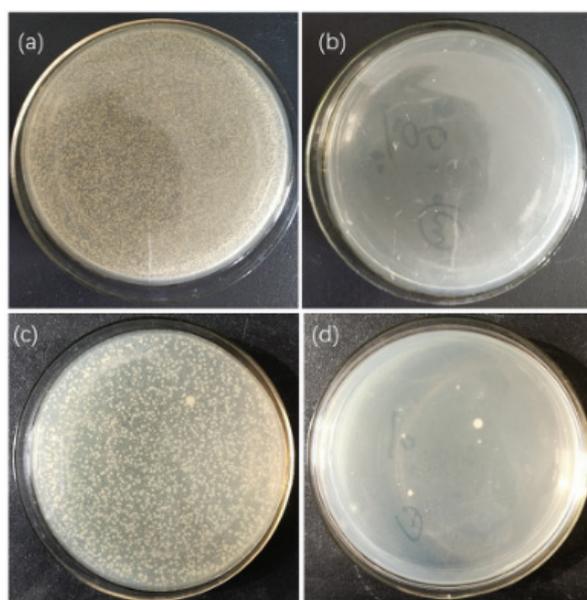


Figure 7. *S. aureus* colonies of (a) amino-treated (b) TiO₂ NP₅-coated cotton fabric and *E. coli* colonies of (c) amino-treated (d) TiO₂ NP₅-coated cotton fabric.

4. Conclusions

In this study, the amino-modified anatase TiO₂ nanoparticles with a morphology size of 12 nm were synthesized by a simple sol-gel method using amino polymer. Due to the numerous amino groups, TiO₂ NPs were adsorbed on cotton fabric. The results of FE-SEM and XRD confirm that the amino-capped TiO₂ NPs were well dispersed. Amino-capped TiO₂ NPs-coated cotton fabric shows great photo degradation of MB under UV irradiation, with the photocatalytic degradation and adsorption rate of 92.03%. In addition, as-prepared cotton fabric exhibits good antibacterial properties under visible light, the bacterial reduction rate of both *S. aureus* and *E. coli* can reach more than 99%.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1944/12/12/2010/s1>, Figure S1: EDS analyze of amino-capped TiO₂ NPs on cotton fabric; Figure S2: FTIR spectra of (a) amino-capped TiO₂, (b) amino polymers; Figure S3: Absorbance of methylene blue (a) absorbance of methylene blue by impregnation of amino treated fabric (b) and TiO₂ NPs coated fabric (c) without UV-light in 7 h; Figure S4: Self-cleaning properties of (a) cotton fabric (b) TiO₂ NPs-coated cotton fabric with UV light; Table S1: Comparison of published data with our research.

Author Contributions: Conceptualization, G.Z. and C.Z.; Methodology, D.W. and Y.X.; Investigation, W.G.; Software, J.Y.; Writing—Original Draft Preparation, G.Z. and D.W.; Writing—Review & Editing, G.Z. and C.Z.; Project Administration, G.Z.; Funding Acquisition, G.Z. and C.Z.

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Conflicts of Interest: The authors declare no conflict of interest.

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