Cellulose (2020) 27:1055–1069
https://doi.org/10.1007/s10570-019-02832-z

ORIGINAL RESEARCH

Silicone quaternary ammonium salt based nanocomposite: a long-acting antibacterial cotton fabric finishing agent with good softness and air permeability

Dangge Gao · Yajuan Li · Bin Lyu · Dina Jin · Jianzhong Ma

Received: 6 July 2019 / Accepted: 30 October 2019 / Published online: 5 November 2019

Abstract A silicone quaternary ammonium salt based nanocomposite was synthesized and the chemical structure and stability of the nanocomposite were investigated. The results showed that the OQAS/(Ag/ZnO) nanocomposite had prepared successfully. The cotton fabrics were treated with different concentration of OQAS/(Ag/ZnO) nanocomposite and its antibacterial, durability, softness, hydrophilicity, and air permeability were also be examined using diverse characterization techniques. The antibacterial rate of treated cotton can reach to over 90%. After 10 cycles washing, antibacterial rate retain over 85% for both *E. coli* and *S. aureus*, because the chemical bond had formed between nanocomposite and cotton from the FT-IR result. In addition, a model bacterium, *E. coli* was used to evaluate the antibacterial mechanism and kinetics of nanocomposite. The hydrophilicity, air permeability and softness of the treated cotton fabrics were also had an improvement to some extent.

D. Gao (✉) · Y. Li · B. Lyu · D. Jin · J. Ma
College of Bioresources Chemical and Material Engineering, Shaanxi University of Science and Technology, Xi'an 710021, Shaanxi, China
e-mail: dangge2000@126.com

D. Gao · Y. Li · B. Lyu · D. Jin · J. Ma (✉)
National Demonstration Center for Experimental Light Chemistry Engineering Education, Shaanxi University of Science and Technology, Xi'an 710021, Shaanxi, China
e-mail: majz@sust.edu.cn

Keywords Cotton fabric · Antibacterial · Softness · Nanocomposite

Introduction

As public health issue attract much attention, more and more people pay attention to this topic to avoid bacterial infection (Tian et al. 2014). One of the effective ways to prevent the spread of bacteria is to use antimicrobial textiles to greatly reduces the probability of cross-infection caused by bacteria (Yang et al. 2018a, b; Gao et al. 2015a, b). In addition, endowing cotton fabric with antibacterial activity can also effectively prevent bacteria destroying the structure of cotton textiles and prolong their service life (Sharkawy et al. 2017; Gao et al. 2014).

Antibacterial materials mainly include inorganic and organic antibacterial agents (Dong et al. 2017; Wei et al. 2017; Tu et al. 2018). Inorganic antibacterial agents are usually photocatalytic metal oxide materials that belongs to semiconductor compounds generally (MN Karim et al. 2018). This type of antibacterial agent is widely used in both scientific research and industrial application because of their effective antibacterial effect, no secondary pollution, good stability and biocompatibility (Duan et al. 2018; Qian et al. 2018; Guo et al. 2017). Among them, ZnO attract the most attention because its excellent biocompatibility and antibacterial activity and are widely used in cosmetics, food packing and medicine field. However, the photocatalytic antibacterial performance of ZnO can be reduced because of the high recombination rate of electron–hole pair. Moreover, the excitation light of ZnO is in ultraviolet region, which means the low utilization for daylight (Gao et al. 2017). There are many ways to promote the photocatalysts antibacterial activity of ZnO, such as dope with noble metal or combination with other semiconductor photocatalysts (Yang et al. 2018a, b; Liu et al. 2018a, b; Sathya and Pushpanathan 2018).

Ag nanoparticles are a gold standard bacteriostatic agent. They can modify ZnO and enhance its antibacterial activity due to synergistic charge transfer (Hong et al. 2018; Li et al. 2019). The utilization of Ag/ZnO nanoparticles with photocatalytic and antimicrobial activity for textile treatment has received much attention in recent years. The researchers coated Ag/ZnO nanoparticles on fabrics to obtained the conclusions that even very small (0.1 at.%) and relatively small (15 at.%) amount of Ag in ZnO based composites led to substantial increases of antimicrobial effect (Ibanescu et al. 2014). Whereas utilizing inorganic nanoparticles to finish cotton fabric directly decrease the softness of cotton fabric, and the antibacterial activity needs further improvement (Ali et al. 2018).

The introduction of inorganic antimicrobial agents into polymer system was an effective way to solve the above mentioned problems. The active groups in the organic chain can anchor inorganic nanoparticles on the matrix more firmly and have a more durable effect. Lu et al prepared the physical mixture of Ag NPs and ZnO nanoparticles and then incorporated the mixture into chitosan to form the Ag/ZnO loaded chitosan dressing. The results demonstrated that the prepared chitosan-Ag/ZnO composite dressing showed high porosity and swelling as well as enhanced antibacterial activity (Lu et al. 2017). Jin et al. synthesized silicone softener (PTSO-PEG) and applied this material on cotton fabric. The results showed that PTSO-PEG treated cotton fabric expressed better softness and hydrophilicity than traditional amino silicone treated sample (Jin et al. 2015).

Polymer-based antibacterial agents containing cationic groups are another kind of important synthetic biocides (Yan et al. 2019). This kind of antibacterial agents can kill bacteria through contact mechanism, which is quite different from leachable and photocatalytic biocides. Quaternary ammonium salts are widely used as cationic polymers-based antibacterial agents in textile finishing processing (Elena and Miri 2018). When applied to the textile, it could endow textile with excellent performance such as antibacterial, soft and hygroscopic properties for it contain cationic quaternary ammonium group, polysiloxane and aliphatic hydrocarbon chains.

We have prepared a kind of polymer-based matrix nanocomposite previously, which can endow cotton fabric excellent antimicrobial activity, but the air permeability of cotton fabrics after finishing decreased obviously, and the softness of cotton fabric need to be further improved than that of the original cotton fabric. In this work, we report a cotton fabric finishing agent with excellent comprehensive properties containing excellent antibacterial activity, better softness, air permeability and hydrophilicity compared with native cotton fabric. For these purposes, an organic–inorganic hybrid OQAS/(Ag/ZnO) nanocomposite was synthesized via free radical polymerization. The antibacterial activity of the OQAS/(Ag/ZnO) nanocomposite treated cotton fabric, along with its durability, softness, hydrophilicity and air permeability will be examined using diverse characterization techniques. The results obtained were expected to provide valuable findings for manufacturing high value-added cotton fabric with multiple functionalities.

Experimental section

Materials

Zinc oxide (AR, Shanghai Naiou Nano Technology Co. Ltd., China), Silver nitrate, Sodium hydroxide and Ethanol (AR, Tianjin Hongyan Reagent Plant, China), DMDAAC (60%, Shandong Luyue Chemical Industry Co. Ltd., China), AGE (AR, Hangzhou Silong Material Technology Co. Ltd., China), Vinyl terminated silicone oil (AR, Guangzhou Juchengzhaoye Youjiguiyuanliao Co. Ltd., China), Potassium per sulfate (KPS, AR, Tianjin Hengxing Chemical Reagents Manufacturing Co. Ltd., China), KH-570 and Hydrochloric acid (CP, Xi'an Chemical Reagents Co. Ltd., China) were all used without further purification. Selected bacteria *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were saved by our laboratory and incubated at 37 °C on a nutrient agar plate for 24 h before use.

Preparation of Ag/ZnO nanocomposite

1.0 g of commercial ZnO NPs was dispersed in 50 mL of distilled water, followed by addition of 100 mL of 3-aminopropyltriethoxysilane with reaction mixture and was stirred for 30 min to get a homogeneous mixture of KH-550/ZnO. Then 0.125 g of $AgNO_3$ was gradually added to the above reaction mixture and stirring was continued for 30 min. The trisodium citrate solution was added drop-wise into reaction mixture until brownish yellow color obtained and the reaction mixture was vigorously stirred for another 60 min. Then the obtained Ag/ZnO nanoparticles were collected by centrifugation and washed with distilled water and ethanol. The centrifugation and washing was repeated for four times to remove the loosely bound Ag NPs and impurities. The synthesized nanocomposite material was dried in hot air oven at 80 °C for 1 h to remove the moisture completely.

Synthesis of OQAS/(Ag/ZnO) nanocomposite

DMDAAC (37.5 g), Ag/ZnO (0.1 g), Silane coupling agent KH-570 (0.05 g) and KPS solution (14.3 g) was added to a 100 mL three-necked round-bottom flask with a digital agitator and a reflux condenser under continuous stirring at 400 rpm, followed by AGE (0.625 g), Si-vi (0.625 g) and KPS solution (13.3 g), and the reaction was run at 80 °C. The reaction was allowed to proceed for 4 h before the solution was cooled to room temperature, the pH was adjusted to 3 by using HCl, and the expected nanocomposite was obtained and marked as OQAS/(Ag/ZnO).

Application to cotton fabric

Cotton fabric (30 cm $\times$ 30 cm) were treated with OQAS/(Ag/ZnO) nanocomposite with different concentrations (5–25 g/L). The clean cotton samples were immersed in the dispersions of the above five materials solution for padding and dried at 90 °C for 5 min in a preheated oven to remove the moisture, and then cured at 120 °C for 15 min. The specific finishing process steps are shown in the Scheme 1. The ZnO and Ag/ZnO nanoparticles were also applied onto the fabric in the same manner as control groups.

Antimicrobial assay

The antibacterial activity of the OQAS/(Ag/ZnO) treated cotton fabric was tested according to FZ/T 73023-2006 standard method (Gao et al. 2018). The *Staphylococcus aureus* (*S. aureus*, ATCC6538), and *Escherichia coli* (*E. coli*, ATCC25922) were selected as the tested bacterium. The detailed antibacterial method was described as following: Firstly, the bacteria were diluted 10 times by sterile PBS solution to the concentration of bacteria was 1×10^8 CFU/mL, then put control and treated cotton textile into flasks containing 70 mL PBS buffer solution and 5 mL diluted bacterial solution, and seal the flasks in a constant temperature water bath oscillator with a rotating speed of 180 rpm and a temperature of 25 °C for 18 h. After the oscillation, 1 mL test solution was extracted from each flask and diluted in a series of 10 times with PBS buffer in the test tube. Then, 1 mL test solution was taken from the test tube and cultured on agar medium plate and the number of bacterial colonies in the plate was calculated after 24–48 h at 37 °C. Finally, the bacterial were cultivated under light conditions and the specific illumination conditions were 8 W fluorescent lamp. The antibacterial rate was calculated in accordance with the following equation:

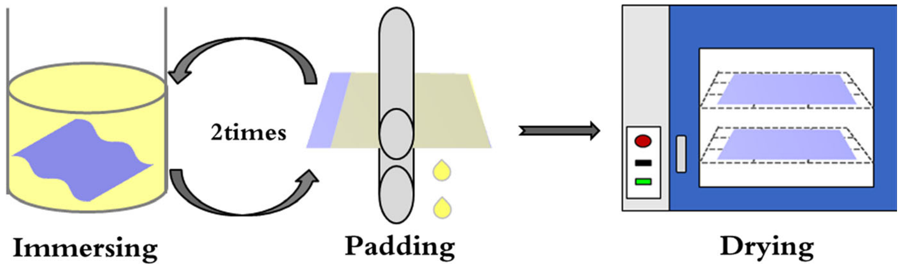
$$Antibacterial\, rate = (Nc - Ns)/Nc$$

where Nc is the number of the of bacteria recovered from the control cotton samples, Ns is the number of bacteria recovered from the OQAS/(Ag/ZnO) treated cotton samples.

The antibacterial durability of cotton fabric was tested by the AATCC test method 61-2007: "Colorfastness to Laundering: Accelerated" (Gao et al. 2019a, b). The treated cotton fabric was soaked in a 200 mL washing cup containing ten steel balls and soap powder and washed at 40 °C for 45 min noted as 1 cycle. (1 cycle was equivalent to 5 cycles household washing)

In order to further evaluated the dissolution of the nanocomposite, the antibacterial activity of the OQAS/(Ag/ZnO) nanocomposite was also test according to inhibition zone method.

Scheme 1 Finishing process of OQAS/(Ag/ZnO) coated cotton fabric



Performance properties of cotton fabric

The softness of treated control and treated cotton fabric were measured by GT-303 softness tester. The air permeability of treated cotton fabric was measured by pervapour device. The hydrophilicity of treated cotton fabric were measured according to FZ/T01071 (2008) and ISO 9073-6 (2000) standard. Each sample was measured three times in parallel.

Characterization

Structural characterization of the synthesized OQAS/(Ag/ZnO) nanocomposite

Fourier transform infrared spectroscopy (FT-IR) OQAS/(Ag/ZnO) nanocomposite were purified and dried firstly, and then tableted with potassium bromide. The purified nanocomposite was conducted on VECTORY-22 Fourier Transform Infrared Spectrometer (Bruker). The wavenumber range was 450–4000 cm^{-1} and the resolution was 1 cm^{-1}.

X-ray diffraction (XRD) OQAS/(Ag/ZnO) nanocomposite were purified and dried firstly. The XRD patterns of the samples were obtained on D8 Advance (Bruker, Germany). The scanning speed was 4°/min and the scanning angle was 10°–80°.

Storage stability When the OQAS/(Ag/ZnO) nanocomposite was storage for one month, the changes of particle size in time as a measure of the nanocomposite stability were investigated with Turbiscan LAB equipment.

Structure and properties characterization of the cotton fabric

Scanning electron microscope (SEM) The cotton fabric was coated with gold in vacuum for 60 s firstly before scanning. Surface morphology of OQAS/(Ag/ZnO) nanocomposite treated cotton fabric was studied on Vega 3 SBH (Tescan, Czech) at an accelerating voltage of 5 kV.

Atom force microscope (AFM) The cotton fabric was dried firstly before scanning. Surface smoothness of OQAS/(Ag/ZnO) nanocomposite treated cotton fabric was recorded on SPI3800N/SPA400 (Seiko, Japan) and the scanning range was 5 $\mu m \times 5$ μm. In addition, the morphology of the bacterial treated by OQAS/(Ag/ZnO) nanocomposite was also observed by AFM.

Laser confocal fluorescence microscopy (CLSM) The images of *E. coli* and OQAS/(Ag/ZnO) nanocomposite treated *E. coli* were captured by LSM800 (Carl Zeiss, Germany) and the scanning range was 10 $\mu m \times 10$ μm.

Results and discussion

Characterization of synthesized OQAS/(Ag/ZnO) nanocomposite

The XRD patterns of ZnO, and OQAS/(Ag/ZnO) nanocomposite are shown in Fig. 1a. The peaks at 37°, 40° and 42° can be assigned to the (100), (002) and (101) lattice plane of nano ZnO, which were in good agreement with the JCPDS no. 36-1451 (Svetlichnyi et al. 2016). The diffraction patterns of OQAS/(Ag/ZnO) nanocomposite showed peak at 30.4° and 31.3°, which correspond to the diffractions of ZnO (002) and (101) planes. In the synthesis process, the silver content in the nanocomposite material was trace. Therefore, the relevant peaks of nano-silver couldn't be detected in the OQAS/(Ag/ZnO) nanocomposite. Notably, the diffraction peaks of OQAS/(Ag/ZnO) nanocomposite were less intense and broader than those of ZnO that was because

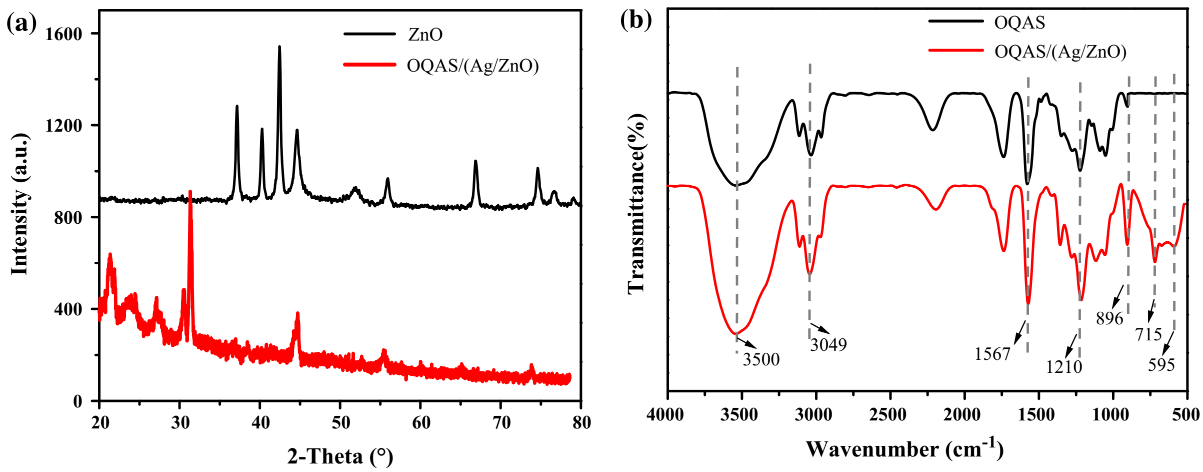


Fig. 1 **a** XRD patterns of ZnO and OQAS/(Ag/ZnO) nanocomposite; **b** FT-IR spectrum of OQAS/(Ag/ZnO) nanocomposite

polymers belonged to amorphous structure and disorderly arrangement, so their crystallinity was poor.

In order to further confirm the chemical structure of our synthesized OQAS and OQAS/(Ag/ZnO) nanocomposite, we analyzed the FT-IR spectra of OQAS and OQAS/(Ag/ZnO) samples as shown in Fig. 1b. Both in the OQAS and OQAS/(Ag/ZnO) samples, the peaks at 3049 cm^{-1} could ascribed to the $-CH_3$ and the peak at 1567 cm^{-1} was corresponding to the $-CH_3$ conjoint with N^+ from the polymer chains (Mai et al. 2018). The characteristic absorption of 1210 cm^{-1} and 896 cm^{-1} were separately assigned to –Si–O–Si and C–O–C bonds from the OQAS polymer segments. In addition, in the spectra of OQAS/(Ag/ZnO) nanocomposite, the peaks at 715 cm^{-1} could correspond to the Si–O–Zn bond very well and the peak at 595 cm^{-1} was the typical characteristic peak of Ag/ZnO (Gao et al. 2019a, b). All in all, the FT-IR result indicated that the OQAS/(Ag/ZnO) nanocomposite was fabricated successfully.

Storage ability

Generally speaking, the storage stability of polymer-inorganic composite was anneglectable concern in the practical application. Based on this principle, the changes of particle size in time as a measure of the composite stability were investigated with Turbiscan LAB equipment. Figure 2a shows the result as the variation of the transmission profile DT with the height of the samples as measured every minute for 30 min. The principle of transmission is based on the change of light transmission caused by particle size changes on the sample pool. The transmission curve varied with the height and time of the sample when the size of composite had changed. It should be noted that the transmission curve only makes sense at a height more than 1 mm, which is the thickness of the bottom of the container. Obviously, the transmission density kept homogeneity with the height and time of the sample, which meant that the sample had no sedimentation.

Dispersion is an evaluation of the stability of the whole dispersion system. In order to reveal the stability of the composite for a month, we used the stability coefficient (TSI–Turbiscan Stability Index) introduced by Chibowski:

$$\mathbf{TSI} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{BS})^2}{n-1}}$$

where x_i is the backscattering for each minute of measurement, x_{BS} is the average x_i, and n is the number of scans.

The higher the TSI, the more unstable the system. The TSI curve over time is shown in Fig. 2b by calculation. The slope of the TSI curve decreases with time increase, which meant that the composite presented a homogeneous phase and have no sediment. Therefore, we could obtain composite materials with good stability by in situ polymerization (Gao et al. 2015a, b).

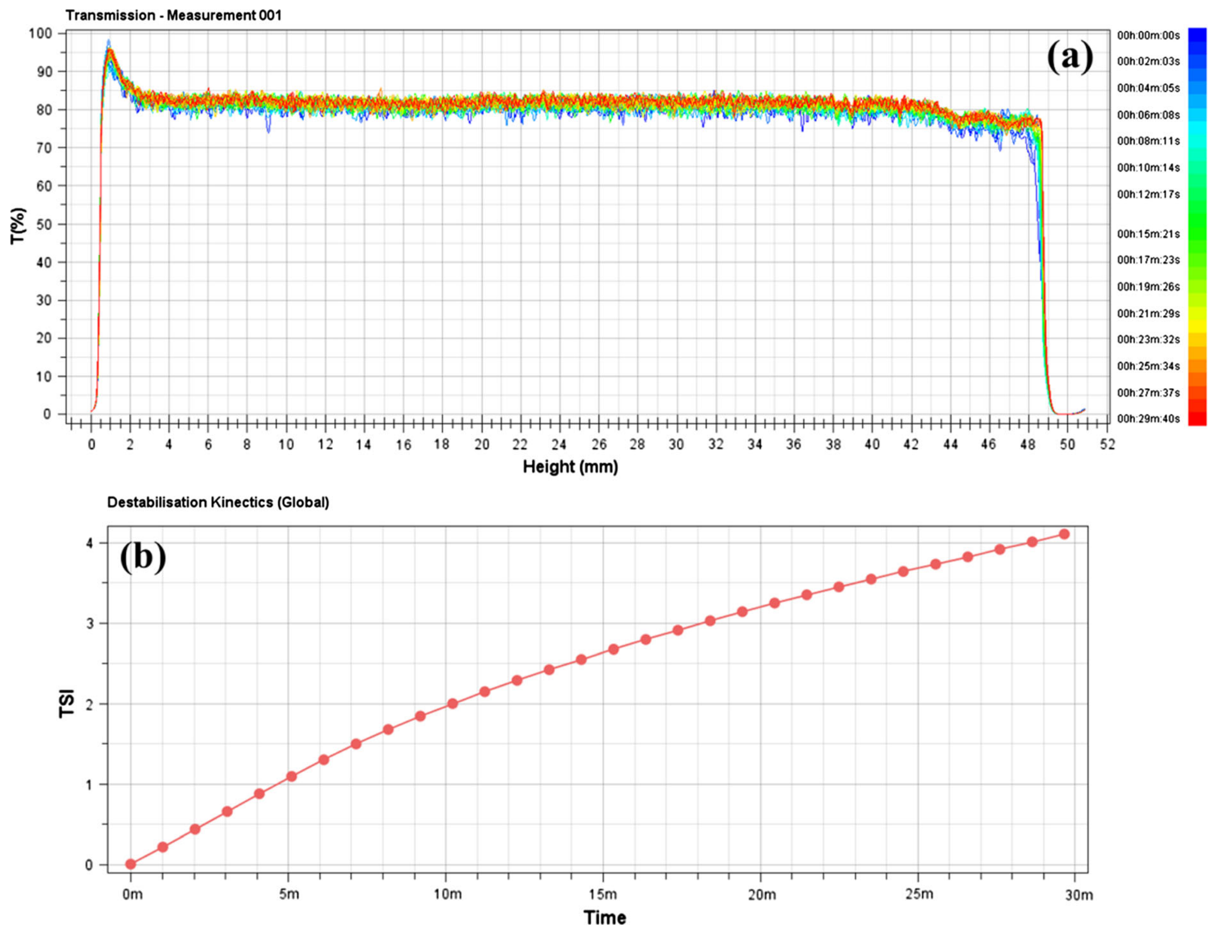


Fig. 2 **a** Transmission DT profile along the sample height as measured at every minute for 30 min; **b** time dependence of the stability coefficient TSI of OQAS/(Ag/ZnO) nanocompsite

Antibacterial activity assay

Figure 3a, b shows the antimicrobial rate of cotton fabric treated with different concentrations of OQAS/(Ag/ZnO) nanocomposites against *E. coli* and *S. aureus*. It can be seen from Fig. 3a, b that the antimicrobial rate of cotton fabric treated with OQAS/(Ag/ZnO) nanocomposite improve with the increase of nanocomposite concentration. For *E. coli* (Fig. 3a), even when the concentration of OQAS/(Ag/ZnO) nanocomposite was 5 g/L, its antimicrobial rate was over 90%. When the concentration reached to 25 g/L, its antimicrobial rate almost closed to 100%, which proven that the treated cotton fabric could results in bacterial death completely. For *S. aureus* (Fig. 3b), a similar conclusion was reached. When the minimum concentration was 5 g/L, the antibacterial activity to *S. aureus* was higher than 90%. When the concentration reached to 15 g/L, the growth and reproduction of bacteria could be completely inhibited. The higher concentration of the OQAS/(Ag/ZnO) nanocomposite treated, the more active ingredients in the cotton fabric existed, and the stronger the killing effect was. The synergistic effect between Ag/ZnO nanoparticles and quaternary ammonium salt was the greatest contribution to the high efficiency and broad-spectrum antimicrobial activity of treated cotton fabric (Gao et al. 2019a, b).

As we know, cotton fabric, as common clothing fabric daily necessity, inevitably need to undergo multiple mechanical washing process, so it is necessary to study its antibacterial activity after repeated washing. It can be seen that the antimicrobial activity of OQAS/(Ag/ZnO) treated cotton fabric decreased

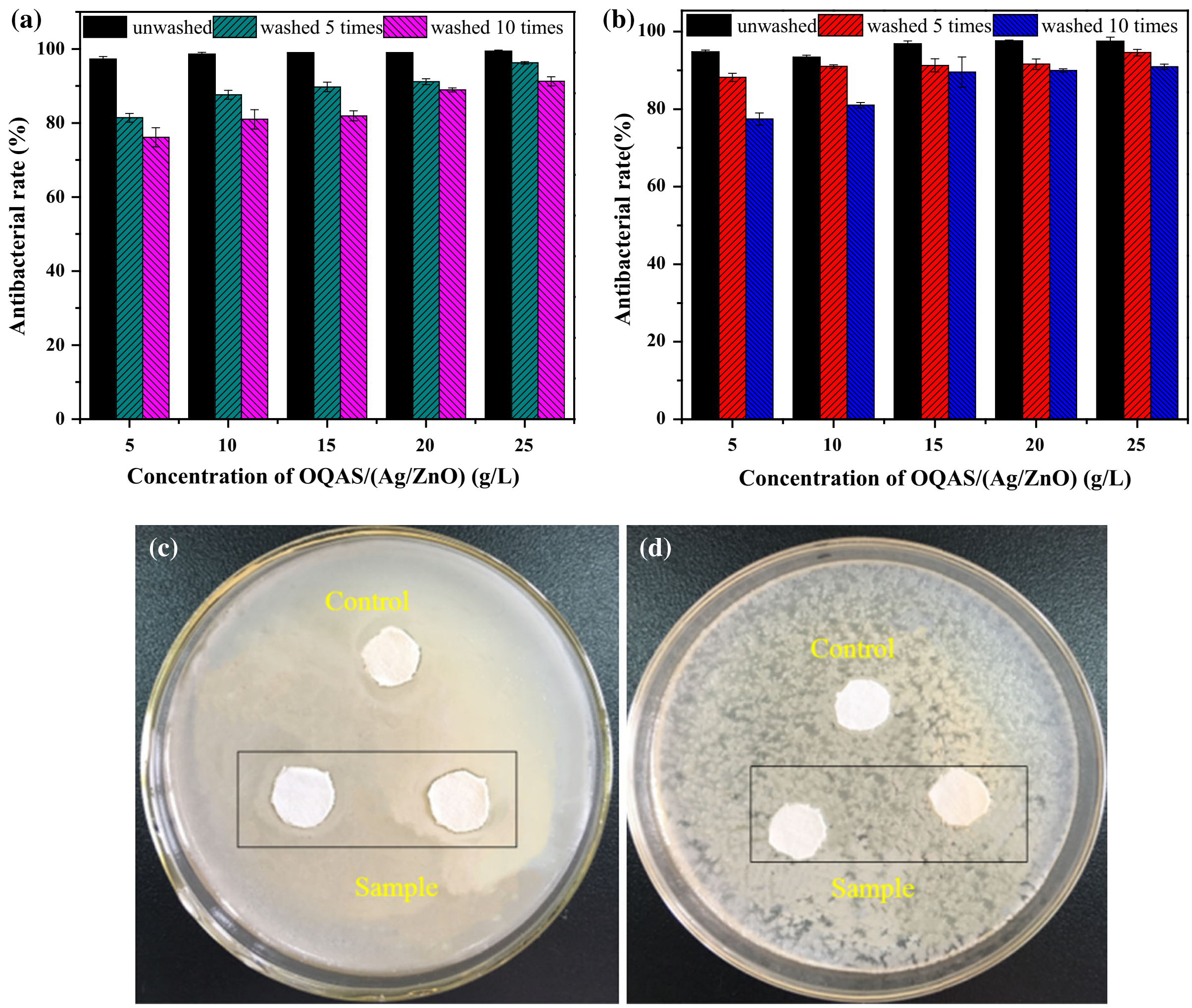


Fig. 3 The antibacterial activity of OQAS/(Ag/ZnO) nanocomposite treated cotton fabric against *E. coli* (**a**) and *S. aureus* (**b**); photograph of the zone of inhibition against *E. coli* (**c**) and *S. aureus* (**d**) for control and OQAS/(Ag/ZnO) treated cotton samples

slightly after 5 washing cycles (equivalent to 25 cycles household washing). When the concentration was 25 g/L, the antimicrobial rate of treated cotton fabric to *E. coli* and *S. aureus* could be maintained more than 90%. This indicated that strong covalent bond have formed between nanocomposite materials and cotton fabric (Druvari et al. 2016). With the further increase of washing machine strength, when cotton fabric experienced 10 cycles washing (equivalent to 50 cycles household washing), the antimicrobial activity of treated cotton fabric obviously decreases in lower concentration. This may be due to the slight damage of the covalent bond under the strong mechanical action in the washing process, resulting in the falling off of nanocomposite materials. However, at the concentration of 25 g/L, the antimicrobial rate of *E. coli* and *S. aureus* was still more than 80%, which meets the market requirements for AAA grade antimicrobial textiles (70%~*E. coli*, 80%~*S. aureus*) (Chen et al. 2014).

It can be seen from the Table 1 that the antibacterial rate of ZnO to *S. aureus* and *E. coli* was 73% and 79% respectively. After modification with nano silver, the antibacterial rate to *S. aureus* and *E. coli* was close to 100%. However, because ZnO and Ag/ZnO belong to inorganic nanoparticles, they are lacking of groups to form covalent bonds with cotton fabrics, so after washing, a large number of nanoparticles were lost from the fabric, resulting in a significant decline in antimicrobial activity, which

Table 1 Antimicrobial activity of cotton textile treated with ZnO, Ag-ZnO, OQAS/ZnO and OQAS/(Ag-ZnO) materials after different washing cycles

Sample	The antibacterial rate of cotton fabric after different washing cycles (%)					
	S. aureus (0 times)	*S. aureus* (5 times)	*S. aureus* (10 times)	*E. coli* (0 times)	*E. coli* (5 times)	*E. coli* (10 times)
ZnO	(73.2 ± 0.9)	/	/	(78.9 ± 0.4)	/	/
Ag-ZnO	(99.4 ± 0.4)	/	/	(99.6 ± 0.2)	/	/
OQAS	(82.1 ± 0.1)	(78.1 ± 0.3)	(70.2 ± 0.7)	(86.2 ± 0.4)	(81.6 ± 0.3)	(74.2 ± 0.4)
OQAS/ZnO	(95.8 ± 0.5)	(89.9 ± 0.3)	(81.2 ± 0.3)	(90.2 ± 0.1)	(85.3 ± 0.2)	(80.1 ± 0.3)
OQAS/(Ag/ZnO)	(96.5 ± 1)	(95.4 ± 0.8)	(90.2 ± 0.6)	(99.1 ± 0.3)	(96.2 ± 0.3)	(91.2 ± 0.2)

can not meet the market requirements for antimicrobial activity. Instead, a unmodified ZnO was directly introduced into the polymer containing reactive groups to obtain OQAS/ZnO nanocomposite, antibacterial rate of ZnO to *S. aureus* and *E. coli* was 96% and 90% respectively. After 10 washing cycles, their antibacterial rate against *S. aureus* and *E. coli* were both about 80%. The antimicrobial activities needed to be further improved. The introduction of Ag/ZnO into polymers showed that the antimicrobial rates for *S. aureus* and *E. coli* were 97% and 99%, respectively. Even after 10 washing cycles, the antimicrobial rate of OQAS/(Ag/ZnO) nanocomposite to *S. aureus* and *E. coli* was still over 90%, which indicated that it has excellent and lasting antimicrobial activity. Therefore, we get the conclusion that there was synergistic antimicrobial effect between Ag, ZnO and OQAS component.

To further investigate the bactericidal action, we also measured the inhibition zone of the control and OQAS/(Ag/ZnO) nanocomposite treated cotton fabric to study whether our synthesized nanocomposite would dissolve or migrate from the cotton surface. A solution containing *S. aureus* and *E. coli* at 1×10^8 CFU/mL was used to perform the test, respectively. The control and treated cotton fabric were cut into discs with a radius of 1.5 cm, were placed onto the surfaces of the bacteria containing agar cultural plate. The inhibition zones around the discs were measured after incubation at 37 °C for 18 h. As can be seen in the Fig. 3c, d, no bacteriostatic rings appear around the control cotton fabric, whether for *E. coli* or *S. aureus*. For the OQAS/(Ag/ZnO) nanocomposite treated cotton fabric, there was no obvious dissolution of the samples for *S. aureus*. For *E. coli* (Fig. 3c), there was a slight inhibition zone around the OQAS/(Ag/ZnO) nanocomposite treated cotton fabric. Because trace zinc and silver ions contained in the nanocomposite were dissoluble, which could be released to play an important role in antimicrobial activity. There was no obvious dissolution of the samples for *S. aureus* (Fig. 3d). The main reason was that the antimicrobial mechanism of our obtained nanocomposites was mainly contact and photocatalytic antimicrobial mechanism. Overall, the possibility of dissolution and migration the nanocomposite was very small, indicated that it will not migrate from the cotton surface to the human body in the application process, and can be widely used safely.

Antibacterial mechanism

Confocal laser scanning microscopy (CLSM) was also used for assaying the viability of bacteria in the presence of OQAS/(Ag/ZnO) nanocomposite. Among various dyes used as probes to stain bacteria from CLSM, fluorescein isothiocyanate (FITC) can label all bacterial including alive and dead by forming a covalent bond between dye and protein nonspecifically. FITC can be excitated at 488 nm and all bacterial fluoresce green (Song et al. 2018). Figure 4a, a′ shows the images of *E. coli* untreated and treated by OQAS/(Ag/ZnO) nanocomposite at various conditions. As can be seen, for fresh *E. coli* (Fig. 4a), all bacteria were stained green, most of bacteria were vigorous and the cell wall could be seen clearly. For OQAS/(Ag/ZnO) nanocomposite with high antimicrobial efficiency (Fig. 4a′), a small portion of bacteria stained green was observed after

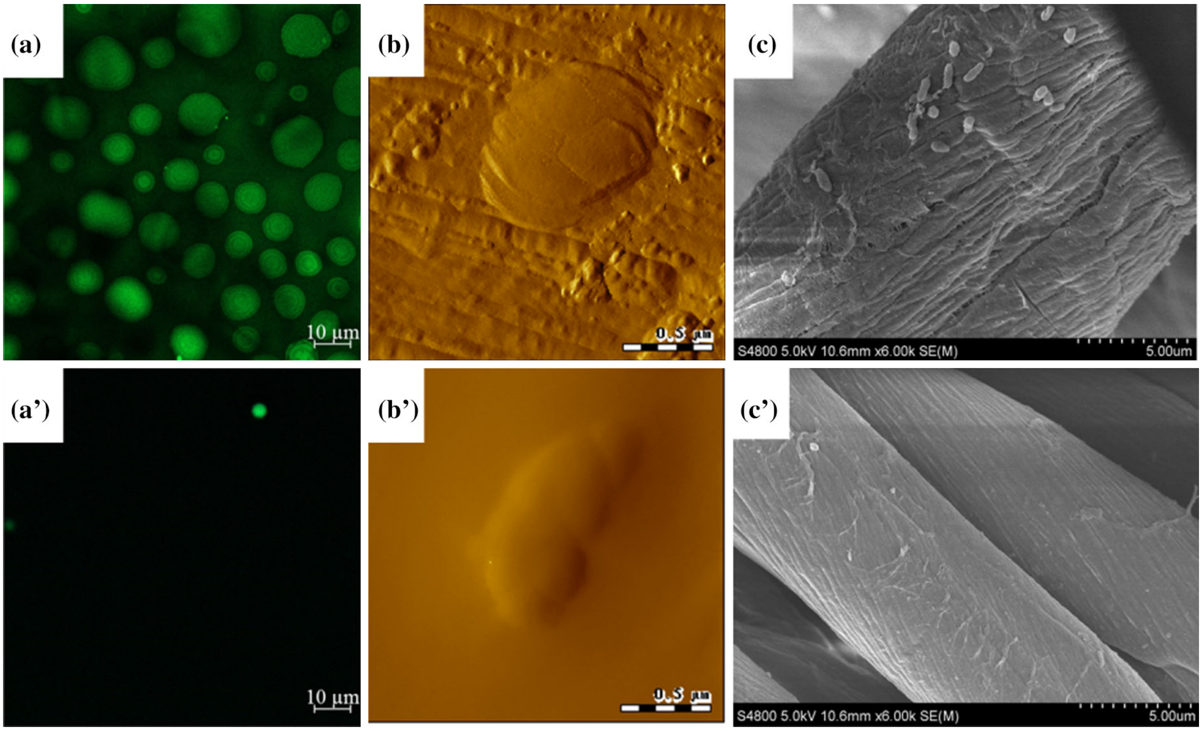


Fig. 4 Live cells images of *E. coli* treated with OQAS/(Ag/ZnO) nanocomposite at initial stage (**a**) and after 24 h contact (**a**′); AFM images of *E. coli* before (**b**) and after treated with OQAS/(Ag/ZnO) nanocomposite (**b**′); SEM photograph of control (**c**) and OQAS/(Ag/ZnO) treated cotton samples (**c**′) after incubation in the *E. coli* suspension for 18 h

24 h incubation and the cell wall was disappear, almost no alive bacteria left in the sight, which was agrees with the previous conclusions.

In order to investigate the mechanism of OQAS/(Ag/ZnO) nanocomposite for antibacterial activity, the bacterial morphology of after contact with OQAS/(Ag/ZnO) nanocomposite was observed by AFM. According to previous literature reported that the destruction of bacterial cell wall plays a crucial role in the quaternary ammonium salt-based polymers induced antibacterial process. The positively quaternary ammonium salt could attach on the cell wall of the bacterial by electrostatic interaction and then destroyed the cell wall, induce leakage of cell contents, and cause cell death. As shown in Fig. 4b, b′, the original *E. coli* cells have smooth surfaces with complete cell wall (Fig. 4b). After treated with OQAS/(Ag/ZnO) nanocomposite (Fig. 4b′), the grooves and holes were obviously seen on the cell surface of *E. coli*, which was the main reason that cause the bacterial death (Liu et al. 2018a, b).

The antimicrobial mechanism of quaternary ammonium salt was to absorb bacteria and kill bacteria. In this process, it is easy to accumulate dead bacteria or intracellular substances released by bacteria, causing defects such as yellowing and stinking of cotton fabric (Zhang et al. 2018). Therefore, we observed the adhesion of bacteria on the surface of cotton fabric cultured with bacterial suspension. As shown in Fig. 4c, after 18 h of bacterial culture, a large number of bacteria with rod shape and structurally intact adhered to the surface of control cotton that made the fibers rougher, that was, there were no apparent antibacterial activities for these fibers. While the fibers treated with OQAS/(Ag/ZnO) nanocomposite materials (Fig. 4c′), the adherent bacteria were few, in addition, the walls of *E. coli* were disrupted and deformed and the bacterial morphology was particularly small, and the micromorphology of fibers was still relatively complete.

Based on the above experimental results, we speculated the antibacterial mechanism of OQAS/(Ag/ZnO) in our research. As shown in the Fig. 5, on

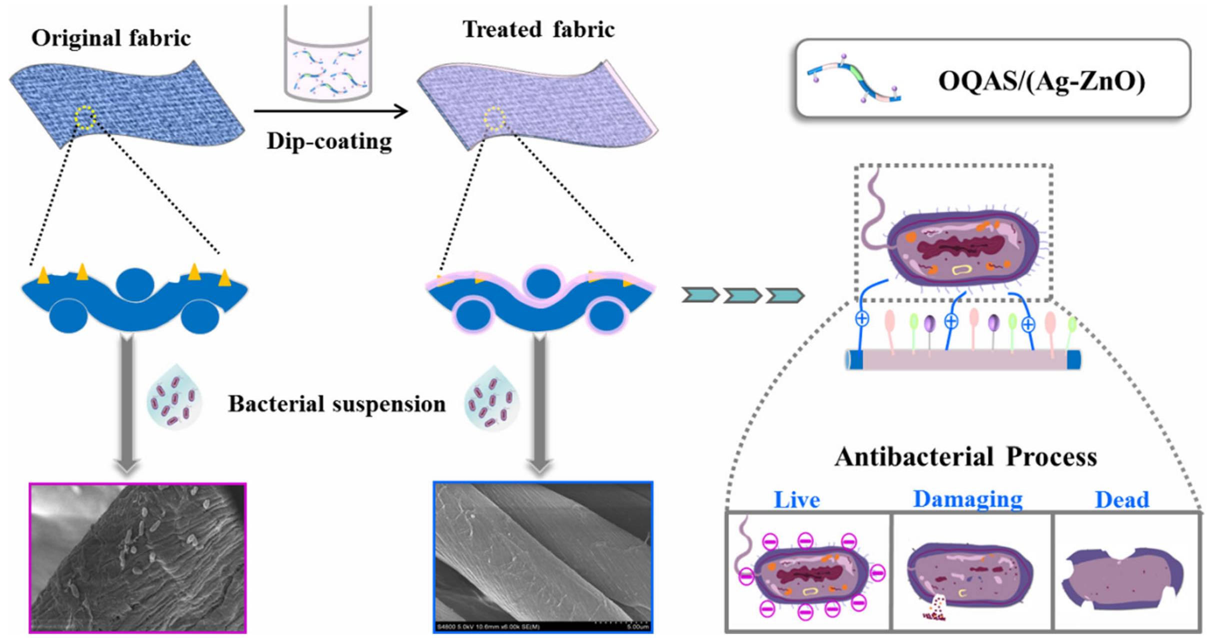


Fig. 5 Antibacterial mechanism of OQAS/(Ag/ZnO) nanocomposite treated cotton fabrics

the one hand, positive quaternary ammonium salt adsorbed on the outside of negative cells, resulted in cell membrane rupture, which leaded to leakage of cell contents and caused cell death, on the other hand, there were some organosilicon chains in the nanocomposite materials, which can be adsorbed on the surface of textiles to initiate hydration, so that the surface can form a tight bound water layer and prevent bacterial adhesion (Chen et al. 2016; Cai et al. 2018).

Surface morphology

Figure 6a, a′ presents AFM images of the cotton fabric before and after the OQAS/(Ag/ZnO) nanocomposite treated. Obviously, a natural ravines and burr peaks were existed on the surface of control cotton fabric (Fig. 6a). After treated with OQAS/(Ag/ZnO) nanocomposite, consequently, the roughness of the native cotton had also been greatly reduced and the value of the roughness decreased from 9.442 to 1.488 nm (Fig. 6a′). This was because the OQAS/(Ag/ZnO) nanocomposite formed covalent bond with cotton fabric, which could fill the ravines and burrs to endow cotton fabric with a relatively smooth surface.

Furthermore, we investigated the softness of the cotton after treated with OQAS/(Ag/ZnO) nanocomposite. The larger the value showed, the better the softness of the cotton fabric have. The softness of the native cotton was 6.08 mm, while the OQAS/(Ag/ZnO) treated cotton had a great improvement about 9.4% with a softness value of 6.65 mm. This result was consistent with the conclusion of AFM. In conclusion, after treated with nanocomposite, the formed film could cover some natural defects and burrs of raw fibers (as shown in Fig. 5). In addition, silone skeleton has good flexibility because the bonds of silicon-oxygen bond are longer than those of carbon–carbon bond and the steric hindrance is relatively weak. When the cotton fabric was subjected under the external stress, it is easier to bend to showing a soft effect. In addition, the composite film coated on cotton fiber play a key role in isolation and lubrication of cotton fibers, so that the fiber has a fluffy soft feel (Jin et al. 2015).

To observed the effect of OQAS/(Ag/ZnO) nanocomposite on the surface morphology of cotton fibers, SEM analyse were carried out, as shown in Fig. 6b–e. Figure 6b was the SEM photograph of control cotton fabric, the surface of native cotton fabric was clean with some natural gullies and defects on its surface. Figure 6c was the surface morphology of cotton fabric treated with OQAS/(Ag/ZnO) nanocomposite. Compared with raw cotton fibers,

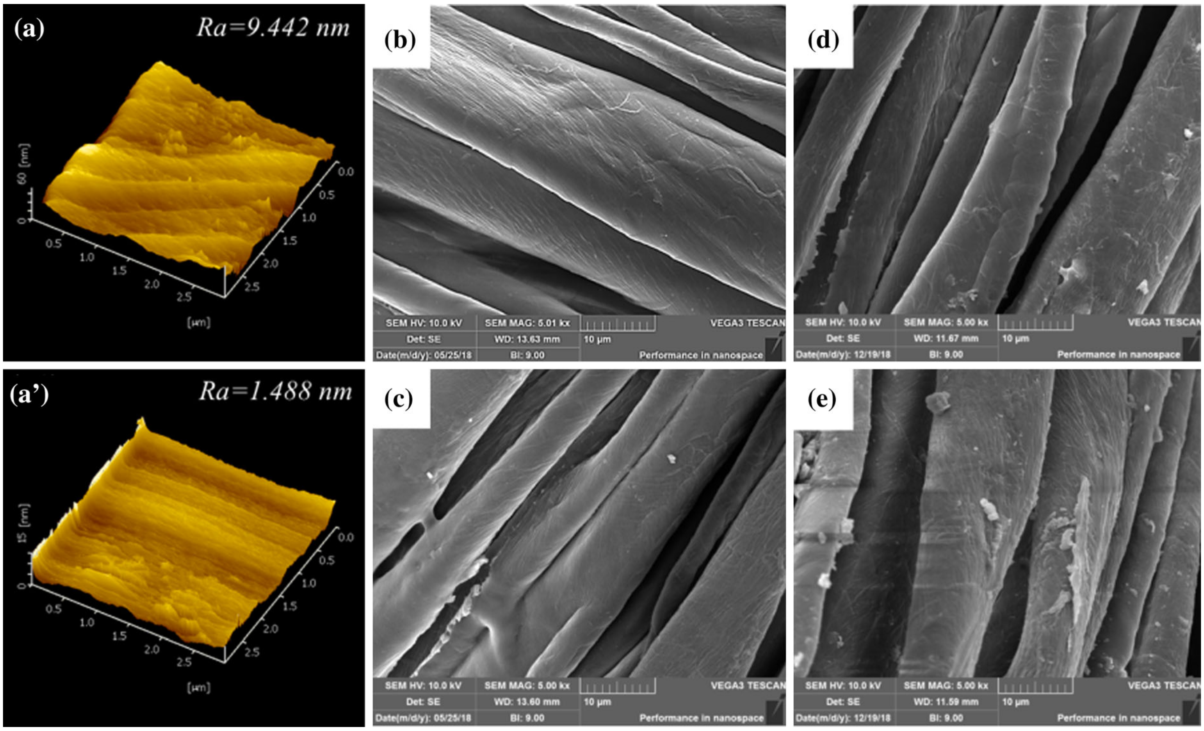


Fig. 6 The AFM images of control cotton (**a**) and OQAS/(Ag/ZnO) treated cotton (**a′**); SEM images of cotton fabrics: untreated cotton (**b**); OQAS/(Ag/ZnO) treated cotton (**c**); OQAS/(Ag/ZnO) treated cotton after 5 cycles washing (**d**) and OQAS/(Ag/ZnO) treated cotton after 10 cycles washing (**e**)

OQAS/(Ag/ZnO) nanocomposite form a thin layer of film between fibers, which made cotton fabric have a smoother surface structure. Figure 6d was SEM photograph of the OQAS/(Ag/ZnO) treated cotton fabric after 5 cycles of washing (equivalent to 25 cycles of household washing). It can be seen that OQAS/(Ag/ZnO) polymer films deposited between the fibers had a slight broken under mechanical friction and form discontinuous fragments on the surface of the fibers. Figure 6e was the micromorphology of OQAS/(Ag/ZnO) treated cotton fabric after 10 cycles of washing (equivalent to 50 cycles of household washing). After 10 cycles of washing, steel beads destroyed the film formed by the OQAS/(Ag/ZnO) nanocomposite materials in the process of washing, and a large number of polymer aggregates were formed on the surface of the fibers.

Analysis of the surface chemical composition

EDX spectra of cotton textiles treated by OQAS/(Ag/ZnO) polymer matrix composites after different washing cycles and FT-IR spectra are shown in Fig. 7. In the Fig. 7a, there were C, O, N, Si, Cl, Ag and Zn elements existed in cotton textiles treated by OQAS/(Ag/ZnO) nanocomposite, among which C and O elements were the most abundant, mainly because the main elements composition in cotton fibers and polymer chains were C and O. Figure 7b was the element content of cotton textiles treated by OQAS/(Ag/ZnO) nanocomposite after 5 cycles of washing process, the contents of Zn and Cl elements in the cotton fibers were slightly reduced, which was mainly due to the slight damage of the covalent bond formed by the nanocomposite on the surface of the cotton textiles during the washing process. Figure 7c was the element content of the treated cotton textiles after 10 washing cycles, with the further increase of the washing strength, the contents of Zn and Ag was decreased further compared with as that of blank the control cotton textiles, which indicated that most of the factors with antimicrobial activity could still be retained in cotton textiles after 10 cycles washing,

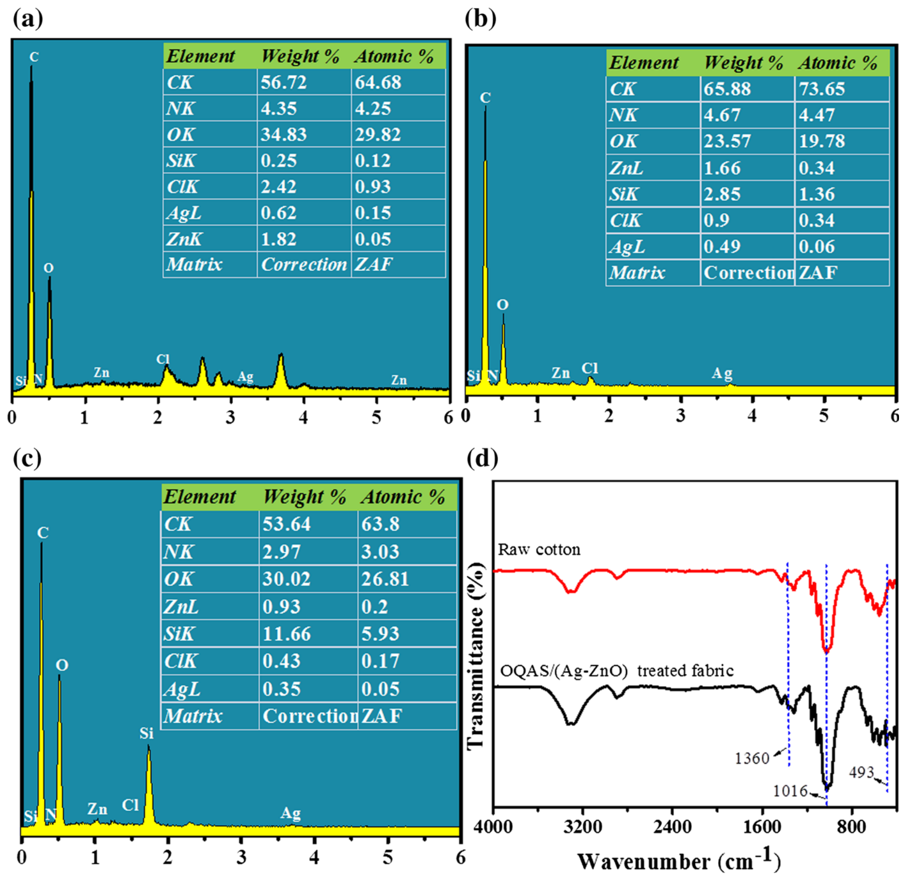


Fig. 7 EDX patterns of OQAS/(Ag/ZnO) treated cotton (**a**); OQAS/(Ag/ZnO) treated cotton after 5 cycles washing (**b**) and 10 cycles washing (**c**); FT-IR spectrum of control cotton and cotton treated with OQAS/(Ag/ZnO) nanocomposite (**d**)

thus enabling cotton textiles to obtain long-lasting antimicrobial activity.

Figure 7d shows the FT-IR spectra of control cotton and OQAS/(Ag/ZnO) nanocomposite treated cotton fabric respectively. It can be seen from the Fig. 7d that the control cotton fabric had the peak of -OH at 3200–3500 cm^{-1}, and has the stretching and deformation vibration of CH at 2895 cm^{-1} and 1307 cm^{-1}, respectively. The characteristic absorption peaks of Si–O–Si bond appeared at 1016 cm^{-1} in treated cotton fabric, which indicated that there were organosilicon chain segments in the treated cotton fabric, and the typical peaks of ZnO appeared at 495 cm^{-1}. What's more, a new peak appeared at 1360 cm^{-1}. It indicated that the covalent bonding had been formed successfully between OQAS/(Ag/ZnO) nanocomposite and cotton fabric, which greatly enhanced the bonding fastness between the nanocomposite and cotton fabric.

Wearability of cotton textiles

Figure 8a shows the hydrophilic effect of OQAS/(Ag/ZnO) nanocomposite on cotton fabric. The degree of hydrophilicity of cotton fabric was determined by measuring the wetting height of cotton fabric during the wetting process. As shown in the inset of Fig. 8a, the hydrophilicity of cotton fabric treated with OQAS/(Ag/ZnO) nanocomposite was obviously higher than that of control cotton fabric. After 50 min, the adsorption height of water molecules on control cotton fabric rose to 0.4 cm and almost had no change until 300 min. While the adsorption height of water molecules on the treated cotton fabric could rise to 8.9 cm in 300 min and the adsorptive height increased with time. As the Fig. 8b illustrated, the surface of OQAS/(Ag/ZnO) nanocomposite contains strong hydrophilic groups such as quaternary ammonium group (Yan et al. 2017). When water molecules contacted with treated cotton fabric, hydrophilic groups on the surface of cotton fabric from OQAS/

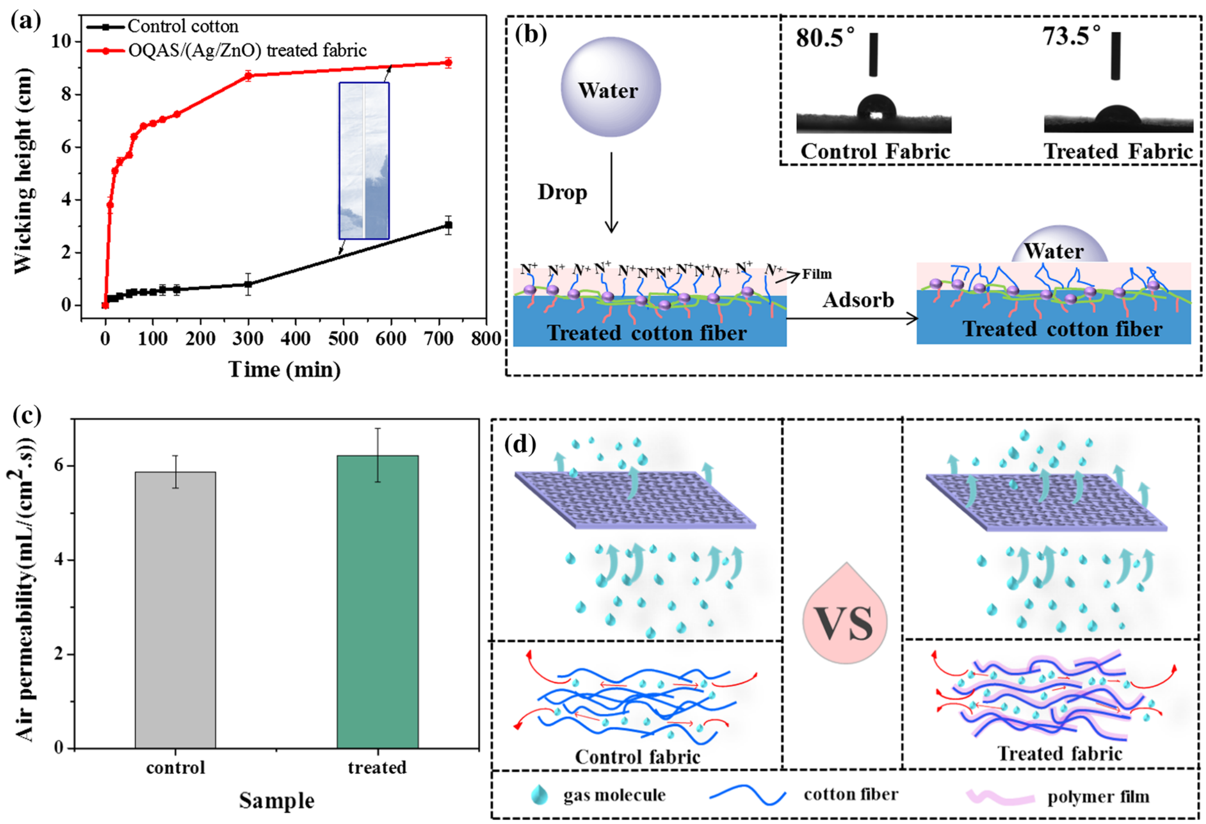


Fig. 8 **a** Hydrophilicity of control cotton and OQAS/(Ag/ZnO) treated cotton; **b** schematic diagram for hydrophilicity of OQAS/(Ag/ZnO) treated cotton; **c** air permeability of the control cotton and OQAS/(Ag/ZnO) treated cotton; **d** schematic diagram for air permeability of OQAS/(Ag/ZnO) treated cotton

(Ag/ZnO) nanocomposite can quickly absorbed water molecules, resulted in good hydrophilicity of the cotton fabric. By testing the contact angle of cotton fabric to water, we found that the contact angle of control cotton fabric to water molecule was 80.5°, while the contact angle of OQAS/(Ag/ZnO) treated cotton fabric to water molecule was reduced to 73.5°, which further proven that the treated of nanocomposite had a significant effect on improving the hydrophilicity of cotton fabric.

Figure 8c shows the air permeability of cotton fabric treated with OQAS/(Ag/ZnO) nanocomposite. It can be seen from the Fig. 8c that the air permeability of the treated cotton have a slight improvement compared with control cotton, this indicated that our synthesized nanocomposite didn't affect the air permeability of the cotton fabric (Lyu et al. 2019). We speculated about this phenomenon as shown in the Fig. 8d, the film formed by the OQAS/(Ag/ZnO) nanocomposite was coated on the outside of a single fiber. When the cotton fabric was baked at high temperature in the finishing process that could cause the movement of the polymer chain coated on the outside of the fiber, which resulted in the change of the porosity between the fibers, so the air permeability of the fabric was slightly improved (Irfan et al. 2017).

Conclusion

In this work, an organic–inorganic hybrid OQAS/(Ag/ZnO) nanocomposite was prepared and utilized on the cotton fabric to investigate its influence on the antimicrobial, softness, hydrophilicity and air permeability of the cotton fabric. The results indicated that cotton fabric functionalized by this nanocomposite exhibited outstanding antibacterial activity and also excellent laundering durability, inhibiting more than 87% of both *E. coli* and *S. aureus* even after 10 laundering cycles (equivalent to 50 cycles commercial or household laundering). Antibacterial adhesion test showed that this nanocomposite can prevent bacteria from adhering to textile surfaces. In addition, the treated cotton performed better softness, air permeability and hydrophilicity. What' more, the nanocomposite would not migrate from the treated cotton fabric to cause other health hazard. The materials of this study can be used in cotton textile industry as a textile finishing agent with excellent comprehensive properties.

Acknowledgments The authors acknowledge the support for this study from the Key Laboratory of Light Chemical Auxiliary Chemistry and Technology Jointly Established by the Ministry of Education (Shaanxi University of science and Technology) (Grant Number KFKT2019-01), Shaanxi Province "Special Support Plan for High Level Talents" Project and National Natural Science Foundation Project (Grant Number 21878182).

Compliance with ethical standards

Conflict of interest All the authors declare that they have no conflict of interest.

References

Ali BR, Majid M, Mahnaz MR et al (2018) Environmentally friendly low cost approach for nano copper oxide functionalization of cotton designed for antibacterial and photocatalytic applications. J Clean Prod 204:425–436

Cai Q, Yang S, Zhang C et al (2018) Facile and versatile modification of cotton fibers for persistent antibacterial activity and enhanced hygroscopicity. ACS Appl Mater Interfaces 10(44):38506–38516

Chen S, Guo Y, Zhong H et al (2014) Synergistic antibacterial mechanism and coating application of copper/titanium dioxide nanoparticles. Chem Eng J 256:238–246

Chen S, Yuan L, Li Q et al (2016) Durable antibacterial and nonfouling cotton textiles with enhanced comfort via zwitterionic sulfopropylbetaine coating. Small 12:3516–3521

Dong A, Wang YJ, Gao Y et al (2017) Chemical insights into antibacterial *N*-halamines. Chem Rev 117(6):4806–4862

Druvari D, Koromilas ND, Lainioti GC et al (2016) Polymeric quaternary ammonium-containing coatings with potential dual contact-based and release-based antimicrobial activity. ACS Appl Mater Interfaces 8:35593–35605

Duan C, MengJ Wang X et al (2018) Synthesis of novel cellulose-based antibacterial composites of Ag nanoparticles@metal-organic frameworks@carboxymethylated fibers. Carbohyd Polym 193:82–88

Elena P, Miri K (2018) Formation of contact active antimicrobial surfaces by covalent grafting of quaternary ammonium compounds. Colloids Surf B 169:195–205

Gao D, Chen C, Ma JZ et al (2014) Preparation, characterization and antibacterial functionalization of cotton fabric using dimethyl diallyl ammonium chloride-allyl glycidyl ether-methacrylic/nano-ZnO composite. Chem Eng J 258:85–92

Gao D, Duan X, Chen C et al (2015a) Synthesis of polymer quaternary ammonium salt containing epoxy group/nano ZnO long-acting antimicrobial coating for cotton fabrics. Ind Eng Chem Res 54:10560–10567

Gao D, Zhang W, Ma J et al (2015b) Influence of alcohols on stability and mechanical properties of polyacrylate coating material. J Coat Technol Res 12(6):1–8

Gao D, Lyu L, Lyu B et al (2017) Multifunctional cotton fabric loaded with Ce doped ZnO nanorods. Mater Res Bull 89:102–107

Gao D, Zhang J, Lyu B et al (2018) Poly(quaternary ammonium salt-epoxy) grafted onto Ce doped ZnO composite: an enhanced and durable antibacterial agent. Carbohyd Polym 200:221–228

Gao D, Li Y, Lyu B et al (2019a) Construction of durable antibacterial and anti-mildew cotton fabric based on P (DMDAAC-AGE)/Ag/ZnO composites. Carbohyd Polym 204:161–169

Gao D, Zhang Y, Lyu B et al (2019b) Nanocomposite based on poly(acrylic acid)/attapulgite towards fame retardant of cotton fabrics. Carbohyd Polym 206:245–253

Guo X, Guo B, Wang Y et al (2017) Preparation of spherical metal-organic frameworks encapsulating Ag nanoparticles and study on its antibacterial activity. Mater Sci Eng C 80:698–707

Hong D, Cao G, Qu J et al (2018) Antibacterial activity of Cu_2O and Ag co-modified rice grains-like ZnO. J Mater Sci Technol 34:2359–2367

Ibanescu M, Musat V, Textor T et al (2014) Photocatalytic and antimicrobial Ag/ZnO nanocomposites for functionalization of textile fabrics. J Alloys Compd 610:244–249

Irfan M, Perero S, Miola M et al (2017) Antimicrobial functionalization of cotton fabric with silver nanoclusters/silica composite coating via RF co-sputtering technique. Cellulose 24(5):2331–2345

Jin Y, Pu Q, Fan H (2015) Synthesis of linear piperazine/polyether functional polysiloxane and its modification of surface properties on cotton fabrics. ACS Appl Mater Interfaces 7:7552–7558

Karim MN, Singh M, Weerathunge P et al (2018) Visible-light-triggered reactive-oxygen-species-mediated antibacterial activity of peroxidase-mimic CuO nanorods. ACS Appl Nano Mater 1(4):1694–1704

Li X, He S, Liu X et al (2019) Polymer-assisted freeze-drying synthesis of Ag-doped ZnO nanoparticles with enhanced photocatalytic activity. Ceram Int 45(1):494–502

Liu L, Liu Z, Yang Y et al (2018a) Photocatalytic properties of Fe-doped ZnO electrospun nanofibers. Ceram Int 44 (16):19998–20005

Liu Q, Li J, Zhong X et al (2018b) Enhanced antibacterial activity and mechanism studies of Ag/Bi_2O_3. Adv Powder Technol 29(9):2082–2090

Lu Z, Gao J, He Q et al (2017) Enhanced antibacterial and wound healing activities of microporous chitosan-Ag/ZnO composite dressing. Carbohyd Polym 156:460–469

Lyu B, Cheng K, Gao D et al (2019) Enhanced hygienic property of solvent-free polyurethane film by hollow TiO_2 microspheres. J Clean Prod 209:608–616
Mai Z, Xiong Z, Shu X et al (2018) Multifunctionalization of cotton fabrics with polyvinylsilsesquioxane/ZnO composite coatings. Carbohyd Polym 199:516–525
Qian L, Lei D, Duan X et al (2018) Design and preparation of metal-organic framework papers with enhanced mechanical properties and good antibacterial capacity. Carbohyd Polym 192:44–51
Sathya M, Pushpanathan K (2018) Synthesis and optical properties of Pb doped ZnO nanoparticles. Appl Surf Sci 449:346–357
Sharkawy A, Fernandes IP, Barreiro MF et al (2017) Aroma-loaded microcapsules with antibacterial activity for eco-friendly textile application: synthesis, characterization, release and green grafting. Ind Eng Chem Res 56 (19):5516–5526
Song Y, Jiang H, Wang B et al (2018) Silver-Incorporated Mussel-Inspired PolydopamineCoatings on Mesoporous Silica as an Efficient Nanocatalyst and Antimicrobial Agent[J]. ACS Appl Mater Interfaces 10(2):1792–1801
Svetlichnyi V, Shabalina A, Lapin I et al (2016) ZnO nanoparticles obtained by pulsed laser ablation and their composite with cotton fabric: preparation and study of antibacterial activity. Appl Surf Sci 372:20–29
Tian T, Shi X, Cheng L et al (2014) Graphene-based nanocomposite as an effective, multifunctional, and recyclable antibacterial agent. ACS Appl Mater Interfaces 6(11):8542–8548
Tu X, Hu F, Thakur K et al (2018) Comparison of antibacterial effects and fumigant toxicity of essential oils extracted from different plants. Ind Crops Prod 124:192–200
Wei T, Tang Z, Yu Q et al (2017) Smart antibacterial surfaces with switchable bacteria-killing and bacteria-releasing capabilities. ACS Appl Mater Interfaces 9(43):37511–37523
Yan X, Li J, Yi L (2017) Fabrication of pH-responsive hydrophilic/hydrophobic janus cotton fabric via plasma-induced graft polymerization. Mater Lett 208:46–49
Yan J, Zheng L, Hu K et al (2019) Cationic polyesters with antibacterial properties: facile and controllable synthesis and antibacterial study. Eur Polymer J 110:41–48
Yang H, Zhang Q, Chen Y et al (2018a) Microwave-ultrasonic synergistically assisted synthesis of ZnO coated cotton fabrics with an enhanced antibacterial activity and stability. ACS Appl Bio Mater 1(2):340–346
Yang H, Zhang Q, Chen Y et al (2018b) Ultrasonic-microwave synthesis of ZnO/BiOBr functionalized cotton fabrics with antibacterial and photocatalytic properties. Carbohyd Polym 201:162–171
Zhang S, Yang X, Tang B et al (2018) New insights into synergistic antimicrobial and antifouling cotton fabrics via dually finished with quaternary ammonium salt and zwitterionic sulfobetaine. Chem Eng J 336:123–132