In order to improve the anti-ultraviolet property and laundering durability of cotton fabrics, the cotton fabrics were cationized with epoxy propyl trimethylammonium chloride, and then boron-nitrogen-doped carbon quantum dots (BN-CQDs) were grafted onto the cationized cotton fabrics by the chemical reaction between the quaternary ammonium cation on the cotton fabrics and the carboxyl functional group on the surface of BN-CQDs. The structure, the ultraviolet protection performance and washing durability of the cotton fabrics grafted with BN-CQDs were characterized and tested. The results showed that the resultant cotton fabrics modified with BN-CQDs exhibited a very high ultraviolet protection factor (UPF). Even after 20 consecutive washings, the UPF value was still as high as 75.3, suggesting the promising potential of the modified fabrics as UV protective materials and their excellent laundering durability.

**Keywords**: carbon quantum dots, cotton fabrics, quaternary ammonium cations, anti-ultraviolet property, UPF value

**INTRODUCTION**

With the development of science and technology and the improvement of living standards, the impact of ultraviolet rays on human health has attracted more and more attention. Proper sunlight exposure is very beneficial to human health. However, excessive ultraviolet radiation can cause skin burns and erythema, accelerate skin aging, and even cause skin cancer.\(^1\) It is generally believed that the wavelength range of sunlight reaching the ground is 290-3000 nm, of which ultraviolet radiation (UVR) accounts for 6%. The ultraviolet radiation is divided into three bands: long-wave UVA (315-400 nm), medium-wave UVB (280-315 nm) and short-wave UVC (200-280 nm).\(^2\) The effect of ultraviolet radiation on human skin depends not only on the type of ultraviolet light, but also on the skin color. UVC can basically be completely absorbed by the outer epidermis and dermal tissue. Only UVA can be transmitted under the dermal tissue to accelerate the aging of the skin, while the transmittance of UVB is worse than that of UVA. Therefore, the ultraviolet radiation protection of cotton fabrics is aimed at UVB and UVA.

Cotton fiber has the characteristics of breathability, sweat absorption, softness and non-stimulation, so it is the preferred material for summer clothing. However, the chemical structure of cotton does not contain the functional groups that absorb in the near-ultraviolet region, resulting in the highest UV transmittance among all fabrics.\(^3\) Therefore, the anti-ultraviolet finishing of cotton fabric is particularly important. At present, there are two main methods for the production of UV-resistant textiles. One is to add ultraviolet reflection agent or absorbing agent into the fibers in the process of blending spinning. Common reflectors mainly include silica particles, nano metal organic framework, graphene oxide, zinc oxide nanoparticles etc.\(^4,5\) Common ultraviolet absorbers include benzotriazole, benzophenone, triazine, metal organic complex light conversion agent and tea extract.\(^8,10\) Such UV resistant textiles have excellent UV resistance and water resistance, but they have high technical requirements and high cost, and are not suitable for natural fibers. Other methods to achieve UV resistance of fabrics include coating, sol-gel technology, printing etc. to endow textiles with
anti-ultraviolet function during fabric finishing.\textsuperscript{11-13} The anti-ultraviolet cotton fabrics obtained in this way have poor water resistance and the finishing will have a certain impact on the surface morphology of the cotton fabric.

Carbon quantum dots (CQDs) are a new type of carbon nanomaterials with a quasi-spherical structure and stable fluorescent properties that are smaller than 10 nm in size. Compared with traditional semiconductor quantum dots and organic dyes, CQDs have high fluorescence intensity, strong photobleaching resistance, good biocompatibility, low toxicity, good dispersibility, strong chemical inertness, simple functionalization, and good light stability. Their good physical and chemical properties have attracted more and more attention.\textsuperscript{14-15} Therefore, they are widely used in the fields of biosensors, chemical sensors and cell imaging.\textsuperscript{16-18} In the early stage, our research group prepared boron-nitrogen co-doped carbon quantum dots (BN-CQDs) by a one-pot hydrothermal synthesis method. The prepared BN-CQDs had good water solubility, emit blue fluorescence, and the emission behavior did not depend on the excitation wavelength. The particles were approximately spherical with a size of 5-10 nm, and an interplanar spacing of about 0.30 nm, which was close to the graphite carbon (002) plane lattice. The surface of BN-CQDs contains a lot of hydrophilic functional groups of hydroxyl, carboxyl and amino groups. The cotton fabric finished with BN-CQDs showed good UV protection performance, but poor laundering durability.\textsuperscript{19}

In order to enhance the binding force between BN-CQDs and the cotton fabric, the cotton fabric was chemically modified to produce some functional groups on its surface, and then BN-CQDs were fixed on the fabric by chemical reaction among the functional groups of the cotton fabric and BN-CQDs. BN-CQDs was grafted on the surface of cotton fabric. However, because the oxidation of cotton fabric was carried out in a heterogeneous system, the effect of oxidation modification was not very good, and the conditions for the acylation reaction and the Schiff base reaction between the oxidized fabric and BN-CQDs surface groups were harsh, so there were not many BN-CQDs grafted onto the surface of cotton fabric, and the combination between cotton fabric and BN-CQDs was not firm, so the water washing durability of the fabric was too poor. The anti-ultraviolet effect of cotton fabric could not be improved.

In this research, based on previous work, the surface of cotton fabric was modified with 2,3-epoxy propyl trimethyl ammonium chloride solution (EPTC). EPTC reacted with C6-OH on cellulose in cotton fabric to generate ammonium salt cationic cellulose ether, which made the surface of cotton fabric contain quaternary ammonium cations.\textsuperscript{20} The surface modified cotton fabric was put into the solution of BN-CQDs, and the quaternary ammonium cations on cotton fabric reacted with the carboxyl functional groups on the surface of BN-CQDs to generate quaternary ammonium salt with stable ionic bond. Then, BN-CQDs were grafted onto the cotton fabric. BN-CQDs on the cotton fabric improved the anti-ultraviolet ability of cotton fabric, and the stable ionic bonds between BN-CQDs and the cotton fabric enhanced the water washing durability. The formation of the stable quaternary ammonium salts was much easier than the amidation or Schiff base reaction between BN-CQDs and the fabric oxidized by the TEMPO/NaBr/NaClO system and NaIO\textsubscript{4}. The schematic diagram of cotton fabric modification and BN-CQDs grafting is shown in Figure 1.

**EXPERIMENTAL**

**Materials**

Citric acid monohydrate, ethylenediamine, borax, 2,3-epoxy propyl trimethyl ammonium chloride (EPTC) and sodium hydroxide were purchased from the Sinopharm Chemical Reagent Ltd. Co. All of them were used as received without further purification. Plain white cotton fabrics (F0) were purchased from...
Cotton fabrics

Jinqiu Textile Company (Zhejiang, China). The fabrics had an area density of 85.6 g/m², thickness of 0.24 mm, warp density of 298 pieces/10 cm, and weft density of 312 pieces/10 cm.

Synthesis of BN-CQDs

BN-CQDs were synthesized according to the previously described method. 0.42 g citric acid (CA), 0.5 mL ethylenediamine (EDA) and 0.042 g borax were firstly dissolved in 80 mL water under stirring. Then, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and held at 180 °C for 5 h in an oven. After the autoclave was cooled to room temperature naturally, the resulting yellow and transparent solution of BN-CQDs was obtained.

Figure 1: Schematic diagram of cotton fabric modification and BN-CQDs grafting

Figure 2: Cellulose modification mechanism of cotton fabric

Figure 3: The principle of grafting BN-CQDs onto the cationized cellulose of cotton fabric

Cationization of cotton fabrics and grafting of BN-CQDs onto cationized fabrics

20 cm × 20 cm cotton fabric (marked F0) was put into 100 mL of 30% NaOH solution for alkalization for 1 h, and washed with deionized water for several times. The cotton fabric was transferred to 100 mL of 4% 2,3-epoxy propyl trimethyl ammonium chloride solution (EPTC), stirred in a water bath for 4 h, washed with water, and vacuum dried at 60 °C for 3 h. The cationized cotton fabric (marked F1) was obtained. The chemical reaction mechanism of cationization of cotton fabrics is shown in Figure 2.

The cationized cotton fabric (F1) with quaternary ammonium cations was put into a beaker containing 100 mL of BN-CQDs aqueous solution, stirred in a water bath at 40 °C for 2 h, washed with deionized
water, and vacuum dried at 60 °C. The cotton fabric with grafted BN-CQDs was prepared (denoted as F1-CQDs). The schematic diagram of grafting BN-CQDs onto the surface of modified cotton fabric is shown in Figure 3.

For comparison, BN-CQDs/cotton fabric was prepared by the spray-rolling method. 100 mL of BN-CQDs aqueous solution was sprayed on a 20 cm x 20 cm cotton fabric, then the cotton fabric was rolled on a small pad for 3 times, and finally dried in a 60 °C vacuum oven to obtain BN-CQDs finished cotton fabric, denoted as F0-CQDs.

Characterization and testing

The surface composition of BN-CQDs, cotton fabric, cationized cotton fabric and grafted BN-CQDs cotton fabric was characterized using a VERTEX70 Fourier Transform infrared spectrometer (Bruker, Germany). The surface morphology of warp cotton fabric was observed by a JSM-IT300 electron microscope (SEM, JEOL, Japan).

An HD902C (Nantong Hongda) anti-ultraviolet penetration test system was used to test the UV protection factor (UPF) of cotton fabric. Each sample was tested at 10 different positions on the front and back, and finally the average value was taken.

The moisture permeability of cotton fabric was tested in a computerized fabric moisture permeability meter (YG601H, Ningbo Textile Instrument Factory), at the temperature of 38 °C, relative humidity of 2%, and the airflow of 0.5 m/s. 10 mL of water was added to the moisture-permeable cup, which was covered with the test surface of the sample downward. Then, the moisture permeable cup was put into the test chamber and allowed to achieve equilibrium for half an hour, then it was weighed, and repeatedly weighed after one hour (the temperature difference was ensured to be lower than 3 °C when weighing outside the chamber). The moisture permeability was calculated according to the following formula:

\[
WVT = \frac{(24 \times \Delta m)}{S \times t}
\]

where WVT is the moisture permeability of the sample, g/(m²·d); \(\Delta m\) is the difference between two weighings of the moisture-permeable cup, g; S is the experimental area of the sample, m²; t is the experimental time, h.

According to AATCC (American Association of Textile Chemists and Colorists) standard, the fabric was washed by the home laundering test for 5 minutes each time. After washing, the sample was dried, and then other tests were carried out.

RESULTS AND DISCUSSION

Structure of BN-CQDs

In the preliminary work of our research group, the boron nitron-doped carbon quantum dots (BN-CQDs) synthesized from citric acid monohydrate, ethylenediamine and borax were graphite-like nanocrystals with rich hydroxyl and amine groups on the surface. They had good water solubility. The particles were approximately spherical, with a size of 5-10 nm and a crystal plane spacing of about 0.30 nm, close to the graphite-carbon (002) plane lattice. BN-CQDs aqueous solution had strong absorption in the ultraviolet region and emitted blue fluorescence, and the emission behavior was independent of the excitation wavelength. Due to such down-conversion fluorescence emission, BN-CQDs were used as ultraviolet absorber for cotton fabric, and when ultraviolet light was irradiated on BN-CQDs, BN-CQDs converted it into visible blue light. \(^{19}\) In this work, the carboxyl functional groups on the surface of BN-CQDs were used to react with the modified surface of cotton fabric, and BN-CQDs were grafted onto the surface of cotton fabric. The XPS characterization result of BN-CQDs further demonstrated the existence of a large number of hydrophilic groups on the surface of BN-CQDs.

The elemental composition of BN-CQDs was characterized by XPS. As shown in Figure 4A, the XPS spectrum of BN-CQDs has four peaks at 191.7eV, 284.6eV, 400.3eV and 530.4eV, corresponding to the peaks of B1s, C1s, N1s and O1s, respectively. XPS results showed that BN-CQDs were mainly composed of C (64.9%), N (11%), O (22.6%) and B (1.5%). The high-resolution spectrograph of C1s (Fig. 4B) consisted of two peaks at 284.3, 285.7 and 287.8 eV, which were attributed to C-C/C=C, C-N and C-O, confirming that carbon exists in three different environments. The N1s spectrum (Fig. 4 C) consisted of two peaks at 399.1eV and 400.7eV, which existed in the form of C-N-C and N-H, respectively. The O1s spectrum (Fig.4 D) consisted of two peaks at 530.8eV and 531.8, which existed in the form of C=O and C-OH/C-O-C, respectively. In Figure 4E, the B1s peaks were located at 191.5eV and 192.1eV, respectively, indicating that boron mainly exists in the form of B-O and B-C.\(^{21}\) The XPS analysis results were consistent with the FTIR analysis results,\(^{19,21}\) indicating that the prepared BN-CQDs were graphite-like nanocrystals with rich hydroxyl, carboxyl and amine groups on the surface.
Structure of cotton fabrics with grafted BN-CQDs

Figure 5 shows the infrared spectra of the blank cotton fabric (F0), the spray-rolled BN-CQDs cotton fabric (F0-CQDs), the modified cationic cotton fabric (F1) and the grafted BN-CQDs cotton fabric (F1-CQDs). For the blank cotton fabric F0, the characteristic peak at 3309 cm⁻¹ is attributed to the stretching vibration of hydroxyl groups in the glucose units, the peaks at 2906 cm⁻¹ and 1370 cm⁻¹ were assigned to the stretching vibration of -CH and -CH₂ groups and the bending vibration of -CH₂ and -CH₃ groups, the peak at 1645 cm⁻¹ was assigned to the stretching vibration of the absorbed moisture, the absorption peaks at 1420 and 1320 cm⁻¹ were the characteristic bands of -CH oscillating vibration in the cellulose structure of cotton fiber, and a strong adsorption band at 1136, 1082 and 898 cm⁻¹ was the result of the overlapping bands of C–C, C–O, and C–O–C stretching vibrations of cellulose, respectively. For the cationized cotton fabric (F1), the peak at 1082 cm⁻¹ disappeared, and a new absorption peak appeared at 1469 cm⁻¹, which was attributed to the characteristic absorption peak of the stretching vibration of C-N of trimethylquaternary ammonium salt (-N’(CH₃)₃Cl). The results indicated that the cationized cotton fabric contained the characteristic functional groups of...
the target product, and the cotton fabric cellulose was cationized with quaternary ammonium under the designed experimental conditions.

Comparing the infrared spectra of the spray-rolled BN-CQDs cotton fabric (F0-CQDs) and the cotton fabric F0, a stronger absorption peak at 1570 cm\(^{-1}\) was attributed to the bending vibration of -C=O-N in BN-CQDs, which proved that BN-CQDs particles successfully adhered to the surface of cotton fabric. Compared with the infrared spectrum of the cationized cotton fabric F1, F1-CQDs also showed a new absorption peak at 1570 cm\(^{-1}\), which was caused by amide bonds formation between quaternary ammonium cations on the cotton fabric with carboxyl groups on the surface of BN-CQDs. The results showed that the cellulose of cationized cotton fabric had a chemical reaction with the surface of BN-CQDs to form stable ion bonded quaternary ammonium salt.

In order to explain the chemical bond formed between BN-CQDs and the fabric for the F1-CQDs sample, the infrared spectra of F0-CQDs and F1-CQDs fabric were recorded after 10 washes, as shown in Figure 6. In the infrared spectrum of F0-CQDs fabric, the bending vibration peak of -C=O-N at 1570 cm\(^{-1}\) was significantly weakened. This was because the CQDs particles attached to the cotton fabric were reduced after 10 standard launderings, but the absorption peak still existed for F1-CQDs fabric, indicating that there were still some BN-CQDs particles attached to the cotton fabric after multiple washes. The intensity of the absorption peak of F1-CQDs fabric at 1570 cm\(^{-1}\) hardly changed, indicating that BN-CQDs was grafted to the cationized fabric in the form of chemical bonding, and the laundering had little effect on BN-CQDs grafted to the cationized cotton fabric.

![Infrared spectra of different cotton fabrics](image1)

**Figure 5:** Infrared spectra of different cotton fabrics

![IR spectra of different cotton fabrics after washings](image2)

**Figure 6:** IR spectra of different cotton fabrics after washings

**UV resistance and laundering durability of cotton fabrics**

UPF levels were divided according to the Australian AS/NZS 4399 clothing sunscreen standard,\(^{25}\) and the UV protection ability of finished cotton fabric was evaluated. The ratings were as follows: providing good protection (UPF: 15-24), very good protection (UPF: 25-39) and excellent protection (UPF>40). The UPF value of cotton fabric (F0) in this work was 31.2, which rates it a very good UV resistant fabric.

The initial UPF of BN-CQDs finished cotton fabric (F0-CQDs) and the grafted BN-CQDs cotton fabric (F1-CQDs) and the UPF after washes are listed in Table 1. Thus, it can be noted that the UPF of F0-CQDs was up to 165.5. This was because the cotton fabric absorbed more BN-CQDs particles, and it had excellent UV resistance. However, after the same number of standard launderings, the UPF of F0-CQDs cotton fabric decreased significantly. After 10 launderings, the UPF value dropped to 56.3, which was 34.01% of the initial value. This was mainly because the BN-CQDs in F0-CQDs fabric were mainly attached to the fabric surface or fiber gaps by physical adsorption. Washing easily made the BN-CQDs fall off, so the UPF value decreased significantly, and the washing resistance of F0-CQDs cotton fabric was poor. The UPF value of the cotton fabric grafted with BN-CQDs (F1-CQDs) was as high as 81.4, achieving excellent UV protection performance.
After washing one time, the UPF decreased, which may be explained by the fact that the attached BN-CQDs particles that did not participate in the grafting reaction were removed by washing. However, with further washing F1-CQDs cotton fabric, its UPF value tended to be stable. After washing for 10 times, the UPF value was 75.3, which was 92.51% of the initial value. Overall, the UPF of F1-CQDs fabric decreased little, and the washing resistance was superior. For F1-CQDs fabric, the quaternary ammonium cation on the fabric surface reacted with the carboxyl (-COOH) on the surface of BN-CQDs to form a stable quaternary ammonium salt ion bond. The formation of chemical bonds made the BN-CQDs particles remain stable on the surface of the fabric, thus improving more effectively the UV resistance and laundering durability of cotton fabric.

As can be seen from the photos of cotton fabric under the 365 nm UV lamp (Fig. 7), the untreated cotton fabric (F0) was grey and white under the UV lamp, while the cationized cotton fabric (F1) was white. Because BN-CQDs absorbed ultraviolet light and emitted blue fluorescence, the BN-CQDs finished cotton fabric (F0-CQDs) and the BN-CQDs grafted cotton fabric (F1-CQDs) emitted bright blue light under the UV lamp. After 10 washings, F1-CQDs fabric still maintained the bright blue light under the UV lamp. It showed that BN-CQDs were successfully grafted onto cotton fabric cellulose, which enhanced the durability of its UV resistance. While F0-CQDs fabric under the UV lamp emitted blue light, it could be concluded that most of the BN-CQDs on the fabric had fallen off during washings, the laundering durability of F0-CQDs fabric was poor and its UV resistance reduced.

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial sample</th>
<th>1 washing</th>
<th>5 washings</th>
<th>10 washings</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>31.2</td>
<td>31.2</td>
<td>30.8</td>
<td>30.7</td>
</tr>
<tr>
<td>F0-CQDs</td>
<td>165.5</td>
<td>116.5</td>
<td>85.3</td>
<td>56.3</td>
</tr>
<tr>
<td>F1-CQDs</td>
<td>81.4</td>
<td>75.6</td>
<td>75.2</td>
<td>75.3</td>
</tr>
</tbody>
</table>

Figure 7: Pictures of different cotton fabrics under 365 nm UV lamp

#### Surface morphology of cotton fabrics

Figure 8 shows SEM images of different cotton fabrics. It can be seen that the untreated cotton fabric (F0) fiber had a smooth surface. The fiber surface of the cationized cotton fabric (F1) became rough, with loose fibers. The cotton fabric (F0-CQDs) finished by BN-CQDs coating had a rough surface, but due to the small particle size of BN-CQDs, the particles are not obviously seen. The surface of cotton fabric (F1-CQDs) grafted with BN-CQDs was also rough, and a large number of nanoparticles were attached to
the fiber. After 10 washings, the surface of F0-CQDs has little change, and a large number of nanoparticles were still attached to the fiber of F1-CQDs cotton fabric.

Figure 8: SEM images of different cotton fabrics

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Moisture transmission (g/m²·d)</th>
<th>Initial sample</th>
<th>10 washings</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>2863.94</td>
<td>2979.95</td>
<td></td>
</tr>
<tr>
<td>F0-CQDs</td>
<td>2728.69</td>
<td>2836.38</td>
<td></td>
</tr>
<tr>
<td>F1-CQDs</td>
<td>2749.15</td>
<td>2841.49</td>
<td></td>
</tr>
</tbody>
</table>

Moisture permeability of cotton fabrics

The moisture permeability of different cotton fabrics is listed in Table 2. The moisture permeability of the raw cotton fabric before and after 10 washings reached 2863.94 and 2979.95 g/m²·d, respectively. Due to the absorption of a large number of BN-CQDs, the initial moisture permeability of F0-CQDs cotton fabric was 2728.69 g/m²·d, which was much lower than that of the raw cotton fabric. After 10 washings, due to BN-CQDs adsorbed on the fabric surface falling off during the washing process, the...
The moisture permeability of the fabric was 2841.49 g/m²d. After 10 times of washing, BN-CQDs absorbed on the surface fell off, but the BN-CQDs grafted on the fabric still existed, the moisture permeability of F0-CQDs cotton fabric increased to 2841.49 g/m²d. Compared with the initial value, it increases by 3.36%. Compared with raw cotton fabric F0, the moisture permeability of F1-CQDs cotton fabric and F1-CQDs cotton fabric decreased, but the decrease amplitude was small, which did not affect the wearable performance of the fabric.

CONCLUSION

The cotton fabric was modified with epoxy propyl trimethylammonium chloride to make the cotton fabric cellulose contain quaternary ammonium cations. The quaternary ammonium cation reacted with -COOH on the surface of BN-CQDs, and BN-CQDs were grafted onto the cotton fabric to obtain BN-CQDs grafted cotton fabric. The BN-CQDs grafted cotton fabric showed excellent UV resistance and washing resistance. The UPF value was as high as 81.4, and it remained 75.3 even after washing 10 cycles. The moisture permeability of the fabric was 2841.49 g/m²d.

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