Construction of a P–N–Si flame retardant coating on the cotton fabric with the integration of biomass carbon dots and ammonium polyphosphate

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Abstract In order to improve the flame retardancy of cotton fabric, a kind of biomass carbon dots (CDs) particles were interspersed in the ammonium polyphosphate (APP) layer to achieve a new efficient CDs-based APP (CDs-APP) composite flame retardant by the integration technology. Then the CDs-APP layer was coated on the surface of cotton fabric. The microstructure and thermal stability of CDs-APP particle were characterized by the Transmission electron microscopy (TEM), Fourier infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The mass ratio of CDs to APP was 15.52%, which contains the C, O, N, Si and P elements, accounting for the 28.86%, 42.29%, 19.01%, 2.58% and 6.26%, respectively. The flame-retardant mechanism of CDs-APP was investigated by the limiting oxygen index (LOI), vertical combustion, cone calorimeter, thermogravimetric and thermogravimetric-infrared analysis. The results showed that, when the content of CDs-APP was about 10%, the LOI value of cotton fabric rose to 36.1%. The burning time and damage length have reduced to 4.5 s, 5.6 cm, respectively. And the fabric achieved B1 level. The addition of CDs-APP decreased the total heat release, heat release rate, total smoke emission and smoke emission rate of cotton fabric, among the peak-heat release rate has decreased by 55.78%. By quantifying the flame-retardant modes of CDs-APP, it displayed the superposition of physical barrier effect, flame inhibition effect and catalytic charring effect, accounting for 45.96%, 8.62% and 47.85%, respectively.
Introduction

The fire caused by the fiber and textile is one of the “blasting fuse” leading to casualties. It is predicted that, the total global market of flame-retardant fabrics will increase from 4.379 billion US dollars in 2017 to 5.787 billion US dollars in 2022. As a widely used material, the cotton fabric belongs to the flammable material with the LOI value of only about 18.4%. Due to the worldwide restrictions on the production and use of brominated flame retardant (FR), it is important to realize the halogen-free FR of cotton fabric.

It is one of the effective ways to realize the flame retardancy of cotton fabric by catalyzing the charring of cotton fabric to form a highly-quality carbon layer with thermal stability under high heat environment. Among the various catalytic charring agent, the ammonium polyphosphate (APP) has been proved to own the excellent catalytic charring effect, applied in various textiles, such as polyterephthalic acid (PET) (Fang et al. 2019), polypropylene (PP) (Yu et al. 2019), etc. However, in order to achieve the more efficient barrier effect of carbon layer, the carbon layer should own excellent characteristics (Huang et al. 2020): ① Thermal-oxidative stability, ② Mechanical strength, ③ High char yield. The APP FR mainly functioned on the char yield. For the thermal-oxidative stability and mechanical strength of carbon layer can be improved by the introduction of inorganic nano materials. Therefore, constructing the nano-material to assist in the traditional flame retardant is an important technical mean.

In various nano-FR systems, nano carbon materials (such as fullerenes, carbon nanotubes, graphene, etc.), with halogen-free, heat resistant, fire-resistant characteristics, is a kind of green environmental protection flame retardant materials. The common of carbon materials in flame retardant polymers (Zhang et al. 2013; Dittrich et al. 2015; González Morones et al. 2016; Wang et al. 2017; Adner et al. 2019; Wei and Wang 2019), was especially in enhancing the carbon layer structure of...
polymer, such as increasing the content of non-oxygen elements the density, continuity, graphitization degree, thermal oxygen stability of carbon layer, so as to play the role of enhancing the carbon layer, forming an effective barrier for heat insulation and oxygen insulation, and play a flame retardant role. As a new member of carbon nanoparticle, carbon dots (CDs) is a kind of zero-dimensional material with carbon core as the skeleton, the particle size of less than 10 nm and rich in functional groups on the surface. It has the advantages of simple production process, low cost, and environmental protection. Khose RV confirmed the functional modification of graphene CDs and realize the preparation of CDs based transparent composite FR (Khose et al. 2018). Alongi J reported the cellulose-based CDs and linear polyamide synergistic flame retardant cotton fabric (Alongi et al. 2019). Gu W W has investigated the flame retardant effect of gelatin-based CDs on the PET fiber, and demonstrated the addition of single CDs can’t make the PET fiber pass the vertical combustion level (Gu et al. 2022). These results implied the CDs-based composite FR would become a new way. In addition, under the combined action of silicon, phosphorus and nitrogen elements, the coated textiles exhibit high thermal stability and charring, and thus go out automatically when the fire source is removed (Castellano et al. 2019; Wang et al. 2021; Gu et al. 2022).

Based on these, in this paper, a new kind of CDs and APP powder were firstly constructed through the integration technology in order to enhance the carbon layer and catalyze the charring of cotton fabric. Through coating finishing, an efficient flame-retardant coating containing P–N–Si elements was formed on the cotton fabric. The flame-retardant mechanism was investigated and qualified by many methods.

**Experimental**

**Materials**

Citric acid, anhydrous thanol, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (KH-792), ammonium polyphosphate (APP), self-crosslinking silicone acrylic emulsion, and 3-Aminopropyltriethoxysilane (KH-550) were all analytical grade and purchased from Tianjin Langyi Funcional Materials Co. Ltd., China. Deionized water is lab-made. The fabric composition used is 100% cotton, the weave type is plain weave, the fabric weight is 344.6 g/m², and the yarn count is about 50 tex × 2 / 52 tex × 2.

**Preparation of CDs-APP composite FR**

The CDs was prepared from the citric acid by the one-step hydrothermal synthesis (Xie et al. 2020). First, 1.507 g of citric acid, 21.8 mL of KH-792 and 40 mL of deionized water were added to the beaker. After stirring evenly, the solution was transferred to a high-temperature reaction kettle and reacted in a vacuum dryer at 200 °C for 6 h. After the reaction, the solution was cooled to room temperature and dialyzed for three times. Then freeze it for 12 h, and put into a freeze dryer for 24 h to obtain the pale-yellow CDs powder.

The 1 g APP powder, 0.1 mL KH-550, and 100 mL anhydrous ethyl alcohol were successively added into a beaker. The above solution was heated to 70 °C with the magnetic stirring for 1 h. Then 0.5 g of CDs was added in the above solution and ultrasonic dispersed for 30 min. Finally, the solution was heated at 50 °C for 2 h at a constant speed. After dialysis and lyophilization, the CDs-APP powder was obtained.

The chemical synthesis schemes of CDs and CDs-APP is shown in Fig. 1.

**Flame retardant coating finish on cotton fabric**

A certain amount of self-crosslinking silicone-acrylic emulsion and distilled water were mixed with CDs-APP powder by the ultrasonic dispersion for a certain period of time. And the mass fraction of FR powder accounted for 30%. Then, it was evenly coated with 2, 4, and 6 layers on both sides of the cotton fabric with a scraper, and dried at 50 °C to form a coating film. The flame-retardant cotton fabric with different weight gain rates was obtained. The specific coating formula is shown in Table 1.

**Characterization**

Transmission electron microscope (TEM) images of CDs and CDs-APP powder were performed by a JEOL JEM-2100 electron microscope.
The changes in functional groups were tested by the 1730 Fourier Transform Infrared (FT-IR) with the scanning range of 450–4000 cm⁻¹. The powder was analyzed by TD-3700 X-ray diffractometer (XRD) with the scanning rate of 5°/min and scanning range of 5–80°.

The flame retardancy cotton fabric was evaluated by the limit oxygen index test (LOI), M601 vertical combustion instrument according to GB/T5455-1997 standard, and the FTT007 cone calorimeter (the irradiation was 35 kW/m²) in accordance with ISO 5660–1 standard.

Thermogravimetric analysis (TGA) testing was performed on the samples using a TGA4000 thermogravimetric analyzer. In N₂ atmosphere, the temperature was raised to 100 °C at a heating rate of 10 °C/min for 3 min, and then continued to heat up to 700 °C for 1 min.

The X-ray photoelectron spectrometer (XPS) test was carried out on thermos Fisher ESCALAB 250XiXPS probe, using Al Kα (1486.6 eV) as X-ray source, Shirley baseline and Lorentzian Gaussian fitting as peak. Thermogravimetric infrared spectroscopy (TG-IR) was set in N₂ atmosphere with a temperature range of 100–650 °C at a heating rate of 10 °C/min.

The whiteness of the fabric was tested with WSB whiteness meter; the air permeability of the fabric was tested with YG461E-III fully auto permeability instrument; the bending performance of the fabric was tested with HD207 automatic fabric stiffness tester.

Table 1 CDs-APP treated cotton fabric sample loading data

| Sample          | Untreated | CP-C1            | CP-C2            | CP-C3            |
|-----------------|-----------|------------------|------------------|------------------|
| Weight gain/wt% | 0         | 15.25 ± 2.03     | 30.12 ± 1.05     | 50.24 ± 0.86     |
| Weight ratio of CDs-APP/wt% | 0 | 5.03 ± 0.61     | 9.94 ± 0.35     | 16.58 ± 0.28     |

Fig. 1 The chemical synthesis schemes of CDs (a) (Xie et al. 2020) and CDs-APP (b)
Results and discussion

Microstructure and molecular structure of CDs-APP

The microstructure of CDs and CDs-APP were analyzed by TEM method. The particle size of CDs (Fig. 2a) is all less than 10 nm. By comparison, it was found in Fig. 2b that CDs were distributed between the CDs-APP layer. In order to further verify the composition of CDs-APP for qualitative and quantitative analysis, the molecular composition of CDs-APP powder was analyzed by the IR (Fig. 3), XRD (Fig. 4) and XPS (Fig. 5).

Combined with the APP IR curve in Fig. 3, the absorption peaks located at 1660 cm\(^{-1}\), 1479 cm\(^{-1}\) were divided into symmetric and asymmetric angular vibration of NH\(_4^+\). According to the IR curve of CDs, the peaks at 3223 cm\(^{-1}\), 1442 cm\(^{-1}\), 1735 cm\(^{-1}\), and 3057 cm\(^{-1}\) were the stretching vibration of –OH, –COOH, –CONH, and –NH\(_2\), respectively. And the symmetric stretching vibration peak of Si–O was scattered at 1070 cm\(^{-1}\). These data demonstrated the surface of CDs turns out to be active. In addition, a vibrational absorption peak of C–N–O was observed at 1660 cm\(^{-1}\) from the IR curve of CDs-APP, which indicated the successful incorporation of APP.
Further qualitative analysis was carried out by comparing the X-ray diffraction patterns of CDs and CDs-APP. In the pattern of APP, there were two characteristic diffraction peaks at 17.4° and 18.9°, with narrow width and small peak area, which conformed to the peak shape corresponding to APP-I (JCPDS: 44-0739) (Shen et al. 1969). In the diffractogram of CDs, the characteristic peak located at 25° was wider and the peak area was larger, which certified that the crystallinity in this region was low and the carbon atoms

Fig. 5 XPS wide scan survey, C1s, Si2p, N1s and O1s spectra of CDs
were randomly arranged (Xie et al. 2020). There were characteristic diffraction peaks of APP and CDs in the diffraction pattern of CDs-APP, which proved that the integration process of APP and CDs was realized.

The components of CDs and CDs-APP FR were quantitatively analyzed by XPS, as shown in Figs. 5 and 6, and the corresponding data are listed in Table 2. The CDs itself contained four elements

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**Fig. 6** XPS wide scan survey, C1s, Si2p, P2p, N1s and O1s spectra of CDs-APP

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including C, O, N and Si, accounting for 47.34%, 35.20%, 10.46% and 7.00%, respectively. CDs-APP was composed of five elements including C, O, N, Si and P, with specific gravity of 28.86%, 42.29%, 19.01%, 2.58% and 6.26%, etc. The appearance of P element further demonstrated the conclusions of IR and XRD.

Furthermore, the C element in CDs mainly belonged to C–C/C═C (284.74 eV), C–O (286.13 eV), C═O (288.97 eV) and C–N (285.14 eV), the existence forms of O element were C–O (531.4 eV) and C–OH/C–O–C (532.90 eV), which further verified the existence of hydroxy-rich functional groups on the surface of CDs. The peak fitting of N and Si elements showed that Si element only exists in the single form of Si–O, and N element mainly exists in the form of O═C–NH (399.25 eV), –NH– (398.90 eV), C–N (400.65 eV). By comparing the XPS analysis of CDs-APP, it was spotted that the existence form of element C was basically similar to that of CDs, while the existence form of O element was added with P═O bond (532.52 eV). And it can be seen from P2p spectra that, the occurrence of P–O–P (134.25 eV) and P═O (133.60 eV) bond is mainly due to the APP powder, and the C–O–P (133.74 eV) bond verify the connection of CDs and APP powder. These data once again substantiated that CDs and APP have been successfully constructed as an integrated structure.

### Thermal stability of flame retardants

Figure 7 shows the thermogravimetric curves of APP, CDs and CDs-APP, from which the thermal degradation rate, temperature and carbon residue of each polymer can be seen to analyze its thermal stability. It can be seen from the figure that the initial decomposition temperature of APP was 327 °C, and rapid degradation occurs after 560 °C. The weight loss rate reached the highest at 649 °C, and the carbon residue at 700 °C was 20.20%. CDs began to degrade at a lower temperature, the initial decomposition temperature was 137 °C, the weight loss rate was the highest at 515 °C, and the carbon residue was 52.16% at 700 °C. Due to the lower degradation temperature of CDs, the initial decomposition temperature of CDs-APP was earlier than that of APP to 275 °C, the weight loss rate reached a peak at 362 °C, and the carbon residue at 700 °C was 57.11%. The proposed mechanism of thermal decomposition of APP, CDs and CDs-APP suggested that a weight ratio of about 15.52% for APP in CDs-APP could easily be obtained. This approach of weight ratio had resulted from the change in the weight loss.
Relationship between flame retardant loading and flame retardant properties of fabrics

LOI and vertical combustion test analysis

The flame retardancy of flame retardants under different loadings on the surface of cotton fabrics were studied. The corresponding LOI value and vertical burning test results are listed in Table 3, and the digital photo of the vertical burning test is shown in Fig. 8.

The limit oxygen index of pure cotton cloth is 16.2%, which is easy to be ignited in the air. In the vertical combustion test, it was completely burned,
the after-flame time and after-glow were 31.5 s, 73.5 s, respectively. The damage length of cotton was 30 cm. With the increase of the flame-retardant coating content, the LOI value of the cotton fabric has also gradually increased. The LOI value of CP-C1, CP-C2 and CP-C3 increased from 16.2% to 20.1%, 36.1% and 54.5%, respectively. The LOI value of CP-C2 was 1.2 times higher than that of pure cotton fabric, reaching the nonflammable level, indicating that the CDs-APP improved the self-extinguishing ability of cotton fabrics. In the vertical combustion test of the flame-retardant coated fabric, it was found that, there was almost no smoldering phenomenon.

**Table 4** Cone calorimeter test data of each sample

| Sample     | Untreated | CP-C1 | CP-C2 | CP-C3 |
|------------|-----------|-------|-------|-------|
| TTI/s      | 9         | 15    | 24    | 79    |
| THR/(MJ m⁻²) | 19.16  | 14.61 | 13.91 | 10.18 |
| pk-HRR/(kW m⁻²) | 299.79 | 259.35 | 117.61 | 113.68 |
| FPI/(m²s/kW) | 0.0300 | 0.0578 | 0.2041 | 0.6949 |
| TSP/m²     | 1.74      | 1.24  | 1.28  | 1.01  |
| MLR/(g(s m⁻²)) | 4.72    | 3.38  | 2.54  | 2.33  |
| TML/wt%    | 97.28     | 59.29 | 50.73 | 42.50 |
| MEHC/(MJ kg⁻¹) | 22.02  | 20.84 | 20.02 | 13.76 |

![Fig. 9 Combustion curve of cotton fabric before and after finishing](image-url)
In Fig. 8b, it was found that an obvious charring area appeared on the surface of CP-C1 after burning. With the increase of layer liquid, the after-flame time of CP-C2 was reduced to 4.5 s, the damage length was also reduced from 30 to 5.6 cm, and the combustion level reached the B1 level, which met the flame-retardant requirements of fabrics in real life.

**Cone calorimeter test analysis**

Table 4 shows the cone calorimeter test data of each sample, and Fig. 9 shows the total heat release (THR), heat release rate (HRR), total smoke production (TSP), and smoke production rate (SPR) curves corresponding to the samples. The ignition time (TTI) of pure cotton fabric was only 9 s, and the ignition time of flame-retardant coated fabric was greater than 9 s, indicating that the flame resistance of the fabric was improved after adding CDs-APP flame retardant. Combined with the combustion curve in Fig. 8, it can be indicated that CDs-APP reduced the THR, HRR, and TSP of cotton fabrics. Combining with Table 4, it can be seen that the peak heat release rate (pk-HRR) of pure cotton cloth was 299.79 kW/m². Compared with that, the pk-HRR of CP-C1, CP-C2, and CP-C3 decreased to 259.35 kW/m², 117.61 kW/m², 113.68 kW/m², respectively. The pk-HRR value of CP-C2 decreased by 55.78%, and the THR value decreased from 19.16 to 13.91 MJ/m². Fire hazard index (FPI) is the ratio of TTI to pk-HRR, which reflects the fire hazard. The larger the value, the smaller the fire hazard. Compared with pure cotton cloth (0.0300), the FPI values of CP-C1, CP-C2, and CP-C3 were 0.0578 m²s/kW, 0.2041 m²s/kW, and 0.6949 m²s/kW, respectively. It shows that the CDs-APP coating film had a protective effect on cotton fabrics, and significantly reduced its fire hazard.

In addition, the average effective heat of combustion (MEHC) of pure cotton fabrics was 22.02 MJ/kg, and the EHC values of CP-C1, CP-C2, and CP-C3 dropped to 20.84 MJ/kg, 20.02 MJ/kg, and 13.76 MJ/kg, respectively. MEHC characterizes the heat released by the combustion of flammable volatile components formed by thermal decomposition of the sample, which usually occurs in the gas phase. The reduction of MEHC was mainly due to two reasons. First, the content of combustible volatile components produced by the decomposition of the condensed phase of the material itself was reduced, and the heat generated by the final combustion was reduced (Abdelkhalik et al. 2019; Makhlof et al. 2020). Second, the volatile compounds (such as phosphorus compounds) released by the material itself can be used as effective flame inhibitors (Ma et al. 2010), preventing the combustion of flammable volatile products. In addition, the mass loss rate (MLR) of the flame-retardant coated fabrics in Table 3 decreased from 4.72 g/(s m²) to 3.38 g/(s m²), 2.54 g/(s m²), and 2.33 g/(s m²), respectively. It shows that the CDs-APP coating film reduced the MLR of the cotton fabric during the combustion process, and the total mass loss (TML) of the flame-retardant cotton fabric decreased from 97.28 wt% to 59.29 wt%, 50.73 wt%, and 42.50 wt%, respectively. And according to the smoke production rate (SPR) and total smoke production (TSP), it was found that the CDs-APP coating film reduced the smoke production rate and smoke production of cotton fabrics, and the TSP value of CP-C2 decreased from 1.74 to 1.28 m². Therefore, it was inferred that the main reasons for the decrease in heat and smoke production of flame-retardant cotton fabrics are as follows. On the one hand, the total amount of flame-retardant cotton fabrics decomposed by combustion decreases, which reduces the content of combustible volatile components and reduces the total heat released (Hu et al. 2013). On the other hand, the decomposition and combustion of the CDs-APP coating film on the cotton fabric volatilized phosphide (Liu et al. 2021; Zhang et al. 2021), which effectively inhibited the flame and interrupted the combustion and smoldering process in advance.

As can be seen from the above data that the flame retardancy of CP-C2 can meet the requirements of use, and its flame-retardant mode was quantitatively deduced according to the following formula (Table 4). It was found that the flame-retardant mode was the superposition of three action modes: physical barrier effect, flame inhibition effect, and catalytic charring effect, accounting for 45.96%, 8.62%, and 47.85%, respectively. It is clear that the CDs-APP flame retardant cotton fabric was mainly through the physical barrier effect and catalytic charring effect.

| Sample | Physical barrier | Flame inhibition | Charring |
|--------|-----------------|------------------|----------|
| CP-C2  | 45.96           | 8.62             | 47.85    |

Table 5 Quantitative assessment of the flame-retardant modes for CP-C material
According to the following formula (Tang et al. 2017), the flame retardant mode of the flame retardant pure cotton cloth was quantitatively calculated, and the results were listed in Table 5.

\[
E_{\text{Physical-barrier}} = 1 - \left( \frac{p_k - \text{HRR}_{\text{CP-C}}}{p_k - \text{HRR}_{\text{untreated}}} \right) \left( \frac{\text{THR}_{\text{CP-C}}}{\text{THR}_{\text{untreated}}} \right)
\]  

(1)

\[
E_{\text{Flame-inhibition}} = 1 - \frac{\text{MEHC}_{\text{CP-C}}}{\text{MEHC}_{\text{untreated}}}
\]  

(2)

\[
E_{\text{Charring}} = 1 - \frac{\text{TML}_{\text{CP-C}}}{\text{TML}_{\text{untreated}}}
\]  

(3)

In the formula, \( E_{\text{Physical-barrier}} \), \( E_{\text{Flame-inhibition}} \), and \( E_{\text{Charring}} \) refer to physical barrier effect, flame inhibition effect and catalytic charring effect respectively, and CP-C refers to flame retardant cotton fabric.

TG-IR analysis of flame-retardant cotton fabrics

First, the TG comparison analysis of pure cotton fabric and CP-C2 flame retardant fabric was carried out, as shown in Fig. 10. The decomposition paths of the two sample curves tend to be similar. The initial decomposition temperature \( T_{\text{onset}} \) of pure cotton fabric was 212.85 °C, the temperature corresponding to the maximum weight loss rate \( T_{\text{max}} \) was 445.71 °C, and the carbon residue at 600 °C was 13.44%. The \( T_{\text{onset}} \) of CP-C2 was 212.12 °C, almost unchanged, and the \( T_{\text{max}} \) was advanced to 423.21 °C, but the carbon residue at 600 °C increased by 29.94%, an increase of 1.22 times. It was verified again that the CDs-APP flame retardant layer promoted the thermal decomposition of cotton fabrics into char, in other words, the effect of catalytic char formation was exerted, which was consistent with the flame retardant test results of cotton fabrics in “Relationship between flame retardant loading and flame retardant properties of fabrics”. This phenomenon might be caused by the phosphoric acid generated during the degradation of CDs-APP or by promoting the dehydration reaction of cotton cellulose (Zhang et al. 2021).

Second, based on the above TG and cone calorimeter tests, CDs-APP was found to promote the dehydration of cellulose to form a carbon layer. The carbon layer can isolate the heat and unburned parts from the flame, and the gas-phase decomposition products of thermal cracking before and after the coating of cotton fabrics were analyzed by the combined thermal infrared technique (Fig. 11). The two peaks at 3559 cm\(^{-1}\) were attributed to –OH in water, 2967 cm\(^{-1}\) was the contraction vibration peak of C–H, the absorption peak at 2359 cm\(^{-1}\) was attributed to CO\(_2\), 1746 cm\(^{-1}\) was the contraction vibration peak of C=O and 1176 cm\(^{-1}\) was the stretching vibration of the C–O–C bond. According to the Gram-Schmidt curve, it was found that the pyrolysis gas intensity of CO\(_2\), H\(_2\)O, CO and carbonyl compounds of CP-C2 was lower than that of pure cotton fabrics, and the
absorption peaks of each pyrolysis gas appeared to move forward in different degrees. Combined with the significant increase in the quality of carbon residue in TG analysis, it can be shown that the addition of CDs-APP flame retardant coating can effectively promote and catalyze the pyrolysis of cotton fabrics into carbon in advance. The generated carbon layer covered the surface of the fabric and played a good role in thermal insulation.

Fig. 11 TG-IR curves of cotton fabrics (a) and CP-C2 (b) before and after finishing.
role in heat insulation and oxygen isolation, inhibited the cracking of gas phase products, and hindered the release of pyrolysis products during the thermal decomposition process, thereby improving the flame-retardant effect of cotton fabrics.

Analysis of carbon residual structure of cotton fabrics

Figure 12 shows the carbon residue morphology and structure of pure cotton fabric and CP-C2 coated fabric after cone calorimeter test. The pure cotton fabrics (a, c) were almost completely burned, and a little carbon residue was in the form of powder, and its own carbon formation was poor. By comparison, it was found that the CDs-APP coated fabric in figures (b, d) was covered with a dense carbon layer after combustion, which expanded and foamed. And combined with the SEM image, it was found that the carbon layer can still maintain complete fiber bundles. The carbon residue of CP-C2 was analyzed by SEM–EDS and found that it contains C, O, N, Si, and P elements. The analysis showed that the CDs-APP coating film will form a carbon layer on the surface of the fabric under high temperature combustion, exerting a physical barrier effect, inhibiting the generation of flammable gas, preventing contact with oxygen, thereby reducing heat transfer and flue gas release. This result was consistent with the quantification of flame retardancy in “Microstructure and molecular structure of CDs-APP”. When APP was heated, it would form a...
strong dehydrating agent called polyphosphoric acid, which would dehydrate the surface of cotton fabric, and then formed carbide. At the same time, the polyphosphoric acid produced by the reaction would also cover the surface of the material, and generated incombustible CO₂, H₂O and other gases due to heat, both of which play a role in isolating and blocking oxygen (Qin et al. 2020). The carbides harden, agglomerate, and eventually formed a dense layer of carbon. When CDs were heated, a fluffy carbon layer can be formed on the surface of the material with a network structure. The carbon layer not only prevented the transfer of heat, but also obstructed the flow of O₂, and at the same time reduced the heat release rate (Gu et al. 2022). When CDs and APP were compounded, it had a synergistic flame-retardant effect, and the morphology features of (b), (c), (d) in Fig. 12 were formed, the surface was smooth, and the carbon layer was fluffy and dense, without faults and cracks. The addition of CDs can effectively improve the APP carbon layer to form a stable network structure. These network structures can improve the physical properties of the carbon layer, make the carbon layer denser, and greatly block the heat transfer and the spread of oxygen. Therefore, CDs-APP can effectively improve the flame-retardant effect of the fabric.

Mechanism of CDs-APP flame retardant cotton fabric

Through the flame retardancy test of CDs-APP coated cotton fabric, the characterization of thermal stability and the analysis of the structure and morphology of the carbon residue, the flame-retardant mechanism was speculated. Figure 13 shows the flame-retardant mechanism of CDs-APP coated cotton fabric. Under the action of the flame, the APP in the CDs-APP coating film would be thermally decomposed to form a strong dehydrating agent of polyphosphoric acid, which catalyzes the dehydration and carbonization of the surface of the cotton fabric to form carbides (Liu et al. 2021; Zhang et al. 2021). CDs can make these carbides form a network-like structure fluffy carbon layer. This dense and stable carbon layer can block the transmission of heat and the spread of flammable gas and smoke, and play the role of flame retardant and smoke suppression. At the same time, the polyphosphoric acid produced by the decomposition of APP and the non-combustible gases such as CO₂ and H₂O produced by heating also covered the surface of the CDs-APP coated cotton fabric, which plays the role of isolating and blocking oxygen and preventing the fabric from further burning. The CDs that enhance the carbon layer and the APP that catalyzes carbonization constitute a high-quality flame-retardant system of CDs-APP synergistic carbonization. Through the physical barrier effect and catalytic

Table 6 LOI values and WL of each sample before and after washing

| Sample  | LOI-before/% | LOI-after/% | WL/% |
|---------|--------------|-------------|------|
| Untreated | 16.2         | 15.6        | 2.4  |
| CP-C1   | 20.1         | 18.9        | 4.6  |
| CP-C2   | 36.1         | 34.8        | 5.1  |
| CP-C3   | 54.5         | 50.1        | 6.5  |
char formation, the combustion reaction was inhibited, the thermal stability of the cotton fabric was improved, and the flame-retardant effect of the cotton fabric was effectively improved.

Test for water resistance of flame-retardant cotton fabrics

In order to characterize the water resistance of flame-retardant cotton fabrics, the following washing procedure was carried out for fabrics. The fabric samples were immersed in warm water containing 0.5% detergent at 40 °C for 20 min, and then washed with deionized water for 20 min. The excess washing liquid on the fabric surface was washed with water by repeated 10 times, and finally dried at 50 °C for 12 h. Table 6 shows the LOI values and mass loss (WL) of each sample before and after washing.

As can be seen from the Table 6, the LOI values of all fabrics after washing have reduced, and the quality of sample is also reduced, compared with that of unwashed fabrics. This may be caused by the yarn shedding at fabric edges and loss of flame-retardant coating during washing. The fabric CP-C2 and CP-C3 (treated by CDs-APP) still retain good flame retardancy after washing, and the LOI values are 34.8% and 50.1%, respectively, which meet the flame-retardant requirements. This is because CDs-APP flame retardant coating own a certain water resistance, so the fabric after flame retardant finishing still retains certain flame-retardant property, even after the repeated washing.

Other properties of flame-retardant cotton fabric

In order to characterize the appearance quality and internal quality of flame-retardant cotton fabrics, the whiteness, air permeability and bending properties of fabrics were tested. The results are expressed in below Table 7.

It can be found that, the whiteness, air permeability and bending properties of the fabrics treated with CDs-APP coating have decreased to a certain extent. The whiteness and air permeability of the fabric gradually decreased with the increase of the coating loading, because the CDs-APP flame retardant coating was light yellow (the colour of CDs powder is yellow), which would reduce the whiteness of the fabric. At the same time, the coating will cover a part of the voids created by the interlacing of the warp and weft yarns of the fabric, reducing the breathability of the fabric. For CP-C2, the Permeability has decreased by 36.10%, from 83.36 to 57.12 mm s⁻¹. However, the difference in extension length of CP-C1, CP-C2 and CP-C3 after flame retardant finishing is not obvious. In general, although the appearance and intrinsic quality of the coated fabrics have decreased, they still meet the requirements for the use of the fabrics in some special industry field.

**Conclusion**

In this paper, through the integrated technology, the CDs of the reinforced carbon layer and the APP that catalyzes the formation of carbon formed a carbon dot-ammonium polyphosphate (CDs-APP) synergistic flame-retardant system, and then loaded on the surface of the cotton fabric through coating finishing, forming a kind of efficient flame-retardant coating containing P–N–Si elements. The results showed that the integrated structure of CDs-APP was successfully constructed by combining C–O–P and C–N–O. The mass ratio of CDs to APP in the flame-retardant coating film was 15.52%, including C, O, N, Si, and P elements, accounting for 28.86%, 42.29%, 19.01%, 2.58%, and 6.26%, respectively. When the flame-retardant content was about 10%, the LOI of the flame-retardant coated cotton fabric CP-C2 reached 36.1%, the afterburning time was reduced to 4.5 s, and the damage length was reduced to 5.6 cm, and the fabric achieved B1 level flame retardant. The addition of CDs-APP reduced the total heat release, heat release rate, total smoke generation and smoke generation rate of cotton fabrics, and the peak heat release rate of CP-C2 decreased by 55.78%. Through quantitative comparison of their flame-retardant modes, it
was found that the quantitative flame-retardant mode is the superposition of three action modes: physical barrier effect, flame suppression effect, and catalytic carbonization effect, accounting for 45.96%, 8.62%, and 47.85%, respectively.

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**Declarations**

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

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