

Environmental and Performance Assessment of Fabricated Hydrophobic and Flame-Retardant Cotton Fabrics with Functional Integrated Graphene

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Research Article

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Abstract

There is a conflict between enhancing the functionality of products and reducing the environmental impact of manufacturing in the materials industry. Using green chemicals or adopting cleaner production processes can help overcome this conflict. However, researchers usually neglect the substitution effect when selecting green technology, namely, that investing more in chemical development decreases the resources used in cleaner process techniques. This study demonstrated this substitution effect in the modification of cotton fabrics. We fabricated hydrophobic and flame-retardant cotton fabrics with functional integrated graphene. It was found that these fabrics can be prepared in one step. As seen from an environmental assessment, applying functional integrated graphene can decrease the time required, reduce the energy consumption, and reduce the wastewater discharge. Based on the hydrophobicity-flame retardancy quadrant, we found that functional integrated graphene can improve the compatibility of different functionalities. On the other hand, compared to the use of commercial finishing agents, using functional integrated graphene can reduce organic discharge by up to 92%. This study demonstrates that using green chemicals can reduce pollution discharge and result in a cleaner production process. This study also provided atom economic ideas for green modification of cellulosic materials.

Introduction

The development of green chemicals or the adoption of cleaner production processes are approaches used by enterprises to achieve environmental protection(Almeida et al. 2015). Pavel Chakraborty et al. (Chakraborty 2018) studied the impact of Germany's ban on azo dyes on India's printing and dyeing industry in 2017 and found that environmental regulation would increase the R&D investment for environmental chemical development in the chemical sector in India but reduce the investment in processing technology upgrading. The results indicated that there is a substitution effect on resources between chemical development and sustainable process upgrading. In other words, increasing the R&D investment in developing new chemicals in upstream enterprises of the industrial chain decreases the resource available for new techniques downstream(Peng and Liu 2016). Previous studies did not investigate the specific mechanism of this substitution effect between developing green chemicals and reducing process techniques in cleaner production.

The failure to allocate resources effectively between process innovation and product innovation occurs frequently in research on material surface modification due to the neglect of the substitution effect(Maine et al. 2012). Therefore, this study investigated the above substitution effect via an environmental assessment of cotton modification. Through deliberate functional molecular design, functional integrated graphene was synthesized and used to prepare hydrophobic and flame-retardant cotton fabrics. Compared with the existing chemical modification process, the use of functional integrated graphene can reduce pollution discharge during processing.

Specifically, in this study, functional integrated graphene was prepared by the construction of chemical bonds between hexachlorocyclotriphosphazene (HCCP), hexafluorocarbon and hydroxyl groups on a

graphene oxide (GO) surface. There is synergy between the flame retardancy and hydrophobicity of cotton fabric treated by functional integrated graphene in one pot. Compared with the commercial treatment process using both flame-retardant agents and hydrophobic agents, treatment employing functional integrated graphene decreased the potential environmental pollution during the preparation, reduced the chemical additives used in the modification, and reduced the corresponding pollution discharges and energy consumption.

The key to functional integrated material design is the selection of nanocarriers (Mohanty and Swain 2019; Prusty and Swain 2020). Graphene was used as a nanocarrier for three main reasons: (1) Nanomaterials have a high adsorption activity. With a decrease in the size of nanoparticles, the specific surface area increases accordingly, and the nanomaterials have an obvious surface effect (Fang et al. 2009), which leads to the excellent adsorption performance of auxiliaries (Shi et al. 2019; Xu et al. 2017). (2) Graphene has a high functional group loading capacity. Graphene, as a two-dimensional nanomaterial, has attracted extensive attention since its discovery (Novoselov et al. 2004). The oxidation-reduction method (Hummers and Offeman 1958) is a common method for preparing graphene. GO is an intermediate product of this oxidation-reduction method. There are many oxygen-containing groups on the surface of GO (Lerf et al. 1998), which can react with active groups to introduce functional components on the graphene surface (Garg et al. 2017; Ji et al. 2017; Wang et al. 2018). As a two-dimensional material, graphene has a high adsorption capacity (Li et al. 2020). (3) GO can be well dispersed in some solvents (Gan et al. 2020). At the same time, due to the presence of a large number of polar groups on its surface, GO has good affinity for and can bind strongly with cellulose fibers (Fang et al. 2018; Zhang et al. 2020), and such binding directly improves the effectiveness of the surface modification of cellulose materials. The products will not decompose but remain in the environment after desorption.

The purpose of this study is to demonstrate the substitution effect between chemical development and process technology upgrading. This study realized and evaluated an environmentally friendly modification approach for the preparation of flame-retardant and hydrophobic cotton fabrics using graphene. Research has shown that functional integrated graphene can be used for one-step modification of cotton fabrics, thus decreasing the process flow, reducing chemical consumption, improving the atom economy, and decreasing the difficulty of green process development in the dyeing and printing industry.

Experimental

Materials

Cotton fabric ($80^S/2 \times 80^S/2$, 160×72 after desizing, scouring and bleaching) was used without any further purification. HCCP was purchased from Shandong Lanyin Chemical Company, Ltd., and was recrystallized from n-heptane before use. Graphite powder (burned residue $\leq 0.15\%$, granularity (≤ 30

$\mu\text{m}) \geq 95\%$), and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All of the abovementioned materials and DI water were used directly without further purification.

Preparation of functional integrated graphene

HCCP and long-chain hexafluorocarbon were linked to a GO surface through four steps. A schematic diagram of the preparation of functional integrated graphene, named the GO-HCCP-F synthesis reaction, is shown in Fig. 1.

GO was prepared by stirring 2 g of graphite powder and 1.6 g of sodium nitrate into 60 mL of concentrated sulfuric acid. The ingredients were mixed in a 2 L beaker that had been cooled to 0–5°C in an ice bath. While maintaining vigorous agitation, 10 g of previously porphyrized potassium permanganate was added to the suspension over 2 h. The ice bath was removed, and then the temperature of the suspension was brought to 45°C and maintained for 1 h. After that, 120 mL of water was added dropwise, and the solution was stirred for another 30 min. The suspension was then further diluted with 280 mL of water and treated with 20 mL of hydrogen peroxide. The solution was centrifuged to remove the liquor, and the yellowish-brown deposit was washed with 2 L of 1 M hydrochloric acid. Half of the above GO deposit and 1.3 g of ethanolamine were dispersed in 300 mL of water at pH 1–2 adjusted by aqueous HCl (1 M) and ethanolamine. The mixture was stirred for 48 h at room temperature. Subsequently, the suspension was washed three times with a mixture of water and ethanol. The undried deposit was washed with THF to remove the water and collected to obtain GO-OH. Approximately 900 mg of GO-OH and 240 mL of THF were added to a 500 mL of three-necked flask flushed with nitrogen. The mixture was sonicated for 1 h with a probe tip apparatus (5 s on, 5 s off) at room temperature. HCCP (10 g) was dissolved in 35 mL of THF and then poured into the flask. After dropwise addition of 25 g of TEA dissolved in 25 mL of THF, the reaction was continued with stirring at 30°C for 72 h. The product GO-HCCP was washed extensively with CHCl_3 and THF. Approximately 300 mg of GO-HCCP and 240 mL of THF were added to a 500 mL three-necked flask flushed with nitrogen. The mixture was sonicated for 1 h with a probe tip apparatus (5 s on, 5 s off) at room temperature. Then, 0.9 g of Rf-OH was dissolved in 15 mL of THF and poured into the flask, followed by the dropwise addition of 0.85 g of TEA dissolved in 10 mL of THF. The reaction was carried out with stirring at 45°C for 26 h. The obtained mixture was centrifuged and washed sequentially with CHCl_3 and THF to remove residual TEA, Rf-OH and other impurities, and the final multifunctional GO was obtained and denoted as GO-HCCP-F. Small portions of GO, GO-OH, GO-HCCP and GO-HCCP-F were dried at 50°C for 96 h for characterization.

Preparation of a functional integrated graphene/cotton composite

One hundred milligrams of GO were sonicated in 10 mL of water with a probe tip apparatus to form a homogeneous suspension. The cotton fabric (5×10 cm) was dipped in the suspension and dried at 60°C. The dip-dry process was repeated until GO was completely adsorbed on the cotton fiber and a GO/cotton composite was produced. The rGO/cotton composite was produced by a reducing procedure in which the GO/cotton was immersed in 200 mL of aqueous sodium hydrosulfite solution (0.5%) for 45 min under

oscillation, followed by drying for 30 min at 60°C. The GO-HCCP/cotton composite was produced by dipping cotton fabric (5×10 cm) into a suspension of 150 mg of GO-HCCP and 10 mL of SDS solution (0.02%), followed by the same process used for GO/cotton. The GO-HCCP-F/cotton composite was produced by dipping cotton fabric (5×10 cm) into a suspension of 350 mg of GO-HCCP and 15 mL of 1,1,1,3,3,3-hexafluoro-2-propanol, followed by the same process used for GO/cotton.

Characterization and environmental evaluation

Structural characterization of carbon nanoparticles

The chemical composition and the structure of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos, UK) with a monochromatic Al K α X-ray source (1486.6 eV photons) at 180 W (12 kV and 15 mA) and a pressure of 2×10^{-7} Pa. Survey spectra and detailed C1s spectra were obtained at a photoelectron take-off angle (α , with respect to the sample surface) of 20°. The morphology was examined by field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Ltd., Japan). All samples were fixed directly to the support.

The thermal stability of the particles was examined by a thermogravimetric analyzer (TGA TG209 F1, NETZSCH, Germany) under nitrogen flow. In each typical experiment, approximately 5 mg of sample was placed in a clean platinum pan and heated from room temperature to 800°C at a rate of 10°C/min.

Functional characterization of cotton

The flammability of the GO-HCCP-F/cotton was tested by match lighting. A 1×7 cm strip of fabric was held by one end, and the angle between the fabric surface and the flame was 135°. A WCA measurement was carried out on a DSA30 contact angle system (Kruss, Germany) using a 5 μ L water droplet at ambient temperature.

Environmental performance evaluation

Phosphorus-containing flame-retardant agents and fluorine-containing waterproof agents for cotton were selected, and the specifications were as follows:

- Flame retardant 1 (nondurable): flame-retardant ZR-2; main component, PYROVATEX CP; solid content, 52%; Suzhou Liansheng Chemical Co., Ltd.
- Flame retardant 2 (durable): durable flame-retardant LZR-CH for cotton, mainly composed of PYROVATEX CP; solid content, 76%; Suzhou Liansheng Chemical Co., Ltd.
- Waterproof agent 1 (trade name: T6-5671): Dajin Fluoro Coating Co., Ltd. (Shanghai), with a fluorine content of 6 wt% and a solid content of 6%.
- Waterproof agent 2 (trade name: T6-5574): Dajin Fluoro Coating Co., Ltd. (Shanghai), with a fluorine content of 6 wt% and a solid content of 9%.
- Cross-linking agent (trade name: C-802A): Suzhou Liansheng Chemical Co., Ltd.

Table 1
Agent selection for two-step cotton fabric treatment

Commercial agents	Example of Control I	Example of Control II	Example of Control III	Example of Control III _A	Example of Control III _B	Example of Control IV
Flame retardant 1	+	+				
Flame retardant 2			+	+		+
Waterproofing Agent 1	+		+		+	
Waterproofing Agent 2		+				+
Note: the finishing process is a two-step process that is described in the corresponding commercial manual in detail.						

Results And Discussion

Structural analysis of functional integrated graphene

Structure and chemical properties of functional integrated graphene

The XPS spectra of GO-HCCP and GO-HCCP-F are shown in Fig. 2 (a). The peaks at binding energies of 135.2, 192.2, 201, 284, 400, 534 and 690 eV correspond to P_{2p}, P_{2s}, Cl_{2p}, C1s, N1s, O1s and F1s, respectively, consistent with the results shown in Fig. 1. There were 3 mol of P atoms on GO-HCCP after grafting 1 mol of HCCP onto the surface of GO. There were 13 mol of F atoms and 8 mol of C atoms on GO-HCCP-F after grafting 1 mol of perfluorohexyl ethanol. According to the elemental composition in Fig. 2(a), the number of HCCP rings grafted on every 100 carbon atoms on the GO lamellae was $[(3.14/3)/43.5] * 100 = 2.4$; the number of perfluorohexyl chains grafted was $((27.37/13/[43.5 - (27.37/13) * 8]) * 100 = 7.9$. According to the elemental composition of GO-HCCP, P/Cl is 1.3, indicating that the number of remaining -P-Cl moieties on each phosphonitrile ring grafted on its surface is less than 3. Even if all are involved in the graft reaction with fluorinated hexyl ethanol, the number of fluorine-containing chains should not exceed 7/100 C atoms. Moreover, there were still residual Cl atoms in the GO-HCCP-F particles. The higher fluoride content than expected may be because, in addition to reacting with the phosphonitrile ring, fluorinated hexyl ethanol also reacts with other active sites on GO.

The C 1s spectra of the GO-HCCP and GO-HCCP-F particles are shown in Fig.2(b) and Fig.2(c). In Fig.2(b), the peak at 284.5 eV corresponds to the sp² hybrid skeleton carbon atom. The peak at 285.6 eV corresponds to the C-O-P bond formed by the indirect branching reaction between GO-OH and HCCP. The

characteristic peaks at 286.7 eV and 288.4 eV correspond to C-O-C and -COOH, respectively, which do not react on the GO-OH surface. In Fig.2(c), the characteristic peaks of -CF₂ and -CF₃ appear at 291 eV and 293.3 eV, respectively. By combining these results with the element composition in the full spectrum, it can be proven that HCCP and perfluorinated hexyl chains were successfully grafted onto the GO surface.

The thermogravimetric analysis curves of the GO-HCCP and GO-HCCP-F nanoparticles are shown in Fig.3. The main data obtained from the figure are listed in Table2. Both GO-HCCP and GO-HCCP-F have two obvious thermal weight loss peaks. The first weight loss begins at approximately 167°C and corresponds to the decomposition of the unreacted oxygen-containing functional groups on the surface of modified GO. The second weight loss starts at 260°C and 240°C, respectively, may be due to the shedding or decomposition of the grafted organic components (including HCCP and perfluorohexyl chains). At 600°C, the weight loss of the two carbon nanoparticles is 42.19% and 29.19%, respectively.

Table 2
TGA data for GO-HCCP and GO-HCCP-F

Sample name	Initial decomposition temperature (°C)	Decomposition end temperature (°C)	Maximum decomposition rate (%/min)	Maximum decomposition rate temperature (°C)	Weight loss (%) (100–600°C)
GO-HCCP	167	206	4.3	203	42.2
	260	304	1.7	291	
GO-HCCP-F	169	202	3.1	194	29.2
	240	301	2.5	274	

Selection of nanocarrier and functional group grafting methods

To introduce surface properties onto cellulose materials and to make the modification process as green and efficient as possible, we have conducted the following procedures.

Carbon nanotubes (CNTs) modified with dimethyl phosphate, cyanuric chloride and perfluorohexyl chains, CNTs or modified CNTs can be used as flame-retardant additives and can be added to the polymer matrix by physical mixing and in situ polymerization. The synergistic effect between CNTs and halogen-free organic flame retardants results in environmentally friendly flame retardants. At the same time, low-surface-energy perfluorohexyl chains and nanorough carbon nanotubes were used to construct multifunctional surfaces on cellulose substrates. However, the final effect did not meet expectations(Xu et al. 2020) because of the low grafting rate. We conjectured that this finding was a result of the small number of active groups and the agglomeration of carbon nanotubes due to the large specific surface area and large aspect ratio.

Therefore, we replaced the nanocarrier with GO and selected the above three functional groups for the graft reaction. The experimental results(Xu et al. 2019) showed that with monofunctional modification, taking hydrophobic monofunctional groups as an example, better hydrophobicity was obtained by using GO than by using carbon nanotubes. The functional performance of the bifunctional modified GO on the surface of cellulose has been improved to some extent, but it is still limited by the grafting rate, which makes the functional effect unsatisfactory. The low grafting rate was caused by steric hindrance and the competition reaction between the hydroxyl groups and all three functional components.

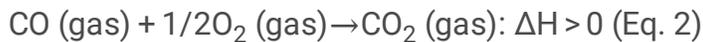
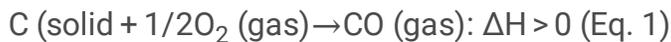
On this basis, we designed the reaction shown in Fig. 1. Increasing the phosphorus content is a way to improve the flame retardancy. Therefore, the following two factors should be considered: First, the reaction efficiency can be improved by replacing dimethyl phosphate with HCCP. The reactivity of P-Cl in HCCP is very high, and it can easily react with hydroxyl compounds by a simple nucleophilic substitution reaction. Second, the phosphorus content of a single small molecule was increased. Three phosphorus atoms could be introduced for each HCCP grafted on the molecule. HCCP is a new kind of organophosphorus flame-retardant framework material with good thermal stability, and its derivatives are widely used as flame retardants. HCCP contains both phosphorus and nitrogen, and its derivatives have synergistic effects between these elements. It is mainly used for flame retardancy of thermosetting materials such as epoxy resin, polyurethane and fiber(Kumar et al. 1986). The thermal stability and flame retardancy of materials can be greatly improved with lower addition. The flame retardancy of phosphazene flame retardants on cellulose materials has been reported(Edwards et al. 2015). These flame retardants act by a coagulation mechanism to increase the amount of carbon formed in the matrix, thus blocking the heat and oxygen exchange between cellulose and the environment and inhibiting combustion. This point has also been verified by the match test and TG experimental results in this paper. Another consideration for selecting HCCP is that as a multi-active-group molecule, HCCP can continue to be grafted as long as there is residual P-Cl after the reaction with GO. If perfluorohexyl ethanol with a hydroxyl group at the end is selected to react with the remaining P-Cl, hydrophobic functional groups can be introduced into GO. HCCP acts both as a flame retardant and as a bridge foundation. Such a design makes it unnecessary to reserve GO surface hydroxyl groups in the first reaction in the encapsulation process for use in the second step, avoids competition reactions, and thus maximizes the grafting amount of the two functional components. GO-HCCP-F was synthesized under optimized conditions, and its chemical formula was $C_{43.5}O_{19.12}N_{5.35}P_{3.14}C_{11.53}F_{27.37}$; the contents of P, N and F were 6.18, 4.76 and 33.0 wt.%, respectively; GO-multi²¹ was synthesized under optimized conditions, its chemical formula was $C_{74.6}O_{15.77}F_{4.06}N_{4.44}P_{1.12}$, and the contents of P, N and F were 2.63, 4.70 and 5.84 wt.%, respectively. The F content of GO-HCCP-F was higher than that of GO-multi, which indicates that when using the same nanocarrier, the modified groups arranged in series are better than those arranged in parallel, and the corresponding multifunctional particles can obtain better functionality on the surface of cotton fabric, which indicates the rationality of the green design.

Performance analysis of the functional integrated graphene/cotton composite

Cotton fabric was treated with GO-HCCP and GO-HCCP-F. The P and N contents of GO-HCCP/cotton were 1.38 and 1.3 wt%, respectively, and the P, N and F contents of GO-HCCP-F/cotton were 2.05, 2.35 and 10.9 wt.%, respectively.

Combustion performance

Match tests were conducted on untreated cotton, GO-HCCP/cotton and GO-HCCP-F/cotton. Digital photographs obtained before and after the test are shown in Fig. 4. The combustion process showed that all three samples could be ignited by standard matches and continued burning for a certain time. The untreated cotton sample was burned to ash after igniting without any residue. The GO-HCCP/cotton and GO-HCCP-F/cotton samples resulted in a large amount of residue after combustion and could maintain the original fabric skeleton structure. Notably, the GO-HCCP/cotton and GO-HCCP-F/cotton samples did not smolder after combustion, which was previously explained by the flame retardant mechanism of phosphorus flame retardants (Laoutid et al. 2003). Cotton smoldering was carried out at 600°C, including the following two steps:



In the first step, the carbon layer continued to be oxidized to produce CO and release heat, and the generated CO continued to be oxidized in the second step under the action of heat and O₂. After the cotton fabric was covered by modified GO, the phosphoric acid generated by the decomposition of phosphorous-containing components grafted on the surface of carbon material changed the decomposition process of the cotton and will cover the surface of the formed carbon layer, preventing the first step of the reaction. At the same time, the ordered structure of modified GO contained defects, and its thermal conductivity worsened, making it more difficult to transfer heat from external combustion. Therefore, the temperature of the carbon layer could not reach the temperature needed for smoldering, and smoldering could not continue.

To further verify the effect of the interaction between the carrier graphene and phosphorus components on the combustion performance of cellulose fiber, the morphology of the fiber before and after combustion was characterized. The SEM images of GO-HCCP/cotton and GO-HCCP-F/cotton before and after burning are shown in Fig.5. The dispersibility of GO-HCCP grafted with HCCP in water is different from that of GO in water. When applied to the fabric, a continuous film was formed. At the same time, some aggregated lamellar structures can be seen in Fig.5 (b). The images after combustion show that the membrane structure was destroyed, but there were still many GO-HCCP lamellar structures formed after thermal decomposition, which were coated and fused on the surface of the carbon fiber residue. This finding is consistent with previous research results, suggesting that two-dimensional graphene materials can play a role in the flame retardancy of polymers through the covering effect (Huang et al. 2011; Huang et al. 2012). The dispersion of GO-HCCP-F in hexafluoroisopropanol is different from that of the above

two kinds of carbon nanomaterials in water; the surface of cotton fiber was layered and fused on the surface of fiber carbon residue, but radial shrinkage of carbon with a lamellar structure was observed. Similarly, after combustion, GO-HCCP-F decomposition products and a residue were observed.

Hydrophobic performance

The wettability of a solid surface is determined by two factors: surface roughness and surface free energy (Barthlott and Neinhuis 1997; Daiki et al. 2014). For a specific substrate, the influencing factors of the wettability of the fabric surface include the macroscopic surface structure, microscopic surface properties and capillary effect (Bahners et al. 2008). Therefore, in the construction of hydrophobic surface of textiles by spinning and weaving of hydrophilic cotton fibers, the following two factors should be concerned: first, the surface free energy should be reduced; second, while reducing the surface free energy, the rough woven surface of the fabric itself should be utilized as much as possible, as confirmed by Yuyang Liu's research during the construction of micro-nano secondary structure on the surface of cotton fabric, which greatly increased the hydrophobicity of CNT-treated cotton fabric (Liu et al. 2008). In this paper, F atoms with low surface energy were loaded on graphene to construct a controllable hydrophobic surface on cotton fiber, and GO-HCCP-F was applied to cotton at different additive amounts to investigate the relationship between the additive amount of GO-HCCP-F on the fabric and the static contact angle of the fabric, as shown in Fig.6. The appearance of GO-HCCP-F/cotton with 49.5 wt % added and the shape of water droplets on its surface are shown in the inline diagram in Fig.6. The static contact angle of GO-HCCP-F/cotton was determined to be 131.3°. The hydrophobicity was increased for the following reasons: first, there were a large number of low-surface-energy F atoms. During the synthesis of GO-HCCP-F, HCCP reacted with the hydroxyl group on the GO surface and then with the fluorine-containing component. This synthesis route did not involve competition for GO surface active groups, so the amount of grafting of the two functional components was maximized. Second, the roughness of the fiber surface was higher after introduction of the modified GO nanostructure. With the gradual increase in the amount of GO on the fiber, the increase rate of contact angle gradually decreased, and the damage degree of micro-nano secondary structure caused by the increase in GO accumulation and coverage was intensified. Therefore, further studies on the relationship between the fiber surface properties and the nanocarrier loading capacity as well as the structure-activity relationship can be conducted from this perspective.

Comprehensive evaluation of functional integration effectiveness

To evaluate the compatibility between the different functionalities of the products, two kinds of typical phosphorus-containing flame retardants and two kinds of fluorine-containing water repellents widely used on the market were selected. A certain flame retardant and a certain waterproof agent were randomly combined and then finished on the fabric by multiprocess treatment. The contents of the

effective flame-retardant element (P) and the low-surface-energy element (F) on the fabric were the same as those on the cotton fabric treated with GO-HCCP-F.

The flame-retardant mechanism of the phosphorus-containing flame retardant was realized by a condensed phase flame retardant, that is, by promoting the carbon formation of the fiber. Therefore, the weight loss rate of the 100–600°C sample was used to quantitatively describe the flame-retardant performance (Zheng et al. 2018), and the static contact angle between the sample surface and water was used to quantitatively describe the hydrophobic performance.

The flame retardancy and hydrophobicity of the GO-HCCP-F/cotton and the four samples prepared by two-step treatment are compared in Fig. 7. The corresponding process of each sample in the figure is shown in Table 1. A weight loss rate of 45.6% was obtained when flame retardant II is applied to cotton fabric alone (as shown in control III_A), indicating an excellent char-forming effect. When water repellent agent I was applied to cotton fabric alone, a flexible rough surface with a static contact angle of 138.4° was obtained (as shown in control III_B), indicating excellent water repellency. Two functional finishing agents were applied to the cotton fabric in two steps, and the weight loss rate of the fabric was 80.4%. The hydrophobicity and flame retardancy were both weakened using two-step treatment rather than the expected synergism. In addition, it can be seen from Fig. 7 that with the same effective element content, the functional effects of the four-control sample are in the second quadrant; that is, the hydrophobic effect is better, but the promotion effect on the carbon formation of cellulose fiber is poor. This shows that the multistep treatment process easily guarantees surface function (such as water repellency), while body function (such as flame retardancy) is more dependent on the superposition of processes, which reflects the green and sustainable development of functional integrated production in the printing and dyeing industry. Compared with the surface treated by the two-step treatment method, the fabric surface treated by functional integrated graphene in this paper can obtain excellent flame-retardant and hydrophobic properties synergistically.

Assessing the substitution effect between using functional integrated graphene and adopting a cleaner process

The application of cleaner production can effectively reduce the negative impact of industrial manufacturing on the environment to realize the real sustainable development of society. At the level of individual enterprise strategies, the two strategies of promoting the innovation of ecological product design and improving process control are combined. The latest development of green chemistry, green engineering and sustainable materials provides opportunities for the above processes.

Researchers can achieve cleaner production by promoting the innovation of ecological products, such as using sodium dodecyl sulfate instead of sodium dodecyl benzene sulfonate as a dispersant, and they can also achieve cleaner production by improving process control, such as by using the pad-batch-steam dyeing process instead of the pad-steam dyeing process to enhance the dye fixation rate and reduce the dyeing effluent (Shu et al. 2018).

In continuous research, people find that there is a substitution effect between ecological product design innovation and improved process control. Ferrero et al.(Ferrero et al. 2015) chose the sustainable material chitosan to treat cotton fabrics to obtain antibacterial fabrics. This process uses the spray method instead of the impregnation method to graft chitosan onto cotton fabric under UV rays at a minimum dose to achieve a sustainable process that can replace other antimicrobial treatments based on synthetic or even dangerous chemicals. In other words, process innovation needs the support of upstream product innovation to achieve cleaner production.

In this paper, graphene was chosen as a nanocarrier to encapsulate flame-retardant and hydrophobic functional components, and product innovation was carried out by this method. The water consumption and total organic discharge of graphene-integrated graphene and the traditional two-step treatment process were compared, in which the same effective flame-retardant element phosphorus (2.05 wt%) and effective hydrophobic element fluorine (10.9 wt%) were equally applied to treat 1000 kg cellulose fiber (shown in Table 3). It can be seen from the data that in addition to the carrier, the consumption of organics by the functional integrated graphene is reduced by 84%-92%, and there is no discharge and no water consumption in the exhaust method. It can be seen that upstream product innovation can greatly reduce the environmental load caused by process superposition, and product innovation can also trigger process innovation to achieve cleaner production. In the field of textile dyeing and printing, product innovation can indirectly save energy and reduce consumption by choosing green material from the source, which makes this process easier and more applicable(Zhu et al. 2021). To achieve cleaner production, the substitution effect plays an important role under the control of limited resources. However, scholars are more inclined to increase investment in product innovation to achieve cleaner production(Chakraborty 2018). The substitutability of product innovation and process innovation proved in this paper supports this view.

Table 3

Comparison of organics and water consumption of 1000 kg cellulose fiber treated by a multichannel process using green packaging technology

Sample name	Total organics consumption (mol)	Total organics discharges (mol)	Water consumption (t)
GO-HCCP-F/cotton	6920	0*	0
Example of Control I	48811	23350	23.21
Example of Control II	43577	23350	23.16
Example of Control III	90412	42315	19.56
Example of Control IV	85178	42315	19.50

**Note that organic solvents used in the treatment process are all recovered.*

Conclusions

The substitution effect in the selection of green technology, namely, that investing more in chemical development leads to suppression of resources used in a cleaner process technology upgrade, was demonstrated in this study in the context of cotton fabric modification. Cotton fabric was treated with functional integrated graphene, which was prepared by introducing hydrophobic perfluorohexyl chains and flame-retardant HCCP onto the surface of graphene sheets. Compared with fabric prepared by the two-step treatment method, the fabric surface treated by functional integrated graphene in this research can obtain excellent flame-retardant and hydrophobic properties synergistically. By assessing the environmental impact of using functional integrated graphene and a commercial two-step treatment process, it can be seen that upstream product innovation can greatly reduce the environmental load caused by process superposition, and product innovation can also trigger process innovation to achieve cleaner production.

In a case study of cotton fabric surface modification, the functional flexibility of integrated graphene has not received enough attention. Better design of functional integrated materials will result in a wider range of applications in the future. Through reasonable design of the product, the process superposition can be stimulated to promote clean production. Finally, considering human and economic costs, there is a substitution effect between product innovation and process innovation. It is suggested that researchers evaluate the environmental impact of product innovation and process innovation before devoting time to innovation activity to allocate resources reasonably.

Declarations

Acknowledgments

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Figures

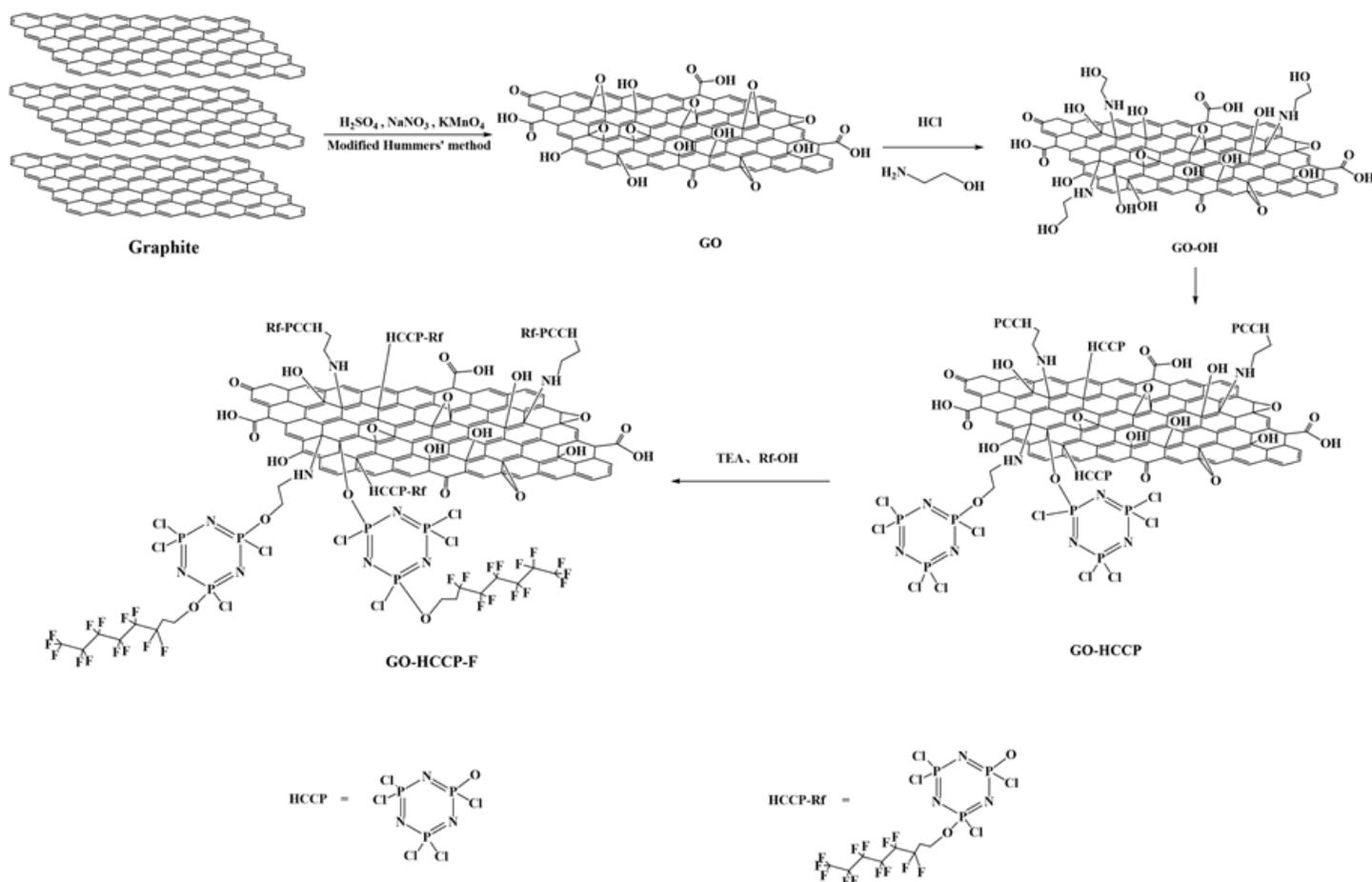


Figure 1

Schematic diagram of the GO-HCCP-F synthesis reaction

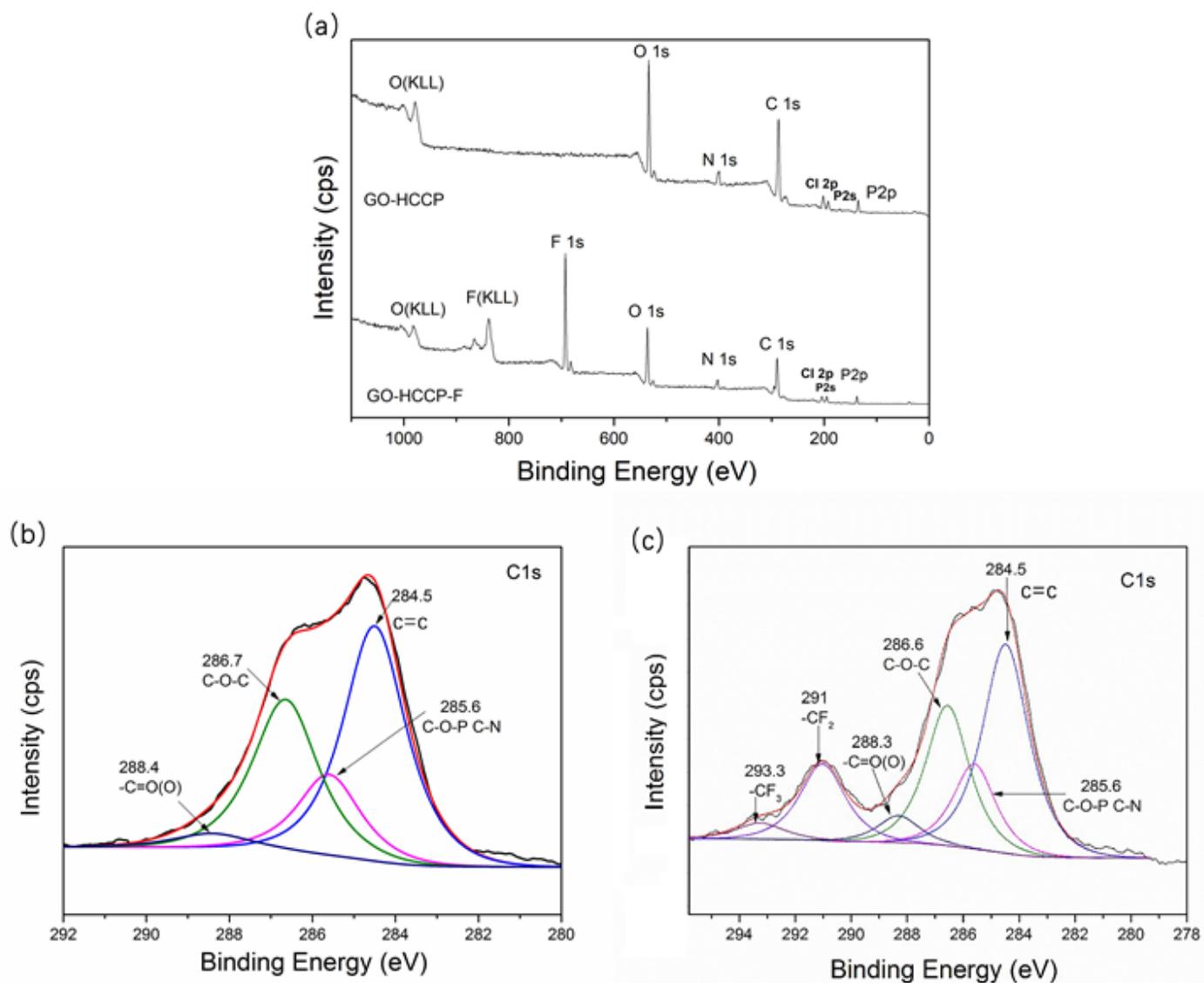


Figure 2

XPS full spectrum of GO, GO-HCCP, and GO-HCCP-F (a), C1s spectrum of GO-HCCP (b) and C1s spectrum of GO-HCCP-F (c).

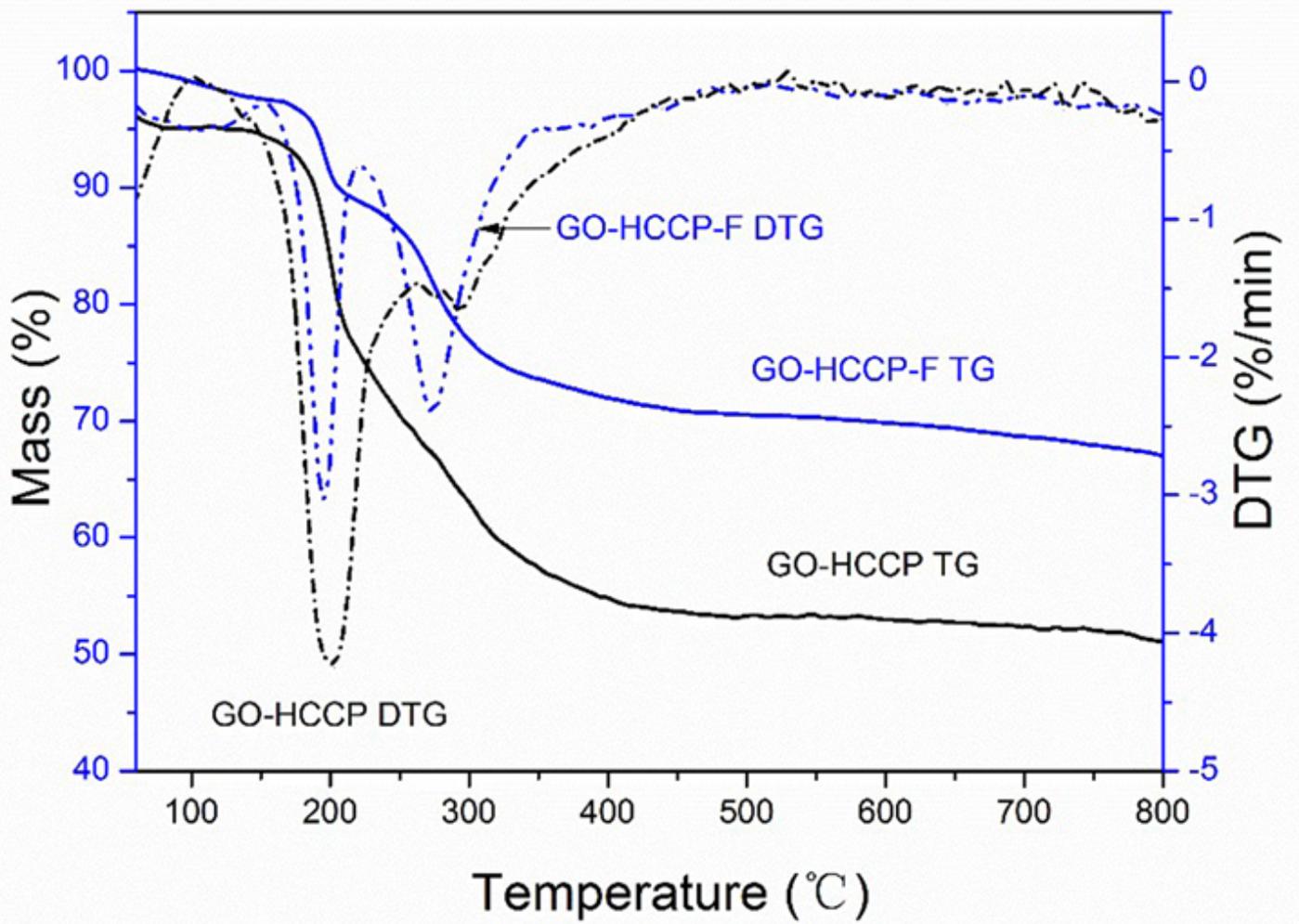


Figure 3

TG and DTG curves of GO-HCCP and GO-HCCP-F

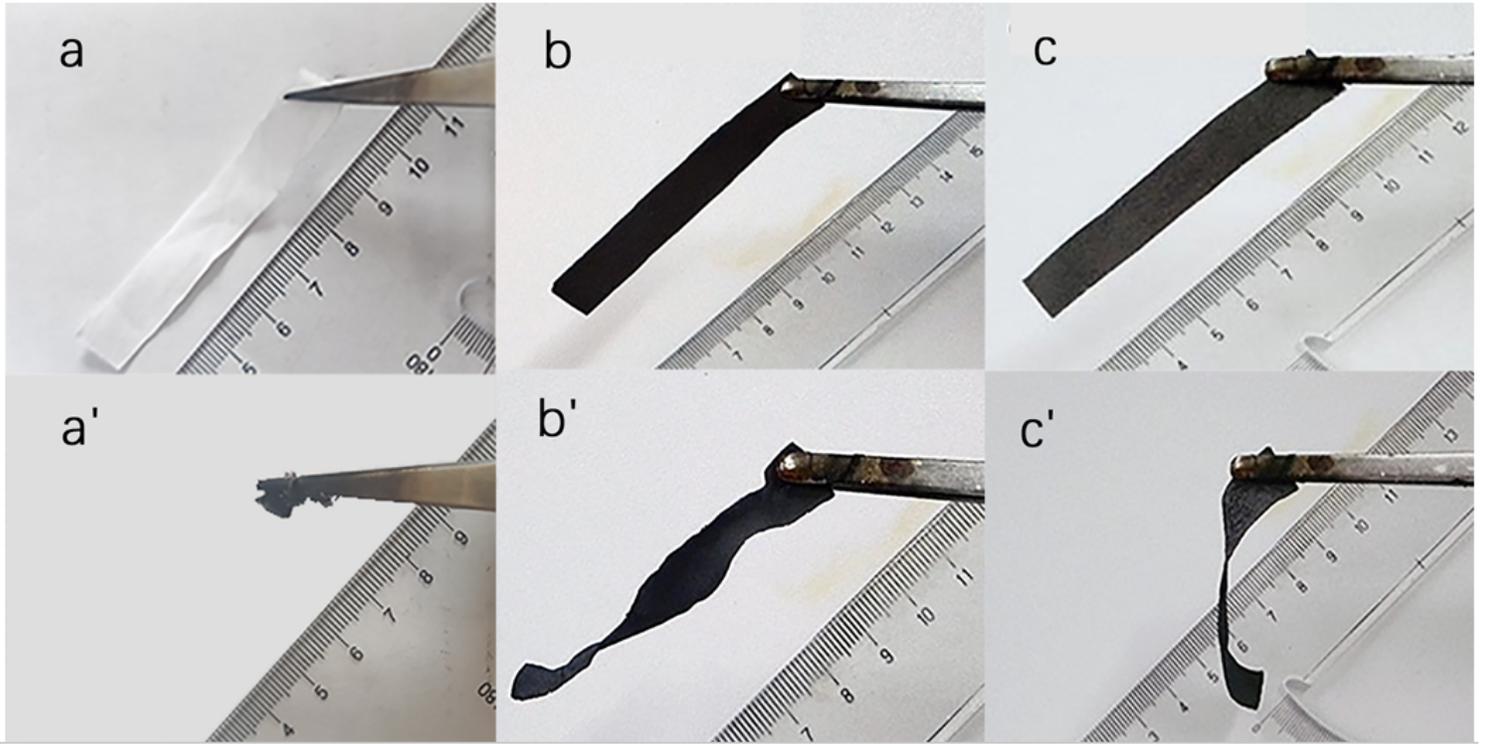


Figure 4

Match test photographs of cotton, GO-HCCP/cotton, and GO-HCCP-F/cotton (a, before cotton combustion; a', after cotton combustion; b, GO-HCCP/cotton before combustion; b', GO-HCCP/cotton after combustion; c, GO-HCCP-F/cotton before combustion; c', GO-HCCP-F/cotton after combustion)

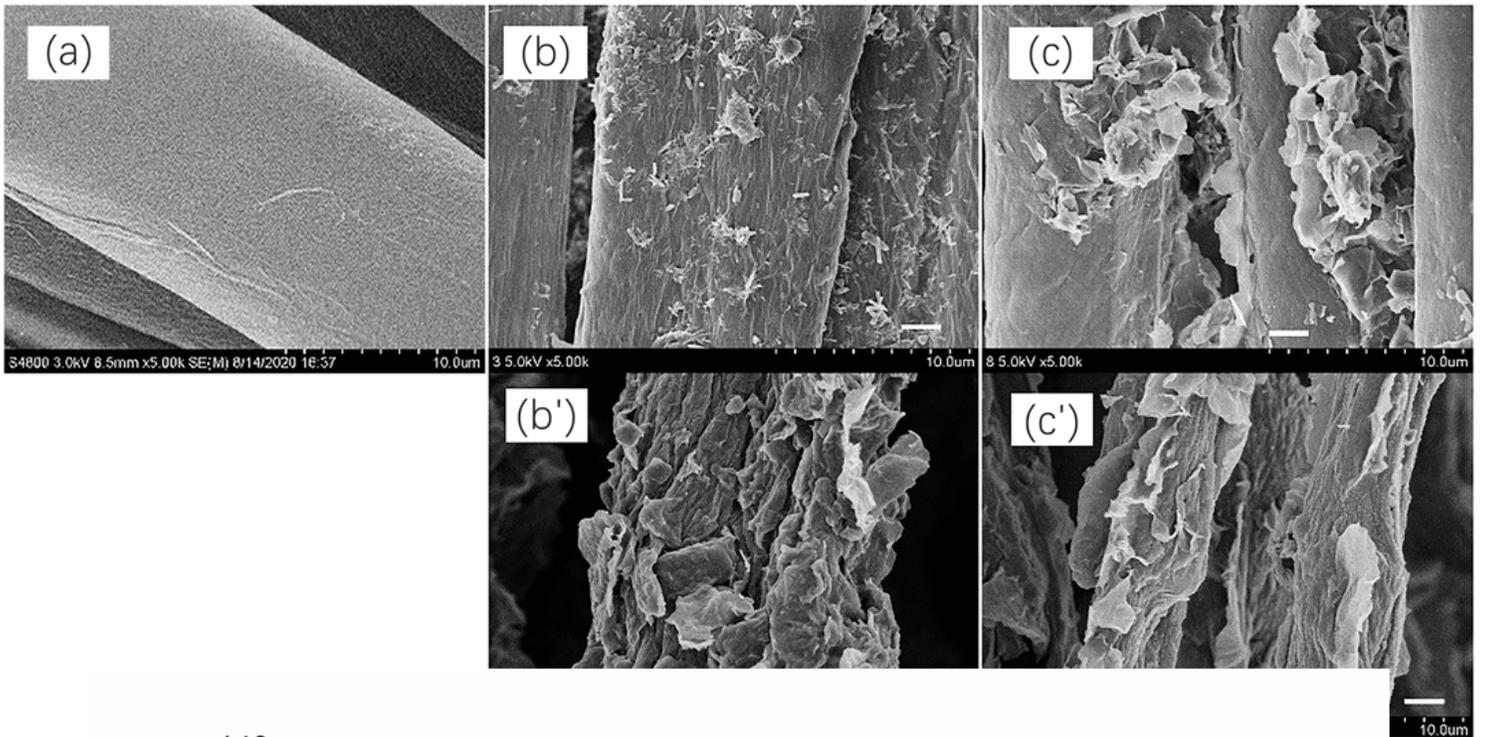


Figure 5

SEM images of the match method test before and after combustion (bar=2 μm): (a) cotton before combustion, (b) GO-HCCP/cotton before combustion, (b') GO-HCCP/cotton after combustion; (c) GO-HCCP-F/cotton before combustion, (c') GO-HCCP-F/cotton after combustion.

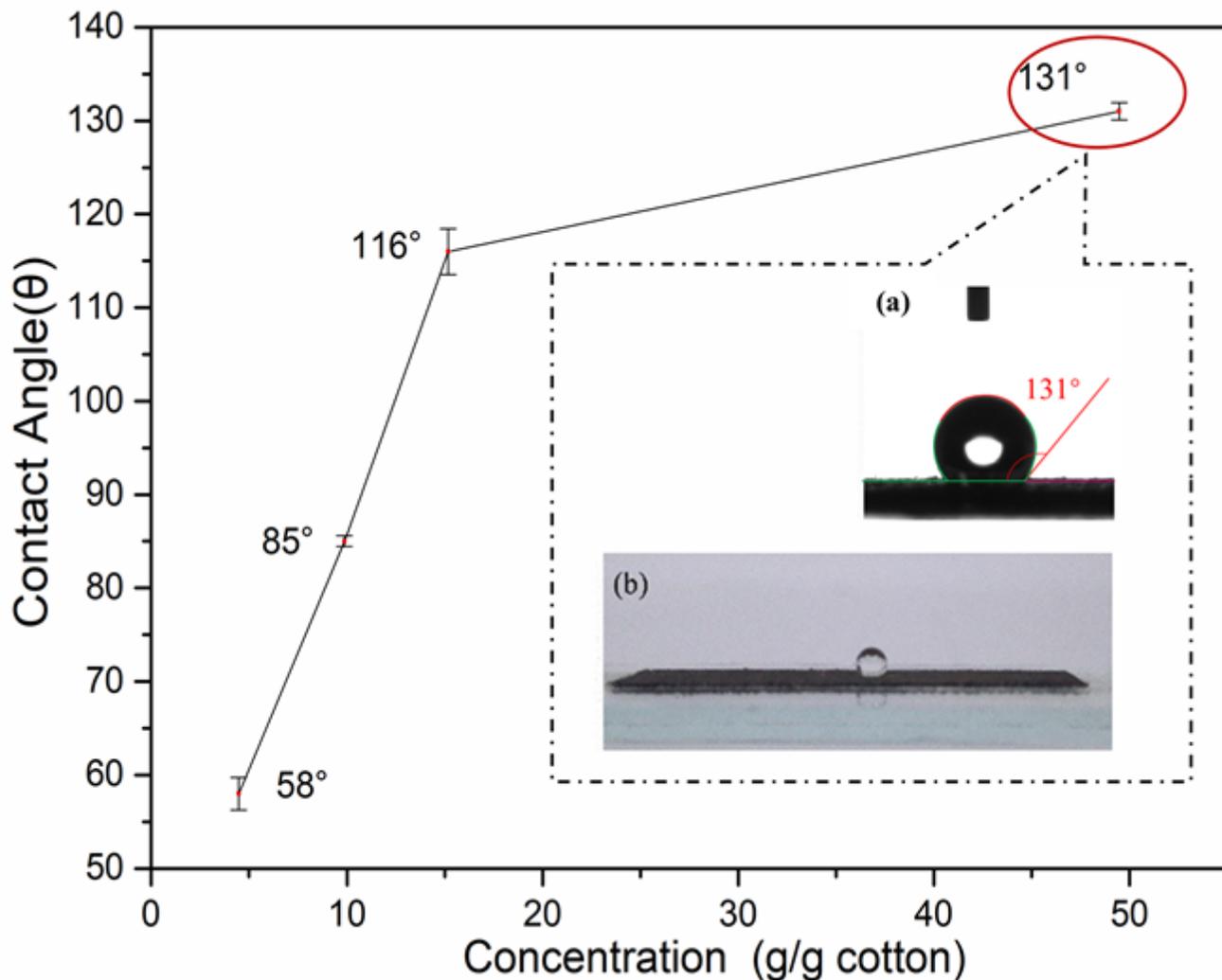


Figure 6

GO - HCCP - F/cotton static water contact angle and the applied quantity relation line chart; (inset a): Photograph of the GO-HCCP-F/cotton samples and the static water contact angle (5 μL); (inset b): Digital photograph of water droplets placed on the GO-HCCP-F/cotton sample

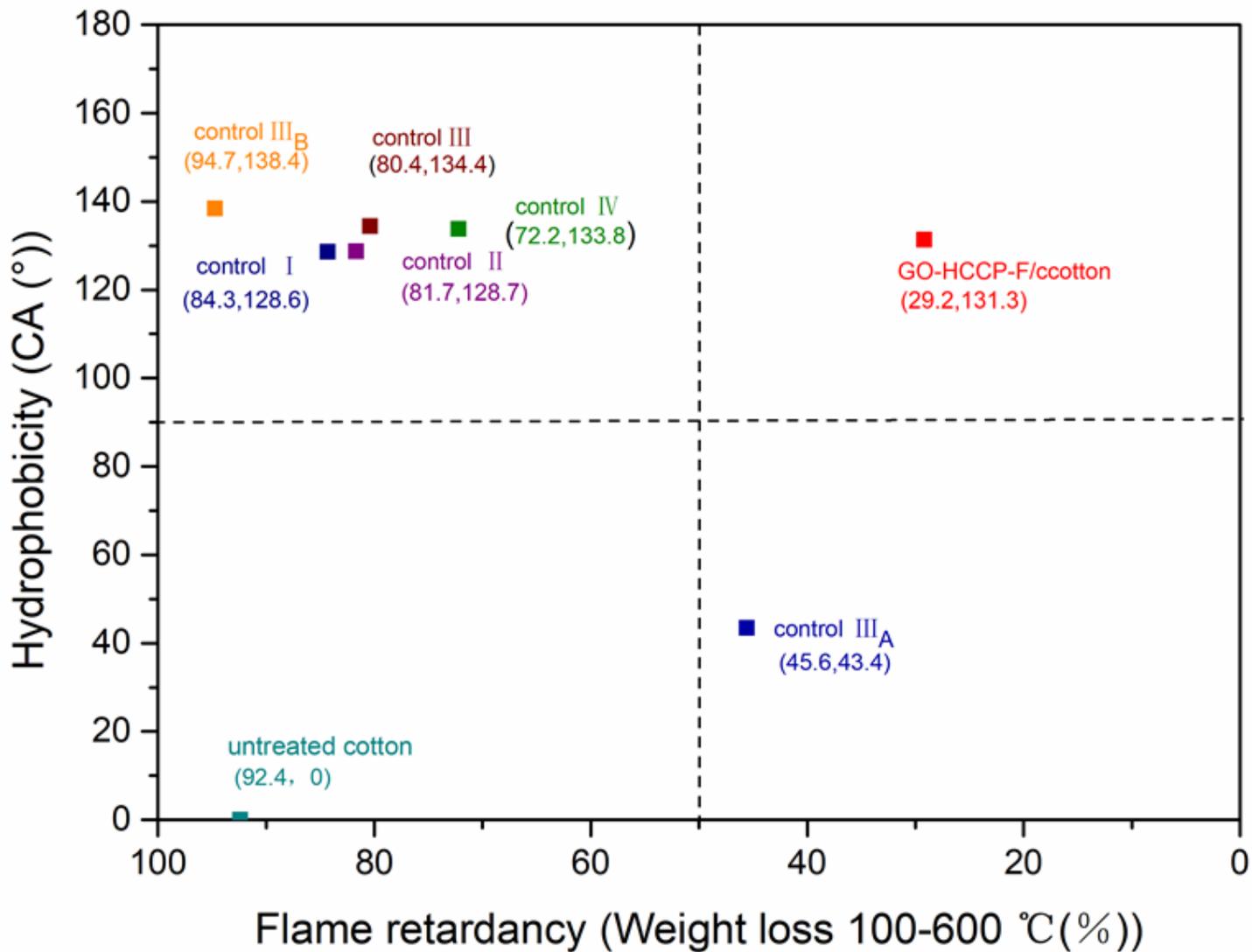


Figure 7

Hydrophobicity-flame retardancy quadrant of untreated cotton, two-step treatment of cotton and GO-HCCP-F/cotton.