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Interlayer-Functionalized Graphene with Phosphorus–Silicon-Containing Elements for Improving Thermal Stability and Flame Retardance of Polyacrylonitrile

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Abstract: Highly-effective non-halogenated flame retardants have received widespread attention because they are environmentally friendly, with low toxicity and low smoke density. In this work, interlayer-functionalized graphene (fRGO) containing silicon and phosphorus elements was synthesized via hydrolytic condensation with 3-(methacryloyloxy)propyltrimethoxysilane and addition reaction with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. Interlayer spacing and oxygencontaining groups of reduced graphene oxide (RGO) were regulated by controlling the hydrazine hydrate dosage. Then, phosphorus–silicon-containing organic molecules were inserted into RGO interlayers; this was verified by FTIR, XPS, TEM, etc. The fRGO was added to a polyacrylonitrile (PAN) matrix using a solution blending method to prepare polyacrylonitrile (PAN) composites. The fRGO addition caused the significant decrease in cyclization heat and the considerable increase in char residues, indicating improved thermal stability. Importantly, PAN composites exhibited outstanding flame-retardant properties, with the peak heat release rate reduced by 45%, which is ascribed to the dense graphitic carbon layers induced by phosphorus–silicon-containing organics and the 2D barrier effect of RGO layers to prevent the heat and mass transfer.

Keywords: interlayer-functionalized graphene; thermal stability; flame retardance; polyacrylonitrile

1. Introduction

Polyacrylonitrile (PAN) has features of strong resistance to weather and chemicals, compression elasticity and good warmth, and thus has widespread applications in the fields of textiles, construction and aerospace [1-3]. However, its flammability and tendency to release toxic compounds pose significant challenges [4,5]. To enhance its flame retardancy, flame retardants are incorporated into PAN through various processing techniques, including copolymerization, solution blending, melt compounding and surface modification [6–8]. Copolymerized flame-retardant PAN has excellent flame retardancy performance and long-lasting effectiveness Typically, copolymerized fragments contain halogens, phosphorus, or nitrogen, as well as chloroethylene, organic phosphate and dopamine-methylacrylamide [7,9,10]. Of these, only halogen-containing copolymerized PAN has been industrially scaled, despite the release of substantial toxic and corrosive gasses during combustion [11,12]. Therefore, numerous studies focus on the fabrication of the environmentally friendly alternatives, often utilizing the blending method due to its simplicity, low cost and ease of industrial scaling [9,13,14]. The key issues with this method lie in the design of highly -effective flame retardants and the compatibility between flame retardant and PAN [2,14].

Interlayer functionalization of two-dimensional (2D) nanosheets provides broad applied potentials owing to their enhanced electrical conductivity, increased mechanical



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). strength and new and improved functions [15,16]. Graphene oxide (GO) nanosheets are one of the 2D materials capable of delaying the heat transfer between polymer matrix interfaces and resisting the escape of pyrolysis products [17–22]. However, GO alone does not achieve the required flame-retardant efficiency. Therefore, modifying GO with flameretardant components via reactions with oxygen-containing functional groups and C=C bonds on GO's surface improves its flame-retardant efficiency [17,23]. As reported, the heat release rate (HRR) and mass loss rate (MLR) for the polymer can be significantly decreased by the addition of modified GO and the morphology of modified GO plays a crucial role in flame-retarding effects [19,23–28]. Layered structured modified GO exhibits an outstanding flame-retardant efficiency, with the structure providing excellent flame retardancy [11,29] and the modified flame-retardant components such as P- [27,30–32], Si- [33,34], B- [31,35], or N-containing molecules [18,27] or other nanoparticles [35–41] contribute to a synergistic flame-retarding effect. Thus, it is feasible to facilitate the flame-retardant properties of GO by interlayer functionalization with flame-retardant components based on preserving the layered structure [42].

Phosphorus—silicon synergistic flame-retardant components can enhance flame retardancy by utilizing the benefits of both organophosphorus and organosilicon compounds [43,44]. Phosphorus serves as a catalyst for carbon formation at high temperatures, while the layered silica produced via oxidation decomposition of siloxanes prevents the oxidation of the carbon layer. Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) is an important organophosphorus flame retardant intermediate due to its unique molecular structure and high flame-retardant efficiency. DOPO can generate derivatives by reacting its P-H bonds with C=C, C=N and other compounds, showing low toxicity and minimal smoke and toxic gas release during combustion, making it promising for use in flame-retardant polymers [45].

In this paper, we describe an interlayer-functionalized graphene (fRGO) that was created by inserting 3-(methylacryloxy) propyl trimethoxysilane (KH570) and DOPO into reduced GO interlayers. The structure and components of fRGO are characterized by FTIR, SEM, XRD, AFM, XPS, TG and Raman. The flame-retardant PAN composite was prepared by introducing fRGO into PAN by a solution-blending method. The flame-retardant properties of GO can be effectively improved by interlayer functionalization with multiple flame-retardant elements (P and Si) based on preserving the layered structure, which has an effective synergistic effect on PAN. The influence of functionalized RGO (fRGO) on the thermal stability and flame retardance of PAN was investigated and potential flame-retardant mechanisms were inferred by analyzing char residues of PAN composites post-combustion.

2. Experimental Section

2.1. Materials and Chemicals

Analytically pure graphite powder, hydrazine hydrate, dimethylbenzene, 1,4-dioxane, *N*,*N*-dimethylformamide (DMF), sodium nitrate and potassium permanganate, Dilute hydrochloric acid with a purity of 10%, concentrated sulfuric acid with a purity of 98% and hydrogen peroxide with a purity of 30% were obtained from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). 3-(methylacryloxy) propyl trimethoxysilane (KH570, 97%) and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO, 97%) were purchased from Shanghai McLean Reagent Co., Ltd. (Shanghai, China). Chemically pure polyacrylonitrile (PAN, average Mw 250,000) was purchased from Meryer (Shanghai) Biochemical Technology Co., Ltd. (Shanghai, China).

2.2. Synthesis of Interlayer-Functionalized Graphene (fRGO)

Figure 1 demonstrates the fabrication of interlayer-functionalized graphene with phosphorus and silicon elements, including the partial reduction of graphene oxide to prepare multilayer graphene nanosheets by regulating the hydrazine hydrate dosage, interlayer functionalization with KH570 molecule by hydrolytic condensation and subsequent addition reaction with DOPO molecule. The hydroxyl groups at one end of the KH570 hydrolysis product molecule undergo dehydration condensation with hydroxyl groups of RGO nanosheet, and then the C=C on the KH570 at the other end react with the P-H of DOPO via an addition reaction, thus achieving the interlayer modification of RGO. Specific operations are as follows:



Figure 1. Schematic diagram of the fabrication of interlayer-functionalized graphene.

Graphene oxide was prepared by the commercial graphite powder via the modified Hummers method. Hydrazine hydrate (10 μ L) was added to 200 mL GO dispersion (2 mg/mL) under sonication for 5 min. The reduction reaction was executed at 100 °C and mechanical stirring took place for 12 h. The resultant reduced graphene oxide (RGO) dispersion was then washed and centrifuged three times to prepare RGO-1. Analogously, RGO-2 was obtained using 200 μ L hydrazine hydrate).

Next, 0.3 g RGO-1 was homo-dispersed in 250 mL xylene by sonication for 60 min. Then, KH570 (6 g) was added dropwise and sonicated for another 60 min. Then, the mixture was held at 110 °C for 12 h under a nitrogen atmosphere. The silicone-modified RGO was obtained by centrifugal separation and washed with xylene three times and then dispersed in 1,4-dioxane (200 mL) by the solvent exchange method. DOPO (0.5 mol) was added into the above dispersion, and the reaction was then carried out at 80 °C for 12 h. Afterward, the resultant mixture was washed using 1,4-dioxane and dried overnight to obtain fRGO-1. Similarly, fRGO-2 was prepared by replacing RGO-1 with RGO-2.

2.3. Preparation of fRGOPAN Composite

PAN (3 g) was dissolved in DMF (30 mL) under stirring in an 80 $^{\circ}$ C water bath. Then, fRGO (0.34 g) was added, and the mixture was sonicated for 3 h at room temperature. Subsequently, the resulting mixture was poured into a plastic mold and dried in the oven in 60 $^{\circ}$ C. For comparison, PAN and RGO/PAN composite were prepared by the same method.

2.4. Characterization

The morphologies and structures of the sample were characterized by transmission electron microscopy (TEM, JEM-2100 (HR), JEOL, Akishima-shi, Showima City, Tokyo, Japan) and a scanning electron microscope (SEM, su1510, Hitachi, Tokyo, Japan). The surface morphology and thickness of the sample were characterized by Atomic Force Microscopy (AFM, Dimension ICON, Bruker, Karlsruhe, Germany). The crystal structure was analyzed by X-ray diffraction (XRD, D2 PHASER, Bruker AXS, Karlsruhe, Germany) measurements with a scanning speed of 5°/min and range of 5° to 65° under a nitrogen

atmosphere. The full width at half maximum (FWHM) of the XRD peaks was analyzed by Gaussian fitting via origin, and the interlayer spacing (d-spacing) of the samples was calculated by Bragg's equation (D = $\frac{\lambda}{2\sin\theta}$), where $\lambda = 1.54$ Å (Cu tube) and θ is the angle between the incident X-ray and the corresponding crystal plane. The chemical structure was tested by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet is10, Thermo Fisher Scientific Co., Ltd., Waltham, MA, USA). Raman Spectroscopy (SPEX-1403, SPEX, Metuchen, NJ, USA) was tested with a scanning range of 500–2000 cm⁻¹ and excitation provided in backscattering geometry by a 514.5 nm argon laser line. The Raman results were analyzed with the Gauss model using the origin and the integral intensity of the peak was calculated. X-ray Photoelectron Spectroscopy (XPS, ESCALB MK-II, VG Scientific, East Grinstead, West Sussex, UK.) was used to analyses the Elements. The thermal stability of samples was obtained by differential scanning calorimetry (DSC, TA-Q200, TA, New Castle, DE, USA.) with a temperature range of 20 °C to 350 °C at a rate of 10 °C/min under a nitrogen atmosphere. The thermal decomposition behavior of the samples was tested by a thermogravimetric analyzer (TG, Q5000, TA, New Castle, DE, USA) with a heating rate of 20 °C/min under an air atmosphere. The samples' flame-retardant properties were tested by a microscale combustion calorimeter (MCC, Govmark, Farmingdale, NY, USA), and the heat release rate (HRR), peak of heat release rate (PHRR), heat release capacity (HRC), total heat release (THR) and temperature at maximum heat release rate (T_{max}) were calculated.

3. Results and Discussion

3.1. Characterization of fRGO

Figure 2 shows the XRD patterns of GO, RGO-1, RGO-2, fRGO-1 and fRGO-2 and the corresponding FWHM and d-spacing are displayed in Table 1. GO exhibits a sharp diffraction peak at $2\theta = 11.4^{\circ}$ with a FWHM of 2.6°, ascribed to the (002) plane of GO. However, the (002) peaks for both RGO-1 and RGO-2 shift to 13.5° and 25.0° , with FWHM values of 4.4° and 7.1° , respectively. This is because partial reduction of GO occurs with a 10 μ L dosage of hydrazine hydrate, and much more reduction occurs with a 200 μ L dosage. The interlayer spacing decreases from 0.78 nm to 0.66 nm and 0.36 nm, demonstrating that the interlayer spacing of multilayer RGO nanosheets can be adjusted by the dosage of hydrazine hydrate. Compared to RGO-1, the new peak at 8.9° of fRGO-1 indicates the significantly increased interlayer spacing of the (002) plane from 0.65 nm to 1.00 nm, which is attributed to the grafted insertion of phosphorus-silicon-containing organic molecules between RGO-1 layers. Moreover, the peak shift from 13.5° to 21.6°, which is attributed to oxygen-containing functional groups in RGO-1, is partially reduced, resulting in a decrease in the interlayer spacing. In contrast to RGO-2, the (002) peak of fRGO-2 mildly shifts from 25.0° to 23.8° due to a little grafted insertion of phosphorus–silicon-containing organics between RGO-2 layers with the smaller interlay spacing. RGO-2 shows less pronounced peak shifts after functionalization compared to RGO-1, which is attributed to a more significant reduction of RGO-2. There are scarce oxygen-containing groups between its layers that can react with the phosphorus-silicon-containing organic molecules and the interlayer spacing is rather narrow, which is not conducive to the interlayer modification.

As shown in Figure 3, RGO-1, RGO-2, fRGO-1 and fRGO-2 all have two strong peaks at 1348 and 1590 cm⁻¹, corresponding to the D and G bands of graphene, respectively. The G band is principally related to the in-plane bond stretching of sp² C atoms, while the D band is ascribed to defects or lattice distortion. The intensity ratio of D and G band (I_D/I_G) reflects the graphitic degree. Compared with the I_D/I_G (1.29) value of RGO-1, the I_D/I_G (1.07) value of RGO-2 is smaller, which proves that RGO-2 is better reduced. And fRGO-1 and fRGO-2 have a slightly lower I_D/I_G values of 1.23 and 1.02 than RGO-1 and RGO-2, respectively. The result is a combination of the partial restoration of graphitic structure at high temperature during interlayer modification [46,47] and the presence of grafted functional groups at the edges or on the surface of RGO, with the former enhancing structure and the latter potentially causing more defects. The restoration of the graphitic

structure is the more significant factor, leading to an increased graphitic degree in fRGO-1 and fRGO-2 after functionalization.



Figure 2. XRD patterns of GO, RGO-1, RGO-2, fRGO-1 and fRGO-2.

Table 1. FWHM and d-spacing of GO, RGO-1, RGO-2, fRGO-1 and fRGO-2.

Sample	2θ (°)	FWHM (°)	d-Spacing (nm)
GO	11.4	2.6	0.78
RGO-1	13.5	4.4	0.66
	42.7	1.8	0.21
RGO-2	25.0	7.1	0.36
	43.1	2.4	0.21
fRGO-1	8.9	3	1.00
	21.6	6	0.41
	43.1	2.3	0.21
fRGO-2	23.8	9.8	0.37
	43.3	1.9	0.21



Figure 3. Raman spectra of RGO-1, RGO-2, fRGO-1 and fRGO-2.

Figure 4 shows the FTIR spectra of RGO-1, RGO-2, fRGO-1 and fRGO-2. RGO-1 exhibits the characteristic absorption peaks of oxygen-containing functional groups at 3380, 1713, 1210 and 1021 cm⁻¹, corresponding to the stretching vibrations of -OH, C=O, C-O-C and C-OH, respectively. Compared with RGO-1, the hydroxyl peak at 3380 cm⁻¹ disappears in the spectrum of fRGO-1, and the broad peak at 1022 cm⁻¹ derived from the stretching vibration of Si-O-C significantly increases, which is attributed to the hydrolytic condensation between RGO-1 and KH570. Moreover, the characteristic infrared peak of DOPO exists at 751 cm⁻¹, indicating the grafting of DOPO onto graphene. There are only faint peaks observed at 1250 cm⁻¹, 1590 cm⁻¹ and 2000–2250 cm⁻¹ in RGO-2 (Figure S1), because RGO-2 is reduced by the excess hydrazine hydrate, leading to the restoration of its graphitic structure with minimal presence of other functional groups and enhanced absorption properties in the infrared range. The FTIR spectra of fRGO-2 display a more pronounced infrared peak compared to RGO-2, suggesting that a number of organic molecules have been chemically attached to RGO-2. However, the infrared peaks are not clearly defined because of the surface functionalization of RGO-2, which does not impact the graphene nanosheets, resulting in the overlapping of strong absorption [48].



Figure 4. FTIR spectra of RGO-1, RGO-2, fRGO-1 and fRGO-2.

XPS was used to study the elementary composition and chemical status of fRGO-1 and fRGO-2 samples. As shown in Figure 5, five characteristic peaks centered at 532.2 eV, 286.0 eV, 153.4 eV, 133.9 eV and 102.0 eV exist in the XPS spectra of fRGO-1 and fRGO-2, corresponding to O, C, Si_{2s}, P_{2p} and Si_{2p}, respectively. Table 2 clearly lists the atomic ratios of C, O, Si and P elements. The C/O atomic ratio of fRGO-2 reaches up to 4.77 and greatly exceeds the C/O ratio of fRGO-1 (2.60) due to a higher graphitic degree of fRGO-2. The silicon content of fRGO-1 (3.77%) is slightly higher than that of fRGO-2 (3.39%), which is ascribed to more oxygen-containing groups of RGO-1 inducing the hydrolytic condensation of siloxane. However, the phosphorus content of fRGO-1 is 1.21%, which is slightly lower than that of fRGO-2 (1.37%). The abnormal result is possibly attributed to a greater insertion reaction of DOPO molecules into RGO-1 interlayers, but more DOPO molecules are grafted onto the RGO-2 surface.

Figure 6 shows the high-resolution spectra of C_{1s} , Si 2p and P 2p for the fRGO-1 and fRGO-2 samples. As shown in Figure 6A-1, the characteristic peaks at 288.8 eV, 286.6 eV and 284.7 eV in the C_{1s} spectra of fRGO-1 and fRGO-2 are ascribed to C-O, C=O and C-C bonds, respectively. Moreover, the relative peak intensities of C-O/C=O and C-C of fRGO-2 are obviously weaker than those of fRGO-1, indicating a higher graphitic degree of RGO-2. The peak at 102.3 eV in Si 2p spectra and the peaks at 133.7 eV and 132.9 eV in the P 2p spectrum correspond to O-Si-C, O-P=O and P-C, respectively.



Figure 5. XPS spectra of fRGO-1 and fRGO-2.

Table 2. Elemental atomic ratios of fRGO-1 and fRGO-2.

Sample	C (at %)	O (at %)	Si (at %)	P (at %)
fRGO-1	68.60	26.42	3.77	1.21
fRGO-2	78.74	16.51	3.39	1.37



Figure 6. High-resolution C_{1s}, Si_{2p} and P_{2p} spectra of (A-1–A-3) fRGO-1 and (B-1–B-3) fRGO-2.

Figure 7 shows the morphologies of RGO-1, RGO-2, fRGO-1 and fRGO-2. RGO-1 has a smooth surface with minimal wrinkles and a four-layer structure, while RGO-2 shows more prominent wrinkles and layers, attributed to the reduction of oxygen-containing groups by excess hydrazine hydrate, leading to smaller interlayer spacing and agglomeration. After the hydrolysis of organosiloxane and subsequent condensation with DOPO, the fRGO-1 surface becomes rougher, opaquer and thicker, and has more obvious wrinkles, because

P-Si-containing organic molecules are grafted into RGO-1 interlayers and onto surfaces, and RGO-1 is further reduced during thermal reaction. Compared to fRGO-1, fRGO-2 becomes rougher and opaquer because smaller interlayer spacing causes more surface grafting rather than interlayer functionalization.



Figure 7. TEM images of (A-1,A-2) RGO-1, (B-1,B-2) RGO-2, (C) fRGO-1 and (D) fRGO-2.

Figure 8A,B depict the SEM images of fRGO-1 and fRGO-2 powders. fRGO-1 shows the regularly stacked nanosheets while fRGO-2 exhibits the disorderly stacked nanosheets. This is possibly because more hydrolytic condensation products between the fRGO-1 interlayers maintain the stacked nanosheets, and more hydrolytic condensation products grafted onto fRGO-2 surface destroy the regular stacked structure. AFM was employed to further characterize the thickness of fRGO-1 nanosheets in Figure 8C-1,C-2. fRGO-1 exhibits a typical sheet structure of a few hundred nanometers in width. In addition, its thickness is approximately 5 nm and exceeds that of RGO-1 (as shown in Figure 7A-1), indicating the insertion of P-Si-containing organic molecules into RGO-1 interlayers.

Figure 9 shows the TG and DTG curves of RGO-1, RGO-2, fRGO-1 and fRGO-2. RGO-1 exhibits strong peaks of mass loss at 64.4, 211.9 and 592.7 °C, corresponding to the volatilization of absorbed water, the evaporation of bound water and the RGO-1 oxidation, respectively. RGO-2 shows the peaks of mass loss at 388.7 and 562.6 °C, indicating the volatilization of a small number of oxygen-containing functional groups on the surface and acting as an indicator of RGO-2 oxidation. The oxidation peak of RGO-2 is significantly lower than that of RGO-1, indicating that RGO-2 underwent a more effective reduction process and possesses a well-defined graphitic structure. fRGO-1 and fRGO-2 exhibit significant weight loss peaks at 397.3 and 412.9 °C, which are attributed to the thermal degradation of P-Si-containing organic molecules grafted onto RGO-1 and RGO-2. In addition, fRGO-1 and fRGO-2 have the temperatures of the maximum mass loss rates at 678.7 and 733.2 °C, respectively, corresponding to the thermal oxidation. Moreover, the maximum mass loss rate of 0.22 wt%/°C of fRGO-1 is clearly lower than that of 0.48 wt%/°C of fRGO-2, respectively, because interlayer functionalization restrains the pyrolytic behavior of P-N-containing organic molecules between fRGO-1 layers to achieve

better thermal stability. Additionally, RGO-1 has almost no char residue, while the char residues of fRGO-1 significantly increase and reach up to 21.16 wt%. The higher char residues of fRGO-1 indicate its better thermal stability, ascribed to the insertion of P-N-containing organic molecules between RGO-1 interlayers.



Figure 8. SEM images of (**A**) fRGO-1 and (**B**) fRGO-2and AFM image (**C-1**) and its height profile (**C-2**) of fRGO-1.



Figure 9. TG (A) and DTG (B) curves of RGO-1, RGO-2, fRGO-1 and fRGO-2 under air atmosphere.

Based on the above analysis, it can be seen that the reduction degree of GO can be controlled by controlling the dosage of hydrazine hydrate, thereby impacting the oxygencontaining functional groups, layer number, layer spacing and graphitization of RGO, which in turn affects the subsequent functionalization. RGO-1 is preferred for modifying the interlayer function, whereas RGO-2 is predominantly modified on the surface. And TG analysis shows the superior thermal stability of the fRGO-1 interlayer functionalized with phosphorus and silicon elements. Therefore, fRGO-1 was subsequently used in the preparation of fRGO/PAN composite.

3.2. Thermal Stability of fRGO-1/PAN Composites

As shown in Figure 10, PAN exhibits a distinct exothermic peak at 296 °C with a high peak value of 7.4 W/g because the cyclization reaction of the PAN cyanogroup occurs and a lot of heat is released as a result. However, the exothermic peaks of RGO-1/PAN and fRGO-1/PAN composites located at 293 °C and 288 °C decrease to 5.5 W/g and 4.3 W/g, respectively, indicating that the addition of RGO-1 and fRGO-1 into PAN matrix contributes to the insulating effect and slows down the heat release. Moreover, RGO-1/PAN composite exhibits an endothermic peak at 200 °C, which is attributed to the thermal reduction of oxygen-containing groups on RGO-1. And the fRGO-1/PAN composite shows an endothermic peak at 240 °C, corresponding to the heat absorption of phosphorus–silicon-containing organic molecules between RGO-1 interlayers for the following breakage of molecular chains.



Figure 10. DSC curves of pure PAN, RGO-1/PAN and fRGO-1/PAN composites.

Figure 11 shows the TG and DTG curves of PAN, RGO-1/PAN and fRGO-1/PAN composites under air atmospheres. PAN, RGO-1/PAN and fRGO-1/PAN composites exhibit a prominent peak around 700 °C, which is attributed to the oxidation of carbon residues above 600 °C. Another strong peak appears between 300 and 600 °C due to the cyclization of cyanogroups of PAN molecules. Table 3 shows that the thermal decomposition temperatures at 5 wt% and 10 wt% weight loss are significantly reduced after the addition of RGO-1 and fRGO-1 into the PAN, and adding fRGO-1/PAN composites results in a more pronounced decrease. Moreover, char residues at 800 °C increase from 27.9 wt% to 29.9 wt% and 34.3 wt% when RGO-1 and fRGO-1 are added into the PAN matrix, respectively. This is because the phosphorus–silicon-containing organic molecules grafted onto RGO-1 degrade prior to the PAN pyrolysis and facilitate the dehydrated carbonization to prevent the escape of pyrolysis products.

Figure 12 shows the HRR curve of pure PAN exhibits two peaks of heat release rate at 345 and 440 °C, and its peak heat release heat (PHRR) reaches up to 129.9 W/g. However, Table 4 shows the PHRR value of fRGO-1/PAN composites decreases significantly to 71.4 $W \cdot g^{-1}$, corresponding to a 45% reduction compared with pure PAN. Unfortunately, the THR values of pure PAN and fRGO-1/PAN composites are very close. Heat release capacity (HRC) is an important index used to evaluate the flammability of a material. In contrast to pure PAN, the smaller HRC value of fRGO-1/PAN composites indicates its lower potential combustion heat, which indicates a higher level of fire safety.



Figure 11. TG (**A**) and DTG (**B**) curves of PAN, RGO-1/PAN and fRGO-1/PAN composites under air atmospheres.

Table 3. TG and DTG data of PAN, RGO-1/PAN and fRGO-1/PAN composites.

Sample	The Temperatures at the Weight Loss of 5 wt% (°C)	The Temperatures at the Weight Loss of 10 wt% (°C)	Char Residues at 800 $^\circ$ C (%)
PAN	263	319	27.9
RGO-1/PAN	221	314	29.9
fRGO-1/PAN	205	267	34.3



Figure 12. (A) HRR and (B) THR curves of pure PAN and fRGO-1/PAN composites.

Table 4. Relevant data of pure PAN and fRGO-1/PAN composites derived from MCC.

Sample	HRC (J⋅g ⁻¹ ⋅K)	PHRR (W \cdot g ⁻¹)	THR (KJ \cdot g ⁻¹)	T _{max} (°C)
PAN	142	129.9	18.4	345
fRGO-1/PAN	101	71.4	18.7	312

3.3. Flame-Retardant Mechanism of fRGO-1/PAN Composites

SEM was used to observe the morphology of the char residues after the combustion of pure PAN and fRGO-1/PAN composites. As shown in Figure 13, the external char residues of pure PAN have many large pores, resulting in poor barrier action against thermal activity and smoke. In contrast, the external char residues of fRGO-1/PAN composites show a relatively denser appearance, effectively preventing the transfer of combustible heat and pyrolysis gasses.



Figure 13. SEM images of char residues after combustion of pure PAN and fRGO-1/PAN composites.

Figure 14 shows that the I_G/I_D values of the char residues of RGO-1/PAN and fRGO-1/PAN composites are 0.273 and 0.285, respectively; these values are obviously larger than that of PAN (0.198). This indicates that the graphitic degrees of char residues of PAN composites are enhanced when RGO-1 and fRGO-1 are added to the PAN matrix. The higher graphitic degree is conducive to blocking heat and mass transfer. Therefore, according to the above results, the possible flame-retardant mechanism of fRGO-1/PAN is that the RGO acts as a barrier to restrain the volatilization of flammable gasses and exchange of heat during combustion. Meanwhile the organic phosphorus and silicone molecules grafted onto RGO interlayers promote catalytic carbonization during combustion, effectively forming a dense char layer to block heat and mass transfer.



Figure 14. Raman spectra of char residues after combustion of PAN and fRGO-1/PAN composites.

4. Conclusions

This study successfully synthesizes functionalized reduced graphene oxide (fRGO) with phosphorus and silicon-containing organic molecules to enhance the flame retardancy of polyacrylonitrile (PAN) through molecular design. The reduction degree of GO can be controlled by the dosage of hydrazine hydrate, thereby impacting the oxygen-containing functional groups, layer number, layer spacing and graphitization of RGO, which in turn affects the subsequent functionalization. RGO-1 is preferred for modifying the interlayer function, whereas RGO-2 is predominantly modified on the surface. And TG analysis shows the superior thermal stability of fRGO-1 interlayer functionalized with phosphorus and silicon elements. The addition of fRGO-1 in PAN notably increases char residue from 27.9 wt% to 34.3 wt% at 800 °C, underscoring its effectiveness in substrate protection during combustion. Further, the integration of fRGO-1 in PAN leads to a marked reduction in the peak heat release rate and heat release capacity by 45% and 28.9%, respectively, demonstrating the composite's strong flame-retardant properties. Analysis reveals that

fRGO-1 fosters the formation of a dense graphitic carbon layer, which acts as a barrier to flammable gas and heat transfer, enhancing flame retardancy. Overall, this innovative flame retardant offers substantial promise for improving flame-retardant efficiency by leveraging a synergistic effect between 2D nanosheets and multiple flame-retardant components.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/pr12112511/s1, Figure S1. FTIR spectra of RGO-2 and fRGO-2; Figure S2: TEM image of GO; Table S1: The intensities of D and G peaks of the obtained samples measured from Raman results.

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References

- 1. Reich, S.; Burgard, M.; Langner, M.; Jiang, S.; Wang, X.; Agarwal, S.; Ding, B.; Yu, J.; Greiner, A. Polymer nanofibre composite nonwovens with metal-like electrical conductivity. *NPJ Flex. Electron.* **2018**, *2*, 5. [CrossRef]
- Peng, H.; Wang, D.; Fu, S. Biomimetic construction of highly durable nacre-like MoS₂ bio-nanocomposite coatings on polyacrylonitrile textile for intumescent flame retardation and sustainable solar-thermal-electricity conversion. *Compos. Part B Eng.* 2021, 215, 108742. [CrossRef]
- 3. Lim, S.J.; Park, Y.-K.; Kim, H.; Kwon, J.; Moon, H.M.; Lee, Y.; Watanabe, A.; Teramae, N.; Ohtani, H.; Kim, Y.-M. Selective solvent extraction and quantification of synthetic microfibers in textile laundry wastewater using pyrolysis-gas chromatography/mass spectrometry. *Chem. Eng. J.* **2022**, *434*, 134653. [CrossRef]
- 4. Chen, Y.; Chu, F.; Zhou, Y.; Jiang, X.; Song, L.; Hu, Y.; Hu, W. Bismaleimide with high thermal stability, toughness and flame retardancy modified by synergistic hyperbranched flame retardant. *Chem. Eng. J.* **2024**, *483*, 149396. [CrossRef]
- 5. Bevington, C.; Williams, A.J.; Guider, C.; Baker, N.C.; Meyer, B.; Babich, M.A.; Robinson, S.; Jones, A.; Phillips, K.A. Development of a Flame Retardant and an Organohalogen Flame Retardant Chemical Inventory. *Sci. Data* **2022**, *9*, 295. [CrossRef]
- Gong, H.; Patino, D.U.; Ilavsky, J.; Kuzmenko, I.; Peña-Alcántara, A.E.; Zhu, C.; Coffey, A.H.; Michalek, L.; Elabd, A.; Gao, X.; et al. Tunable 1D and 2D Polyacrylonitrile Nanosheet Superstructures. ACS Nano 2023, 17, 18392–18401. [CrossRef]
- 7. Mujtaba, M.; Fernández-Marín, R.; Robles, E.; Labidi, J.; Yilmaz, B.A.; Nefzi, H. Understanding the effects of copolymerized cellulose nanofibers and diatomite nanocomposite on blend chitosan films. *Carbohydr. Polym.* **2021**, 271, 118424. [CrossRef]
- 8. Guo, Y.; Zuo, C.; Liu, Y.; Chen, X.; Ren, Y.; Liu, X. Construction of a fully bio-based intumescent flame retardant for improving the flame retardancy of polyacrylonitrile. *Polym. Degrad. Stab.* **2023**, *214*, 110385. [CrossRef]
- 9. Wang, L.; Gao, L.; Zuo, C.; Tan, W.; Ren, Y.; Liu, X. A novel phosphorus/nitrogen-containing polyacrylonitrile fiber with excellent flame retardancy and mechanical properties. *Polym. Degrad. Stab.* **2024**, *223*, 110716. [CrossRef]
- Liu, Y.; Yu, X.; Guo, Y.; Ren, Y.; Liu, X. Preparation of flame retardant, smoke suppression and reinforced polyacrylonitrile composite fiber by using fully biomass intumescent flame retardant system and its sustainable recycle application. *Compos. Part A Appl. Sci. Manuf.* 2023, 173, 107705. [CrossRef]
- 11. Ioni, Y.; Sapkov, I.; Kirsanova, M.; Dimiev, A.M. Flame modified graphene oxide: Structure and sorption properties. *Carbon* **2023**, 212, 118122. [CrossRef]
- 12. Tretsiakova-McNally, S.; Joseph, P. Thermal and Calorimetric Evaluations of Polyacrylonitrile Containing Covalently-Bound Phosphonate Groups. *Polymers* **2018**, *10*, 131. [CrossRef] [PubMed]
- Rahimi-Aghdam, T.; Shariatinia, Z.; Hakkarainen, M.; Haddadi-Asl, V. Nitrogen and phosphorous doped graphene quantum dots: Excellent flame retardants and smoke suppressants for polyacrylonitrile nanocomposites. *J. Hazard. Mater.* 2020, 381, 121013. [CrossRef] [PubMed]
- 14. Li, M.; Mu, B. Effect of different dimensional carbon materials on the properties and application of phase change materials: A review. *Appl. Energy* **2019**, 242, 695–715. [CrossRef]

- 15. Guo, W.; Yu, B.; Yuan, Y.; Song, L.; Hu, Y. In situ preparation of reduced graphene oxide/DOPO-based phosphonamidate hybrids towards high-performance epoxy nanocomposites. *Compos. Part B Eng.* **2017**, *123*, 154–164. [CrossRef]
- 16. Anderson, L.; Yu, E.; Chen, W.-T. Chemical Recycling of Mixed Plastics in Electronic Waste Using Solvent-Based Processing. *Processes* **2021**, *10*, 66. [CrossRef]
- Zhu, M.; Li, S.; Sun, Q.; Shi, B. Enhanced mechanical property, chemical resistance and abrasion durability of waterborne polyurethane based coating by incorporating highly dispersed polyacrylic acid modified graphene oxide. *Prog. Org. Coat.* 2022, 170, 106949. [CrossRef]
- 18. Gao, M.; Wang, T.; Chen, X.; Zhang, X.; Yi, D.; Qian, L.; You, R. Preparation of ionic liquid multifunctional graphene oxide and its effect on decrease fire hazards of flexible polyurethane foam. *J. Therm. Anal. Calorim.* **2021**, 147, 7289–7297. [CrossRef]
- 19. Yuan, B.; Sun, Y.; Chen, X.; Shi, Y.; Dai, H.; He, S. Poorly-/well-dispersed graphene: Abnormal influence on flammability and fire behavior of intumescent flame retardant. *Compos. Part A Appl. Sci. Manuf.* **2018**, *109*, 345–354. [CrossRef]
- Wang, Y.; Zhao, J. Effect of graphite on the flame resistance of silica fume-based geopolymeric coatings. *Mater. Chem. Phys.* 2020, 239, 122088. [CrossRef]
- Nabipour, H.; Wang, X.; Song, L.; Hu, Y. Graphene oxide/zeolitic imidazolate frameworks-8 coating for cotton fabrics with highly flame retardant, self-cleaning and efficient oil/water separation performances. *Mater. Chem. Phys.* 2020, 256, 123656. [CrossRef]
- Liao, S.-H.; Liu, P.-L.; Hsiao, M.-C.; Teng, C.-C.; Wang, C.-A.; Ger, M.-D.; Chiang, C.-L. One-Step Reduction and Functionalization of Graphene Oxide with Phosphorus-Based Compound to Produce Flame-Retardant Epoxy Nanocomposite. *Ind. Eng. Chem. Res.* 2012, 51, 4573–4581. [CrossRef]
- 23. Wang, N.; Liu, H.; Zhang, J.; Zhang, M.; Fang, Q.; Wang, D. Synergistic effect of graphene oxide and boron-nitrogen structure on flame retardancy of natural rubber/IFR composites. *Arab. J. Chem.* **2020**, *13*, 6274–6284. [CrossRef]
- 24. Qu, L.; Sui, Y.; Zhang, C.; Li, P.; Dai, X.; Xu, B. Compatible cyclophosphazene-functionalized graphene hybrids to improve flame retardancy for epoxy nanocomposites. *React. Funct. Polym.* **2020**, *155*, 104697. [CrossRef]
- 25. Tang, X.-Z.; Li, W.; Yu, Z.-Z.; Rafiee, M.A.; Rafiee, J.; Yavari, F.; Koratkar, N. Enhanced thermal stability in graphene oxide covalently functionalized with 2-amino-4,6-didodecylamino-1,3,5-triazine. *Carbon* **2011**, *49*, 1258–1265. [CrossRef]
- Li, J.; Gao, M.; Zheng, Y.; Guan, Y.; Yi, D. Effects of Low-Load Boron/Silicon-Based Graphene Oxide on Combustion and Thermal Degradation of Flame-Retardant Unsaturated Polyester Resin. *Macromol. Mater. Eng.* 2020, 305, 2000454. [CrossRef]
- 27. Zhu, M.; Liu, L.; Wang, Z. Iron-phosphorus-nitrogen functionalized reduced graphene oxide for epoxy resin with reduced fire hazards and improved impact toughness. *Compos. Part B Eng.* **2020**, *199*, 108283. [CrossRef]
- Chen, Y.; Xia, S.; Ren, W.; Zheng, Z.; Chen, J.; Ma, K.; Yu, C.; Zhou, X.; Zhang, W. A Favorable Improvement in Reactivity between n-Al and Sheet-like Porous CuO as a Nanoenergetic Composite by Graphene Oxide Additives. *Ind. Eng. Chem. Res.* 2020, 59, 12934–12942. [CrossRef]
- Li, K.-Y.; Kuan, C.-F.; Kuan, H.-C.; Chen, C.-H.; Shen, M.-Y.; Yang, J.-M.; Chiang, C.-L. Preparation and properties of novel epoxy/graphene oxide nanosheets (GON) composites functionalized with flame retardant containing phosphorus and silicon. *Mater. Chem. Phys.* 2014, 146, 354–362. [CrossRef]
- 30. Luo, F.; Wu, K.; Shi, J.; Du, X.; Li, X.; Yang, L.; Lu, M. Green reduction of graphene oxide by polydopamine to a construct flexible film: Superior flame retardancy and high thermal conductivity. *J. Mater. Chem. A* 2017, *5*, 18542–18550. [CrossRef]
- 31. Zheng, H.; Liu, H.; Duan, H. Enhancing flame retardant property of graphene oxide via phosphorus and nitrogen co-doping. *Mater. Lett.* **2023**, *330*, 133351. [CrossRef]
- 32. Zhu, Y.; Kong, G.; Che, C. Ultra-sensitive fan-folded thermally expandable surface reduced graphene oxide strips for fire early warning response. *Colloids Surf. A Physicochem. Eng. Asp.* **2023**, *669*, 131478. [CrossRef]
- Guan, F.-L.; Gui, C.-X.; Zhang, H.-B.; Jiang, Z.-G.; Jiang, Y.; Yu, Z.-Z. Enhanced thermal conductivity and satisfactory flame retardancy of epoxy/alumina composites by combination with graphene nanoplatelets and magnesium hydroxide. *Compos. Part B Eng.* 2016, *98*, 134–140. [CrossRef]
- Lin, G.; Fu, T.; Qiu, Y.; Li, F.; Sun, W. Flame retardancy and anti-impact performance of polyurea composite coating reinforced by modified ammonium polyphosphate and two-dimensional nano-fillers. *Prog. Org. Coat.* 2023, 180, 107554. [CrossRef]
- 35. An, W.; Ma, J.; Xu, Q.; Zhang, H.; Wei, L.; Yuan, L. Construction of hetero-structured fillers to significantly enhance the fire safety of bio-based nanocomposite coating. *Appl. Surf. Sci.* 2022, 575, 151767. [CrossRef]
- Xu, W.; Zhang, B.; Wang, X.; Wang, G.; Ding, D. The flame retardancy and smoke suppression effect of a hybrid containing CuMoO₄ modified reduced graphene oxide/layered double hydroxide on epoxy resin. *J. Hazard. Mater.* 2018, 343, 364–375. [CrossRef]
- 37. Damian, C.M.; Necolau, M.I.; Neblea, I.; Vasile, E.; Iovu, H. Synergistic effect of graphene oxide functionalized with SiO₂ nanostructures in the epoxy nanocomposites. *Appl. Surf. Sci.* **2020**, *507*, 145046. [CrossRef]
- Zhou, Y.; Chu, F.; Qiu, S.; Guo, W.; Zhang, S.; Xu, Z.; Hu, W.; Hu, Y. Construction of graphite oxide modified black phosphorus through covalent linkage: An efficient strategy for smoke toxicity and fire hazard suppression of epoxy resin. *J. Hazard. Mater.* 2020, 399, 123015. [CrossRef]
- 39. Liu, Y.; Lu, M.; Hu, Z.; Liang, L.; Shi, J.; Huang, X.; Lu, M.; Wu, K. Casein phosphopeptide-biofunctionalized graphene oxide nanoplatelets based cellulose green nanocomposites with simultaneous high thermal conductivity and excellent flame retardancy. *Chem. Eng. J.* **2020**, *382*, 122733. [CrossRef]

- Dong, S.; Xiao, G.; Chen, C.; Chen, C.; Yang, Z.; Zhong, F.; Wang, M.; Zou, R. Zn-Al layered double metal hydroxide anchored reduced graphene oxide for enhancing the fire performance of composite coatings. *Colloids Surf. A Physicochem. Eng. Asp.* 2022, 632, 127736. [CrossRef]
- 41. Rashid, M.; Al-Zaqri, N.; Guerrero-Barajas, C.; Hussain, F.; Ibrahim, M.N.M. Waste Derived Graphene Oxide-ZnO: An Efficient Photocatalyst for Rhodamine 6G. *Processes* **2022**, *10*, 2266. [CrossRef]
- 42. Wang, D.; Ma, J.; Liu, J.; Tian, A.; Fu, S. Intumescent flame-retardant and ultraviolet-blocking coating screen-printed on cotton fabric. *Cellulose* **2021**, *28*, 2495–2504. [CrossRef]
- 43. Zhang, Z.; Dong, C.; Liu, J.; Kong, D.; Sun, L.; Lu, Z. Preparation of a synergistic reactive flame retardant based on silicon, phosphorus and nitrogen and its application to cotton fabrics. *Cellulose* **2020**, *27*, 1799–1815. [CrossRef]
- 44. Yu, M.; Zhang, T.; Li, J.; Tan, J.; Zhu, X. Synthesis of a Multifunctional Phosphorus/Silicon Flame Retardant via an Industrial Feasible Technology. *ACS Sustain. Chem. Eng.* **2023**, *32*, 11965–11977. [CrossRef]
- 45. Varganici, C.; Rosu, L.; Bifulco, A.; Rosu, D.; Mustata, F.; Gaan, S. Recent advances in flame retardant epoxy systems from reactive DOPO–based phosphorus additives. *Polym. Degrad. Stab.* **2022**, 202, 110020. [CrossRef]
- 46. Wang, D.; Xing, W.; Song, L.; Hu, Y. Space-confined growth of defect-rich molybdenum disulfide nanosheets within graphene: Application in the removal of smoke particles and toxic volatiles. *ACS Appl. Mater. Interfaces* **2016**, *8*, 34735–34743. [CrossRef]
- Wang, D.; Peng, H.; Yu, B.; Zhou, K.; Pan, H.; Zhang, L.; Li, M.; Liu, M.; Tian, A.; Fu, S. Biomimetic structural cellulose nanofiber aerogels with exceptional mechanical, flame-retardant and thermal-insulating properties. *Chem. Eng. J.* 2020, 389, 124449. [CrossRef]
- Li, D.; Müller, M.; Gilje, S.; Kaner, R.B.; Wallace, G.G. Processable aqueous dispersions of graphene nanosheets. *Nat. Nanotechnol.* 2008, *3*, 101–105. [CrossRef]

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