



## Superior flame retardancy and smoke suppression of epoxy-based composites with phosphorus/nitrogen co-doped graphene

Yuezhan Feng<sup>a</sup>, Chengen He<sup>a</sup>, Yingfeng Wen<sup>a</sup>, Yunsheng Ye<sup>a,\*</sup>, Xingping Zhou<sup>a,\*</sup>, Xiaolin Xie<sup>a,b</sup>, Yiu-Wing Mai<sup>a,c</sup>

<sup>a</sup> Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

<sup>b</sup> State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology Wuhan 430074, China

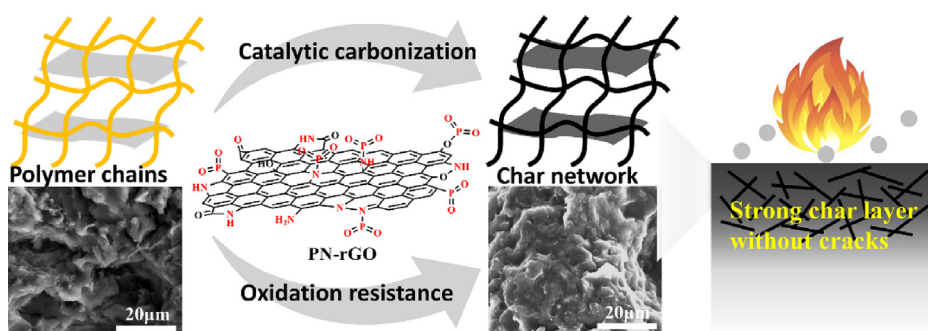
<sup>c</sup> Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronic Engineering J07, The University of Sydney, Sydney, NSW 2006, Australia



### HIGHLIGHTS

- Phosphorus/nitrogen co-doped graphene (PN-rGO) was synthesized via a scalable and green hydrothermal and microwave process.
- PN-rGO was used as an additive for the first time to improve the flame retardancy and smoke suppression of epoxy resin.
- Char (condense phase) and volatile (gaseous phase) analyses were measured to investigate the flame retardation mechanism.
- Phosphorus/nitrogen co-doping is a viable approach to improve the efficiency of graphene as a flame retardant additive.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 19 August 2017

Received in revised form 5 December 2017

Accepted 6 December 2017

Available online 7 December 2017

#### Keywords:

Phosphorus/nitrogen co-doping

Graphene

Epoxy resin

Flame retardancy

Smoke suppression

### ABSTRACT

Phosphorus and/or nitrogen doping is an effective method of improving the physical and chemical properties of reduced graphene oxide (rGO). In this work, phosphorus and nitrogen co-doped rGO (PN-rGO), synthesized using a scalable hydrothermal and microwave process, was used as an additive to improve the flame retardancy of epoxy resin (EP) for the first time. Chemical structure and morphology characterization confirmed that the nitrogen and phosphorus atoms were doped into the graphite lattice adopting pyrrolic-N, pyridinic-N, quaternary-N and pyrophosphate and metaphosphate forms. Doping increased the oxidation resistance of rGO and the thermal-oxidative stability of its composites' char, while also improving the catalytic charring ability of polymer. Both effects resulted in the formation of a stable char protective layer during burning and to a significant improvement in flame retardation and smoke suppression in the final composites. The peak heat release rate (PHRR), total heat release (THR) and total smoke production (TSP) for the EP-based composite (containing 5 wt% PN-rGO) decreased by 30.9%, 29.3% and 51.3%, respectively, compared to neat EP. Our work has produced a promising graphene-based flame retardant additive for the mass production of high-performance composites, also expanded the application of heteroatom-doped graphene.

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\* Corresponding authors.

E-mail addresses: [ysye@hust.edu.cn](mailto:ysye@hust.edu.cn) (Y. Ye), [xpzhou@hust.edu.cn](mailto:xpzhou@hust.edu.cn) (X. Zhou).

## 1. Introduction

The rapid development and widespread use of polymers in e.g. buildings, electric devices, medicines, energy transfer and storage materials, has drawn attention to their fire safety (flammability) related problems [1–4]. The incorporation of flame retardants into polymers has been widely used to address such issues [5]. However, traditional flame retardants, due to harmful by-products generated during combustion (halogenated flame retardants) [6], or because of the deterioration in their mechanical and thermal properties that results from high-loadings (phosphorus-containing compounds and metal hydroxides) [7–9], are often considered not to meet the requirements of high-performance and eco-friendly polymer applications. Therefore, developing eco-friendly and chemically stable flame retardant additives that do not degrade the polymer matrix's sought after properties will be key to preparing future high-performance materials.

Reduced graphene oxide (rGO) with its two-dimensional (2D) monolayer  $sp^2$ -hybridized carbon lattice structure has been extensively studied for potential applications in e.g. capacitors, sensors, catalysts, and electric/thermal conductive composites [10–13]. Recently, close attention has been paid to potential flame-retardant additives for polymers, which may a route to improving the flame resistance of polymers without damaging their mechanical and thermal properties, while minimizing environmental impact [14–18]. Unfortunately, rGO's weak compatibility with polymer matrices, its poor thermal-oxidative stability and its low charring capacity seriously restrict its application as a flame retardant additive [19,20]. Literature reports commonly offer two possible solutions: i.e., blending and surface functionalizing the graphene with organic or inorganic flame retardants [21,22]. However, in the blending flame retardant system, relatively high loadings of organic or inorganic flame retardants are still needed, which induce the deterioration in mechanical properties [23,24]. On the other hand, although the compatibility and charring capacity of rGO can be improved by surface functionalization, the poor oxidation resistance that reduces charring properties has not been addressed [25]. Moreover, the complicated functionalization process is not industrially scalable and eco-friendly [26–28]. Therefore, the search for new graphene derivatives to meet industrial requirements (i.e. scalable and eco-friendly) is still a huge challenge in the quest to prepare high-performance flame retardant polymer composites.

Recent studies have demonstrated that nitrogen or/and phosphorus doping can improve the thermo-oxidative stability of GO and rGO [29–33]. Yuan et al. [29] showed that the 50% mass loss rGO thermal degradation temperature increased by 131 °C when co-doped with phosphorus and nitrogen. Kim et al. [31] and Some et al. [33] have confirmed that the phosphorus-doped graphene, or GO, were able to be used as effective flame retardant protective layers for cloth or paper. The positive role of phosphorus and/or nitrogen doping in enhancing thermal-oxidative stability and fire resistance, has indicated the potential of doped rGO as a polymer flame retardant additive. Even so, to the best of our knowledge, very few studies on the improvement of polymer flame retardancy by the incorporation of phosphorus or/and nitrogen doped rGO have been reported. Very recently, Shabestari et al. [34] reported that nitrogen and oxygen doped carbon nanotubes (CNTs), prepared by chemical vapor deposition (CVD) method, were used as flame retardant additives to improve the flame resistance of epoxy resin. In contrast, phosphorous/nitrogen doping graphene, with 2D structure and higher aspect ratio than CNTs, was expected to be the more promising flame retardant additive for polymers. Moreover, in comparison to traditional flame retardant functionalization, the doping process for graphene is usually 'green' i.e. without the need for any organic solvents and suitable for mass production, such as CVD method [35], pyroprocessing [29,36], and microwave treat-

ment [37]. Therefore, it is very significant and meaningful to explore the effect of phosphorus/nitrogen doped graphene on the flame retardancy of polymers.

In this study, phosphorus/nitrogen co-doped rGO (PN-rGO) was prepared using a scalable, low-energy, solvent-free green hydrothermal and microwave process. The influence of PN-rGO on flame retardation and smoke suppression of epoxy-based composites was investigated using a cone calorimeter, char and volatile gas analysis. Our work has produced a promising graphene-based flame retardant additive for the mass production of high-performance composites, also expended the application of heteroatom-doped graphene.

## 2. Experimental

### 2.1. Materials

The diglycidyl ether of bisphenol-F epoxy (DGEBF, YDF-170) was supplied by KUKDO Chemical Co., Ltd (China). The curing agent [2-ethyl-4-methylimidazole (EMI-2,4, AR)] was purchased from Aladdin Industrial Corporation (USA). Polyvinylpyrrolidone (PVP,  $M_w = 130,000 \text{ g mol}^{-1}$ ) was provided by Beijing J&K Technology Co., Ltd. (China). Phosphoric acid (80%), polyphosphoric acid (PPA, AR), urea (AR), ethyl alcohol (AR), acetone (AR) and *N, N*-Dimethylformamide (DMF, AR) used without further purification were supplied by Sinopharm Chemical Reagent Co., Ltd. (China).

### 2.2. Preparation of phosphorus/nitrogen co-doped rGO (PN-rGO)

Graphene oxide (GO) was prepared from natural graphite by using a modified Hummers' method based on our previous work [38]. PN-rGO was prepared by a simple hydrothermal and microwave processes (Fig. 1a). Typically, GO sheets (1.0g) with phosphoric acid (5g), PPA (1g) and urea (10g) were dispersed in deionized water by ultrasonication for 1h. The obtained suspension was subsequently hydrothermally processed at 90 °C for 24h with stirring and then the suspension was concentrated and lyophilized to obtain brown powders, which were treated by microwave-thermal reduction (Galanz, 700W microwave oven) at ambient temperature for 2 min. The product, i.e., PN-rGO, was washed with deionized water to remove the residual compounds and then treated by freeze-dried process to obtain PN-rGO powder. GO sheets without any heteroatom sources were also treated under the same conditions (i.e. hydrothermal and microwave processing) to obtain rGO (i.e., microwave reduced graphene oxide, denoted as WrGO) to be used a reference material.

### 2.3. Stabilized dispersion of PN-rGO by PVP

Due to the lack of organic groups, the resulting PN-rGO created using microwave reduction exhibited a poor dispersion in organic solvents, such as ethanol and DMF (see Fig. 1b), resulting in irreversible agglomerations in composites. To overcome this problem, we employed PVP (10 wt% relative to PN-rGO) as a surfactant to improve its dispersibility in organic solvents [39,40]. Fig. 1b shows the improvement of PN-rGO dispersion in ethanol and DMF found using PVP modification. The Tyndall effect (Fig. 1b) confirms the stabilized dispersion of PN-rGO in DMF assisted by PVP. Hydrogen bond linking between PN-rGO and PVP is thought to be the main dispersion mechanism (Fig. 1c), which possibly results from the enhancement of interfacial interactions between PN-rGO and EP.

### 2.4. Preparation of EP/PN-rGO composites

Epoxy-based composites containing PN-rGO sheets were fabricated using the following procedure. PN-rGO was ultrasonically-

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