

# Halogen-free, phosphorus decorated, bio-waste derived nanocomposite for highly efficient flame retardant for cotton fabric

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## Research Article

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# Abstract

We have prepared an efficient flame retardant composite using biowaste derived phosphorous groups decorated graphene supported nanomaterial. The eggshell was utilized as a source of calcium carbonate, which was converted to monocalcium phosphate (CP) by phosphoric acid treatment. As-prepared monocalcium phosphate was functionalized with graphene to prepare graphene functionalized monocalcium phosphate (GCP). The GCP-coated fabric didn't ignite during the flame test and sustained more than 600s on continuous exposure to flame without changing its initial length and shape. Whereas, graphene oxide (GO), and CP coated cotton fabric burnt out very easily within a short time. The synthesized GCP coated cotton fabric also confirmed efficient flame retardant property with a high limiting oxygen index (34.1) and char length of 2.5cm was generated from the VFT test. This facile method enables an easy process for mass production of cost-effective, bio-waste derived nanomaterial for a significantly highly efficient candidate for different applications in sustainable chemistry, including flame-retardant application.

## Introduction

Fire is the major revolutionary discovery of humans with a two-edged sword in that it is used in almost every aspect of daily life and industry, but it also causes significant damage. Every year approximately 0.2% of the global economy is lost due to fire disasters without counting its reconstruction and other medical-related issues (Li et al., 2011; Chen et al., 2015; Li et al., 2010). The primary benefit of flame-related research is the development of highly effective materials capable of protecting both human life and society. Among the various flame retardants available, the fabric containing flame retardants is gaining popularity due to its mechanical properties and lack of comfort (Weil et al., 2008; Horrocks et al., 2005). These fabrics are used for soft furnishings, and unmodified cotton fabric are highly flammable (Li et al., 2011; Devaux et al., 2002; Alongi et al., 2014) As a result, the way of making fabric flame retardant is surface modification. Surface modification is cost-effective, simple, frequently utilized, and possess an enormous practical approach (Wang et al., 2020; Zhang et al., 2021; Kim et al., 2014). The choice of the flame retardant is also playing an important role. Originally, boron, silicon, and halogen-based flame retardants were widely employed, but they were phased out because they emit dangerous chemicals into the environment causing deleterious effects on human health's (Wakelyn et al., 2007; Hsiue et al., 1999; Mercado et al., 2006). For the surface modification, dipping (Xu et al., 2019) and layer-by-layer (LBL) (Li et al., 2010; Laachachi et al., 2011) self-assembly were utilized as simple and extensive approaches to improve the flame retardancy of cotton fabric. In that, the cotton fabrics were originally treated with intumescent flame retardant coatings by Li et al. (Li et al., 2011) This sort of coating is extremely effective, beneficial, and versatile in the fabrication of flame retardant coatings on a variety of substrates (Li et al., 2010; Laachachi et al., 2011; Laufer et al., 2012).

The eggshell employed as a bio-filler was commonly utilized as an intumescent flame retardant coating because it includes a high quantity of calcium carbonate ( $\text{CaCO}_3$ ), i.e., about 95% while 5% of other organic components. Intumescent fire-retardant coating, which is largely composed of an intumescent

fire-retardant system, a synergist, a binder, and an auxiliary agent, is considered as one of the most effective materials for shielding substrates from fire hazards (Yan et al., 2018). Researchers are interested in using polymer because of its simple compatibility with bio-filters, fire resistance, and mechanical characteristics (Yew et al., 2018). The intumescent flame retardant has lately become a pandemic FR for polymers because of its low smoke, halogen-free, low toxicity, and excellent efficiency (Xueying et al., 2015; Zhang et al., 2018). Researchers have been drawn to developing novel intumescent flame retardant systems using bio-based flame retardants like starch (Olivares et al., 2019; Oassaure et al., 2019), chitosan (Cheng et al.), and lignin (Song et al., 2016; Liu et al., 2016). Acid was widely utilized to improve the flame retardant characteristic of bio-filler-containing products (Yeh et al., 1995; Duquesne et al., 2004). These flame retardants mainly consist of acid source, blowing agent, and binder. When these types of flame retardants come in contact with the flame, they produce black smoke, heat, and toxic gases (Chen et al., 2016). Also, such type of flame retardants has a limited scope of application, which means they cannot be applicable on cotton fabric.

In addition to the eggshell, seashell (Moustafa et al., 2017), clamshell (Li et al., 2020), and conch shell (Wanf et al., 2021) were utilized as bio-fillers, along with various acid, polymer, and binder sources, to increase the flame retardant characteristics of the composite. The application of these chemicals enhances flame retardant efficiency while also protecting the composition. The usage of these compounds (chemicals) to emphasize the flame retardant characteristic of the composite has a very hazardous effect on the environment and human. These sorts of composites may create health issues such as allergic reactions, skin inflammation, and so on (Tesghai et al., 2019). There is a need to modify the bio-filler in such a way that it should take care of all the aspects of ecology with the enhanced flame retardant property.

Long-lasting phosphorus-containing flame retardant materials have fastened attention due to their efficacy, such as low toxicity, reducing the volatility of fuels, producing the carbon-based char, lowering the pyrolysis temperature, wash fastness resistivity and reducing the afterglow. Phosphorus-containing flame retardants benefit from being effective in both the gaseous and condensed phases by generating chain reactions and producing a shield through char formation, respectively (Fang et al., 2020; Dhumal et al., 2022., Yun et al., 2011). The phosphorous functionalization was done in various techniques, including sponges, poly cables, and textiles (Chen et al. 2012). The phosphorous functions can dehydrate cellulose and increase char formation (Wicklein et al., 2015; Song et al., 2017). Many researchers used the phosphorous-graphene strategy for efficient flame retardancy such as DES functionalized (Pethsangave et al., 2017), polymer-based (Pethsangave et al., 2019), GO in ABS (Higginbotham et. Al., 2009), and FR-GQD (Khose et al., 2018). Graphene is forthcoming as a very attractive support material for flame retardation systems. It is a perfect fit for the skeleton of flame retardant materials due to its large surface area, high oxygen-rich active functionalities, low toxicity potential and thermal stability. As a result, society continues to demand efficient materials that are simple to produce, environmentally benign, cheaper in cost, and gentle in nature. According to the literature, the modified bio fillers-based flame retardant may be enhanced by the functionalization of phosphorous groups in the presence of graphene as a high surface area containing a suitable carbon-based skeleton.

As a result of the need for an environmentally friendly, easy-to-prepare flame retardant nanocomposite, we synthesized one from biowaste. In this, the biowaste (eggshell) was treated with phosphoric acid before being reacted with graphene oxide to prepare a nanocomposite for flame retardant applications. Eggshell was converted to monocalcium phosphate by phosphoric acid treatment, which was functionalized with graphene to prepare graphene functionalized monocalcium phosphate (GCP). The prepared composite can sustain in the continuous flame for more than 10 min (600 s) as compared to the blank cotton fabric (5 s), coated fabric GO (15 s), and CP coated fabric (10 s). The coating of the GCP is a very simple and easy method that requires a concise time. Compared to the blank cotton fabric, GO coated cotton fabric, and CP coated fabric, the produced composite can maintain the flame for more than 10 minutes.

## Experimental

### 2.1 Material and Methods

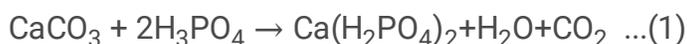
Graphite powder (325 mesh, Alfa Aesar), sulphuric acid (98% assay with 99% purity, Merck), hydrochloric acid, hydrogen peroxide (30%, S D Fine Chemicals, Ltd.), potassium permanganate (99%, Alfa Aesar), and ethanol (99.5%, Merck). Chemicals and solvents were used as obtained without further purifications. Eggshell was collected from the local canteen.

### 2.2 Preparation of graphene oxide (GO):

As mentioned in the preceding paper, the graphene oxide was synthesized using a modified Hummers technique (Dhumal et al., 2021).

### 2.3. The preparation of monocalcium phosphate (CP)

The waste eggshell was collected as a source of  $\text{CaCO}_3$  from the local canteen and washed several times with water. The washed shells were dried at room temperature first, then in an oven at  $80^\circ\text{C}$  for 6 hrs. To make powder, the dried shells were crushed in a grinder. This eggshell powder was then mixed in a 1:2 ratio with the phosphoric acid solution, as shown in equation 1. Subsequently, the solution was stirred for an hour and water was added to this solution. After that, the solution was filtered, and the white solid was collected. This white mass was then dried in an oven at  $100^\circ\text{C}$  for an overnight period.



### 2.4. The preparation of the GCP

GO (50 mg) was dispersed in deionized water (50 mL) for GCP preparation. 100 mg of CP were dissolved in 1N HCL solution (15 mL). Both solutions were poured into a 250 mL round bottom flask and stirred at  $85^\circ\text{C}$  for 2 h. The reaction mixture was cooled at room temperature after 2 h. of stirring and used as GCP for further experiment.

## Results And Discussion

X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy was used to characterize the as-prepared materials (SEM).

The surface morphology of the as-prepared materials was studied by scanning electron microscopy (SEM). In the case of GO, it has a thin, wrinkled sheet-like structure (Some et al., 2012). The morphological changes have been traced by performing SEM of GCP coated material before and after the fire test and SEM pictures are displayed in Figure 1. The shape of the GCP in these images makes it appear like the CPs are evenly dispersed on the graphene surface. The CP particles are clustered together in a form that resembles a bundle (Figure 1a). The morphology of the CP alters following the flame test as it transforms into granular form, which is interesting. It might be because when the CP is exposed to heat, it forms a stable crystal structure in the form of granules or spheres, as shown in Figure 1b (Welzel et al., 2004).

Furthermore, as shown in Figure 2a, the cotton fabric was being uniformly coated by the composite throughout the surface, and its elemental mapping contains carbon, phosphorous, oxygen, and calcium (Figure 2c). In addition, the cotton fabric retained its morphology and structure (Figure 2b) as well as its elemental mapping, depicting an equal distribution of the carbon, phosphorous, oxygen, and calcium elements, as shown in Figure 2d. The EDX mapping of the GCP composite was described on the Table S1.

XPS analysis was used to study the surface electronic state and atomic composition of the composite. The surface electrical state of the composite and its atomic composition was investigated using XPS analysis.

The GCP has a high oxygen content i.e., the C/O ratio of 0.95 as shown in Table S1. In the spectra survey of GCP (Figure 3a), the C1s, O1s, P2p, P2s, and Ca2p peaks were seen. At 531.2 and 533.2 eV, respectively, the O1s spectra (Figure 3b) comprise the C=O/P=O and C-O/P-O bonding. The GCP's C1s spectra (Figure 3c) reveals a strong peak for C-C bonding at 284.6 eV, a peak for C-O and C-P at 285 eV, and a peak for C-O and C-P at 285 eV. The existence of P2p and P2s at 133.2 and 134.6 eV, respectively, is confirmed in the GCP spectra, as shown in Figure 3d (Kim et al., 2014; Blundell et al., 2014).

The TGA was performed in an air environment with a flow rate of 20°C to assess the thermal stability of the GCP composite. Because of its thermal stability, there is no notable change in weight in the TGA spectra of CP and calcium carbonate (Figure 4a). Both curves have excellent thermal stability, with weight loss ranging from 15-20% in each case. The first loss was noticed in the GCP curve at 100°C owing to the loss of intercalated water molecules. After that, at 240°C, a second weight loss was observed due to the burning of the carbon skeleton (Yilmaz et al., 2004). The GCP has lost about 41% of its total weight, demonstrating the composite's thermal stability. The crystallite structure of the GCP composite material has shown by the XRD pattern (Figure 4b). The usual graphene peak at 26.2° and the peak at 32.2°

suggest the presence of CP crystals (Kamalanathan et al., 2014). Figure S1 depicts the graphene oxide XRD pattern, which exhibits a characteristic peak at  $10^\circ$ .

The FT-IR spectra of GO revealed the following peaks as shown in Figure 5. The peak indicates the wide vibration of the O-H band at  $3424\text{ cm}^{-1}$ . The presence of C=O stretching of acid and C=C stretching vibration of aromatic carbon atoms was verified by the appearance of peaks at  $1728$  and  $1623\text{ cm}^{-1}$ , respectively. Peaks were found at  $1412$  and  $1053\text{ cm}^{-1}$ , suggesting C-H bending and C-O stretching, respectively (Higginbotham et. Al., 2009).

In the spectra of the CP, the peaks found at  $569$ ,  $950$ , and  $1092\text{ cm}^{-1}$  attributed to the vibrations of phosphate group  $\text{PO}_4^{-3}$  (Yelteen et al., 2016). Also, the hydroxy group (-OH) is represented by the steep peak at  $3467\text{ cm}^{-1}$  and the peak at  $650\text{ cm}^{-1}$ . Peaks for the phosphate group ( $\text{PO}_4^{-3}$ ) at  $599$ ,  $977$ , and  $1024\text{ cm}^{-1}$  in the GCP spectra demonstrate the incorporation of monocalcium phosphate into the graphene core. At  $1440\text{ cm}^{-1}$ , the peak for C-H stretching was also seen. From the peak at  $1627\text{ cm}^{-1}$ , the C=C stretching vibration bonding was confirmed.

### **Flame retardant test of the GCP coated cotton fabric**

An ethanol lamp was utilized to conduct the flame retardant test.

A dipping procedure was used to coat the GCP sample on the fabric. The GO and CP coated cotton fabrics were treated in the same way. The GO coated cotton fabric and blank cotton fabric were tested for the flame experiment in the air atmosphere, as shown in Figure (6 a-c) and Video V1. The GO coated fabric burnt out within 15 s, whereas the blank cotton fabric burnt out within 5 s. The CP coated burnt out in 10 s, exhibited the same phenomena in comparison to other control samples (Figure 6d-f and Video V2). In the case of GCP, the coated fabric did not catch fire for more than 10 minutes (600s) on continuous flame and retained its original shape and size, as illustrated in Figure (6 g-i and Video V3). The plausible mechanism of the GCP composite for flame retardancy is shown in Figure S2. As a result, GCP coated fabric was the most promising flame retardant material compared to GO and CP coated cotton fabric. The chemistry of flame retardancy is determined by the recurrence of chemical structural elements and their interaction during combustion. Because of the strong bonding interaction, the energy required to break the  $\text{sp}^2$  hybridized carbon atom is higher. As a result, any compounds containing the  $\text{sp}^2$  carbon's strong backbone, are more flame resistant (Walters et al., 2002; Lyon et al., 2009).

To evaluation of the flame retardant property of the GCP composite, the vertical flammability test (VFT) was performed. The test was done as per the ASTM D6413-09 standard method for the flame-resistant test of cotton fabric. The flame height was 38 mm and the sample dimensions were  $30 \times 7.6\text{ cm}^2$ . The bottom cut edge of the fabric was subjected to a controlled flame for 12 s, followed by flashing over the surface, burning with flame time, burning with afterglow after flame stop, and char length measured as shown in Figure 6. Table S2 shows the results of the vertical flammability test, which were outstanding, as well as detailed flammability data. The blank fabric lit quickly and burned up completely in less than

18 s (Figure 7a), with flashes throughout the surface. The GO covered fabric was entirely burned out in 11 s (Figure 7b), with flashing across the surface afterwards. The GCP coated fabric did not display flash across the surface and did not burn, although it did have a 2s afterglow, resulting in a total burning time of 2s (Teli et al., 2017) and measured char formation is 2.5 cm (Figure 7c). Table S3 summarizes the data and LOI explanations for the composite. Also, table S4 contains a comparative study of the char length of similar materials.

The mechanical property of the flame retardant composite plays important role. Tensile strength of the GCP composite was discussed in the S3. Whereas, the washing fastness of calcium carbonate, CP, and GCP coated cloth/binder before and after washing was analyzed and weight percent loss calculated and mentioned in Figure S5.

## Conclusions

We have synthesized halogen-free, phosphorus functional groups decorated, sustainable, bio-waste derived nanocomposite for efficient flame retardant for cotton fabric. Leftover eggshells were treated with phosphoric acid to prepare monocalcium phosphate, which was functionalized with graphene to prepare GCP. The as-prepared GCP composite coated cotton fabric can prevent a continuous flame for more than 600 s, whereas the CP and GO coated cotton fabrics burn out in 10 and 15 s, respectively, with smoke formation. The major advantage of the GCP coated fabric is to protect its initial shape and size after being exposed to a continuous flame for 10 minutes. The both LOI and vertical flammability test confirmed the GCP's flame retardant properties. The GCP coated fabric has a high LOI value of 34.1, indicating good flame retardant properties. The phosphorus decorated bio filler functionalized graphene nanocomposite was synthesized by using a simple and green approach, which has high efficiency as flame retardancy for cotton fabric. The present study indicates the environmentally benign, sustainable efficient flame retardant nanocomposite deserves exploration for different fabrics.

## Declarations

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## Author Contributions

P.S.D. and S.S. wrote the manuscript, P.S.D. performed experiment, P.S.D., K.D.L., M.A.B. and M.P.B. prepared graphene oxide and nanocomposite. P.S.D. analyzed all data, S.S supervised all work.

## Compliance with ethical standards

**Conflict of interest:** The authors declare that they have no conflict of interest.

**Ethical approval:** The authors have no statement about ethical approval. Because, this research does not involve human and animal.

**Informed consent:** This research does not involve human participants that's why author have no statement about informed consent.

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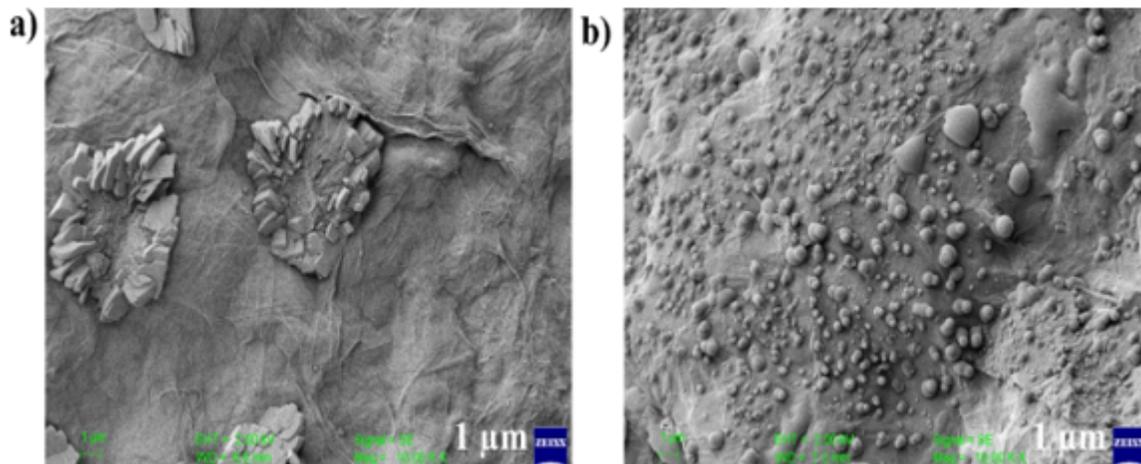
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# Figures



**Figure 1**

SEM image of the GCP a) before the flame test and b) after the flame test

**Figure 2**

SEM images of GCP composite a) before flame and b) after the flame retardant experiment. Corresponding EDX element mapping c) before flame test contains carbon (blue), phosphorous (green), oxygen (orange), and calcium (yellow) and d) after flame test contains carbon (blue), phosphorous (green), oxygen (orange), and calcium (yellow).

**Figure 3**

a) XPS survey spectra of the GCP, b) XPS spectra of GCP O1s spectra, c) XPS spectra of GCP C1s spectra, and d) XPS spectra of GCP P2p

**Figure 4**

a) TGA graph of calcium carbonate, monocalcium phosphate (CP), and GCP, b) XRD pattern of GCP

**Figure 5**

## Figure 6

Snapshots of the flame retardant test of the GO coated cotton fabric (right) with and blank cotton fabric (left) concerning time from (a-c) 0-15s. Snapshots of the flame retardant test of the CP coated cotton fabric (right) with and blank cotton fabric (left) concerning time from (d-f) 0-10s. Snapshots of the flame retardant test of the GCP coated cotton fabric (right) with and blank cotton fabric (left) concerning time from (g-i) 0-600s.

## Figure 7

Snapshot of the vertical flammability test (a) blank cotton fabric, (b) GO coated cotton fabric, and c) GCP coated cotton fabric.

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformation.docx](#)
- [V1GOcoated.mov](#)
- [V2CPcoated.mov](#)
- [V3GCPcoated.mp4](#)