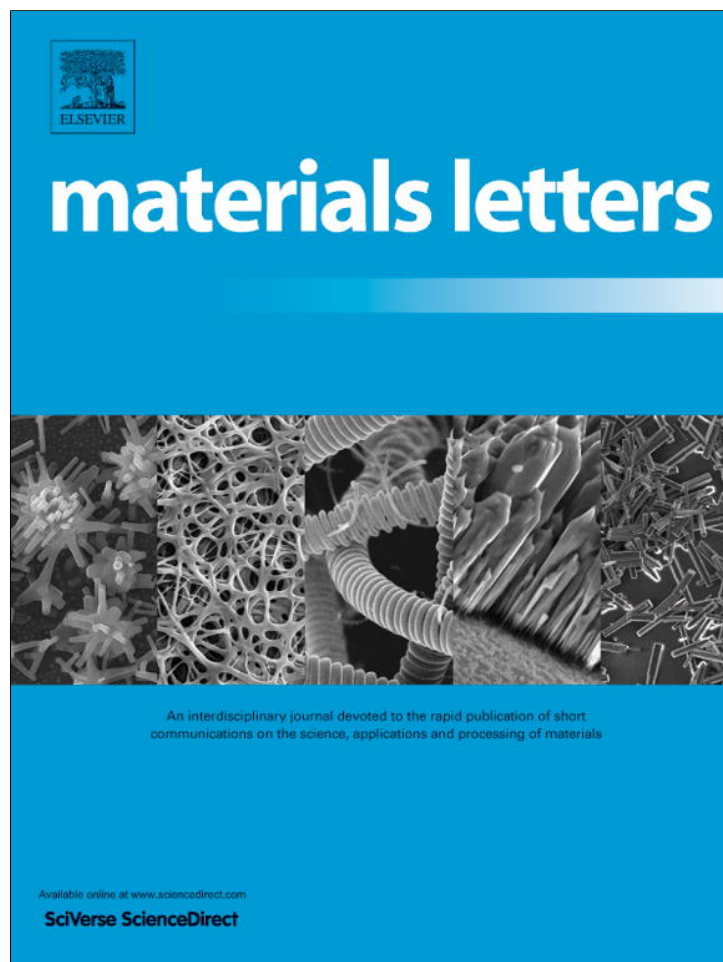


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# Hydrothermal co-doping of boron and phosphorus into porous carbons prepared from petroleum coke to improve oxidation resistance<sup>☆</sup>

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## ABSTRACT

Porous carbons (PC) have been extensively used in a wide variety of industries. However, their poor oxidation resistance, especially at high temperature (e.g. > 370 °C), has severely limited their applications such as catalysts under high temperature. Hydrothermal doping technology, as a newly emerged efficient approach for chemical modification, was for the first time introduced towards PC modification. The PCs used in this work were, by KOH activation, prepared from petroleum coke. The modified porous carbons (MPC) were achieved using hydrothermally co-doping boron and phosphorus into the PC followed by a heating treatment. The results revealed that the onset oxidation temperature of the MPC was greatly improved from 370 °C to 600 °C. The residual weight percent for MPC, an immediate and most critical indication of the oxidation resistance, was observed as high as 49% at 850 °C, while that of the blank sample was <10% at an even lower temperature of 600 °C. The achieved remarkable improvements on onset oxidation temperature and residue weight, substantiated by TGA, FTIR and Raman spectroscopy, confirmed the success of our unprecedented combination of co-doping and hydrothermal technologies to improve the oxidation resistances of PC materials.

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## 1. Introduction

Due to their abundant pores, beneficial mechanical property and chemical stability, PCs have been widely used in fields of adsorption and separation, electronics, energy storage, catalysts etc. [1–3]. However, their poor oxidation resistance under high temperature has greatly restrained their industrial application in oxygen-exposed environments. The anti-oxidation approaches that have received extensive concerns are doping certain additives into the carbon composite materials, the most commonly used doping additives vary from boron, halogen, phosphorus etc. [4–8]. All those treatments, while still preliminary, have proven to be promising in improving the oxidation resistance. However, to date little work has been reported for the PC modification using this doping technology.

In this paper, hydrothermal method was employed to help form an even diffusion of boron atoms into the PC pores. H<sub>3</sub>PO<sub>4</sub> solution, acting both solvent and doping additive, was used in hydrothermal treatment.

## 2. Experimental procedure

PCs were prepared from petroleum coke by KOH activation at 850 °C. In the hydrothermal treatment, B<sub>2</sub>O<sub>3</sub> was used as the boron source, and phosphoric acid as phosphorus source and solution.

PCs were thoroughly mixed with B<sub>2</sub>O<sub>3</sub> powder and H<sub>3</sub>PO<sub>4</sub> solution (85 wt.%), and placed into a hydrothermal reactor, increased the temperature to 200 °C and kept for 96 h. This step was to ensure a thorough filling of B<sub>2</sub>O<sub>3</sub> and intermediates into the PC pores. After hydrothermal treatment, the samples were taken out of the reactor and rinsed by distilled water, and then dried in an oven under 110 °C. The dried PCs were heated at 900 °C for 5 h. N<sub>2</sub> protective atmosphere was used throughout the heating process.

The PC without doping was considered as blank, whereas PC with heating treatment (5 h at 900 °C) was labeled as PC-HT. The boron-phosphorus doped sample was labeled as MPC.

Weight loss at high temperature is a direct parameter which determines the oxidation resistance performance of any specific PC. Oxidation resistance was examined by TGA. 10 mg PC was placed in a platinum crucible and heated to 850 °C at 10 °C/min with air flowing

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into the furnace at 50 mL/min. FTIR and Raman Spectroscopy were utilized to characterize the changes in microstructure and chemistry of the PCs after co-doping treatments.

### 3. Results and discussion

Our group has previously doped the PC, using solid-state boron, and observed certain positive improvements on the oxidation resistance of resultant PC materials [9]. However, due to the lack of an appropriate mixing approach for a uniform dopant distribution, the resulting improvement on the oxidation resistance was somewhat limited. Based on this finding, hydrothermal doping technology, as a thorough mixing approach, was adopted in this work for a homogeneous distribution of the doping additives into the PC microstructure.

Fig. 1 presents the weight loss curves of the following samples 1) blank PC, 2) PC-HT and 3) MPC prepared from various ratios of KOH/petroleum coke. When compared to that of PC, the onset oxidation temperature of PC-HT was improved from 370 °C to 530 °C, likely due to the carbonization which gave rise to the order degree of the PC-HT microstructure. A similar trend was revealed by Raman spectra (see Fig. 2 for details). In a sharp contrast to the blank sample, the MPC's onset oxidation temperature was greatly improved from 370 °C to as high as 600 °C. More importantly, the oxidation rate of MPC was remarkably reduced (as clearly suggested by slopes of TGA curves). Positively, the MPC residue percent was as high as 49% at 850 °C, while that of the blank was only < 10% at even a lower temperature of 600 °C. This outcome clearly suggested that co-doped boron and phosphorus must be responsible for the improvement of the observed oxidation resistance. Previous study on boron-alone doping, as described elsewhere, had demonstrated an improved onset temperature to 530 °C, much lower than 600 °C achieved in this work [2]. It is very likely that synergy of co-doped boron and phosphorous should be responsible for this remarkable improvement of oxidation resistance.

Fig. 1 also presents the effect of KOH/petroleum coke ratio on the oxidation resistance. Very interestingly, with decreasing the KOH/petroleum coke ratio within the tested ranges, the onset oxidation temperature steadily increased, and the oxidation rate significantly dropped. It is noteworthy that the onset oxidation temperature and weight loss rate are two crucially important factors that determine the oxidation resistance of any PC materials. The improvement of those two parameters successfully achieved in this work, definitely showed a promising prospect of the co-doping approach. On one hand, the co-doping successfully created synergy of co-doped elements, and on the other hand, our unprecedented combination of co-doping with hydrothermal process as a powerful mixing means may provide an inspiring new route to control the properties of the resulting PC materials.

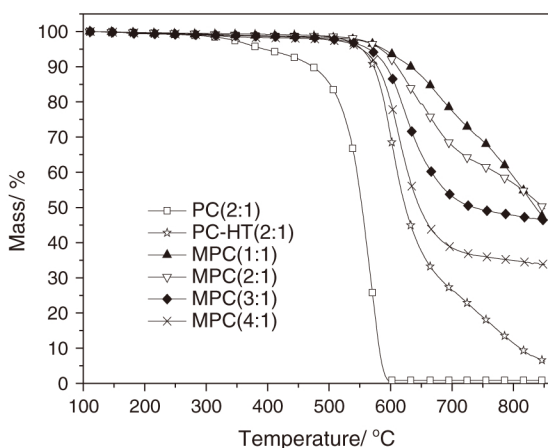


Fig. 1. TGA curves of PCs.

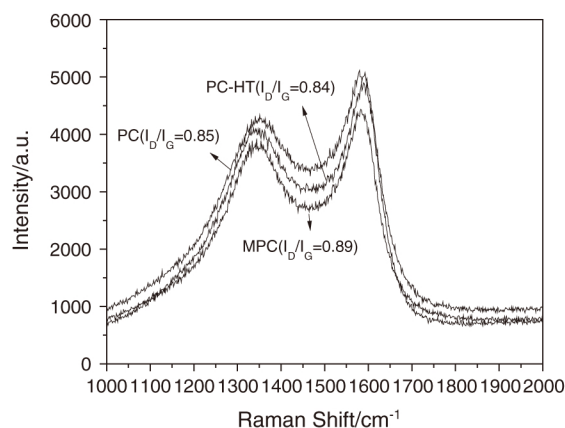


Fig. 2. Raman spectra of PCs.

For carbon materials, Raman spectroscopy is recognized as a sensitive probe for the presences of defects and disorder. Fig. 2 presents the Raman spectra of PCs treated under various conditions. Two noticeable bands, i.e. 1340  $\text{cm}^{-1}$  (D-band) and 1592  $\text{cm}^{-1}$  (G-band), were shown for all carbon samples, corresponding to the defects and disorder [10]. The intensity ratio of D-band to G-band ( $I_D/I_G$ ) relates to the degree of disorder [11,12]. The results showed that the  $I_D/I_G$  of PC-HT was decreased to 0.84 from 0.85 of PC, while the  $I_D/I_G$  of MPC was increased to 0.89. It is believed that the graphitization created by heat treatment was responsible for the decrease in the degree of disorder. We would interpret this increase in degree of disorder as a result of the introduction of certain functional groups (e.g. –COOH and –OH) into the PC by hydrothermal co-doping process. Formation of those functional groups was a result of site-selective reactions activated by the added  $\text{H}_3\text{PO}_4$  within the PC.

Fig. 3 presents the FTIR spectra for blank, PC-HT and MPC samples. When compared to blank and PC-HT samples, MPC exhibited a new pronounced peak at 1030  $\text{cm}^{-1}$ , which we would interpret as a result of the formation of P–O–C bond, indicative of the successful doping of phosphorus. For some reason, the baselines of all spectra were rather coarse, yet a careful comparison still showed that MPC displayed a weak yet unique peak at 1382  $\text{cm}^{-1}$ , which we would interpret as a result of the formation of B–C bond, boron containing peak, by nature, has often been shown rather weak [13,14]. However, its presence further implied herein the successful doping of boron into PC. (For unambiguous confirmation, an energy dispersive spectroscopy analysis will be done to obtain the levels of co-doped boron and phosphorous).

Taken together, the doped boron and phosphorus were found highly effective to improve the PC oxidation resistance. It was believed

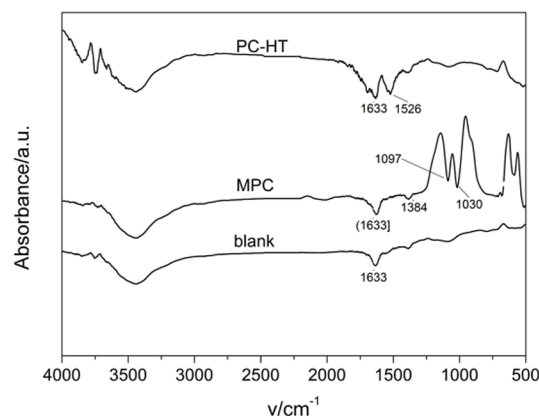


Fig. 3. FTIR spectra of blank, PC-HT and MPC samples.

the co-doping allowed boron/phosphorus molecules into the carbon lattice to form C–B and C–O–P groups, which blocked the otherwise accessible active sites within the PC to protect them from direct contact with oxygen molecules [15–18].

#### 4. Conclusions

PC materials offer a series of technical advantages and have been widely used in various fields. However, their poor oxidation resistance under high temperature has greatly restrained their industrial application in oxygen-exposed environments. To overcome this major weakness, hydrothermal and co-doping technologies were adopted for the first time in the work to control the oxidation resistance of PC at molecular levels. Our findings have clearly proved that hydrothermal co-doping of boron and phosphorus was an effective approach to improve the oxidation resistance of PC. The results demonstrated considerable improvement in both the onset oxidation temperature and residue weight of the modified PC. The creative combination of co-doping technology with the hydrothermal process may provide a new approach to control the properties of those PC materials.

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