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The microwave adsorption behavior and microwave-assisted heteroatoms doping of graphene-based nano-carbon materials

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Microwave-assisted heating method is used to treat graphite oxide (GO), pyrolytic graphene oxide (PGO) and hydrogen-reduced pyrolytic graphene oxide (HPGO). Pure or doped graphene are prepared in the time of minutes and a thermal deoxygenization reduction mechanism is proposed to understand their microwave adsorption behaviors. These carbon materials are excellent catalysts in the reduction of nitrobenzene. The defects are believed to play an important role in the catalytic performance.

Microwave irradiation is an efficient, green and non-contacting heating method[1] which has been widely used not only on household appliances, but also in scientific research fields, such as the high-speed microwave-assisted organic synthesis (MAOS)[2], materials manipulation[3], polymer chemistry[4], and the synthesis of nanoparticles[5]. In a typical microwave heating reaction in liquid phase, the microwave irradiation provides an inverted temperature gradient. And the selective wave-absorption of polar solvents or substrates as well as the potential superheating effect would make the process energy-efficient and time-saving[1,6]. Microwave irradiation heating, mediated by the dielectric relaxation or ionic conduction, provides an approach to heat a system homogeneously from the interior and more importantly, the differences in the wave-adsorption ability of materials made it possible to heat the substrates selectively. Since the microwave irradiation is a penetrating and adsorption-selective heating method, it is also suitable to be used in the solid phase reactions[2,3]. Without mechanical stirring and energy loss to the environment, the solids which absorb microwave can be heated homogeneously and efficiently.

Due to their excellent properties and widely potential applications, many methods have been developed to prepare the nano-carbon materials, such as chemical vapor deposition (CVD), arc-discharge, epitaxial growth and the bottom-up synthesis[7,8]. However, high temperature treatment is usually required to get a good crystallinity for these nano-carbon materials which is closely associated with their properties. For example, the widely-used CVD process needs a temperature of 873–1273 K and a time of several hours[9]. In particular, despite the extremely high temperature, metal is still needed to catalyze the decomposition of carbon precursors. Among these metals, the environmentally unfriendly nickel and copper metals are the most commonly chosen ones. What is more, the products of the mild bottom-up synthesis are usually of low qualities. Only in recent years, it was found that the nanocarbon materials itself could be responsive to the microwave irradiation[10–15]. These features of microwave-assisted heating have also been utilized in the production and modification of graphene materials[10–12] and in the formation of the graphene composites in liquid phase[13–15].

Our previous studies have reported that by microwave irradiation, the hollow carbon nanospheres or porous graphitic carbon can be synthesized in time of minutes[16,17]. Here, we report that graphene-based materials (graphite oxide, pyrolytic graphene oxide and hydrogen-reduced pyrolytic graphene oxide) can absorb microwave intensively. The process can be used to produce graphene with high purity from graphene oxide precursor in minutes. By using X-Ray diffraction (XRD), transmission electron microscope (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), element analysis (EA) and Near Edge X-ray absorption spectroscopy (NEXAS), a thermal deoxygenization reduction mechanism of the synthetic process was proposed. More impor-
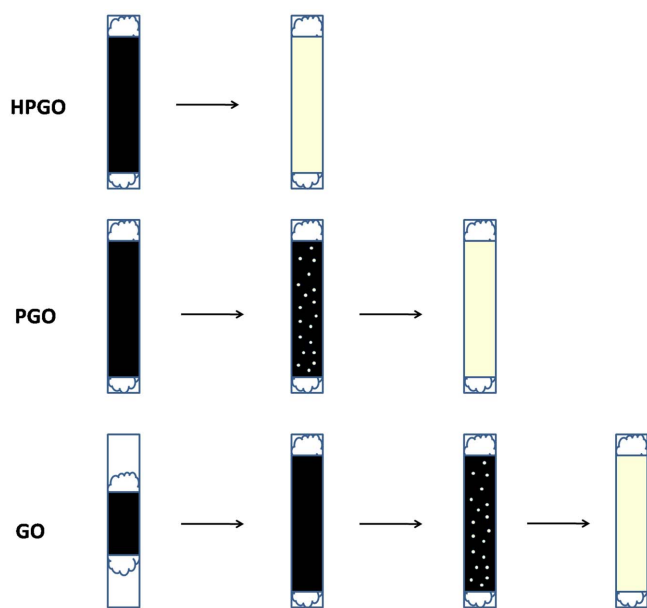
Figure 1 | Schematic diagram of the wave-adsorption/light-emission behaviors of the graphene-based carbon materials under microwave irradiation. (black color for the carbon substrate and the yellowish color for the light-emission areas).

tantly, a convenient and general method, which only needed less than 3 minutes, to prepare heteroatom-doped (N, P, B) graphene from graphene-based nano-carbon materials was developed. The catalytic performance of these nano-carbon materials was evaluated in the nitrobenzene reduction reaction. It was found that the heteroatom-doped nano-carbon exhibited a better catalytic activity than other materials.

Results

Various kinds of graphene-based nano-carbon materials (GO, PGO and HPGO) were treated by microwave irradiation. Pure graphene materials with excellent crystallinity could be obtained under microwave irradiation for just 1 min and their microwave adsorption behaviors (Figure 1) are found to be in line with their electrical conductivities (Supplementary Figure S1). The data of XRD, Raman (Figure 2)and EA (Table 1) illustrate that their composition, structures (Figure 3) and electrical conductivity change under microwave irradiations. A thermal deoxygenization reduction mechanism is proposed to understand their chances under microwave irradiations.

Furthermore, heteratoms (N,P,B) could dope into the graphene sheets under microwave irradiation. The dopants in graphene sheets are confirmed by the results of NEXAS (Figure 4) and XPS (Figure 5)

and the Raman data (Figure 6) show that the dopants create defects in these materials. These doped graphene-based nano-carbon materials are excellent catalysts in the reduction of nitrobenzene and the B-graphene materials with the biggest I_D/I_G ratio show the highest catalytic capabilities in this reaction. (Table 2).

Discussion

Thermal deoxygenization reduction of the graphene-based carbon materials under microwave irradiation. Three types of graphene-based carbon materials were used as the precursors, which were graphite oxide (GO), pyrolytic graphene oxide (PGO), and hydrogen-reduced graphene oxide (HPGO). These carbon materials were then treated in the microwave under inert atmosphere. After irradiation for 1 min, the weight loss of these carbon materials were recorded and the carbon materials before and after microwave irradiation were analyzed by EA, XRD, TEM and Raman spectroscopy.

The three carbon materials exhibited quite different phenomena under microwave irradiation. For HPGO, when the microwave treatment was on, an instant yellowish to white light emission from HPGO could be observed in less than 2 s. No color gradient was observed on the bulk material. This phenomenon suggested that there is no heat gradient over HPGO sample in the microwave irradiation process (as shown in the picture in Supplementary Figure S2). Under the protection of inert atmosphere, all through the experimental process (3 min), the intensity of light emission of HPGO exhibited no observable decay, indicating that HPGO may be used as the lighting source under microwave irradiation. A similar light-emission phenomenon of carbon nanotube under microwave irradiation had been reported by Tour *et al*[20].

For layered nano-carbon materials with higher oxygen content, such as GO and PGO, an induced period for wave-adsorption/light-emission was observed under the microwave treatment (see Figure 1). As shown in Figure 1, when GO was irradiated by the microwave, GO first expanded in volume and an obvious pyrolytic process with a large amount of gas emission was observed. After the pyrolytic process, the material experienced a twinkling light emission period at the beginning and gradually a homogeneous emission. In the full emission step, both the intensity and the color of the light were similar to those of HPGO under irradiation. Based on these phenomena, we proposed that GO, with a much higher oxygen content, was firstly pyrolyzed to form PGO[21,22], which then underwent a deoxygenization process under microwave irradiation. With further decrease of the oxygen content, the HPGO-like sample will couple with microwave field intensively, resulting in a strong light-emission, very similar to that of HPGO sample.

As a further verification of the proposal, the PGO (with an oxygen content of 18%) prepared through the thermal heating process of GO[18,23] was used for microwave irradiation under the same conditions mentioned above. PGO materials also showed a twinkling light-emission period at first and then a homogeneous emission of light as
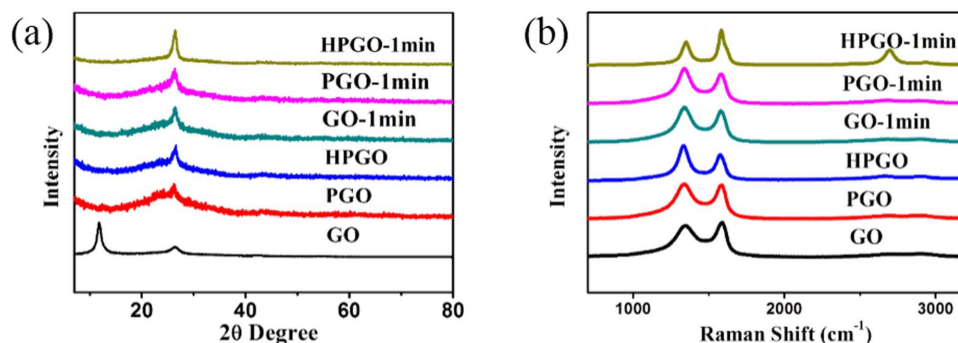

Figure 2 | (a) XRD profiles and (b) Raman spectra of the graphene-based carbon materials before and after microwave irradiation.

Table 1 | The content of oxygen in different nano-carbon materials (determined by EA) and the weight loss of those materials after microwave irradiation

Carbon materials	Oxygen (wt%)	Weight loss (wt%)
GO	46	57
PGO	18	37
HPGO	2.4	7.6
GO-1 min	1.2	--
PGO-1 min	1.4	--
HPGO-1 min	0.4	--

shown in Figure-1. In brief, besides the initial pyrolytic process for GO material under microwave irradiation, PGO and GO underwent the same reaction processes and exhibited the very similar light-emission phenomena.

As shown in Table 1, before irradiation, the oxygen content of GO is 46%. It is clear that the pyrolysis of GO can greatly reduce the concentration of oxygen species over the GO framework, and the resulting PGO has a relatively lower oxygen content of 18%[24]. Even after the hydrogen treatment at 1123 K for 8 h, there is still a 2.4% oxygen content on the surface of HPGO. However, to our surprise, after 1 min microwave irradiation, the oxygen content in those samples drops dramatically to 1.2%, 1.4% and 0.4%, respectively. This result demonstrates that microwave treatment is an efficient method for the removal of structural oxygen over graphene-oxide related nano-carbon materials. The removal of oxygen from the graphene framework is accompanied with the expelling of adjacent carbon atoms, normally in form of CO or CO_2. This is evidenced by the fact that the overall weight loss of the samples is usually higher than the loss of oxygen element. It is worth noting that the samples with a large amount of oxygen (GO and PGO) experienced a very fast deoxygenization process as well as the high overall weight loss during the irradiation. The oxygen contents of these two samples decreased by 97.4% and 92.2%, respectively. Instead, for HPGO with less oxygen, although more than 16% of the original oxygen species were still preserved after irradiation, the oxygen content is just 0.4%, most possibly in the form of OH group on the surface[25].

The structure of the samples was examined by XRD, Raman and TEM. Figure 2a presents the XRD profiles of the various carbon materials before and after microwave irradiation. GO showed a sharp reflection at 11° and a minor signal at 26°. The signal at 26° was a typical graphitic (001) reflection associated with an interlayer spacing of 0.3 nm, which shifted down to 11° due to the intercalation of oxygen atoms in the interlayer gallery, consequently generating an increased interlayer spacing of 0.7 nm after oxidation[21,23]. The appearance of this 26° minor graphitic signal suggests that part of the graphitic structure survived the oxidation process and the interlayer distance remained unchanged although the majority of the graphitic structure was intercalated by oxygen. For PGO and GO-1 min samples, no apparent signal at 11° was recorded, which suggests a delamination of the layered structures as a consequence of the deoxygenization process.

The Raman spectra of all the materials (Figure 2b) exhibit a D band at 1350 cm^{-1} and a G band at 1580 cm^{-1} [15,22]. The I_D/I_G ratios of GO-1min and PGO-1min show little variation, indicating a similar chemical status of the carbon structures in these samples. After the deoxygenization process, such as the pyrolytic transformation from GO to PGO, hydrogen treatment from PGO to HPGO and the microwave treatment of GO/PGO, the I_D/I_G ratios increased. Combined with the XRD results, the phenomenon can be rationalized by the improved crystallinity at the same time of the generation of smaller graphitic/conjugated domain of the samples, as a result of the expelling of the oxygen/carbon from the carbon materials[25]. Instead, for HPGO sample with much lower oxygen content, the healing of the surface defects becomes the dominant process under the irradiation. Therefore, the I_D/I_G ratio decreases after microwave treatment. The XRD profiles of both the HPGO and PGO-1min showed a sharper basal reflection than PGO at 26°, suggesting a better crystallinity of these two materials than the PGO precursor, as the result of the deoxygenization treatment of the materials[13,23,26]. For HPGO-1 min, the basal reflection at 26° becomes the dominant diffraction in XRD profile, strongly suggesting that a highly crystallized sample was obtained. These results in combination suggest that the reduction process of graphene-based nano-carbon materials by high temperature treatment or the microwave irradiation alone can generate highly crystallized graphitic structures with smaller graphitic/conjugated domain[25]. While a combination of high temperature hydrogen reduction and microwave irradiation could produce layered graphitic nano-carbon materials with good crystallinity and very few defects.

The electrical conductivity of selected samples was also measured. According to the current-voltage curves in Supplementary Figure S1, a big difference in the conductivity of GO, PGO, HPGO before and after microwave irradiation was observed. HPGO exhibited a much better conductivity than that of GO and PGO samples, which may be associated with its relatively lower oxygen content. For samples with even lower oxygen content (those after microwave irradiation), the conductivities are even higher. These results are in good agreement with previous reports that both the chemical and thermal reduction processes could improve the conductivity of GO[13,14,23]. It is worth
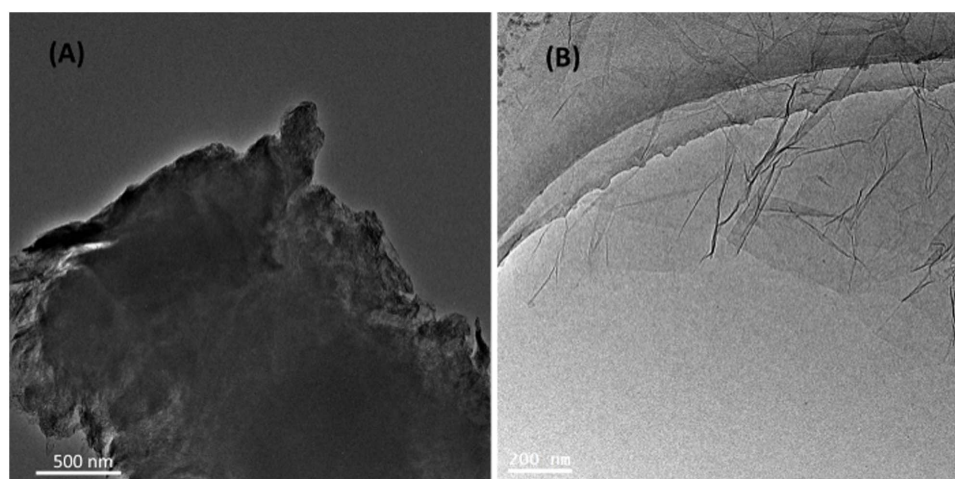

Figure 3 | TEM images of (A) GO and (B) GO-1 min.

noting that the samples performing violent lighting phenomenon (HPGO, GO-1 min, PGO-1 min and HPGO-1 min) have higher conductivity. Clearly, after the microwave irradiation process, GO and PGO samples exhibited a remarkable improvement in electrical conductivity. It was therefore proposed that the microwave-induced structural transformation in these graphene materials could be divided into two stages. In the first stage, the conductivity was low, and most possibly, it is the dielectric relaxation effect that dominated the microwave heating process; as a result, the oxygen element was deprived from the graphene oxide-based materials. The observed scintillation of the light of GO and PGO was due to the regeneration of π-conjugated structures (*i.e.*, crystallized graphitic structures) which could couple with microwave field extensively. At the same time, after the initial deoxygenization reduction process, the conductivity of PGO and GO greatly improved, and the ions/electrons conduction started to dominate the microwave absorption process. As a result, a homogeneous microwave absorption, heating and temperature distribution were observed. In this process, it is the thermal effect initiated by the microwave irradiation that dominates the pyrolytic and the consecutive reduced transformation of these materials.

The rapid production of N, P and B-doped graphene materials by microwave irradiation. At present, the preparations of doped graphene materials are primarily based on the high temperature chemical vapor deposition or annealing at 773–1373 K. The N and B atoms were incorporated into the lattice of graphene sheets while the oxygen elements came off[27,28]. Normally, it takes several hours for such reactions to complete at high temperatures. As microwave irradiation is a unique method for homogeneous heating, it would be very interesting to employ this efficient method for the preparation of doped graphene materials. Considering the relatively large volume change of GO under microwave irradiation, PGO was used as the precursors.

As a verification that the microwave assisted doping is a general method for graphene doping, nitrogen-, phosphorus- and boron-doped PGO materials were prepared, with ammonia, triphenyl phosphate and sodium tetraphenyl boron as the source of N/P/B, respectively. The mixture of PGO and the heteroatom precursors were microwave irradiated for three minutes, and the products were denoted as N-PGO, P-PGO and B-PGO, respectively. During the irradiation, a similar wave-adsorption/light-emission phenomenon was observed. The heteroatom contents of the obtained products were determined by XPS, with that of N in N-PGO 2.7%, B in the B-PGO 1.4%, and the P content in P-PGO 1.0%. Meanwhile, the oxygen content drops greatly for each of the doped samples to around 1%, respectively.

The raw PGO sample shows three main absorptions on C *K-edge* XAS spectrum. The peaks at ~285.4 eV and ~292.5 eV can be assigned to unoccupied π* and excited σ*, respectively in a C6 cell of graphene, while the peak at ~288 eV is attributed to C-O bonding (Figure 4)[29,30]. After microwave-assisted doping, the π electron system was well preserved. The intensity of characteristic π peak at ~285.4 eV slightly increases with the removal of large amount of oxygen, indicating the reinforcement of π-conjugated electron system. For the heteroatom-doped PGO samples, as the C-X bonding (X = N, P, B) might also appear at around 288 eV, no significant change was observed on the peaks of this region. However, as the oxygen content dropped extensively, the retaining of the peak at around 288 eV indicated the successive incorporation of heteroatom into the graphene framework[31].

The incorporation of the heteroatoms was further investigated by XPS method (Figure 5). Four N species can be resolved based on the N 1s spectrum of N-PGO, including C-N-O species at 403.2 eV, graphitic or quaternary N species at 401.1 eV, the aniline N species at 399.7 eV and pyridinic N species at 398.4 eV. The existence of those peaks indicates that after a 3-min microwave treatment,
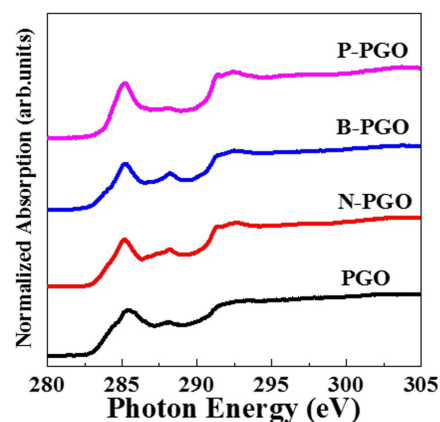

Figure 4 | C *K-edge* XAS spectra of PGO and those after doping.

nitrogen atoms were indeed incorporated into the lattice of those graphene-based nano carbon materials. The graphitic and pyridinic N species are the main N speices in the N-PGO[19,27]. Similarly, on the P 2p spectrum of P-PGO, the P-C species at 130.7 eV and P-O species at 132.5 eV were observed. The appearance of the major P-C peak at 130.7 eV suggests the incorporation of P species into the lattices[32,33]. For the B elements of B-PGO, three B species can be discriminated based on the analysis of B 1 s spectrum. The B-C$_4$ signal at 180.7 eV suggests the existence of B element at the boundaries or defects of the graphene sheets. B-C$_3$ signal at 189.6 eV is resulted from the B element incorporated into the lattices of the graphene sheets. The appearance of B-C-O signal at 192.3 eV is due to the residual O element in the PGO and the B precursors[22,34]. All these results demonstrate that microwave assisted doping is a simple and efficient method for the heteroatom dopants in the graphene sheet frameworks. In particular, the doping process can be completed in a very short time of several minutes.

Raman spectroscopy was also employed to investigate the doping process (Figure 6). As a control, the PGO was treated under the same microwave irradiation conditions for 3 minutes (denoted as PGO-3 min). Apparently, after the doping process, all the doped graphene-based carbon materials (N-PGO, P-PGO and B-PGO) presented a much higher I_D/I_G ratio than the PGO-3 min sample, indicating that the doping of heteroatoms in the graphene sheets created more defects[28,29]. Furthermore, the relatively high I_D/I_G ratio of B-PGO is consistent with the XPS results that most of the B atoms were located at the defected sites of the graphene sheets.

Based on these results, it is suggested that the reactions of doping and deoxygenization reduction occurred simultaneously. In order to verify this hypothesis, HPGO with much lower O content than that of PGO was used as a precursor for the same doping treatment to prepare the N-HPGO sample. XPS analysis suggests the N content in N-HPGO sample is only 1%, much less than that of N-PGO (2.7%), which confirms the simultaneous deoxygenization/doping hypothesis.

In this part, we reported an energy-efficient and rapid method for the preparation of N, B and P doped graphene materials. The contents of the doping elements in the final products are dependent on the O contents in the carbon precursors.

Catalytic capabilities of the graphene-based carbon materials. Recently, carbon materials have attracted many interests as the catalysts in the field of heterogeneous catalysis[35,36]. Among those efforts, graphene-based carbon materials have been reported as an efficient catalyst for the reduction of nitrobenzene reaction[18,37,38]. Herein, the reduction of nitrobenzene by hydrazine hydrate was selected as a probing reaction to evaluate the catalytic performance of each of the carbon materials prepared from the microwave irradiation.
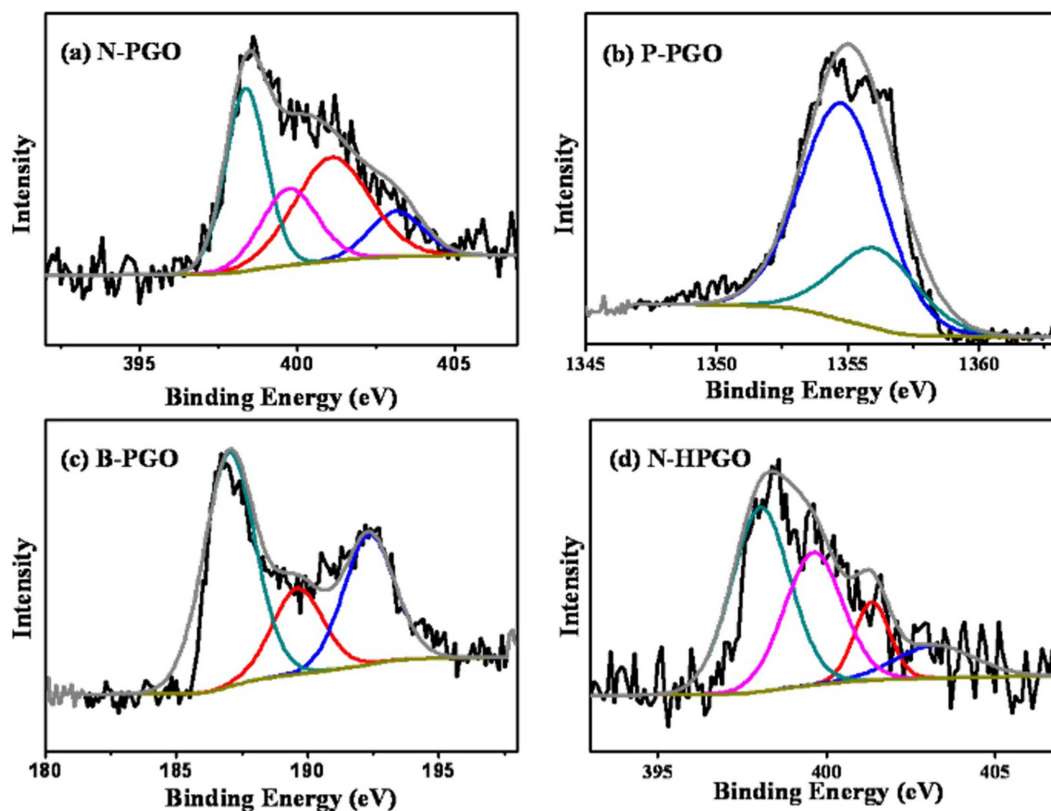
Figure 5 | XPS spectra of various nano-carbon materials; (a) N 1s spectrum of N-PGO; (b) P 2p spectrum of P-PGO; (c) B 1s spectrum of B-PGO; (d) N 1s spectrum of N-HPGO.

Graphene-based nano-carbon materials were found to be an efficient catalyst for the reduction of nitrobenzene, while the defects were believed to play an important role in the reaction[24]. Although graphene or graphene oxide is very active for the reaction[24], after microwave irradiation, PGO-3 min shows relatively low catalytic activity, possibly due to the decreased density of the defect sites. However, when heteroatoms were introduced into the framework of PGO, better catalytic performances were observed (Table 2, entries 1–3), suggesting that the doping elements improved the catalytic activity. Among those three catalysts, B-PGO material with the highest I_D/I_G ratio exhibited the highest catalytic activity, which also supported the proposal that the incorporated heteroatom-induced morphological and electronic structural changes make the material very active in the reaction[25].
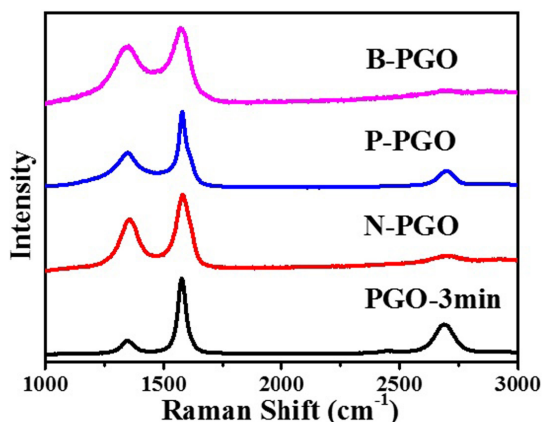
Conclusion

The microwave-adsorption behaviors of a series of graphene-based nano-carbon materials were investigated. Under microwave irradiation, structural, compositional changes as well as the alternation in the electrical conductivity of those nano-carbon materials (GO, PGO and HPGO) were observed. All those graphene-based nano-carbon materials have a strong coupling with the microwave field, and an extensive deoxygenization and light-emission phenomenon were observed under microwave irradiation. Based on the results obtained, a thermal deoxygenization reduction mechanism for those graphene-based nano-carbon materials was proposed. It is suggested that the microwave adsorption behaviors are in line with the different electrical conductivity of those materials. Significantly, under microwave irradiation, N, B and P can be introduced into the graphene lattice in a short period of three minutes, generating N/B/P doped graphene materials. This study discloses the microwave-adsorption behavior of graphene-based carbon materials, which may be used to facilitate the design and synthesis of the graphene-related carbon materials via this energy and time efficient microwave irradiation method.

Methods

Chemicals. The graphite (99.9%) was purchased from LiuMao graphite mine Company. All the other chemicals were commercially available, at least analytical reagent grade and were used without further purification. Sodium tetraphenyl boron and triphenyl phosphate were purchased from Alfa Aesar.

Characterizations. XRD patterns of the catalysts were recorded using a Rigaku D/max-2400 diffractometer with a Cu-Kα radiation source operating at 40 kV and 100 mA. TEM images were obtained with a Tecnai G220 S-Twin microscope operating at an accelerating voltage of 200 kV. The elemental analysis was performed on the Elementar Vario Micro Cube (Germany). Raman measurements were performed under ambient conditions using a 532 nm (2.33 eV) laser in the back-scattering configuration on a Jobin-Yvon HR800 Spectrometer. XPS spectra were obtained using an Axis Ultra spectrometer (Kratos, UK). A mono Al-Kα (1486.6 eV) X-ray source was used at a power of 225 W (15 kV, 15 mA). To compensate for

Figure 6 | Raman spectroscopy of various nano-carbon materials.

Table 2 | Reduction of nitrobenzene using the graphene-based carbon materials as catalysts

Entry	Catalysts	Conversion (%)	Yield (%)
1	N-PGO	52.6	48.4
2	P-PGO	77.6	72.9
3	B-PGO	>99	90.7
4	PGO-3min	38.6	35.6
5	Blank	13.5	10.5

Reaction Conditions: Hydrazine hydrate (85%) 2 mL, Temperature 90°C, Initial nitrobenzene 0.5 g, Catalyst 10 mg, 4 h in a 50 mL sealed pressure tube.

surface charge effects, binding energies were calibrated using the C 1s hydrocarbon peak at 284.8 eV. All the current-voltage curves were recorded with a Keithley 4200 semiconductor characterization system equipped with a four-electrode detector. All these carbon materials (50 mg) were pressed into a tablet with a diameter of 1 cm, and the thickness of these tablets varied according to their densities. Then the electrodes are inserted into the edges of this tablet to measure the I–V curves. Carbon K-edge NEXAFS experiments were performed in the "total electron-yield (TEY) mode" at the end station of soft X-ray beam-line U4B at the National Synchrotron Light Source (NSLS). These samples were uniformly spread over adhesive copper tape with sufficient thickness so no interference from the adhesive on the copper tape was expected. The tapes were then pasted on an aluminum bar placed in the UHV chamber with pressure lower than 10^{-8} Torr. The energy resolution in the NEXAFS measurements was about 0.2–0.4 eV depended on the edge. Data calibration and normalization were then analyzed using Athena software.

Synthesis of graphene-based nano-carbon materials. Graphite oxide (GO) was prepared using the modified Hummers' method (details in Supporting Information) and was reported elsewhere[18,19]. GO powder was heated to 523 K at 20 K/min to get pyrolytic graphene oxide (PGO). PGO was heated and treated at 1123 K under H_2 atmosphere (80 mL/min) for 8 h to get hydrogen-reduced pyrolytic graphene oxide (HPGO).

Microwave irradiation experiments. The microwave oven used in this article is a commercially available Panasonic NN-GD576M microwave oven. The microwave output of this oven is at 1 kW and 2450 MHz. A full powder is used for every microwave irradiation experiments. All the microwave irradiation experiments were conducted in a microwave oven. For each sample, 40–60 mg graphene-based carbon materials were stuffed into a small quartz tube (1 cm in diameter and 10 cm in length). The tube was sealed by quartz wool and put into a 50 mL quartz bottle. Before each microwave experiment, the bottle was flushed with 200 mL/min N_2 (>99.999%) flow for 15 min in order to create an inert atmosphere. In a typical experiment, a 100% irradiation power and a 1 min treatment period were used. After the microwave irradiation, the products of GO, PGO and HPGO are denoted as GO-1 min, PGO-1 min and HPGO-1 min, respectively.

In contrast, for the doping process, the sample was rotated at the center of the turntable to obtain a uniform microwave exposure. A 100% irradiation power and a 3-min treatment period were used. For the N-doping process, the PGO or HPGO was used as the carbon precursors. The bottle was flushed with N_2 flow followed with 100 mL/min NH_3 flow (>99%) for 10 min. For the B and P-doping processes, the PGO was used as the precursor. Considering the toxicity of the gaseous B and P compounds such as B_2H_6 and PH_3, sodium tetraphenyl boron and triphenyl phosphate were chosen because of their easy accessibility and high solubility in ethanol. After these precursors were dissolved in ethanol, an incipient impregnation method was used for a homogeneous dispersion of the B and P elements on the PGO substrate. The mixture was then dried at 333 K to obtain a mixture containing 15% B or P. The mixture was irradiated by microwave at the center of the turntable for 3 min under a 100% irradiation powder. The obtained doped PGO materials were denoted as N-PGO, B-PGO and P-PGO.

Catalytic reactions. The nitrobenzene reduction reaction was carried out in a sealed pressure tube at 363 K for 4 h. For each reaction, 0.5 g nitrobenzene and 2 mL hydrazine hydrate (85%) were used as the reactants, and 10 mg carbon materials was used as the catalyst. After the reaction, 0.1 g dodecane and 6 mL CH_2Cl_2 were added into the tube as the internal standard and extraction liquid, respectively. Upon removal of the catalyst, the mixture was analyzed by Agilent GC 7820A equipped with a HP-innowax column and a FID detector.

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Author contributions

P.T. and D.M. designed and performed the experiments. S.Y.Y. and Z.Y.L. performed the EXANF experiments and discussed the results. G.H., Y.J.G. and W.J.L. helped to analyze the results and write the manuscripts.

Additional information

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