

A direct phase separation approach synthesis of hierarchically porous functional carbon as an advanced electrocatalyst for oxygen reduction reaction



Jutao Jin ^{a, b}, Lingzheng Gu ^a, Luhua Jiang ^a, Jing Liu ^a, Gongquan Sun ^{a, b, *}

^a Laboratory of Fuel Cell, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, People's Republic of China

^b Dongguan University of Technology, School of Environment and Architecture, People's Republic of China

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ABSTRACT

Heteroatom-doped hierarchically porous carbon materials have attracted great research interests for applications in both energy conversion and storage devices. Rational constructing the architecture, selecting heteroatoms and tuning their bonding structure are keys for the synthesis of high performance carbon based electrode. Here we develop a phase separation approach for the synthesis of a novel porous exfoliated carbon block. Our protocol allows for simultaneous formation of exfoliated porous structure and heteroatom doping through a simple pyrolysis process. The as obtained sample is composed of graphene-like carbon layers, which are enriched with nitrogen dopants in the basal plane and phosphorus functional groups at the carbon edge. The particular structure and surface chemistry of the sample endow the materials with high catalytic properties for oxygen reduction reaction (ORR). On the one hand, the opened-edge thin carbon layers form open channels for efficient mass and ion transportation; On the other hand, the heteroatom dopants and functional groups change the surface chemistry and thus the electronic structure and the surface wettability of the host materials, further enhancing the intrinsic electrochemical performance of the carbon material.

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1. Introduction

Electrochemical energy storage and conversion devices are at the heart of renewable-energy technologies, and efficient active electrodes based on abundant and low cost materials are essential for the practical applications of these technologies [1–3]. Carbon nanomaterials, including porous carbon, graphene and carbon nanotube, represent attractive advanced materials finding a wide-spectrum potential applications in the field of energy storage and conversion, e.g., lithium ion battery [4–7], supercapacitors [8–10] and fuel cells [11–13], owing to their high stability, high specific surface area as well as excellent electron conductivity. However, the ever-increasing demand of renewable energy requires more efficient and reliable electrochemical devices for energy storage and conversion, which in turn presents new challenges to the

fundamental electrode materials [3,14–19]. In principle, an electrochemical electrode could achieve an improved performance by combining large accessible surface area for electrochemical reactants, high intrinsic electrochemical properties, short ion and electron transfer distance. To this end, great efforts have been focused on the synthesis of novel carbon materials with controlled architecture and desired heteroatom dopants. [12,19–23].

Recently, various hierarchically porous carbons using 2D graphene layers as building blocks have been successfully synthesized. Benefitting from the pore structure controlling and the surface chemistry tuning, they show excellent performance for energy storage and conversion [24–28]. Generally, most of these porous carbons are synthesized by a two-step method: formation of porous structure with a template and then tuning the surface chemistry in a subsequent post treatment step [24,29]. Normally, the porous graphene nanostructures are mainly produced through CVD method using a porous metal as both catalyst and template [30,31] or a template mediated assembly method using graphene oxide as the building unit [32,33]. However, most of these methods are suffered from complicated multistep synthesis as well as potential use of harmful chemicals for the removal of the template. On

* Corresponding author. Laboratory of Fuel Cell, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, People's Republic of China.

E-mail address: gqsun@dicp.ac.cn (G. Sun).

the other hand, the subsequent heat treatment to tune the surface chemistry of carbon materials is also a big challenge. Although various elements, including B, N, S and P etc, have been successfully incorporated into the sp_2 grid lattice, the intrinsic performances of these heteroatoms-doped carbons are largely depended on the category of dopants, the dopant concentration and their bonding environment in the carbon lattice [34–36]. In fact, some dopants only have detrimental effects when doped into the carbon lattice, such as reducing the stability or harming the electron conductivity of the host material. Thus, the direct synthesis of porous graphene nanostructure with desired doping heteroatoms by a scalable method is still a challenge.

Herein, we present a direct phase separation approach to synthesize nitrogen and phosphorus binary doped porous carbon blocks by using melamine, phosphoric acid and glucose as precursor. Our protocol allows for simultaneously tuning the surface chemistry and forming porous structure through a facile and scalable method. Simply, the melamine and glucose molecular are firstly dissolved in water, and then they are coprecipitated with phosphoric acid from water to form a solid organic-inorganic crystal: glucose-melamine-pyrophosphate salt. Upon heat treatment, the glucose-melamine-pyrophosphate phase is transformed into two intercalated layer phases at a moderate temperature: a phosphocarbonaceous phase and a carbon nitride phase, in a lamellar arrangement. When subjected to a higher temperature treatment, the carbon nitride phase was pyrolyzed and the phosphate species were detached from the phosphocarbonaceous phase, leaving a porous exfoliated carbon block. The carbon nitride phase and phosphate species serve as two dimensional templates and molecular templates, respectively, during the formation of the porous exfoliated carbon block. Furthermore, the nitrogen rich species from pyrolyzed products of carbon nitride and the phosphate species from phosphocarbonaceous phase can further afford nitrogen and phosphorus sources for heteroatom doping during the high temperature annealing process. The N dopants can be doped into the carbon lattice, while P dopants are mainly at graphite edge in form of phosphorus functional groups. The as obtained porous carbon blocks, composed of interconnected exfoliated carbon layers, show a high specific surface area and afford open channels for mass transportation. The particular porous structure and the surface chemistry of the exfoliated carbon block endow the materials excellent performance for both energy conversion (ORR) and storage (supercapacitor). The synthesis method is general and can be easily extended for the synthesis of S, N- or B, N- doped porous carbon sheets by simply replacing the glucose-melamine-pyrophosphate salt with glucose-melamine-sulphate and glucose-melamine-borate salt, respectively. We expect that this work would pave a new way to synthesize porous functional carbon materials.

2. Experimental section

2.1. Sample preparation

To prepare P/N co-doped functional exfoliated carbon, glucose (0.2 g), melamine (5.3 g) was dissolved in deionized water (300 mL) at 95 °C by stirring for 30 min. Then phosphoric acid (1.43 mL, 85 wt %) was added to the above solution drop by drop and melamine/pyrophosphate salt precipitated quickly from the transparent solution to form a sticky mixture. Subsequently, the mixture was vacuum-dried using a rotary evaporator to get a white solid powder. Finally, the as-obtained white samples were subjected to annealing under N_2 atmosphere with different temperature varying from 450 to 1050 °C with a heating rate of 5 °C min⁻¹ and kept at the final temperature for 2 h. The corresponding samples were

labeled as G-P/N-T (where T refers to the annealing temperature). Before heating, the furnace was pumped with rotary pump and washed with N_2 three times to remove oxygen in the tube furnace. For comparison, physical mixture of melamine/glucose was also subjected the same annealing procedure and the corresponding sample was labeled as G-N-T.

2.2. Sample characterizations

TEM and HRTEM images were collected on a JEM-2100 transmission electron microscope; SEM images were recorded on a JSM-7800F scanning electron microscope; X-ray photoelectron spectroscopy (XPS) of the catalysts was acquired on ESCA-LAB-250Xi XPS instrument using a Al K α X-ray source; Raman spectra were collected with a LabRAM HR800 Raman spectrometer with a 514.5 nm Ar laser as the excitation source. XRD patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$). FT-IR spectroscopy was made in transmittance mode on samples embedded in KBr pellets on a Avatar370FTIR spectrometer. Thermo-gravimetric analysis (TGA) was performed on a SDT-Q600 analyser over the temperature range 25–900 °C at a heating rate of 5 °C min⁻¹ and under flowing N_2 (50 mL min⁻¹). Nitrogen sorption isotherms were measured at 77 K using a NOVA2000e analyser.

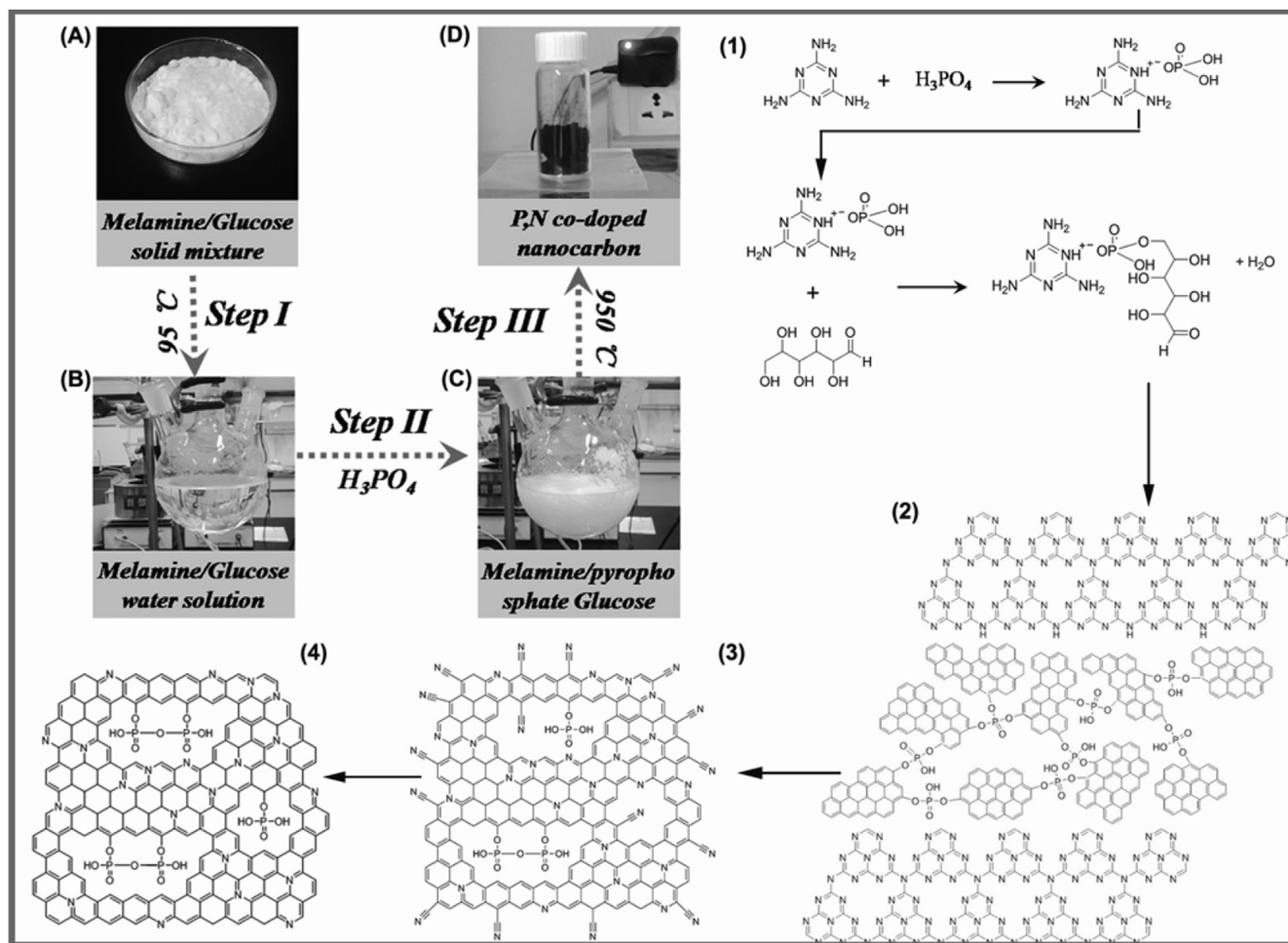
2.3. Electrochemical measurements

To evaluate the electrochemical performance of the as-synthesized samples, thin electrode films were prepared by a simple procedure as follows: Firstly, 4 mg of sample powders were dispersed to 1 mL 0.5 wt % Nafion ethanol solution by at least 60 min sonication to form a homogeneous suspension. Then, 10 μ L of the sample ink was spin coated onto a glassy carbon electrode of 5 mm in diameter at a rotating rate of 500 rpm. The sample was dried at room temperature to form a homogeneous thin film electrode with a mass loading of 0.204 mg cm⁻². The electrode performance was evaluated with a CHI 760C workstation. To evaluate the ORR performance, we conducted both cyclic voltammograms and linear sweep voltammetry in 0.1 mol L⁻¹ NaOH saturated and protected by O_2 . MMO(0.1 M NaOH) and platinum wire served as the reference and counter electrodes, respectively. For comparison, commercially available platinum-loaded carbon black, i.e., Pt/C (with Pt loading of 20%, Johnson Matthey) was also used to conduct the same electrochemical test. The capacitance performances of all the samples were evaluated in both two-electrode and three-electrode systems. For a two electrode measurement, two symmetry electrodes were immersed into a container containing 6 mol L⁻¹ NaOH solution, with a distance of 15 mm between the centers. For a three electrode measurement, MMO(6 M NaOH) and platinum wire served as the reference and counter electrodes, respectively. All experimental were conducted at room temperature (25 °C).

3. Results and discussion

3.1. Materials characterization

The process for the synthesis of hierarchically porous P/N co-doped carbon, as schematically illustrated in Scheme 1, includes the fabrication of glucose-melamine-pyrophosphate salt precursor and subsequent carbonization by high temperature annealing under a N_2 atmosphere (see Experimental Section for details of the synthesis). For simple, the sample were labeled as G-P/N-T according to the synthesis temperature varying from 400 to 1050 °C. (Where T refers to the annealing temperature) For comparison, the



Scheme 1. Schematic illustration of the synthesis of G-P/N samples (A–D) and corresponding the carbonization mechanism (1–4).

sample without adding phosphoric acid was also synthesized and labeled as G-N-T.

The morphology and microstructure of the as-prepared samples were first investigated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. Fig. 1a is the low resolution SEM image of the representative G-P/N-950 sample, showing a flat block morphology. The high resolution SEM image reveals that these carbon blocks are composed of opened-edge graphene-sheet like carbon layers (Fig. 1b). Further TEM image (Fig. 1c) indicates that these thin carbon layers are made up of cross-linked fragment networks. The high resolution TEM image indicates (Fig. 1d) that these entangled thin carbon layers are about 1.5–3.5 nm in thickness, corresponding 4–10 layers of graphene sheets. The layer distance of these entangled wrinkles is about 0.34 nm, a little larger than that of the well crystal graphite phase. For comparison, the sample of G-N-950 without adding phosphoric acid in the precursor also shows graphene-sheet like appearance, but they arranged randomly (Fig. S1). Raman spectroscopy was further used to analyze the structure of the as obtained samples (Fig. S2). The G-P/N-950 sample shows the typical graphite G resonances at about 1585 cm^{-1} , along with a strong D band at 1360 cm^{-1} , indicating a high defect density in the sp^2 hybrid phase. Samples synthesized at different temperature shows identical Raman spectra features, but the intensity ratio of D band to G band (I_D/I_G) varies with the synthesis temperature. The sample of G-P/N-750 and G-P/N-950, synthesized at low temperature and high temperature, shows higher I_D/I_G ratio compared with G-P/N-850

prepared at mediated temperature, suggesting more disordered structure of G-P/N-750 and G-P/N-950. For sample G-P/N-750, the disordered structure may originate from the amorphous carbon phase owing to the low synthesis temperature. While for sample G-P/N-950, the disordered structure may mainly comes from the edge carbon or the lattice defects induced by phosphorus acid etching at ultra high temperature. For comparison, the sample G-N-950 synthesized without adding phosphorus acid in the precursor shows a lower I_D/I_G ratio when compared with the sample G-P/N-950, confirming the phosphorus acid etching effect at high temperature. Nitrogen adsorption-desorption tests were conducted to examine the textural properties of the G-P/N-T sample and the results were summarized in Table 1. As shown in Fig. 1e, obvious hysteresis loops appear for both sample G-P/N-950 and G-N-950, suggesting the mesoporous nature of these samples. The specific surface area and pore structure were calculated by Brunauer–Emmett–Teller (BET) and Density Functional Theory (DFT) methods, respectively. The sample G-P/N-950 shows a BET surface area of $1440\text{ m}^2\text{ g}^{-1}$ and a pore distribution concentrated at 4.5 nm, compared with BET surface area of $550\text{ m}^2\text{ g}^{-1}$ and a widely distributed pore structure from 5 to 25 nm for G-N-950, indicating the role of phosphoric acid etching for the formation of porous G-P/N-950 sample [37,38]. The pore structure and specific surface area of sample synthesized at lower temperature are also analyzed (Fig. S3).

The elemental compositions and their chemical bonding configurations were investigated via X-ray spectroscopy (XPS). The XPS spectra show the presence of P, C, N and O in G-P/N-950 sample

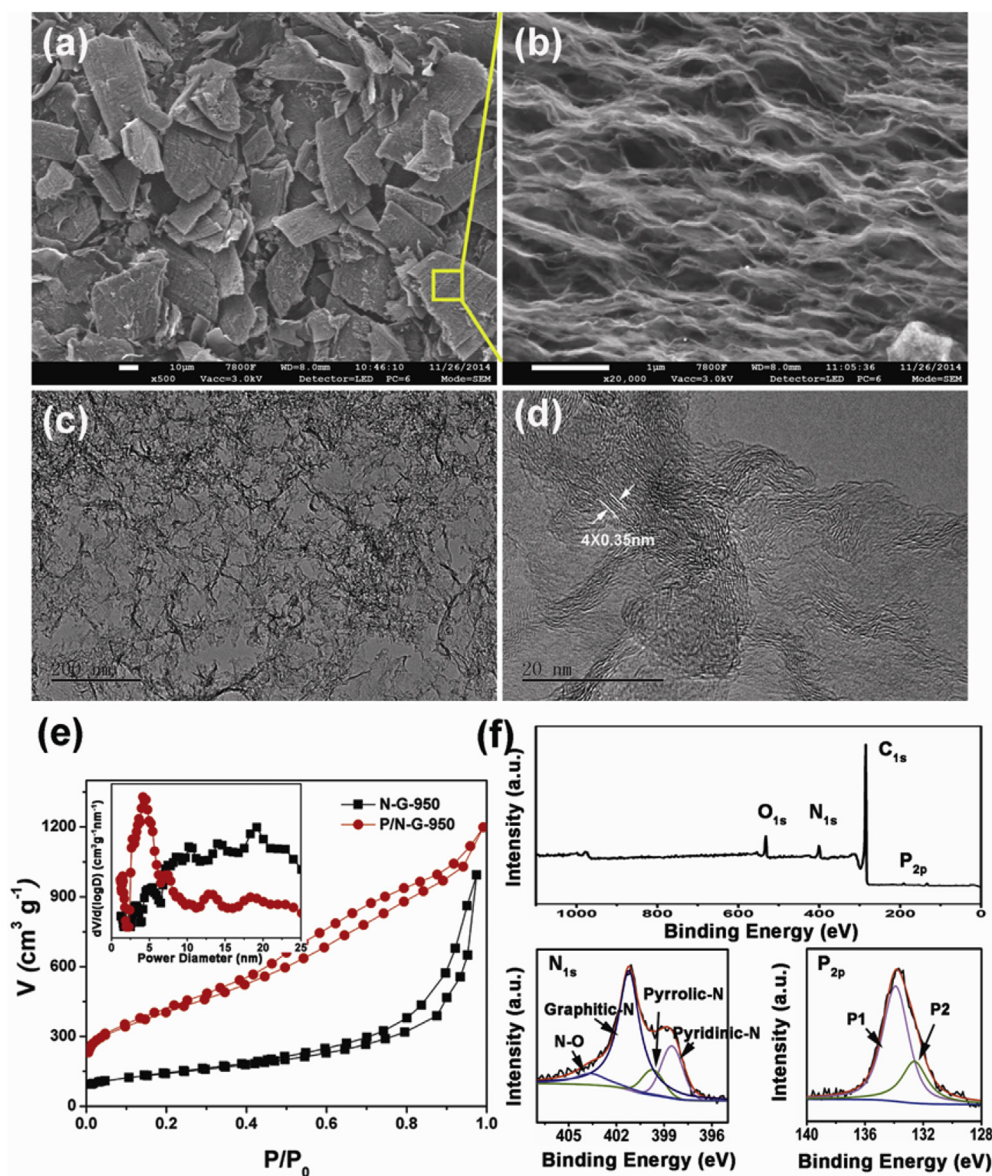


Fig. 1. Structural and compositional analysis of as prepared samples. (a, b) SEM images of G-P/N-950 (a) Low resolution SEM image showing the carbon block morphology (b) high resolution SEM image showing the vertically aligned graphene-like layers. (c, d) TEM images of G-P/N-950 (c) Low resolution TEM image exhibiting wrinkles and pores of the graphene-like layers (d) high resolution TEM image showing the lattice distance and layer thickness of the graphene-like layers. (e) N_2 adsorption/desorption isotherms of G-P/N-950 and G-N-950 (the inset showing the corresponding pore distribution). (f) XPS survey spectra and high resolution N 1s and P 2p spectra of G-P/N-950. (A colour version of this figure can be viewed online.)

Table 1

Texture properties and surface chemistry of as synthesized samples.

Sample	Texture properties			Surface chemistry			
	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	D_p (nm)	C (at.%)	N (at.%)	P (at.%)	O (at.%)
G-P/N-650	36	0.058	2.8	—	—	—	—
G-P/N-750	39	0.054	4	25.67	32.74	24.38	17.21
G-P/N-850	561	0.946	10	31.95	32.66	18.23	17.16
G-P/N-950	1440	1.622	4	85.88	6.13	1.48	6.51
G-N-950	497	1.267	19	89.51	4.02	—	6.47

(Fig. 1f). The compositions of sample synthesized at other temperature were also analyzed (Fig. S4) and listed in Table 1. For sample G-P/N-950, the content of each element are 1.47 at.% P, 6.13 at.% N, 6.51 at.% O. While for sample G-P/N-850 and G-P/N-750 synthesized lower temperature, the corresponding P, N, O elements

content are much higher (18.23 at.% P, 32.66 at.% N, 17.16 at.% O for sample G-P/N-850 and 24.38 at.% P, 32.74 at.% N, 17.21 at.% O for sample G-P/N-750). These results demonstrate that P, N, O elements remain stable at temperature up to 850 °C, but most of them become unstable and are broken out of carbon lattice at

temperature above 950 °C. The bonding configurations of nitrogen in G-P/N-T were further studied on the basis of high-resolution XPS spectra. As shown in Fig. 1f, four types of nitrogen, pyridinic N–C (398.3 eV), pyrrolic-N–C (399.8 eV), graphitic-N (400.9 eV), and oxidic-N (402.9 eV), are present in sample G-P/N-950. For sample G-P/N-950, the graphitic-N (63.1%) is dominant among these four types of N in carbon lattice. While for samples synthesized at lower temperature, pyridinic N–C (398.3 eV) is the main type N structure (Fig. S5). In fact, the graphitic-N, referring to the nitrogen bonding to three carbon atoms in the plane of the graphene matrix, is more stable than pyridinic N–C that bonds to two carbon at edge [39]. When subjected to high temperature annealing, the pyridinic N–C is more feasible to be broken out off the carbon lattice or transferred to more stable graphitic-N [39]. The detailed P spectroscopy was also depicted in Fig. 1f. The P_{2p} can be deconvoluted into two components, centered at 132.3 and 134.2 eV, respectively. The component with band centered at 132.3 eV is attributed to pentavalent tetra coordinated phosphate (PO_4). While the main band centered at 134.2 eV is attributed to P in a higher oxidation state, referring to pyrophosphate groups (PO_3)_n [38]. Notably, No C–P bonding signal (centered at 130 eV) appears [40], suggesting that P atoms are not doped into the graphite lattice but in the form of functional phosphorus groups at the edge site.

3.2. Carbonization analysis

To investigate the carbonization mechanism of G-P/N, the morphology and structure evolution process of the precursor during the annealing process were characterized and shown in Fig. 2. The sample directly precipitated from the solution shows an irregular cubic morphology, and the XRD diffraction patterns confirm the presence of glucose-melamine-pyrophosphate phase (Fig. 2a). After annealing the sample at 400 °C for 2 h, new diffraction peaks besides the patterns of melamine-pyrophosphate appears (Fig. 2b), suggesting the presence of new phases during the annealing process. Thermal analysis results also shows a large endothermic peak at 390 °C, associated with a weight loss of 10% in the range of 370–400 °C (Fig. S6). We propose that microphase separation may occur at this stage, which the melamine segment in glucose-melamine-pyrophosphate phase starts to polymerize to form a carbon nitride phase. The new patterns in the XRD spectra can be ascribed to this phase. At the same time, the carbon rich glucose segments start to carbonize with the help of phosphorus acid to form an amorphous phosphocarbonaceous phase [41,42]. As the temperature increased to 500 °C, the diffraction patterns of melamine-pyrophosphate crystal completely disappeared (Fig. 2c). However, the SEM image shows the presence of homogeneous cubic morphology, instead of separated carbon nitride and carbon particles. We propose that these two phases are intercalated with each other in a lamellar arrangement in the micro-range. Further increasing the temperature above 600 °C, $g-C_3N_4$ becomes unstable and gradually disappears, leaving exfoliated porous carbon layers (Fig. 2e,f). Thermal analysis also shows a sharp weight loss of 18% at this stage, along with a weak endothermic peak at 550 °C.

The evolution of the surface species of the G-P/N samples during annealing process was also characterized by FT-IR. As shown in Fig. 3, the sample obtained at 600 °C shows a typical C–N heterocyclic stretches of $g-C_3N_4$ in the 1100–1600 cm^{-1} region, consistent with the XRD result. The broad band centered at 2180 cm^{-1} can be assigned to nitrile $C\equiv N$ or azide $N\equiv N$ stretching, which is kept up to 800 °C [43]. When increasing the temperature above 600 °C, the typical stretches fingers of $g-C_3N_4$ disappears. Instead, two new broad bands centered at 940 and 1240 cm^{-1} appear. The band centered at 940 cm^{-1} is attributed to the modes of symmetric vibrations of PO_2 and PO_3 . While the band centered at 1240 cm^{-1} can

be assigned to P–O–C bonds. These results together confirm the presence of “phosphatecarbon” complexes during the synthesis process. It should be noted that these phosphocarbonaceous structure may form at lower temperature [42], but their spectra are overlapped with the strong C–N bands at the same region. Further increasing temperature above 850 °C, the spectra of these phosphocarbonaceous structure become very weak, demonstrating that these phosphocarbonaceous phase became unstable and the phosphorus species may detach from the carbon phase. The detachment of phosphorus species in the carbon phase can create rich pores in the carbon phase, which largely improve their specific area to 1440 $m^2 g^{-1}$ for sample G-P/N-950, compared that of 561 and 39 $m^2 g^{-1}$ for sample G-P/N-850 and G-P/N-650, respectively (Fig. S3). The presence of an obvious endothermic peak centered at 850 °C further confirms the changes of the structure at this temperature. In fact, although most of phosphate species may detach from the host carbon material, the XPS results still show the presence of phosphate species at temperature up to 1000 °C, suggesting there are still phosphate functional species at the edge site of carbon materials at such a high temperature.

Drawn from the above results, a carbonization mechanism for the formation of exfoliated P/N-PG is illustrated in Scheme 1:

Stage I: At low temperature (<600 °C), a microphase separation transformation happens, which the glucose-melamine-pyrophosphate was decomposed to release melamine and acidic species slowly. The decomposition products, melamine, can polymerize into layered carbon nitride at relatively higher temperature (450–600 °C). These carbon nitrides afford template and confined nanospace for the carbonization of glucose. The glucose are mainly transformed to small aromatic molecules and (or) carbonaceous segments, which are bridged by phosphate species and confined between carbon nitride layers. Stage II: At medium temperature (600–800 °C), the small aromatic molecules and (or) carbon segments are condensed to form large graphite layers. The phosphate functional groups at the carbon edge can suppress the graphitization of the graphite layers and create pore structures in graphite layers. At this temperature, the carbon nitride polymer become unstable and is pyrolyzed to create nitrogen rich species for nitrogen doping. Stage III: At high temperature (>900 °C), the unstable phosphate species are detached from carbon lattice, creating rich pores in the carbon layers. Meanwhile, the unstable nitrogen species, including nitrile-N, pyrrolic-N and pyridinic-N are either removed from carbon lattice or transformed to more stable graphitic-N structure.

3.3. Electrochemical performances

To investigate the ORR performance, the as synthesized materials were first drop-cast onto the glassy carbon electrode (196 $\mu g cm^{-2}$) for cyclic voltammograms (CV) and rotating-disk electrode (RDE) in N_2 - and O_2 -saturated 0.1 M NaOH, respectively. Samples treated with different temperature were compared with the commercial Pt/C electrocatalyst. (20 wt% Pt/C, Johnson Matthey). As shown in Fig. 4a, the samples G-N-950, G-P/N-950 and Pt/C show negligible reduction peaks (dash line) in N_2 saturated solution (Fig. 4a). In the presence of O_2 , an obvious reduction peak centered at different voltage appear, suggesting the intrinsic catalytic performance of these catalysts for oxygen reduction reaction (ORR). The onset potential (E_0) and half-wave potential ($E_{1/2}$), which reflects the intrinsic catalytic performance of an electrocatalyst [44,45], were got from RDE curves and the results were compared (Fig. 4b). The best catalytic activity was obtained from

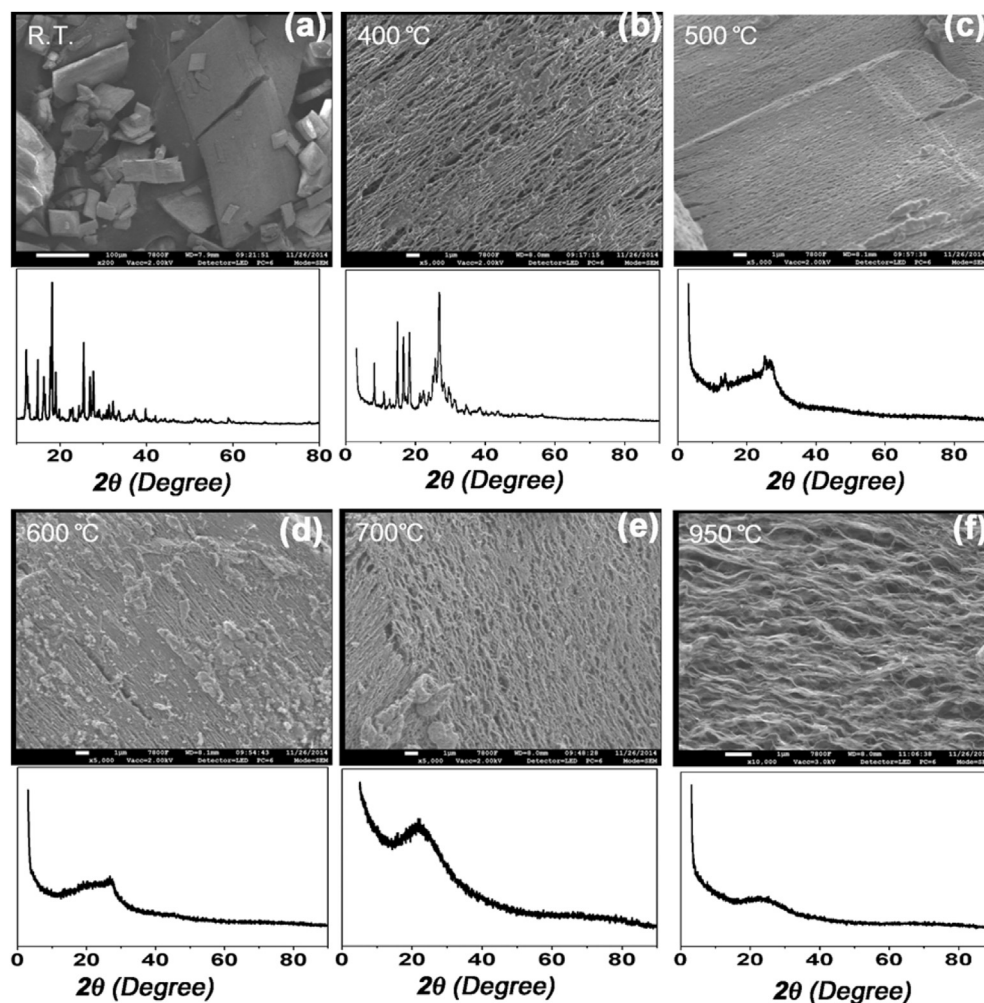


Fig. 2. The morphology and XRD pattern of melamine/pyrophosphate salt and glucose mixture annealing at temperature varied from room temperature to 950 °C.

sample G-N-950, which has an onset potential and half-wave potential of 0.98 and 0.81 V, respectively. The result is just about 50 mV negative than that of Pt/C electrocatalyst. Sharp drops of the ORR activities were observed for samples treated at temperature 850 °C and below. Specially, the sample G-N-950 synthesized without adding phosphoric acid also shows inferior catalytic activity when compared with G-P/N-950 sample, suggesting the role of phosphorus functional groups in host materials in improving the catalytic performance.

To further reveal the ORR kinetics of the samples, RDE measurements at varied rotation rate were carried out. Fig. 4c shows the rotating disk voltammograms of oxygen reduction recorded at the G-P/N-950/GC electrode in 0.1 M NaOH with the rotating rate varied from 400 to 2500 rpm. An obvious diffusion current platform, a feature of the high quality ORR electrocatalyst, appears at all rotating rate for sample G-P/N-950. The corresponding Koutecky-Levich plots are linear at potential varied from 0.5 to 0.85 V (Fig. 4d), suggesting the first order reaction kinetics with respect to the concentration of dissolved O_2 . Two important kinetic parameters, charge transfer number (n) and kinetic-limiting current density (J_k), are calculated from the slope and the reciprocal of the intercept of the K-L plots, respectively (See supporting information for the details of the calculation of J_k and n). The J_k value of G-P/N-950 calculated at 0.6 V is 18.24 mA cm^{-2} , compared with 20.22 mA cm^{-2} for Pt/C catalyst. G-P/N-850 and G-P/N-750 show much lower value of 8.53 and 2.83 mA cm^{-2} at the same potential,

indicating their inferior ORR performance. The n value reaches 3.7 at potential lower than 0.7 V for sample G-P/N-950, suggesting a mainly four electron process was involved in the ORR process. While for sample G-P/N-850 and G-P/N-750, the n value are about 3.0 and 2.3 in the same potential range, indicating mainly 2 e process on these catalysts (Fig. S8). To further reveal the ORR kinetics of the synthesized samples, the tafel plots were got by calculating the J_k value in the potential range from kinetic controlled range to mixed kinetic and diffusion controlled range (Fig. 4e). The tafel slope is 72 mV Dec^{-1} for sample G-P/N-950, just a slight larger than that of Pt/C (65 mV Dec^{-1}). G-N-950 and G-P/N-850 samples show similar tafel slope as Pt/C catalyst, but present much higher overpotential. While sample G-P/N-750 shows a tafel plot as high as 95 mV Dec^{-1} , indicating a completely different reaction process during ORR.

The performance differences can be assigned to the surface chemistry differences of these samples. From the above results, we observed that the dopants structure of the synthesized samples were sensitive to the annealing temperature. The phosphorus species are mainly in the form of phosphocarbonaceous at temperature below 850 °C. While at higher temperature, these phosphocarbonaceous species were broken, leaving rich lattice defects and phosphorus functional groups at carbon edge. For nitrogen species, they are mainly in pyridine or nitrile form for sample synthesized at low temperature. Whereas these nitrogen species are transformed into mainly graphitic form at temperature above 950 °C. The

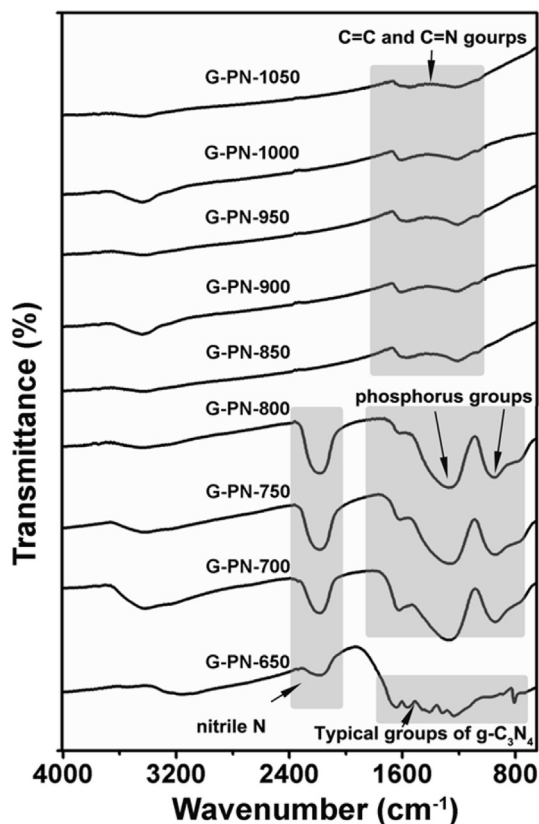


Fig. 3. FTIR spectra of synthetic G-P/N samples obtained at temperature varied from 650 to 1050 °C.

superior catalytic activity of sample G-P/N-950 may mainly originate from the special dopant structure of phosphorus and nitrogen species in the host carbon matrix. On one hand, the graphitic-N, which contributes two π electron to the carbon lattice, was reported to be the most active and stable nitrogen specie for ORR among all the nitrogen species [35,46]. On one hand, the abundant lattice defects and phosphorus functional groups at carbon edge can create new localized electronic states, which are beneficial for the adsorption of oxygen molecular at low temperature. Furthermore, the presence of phosphorus functional groups can also improve the surface wettability of the sample. Combining with its porous structure of the opened-edge carbon layers, it can significantly extend the active electrochemical reaction area for ORR.

The cross-over effect of our catalyst and Pt/C catalyst against the methanol oxidation in O_2 saturated 0.1 M NaOH in the presence of methanol (1.0 M) was also investigated. As shown in Fig. 4f, in the presence of methanol, a sharp performance loss for ORR along with an obvious oxidation peak, can be observed for Pt/C electrocatalyst. Whereas for G-P/N-950 sample, negligible current change was seen under the same experimental conditions, indicating high selectivity and good stability of G-P/N-950 for the ORR compared with Pt/C. To test the electrocatalyst long term stability, the chronoamperometric test of the G-P/N-950 was conducted with the electrode potential hold at 0.5 V in alkaline solution. The result showed that 87% current density was reserved after operation for 24 h, indicating its long-term stability as an ORR electrocatalyst in alkaline solution (Fig. S9).

4. Conclusions

In conclusion, we have designed an effective route to synthesize a novel functional porous carbon block via a “phase

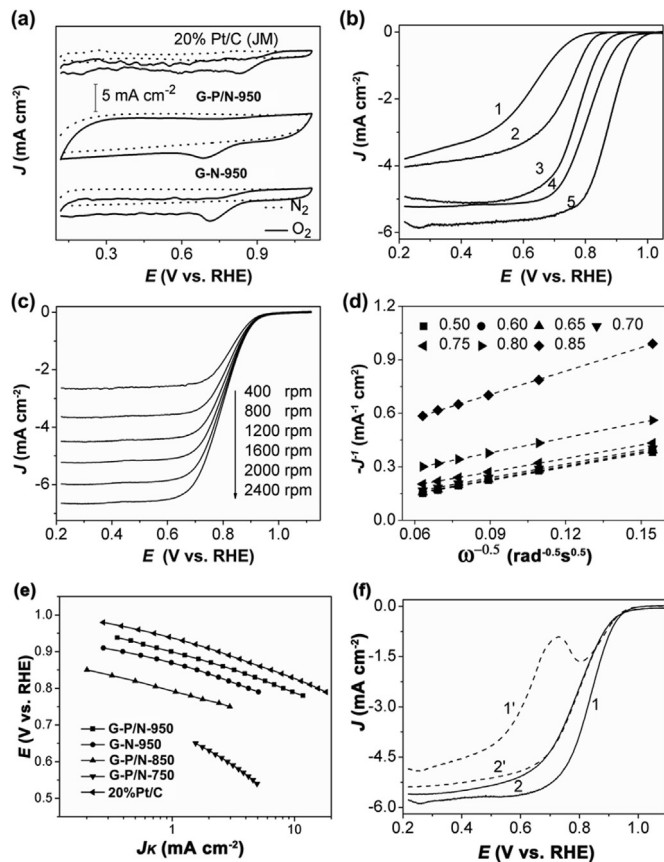


Fig. 4. Electrochemical performance of obtained samples. (a) CVs of G-P/N-950, G-N-950 and 20% Pt/C on glassy carbon electrodes in O_2 -saturated (solid line) or N_2 -saturated 0.1 M NaOH (dash line). (b) LSVs of ORR in an O_2 -saturated 0.1 M NaOH solution at a scan rate of 5 mV^{-1} at rotating rate of 1600 rpm (1: G-P/N-750, 2: G-P/N-850, 3: G-N-950, 4: G-P/N-950, 5: 20%Pt/C (JM)). (c) LSVs of G-P/N-950 at various rotating rate and (d) the corresponding Koutecky–Levich plots (j^{-1} versus $\omega^{-0.5}$) at different potentials. (e) Tafel plots of the obtained samples derived by the mass-transport correction of corresponding RDE data (see details in supporting information) (f) ORR LSVs of G-P/N-950 and 20%Pt/C before (solid) and after (dash) the addition of methanol in 0.1 M NaOH (1, 1': 20%Pt/C; 2, 2': G-P/N-950).

separation” method without using any template or catalyst. The carbonization process of the precursors was carefully examined. During the annealing process, the precursor of glucose-melamine-phosphate salt was separated into two intercalated phases: carbon nitride polymer and phosphocarbonaceous phase. And subsequently at higher annealing temperature, the carbon nitride polymer phase was pyrolyzed and most phosphorus groups were detached from the carbon lattice, leaving porous exfoliated carbon blocks. Specially, the exfoliated carbon block is enriched with nitrogen dopants in the basal plane and phosphorus functional groups at the edge of graphene lattice. The particular structure and surface chemistry of the sample endows the materials with high catalytic properties for oxygen reduction reaction (ORR). We expect this work would provide valuable support for the mass production of functional carbon nanomaterials for energy storage and conversion.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.carbon.2016.07.037>.

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