



# One-pot solvothermal synthesis of doped graphene with the designed nitrogen type used as a Pt support for fuel cells

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## ABSTRACT

Nanoflower-like, nitrogen-doped graphene (NG) with pure  $sp^2$  hybridized carbon and designed nitrogen types was synthesized by a low temperature solvothermal process. HRTEM results indicated that the product consists of many NG sheets with about 6–10 graphitic layers. Electrochemical test showed that NG has a much higher durability as a Pt support for fuel cells than commercial carbon black (Vulcan XC-72). The possible reasons have been analyzed based on the physical and chemical characterization.

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## 1. Introduction

Polymer electrolyte membrane (PEM) fuel cells can both be a high-efficiency and environmentally friendly power sources. One of the most challenging problems facing PEMFCs is the development of cost-effective, highly active, and durable electrocatalysts. Currently, the most promising electrocatalysts are still Pt nanoparticles supported on porous carbon (Pt/C), but the corrosion of carbon leads to the agglomeration and/or detachment of Pt nanoparticles from the support materials and in turn degrades the fuel cell performance [1]. Recently, much effort has been devoted to the durability issues of support materials, which demonstrates that the extent of graphitization of the carbon plays an important role in carbon support stability; more graphitic carbons are more thermally and electrochemically stable [2–5].

Graphene is really a highly graphitized carbon support with a unique graphitized basal plane [6]. Shao et al. reported that graphene is a promising and durable electrocatalyst support for oxygen reduction in fuel cells [7]. However, there are fewer active sites for highly graphitized carbon support, which makes Pt deposition difficult. One solution to the problem is to dope nitrogen atoms to the carbon frameworks. Our previous results have indicated that Pt nanoparticles can be more uniformly deposited on nitrogen-doped carbon nanotubes ( $CN_x$ ) than on pristine carbon nanotubes, due to the higher wettability, additional surface structural defects and active surface created by nitrogen doping [8]. Furthermore, it has been shown that nitrogen-doped carbon materials used as Pt supports have an enhanced catalytic activity and durability toward the oxygen reduction reaction [8–10]. Based on these qualities, it is of significant interest for us to focus on the electrochemical

performance of Pt nanoparticles supported on nitrogen-doped graphene, a subject that has not been studied yet in detail.

So far, chemical vapor deposition, arc-discharge, and post-treatment methods have been proposed for synthesis of NG [11–13]. However, these methods are complex and operated at higher temperatures (800–1100 °C). Recently, solvothermal synthesis [14] and detonation processes [15] were developed to prepare NG, but these reactions usually proceed at temperatures >250 °C, which are too high for hydrothermal reactions and therefore risky. Also usually the transformation of  $sp^3$ -hybridized carbon to  $sp^2$ -hybridized carbon was involved in the synthesis process due to the use of  $sp^3$ -hybridized carbon precursor. Remarkably, it is more difficult to obtain pure  $sp^2$ -hybridized carbon in the product. All of these documented methods use different precursors as the carbon and nitrogen sources, resulting in uncontrollable N-doping (a mixture of pyridine-like, pyrrole-like, quaternary-like, and nitrogen oxides) strongly restricting the quality of the resulting NG. Herein, we report a novel solvothermal method for large-scale preparation of NG that uses pentachloropyridine as both the carbon source and the nitrogen source. The pentachloropyridine is reacted with potassium. The method features a lower synthesis temperature (~160 °C) than previously reported. Moreover, controllable N-doping and  $sp^2$ -hybridized carbon can be realized. The durability of synthesized NG as a Pt support for PEM fuel cells was examined and compared with commercial Pt/C (E-TEK) and homemade Pt/C (Vulcan XC-72).

## 2. Experimental

### 2.1. Sample preparation and characterization

A solvothermal route was employed in the synthesis as described below. Typically, 200 mg of pentachloropyridine was placed in a 25 mL Teflon-lined autoclave. Then an appropriate amount of

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metallic potassium was cut into flakes and rapidly added to the autoclave in the glove box. The autoclave was sealed and heated to the desired temperature, where it was maintained for 10 h before it was cooled to room temperature naturally. The products, dark precipitates, were filtered out and washed with acetone, absolute ethanol and water in sequence, and were then dried in a vacuum at 80 °C for 4 h.

The morphologies of the samples were characterized by scanning electron microscopy (SEM), high resolution transition electron microscopy (HRTEM). Also the detailed structures have been also characterized by Raman spectra. The nitrogen contents on the surface of all catalysts were also determined by X-ray photoelectron spectroscopy (XPS).

## 2.2. Electrochemical test

A three-compartment cell was employed for the electrochemical measurements. Platinum wire and Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode were used as the counter and the reference electrode, respectively. The potentials presented in this study are referred with respect to standard hydrogen electrode (SHE). A glassy carbon electrode casted with a thin film of the same amount of catalysts was applied as the working electrode (Pt loading on GC surface: 30.6 μg cm<sup>-2</sup>). Accelerated durability tests (ADT) were conducted by sweeping electrode between 0.05 and 1.2 V for 4000 cycles in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. All the experiments were carried out at 25 °C.

## 3. Results and discussion

Fig. 1a and b show the morphology and structure of the synthesized NG characterized with SEM and TEM. As observed in Fig. 1a, the product has a flower-like structure consisting of many loose NG sheets. It can be observed from the TEM image in Fig. 1b that the graphene forms small particle-like structures which are 200–300 nm

in diameter. There are a number of small flakes around the particles, indicated by arrows. HRTEM (Fig. 1c) further revealed that the petal-like NG sheets are approximately 6–10 graphitic layers thick. The selected area electron diffraction (SAED) pattern (Fig. 1d) was used to identify that it is a polycrystalline structure. XPS is a commonly used technique to examine the content and features of nitrogen species in carbon materials. Using the current method, approximately 3.0 at.% nitrogen (atomic ratio: N/(N+C)) was obtained in the NG based on the XPS analysis. The high-resolution XPS N1S spectrum is shown in Fig. 2(a). As expected, only pyridine-like (60.1%) and quaternary (39.9%) nitrogen are formed by the designed reaction.

Another goal of this work is to evaluate the durability of NG as a Pt support for PEM fuel cells. To compare its durability with the commercial Pt/C, homemade Pt/C using Vulcan XC-72 was used as the control sample. The deposition of Pt nanoparticles on NG and Vulcan XC-72 was finished by the impregnation-reduction method [16]. Fig. 3a and b depict the TEM images of Pt nanoparticles dispersed on NG and Vulcan XC-72. The sizes of the Pt nanoparticles range from 3 to 5 nm, similar to the sizes obtained on the commercial catalyst. Fig. 3c represents the change in the voltammograms during ADT at different cycles for Pt/NG [17,18]. Normalized by the initial scan, the degradation of the electrochemical active surface area (ESA) is plotted in Fig. 3d. It can be observed that approximately 32% of the initial ESA remained for Pt/C (E-TEK) (from about 248.0 to 81.3 cm<sup>2</sup> mg<sup>-1</sup><sub>Pt</sub>), while 36% (from about 263.3 to 94.8) and 50% (from about 251.5 to 124.6 cm<sup>2</sup> mg<sup>-1</sup><sub>Pt</sub>) of the initial ESA remained for Pt/C (homemade) and Pt/NG, respectively. This suggests that homemade Pt/C has a comparable durability with the commercial version; in other words, Pt deposition using the current method is feasible, and the synthesis-induced difference in the electrochemical performances can be excluded. Thus, Pt/C (homemade) should be suitable to act as the control sample. Furthermore, it can be calculated that Pt/NG retains an ESA that is 1.5 times higher than that of Pt/C (homemade) after 4000 cycles. Based on the above discussion,

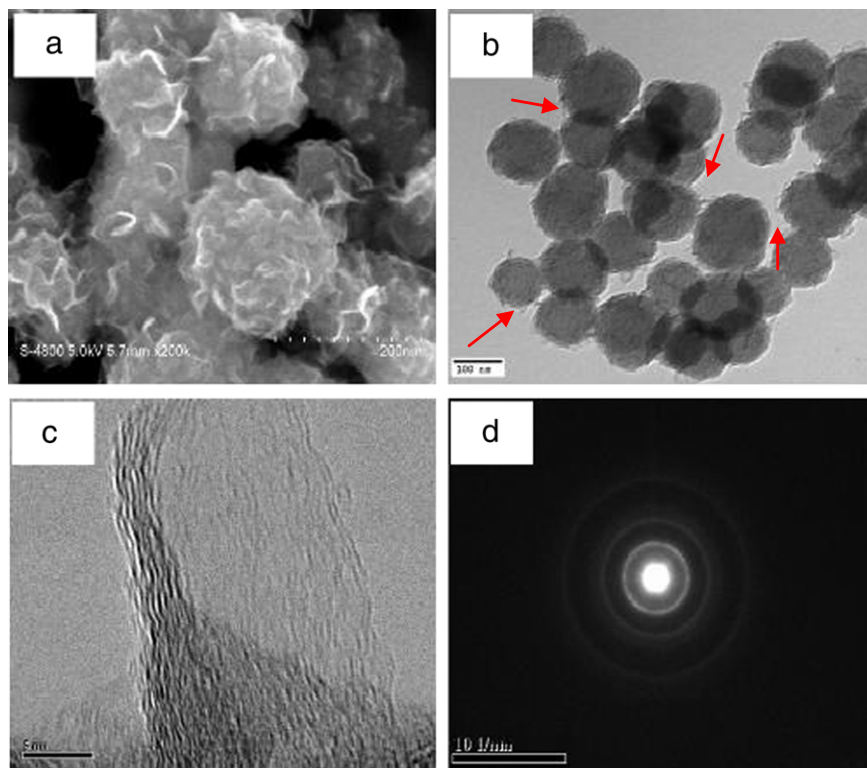
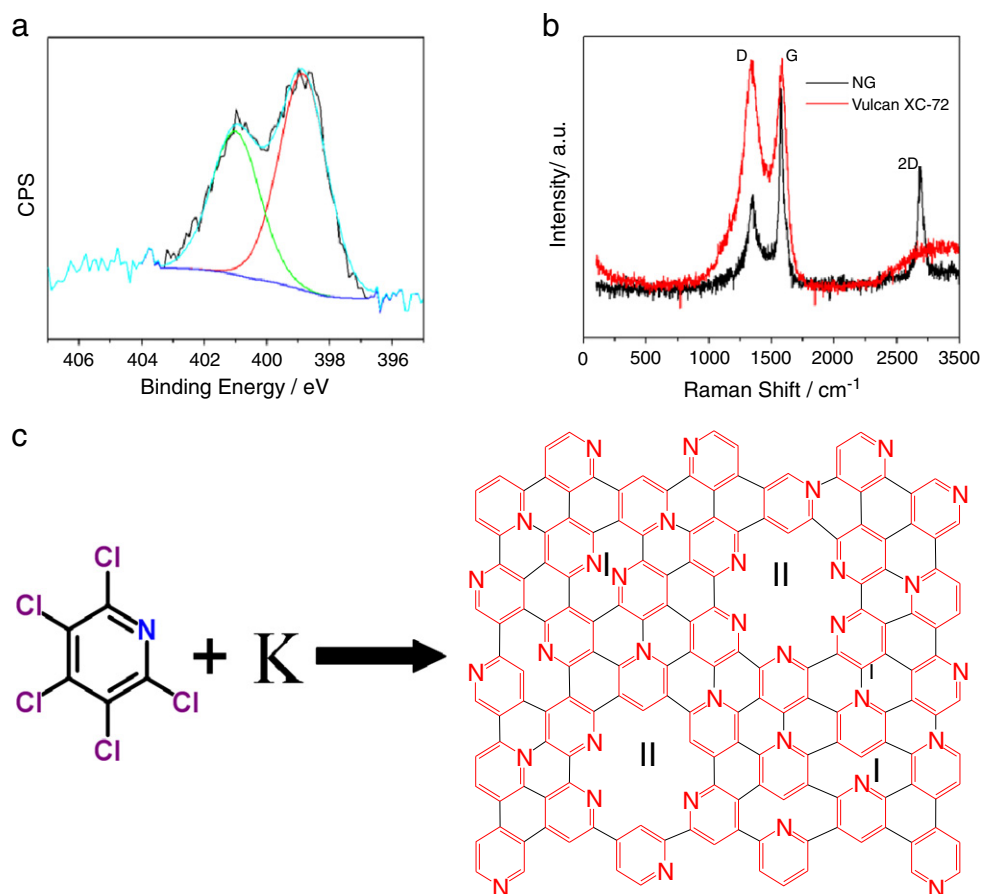


Fig. 1. (a), (b) SEM and TEM images of the synthesized NG. (c) A high-resolution TEM micrograph of NG. (d) Electron diffraction pattern of NG.



**Fig. 2.** (a) The high-resolution N1s spectrum for NG: the black and cyan lines are the raw and fitted spectra; the red and green lines correspond to pyridine-like N (398.5 eV) and quaternary N (401.3 eV), respectively. (b) Raman spectra of NG and Vulcan XC-72. (c) Schematic description of NG formation process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

we can conclude that the flower-like NG has a higher stability than the carbon black (Vulcan XC-72), which can be ascribed to the following three points:

(i) The presence of nitrogen

Nitrogen doping can enhance the interaction between Pt nanoparticles and the delocalized  $\pi$  bond of NG. The existence of the lone electron pair in nitrogen atoms can also stabilize Pt nanoparticles. Our previous experiments also indicated that the presence of nitrogen in carbon nanotubes stabilizes Pt catalysts, resulting in better long-term performance of the catalysts [8]. Using density functional theory, Malardier-Jugroot et al. have demonstrated that the N-doping of graphene increases the binding energy of Pt atoms to the substrate [19]. Currently, it is unclear which kind of nitrogen type plays the key role to improve the durability. However, the quaternary N-doped graphene surface shows the strongest binding energy at  $-2.521$  eV, which is about 1.25 eV higher than the non-doped graphene by theoretical calculation [19]. Further, pyridine-like and quaternary nitrogen usually are believed to contribute to the electrocatalytic activity for oxygen reduction reaction (ORR) when nitrogen doped carbon materials are considered as non-noble metal ORR catalysts [20].

(ii) Higher graphitized structure of NG

Many studies have shown that the greater the extent of graphitization of the carbon material, the greater its durability [2–5]. The polycrystalline structure was confirmed by the SAED pattern. To examine the degree of graphitization,

Fig. 2(b) shows Raman spectra of synthesized NG and the commercial carbon black. Compared with Vulcan XC-72, NG has an obvious 2D band, indicative of the multilayer NG sheets, which is consistent with the HRTEM observations. Importantly, NG has a relatively low  $I_D/I_G$  (the peak intensity ratio of the D to G band; 0.6 vs 1.0), suggesting that the NG layer retained a higher crystalline quality. In the current synthesis, the precursor is pentachloropyridine, which contains only  $sp^2$ -hybridized carbon. It is not difficult to conclude that the resulting graphene will consequently contain only  $sp^2$ -hybridized carbon (see Fig. 2c). Usually, a predominance of  $sp^2$ -hybridized carbon atoms represents a higher level of graphitization. Recently, Deng et al. also reported the solvothermal process to synthesize NG [14], but they used tetrachloromethane ( $CCl_4$ ), which involves the transformation of  $sp^3$ -hybridized carbon in  $CCl_4$  to  $sp^2$ -hybridized carbon in the synthesis process. Remarkably, it is more difficult to obtain pure  $sp^2$ -hybridized carbon in the product than with our technique.

(iii) The presence of ultra-micropores for NG

From the XPS analysis, it is known that not all nitrogen atoms form quaternary N because there is approximately 60.1% pyridine-like N in the product. As shown in Fig. 2c, pyridine-like N should result in some ultra-micropores such as type-I or type-II or even others, in the synthesized NG [21]. So far, it is not clear whether the ultra-micropores are playing an important role in the durability. Further study is necessary.

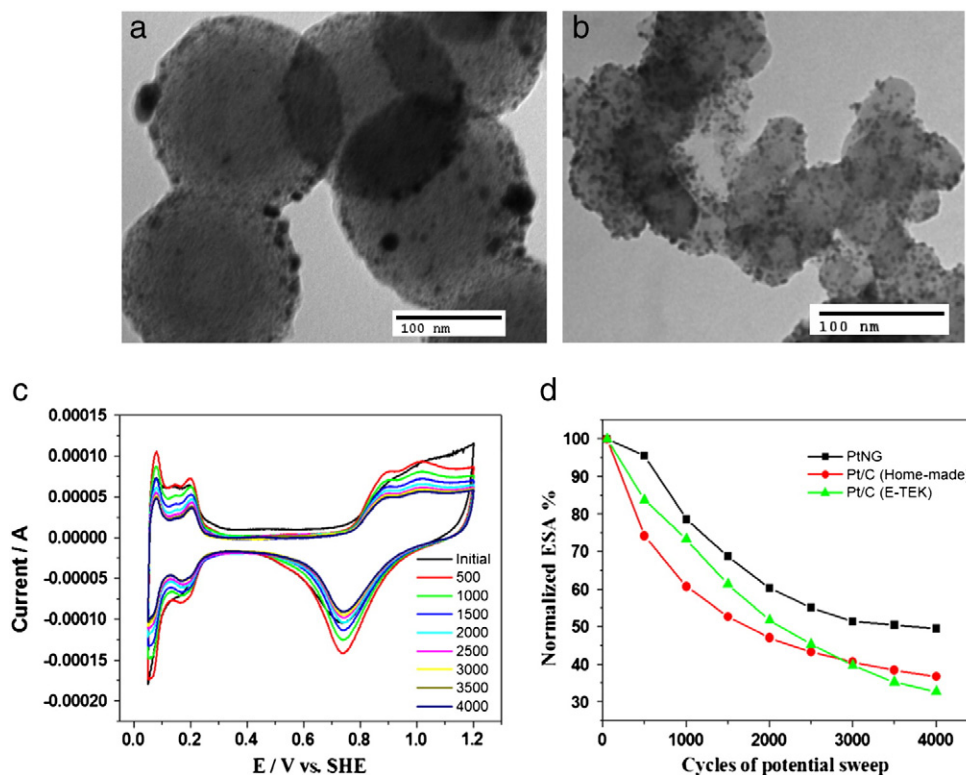


Fig. 3. (a) and (b): TEM images of Pt/NG and Pt/C (homemade). (c) CV curves of Pt/NG for the different cycles. Scan rate: 50 mV/s. (d) Normalized ESA of Pt/NG, Pt/C (homemade), and commercial Pt/C. Pt loading in each carbon: 30 wt.%.

#### 4. Conclusions

In summary, we have shown that nitrogen-doped graphene flowers can be synthesized through a solvothermal process. The resulting material contains  $sp^2$ -hybridized carbon and the designed nitrogen types. This may facilitate new ways to design doped graphene materials with the controllable doping. More importantly, the synthesized NG used as a support for Pt exhibited higher durability than the commercial carbon black due to its special character as a promising electrocatalyst support material for PEM fuel cells.

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