**Boron, nitrogen co-doped graphene: a superior electrocatalyst support and enhancing mechanism
for methanol electrooxidation**

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Abstract: Boron, nitrogen co-doped graphene (BNG) is facilely synthesized by the two-step thermal annealing of graphene in the presence of melamine and boric acid, which is served as a novel support to enhance the catalytic properties of noble metal catalysts for the methanol oxidation reaction (MOR). It is revealed that the BNG support has more defect sites due to the co-doping of boron and nitrogen, so that uniformly dispersed Pt nanoparticles with average size of 2.3 nm are anchored on the surface of BNG support. The BNG supported Pt (Pt/BNG) catalyst exhibits excellent activity and improved stability towards the MOR, which is mainly attributed to the synergetic effects of boron and nitrogen co-doping into graphene support. It is revealed that nitrogen and boron co-doping produces more oxygen-containing species, which accelerates the methanol oxidation by the so-called bifunctional mechanism. Moreover, the boron doping weakens the adsorption energy of poisoning intermediates on Pt surface by lowering the d-band center of Pt, facilitating the oxidative removal of poisoning intermediates and methanol oxidation. The boron and nitrogen co-doping of graphene opens up a new strategy for the catalyst performance optimization.

Keywords: Boron and nitrogen co-doped graphene, catalyst support, electrocatalysis, carbon monoxide tolerance, methanol oxidation

1. Introduction

Metal nanocatalysts dispersed on supports play a pivotal role in the fields of energy storage/conversion, environmental protection and sustainable production of chemicals [1]. It has been demonstrated that the properties of metal catalysts depend highly on their interaction with supports [2]. Graphene, as a unique class of two-dimensional single atomic layer of sp^2 hybridized carbon atoms, has attracted tremendous attention for potential applications in catalysis [3], because of its huge surface area, unique graphitized basal plane structure and high electronic conductivity. In particular for electrocatalytic applications, as a highly stable and conductive platform to anchor catalyst nanoparticles, graphene opens up new possibilities for designing the next generation electrocatalyst supports [4]. Unfortunately, pure graphene is difficult to uniformly anchor catalyst nanoparticles due to its perfect graphitization, low defect level and smooth surface. More importantly, the interaction between metal catalyst and graphene is not strong, which is not good for enhancing the catalytic properties of metal catalysts [5-7].

Heteroatom doping is an effective approach to producing a large number of defect sites in the basal planes and edges of graphene sheets, which can serve as loading sites for anchoring catalyst nanoparticles [8]. Moreover, the interaction of graphene with metal catalyst can be tailored by the heteroatom doping [2]. Doping with heteroatoms of nitrogen [9-11], boron [12], sulfur [13], and phosphorus [14] have been proved to effectively modify the physical, chemical, and electronic properties of graphene materials. Among numerous dopants, nitrogen is commonly considered to be an excellent choice for the chemical doping of graphene materials because it has comparable atomic size and contains five valence electrons available to form strong valence bonds with carbon atoms [15]. The formed C-N bonds promote the dispersion of metal nanoparticles [16-18], which is mainly attributed to the pyridinic type nitrogen species that is a good ligand and interacts strongly with metal catalysts

[19-20].

Nitrogen-doped graphene supported Pt nanoparticles (Pt/NG) have already been employed as the electrocatalyst towards the methanol oxidation reaction (MOR) [2,5,21], which is regarded as one of the most important oxidation reactions of small molecules, especially for direct type fuel cells. It is reported that the Pt/NG catalyst exhibits high MOR catalytic activity and stability [22], which is ascribed to, on the one hand, the well dispersed Pt nanoparticles on NG support, leading to high electrochemical active surface area, and on the other hand, the increased defect level and thus oxygen-containing species on NG support, facilitating the removal of poisoning intermediates by the so-called bifunctional mechanism [19]. However, the MOR kinetics of Pt/NG catalyst is still slow and cannot meet the requirement for practical applications because of the scarce resources and the soaring price of Pt. As we know, the rate-determining step of MOR is the slow adsorption and dehydrogenation of methanol at low potentials or the poisoning of reaction intermediates (commonly CO) at high potentials. Methanol is a polar molecule with negative charge accumulated on oxygen atoms and tends to adsorb on metal surface via lone-pair electrons of oxygen atoms [23]. However, the doping of nitrogen with high electronegativity into graphene decreases the electron density of its supported Pt, increasing the adsorption energy and reducing adsorption rate of methanol on Pt surface at low potentials [24]. Meanwhile, nitrogen doped graphene increases the d-band center of Pt, which enhances the adsorption of CO intermediate on Pt surface according to the d-band center theory from Nørskov [25], slowing down the oxidation removal of methanol at high potentials. Thus, Pt/NG catalyst does not exhibit the desirable MOR kinetics, although its MOR activity is higher than that of Pt/G catalyst because the defect sites and oxygen-containing species on N-doped graphene facilitate the removal of poisoning intermediates by the bifunctional mechanism.

Herein, in order to further enhance the MOR activity, we demonstrate the facile synthesis of boron,

nitrogen co-doped graphene (BNG) by the two-step thermal annealing of graphene in the presence of melamine and boric acid. This BNG material is employed as the electrocatalyst support, onto which Pt nanoparticles are deposited by a microwave-assisted polyol reduction approach. On the one hand, nitrogen doping produces a large number of anchoring sites on graphene for uniformly dispersing Pt nanoparticles, and enhances their MOR activity by the bifunctional mechanism. On the other hand, the doping of boron atoms with low electronegativity can increase the electron density of Pt and lower the d-band center of Pt, which is beneficial to decreasing the bond energy of C-H bond of methanol molecules[26] and the adsorption energy of CO intermediate [27], promoting methanol dehydrogenation and CO oxidation. Our approach integrates the benefits of nitrogen doping and boron doping, which synergistically contribute to the activity and stability of supported Pt catalyst. Therefore, the BNG supported Pt catalyst, Pt/BNG, shows remarkably enhanced electrocatalytic properties than the Pt/NG catalyst. Although the boron, nitrogen co-doped graphene has been employed as a main catalyst for the oxygen reduction reaction [28,29], this is the first report of its usage as the support of Pt catalyst for the MOR.

2. Experimental

2.1 Preparation of graphene oxide

Graphene oxide (GO) was synthesized by the Hummers method [30]. Briefly, 5 g of graphite powder was mixed with 180 mL of concentrated H_2SO_4 , into which 60 mL of concentrated HNO_3 was added and stirred for 1 h. Under vigorous stirring, 25 g of KMnO_4 was slowly added to the suspension. After the mixture was stirred at room temperature for 120 h, the resultant slurry was diluted with 1000 mL of deionized water to terminate the reaction and the mixture turned into bright yellow by adding 30 wt.% H_2O_2 under stirring for 2 h. The product was filtered, washed with a mixture of 35 mL of HCl , 15

mL of H_2O_2 and 500 mL of deionized water and subsequently excess water until pH value was neutral. Finally, the sample was transferred into a Petri dish with diameter of 6 cm, and the product was obtained by freeze-drying at $-50\text{ }^\circ\text{C}$ under vacuum for 12 h.

2.2 Synthesis of B, N co-doped graphene

B, N co-doped graphene (BNG) was prepared by a simple thermal annealing process. First, GO was dispersed into deionized water and ultrasonically treated for 6 h. Then, melamine was added into the GO suspension and ultrasonically treated for another 6 h. After the mixture was freeze-dried, the obtained solid mixture was put into a quartz boat and annealed under H_2/Ar (H_2 5%/Ar 95%) atmosphere at $1000\text{ }^\circ\text{C}$ for 2 h to form the nitrogen doped graphene (NG). Subsequently, the NG sample was sonicated in deionized water for 6 h, and boric acid was added and sonicated for another 6 h. After freeze-drying, the mixture was heat treated at $1000\text{ }^\circ\text{C}$ for 2 h by flowing H_2/Ar gases. The product was dispersed into hot water to remove the impurity, and the BNG product was finally obtained.

2.3 Synthesis of BNG supported Pt (Pt/BNG) catalyst

The BNG supported Pt (Pt/BNG) catalyst with 40 wt.% Pt loading was prepared by a microwave-assisted polyol reduction process in ethylene glycol solution. Briefly, 20 mg of BNG support was added into the mixture of 10 mL of isopropanol and 40 mL of ethylene glycol, and ultrasonicated for 30 min to form a uniform suspension. This suspension was stirred for 6 h at room temperature. After that, 0.6 mL of H_2PtCl_6 solution (0.115 M) was dropwise added to the mixture and its pH value was adjusted to 11 using 1.0 M NaOH solution. The mixture was then subject to microwave heating (2450 MHz, 800 W) for 60 s. After cooling down to room temperature, pH value of the mixture was adjusted to 2 using 1.0 M HNO_3 and magnetically stirred overnight. Finally, the product was separated by

dialysis, filtration, washing with a large amount of hot water and drying in vacuum at 80 °C for 12 h. The NG supported Pt (Pt/NG) catalyst with 40 wt.% of Pt loading was also prepared by the same procedure.

2.4 Physical characterization

Raman spectra were collected on a Raman spectrometer (HR800, JY Company) with 457.9 nm laser. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer using Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The morphology and structure of NG, BNG, Pt/NG and Pt/BNG samples were characterized by transmission electron microscopy (TEM) using an H-7650 (Hitachi, Japan) instrument operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed by a Physical Electronics PHI model 5700 instrument using Al K α radiation (1486.6 eV). The binding energy for all samples was calibrated by the C 1s binding energy of graphite carbon at 284.6 eV. Surface area and pore size distribution of samples were determined by recording nitrogen adsorption-desorption isotherms using a 3H-2000PS1 gas adsorption analyzer (Bei Shi De, China). Pt content in all the samples was determined by inductively coupled plasma mass spectrometry (ICP-MS) using Agilent 7700 instrument.

2.5 Electrochemical measurements

The electrochemical tests were carried out using CHI 604D workstation in a standard three-electrode system with Pt foil and Hg/Hg₂SO₄ as the counter and reference electrode, respectively. The catalyst ink was prepared by dispersing 5 mg of catalyst powder in 5 mL of ethanol solution. 15 μL of the catalyst ink was dropped onto the surface of glassy carbon electrode (4 mm diameter) and allowed to dry at room temperature. Then, 5 μL of 0.05 wt.% Nafion solution was applied onto the surface of the

dried catalyst layer to use as the working electrode. Before the electrochemical tests, the working electrode was pretreated by potential sweep between 0.05 V and 1.2 V in 0.5 M N₂-purged H₂SO₄ solution until a stable voltammogram was obtained and impurity was removed completely. The electrochemical surface area (ESA) was determined by the hydrogen desorption peaks in the obtained cyclic voltammograms (CV) curves based on the following equation:

$$\text{ESA} = \frac{Q_{\text{H}}}{0.21 \times [\text{Pt}]}$$

where Q_{H} is the charge for hydrogen desorption, [Pt] is the Pt loading (mg cm⁻²) in the working electrode, and 0.21 mC cm⁻² represents the charge associated with monolayer adsorption of hydrogen on Pt. The methanol oxidation reaction (MOR) activity was evaluated by CV at a scan rate of 50 mV s⁻¹ and chronoamperometry (CA) test at a potential of 0.6 V in 0.5 M CH₃OH and 0.5 M H₂SO₄ solution. All the performance results were normalised to Pt surface area. CO stripping was conducted in 0.5 M H₂SO₄ solution at a scan rate of 10 mV·s⁻¹. Before the CO stripping test, the electrolyte was bubbled with CO gas by holding the electrode potential at 90 mV for 30 min, followed by purging N₂ gas for 30 min to remove the residual CO. Tafel plots were recorded in potentiostatic mode after the current decayed for 20 s. All the experiments were conducted at room temperature and all potentials were reported with respect to the reversible hydrogen electrode (RHE).

Differential electrochemical mass spectrometry (DEMS) experiment was carried out in a BGM-202 spectrometer (ULVAC, Japan) in vacuum at a heating rate of 5 °C min⁻¹. Before the measurement, the sample was put in a quartz reactor and heated in H₂/Ar at 400 °C for 0.5 h to remove the impurities. Adsorption of CO was performed at room temperature by bubbling CO gas into quartz reactor for 1 h.

Excessive adsorbate was removed by vacuumizing until no significant change for the baseline could be detected.

3. Results and discussion

3.1 Physical characterization

The detailed morphology and structure of N-doped graphene (NG) and B, N co-doped graphene (BNG) are studied by TEM and HRTEM (Fig. 1). Both NG and BNG samples exhibit thin, transparent and curled structure (Fig. 1A and 1B), which is similar to the typical structure of graphene (Fig. S1 in Supporting Information). The thickness of both NG and BNG samples is ~ 5 nm (Fig. 1C and 1D), indicating their multilayered nature, which might be due to the thermal annealing that causes the stacking between graphene layers [31]. Careful observation reveals that the thickness of NG and BNG monolayer is ~ 0.34 nm, which is also identical to that of pure graphene [32]. All these results indicate that the doping process of foreign N and B atoms does not significantly change the morphology graphene sheets.

Fig. 1.

Fig. 2A shows Raman spectra of the NG and BNG samples. The D peak located at 1361 cm^{-1} [33] is a signature of disorder-induced vibration mode and the G peak at 1580 cm^{-1} [34] is commonly observed for the sp^2 bonded graphitic carbons [35]. Therefore, the intensity ratio of D peak and G peak (I_D/I_G) is a factor for judging the degree of graphitization of carbon. The I_D/I_G ratio increases from 0.85 for NG to 1.03 for BNG, which suggests an increase in the defect sites due to the boron atom doping into NG. This increase in defect sites will accelerate the subsequent deposition of Pt nanoparticles. The

chemical composition of NG and BNG samples is characterized by XPS and the results are shown in Fig. 2B and 2C. In Fig. 2B, the N 1s peak of NG is deconvoluted into two kinds of nitrogen: the pyridinic N (398.3 eV [36]) and the pyrrolic N (400.3 eV [36]). In comparison with NG, the deconvoluted results of BNG sample exhibit a new peak located at 397.6 eV [37], which can be assigned to the N-B bond with boron atomic percentage of 3.7%, indicating that boron atoms have already been bonded to NG. It is further revealed that the atomic content of N in NG and BNG samples is around 2.6% and 2.4%, respectively. Moreover, the percentage of pyrrolic N decreases significantly from 13.3% for NG to 6.7% for BNG, while that of pyridinic N increases from 86.7% for NG to 89.8% for BNG. These results indicate that the pyrrolic N can easily react with boron atoms and transforms into the pyridinic N, because the pyrrolic N is less stable [38]. Thus, the pyrrolic nitrogen plays an important role in the boron doping process, which should be the main reaction site with the mechanism shown in Fig. S2. The B 1s peak for BNG (Fig. 2C), whose location (191.0 eV) is higher than that of pure boron (187.0 eV [39]), can be deconvoluted to largely the N-B-C [40] species as well as a small amount of B-C-O species [41].

Fig. 2.

The detailed textural features of support materials are determined by N₂ adsorption/desorption isotherms of graphene, NG and BNG (Fig. 3). All samples show similar type IV adsorption isotherms with a significant hysteresis loop type H₃, which is correlated with slit-shaped mesopores possibly between parallel layers [42]. The pore size distributions of the samples (inset of Fig. 3) show a main distribution of 2-40 nm, indicating that these materials are composed of a large amount of mesopores [43]. Moreover, the BET surface area of graphene, NG and BNG is 315.7 m² g⁻¹, 326.5 m² g⁻¹ and 328.8 m² g⁻¹, respectively, which are close to each other. These results indicate that boron and nitrogen doping

does not significantly change the textural features of graphene.

Fig. 3.

The TEM images of Pt/NG and Pt/BNG catalysts are shown in Fig. 4. It is clear that Pt nanoparticles are uniformly distributed on the NG and BNG supports (Fig. 4A and 4B), confirming that the Pt nanoparticles have been successfully loaded on the supports. From the HRTEM images (Fig. 4C and 4D), the crystalline lattice planes of Pt nanoparticles can be observed. The crystalline lattice planes have the same spacing of 0.227 nm for the Pt/NG and Pt/BNG catalysts, suggesting that the crystalline structure of Pt nanoparticles does not change for Pt/NG and Pt/BNG catalysts. However, the average particle size of Pt/BNG catalyst is 2.3 ± 0.2 nm, which is lower than that of Pt/NG (2.5 ± 0.2 nm) catalyst (Fig. 4E and 4F), in agreement with the XRD results (Fig. S3.). Moreover, the Pt/BNG catalyst shows a narrower size distribution than the Pt/NG catalyst. This improved dispersion can be ascribed to the more defects sites in the BNG support that serve as the preferred sites for Pt nanoparticles anchoring, which is consistent with the observation in Raman results. The Pt loading for Pt/NG and Pt/BNG catalysts is determined by ICP-MS to be 38.9 wt.% and 39.2 wt.%, respectively, which is largely consistent with the designed value.

Fig. 4.

3.2 Electrocatalytic activity

The electrochemical behavior of Pt/NG, Pt/BNG and PtRu/C catalysts is firstly studied by CV in 0.5 M N₂-saturated H₂SO₄ solution at the scan rate of 50 mV s⁻¹ (Fig. 5A). Based on the hydrogen desorption peaks, the electrochemical surface area (ESA) of Pt/BNG catalyst is calculated to be 70.6 m² g_{Pt}⁻¹, which is 1.15 times and 1.21 times that of Pt/NG catalyst (61.2 m² g_{Pt}⁻¹) and PtRu/C (58.5 m² g_{Pt}⁻¹),

respectively. These results should be ascribed to the introduction of boron atoms, which generates additional defect sites for the uniform deposition of Pt nanoparticles as revealed by the TEM images (Fig. 4) [34].

The electrocatalytic activities of Pt/NG, Pt/BNG and PtRu/C catalysts towards the MOR are characterized by CV and CA in a solution of 0.5 M H₂SO₄ and 0.5 M methanol. The CV curves exhibit the well-known features of methanol oxidation on Pt catalysts (Fig. 5B). The forward peak current density for Pt/BNG is 2.46 mA cm⁻², which is 1.56 times and 1.63 times that for Pt/NG (1.58 mA cm⁻²) and PtRu/C (1.51 mA cm⁻²), respectively. For the CA curves (Fig. 5C), the current density for Pt/NG, Pt/BNG and PtRu/C catalysts decreases rapidly in the initial stage, which should be due to the formation of poisoning intermediates (mainly CO_{ads} or CHO_{ads}) during the methanol oxidation process [44]. After 1000 s, however, the current density is 0.18 mA cm⁻² for Pt/BNG, which is 3.0 times and 3.6 times higher than that for Pt/NG (0.06 mA cm⁻²) and PtRu/C (0.05 mA cm⁻²), respectively. Meanwhile, the mass activity of Pt/BNG catalyst is also significantly higher than that of Pt/NG and PtRu/C catalysts (Fig. S4). All these results definitely indicate that the Pt/BNG catalyst has higher methanol oxidation activity than Pt/NG and PtRu/C.

The electrochemical stabilities of Pt/NG and Pt/BNG catalysts are evaluated by the continuous potential cycling between 0.05 V and 1.2 V. Fig. 5D and 5E present the voltammograms at different cycles for Pt/NG and Pt/BNG catalysts. It can be observed that the hydrogen adsorption/desorption peaks of both Pt/NG and Pt/BNG catalysts degrade during the cycling process. The degradation of ESA normalized by the initial values of Pt/NG and Pt/BNG catalysts is plotted along with the cycling number in Fig. 5F. After 1000 cycles, the Pt/NG catalyst maintains 75.71% of its initial ESA, while 79.24% of

the initial ESA remains for the Pt/BNG catalyst. This result indicates that the Pt/BNG catalyst has slightly higher stability than Pt/NG, which should be due to the higher interaction between Pt nanoparticles and BNG support that inhibits the aggregation and dissolution of Pt nanoparticles during the potential cycling.

Fig. 5.

3.3 Mechanism

In order to investigate the enhancing mechanism of Pt/BNG catalyst towards the MOR, Tafel plots for Pt/NG and Pt/BNG catalysts are measured and shown in Fig. 6. Each Tafel plot can be divided into the low and high polarization regions. It has been revealed that, at the potential of 0.4 V~0.5 V [45], the methanol oxidation process on Pt surface involves the dissociative chemisorption of methanol to give a Pt-COH species as follows [46]:

During these processes, the first dehydrogenation step is the rate determining step. For the low polarization region, the Tafel slope for Pt/NG and Pt/BNG catalysts is 104.0 mV dec⁻¹ and 75.8 mV dec⁻¹, respectively. The lower slope for Pt/BNG suggests the higher methanol dehydrogenation rate. The transfer coefficient β and exchange current density i^0 for methanol dehydrogenation processes are obtained from the Tafel plots based on the Butler-Volmer formula:

$$\eta = -\frac{2.3RT}{\beta F n} \lg i^0 + \frac{2.3RT}{\beta F n} \lg i \quad (4)$$

where η is overpotential, R gas constant (8.314 J K^{-1}), T temperature, F Faraday constant (96500 C mol^{-1}), n the number of transferred electrons. Thus obtained β and i^0 values of Pt/NG and Pt/BNG catalysts are 0.3, $6.3 \times 10^{-8} \text{ A cm}^{-2}$ and 0.4, $5.7 \times 10^{-6} \text{ A cm}^{-2}$, respectively, clearly indicating the higher methanol dehydrogenation rate for Pt/BNG catalyst.

Fig. 6.

In the high polarization region, the MOR is complicated by the formation of CO_{ads} poisoning intermediate and oxygen-containing species, formaldehyde, and formic acid et al. However, the poisoning intermediate (CO_{ads}) is attached to Pt surface and blocked subsequent reaction. As a result, the Tafel slopes are different from those in the low potential region, indicating that the varied rate-determining step. The most likely rate determining step in the high polarization region should be the oxidative removal of adsorbed CO_{ads} [44-47]:

The Tafel slope of Pt/BNG catalyst is less than that of Pt/NG in these potential ranges, indicating that the higher rate of CO_{ads} removal. To verify the ability of CO_{ads} removal, CO stripping test is carried out in 0.5 M H_2SO_4 solution (Fig. 7A). The onset and peak potentials for Pt/BNG catalyst shift negatively 30 mV and 10 mV, respectively, in comparison with Pt/NG catalyst, confirming the enhanced CO tolerance by the BNG support material.

DEMS is used to analyze the adsorption strength of CO_{ads} on Pt surface for Pt/NG and Pt/BNG catalysts (Fig. 7B). Apparently, CO_{ads} is desorbed at 170 °C for Pt/BNG catalyst, which is significantly lower than that for Pt/NG catalyst (300 °C). The low desorption temperature for Pt/BNG catalyst

illustrates the weaker adsorption energy between Pt and CO, which should be attributed to the boron doping into the NG support.

Fig. 7.

XPS is employed to analyze the underlying mechanism of high dehydrogenation rate and CO tolerance for Pt/BNG catalyst. Fig. 8A shows Pt 4f XPS spectra for Pt/NG and Pt/BNG catalysts. The Pt 4f peak for Pt/BNG catalyst (71.1 eV) shifts negatively by 0.3 eV compared to Pt/NG (71.4 eV), indicating the higher electron density of Pt, which should be ascribed to the electron transfer to Pt from the B atoms doped in BNG support that have lower electronegativity. This electron transfer lowers the d-band center of Pt, which decreases the bond energy of C-H bond [26,48], and weakens the adsorption of poisoning intermediates according to the d-band center theory by Nørskov [25]. Thus, both the methanol dehydrogenation and the CO oxidation rates on the Pt/BNG catalyst are accelerated [27,49]. Moreover, the Pt/BNG catalyst presents higher metallic Pt content (77.43 %) than Pt/NG (57.83 %), which should be attributed to the fact that B doping can transfer electron to Pt and increase its electron density because B atoms have lower electronegativity [50,51]. The higher metallic Pt content indicates that BNG support facilitates the formation of metallic Pt, which is beneficial to the methanol electrooxidation by providing more active sites for the reactions of methanol dehydrogenation and adsorbed intermediates removal. This mechanism is highly different from that of Pt/NG catalyst [52], which raises the d-band center of Pt by the doped nitrogen with high electronegativity, thus leading to strengthened chemisorption of reaction intermediates.

In addition to the mechanism of weakening the adsorption strength of reaction intermediates, the XPS results also show that the O atomic content is 12.89% and 13.06% for Pt/NG and Pt/BNG (Fig. 8B),

respectively. According to the deconvoluted results of O 1s spectra, the content of C-OH group at 533.3 eV for Pt/BNG is 16.7%, which is higher than that for Pt/NG (14.01%), which might be due to the B-C-O bond introduced by boron atoms, forming a new defect site of oxygen species. The presence of more C-OH groups on the BNG support can promote the oxidation of CO_{ad} on the Pt active sites via the bifunctional mechanism [27]. As a result, the high CO tolerance of Pt/BNG catalyst is attributed to the reduced CO adsorption energy by lowering the d-band center of Pt and also the abundant oxygen-containing functional groups on the BNG surface from the high defects level as revealed by the Raman results.

Fig. 8.

4. Conclusions

We have prepared the boron, nitrogen co-doped graphene (BNG) by the thermal annealing of nitrogen doped graphene and boric acid, which is employed as the support material to disperse Pt nanoparticles by a microwave-assisted polyol reduction procedure. Boron atoms are incorporated into the nitrogen doped graphene mainly in the form of B-N-C and B-C-O bonds, which facilitates the uniform dispersion of Pt nanoparticles. Thus, the obtained Pt/BNG catalyst has 1.15 times and 1.21 times higher electrochemical surface area in comparison to Pt/NG catalyst and PtRu/C, respectively. Furthermore, the Pt/BNG catalyst exhibits greatly enhanced catalytic activity towards the methanol oxidation reaction, which is 3.0 times and 3.6 times higher than that of Pt/NG and PtRu/C catalyst, respectively. The superior catalytic properties of Pt/BNG catalyst is largely attributed to the increased electron density and lowered d-band center of Pt induced by boron atoms doping, which accelerate the

dehydrogenation of methanol and weaken the CO intermediate poisoning. Meanwhile, the nitrogen doping also enhances the oxidation removal of CO intermediate by the bifunctional mechanism. The synergetic contribution of nitrogen and boron co-doping leads to the MOR activity enhancement of Pt/BNG catalyst. Our study provides a new strategy for designing and preparing fuel-cell catalyst supports with tailorable cocatalytic properties.

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Figure captions:

Fig. 1. TEM and HRTEM images of NG (A, C) and BNG (B, D) samples.

Fig. 2. Raman spectrum of NG and BNG (A), N 1s XPS spectra for NG and BNG (B), and B 1s XPS spectra for BNG (C).

Fig. 3. N₂ adsorption/desorption isotherms of graphene (A), NG (B) and BNG (C) and BJH pore size distribution (inset).

Fig. 4. TEM and HRTEM images of Pt/NG (A, C) and Pt/BNG (B, D) catalysts, size distribution of Pt/NG (E) and Pt/BNG (F) catalysts.

Fig. 5. CV curves (specific activity) of Pt/NG, Pt/BNG and PtRu/C catalysts in 0.5 M H₂SO₄ (A), 0.5 M H₂SO₄+ 0.5 M CH₃OH solution (B), CA curves of Pt/NG, Pt/BNG and PtRu/C catalysts in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution (C), stability of Pt/NG (D), Pt/BNG (E) for the different cycles in 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹, and Normalized ESA of Pt/NG and Pt/BNG catalysts with the number of CV cycles in 0.5 M H₂SO₄ solution (F).

Fig. 6. Tafel plots of Pt/NG (A) and Pt/BNG (B) in 0.5 M H₂SO₄ +0.5 M CH₃OH solution.

Fig. 7. CO stripping curves in 0.5 M H₂SO₄ solution (A), DEMS for CO desorption (B) on Pt/NG and Pt/BNG catalysts.

Fig. 8. Pt 4f (A) and O1s (B) XPS spectra of Pt/NG and Pt/BNG catalysts.

Fig. 1.

Fig. 2.

Fig. 3.

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Fig. 6.

Fig. 7.

Fig. 8.