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One-Pot Facile Synthesis of N-Doped Graphene Synthesized from Paraphenylenediamine as Metal-Free Catalysts for the Oxygen Reduction Used for Alkaline Fuel Cells

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***Abstract*—**In the work presented here, nitrogen-doped graphene materials were synthesized and used as metal-free electrocatalysts for oxygen reduction reaction (ORR) under alkaline conditions. Paraphenylenediamine was used as N precursor. The N-doped graphene was synthesized under hydrothermal treatment at 200°C. All the materials have been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM) and X-ray photo-electron spectroscopy (XPS). Moreover, for electrochemical evaluation of samples, Rotating Disk electrode (RDE) and Cyclic Voltammetry techniques (CV) were employed. The resulting material exhibits an outstanding catalytic activity for the oxygen reduction reaction (ORR) as well as excellent resistance towards methanol crossover effects, indicating their promising potential as ORR electrocatalysts for alkaline fuel cells.

***Keywords*—**Alkaline fuel cell, graphene, metal-free catalyst, paraphenylenediamine.

I. Introduction

THE oxygen reduction reaction (ORR) is an important reaction in alkaline fuel cells, in metal-air batteries and in chlorine-alkali electrolysis [1].

So far, Platinum (Pt)-based nanomaterials have been extensively studied as active ORR, catalysts, but the limited Pt resources, poor durability, poisoning effects and crossover are important issues that they suffer [2]. Although, recently, intensive studies have been done on metal-free catalysts with the aim to reducing the cost and improving the performance towards ORR, there are still two undeniable challenges, including the lower onset potential compared to Pt/C catalyst and unclear functions of various nitrogen states towards ORR [3]-[7]. Therefore, considerable researches have been done to substituting Pt-based catalysts by low-cost materials such as palladium alloys [8], MnO_x [9], metalloporphyrins [10], and different heteroatom types (such as N, S, P, and B atom)-doped carbon structures [11]-[14], Non-noble metal and metal-N4 catalysts such as transition metal alloys [15] and transition metal N4-macrocyclic complexes [16], [17], which among, graphene, a single layer of two dimensional aromatic carbon lattices, presents excellent electrical, chemical, and mechanical properties, which is desirable at the harsh ORR conditions. To achieve more applications of graphene, its properties could be moderated by chemical doping and modifications [18]. For example, heteroatom-doped graphene nanosheets introduced by nitrogen, sulfur, boron, and phosphorus, not only enhances the electrical properties of graphene, but also effectively provides the more active site of the catalyst which intensify electrocatalytic performance toward ORR [19]-[23].

Nitrogen-doped graphene (NG) is one this structure has enhanced electronic and catalytic properties than the intrinsic graphene, which can be used for nano-devices and fuel cells.

Different approaches have been used to introduce nitrogen atoms within the graphene framework, for which most are complex, such as high temperatures working in gas phase or plasma and arc discharge or are unable to control the doping degree and nitrogen functionality [2]. So, herein, we report a facile new approach for preparation of N-doped graphene hydrothermally synthesized from paraphenylenediamine under conditions at 200ºC. The prepared electrocatalyst exhibited good electrocatalytic activity. Furthermore, the studied electrode showed superior stability compared to commercial Pt/C catalysts under alkaline condition.

II. Experimental Synthesis of N-Doped Graphene Nanosheets

Graphene oxide was synthesized by Hummer's method [24]. Briefly, $NaNO_3$ (5g), graphite (5g) and H_2SO_4 (225ml) were mixed and stirred for 45 minutes while keeping the temperature less than 10°C. Subsequently, $KMnO_4$ (15g) was gradually added to the slurry and stirred at 35°C for 2 hours. Afterwards, 500 ml deionized water and 30 ml H_2O_2 (30%) were added, respectively; and kept stirring for another 1 hour. After that, the obtained precipitation was centrifuged at 10,000 rpm for 10 minutes and further washed with 500 ml of 5 M HCl solution to eliminate excess metal. Finally, the As-

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prepared graphene oxide was additionally washed with deionized water and dried at 60°C for 24 hours. N-doped graphene was hydrothermally synthesized from the mixture of graphene oxide and paraphenylenediamine as the nitrogen precursor. 150 mg of graphene oxide was dispersed in 150 ml deionized water using cleaner ultrasonic bath. Then, 300 mg of paraphenylenediamine was slowly added to the graphene oxide suspension and stirred for 1 hour. Following, the mixture was poured into a Teflon container and put in an oven at 200°C for 24 hours [24].

A. Characterization

The materials crystallinity was characterized by X-ray diffraction (XRD) using a XPERT- PRO diffractometer with Cu Ka radiation. Elemental analysis was carried out with a Fourier transform infrared spectroscopy (FTIR) using a Bruker spectrometer (IFS-88) with 4 cm^{-1} resolution and X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) test was done at the Sharif University of technology on an ultraviolet spectrometer using an Mg Ka source operating and monochromatic Al Ka source operating. The base pressure was about 1×10^{-10} torr, and operating pressure was around 2×10^{-10} torr.

Morphology and microstructure of the synthesized materials were also investigated by a Transmission electron microscopy (TEM) using a 100 KeV Philips EM-208 instrument.

B. Rotating Disk Electrode (Rde) Experiment

For preparation of the electrodes, the catalyst powder was firstly dispersed in a mixture of water and Nafion with ratio of 9:1 v/v respectively at a concentration of 1 mg mL^{-1}. Afterwards, 5 µL of each suspension was dropped on a 3 mm diameter glassy carbon electrode as a working electrode. Finally, ink was dried at 60°C for 15 minutes forming a thin film on the glassy carbon electrode. Then, for the electrocatalytic evaluation of the catalysts the rotating disk electrode (RDE) experiment was performed at room temperature by linear sweep voltammograms (LSVs). Pt was used as a counter electrode and Ag/AgCl electrode was used as a reference electrode. RDE measurements were carried out in a 0.1 M KOH electrolyte in the potential range from -1 to 0.2 V at a scan rate of 5 mV s^{-1} and measured at 250, 500, 750, 1000, 1250, 1500, 2000, 2500, 3000 and 3500 rpm. Oxygen was purged into the electrolyte to make an O_2-saturated solution. The Koutecky– Levich (K–L) equation was used to calculate the number of electrons transferred with RDE data. The catalyst prepared will be here after referred with GO-NP-200-code

III. Results and Discussion

A. Catalyst Characterization

To characterization of the phase structures of Graphene Oxide (GO) and GO-NP-200, XRD analysis was employed. As can be seen in Fig. 1, the sharp (002) peak of pristine graphite at 11.77° can be assigned to the characteristic value of graphite.

The interlayer spacing calculated from the (002) reflection is 8.98 A° far larger than that of graphene [2].

In GO-NP-200 catalyst, the peak indexed to (002) is broadened and positively shifted to 28.28°, comparatively to GO base. So, the results show that due to the reduction effect at high temperatures, hydrothermal treatment of GO will partially restore the graphitic crystal structure, possibly due to paraphenylenediamine corrosion and defects resulted from nitrogen doping [25].

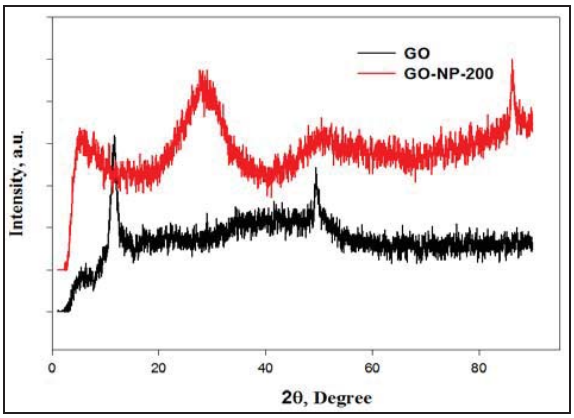

Fig. 1 XRD patterns of GO and GO-NP-200

FTIR spectra were then used to analyze the chemical compositions of GO and GO-NP-200 (Fig. 2).

The main peaks in FTIR spectrum of GO centered at 1044, 1219, 1617, 1720, and 3406 cm^{-1} can be related to alkoxy C–O, epoxy C–O, carboxyl O=C–O, aromatic C=C, C=O (carboxylic acid and carbonyl moieties), and O–H stretches, respectively, confirming the successful oxidation of graphite. After hydrothermal treatment, whereas, the content of these oxygen-containing groups in GO significantly decreased, two new nitrogen-related peaks appeared at 1451 and 1559 cm^{-1}, which could be attributed to C–N stretching and N–H bending bonds of amide, respectively [2].

More detailed information about the catalyst morphology was obtained from TEM (Fig. 3). The TEM image showed the graphene nanosheets had a typical balled surface with random array, which might be attributed to the defective structure formed upon exfoliation and the presence of nitrogen atoms.

To further investigate the elemental composition and nitrogen bonding configurations in GO-NP-200, XPS measurements were carried out.

The peaks at 286.6 eV relating to C-OH group which remarkably decreased after hydrothermal process indicating nitrogen doping has increased the reduction degree of GO.

Significantly, the peak intensities of oxygen-containing groups corresponding to the carbon atoms in different functional groups: C–C (284.8), C–O (286.9) became much weaker in GO-NP-200, whereas an additional component appeared at 285.8 eV, which can be attributed to the C–N bonds [25] (Fig. 4 (d)). Also, the peak at 398.6 corresponds to N1s peak of nitrogen-sp^3 C bonds. Additionally, the peak at 533.9 eV assigns to O1s peak, which can be originated from

C=O (aldehydes, ketones, lactones) [25] (Fig. 4 (c)).

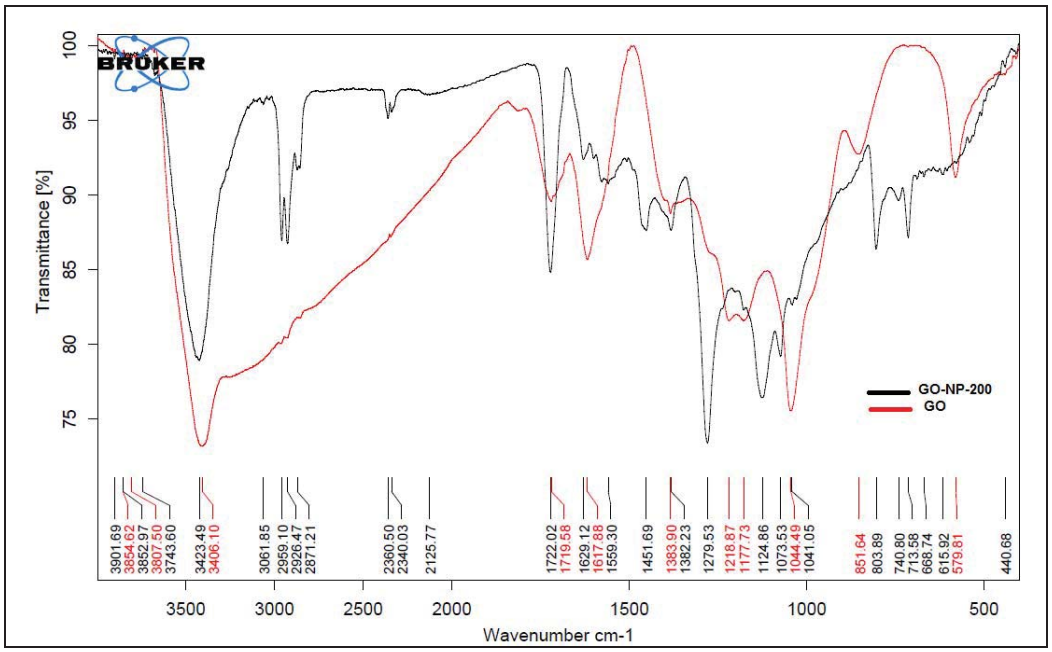

Fig. 2 FTIR spectra of GO and GO-NP-200

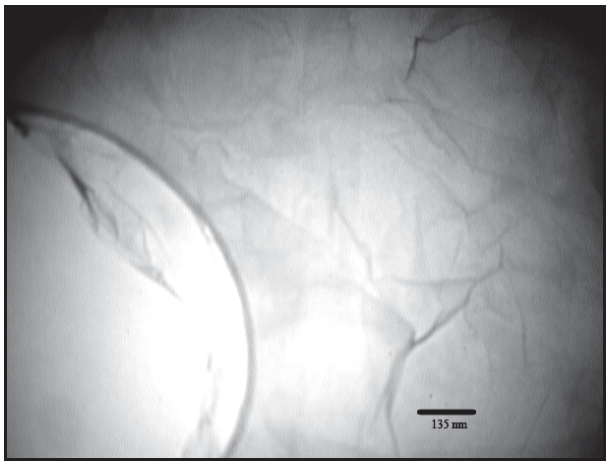

Fig. 3 TEM image of GO-NP-200

The high-resolution N 1s XPS spectrum of GO-NP-200 has been shown in Fig. 4 (b). The peaks located at 398.5 and 401.4 eV are assigned to pyridinic and pyrrolic-type nitrogen atoms doped in the graphene structure, respectively

The FTIR and XPS spectra could clearly support that the pristine GO was adequately reduced and efficiently modified with nitrogen atoms/amino group through low-temperature hydrothermal process, producing nitrogen doped graphene successfully.

B. ORR Activity

Fig. 5 shows the linear sweep voltammograms measured in O_2-saturated 0.1 M KOH at 5 mV/s and 1500 rpm.

The ORR currents at the disk electrode start around -0.03 and reach a limiting current around -0.6V. To obtain quantitatively the number of transferred electrons (n) of the ORR catalysis, by using the Koutechy–Levich equation, the electron transfer numbers were calculated, which is around 3.6, suggesting the almost complete O_2 reduction to H_2O.

In fuel cells, there may exist fuel molecules penetrating through the electrolyte membrane and contact with the cathode catalysts, that is the so-called fuel crossover effects [2], [25]-[27].

Methanol not only influences the anion exchange membrances, but also poisons the catalyst (Pt/C). Therefore, the methanol tolerance is an important criterion to evaluate the quality of an electrocatalyst for ORR.

To evaluate the tolerance of GO-NP-200 toward methanol crossover, CV measurements were recorded when methanol was introduced during the ORR process at the prepared and commercial Pt/C electrodes against the electrooxidation of methanol (Figs. 6 (a) and (b)). It was seen that a decrease in the current occurred at the Pt/C electrode upon the addition of 1 M methanol, while a strong and stable amperometric response remained at the prepared electrode, indicating its excellent tolerance to the crossover effect of methanol. Therefore, the GO-NP-200 catalyst exhibits excellent selectivity and durability, showing superior advantages over the commercial Pt/C when used as long-term running electrocatalysts.

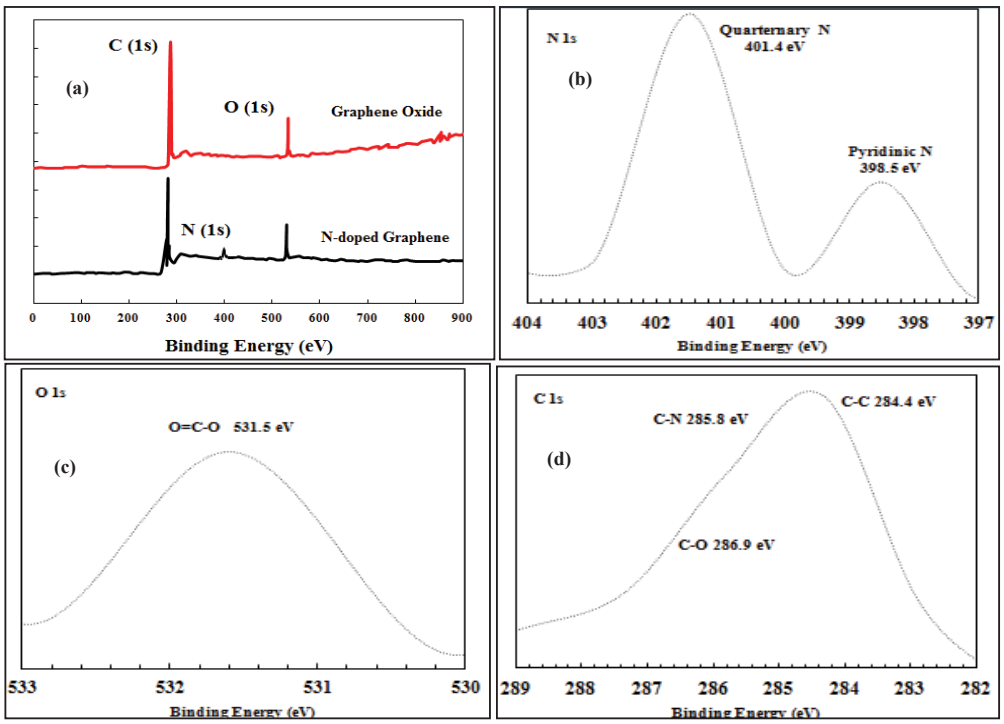

Fig. 4 (a) The XPS survey spectra of GO and GO-NP-200. (b) High-resolution N 1s spectrum. (c) High-resolution O 1s spectrum. (d) High-resolution C 1s spectrum

The excellent performance of the GO-NP-200 catalyst could be attributed to the unique porous structure of graphene intensified, the electrolyte ions, reaction intermediates and products transport. On the other hand, the high amount of active heteroatom species, including pyridinic and pyrolic nitrogen, results in the formation of more active sites which more favor ORR.

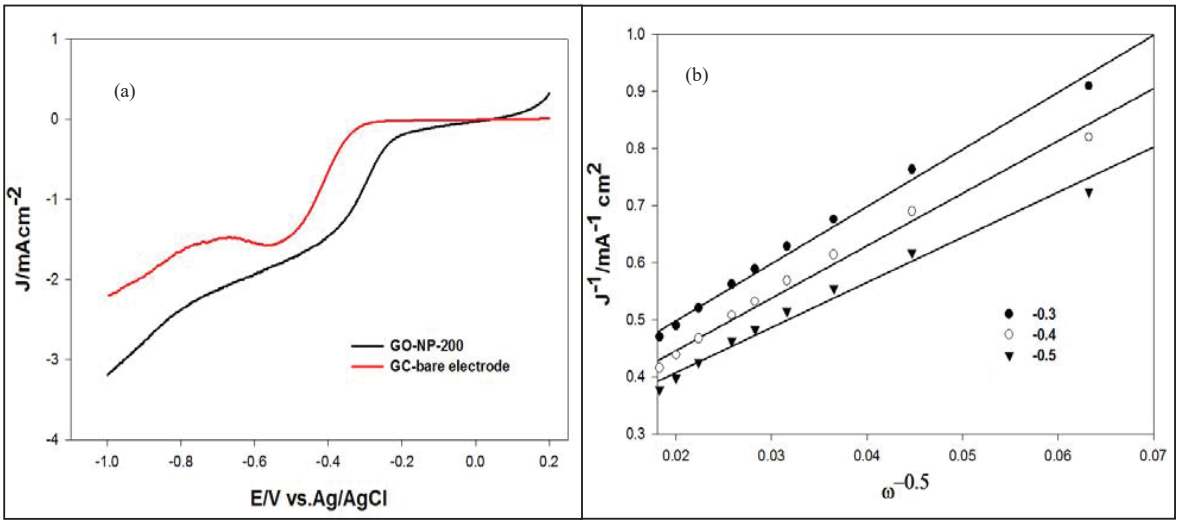

Fig. 5 (a) LSV curves of GC-bare and GO-NP-200 in an O_2-saturated 0.1 M KOH solution at a scanning rate of 10 mV s^{-1} and a rotation speed of 1600 rpm, (b) Koutecky–Levich plot (J^{-1} vs $\omega^{-0.5}$) at different electrode potentials. The experimental data were obtained from lsv results and the lines are linear regressions

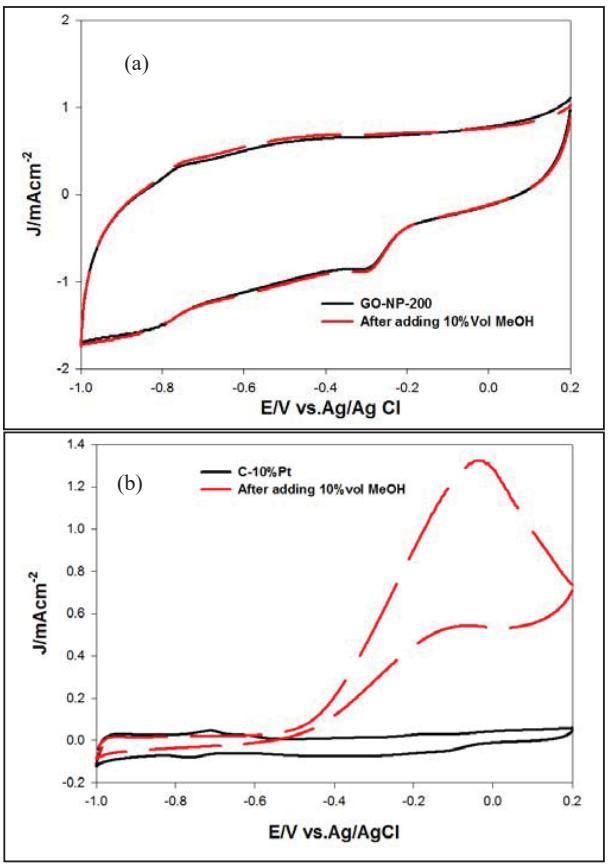

Fig. 6 Cyclic Voltammograms (CVs) of (a) GO-NP-200 and (b) commercial Pt/C in O_2-saturated 0.1M KOH solution upon the addition of 1M CH_3OH. Scan rate: 10mV s^{-1}

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