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Nitrogen and Boron doped hydrothermally reduced Graphene oxide amperometric sensor for sensing Dissolved oxygen

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Abstract:

Dissolved oxygen is an important parameter in fermentation processes. Here we present oxygen reduction activity of Nitrogen, Boron doped reduced graphene oxide and electrochemically reduced graphene oxide (ERGO) and its application as amperometric sensor for dissolved oxygen. Our study shows that N,B-HRGO, which showed high sensitivity of 0.01 µA / % of oxygen, can be used as an amperometric sensor to sense dissolved oxygen at very low concentration at lower polarization voltage (-0.4 V) compared with ERGO which shows less sensitivity (0.04 µA / % of oxygen) at lower polarization voltage .

Key words: Dissolved oxygen, Nitrogen and Boron doping, Reduced graphene oxide, Amperometric sensor, Oxygen reduction.

Introduction

Dissolved oxygen is an important parameter in various biological and environmental processes like aquatic system, water quality maintenance and fermentation processes. Clark type electrochemical sensor and optical sensor have been used for measuring dissolved oxygen in biological process. However, the large size and complex assembly of these electrodes with liquid electrolytes and an oxygen permeable membrane makes it impossible to use it in micro reactor or in any medical application. Optical sensors also have their own limitations.

Graphene is a two dimensional material and has high electronic and thermal conductivity and an excellent chemical stability. Graphene properties can be tuned by functionalizing with different molecules and doping with different hetero atoms. There are many hetero atom doped graphene that have been studied for oxygen reduction reaction (ORR) activity. The presence of heteroatoms make the graphene electron deficient, which increases the ORR catalytic activity [1]. Here we developed an amperometric dissolved oxygen sensor using N,B doped graphene as ORR catalyst. The high ORR activity of N,B-HRGO increased the sensitivity of the oxygen sensor. Oxygen sensing performance of N, B doped graphene is compared with electrochemically reduced graphene oxide.

Experimental details

Nitrogen, Boron doped graphene (N,B-HRGO) is synthesized by Hydrothermal method. In a typical procedure 50 mg of graphite oxide is dissolved in 50 ml of water to get 1 mg/ml GO concentration. The dispersion was sonicated for four hours, and unexfoliated graphite oxide flakes are removed by centrifugation. The resultant GO dispersion is used for functionalization. For Nitrogen and Boron doping, equal amounts of $NH_3.H_2O$ and Boric acid was dissolved in 50 ml GO dispersion and the container was kept in an autoclave for 12 hours at 120^{o}C (0.12 MPa). Then, the black solid was obtained by filtration (Fig. 1). Electrochemically reduced graphene oxide (ERGO) is prepared by electrochemical reduction of GO deposited (2 µl of 0.5 mg/ml) on an electrode by cyclic voltammetry (0 to -1.2V).

Results and discussion

In order to evaluate the ORR activity of N,B-HRGO and ERGO, a 2 mm Gold disc is used as a working electrode and 0.1 M KNO_3 solution is used as an electrolyte. For amperometric sensing, the electrode is polarized at -0.4 V and the current value of the electrode is measured in 0.1 M KNO_3 containing different dissolved oxygen concentration. The different oxygen concentration solutions are achieved by mixing different volumes of nitrogen and oxygen saturated solution as shown in Table 1.

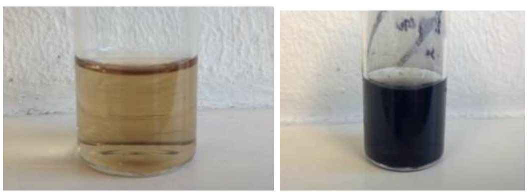

Fig. 1. Photos of Graphene oxide before and after the hydrothermal reduction

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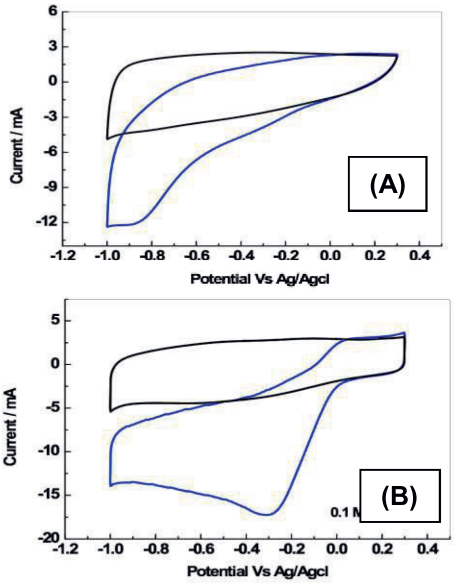

Fig. 2. Cyclic voltammetry of ERGO (A) and N,B-HRGO (B) in 0.1 M KNO_3 solution in nitrogen saturated (Black) and oxygen saturated (Blue)

Tab. 1: Table caption

Air sat. (ml)	**N2. Sat (ml)**	**Air:N2 %**
10	0	100:0
7.5	2.5	75:25
5.0	5.0	50:50
2.5	7.5	25:75
0	10	0:100

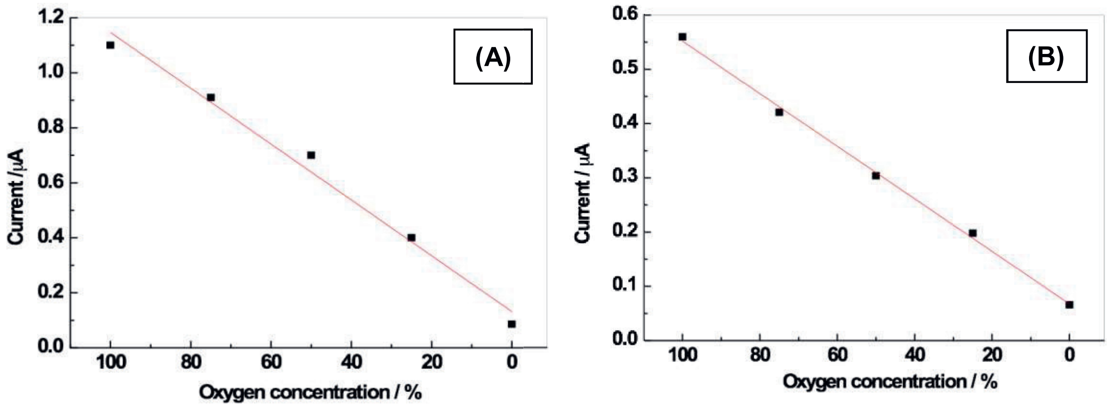

Fig.3. Oxygen sensing performance of N,B-HRGO (A) and ERGO (B) electrode in 0.1 M KNO_3 with 100, 75, 25, 0 % oxygen concentration.

Oxygen reduction potential of N,B-HRGO and ERGO is evaluated by cyclic voltammetry. The electrodes are cycled between the voltage range 0 to -1.0 V at a scan rate of 50 mv/s. CV of N,B-HRGO shows a sharp oxygen reduction peak at -0.3 V with an onset potential less than -0.1 V. This peak disappears completely when the solution is saturated with nitrogen. But CV of ERGO in oxygen saturated solution shows different behaviour. It shows a less intense peak around -0.3 V with an onset potential higher than -0.1 V, but a prominent oxygen reduction peak appeared at -0.8 V with an onset potential of -0.6V. This indicates that N,B-HRGO reduces the oxygen at a lower reduction potential compared with ERGO.

From cyclic voltammetry, -0.4 V is chosen to polarize the electrode for amperometric oxygen sensing. The current values of N,B-HRGO and ERGO is measured in 0.1 M KNO_3 solutions containing different percentages of oxygen. The current values are plotted against the percentage of oxygen concentration (Fig 3) It can be clearly seen that an N,B-HRGO deposited electrode shows a sensitivity of 0.01 µA / % of oxygen. The ERGO deposited electrode shows less sensitivity of 0.04 µA / % of oxygen.

Conclusion

ORR activity of N,B-HRGO and ERGO is demonstrated d and a linear relationship is obtained between the current and the oxygen concentration in the solution..

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References

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