CATALYTIC CARBON NANODOTS FOR OXYGEN REDUCTION REACTION

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ABSTRACT. This report provides a new perspective for practical application of the electronics properties of carbon nanodots as an electrocatalytic layer on the graphite working electrode. For that purpose, ultra-small nitrogen doped carbon nanodots (C-dots) with average diameter between 1.5-2 nm were synthesized by microwave assisted pyrolysis and after that were immobilized chemically onto the graphite surface of the electrode. As environmentally friendly electrocatalyst for oxygen reduction reaction (ORR) our data show that the bare C-dots alone are not able to form stable electro-catalytic film for ORR because of their high water solubility. However, the chemically conjugated nanoparticles exhibit ORR electrocatalytic activity in acid or basic media. These properties open a new range for practical application in the field of ecotechnology and environmental protection.

Keywords: carbon nanodots, environmental friendly electrocatalyst, oxygen reduction reaction

КАТАЛИТИЧНИ ВЪГЛЕРОДНИ НАНОТОЧКИ ЗА РЕДУКЦИЯ НА КИСЛОРОД

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РЕЗЮМЕ. Тази статия предоставя нова перспектива за практическо приложение на електричните свойства на въглеродни наноточки, като електрокаталитичен слой върху графитен работен електрод. За тази цел ултра малки азот-съдържащи въглеродните наноточки (C-dots) със среден диаметър между 1.5-2 nm бяха синтезирани, чрез микровълнова асистирана пиролиза и след това бяха химически имобилизирани върху графитената повърхност на електрода. Като екологосъвместими катализатори за редукция на кислород (ORR) получените данни показват, че C-dots не са в състояние сами по себе си да образуват стабилен електро-каталитичен филм за ORR, поради тяхната висока разтворимост във водни разтвори. Въпреки това, химически конюгираните наночастици проявяват ORR електрокаталитична активност в кисела или основна среда. Тези свойства откриват нови възможности за тяхното практическо приложение в областта на екотехнологиите и опазването на околната среда.

Ключови думи: въглеродни наноточки, *екологосъобразни катализатори, фотоокисление*

Introduction

The negative consequences of the anthropogenic environmental pollution create a prerequisite for the development of modern ecotechnology for clean energy generation. One such approach is the development of membrane fuel cells, microbial fuel cells, etc., which utilize the reduction of oxygen in order to generate electrical energy (known as oxygen reduction reaction or ORR) (Huang et al., 2017). The reduction of oxygen in water solution can proceed basically by two general pathways and the reaction occurred on the cathode electrode. The pathways are dependent on pH conditions and thus ORR mechanism basically differs in basic or acidic conditions (Yeager 1984), as shown on the equation below:

In basic environment:

$O_2 + 4e^- + 2H_2O \rightleftarrows 4OH^-$ $\quad E_0 = 0.401$ V

$O_2 + 2e^- + H_2O \rightleftarrows HO_2^- + OH^-$ $\quad E_0 = -0.065$ V

In acidic environment:

$O_2 + 4e^- + 4H^+ \rightleftarrows 2H_2O$ $\quad E_0 = 1.229$ V

$O_2 + 2e^- + 2H^+ \rightleftarrows H_2O_2$ $\quad E_0 = 0.670$ V

In order to increase the performance of the working electrode (cathode) our efforts are concentrated on the development of effective and low cost electrocatalysts (known as platinum-free) that are able to increase ORR peak current and reduce the electrochemical overpotential. The reason is because the noble metals as platinum and its compounds are considered as the most effective ORR catalysts, however the high cost and poor global distribution limit its practical application (Lin et al., 2014).

During the last decades a lot of efforts have been made to develop an effective and non-precious electro-catalysts as alternatives of the platinum based on light elements (carbon, hydrogen, boron, oxygen, etc.). The recent studies have focused on carbon based nanomaterials, which are of particular interest, because they have various attractive benefits (Li et al., 2012), such as electrocatalytic activity dependent on their structure and morphology, cheap production, easy chemical modification and long-term stability. Herein we employed nitrogen-doped carbon nanodots (C-dots) as electrocatalyst of ORR in both basic and acidic aqueous solutions. C-dots are reported to be composed of polyatomic carbon domains surrounded by amorphous carbon frames (Zhu et al., 2013). The nanoparticles are highly fluorescent and can be fabricated in one step reaction by microwave assisted pyrolysis. Their abundant of organic groups shell allows to be immobilized on the graphite electrode through chemical conjugation. Thus, the presented report suggests a novel approach for producing effective electro-catalyst as alternative to platinum for ORR.

Experimental Procedures

Materials. Citric acid, 1,2-ethylenediamine, sodium nitrite, sodium bicarbonate, potassium hydroxide, sulfur acid and concentrated hydrochloric acid were purchased from Wako. All the chemicals used within the experiments were of an analytical grade without any further purification. All solutions were prepared with deionized water. Graphite rods (model: Uni 0.5 Mm Hb Nano Dia Blended Hi-quality Mechanical Pencil Leads, made in Japan) with 1.2 nm diameter were used as a working electrode (cathode).

Fabrication of graphite electrode chemically coated with carbon nanodots. The nanoparticles were prepared by the so called “bottom up” method. For that purpose 1 g of citric acid was mixed with 10 ml deionized water and 0.2 ml of 1,2-ethylenediamine was subsequently injected in the reaction mixture. The precursors were well mixed by magnetic stirrer to obtain a clean transparent solution. Then the mixture was subjected to microwave pyrolysis in 150 ml Beher glass for 180 sec in conventional microwave oven (600 W). After the pyrolytic reaction a yellow-brown pellet was formed at the bottom of the glass vessel. Its aqueous solution has acidic pH = 3.5. The pellet was dissolved again in 10 ml deionized water and cooled down in an ice bath. In another glass vessel blue nitrous acid (HNO_2) was prepared by simple mixing of ice, concentrated hydrochloric acid and sodium nitrite ($NaNO_2$) at temperature close to 0 °C. 2 ml of the freshly prepared nitrous acid was mixed with the solution of carbon nanodots. During the formation of diazonium salts the fluorescence of nanoparticles disappeared. This fluorescence quenching effect was an indicator for the monitoring of reaction end. The chemically activated nanoparticles [C-dots-N≡N$^+$] Cl$^-$ were mixed with the graphite electrodes in sodium bicarbonate ($NaHCO_3$) buffer solution. Thus, an energetic reaction of chemical conjugation occurred on the graphite surface. During the reaction bubbles were formed on the fabricated electrode surface as a result of neutralization of the bicarbonate buffer with the acidic solution of the nanoparticles.

Electrochemical measurements. The measurements were conducted by a conventional three-electrode system utilizing a Saturated Calomel electrode (SCE) and a platinum wire as a reference and counter electrode. The working electrodes were (i) unmodified graphite electrode, (ii) graphite electrode chemically modified with carbon nanodots and (iii) polycrystalline platinum disk electrode as a control experiment. For ORR measurements, 0.1 M KOH and H_2SO_4 solutions saturated with oxygen were used. Before measurement the solutions were subjected to bubbling with oxygen for 30 min to achieve their complete saturation at ambient temperature (Gara & Compton, 2011). One control experiment with solutions saturated with nitrogen was performed too.

Result and discussion

Physicochemical characterization of the carbon nanodots. The physicochemical characterization of C-dots was performed using Fourier transform infrared spectroscopy (FT-IR), dynamic light scattering (DLS) and X-ray photoelectron spectroscopy (XPS). DLS analysis showed nanoparticles size distribution in the range 1.5-2.5 nm with 2 nm average diameter. By this analysis no aggregations were found. FT-IR analysis showed absorption bands at 3000~3500 cm^{-1}, which were associated to the combination of stretching vibrations of amino (H_2N–), hydroxyl (HO–), and alkyl (C–H) functionalities. These organic groups are responsible also for the hydrophilic nature and stability of C-dots in aqueous solution. The transitions at 1566, 1402, 1184 and 768 cm^{-1} are assigned to ν(C=O), ν(C=C), ν(C–O) and ν(C–C) vibrations, respectively (Zhu et al., 2013). XPS analysis was performed, focusing on the C 1s, N 1s and O 1s regions of the carbon nanodots. XPS analysis for C 1s region shows main binding energy (BE) peaks at 285.1 eV and 287.0 eV, which correspond to functional groups of aliphatic carbons and to carbons in C=O, C-O-H and C-O-C, respectively. The region for nitrogen (N 1s) at 407.5 eV was observable with a dominant peak.

Electrochemical activity of unmodified graphite electrodes. Cyclic voltammograms were measured for the unmodified graphite macroelectrodes (as control experiment) in a range of scan rates in H_2SO_4 solution saturated with either oxygen or nitrogen gas. As we expected, in the majority of experiments with saturated oxygen there was a response for ORR electroactivity of the graphite. Nevertheless, the control experiment with solution saturated with nitrogen gave very little response with most nothing except a response for the breakdown of solvent (in case of organic solvent as methanol).

Electrochemical activity of graphite electrode coated with C-dots. The ORR electroactivity of the immobilized C-dots on the graphite electrode was evaluated in basic and acidic media as explained above. On Fig. 1 are shown typical linear sweep volammograms obtained from (i) unmodified graphite electrode, (ii) graphite electrode coated with carbon nanodots, and (iii) polycrystalline platinum disc electrode. The experiments were performed in oxygen saturated solutions of 0.1 M potassium hydroxide (Fig. 1A) and 0.1 M sulfuric acid (Fig. 1B). The figure shows that the unmodified electrode and the platinum electrode have an ORR peak current (I_p) and ORR onset at –552 μAcm^{-2} and –0.35 V, and at –559 μAcm^{-2} and –0.038 V

(vs SCE), respectively in basic solution. In acidic solution the unmodified electrode and platinum disk have ORR peak current and ORR onset at –662 μAcm^{-2} and –0.51 V, and at –717 μAcm^{-2} and –0.47 V (vs SCE), respectively. In both experiments as theoretically expected the polycrystalline platinum disk electrode displays optimal oxygen reduction reaction activity. It is clear further on both figures that in basic or acidic solution modified graphite electrode becomes less electronegative. In case of KOH the ORR onset of the coated electrode shifted from –0.35 V to –0.27 V (shifting by 0.08 V) and the peak shifted from –552 μAcm^{-2} to –484 μAcm^{-2} (shifting by 68 μAcm^{-2}). In the case of the acidic solution the change is even more significant. The ORR onset of the coated electrode shifted from –0.51 V to –0.16 V (shifting by 0.35 V) and ORR peak current shifted from –662 μAcm^{-2} to –597 μAcm^{-2} (shifting by 65 μAcm^{-2}). The analysis of the figure proved that the modification of the electrode with carbon nanodots enables ORR to occur at a less electronegative overpotential compared to that of unmodified electrode. As a result the electrochemical reaction proceeds at less electronegative ORR onset and the achievable current density is increasing.

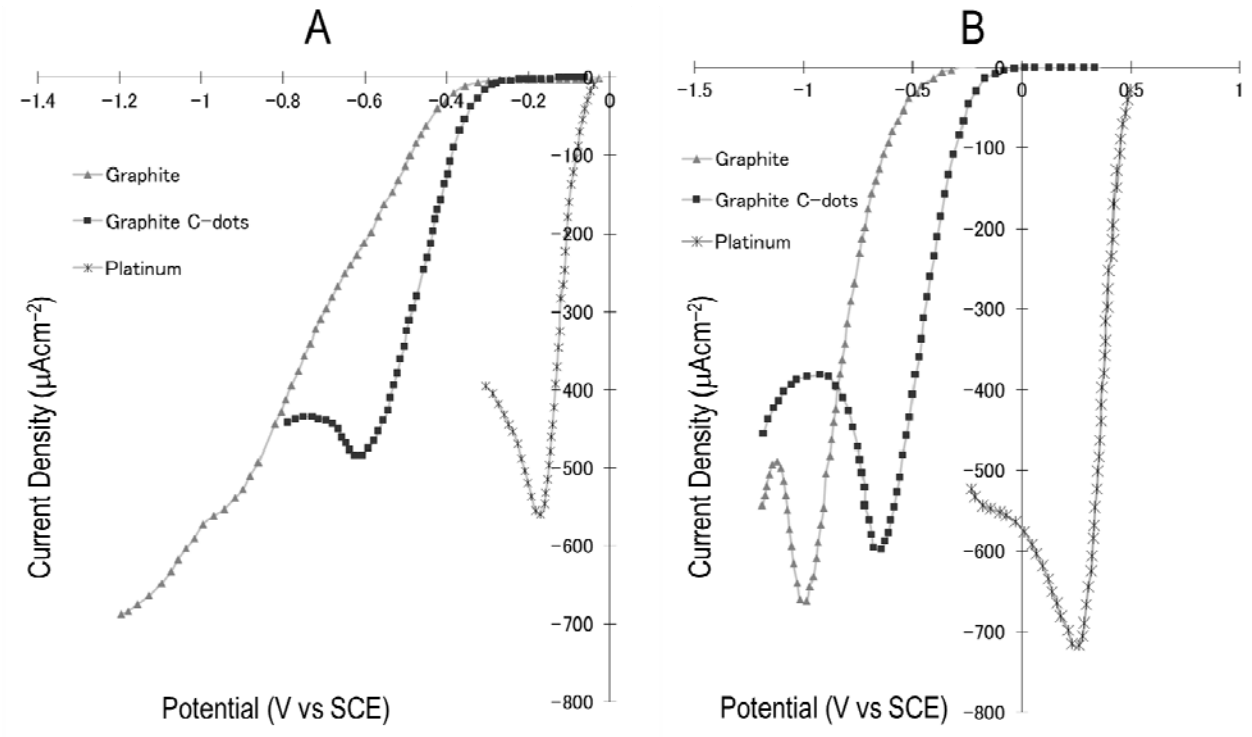

Fig. 1. Linear sweep volammograms of unmodified graphite, graphite electrode chemically coated with nitrogen doped carbon nanodots and platinum disk electrode in (A) 0,1 M solution of KOH and (B) 0,1 M solution of H_2SO_4

The obtained data concluded that the addition of fluorescent nitrogen doped carbon nanodots on the electrode surface caused beneficial alteration to the ORR signal output. The reason is because in both basic and acidic solution the nanoparticles have a 2 electron pathway ORR mechanism. In the case of H_2SO_4 the obtained H_2O_2 was the major reaction product (Martınez-Perinan et al., 2018). It was important to test the operational stability during longer period of exploitation of the modified electrode in order to claim for its practical industrial applications. All experiments show that the modified electrodes have initial increase in their relative current output (during 90 min exploitation). These were important results for the practical use of the electrode as cathode in fuel cells. However, after few hours' exploitation (less than 4) their current gradually decreases. Note that the nature of graphite electrode is with low adhesion which enables dissolution of its rough surface into the electrolyte during the friction with liquids.

Another practical advantage of the fabricated electrode is the resistance of the carbon nanodots to poisoning as inhibition of the catalytic centers with hydrogen sulfide, carbon oxide and methanol. These mentioned compounds have been shown to reduce significantly the ORR activity of all platinum based electrocatalysts. In addition, the presence of the nano-layer on the electrode reduces the charge transfer resistance and thus improves the electrochemical response. This property could find application in the biosensors technologies too.

Conclusion

We reported the fabrication and electrochemical characterization of graphite electrode modified with nitrogen doped carbon nanodots towards the ORR in basic and acidic media. All experiments show increasing of the ORR signal output, which caused increasing of the achievable current too. Thus, the electronegativity of the ORR onset potential of the modified electrode was decreased. Future work is orientated to improve the stability of the nano-layer on the electrode surface. This might offer cheap, stable and effective alternative of the platinum based cathode materials.

Acknowledgment

Funding from Bulgarian National Science Found, Grant № DN07/7, 15.12.2016. This study was accomplished thankful to the bilateral agreement between Saitama University-Japan and the University of Mining and Geology "St. Ivan Rilski"-Bulgaria.

References

Gara, M., R. G. Compton. Activity of carbon electrodes towards oxygen reduction in acid: a comparative study. - New J. Chem. 35, 2011. - 2647–2652.

Haitao, L., K. Zhenhui, L. Yang, L. Shuit-Tong. Carbon nanodots: synthesis, properties and applications. - J. Mater. Chem. 22, 2012. - 24230–24253.

Huang, X., Y. Wang, W. Li, Y. Hou. Noble metal-free catalysts for oxygen reduction reaction. - Sci China Chem. 60, 12, 2017. - 1494–1507.

Lin, L., Q. Zhu, A.W. Xu. Noble-metal-free Fe-N/C catalyst for highly efficient oxygen reduction reaction under both alkaline and acidic conditions. - J Am Chem Soc. 136, 31, 2014. - 11027–11033.

Martinez-Perinan, E., I. Bravo, S.J. Rowley-Neale, E. Lorenzo, C.E. Banks. Carbon nanodots as electrocatalysts towards the oxygen reduction reaction. - Electroanalysis 30, 2018. - 436–444.

Wang, Y., C. Wang, H. Guo, Y. Wang, Z. Huang. A nitrogen-doped three-dimensional carbon framework for high performance sodium ion batteries. - RSC Adv. 7, 2017. - 1588–1592.

Yeager, E. Electrocatalysts for O2 reduction. Electrochim. - Acta. 29, 1984. - 1527–1537.

Zhu, S., Q. Meng, L. Wang, L. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang, B. Yang. Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging. - Angew Chem Int Ed Engl. 52, 14, 2013. - 3953–3957.