Electrochemically modified carbon materials for applications in electrocatalysis and biosensors

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Presented in 2016, Instituto Universitario de Materiales. Universidad de Alicante.

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OBJECTIVES AND NOVELTY

The present work focused in the functionalization of nanostructured carbon materials for their application as electrocatalysts for the oxygen reduction reaction at the cathode of fuel cells and as transducer elements in electrochemical biosensors.

Fuel Cells

Nowadays, there is an increase in the use and consumption of energy in the world and until now the fossil fuels cover this demand. There is the necessity of the use of renewable energies; however, since they are discontinuous, devices for energy storage and production are needed. In this sense, several devices have been developed during the last decades, in which the fuel cells appears as a good alternative to replace/combine the combustion engines. Fuel cells can be applied in various industries such as automotive, stationary and portable energy generation and supply for emergency systems. These devices have several advantages compared to conventional technologies that are used for energy production: (i) can operate with higher efficiency than the combustion engines; (ii) can convert chemical energy from a fuel into electric energy with efficiency close to 60%; (iii) have lower emissions than the conventional combustion engines. However, there are several aspects that still are in development for their use in practical applications.

The reaction that occurs in the cathode is the Oxygen Reduction Reaction (ORR). The ORR is a reaction with a slow kinetics, which makes necessary the use of a catalyst. The challenge is to develop new electrocatalysts with high performance and durability at lower prices. Even though platinum is the best catalyst, when supported on carbon materials, such materials are expensive and vulnerable to poisoning and electrochemical deactivation, which affect their efficiency and useful life. For that reason, it is necessary to explore new electrocatalytic materials of lower costs. Therefore the focus is on catalysts with non-noble metals or metal-free, which are less expensive, robust to the deactivation or poisoning and highly available in nature.

Biosensors

Glucose detection has been studied for many years because of its implication in diseases as diabetes and hypoglycemia. They are caused by metabolic disorders in which the body does not produce the necessary amount of insulin for glucose processing, leading to glucose levels out of the normal concentration range (4.0 to 5.9 mM). The diagnosis and supervision of these diseases leads to a high demand for blood glucose monitoring systems and huge efforts have been done in the development of novel sensors.

The development of biosensors based on glucose oxidase enzyme (GOx) is seen as the most promising technology to achieve accurate, non-invasive and even continuous monitoring of sugar levels, and research on this field has witnessed a remarkable activity. The use of this specific enzyme leads to an increase in the selectivity and the sensitivity of the sensor, minimizing the possible interferences with other analytes present in biological fluids. The limiting factor in the glucose biosensors is the electron transfer between the FAD and the electrode surface. The use of nanostructured carbon materials has been studied as electrode materials in order to enhance the electronic transfer, which results in an increase of the selective recognition, and in an enhancement of the detection limit.

RESULTS

Electrochemical functionalization of carbon nanotubes (CNTs) and Zeolite Templated Carbon (ZTC) with aminobenzene acids

The functionalization of CNTs with aminobenzene acids has been performed using potentiodynamic methods at oxidative conditions. The functionalization was confirmed by XPS and electrochemical measurements. An increase in the nitrogen, sulfur and phosphorus content was seen for the 4-aminobenzoic (4-ABA), 4-aminobenzence sulfonic (4-ABSA) and 4-aminobenzyl phosphonic (4-ABPA) acids functionalized CNTs, respectively. A noticeable increase in the capacitance for the functionalized CNTs points out the formation of an electroactive polymer thin film on the CNTs surface along with covalently bonded functionalities (Fig. 1a).

The ORR activity was studied in basic medium using a RRDE. The ORR activity of the functionalized samples was similar to that of the parent CNTs, independently of the functional group present in the aminobenzene acid. A heat treatment in a slightly oxidizing atmosphere at 800 ºC of the CNTs functionalized with aminobenzoic acid produced a material with high amounts of surface oxygen and nitrogen groups, that seem to modulate the electron-donor properties of the resulting material, which enhance the ORR activity (NT-ABA_800_O in Fig. 1b). These are promising results that validates the use of electrochemistry for the synthesis of novel N-doped electrocatalysts for ORR in combination with adequate heat treatments.

A selective electrochemical functionalization of a zeolite templated carbon (ZTC) with two different aminobenzene acids (2-ABA and 4-ABA) was performed. The optimization of the functionalization conditions was achieved in order to preserve the unique ZTC structure. It was possible to avoid the electrochemical oxidation of the highly reactive ZTC structure by controlling the potential limit of the potentiodynamic experiment. The electrochemical characterization demonstrated the formation of

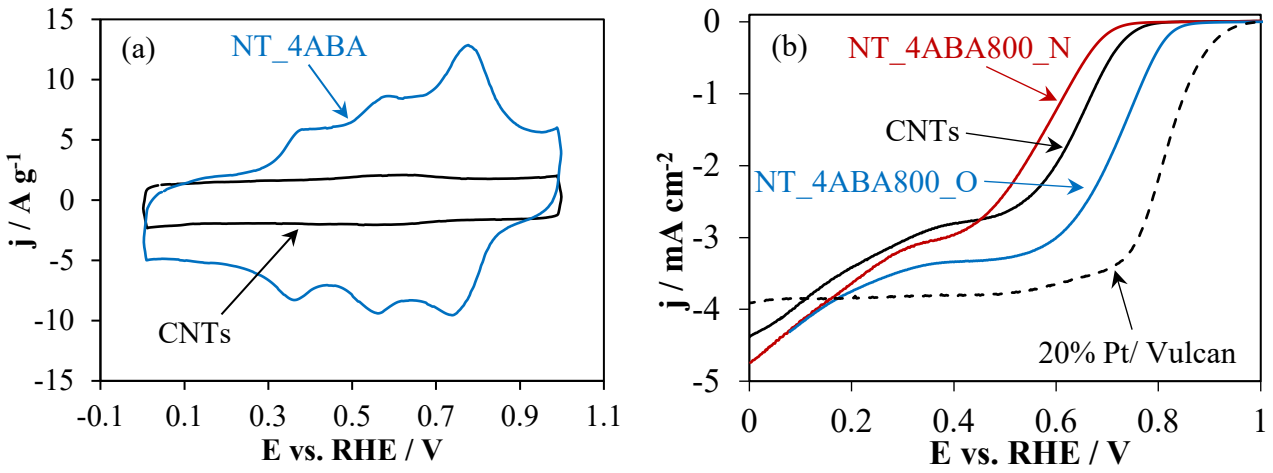

Fig. 1 (a) CV of CNTs and functionalized nanotubes with 4-ABA (NT_4ABA). (b) LSV of NT-4-ABA based samples at 1600 rpm, 5 mV s^{-1}

polymer chains along with covalently bonded functionalities to the ZTC surface (Fig. 2). The success of the proposed approach was also validated by using TPD, XPS and FTIR, which confirmed the presence of different nitrogen groups in the ZTC surface. This method could be used to achieve highly selective functionalization that could enhance the electro-oxidation resistance and increase the capacitance of highly porous carbon materials.

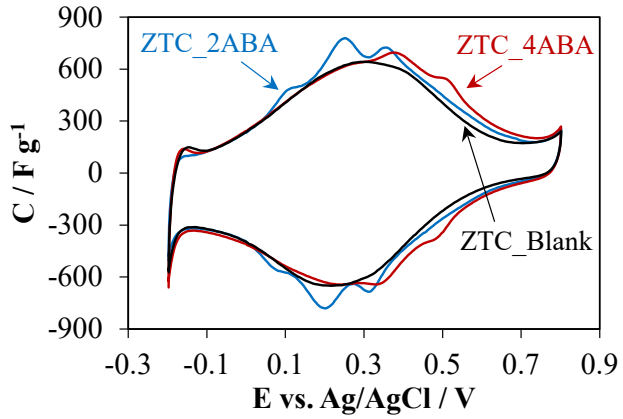

Fig. 2 CV of functionalized ZTC with 2-ABA and 4-ABA.

Iron (FePc) and Cobalt (CoPc) phthalocyanines supported con CNTs as electrocatalysts for the ORR

Catalysts based in FePc and CoPc loaded CNTs were prepared. The catalysts were heat treated at different temperatures and atmospheres in order to change the surface chemistry of the pristine CNTs. The role of those functionalities in the activity and stability as electrocatalysts for the ORR in alkaline medium was studied. The prepared catalysts displayed an enhanced activity towards ORR compared to the pristine CNTs.

The samples based in FePc showed a better performance than the CoPc-based samples, with equivalent performance to the state-of-the-art Pt-C catalyst even with very low amount of metal (Table 1). According to the temperature of the heat treatment, changes in the chemical properties of the materials are produced, which showed an enhanced activity when the samples are heat treated at 400 ºC where a stronger interaction of the FePc with the CNTs is observed. Additionally, the use of functionalized carbon nanotubes with oxidized nitrogen species as support showed that the presence of such functionalities leads to a decrease in the ORR activity, since they prevent the π-π interaction between the CNTs surface and the FePc. Finally, stability tests were performed and it was found that the fast deactivation seems to be related to the H_2O_2 formation during the experiments.

Table 1. Electrochemical parameters calculated from the RRDE experiments of the electrocatalysts

Sample	E_{onset} vs. RHE / V	% H_2O_2 at 0.4 V
NTs	0.74	89
NT_CoPc	0.83	48
NT_CoPc_400	0.83	59
NT_CoPc_800	0.85	83
NT_FePc	0.92	10
NT_ FePc_400	0.94	7
NT_FePc_800	0.88	59
20% Pt-C	0.97	4

Glucose biosensors based on CNTs

The development of glucose electrochemical sensors have been carried out by the immobilization of GOx on CNTs with different structures: tubular and herringbone CNTs. The CNTs were previously modified using chemical and electrochemical methods in order to change the surface chemistry and study the influence in the enzyme immobilization.

The results show that all GOx-loaded materials were active to the glucose detection using different approaches: (i) the detection of the H_2O_2 formed

during the reaction at 0.45 V, (ii) the introduction of a mediator as an electron carrier between the glucose and the FAD at 0.2 V and (iii) the detection at negative potentials, i.e. at -0.4 V, which is close to the potential of the FAD/$FADH_2$ redox processes. The best results were achieved with oxidized samples, which are proposed to immobilize a larger amount of active enzymes owing to the presence of carboxylic functionalities.

The use of negative potentials leads to remove the interference problems with other analytes usually present in the biological fluids. Glucose detection in an O_2 saturated atmosphere at -0.4 V for oxidized herringbone CNTs, this glucose biosensor shows a linear detection range between 0.03 and 4 mM with a sensitivity of 1.07 μA mM^{-1} and a detection limit of 0.01 mM. The biosensor based in oxidized tubular CNTs shows a linear detection range between 0.3 and 7 mM, and a sensitivity of 0.804 μA mM^{-1} with a detection limit of 0.1 mM.

CONCLUSIONS

The main contribution of this work was the the functionalization of nanostructured carbon materials using conventional chemical and thermal treatment methods and novel electrochemical methods. The electrochemical functionalization with different aminobenzene acids was successfully performed using carbon nanotubes and ZTC. The conditions were optimized in order to preserve the structure of the materials, changing the surface chemistry of the pristine materials.

The prepared materials were tested in two different applications; as electrocatalysts for the ORR and as transducer elements of biosensors for glucose detection. The functionalized materials showed an enhanced ORR activity depending on the functionalization and heat treatment performed to the materials. The metal-free catalysts showed a good performance when an oxidant atmosphere was used during the heat treatment, due to the combination of oxygen and nitrogen functionalities that modulate the electron-donor properties in the activity. FePc based catalyst showed an excellent ORR catalyst performance – close to the Pt-based catalyst – with a small amount of metal loading.

Likewise, biosensors for glucose detection were prepared by adsorption of GOx on the modified carbon materials. The glucose detection was performed by using different approaches: the detection of the H_2O_2 formed during the reaction at 0.45 V, the introduction of a mediator as an electron carrier between the glucose and the FAD at 0.2 V and the detection at -0.4 V.

RELATED PUBLICATIONS

[1] González-Gaitán C, Ruiz Rosas R, Nishihara H, Kyotani T, Morallón E, Cazorla-Amorós D. Successful functionalization of superporous zeolite templated carbon using aminobenzene acids and electrochemical methods, Carbon, 2016; 99, 157 - 166.

[2] González-Gaitán C, Ruiz Rosas R, Morallón E, Cazorla-Amorós D. Electrochemical methods to functionalize carbon materials. In Chemical functionalization of Carbon Nanomaterials: Chemistry and Applications, Taylor & Francis Group, 2015; 231 - 249.28/07/2015.

[3] González-Gaitán C, Ruiz Rosas R, Morallón E, Cazorla-Amorós D. Functionalization of carbon nanotubes using aminobenzene acids and electrochemical methods. Electroactivity for the oxygen reduction reaction, International Journal of Hydrogen Energy, 2015; 40, 11242 – 11253.

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