

SILICA-TEMPLATED ORDERED MESOPOROUS N-DOPED CARBON THIN FILMS. A HIGHLY EFFICIENT CATALYST TOWARDS OXYGEN REDUCTION REACTION

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Introduction

Metal-free catalysts are one of the most promising alternatives as cathodes for oxygen reduction reaction (ORR) in fuel cells and metal-air batteries. Among them, N-doped carbon materials are considered as a possible substitute of the commercial platinum-based catalysts used in these devices¹.

The most common preparation method of N-doped carbon materials is based on the heat treatment of a mixture of nitrogen and carbon-containing precursors. However, one of the main limitations of these routes of synthesis is that the pore structure and pore size distribution cannot be controlled².

Therefore, controlling the structure of the materials using a template arises as an important option to overcome this problem. In this study, we report a method to synthesize 2D mesoporous N-doped carbon materials with high control over the nature of active sites towards oxygen reduction reaction and pore size distribution by electropolymerization and carbonization of a thin film of polyaniline on an ordered mesoporous silica template. The promising catalytic performance of the materials emphasizes the relevance of the thickness of polyaniline thin films and the temperature used in the heat treatment, since this permits tailoring the most active sites.

Materials and Methods

Nanostructured 2D ordered mesoporous silica thin films were synthesized via dip-coating onto the graphite current collector and used as the hard-template³.

The electrochemical polymerization of aniline was performed in a conventional three-electrode cell through chronoamperometric experiments in acid medium. Once the polymerization is finished, electrochemical characterization of the G/Si-PANI-X samples (where X is the time of polymerization) were carried out by cyclic voltammetry (CV) in acid medium. The samples were heat treated in a tubular furnace at 900°C. The samples were named as G/Si_PANI_X_900 and they were characterized by cyclic voltammetry in different electrolytes..

The template was removed in the sample obtained after 5 minutes of polymerization. In order to remove the template of the sample was immersed into a 10M NaOH solution during 5 h at 75°C. Then it was washed several times with water. The final sample is named as G/Si_PANI_5min_900-NaOH.

The physicochemical characterization of all materials was done by XPS and TEM analysis.

The electrocatalytic activity towards ORR was studied by linear sweep voltammetry (LSV) in O₂-saturated 0.1M KOH solution.

Results and Discussion

TEM images show a well-formed ordered mesoporous silica thin films. CV profiles after polymerization shows that the time employed during the chronoamperometric experiment is directly related with the electrochemical response of the final materials. The experimental conditions for polymerization not only affect the thickness of the deposited polyaniline, but also the polymer chain length.

All previously characterized G/Si_PANI_X samples were heat treated at 900°C. CV profiles in alkaline and acidic electrolytes of the heat-treated samples show that the thickness of the electropolymerized PANI determines the thickness of the final PANI-derived carbon materials. Interestingly, a new peak is observed in alkaline solution for G/Si_PANI_5min_900 sample that can be related to Si-C-N or Si-O-N species formed during the heat treatment.

The electrocatalytic activity of all materials were studied in O₂-saturated 0.1 M KOH solution. Once the polyaniline is electropolymerized and heat treated within the porosity of the silica template, relevant differences in activity are observed depending on the amount of PANI initially loaded. Higher polymerization times lead to the formation of a well-formed polyaniline, which, after carbonization, produces the N-doped carbon material with the presence of Si-C-N and Si-O-N species. The sample containing the combination of these sites (i.e., sample G/Si_PANI_5min_900) exhibits the highest catalytic activity towards ORR with an initial reduction potential (E_{ONSET}) of 0.91 V vs RHE.

In order to discern whether the Si-C-N or Si-O-N species have an influence in the catalytic activity, the silica template was removed. The removal of the silica results in a decrease in the catalytic activity, what suggests that Si-C-N or Si-O-N species are responsible for the highly efficient catalysis of G/Si_PANI_5min_900 sample.

Conclusions

2D mesoporous N-doped carbon materials were successfully synthesized through electrochemical polymerization of aniline, followed by a heat treatment at 900°C. The polymerization conditions permits to control not only the thickness of the electropolymerized PANI but also of the PANI-derived carbon material. Moreover, the carbonization seems to create Si-C-N or Si-O-N species which have an important influence in the catalytic activity for ORR. Interestingly, the etching of the silica template results in an important decrease of the ORR activity showing the crucial role the Si-containing species in the catalytic activity of the resultant composites.

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