Poster

NANOSTRUCTURES FORMATION FROM PALADIUM-COBALT PRECURSOR ON HIGHLY ORDERED PYROLYTIC GRAPHITE SURFACES

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Nano-sized metal particles continue to attract interest for different researcher areas due to their different physical and chemical properties when compared to bulk material. Nanomaterials synthesis can be done with different techniques and methods. The common methods use many processes to obtain the nanomaterials. Metal nanostructures and nanoparticles can be prepared by chemical methods allowing the control of size and composition distribution of the particles. In this methods molecular or ionic precursors are usually used as the starting material.[1,2] Additionally, the demand for tailored catalytic nanoparticles has encouraged the used of heterobimetallic precursors. For example, palladium-cobalt alloy has resulted in an extremely active catalyst for the oxygen reduction reaction.[3,4] This reaction is of most importance for developing high efficiency, stability, and durability H_2-O_2 fuel cell systems.

Our group has been working in the nanostructures and nanoparticles formation from precursors on highly ordered pyrolytic graphite (HOPG) surfaces.[5,6,7] This research focuses on the development of palladium-cobalt nanostructures with defined size and composition distribution which can be controlled by support chemical structure conditions and the atmosphere used in the deposition process. In this work, we describe the study of deposition and reductive decomposition of the heterobimetallic precursor $CoPd_2(Me_2Ipz)_4Cl_4 \cdot 2NH_4$ ($CoPd_2$) on the HOPG surfaces. We propose an easy and economic methodology for the nanostructures formation. The nanostructures formation were characterized by surface analysis techniques, such as: atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

The HOPG surfaces was imaged by AFM and SEM to study their morphology change in the modification process. AFM image of modified HOPG with $CoPd_2(Me_2Ipz)_4Cl_4 \cdot 2NH_4$ ionic precursors showed the formation of organized circular nanostructures with different sizes (Figure 1). These circles (tubes) have a diameter between 0.46 to 2.15 μm and height between 71 and 390 nm. Figure 2 shows the SEM images for modified HOPG with control of the atmosphere in the deposition process. The $CoPd_2$ precursor was thermally reduced under hydrogen atmosphere, a procedure which removes the organic ligads, forming bimetallic nanoparticles. We observed in the AFM images a particles formation tendency after reduction process of $CoPd_2$ precursor on HOPG surface. Also, the nanostructures persisted after the reduction process.

The composition of the modified surface described was characterized by XPS analysis. Typical elements peaks for modified HOPG surface are present in the XPS spectrum (Figure 3). After the reduction, the characteristic peaks of the ligands disappear and the Pd and Co peaks shift their binding energy. This is due to the adsorption of $CoPd_2$ complex on the surface and the change in oxidation state.

In summary, the deposition with atmosphere control offers an alternative methodology for the nanostructures formation to large-scale production. These results suggest that the Pd-Co structures might be promising new nanomaterials for different applications such as: electronics, sensors, storage and fuel cell. In future work we are going to obtain optimal conditions for the nanostructures formation. Additionally, to study electrocatalytic activity of metallic palladium-cobalt nanoparticles for oxygen reduction reaction.

References:

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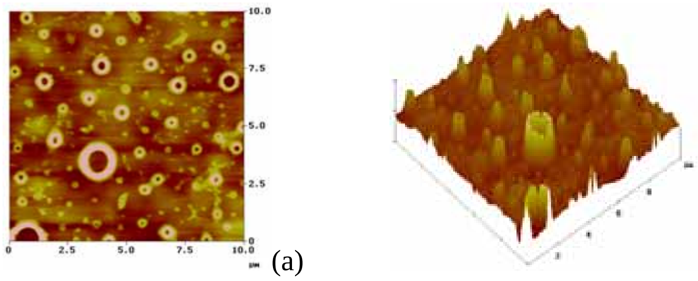
Figures:



(a) (b)

Figure 1. AFM images (a) top and (b) 3D view (z = 380 nm) for deposition of $CoPd_2(Me_2Ipz)_4$•$2NH_4$ on HOPG surface.

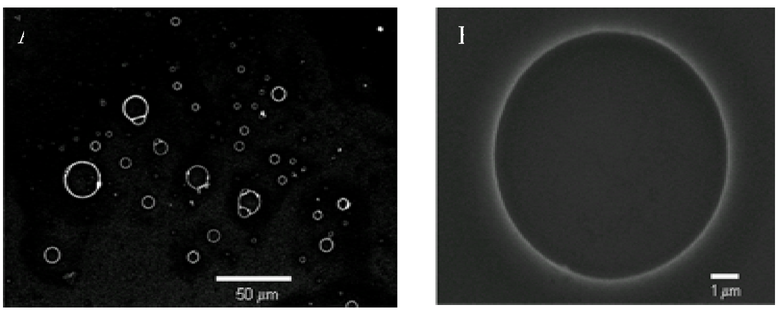


Figure 2. SEM images (A) x500, and (B) x10,000 for deposition of $CoPd_2(Me_2Ipz)_4Cl_4$ on HOPG at 21°C and 77 $\pm$ 1 %RH.

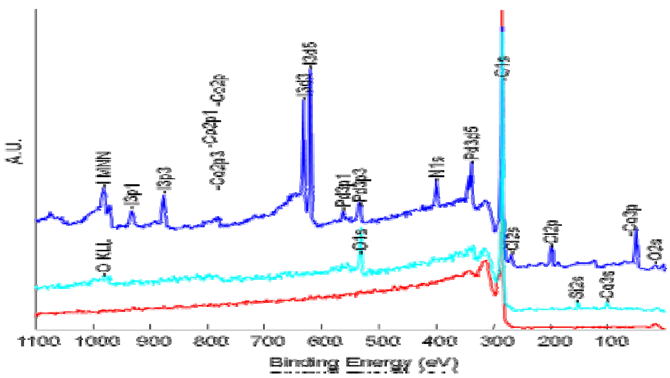


Figure 3. XPS spectrum of the surface of HOPG (red), the $CoPd_2(Me_2Ipz)_4Cl_4$•$2NH_4$ before (blue), and after (clear blue) reduction process on HOPG.