Research Letter

Nanostructural Formation of Pd-Co Bimetallic Complex on HOPG Surfaces: XPS and AFM Studies

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A new single source approach was developed to synthesize Pd-Co nanoparticles using a bimetallic compound, $[\text{Et}_3\text{NH}]_2[\text{CoPd}_2(\mu\text{-4-I-3,5-Me}_2\text{pz})_4\text{Cl}_4]$ (CoPd_2), as a molecular precursor to obtain dispersed catalyst on highly ordered pyrolytic graphite (HOPG) surface, in view of preparing oxygen reduction catalysts for low temperature fuel cells. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques were employed to characterize the nanostructure formations and to determine the composition and morphology of the complex on the HOPG. Results of high resolution XPS analysis (HR-XPS) revealed the binding energies corresponding to the atomic constituents of the precursor. When the precursor solution was placed on the surface of the HOPG, the bimetallic complex assumes a tubular structure and it appears that the surface of the HOPG offers a ground for the self-organization of nanostructural formations.

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1. Introduction

Nanoarchitecture is an emerging area that fuels the interests of scientists and engineers alike, largely due to the novel material properties that can be engineered and tuned at molecular levels. These nanomaterials are mainly used for heterogeneous catalysis. Platinum is used extensively as a catalyst in both anodes and cathodes of low-temperature polymer electrolyte fuel cells. Low-temperature fuel cells are considered alternate power sources for portable and transportation applications [1]. In spite of its excellent electrocatalytic activity, the use of monometallic platinum is disadvantageous due to its intermediate poisoning and high cost. Sophisticated bimetallic, cost-effective Pd-Co catalysts were recently proposed for oxygen reduction reaction in low-temperature fuel cells, especially for direct methanol fuel cell applications due to their methanol tolerance ability and appreciable oxygen reduction efficiency [2].

When bimetallic catalysts are prepared by using multiple precursors, it is difficult to attain homogeneous catalytic system characterized by a uniform particles size distribution.

In order to achieve such objective, in this paper, a single organometallic precursor characterized by a well-defined Pd-Co ratio has been used. This approach would allow the formation of nanostructures and nanoparticles with defined size and composition distribution.

This paper reports on the characterization of a CoPd_2 precursor and deposition for the nanoarchitectural formation on highly ordered pyrolytic graphite surface through surfaces analysis techniques such as X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

2. Experimental

The ionic precursor of $[\text{Et}_3\text{NH}]_2[\text{CoPd}_2(\mu\text{-4-I-3,5-Me}_2\text{pz})_4\text{Cl}_4]$ (CoPd_2) was synthesized following the procedure from [3]. An exfoliated piece of highly ordered pyrolytic graphite (HOPG) spi-2 grade was used as the substrate. Approximately 100 μL of CoPd_2 precursor (0.5 mM) in dichloromethane solution was deposited on HOPG surface and allowed to dry. This sample was placed under vacuum for one hour and analyzed by surface

FIGURE 1: XPS survey spectra of the CoPd₂ precursor.

analytical techniques. The reduction process was performed in a closed tube furnace by increasing the temperature to over 600°C under an H₂ stream. The samples were cool-off in an H₂ atmosphere to ~63°C and they were purged with N₂ until they reached room temperature before opening the stainless steel system.

Our scanning probe microscope was a Nanoscope IIIa-Multimode atomic force microscope (AFM) from Digital Instruments, with a scanning probe microscope controller equipped with He-Ne laser (638.2 nm) and scanner type E. A standard Si₃N₄ cantilever was used for contact mode imaging, and the scan rate was 1 Hz.

X-ray photoelectron spectroscopy (XPS) was used to determine the composition of the precursors. A PHI 5600ci spectrometer with an Al K α monochromatic X-ray source at 15 kV and 350.0 W was used to obtain a survey and multiplex XPS spectra. Spectrum was recorded at a take-off angle of 45° and pass energy of 187.8 eV for the survey and 58.7 eV for the high-energy resolution studies. The binding energies were corrected using the carbon (C1s) contamination peak at 284.5 eV.

3. Results and Discussion

Surface analytical techniques were employed to study the nanoarchitectural formation of a new heterobimetallic compound on the surface of HOPG. The molecular complex had Pd(II) and Co(II) metals with chloride and dimethyliodopyrazolate ligands. The chemical composition of the [Et₃NH]₂ [CoPd₂(μ -4-I-3,5-Me₂pz)₄Cl₄] (CoPd₂) complex and the modified HOPG surface were determined by XPS analysis. The XPS survey spectrum for the CoPd₂ precursor showed the peaks attributed to C, N, I, Cl, Pd, and Co atoms (see Figure 1).

The high-resolution XPS (HR-XPS) was used to identify the metals present in the precursor. The observed HR-XPS binding energy (BE) peaks are summarized in Table 1.

Figure 2 shows the high-resolution XPS spectrum corresponding to palladium (3d) and cobalt (2p) binding energy regions for the CoPd₂ precursor. In the Pd 3d_{5/2} region,

(a)

(b)

FIGURE 2: HR-XPS spectra corresponding to Pd 3d and Co 2p binding energy regions of the CoPd₂ precursor.

the HR-XPS spectrum shows two peaks with binding energy values of 337.9 and 339.5 eV for the Pd-Cl and Pd-N, respectively. These values are in agreement with the binding energy values of 337.8 and 337.9 eV for PdCl₂ and 339.0 eV for K₂Pd(NO₂)₄ compounds [4, 5].

In the Co region, the peak with BE of 781.3 eV is attributed to cobalt at precursor and a shakeup satellite peak at 787.0 eV [6]. The binding energy values for Co 2p_{3/2}, in the precursor, were similar to those reported in literature for other cobalt compounds with Cl-Co-N bonds [4]. The other binding energy values were as follows: I in 4-I-pz, 661.9 eV; and Cl in Cl-Co and Cl-Pd, 197.3 eV and 198.1 eV, respectively. The binding energy obtained for nitrogen in the pyrazolate was found at different regions such as 339.1, 400.1, 401.5, and 402.6 eV, and this has been due to the different chemical environments prevailing in the precursor. The C-C, C-I, and C-N bonds in the pyrazolate can be ascertained from corresponding binding energy values such as 284.5, 285.3, and 286.1 eV, respectively.

The XPS spectrum for the unmodified HOPG surface was used as a reference. A clean HOPG survey spectrum showed only the typical C(1s) and O(1s) peaks. On the other hand, the XPS survey spectrum confirmed the modification of the HOPG surface with the complex CoPd₂. Typical

TABLE 1: Binding energy (BE) values obtained from HR-XPS studies for the free standing CoPd_2 precursor and CoPd_2 precursor on HOPG surface.

Elements	Binding energy (eV)	
	Free precursor	Precursor on HOPG
Pd ($3d_{5/2}$)	337.9	338.4
	339.5	339.6
Co ($2p_{3/2}$)	781.3	781.9
	787.0	787.0
I ($3d_{5/2}$)	621.9	621.3
Cl ($2p$)	197.3	198.4
	198.1	199.7
N ($1s$)	399.1	399.7
	400.1	400.6
	401.5	401.7
	402.6	402.7
C ($1s$)	284.5	284.5
	285.3	285.4
	286.1	286.3

element peaks for Pd(3d), Co(2p), I(3d), N(1s), Cl(2p), C(1s), O(1s), and Si(2p) were present in this spectrum. This has been attributed to the adsorption of CoPd_2 precursor on the HOPG surface. The Si (2p) and O (1s) impurities might have originated from the glassware used in the preparation of the sample.

It is known that the deposition is highly influenced by the substrate surface characteristics. Also, the shape and size of the deposit depends on the substrate employed. Highly ordered pyrolytic graphite is a nonpolar, highly pure carbon, with a smooth surface and basal plane featuring a few defects. The HOPG surface image was obtained using an AFM to study the morphological change which would arise as a result of the modification process. AFM images of HOPG modified with a CoPd_2 precursor showed the formation of organized circular nanostructures of different sizes (Figure 3). These nanostructures on HOPG exhibited a tube-like shape in micro- to nanosize regime diameter and height. The AFM section analysis has been used for size determination of the nanostructures.

In Figure 3(a), the rings exhibit diameters which range from 156 nm to $2.03\ \mu\text{m}$ and heights between 25 and 385 nm. Figure 3(b) shows rings with diameters ranging from 234 nm to $1.86\ \mu\text{m}$ and heights between 14 and 200 nm. Their inner diameters span from 30 to 898 nm and wall thickness between 117 and 391 nm. Some structures are volcano-like shapes with the top end of the wall smaller in diameter than the bottom.

Other samples examined by AFM and scanning electron microscopy (SEM) showed diameters ranging from 150 nm to $8.1\ \mu\text{m}$ and the heights between 10 and 400 nm with a maximum frequency at 60 nm. Similar results were observed with palladium precursors [7, 8]. The interaction between

FIGURE 3: AFM images top and 3D view (a) $10\ \mu\text{m} \times 10\ \mu\text{m} \times 380\ \text{nm}$ and (b) $10\ \mu\text{m} \times 10\ \mu\text{m} \times 160\ \text{nm}$ for deposited of CoPd_2 precursor on HOPG surfaces.

precursor-solvent-substrate and the evaporation process play an important role in the rings structure formation [8, 9]. Gómez-Segura et al. reported the self-assembly of Mn_{12} microrings in the HOPG surfaces [9]. CoPd_2 precursor is a nonpolar complex allowing the interaction with the HOPG surface. The organic ligands ($(\mu\text{-4-I-3, 5-Me}_2\text{pz})_4\text{Cl}_4$) in the precursor prevent the random particles dispersion, and hence the solution drops evaporate to form the same type of structures. Different structural size formations can be seen when the samples are prepared in different days, perhaps due to the humidity change on a given day. It is assumed that the structural difference causes this change. Development of palladium-cobalt nanostructures with defined sizes can be controlled by the characteristics of the support surface and the environment used in the deposition process. The process of circular structure formation is not fully understood and a study with humidity control is underway.

The CoPd_2 precursor was thermally reduced under hydrogen atmosphere, a procedure which removes the organic ligands. The rings formation tendency is preserved after the reduction process. This nanostructures show different size distributions on the surface. Moreover, in the images of the AFM, it is possible to observe the rings formed by bimetallic particles (see Figure 4).

In the survey spectrum after the reduction process, the corresponding peaks of pyrazolate ligands disappear while the Pd and Co peaks shift their binding energy. The CoPd_2 precursor reduced has a BE at 335.0 eV, 335.9 eV,

FIGURE 4: AFM images top and 3D view ($10\ \mu\text{m} \times 10\ \mu\text{m} \times 100\ \text{nm}$) after thermal reduction of CoPd_2 precursor on HOPG surface.

and 337.4 eV for Pd $3d_{5/2}$, which shows the presence of three different species. The literature reports binding energy values of 335.1 eV for Pd metallic [4], 335.7 eV for PdCo alloy [10, 11], and 337.9 eV for PdO_2 and PdCl_2 [4, 5, 12]. For the Co region, the peak at 781.5 eV is higher than the cobalt metallic [5] and can be attributed to cobalt bimetallic because they are similar to reported value (781.9 eV) at literature for PtCo bimetallic [13]. On the other hand, the BE at 787.3 eV is for the shakeup satellite of cobalt. The binding energy shifts could be caused by the Pd-Co alloy formation. We can observe similar results with the precursor reduced on HOPG surface. For the Pd $3d_{5/2}$ region, the BE is of 335.3 eV, 336.1 eV, and 338.1 eV. The binding energies of 781.3 eV, 783.8 eV, and 788.2 eV correspond to Co region. Also, the binding energy displacement in the Pd and Co regions shows the change of oxidation state and demonstrates that the modified HOPG surface changes after the reduction process.

HOPG provides the surface for the nanostructures preparation and it can be used as an electrode for electrochemical analysis. In addition, these nanostructures with different size distribution in the HOPG surfaces may lead to its development for diverse applications.

Our future work would be focused on optimizing the conditions (e.g., relative humidity) for the nanostructures formation at HOPG surfaces. We are also studying different precursors and surfaces to see if they exhibit a similar behavior. These precursors have the same ligands but with different metal combinations like Pd-Ni, Pd-Cu, Pt-Co, among others. These combinations open the possibility of straightforward development of nanomaterials for various applications. Furthermore, the obtained novel metallic nanostructures and nanoparticles from CoPd_2 precursor will be evaluated for oxygen reduction reaction in fuel cell cathode applications.

4. Conclusion

We prepared a promising bimetallic nanocatalyst by chemical method from single precursor. The XPS spectrum of the $[\text{Et}_3\text{NH}]_2[\text{CoPd}_2(\mu\text{-}4\text{-I-}3,5\text{-Me}_2\text{pz})_4\text{Cl}_4]$ precursor and modified HOPG surface confirmed the interaction between the precursor and the substrate. HR-XPS allowed the analysis of different species present in the precursor. The AFM image showed circular structures in the range of micro- to

nanometer with the precursor's deposition at HOPG surface. Hence, this study is vitally important in the aspects of developing nanostructures and nanoparticles in well-defined support surfaces. This precursor is a promising new material for obtaining Pd-Co nanorings with self-formation at HOPG surfaces.

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References

- [1] B. Viswanathan and M. A. Scibioh, *Fuel Cells: Principles and Applications*, CRC Press, Boca Raton, Fla, USA, 2008.
- [2] O. Savadogo, K. Lee, K. Oishi, S. Mitsushima, N. Kamiya, and K.-I. Ota, "New palladium alloys catalyst for the oxygen reduction reaction in an acid medium," *Electrochemistry Communications*, vol. 6, no. 2, pp. 105–109, 2004.
- [3] H. N. Miras, H. Zhao, R. Herchel, C. Rinaldi, S. Pérez, and R. G. Raptis, "Synthesis and characterization of linear trinuclear Pd, Co, and Pd/Co pyrazolate complexes," *European Journal of Inorganic Chemistry*, vol. 2008, no. 30, pp. 4745–4755, 2008.
- [4] J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*, Perkin-Elmer, Eden Prairie, Minn, USA, 1992.
- [5] G. Kumar, J. R. Blackburn, R. G. Albrige, W. E. Moddeman, and M. M. Jones, "Photoelectron spectroscopy of coordination compounds—II. Palladium complexes," *Inorganic Chemistry*, vol. 11, no. 2, pp. 296–300, 1972.
- [6] F. B. Noronha, M. Schmal, B. Moraweck, et al., "Characterization of niobia-supported palladium—cobalt catalysts," *The Journal of Physical Chemistry B*, vol. 104, no. 23, pp. 5478–5485, 2000.
- [7] R. Díaz-Ayala, L. Arroyo, R. G. Raptis, and C. R. Cabrera, "Thermal reduction of Pd molecular cluster precursors at highly ordered pyrolytic graphite surfaces," *Langmuir*, vol. 20, no. 19, pp. 8329–8335, 2004.
- [8] R. Díaz-Ayala, E. R. Fachini, R. G. Raptis, and C. R. Cabrera, "Palladium nanostructures and nanoparticles from molecular precursors on highly ordered pyrolytic graphite," *Langmuir*, vol. 22, no. 24, pp. 10185–10195, 2006.
- [9] J. Gómez-Segura, O. Kazakova, J. Davies, P. Josephs-Franks, J. Veciana, and D. Ruiz-Molina, "Self-organization of Mn_{12} single-molecule magnets into ring structures induced by breath-figures as templates," *Chemical Communications*, no. 45, pp. 5615–5617, 2005.
- [10] K. Lee, O. Savadogo, A. Ishihara, S. Mitsushima, N. Kamiya, and K.-I. Ota, "Methanol-tolerant oxygen reduction electrocatalysts based on Pd-3D transition metal alloys for direct methanol fuel cells," *Journal of the Electrochemical Society*, vol. 153, no. 1, pp. A20–A24, 2006.

- [11] L. Zhang, K. Lee, and J. Zhang, "Effect of synthetic reducing agents on morphology and ORR activity of carbon-supported nano-Pd-Co alloy electrocatalysts," *Electrochimica Acta*, vol. 52, no. 28, pp. 7964–7971, 2007.
- [12] D. Bera, S. C. Kuiry, Z. U. Rahman, and S. Seal, "Template-assisted deposition of palladium nanoarrays preparation, microscopic, and spectroscopic studies," *Journal of the Electrochemical Society*, vol. 152, no. 8, pp. C566–C570, 2005.
- [13] Z. Zsoldos and L. Guzzi, "Structure and catalytic activity of alumina supported platinum-cobalt bimetallic catalysts. 3. Effect of treatment on the interface layer," *The Journal of Physical Chemistry*, vol. 96, no. 23, pp. 9393–9400, 1992.