Deposition and Characterization of Platinum Nanoparticles on Highly Orientated Pyrolytic Graphite

Nora Elizondo Villarreal[*,**], Carlos Novar[**], Ji Ping Zhou[**], Lorena Álvarez Contreras[***] and Ran Tel Vered[****]

[*]Department of Physics, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N. L., C.P. 66451, México, nelizond@mail.uanl.mx

[**]Department of Chemical Engineering and Texas Materials Institute, University of Texas at Austin, TX 78712, USA, jpzhou@ccwf.cc.utexas.edu, norae@che.utexas.edu

[***]Department of Chemical Materials, Research Center on Advanced Materials, S. C., Miguel de Cervantes 120, Complejo Ind. Chih., 31109 Chihuahua, Chih., México, lorena.alvarez@cimav.edu.mx

[****]Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel, telvered@gmail.com

ABSTRACT

Pt nanoparticles were synthesized by polyol method and then deposited on a highly orientated pyrolytic graphite (HOPG) substrate. They also were obtained by direct reduction of chloroplatinic acid on HOPG in a H_2 flow and by immersing the graphite electrode into a platinum plating solution, 0. 1 mM H_2Cl_6Pt and 0.1 M H_2SO_4 solution. The density of particles as well as their dimension depend in this case on the time of immersion in the hexachloroplatinic solution. Pt nanoparticles formed for these methods are mainly quasi hemispherical small Pt nanoparticles in size. The characterization of these systems was studied by high angle annular dark field (HAADF) technique and transmission electron microscope (HRTEM). The combination of these experimental techniques allowed, the determination of the structure and the distribution of Pt nanoparticles on HOPG. A rotation between the layers of HOPG was observed in the direction perpendicular to the basal plane by effect of heating in H_2.

Keywords: platinum nanoparticles, characterization, deposition, transmission electron microscope

INTRODUCTION

Platinum is considered one of the best electrocatalyst for low temperature reactions in a H_2/O_2 fuel cell. Metallic nanoparticles are of great interest because of the modification of properties observed due to size effects, modifying the catalytic, electronic, and optical properties of the monometallic nanoparticles. Interest in platinum nanoparticles derives mostly from the importance of highly dispersed platinum in catalysis. An "ideal" model system for investigating a particle size effect in electrochemical reactions-such as the methanol oxidation and oxygen reduction reactions- would possess all of the following characteristics: (1) Platinum nanocrystals should be size and shape monodisperse. (2) Nanocrystals should be dispersed on, and electrically connected to, a technologically relevant support surface that facilities spectroscopic characterization of the particles and of adsorbed intermediates. For many electrocataysis reactions the preferred support material is graphite. (3) Individual platinum particles on this support should be well-separated from one another. (4) The structure of the platinum nanocrystals on the support surface should be accessible both before and following the involvement of these particles in the catalytic process of interest. (5) Supported and platinum nanoparticles should be stable for days [1-5].

In this paper, a colloidal method of synthesis has been proposed to obtain metallic nanoparticles; the polyol method has been reported to produce small nanoparticles as the final product, easily changing composition and surface modifiers [6-9].

The gas-phase method of platinum salt particles disposed on a graphite surface by H_2 was used in this work. This method has the potential to yield nanocrystals that are disposed in direct contact with a substrate surface [10].

We describe also, an electrochemical method for preparing dispersions of platinum nanocrystals on a graphite basal plane surface involving the pulsed potentiostatic deposition of platinum from dilute $PtCl_6^{2-}$ using large overpotentials ($E_{overvoltage} \approx 500$ mV) [11-13].

A novel approach to characterize this kind of particles is based on the use of HAADF technique, in a high resolution transmission electron microscope (HRTEM), which allowed us the observation of the elements due to atomic number, densities, or the presence of strain fields due to differences in lattice parameters, structure, the presence of surfactants or any other surface modifier besides the size of the particle [14].

The HOPG is described as consisting of a lamellar structure The freshly cleaved surface consists of atomic steps and steps of several or dozens of atomic layers. The crystallographic planes do have a definite structure and the

NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8503-7 Vol. 1

height of a single step is 0.34 nm [15]. The Moiré patterns were observed and rotations between the first and second layers of HOPG in the direction perpendicular to the basal plane by effect of heating Pt nanoparticles on HOPG in H_2 flow [14, 16].

EXPERIMENTAL SECTION

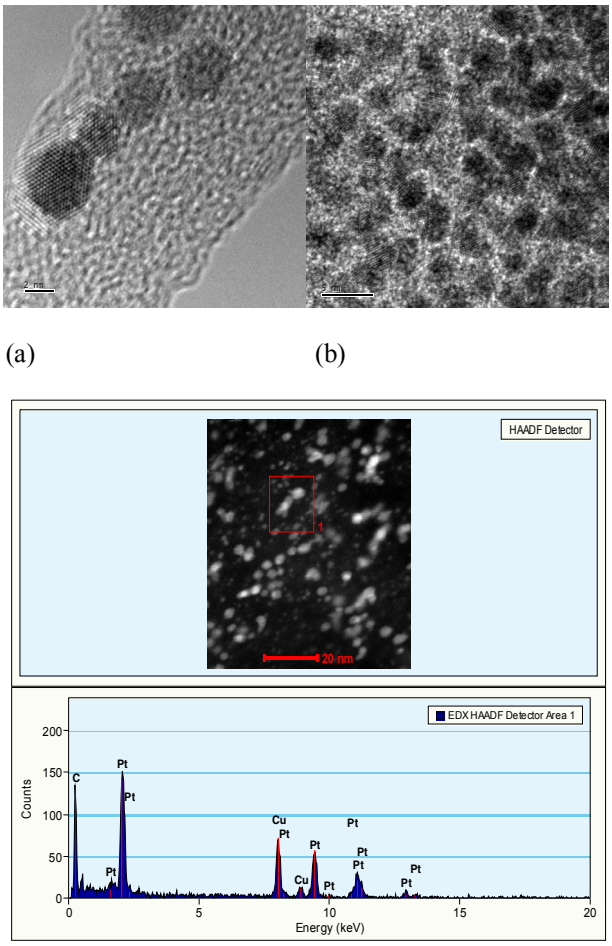
The polyol method was followed to obtain platinum metallic nanoparticles passivated with poly(vinylpyrrolidone) (PVP). Hexachloroplatinic (IV) acid (H_2PtCl_6) hydrate (99.99%), and poly (N-vinyl-2-pyrrolidone) (PVP-K30, MW = 40000) were purchased from Sigma Aldrich, and 1,2-ethylenediol (99.95%) was purchased from Fischer Chemicals; all the materials were used without any further treatment.

A 0.4 g sample of Poly (N-vinyl-2-pyrrolidone) (PVP) was dissolved in 50 mL of 1,2-ethylenediol (EG) under vigorous stirring, heating in reflux, until the desired temperature was reached (working temperatures ranged from 100 to 190 °C in increments of 10 °C). For the Pt metallic nanoparticles, a 0.1 mM EG-solution of the metal precursor was added to the EG-PVP solution, with continuous agitation for 3 h in reflux. When preparing the Pt metallic nanoparticles, the following criterion was used: after complete dissolution of PVP in EG, 2 mL of an EG solution of H_2PtCl_6 (0.05 M) was added to the EG-PVP solution in a period of 1 h. The reaction was carried out for 3 h at constant temperature. For this work the Pt nanoparticles presented the smaller average size for a synthesis performed at 130 °C. These Pt nanoparticles in a solution of ethanol were impregnated on HOPG and dried in a oven at 80°C.

The Pt nanoparticles preparation on HOPG by direct reduction of Platinum salts in H_2 flow on HPOG (the gas phase method) consisted in the partial oxidation of the support in a muffle furnace at 600°C for 24 hours. Then the impregnation of preoxidized HOPG with chloroplatinic acid solution in a four to one mixture of benzene to ethanol (absolute). The metal concentration was adjusted to produce the desired total metal loading (10 Wt % Pt). The amount of solvent was fixed using 50 ml/g of HOPG. A mixture of salt solution and HOPG was shaken while nitrogen was bubbled through the suspension at flow rate of 200-500 cc/min until to solution evaporated to dryness, i.e., after 40-60 hr for a 10 g sample in 500 ml of solution.

The samples prepared by these methods (Pt nanoparticles on HOPG) were heated in a H_2 flow at a temperature range from 450 ºC to 1000 ºC during time intervals from 2hr to 5 hr. Samples were then exfoliated with a scotch tape for TEM observation.

Pt nanoparticles were electrochemically deposited on a highly ordered pyrolytic graphite (HOPG, grade-1) which was obtained from SPI Supplies (West Chester, PA). Platinum deposition was carried out by immersing the potential in which electroless platinum deposition was not observed), followed by stepping the potential of the graphite surface to a deposition potential of -0.6 V, for 100 ms. Following the application of the deposition pulse, the



(c)

Figure 1. A microscopy images by HRTEM, shows a platinum nanoparticle synthesized by polyol method at: (a) and (b) synthesized at 145 °C. (c) HAADF shows of Pt nanoparticles and EDX HAADF analyze of Pt nanoparticles.

electrode potential was stepped back to 0.2 V, and the working electrode was removed from the plating solution. All electrochemical experiments were performed using a CH Instruments potentiostat model CHI 900B (CH Instruments, Austin, TX). A platinum coil (d=0.5 mm) and a Hg/Hg_2SO_4 were used as the counter and reference electrodes, respectively.

The Pt nanoparticles on HOPG for the electron microscopy analysis were prepared over lacey carbon TEM grids. HAADF images were taken with a JEOL 2010F microscope in the STEM mode, with the use of a HAADF detector with collection angles from 50 mrad to 110 mrad

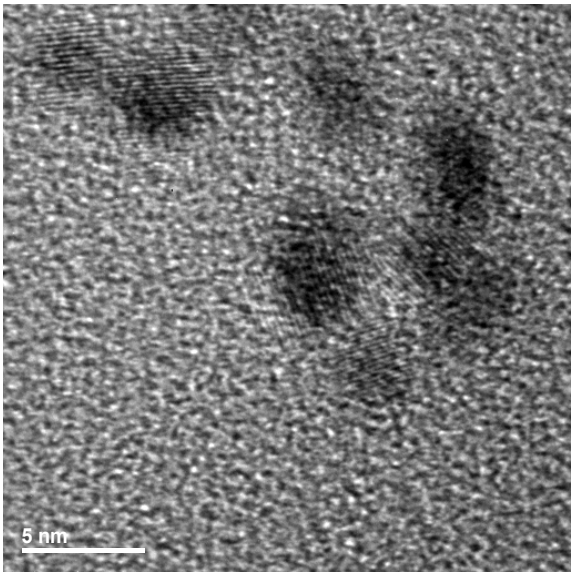


Figure 2. HRTEM image of Pt nanoparticles on HOPG synthetized by polyol heated in H_2 flow at 450ºC.

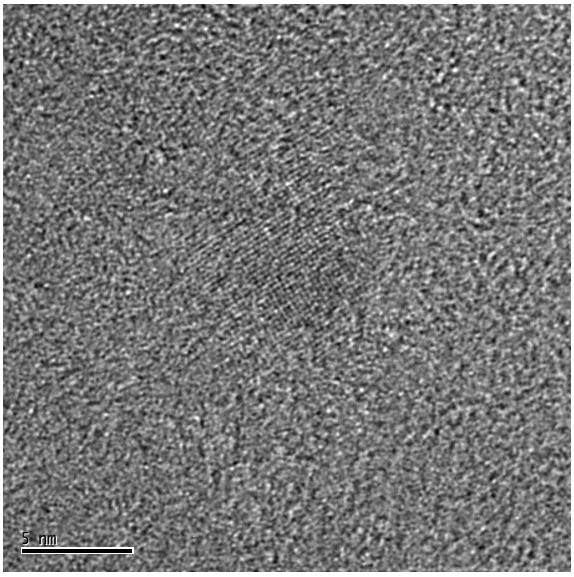


Figure 3. HRTEM image of Pt nanoparticle synthesized on HOPG graphite by direct reduction of chloroplatinc acid impregnated on HOPG and heated in H_2 flow at 950 ºC.

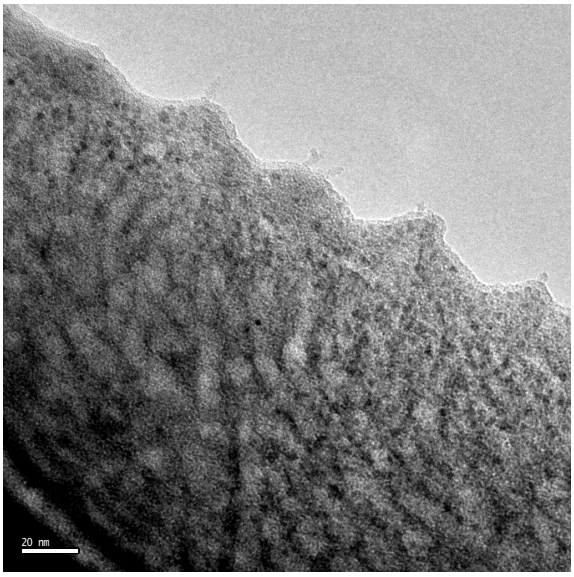


Figure 4. HRTEM image of Pt nanoparticle synthesized on HOPG by the electrochemical method.

RESULTS AND DISCUSSION

By the polyol method with ethylene glycol as solvent-reductor, was possible to obtain monometallic platinum nanoparticles with narrow size distributions in systems with small particles (2-4 nm) and different structures depending on the temperature of reaction. The structure of a platinum nanoparticle is cubic, face centered has can be seen from Figure 1 (a). The monometallic synthesis of Pt nanoparticles by itself showed a distinctive morphology of quasi hemispherical small Pt nanoparticles, which does not depend on the temperature of reaction has can be seen from Figure 1 (a) and (b). In the figure (c) a image of HAADF of Pt nanoparticles with its respective analyze is shown.

The Pt nanoparticles synthesized by polyol method, were deposited successfully on the HOPG has can be seen from figure 2.

In the case when the Pt nanoparticles were synthesized by direct reduction of platinum salt in H_2 flow on HPOG we obtained nanoparticles with a considerable size distributions in systems of Pt nanoparticles and different structures depending on the temperature of reaction [17-18]. We obtained good results also in the preparation of Pt nanoparticles on HOPG by this method as can be seen in figure 3.

By immersing the graphite electrode into a platinum plating solution were obtained Pt nanoparticles in a narrow particle size distribution also for mean crystallite diameters smaller than 4 nm.

NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8503-7 Vol. 1

It is important to observe that several patterns of diffraction of the samples Pt nanoparticles on HOPG presented rotations of some degrees between the layers of HOPG in the direction perpendicular to the basal plane by effect of heating these samples in H_2. Also Moire patterns were observed in some of these samples. Honeycomb structures were observed on the HOPG surface.

For preparing supported platinum nanoparticles on HOPG graphite for investigations of electrocatalysis, the advantage of the polyol method is the small size of the particles and the narrow distribution sizes of them. The second method have the potential to yield nanocrystals that are disposed in direct contact with HOPG; however, in neither case has it been possible to achieve good particle size monodispersity for platinum across a wide range of particle sizes.

Electrochemical deposition resulted an effective method to obtain directly nanoscale platinum particles on HOPG with a narrow distribution sizes.

ACKNOWLEDGMENT

Authors would like to acknowledge Professor Allen J. Bard for their support.

REFERENCES

[1] J. V. Zoval, J. Lee, S. Gorer, R. M. Penner, J. Phys. Chem. B, 102, 1166-1175, 1998. [2] D. Snow, M. Major and L. Green, Microelectronic Engr. 30, 969, 1996.

[2] J. M. Thomas, R. Raja, B. F. G. Johnson, S. Hermans., M. D. Jones, T. Khimyak, *Ind. Eng. Chem. Res.* 2003, *42*, 1563.D. Snow, M. Major and L. Green, Microelectronic Engr. 30, 969, 1996.

[3] L. M. Bronstein, D. M. Chernyshov, I. O. Volkov, M. G. Ezernitskaya, , P. M. Valetsky, V. G. Matveeva, E. M. Sulman, *J. Catal. 196*, 302, 2000.

[4] S. W. Han, Y. Kim, K. Kim, *J. Colloid Interface Sci.*, *208*, 272,1998.

[5] T. Freelink, W. Visscher, J. A. R. van Veen, J. Electroanal. Chem. 382, 65, 1995.

[6] M. M. Alvarez, J. T. Khoury, G. Schaaff, M. N. Shafigullin, I. Vezmar, R. L. Whetten, *J. Phys. Chem. B 101*, 3706, 1997.

[7] A. Henglein, *J. Phys. Chem. B*, *104*, 2201, 2000.

[8] K. C. Grabar, R. G. Freeman, M.B. Hommer, M. J. Natan, Anal. Chem. 34, 735, 1995.

[9] B. E. Baker, N. J. Kline, P. J. Treado, M. J. Natan, J. American Chemical Society, 118, 8721, 1996.

[10] C. H. Bartolomew, M. Boudart, J. Catalysis, 25, 173, 1972.

[11] M. T. Reetz, W. Helbig, J. Am. Chem. Society, 116, 7401, 1992.

[12] P. Allongue, E. Souteyrand, J. Electroanal. Chem., 362,79, 1993.

[13] H. Cachet, M. Froment, E. Souteyrand, Denning C. J. Elecrochem. Soc. 139, 2920, 1992.

[14] D. B. Williams, C. B. Carter, *Transmission Electron Microscopy*, Plenum Press, New York, 1996.

[15] L. Pauling, The Nature of the Chemical Bond, p. 235, 3rd. Edition 1960.

[16] H. Beyer, M. Müller, T. Schimmel, Applied Physics A, Science and Prosessing, 68,2, 0947-8396, 1999.

[17] A. Tomita and Y. Tamai, J. Phys. Chem., 78, 2254, 1974.

[18] R. T. Baker, R.S. Sherwood and E. O. Derouane, J. Cat. 75, 382,1982.