Journal of Nano Research Vol. 14 (2011) pp 93-103
Online available since 2011/Apr/14 at www.scientific.net

doi:10.4028/www.scientific.net/JNanoR.14.93

New Synthesis Method to Obtain Pd Nano-Crystals

M. Ugalde[1,a], E. Chavira[2,b], M. T. Ochoa-Lara[1,c], Carlos Quintanar[3,d]

[1]Centro de Investigación en Materiales Avanzados, S.C., Av. Miguel de Cervantes #120, C.P. 31109, Chihuahua, México

[2]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A. P. 70-360, 04510 México, DF, México

[3]Facultad de Ciencias, Universidad 3000 Circuito Exterior S/N, C.P. 04510 Ciudad Universitaria

[a] magali.ugalde@cimav.edu.mx, [b] chavira@servidor.unam.mx
[c] martha.ochoa@cimav.edu.mx, [d] cqs@matrix.super.unam.mx

Submitted: September 25, 2010; revised: November 29, 2010; accepted: December 10, 2010

Keywords: palladium nano-crystal, sol-gel method, TGA, XRD, HRSEM, TEM

Abstract. We report a new synthesis method to obtain palladium nano-crystals by sol-gel polymerized with acrylamide. From thermogravimetric analysis (TGA) studies, we found PdO and Pd compounds in the xerogel sample, at 550 ºC, and over 900 ºC we detected only metallic Pd. These results were corroborated by powder X-Ray Diffraction (XRD), High Resolution Scanning Electron Microscopy (HRSEM), and Transmission Electron Microscopy (TEM). XRD studies exhibit the lines from the tetragonal structure (PDF 41-1107) of PdO compound and from the cubic structure (PDF 46-1043) of Pd metallic. HRSEM micrographs show morphologies from the sample very sensitive to heat treatment. Finally, TEM images show crystals of ~8 nm in diameter.

Introduction

Recently, considerable attention has been paid to the nano-sized metal colloids and clusters due to their unique properties and potential applications in several areas such as catalysis, optoelectronics, microelectronics, magnetic materials and others [1–7]. The catalytic activity and selectivity, as well as electrical, thermo-dynamical and chemical properties of the nano-crystals are strongly dependent on its nano-size [8]. Therefore, development of synthesis methods of nano-size control has been created such as hydrothermal [9], coprecipitation [10], microemulsion [11-15], nano-crystals stabilized in micelles [16], sputtering [17], gas-evaporation [18,19] and specially sol– gel method proposed in this work [20]. For example, to synthesize palladium nano-crystals is very important, because they can be used as primary catalyst for many organic reactions, such as C–C coupling of Heck, Suzuki, and hydrogenation of alkenes and allylamines [21-26], etc. For this purpose, the ultra fine crystals have to be as small as possible presenting more accessible surface. Furthermore Palladium oxide (PdO) is an important platinum group metal oxide, which supported or modified PdO has been used as a catalyst in catalytic combustion of natural gas (methane) or as a liquid-phase oxidation of alcohols with oxygen in recent years [26-29].

Nowadays, control of crystal size and its dispersion is one of the main goals of nano-crystals preparation technology. That is the reason why the aim of this work is to produce nano-sized palladium crystals using a new modified polyacrylamide sol-gel method with microwave irradiation.

Although some chemical approaches are available for the preparation of Pd nano-crystals, and due to few reports on size-controlling synthesis of Pd nano-crystals have been published, it is required to develop a convenient method to generate nano-crystals with controlled sizes. Microwave irradiation, as a fast, simple, uniform and energy efficient heating method has been widely used in chemistry [30, 31]. By the other hand, recently, microwave-assisted synthesis has been used to prepare nano-sized materials [32–42] and small and homogeneous metal nano-crystals.

Experimental Procedure

Pd nano-crystals were prepared using an acrylamide sol-gel technique [43]. This is particularly useful, since the polyacrylamide network inhibits the aggregation of nano-crystals [44]. At first, Palladium acetate (99%, Aldrich) was dissolved in a solution of distilled water (300 ml) at 80 °C mixing 12 ml of nitric acid (HNO_3; 70%, J. T. Baker) and hydrogen peroxide (11 wt% in H_2O). Later 10.2 mmol of chelating agent ethylene-diaminetetraacetic acid (EDTA) [CH_2N $(CH_2CO_2H)_2]_2$ (99%, Fluka) was added to the Pd dissolution obtained in order to encapsulate the Pd ion. We use this reagent, to trap the Pd metal ion preventing formation of ion complexes until the reaction starts. Thus, Pd ions remain stable during the decomposition of EDTA [45].

The formation of Pd gel takes place from the transparent dissolution. The pH of the dissolution was adjusted to 6 mixing ammonium hydroxide (NH_4OH; 28 – 30%, J. T. Baker) and water. Then, to start the polimerization, we added 562.7 mmol of acrylamide monomer ($H_2C=CHCONH_2$ (99%, Aldrich)), 129.7 mmol of the cross-linker N–N' metilenebisacrylamide (C_7H_{10} N_2O_2 (99.5%, Fluka)) and 3.68 mmol of a chemical initiator α–α' azodiisobutyramidine dihydrochloride ($C_8H_{18}N_6$.2HCl (98%, Fluka)), to increase interconnections velocity [43]. The correct concentration of EDTA allows Pd to react with acrylamide monomer, forming the gel. The polymerization was performed heating at 80 °C during 5 s, under continuous magnetic stirring.

The procedure for obtaining xerogel involves the gel decomposition, heating this material inside a microwave oven, from 80 °C up to 170 °C, raising the temperature slowly under an argon flux, during 3 min. The produced xerogel was pulverized using an agate electric mortar and then heated at 600 ± 4 °C for one week in air. The resultant powder was characterized by XRD technique for recognizing the compounds and phases obtained. Then this powder was again heated at 900 ± 4 °C, for 2 hours, under an argon flux and was later characterized by XRD, SEM and TEM.

Characterization

Powder diffraction analysis was used to determine the crystalline structure and the residual polymer material present in the sample applying a Bruker-axs D8-advance diffractometer, with Cu Kα radiation (λ= 1.5406 Å), 40 KV and 30 mA, equipped with a graphite diffracted beam monochromator. Diffractograms patterns were collected at room temperature over the 2θ range 2.5°–70°, with a step size of 0.02°, and time per step of 0.6 s.

Thermo-gravimetric analysis (TGA) studies were carried out by a TA-Instruments model STD Q600, using a standard alumina pan at a heating rate of 10°C min^{-1} in air over a temperature range from 20°C to 1000°C.

The microstructure and morphology were observed by scanning electron microscopy (SEM) and by transmission electron microscopy (TEM). SEM studies were performed using a Cambridge-Leica Stereoscan 440 electron microscope. The micrographs were taken with a voltage of 20 kV, current intensity of 1,000 pA and WD = 25 mm. TEM analyses were performed on a JEOL-1200EX electron microscope, operating at 120 KV. TEM samples were prepared by slow evaporation of a drop of the colloidal solution (dissolving the sample in toluene) deposited onto a carbon-covered copper grid.

Results and Discussion

The evolution of the sample under different treatments is illustrated by Figure 1. Fig. 1 a) shows the dehydrated gel, while Fig. 1 b) exhibits the xerogel, which means gel heated up to 170 ºC with microwaves. Fig. 1 c) presents the pulverized xerogel after being heated up to 600 ºC, and finally, we can see in Fig. 1 d), the pulverized xerogel after been heated up to 900ºC. In this Figure, it is possible to appreciate how the material undergoes changes in color as well as in physical appearance, from a dehydrate gel, then a xerogel, until a sample with Pd and PdO compound and finally a sample with only Pd was obtained. We remark that we obtained the dehydrated gel after pressing the sample between two glass plates at room temperature. We attribute the different color

in some cases to the oxidation state of the metal, but we need to make more work to explain in detail these changes.

Fig. 1 *a*) Dehydrated Pd gel, *b*) xerogel, Pd gel after heating up 170 °C *c*) Pd sample heated at 600 ºC and *d*) Pd xerogel powder after a heat treatment at 900 ºC.

X-Ray Diffraction

Figure 2 reproduces the xerogel XRD pattern (above) and a dehydrated gel XRD pattern (below). Gel diffratogram only shows amorphous material due to the polymer is encapsulating Pd ions. By the other hand, some new lines appear and they become more sharply defined. Xerogel XRD pattern shows A labeled peaks corresponding to the tetragonal structure (PDF 41-1107) of PdO compound, and the B labeled peaks are related to the face centered cubic structure (FCC) (PDF 46-1043) of Pd metal. The C labeled peaks are associated with the orthorhombic phase of Pd $(NO_3)_2$ $(H_2O)_2$ (PDF 85-2483) and finally, the D labeled peaks are corresponding to the orthorhombic phase of NH_4N0_3 (PDF 8-0452). These last two compounds are residues generated during the production of sol-gel.

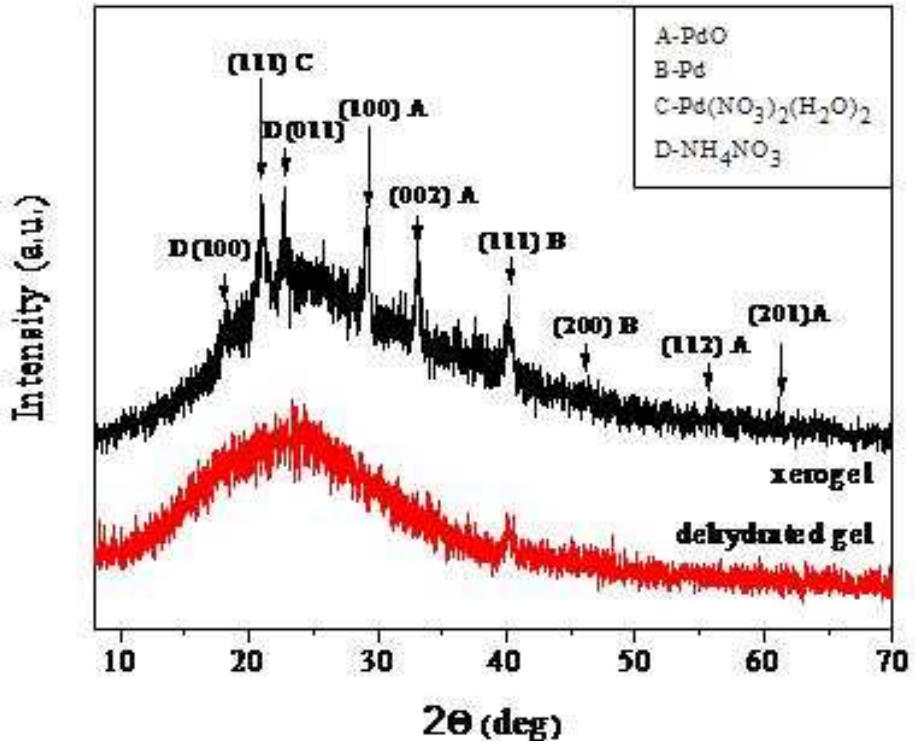

Fig. 2 XRD patterns from dehydrate gel and xerogel. The planes corresponding to: *A* (PdO), *B* (Pd), *C* (Pd $(NO_3)_2$ $(H_2O)_2$) and *D* (NH_4NO_3) are marked.

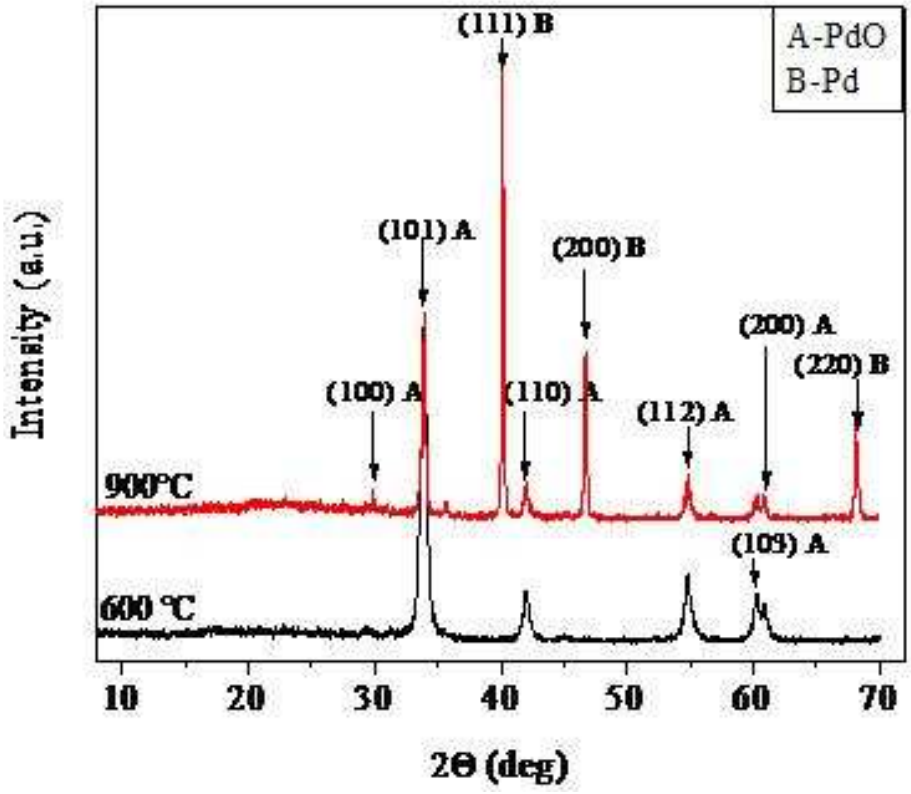

Fig. 3 XRD patterns from nano-crystalline PdO compound heated at 600 °C for 168 hours (below), and mixed Pd-PdO treated at 900 °C for 3 hours (above).

Figure 3, shows how the amorphous phase vanished after heating the material at 600 °C and the PdO phase is mostly observed. Although, at 900 ºC (above) the Pd metal dominates, even though there are still some impurities of PdO phase. This suggests that increasing the temperature beyond 900 ºC, the metallic Pd phase would also increase, but the nano-crystal size would increase as was observed from HRSEM and TEM techniques and illustrated later.

Thermogravimetric analysis

Results obtained from TGA are very important to determine the temperatures corresponding to the formation of organic matter and sub-products, during the synthesis of the sol because this process allows generating purer palladium phases. The curves obtained from TGA of gel and xerogel samples are showed in Figure 4. In the case of gel, its curve exhibits three large lost of weight at 210 ºC, 400 ºC and at 515 ºC, data corresponding to the decomposition of (NH_4NO_3) compound, (Pd (NO_3) $_2$ (H_2O) $_2$) compound, and to PdO compound**,** respectively. The curve of the xerogel, presents two larges lost of weight, at 400 ºC and at 515 ºC, corresponding to the decomposition of (Pd (NO_3) $_2$ (H_2O) $_2$) compound, and PdO compound respectively

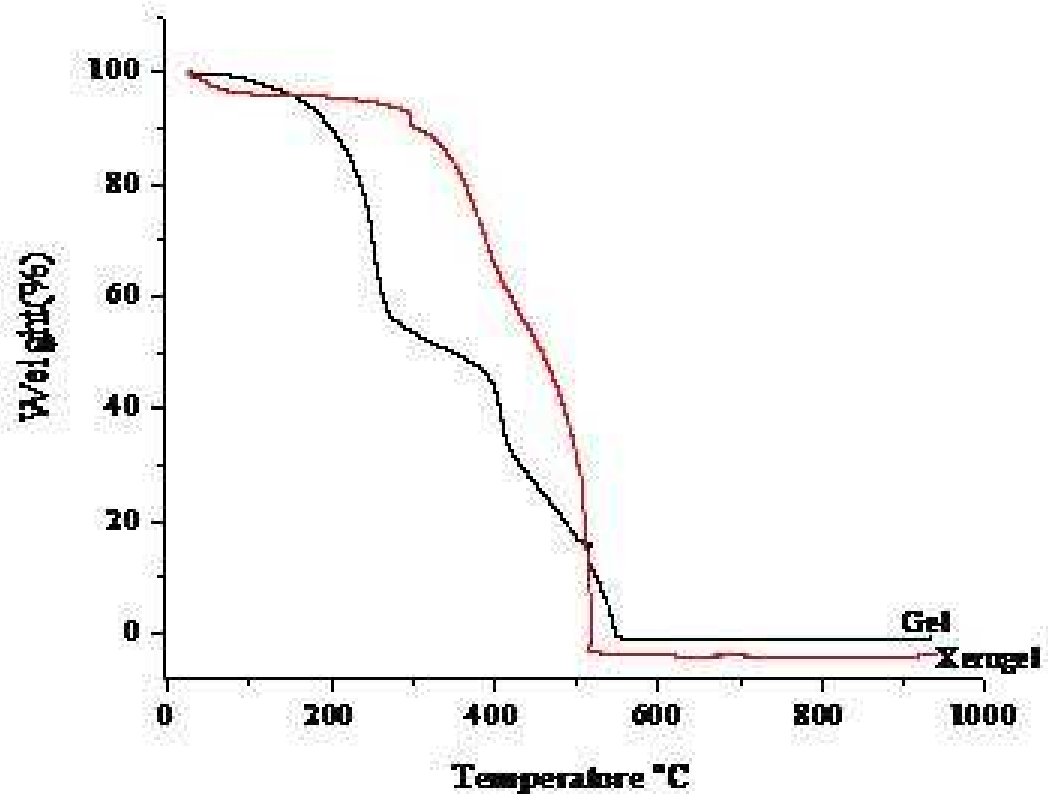

Fig. 4 TGA curves from gel and xerogel showing its respective depuration.

Interpreting TGA curves from Fig. 4, it is important to observe at 515°C, the mass is not totally lost since at 900°C organic matter reveals it's lost as intermediate compounds and impurities, though Pd compounds still remain because Pd melting point is 1555 °C, allowing a wide range of temperature for eliminating parasite reaction from the sol-gel. It is supported when we compare with the result of heating in the oven around 20 g of the material at high temperatures. The final amount obtained is only some few mg. This result agrees with TGA curves.

Electron Microscopy

Representative SEM micrographs of synthesized samples by the sol–gel technique showed PdO clusters formed in turn by spherical nano-clusters, after heating the system at 600 °C (Fig. 5a)). After heating at 900 °C bigger spherical clusters and nano-clusters appeared (Fig. 5b)). Elemental analysis from SEM showed the presence of Pd metal and a minimum amount of PdO.

By the other hand, TEM images from Figure 6 a), show some clusters and nano-crystals, after heating the material at 600 °C. The principal of them, in the micrograph, looks like a conformation of clusters of nano-metric size. When temperature is increased at 900 °C, only dispersed nano-crystals of around 8 nm were observed, corresponding to Pd metal and PdO compound, however clusters were not found (Fig. 6b) in contrast to SEM results. The difference between SEM and TEM results is due to TEM sample preparation because the powder is dispersed using 2- propanol and an ultrasonic bath. By the other hand, analysis elemental from TEM shows the same result than SEM, we mean the presence of Pd metal and PdO compound again. This fact points out Pd nano-crystals can be obtained from the proposed method in this work. In addition, this method can be improved until producing Pd metal pure.

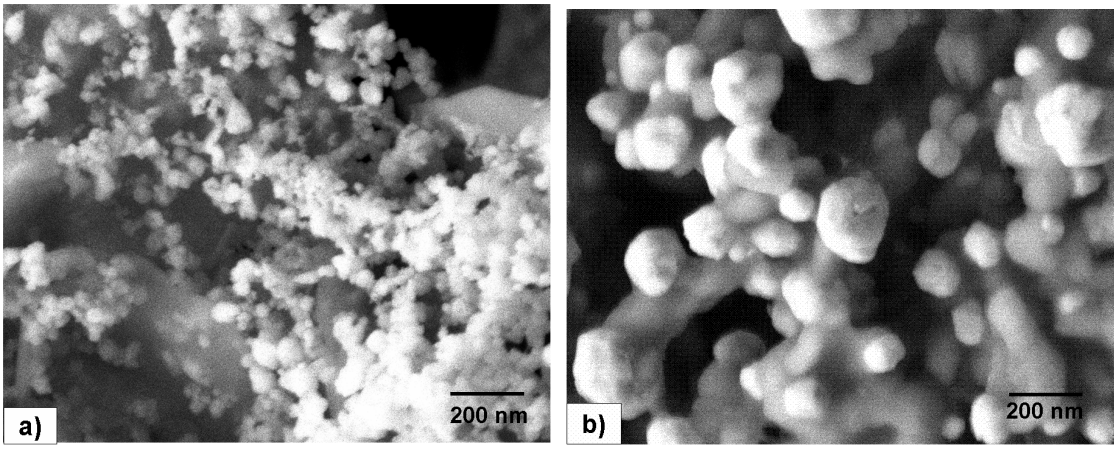

Fig. 5 SEM images show a) PdO nano-clusters after heat treatment at 600 °C. b) Pd and PdO nano-clusters after heat treatment at 900 °C.

The size of the Pd nano-crystals was estimated from X-ray peak broadening in the diffractograms and from the TEM and SEM images. There are two different levels of crystal sizes in our experiments. Comparing the size of Pd crystallites estimated from X-ray diffraction data, it differs from the scale data obtained for Pd nano-sizes for crystals, from electron microscopy images. The clusters are formed by these nano-crystals.

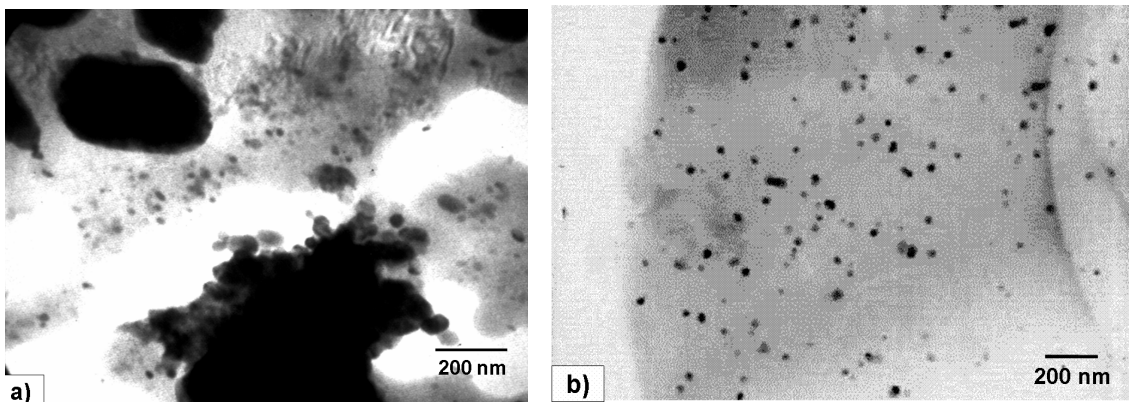

Fig. 6 TEM images show a) Clusters with a size distribution between 50 nm and 600 nm or more and some nano-crystals, after heat treatment at 600 °C. b) Pd and PdO nano-crystals, after heat treatment at 900 °C.

Table 1 contains the average crystallite size data obtained between 600 °C and 900 °C, calculated from the Debye-Scherrer equation ($D = 0.9\lambda/B \cos\theta$), where λ is the X-ray wavelength, θ the Bragg angle and B the full width of the diffraction line at one half of the maximum intensity. The average crystallite size rose when the temperature increased up to 900 °C and the growing of Pd metal was favored. This result was confirmed by TEM.

Table 1. The crystallite size estimated from Scherrer equation

Temperature ºC	PdO	Pd
600	2 nm	-
900	7 nm	8 nm

The crystals size obtained by our method is of around 2-8 nm, compared with the ones resulting from microemulsion of water where the obtained crystals are between 4-8 nm, depending on the composition of the microemulsion [46]. The reduction method by thermal decomposition of Pd-surfactant complexes gives us as result a monodispersed crystal distribution of Pd with sizes of 3, 5 and 7 nm respectively. The size varies with the temperature of the process and the dissolvent is used like a reducer. [47]

Summary

Analyzing the different results obtained from the techniques used in this work we have concluded that after heating the material at 600 °C it is possible to obtain nanometric- crystals, although there are a great quantity of clusters formed or nano-clusters and nano crystals. However if the material is heated at 900 °C for 5 hours in Ar_2 flux**,** nano-metric crystals are obtained and almost no clusters there are. The size of the clusters is bigger after applying a heat treatment at 600° C than in the case of the heat treatment applied at 900 °C. Nevertheless the size change is very small.

The grain size was calculated from Scherrer equation resulting to be between 2-8 nm after heat treatment at 600 °C. TEM images show bigger clusters, but many of them are little clusters conformed for nano clusters and nano-crystals. Additionally, TEM images taken after heating at

900 °C show nano-crystals with a size similar to predicted for Scherrer equation**,** however SEM images show clusters only smaller than at 600 °C, but the crystal size looks larger than the shown by TEM micrographs. The difference is due to the different sample preparation for these techniques. In the case of TEM preparation, the sample was dispersed in 2-propanol separating the little clusters after ultrasonic treatment.

Our synthesis method to produce nano-crystals of Pd presents advantages over the others, [9-20] because the reduction does not require special conditions but very high temperatures are necessary and short reaction times (~3s). Also it allows obtaining materials with bigger superficial area respect to the obtained ones by reaction in solid state.

We conclude that this method allows easily the synthesis of nanometric size Pd metal crystals and it is possible to separate them from the clusters formed initially. However this method has to be improved.

Acknowledgement

This work was supported by IMPULSA-PUNTA-UNAM, UNAM-IN109308, CONACyT 80380 projects and IIM-HITACHI. M. Ugalde acknowledges financial support from CONACyT through scholarship 207277. The authors express their grateful acknowledgment the technical support from Adriana Tejada, Carlos Flores, Esteban Fregoso-Israel, Omar Novelo, Karla Campos Venegas and Willber Antunez Flores for useful discussions.

Reference

[1] Bonnemann, H, Richards, RM, Nanoscopic metal particles- Synthetic methods and potential applications, Eur. J. Inorg. Chem. 10 (2001) 2455-2480.

[2] Dutta, J., Hofmann, H., Hollenstein, C. and Hofmeister, H. Plasma-Produced Silicon Nanoparticle Growth and Crystallization Processes, in Nanoparticles and Nanostructured Films: Preparation, Characterization and Applications (ed. J. H. Fendler), Wiley-VCH Verlag GmbH, Weinheim, Germany (2007).

[3] Prashant V. Kamat, Photophysical, Photochemical and Photocatalytic Aspects of Metal Nanoparticles, J. Phys. Chem. B 106 (2002) 7729–7744.

[4] M.-C. Daniel, D. Astruc, Chem. Rev. 104 (2004), 293–346 M.-C. Daniel, D. Astruc, Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-size Related Properties, and Applications towards Biology, Catalysis and Nanotechnology, Chem. Rev. 104 (2004) 293-346.

[5] Karical R. Gopidas, James K. Whitesell, and Marye Anne Fox Synthesis, Characterization, and Catalytic Applications of a Palladium-Nanoparticle-Cored Dendrimer Nano Letters 3 (12) (2003) 1757–1760.

[6] D.J. Maxwell, J.R. Taylor, S. Nie, Self-Assembled nanoparticle probes for recognition and detection of biomolecules, J. Am. Chem. Soc. 124 (2002) 9606–9612.

[7] M.M. Oliveira, E.G. Castro, C.D. Canestraro, D. Zanchet, D. Ugarte, L.S. Roman,A.J.G. Zarbin, A Simple Two-Phase Route to Silver Nanoparticles/Polyaniline Structures J. Phys. Chem. B, 110 (2006) 17063–17069.

[8] D.V. Leff, P.C. Ohara, J.R. Heath, W.M. Gelbart, Thermodynamic Control of Gold Nanocrystal Size: Experiment and Theory, J. Phys. Chem. 99-18 (1995), 7036–7041.

[9] S. Komarneni, R. Roy, E. Breval, M. Ollinen, Y. Suwa, Hydrothermal Route to Ultrafine Powders Utilizing Single and Di-Phasic Gels, Adv. Ceram. Mater. 1 (1986) 87.

[10] Z.X. Tang, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, Preparation of manganese ferrite fine particles from aqueous solution, J. Colloid Interf. Sci. 146 (1991) 38-52.

[11] J.H. Fendler, Atomic and molecular clusters in membrane mimetic chemistry, Chem. Rev. 87 (1987) 877–899

[12] A. Henglein, Small-particle research: physicochemical properties of extremely small colloidal metal and semiconductor particles, Chem. Rev. 89 (1989) 1861-1873.

[13] K. Osseo-Asare, F.J. Arriagada, Synthesis of nanosize particles in reverse microemulsions, Ceram. Trans. 12 (1990) 3-16.

[14] M.P. Pileni, Reverse micelles as microreactors, J. Phys. Chem. 97 (1993) 6961.

[15] Pillai, P. Kumar, M.J. Hou, P. Ayyub, D.O. Shah, Preparation of nanoparticles of silver halides, superconductors and magnetic materials using water-in-oil microemulsions as nano-reactors, Adv. Colloid Interf. Sci. 55 (1995) 241.

[16] Irina P. Beletskaya, Alexander N. Kashin, Alexander E. Litvinov, Vladimir S. Tyurin, Petr M. Valetsky, and Gerard van Koten Palladium Colloid Stabilized by Block Copolymer Micelles as an Efficient Catalyst for Reactions of C−C and C−Heteroatom Bond Formation, Organometallics 25 (1) (2006) 154-158.

[17] P. Fayet, L.Z. Wöste, Atoms, Molecules and Clusters, Phys. D 3 (1986) 177.

[18] R.W. Siegel, S. Ramasamy, H. Hahn, L.i Zongquan, L.u Ting, R. Gronsky, Synthesis, Characterization, and Properties of Nanophase TiO_2, J. Mater. Res. 3 (1988) 1367.

[19] R. Uyeda, The morphology of fine metal crystallites, J. Cryst. Growth 24 (1974) 69-75.

[20] B. Fegley Jr, P. White, H.K. Bowen, Processing and characterization of ZrO_2 and Y-doped ZrO_2 powders, Am. Ceram. Soc. Bull. 64 (1985) 1115.

[21] M. Chen, Y. Feng, L. Wang, L. Zhang, J.-Y. Zhang, Study of palladium nanoparticles prepared from water-in-oil microemulsion, Colloid Surf. A: Physicochem. Eng. Asp. 281 (2006) 119–124.

[22] K.R. Gopidas, J.K. Whitesell, M.A. Fox, Synthesis, Characterization, and catalytic applications of a palladium-nanoparticle-cored dendrimer, Nano Lett. 3 (2003) 1757–1760.

[23] J. Liu, J. Alvarez, W. Ong, E. Román, A.E. Kaifer, Tuning the catalytic activity of cyclodextrin-modified palladium nanoparticles through host−guest binding interactions, Langmuir 17 (2001) 6762 6764.

[24] Y. Li, M.A. El-Sayed, The effect of stabilizers on the catalytic activity and stability of Pd colloidal nanoparticles in the Suzuki reactions in aqueous solution, J. Phys. Chem. B 105 (2001) 8938–8943.

[25] J. Alvarez, J. Liu, E. Román, A.E. Kaifer, Water-soluble platinum and palladium nanoparticles modified with thiolated β-cyclodextrin, Chem. Commun. (2000) 1151–1152.

[26] N.A. Dhas, A. Gedanken, J. Mater. Chem. 8 (1998) 445–450.Sonochemical preparation and properties of nanostructured palladium metallic clusters, N. Arul Dhas and A. Gedanken, J. Mater. Chem. 8 (1998) 445.

[27] Y. Ozawa, Y. Tochihara, M. Nagai, S. Omi, PdO/Al_2O_3 in catalytic combustion of methane: stabilization and deactivation, Chem. Eng. Sci. 58 (2003) 671–677

[28] J.G. McCarty, Kinetics of PdO combustion catalysis, Catal. Today 26 (1995) 283–293.

[29] T.L. Stuchinskaya, I.V. Kozhevnikov, Liquid-phase oxidation of alcohols with oxygen catalysed by modified palladium(II) oxide, Catal. Commun. 4 (2003) 417–422.

[30] P. Euzen, J-H.L. Gal, B.R. Rebours, G. Martin, Deactivation of palladium catalyst in catalytic combustion of methane, Catal. Today 47 (1999) 19–27.

[31] R. Gedye, F. Smith, K.Westaway, H. Ali, L. Baldisera, L. Laberge, J. Rousell, The use of microwave- ovens for rapid organic-synthesis Tetrahedron Lett. 27 (1986) 279–282.

[32] X. Xu,W. Yang, J. Liu, L. Lin, Synthesis of a High-Permeance NaA Zeolite Membrane by Microwave Heating, Adv. Mater. 12 (2000) 195–204.

[33] W. Yu,W. Tu, H. Liu, Synthesis of Nanoscale Platinum Colloids by Microwave Dielectric Heating, Langmuir 15 (1999) 6–9.

[34] Weixia Tu and Hanfan Liu W. Tu, H. Liu, Rapid synthesis of nanoscale colloidal metal clusters by microwave irradiation, J. Mater. Chem. 10 (2000) 2207–2211.

[35] W. Tu, H. Liu, Continuous Synthesis of Colloidal Metal Nanoclusters by Microwave Irradiation, Chem. Mater. 12 (2000) 564–567.

[36] T.C. Deivaraj,W. Chen, J.Y. Lee, T. C Preparation of PtNi nanoparticles for the electrocatalytic oxidation of methanol, J. Mater. Chem. 13 (2003), 2555–2560.

[37] F.-K. Liu, Y.-C. Chang, F.H. Ko, T.-C. Chu, Microwave rapid heating for the synthesis of gold nanorods, Mater. Lett. 58 (2004) 373.

[38] Y.-J. Zhu, X.-L. Hu, Microwave-assisted polythiol reduction method: a new solid–liquid route to fast preparation of silver nanowires, Mater. Lett. 58 (2004) 1517–1519.

[39] B. He, J.J. Tan, K.Y. Liew, H. Liu, Synthesis of size controlled Ag nanoparticles, J. Mol. Catal. A: Chem. 221 (2004) 121–126.

[40] Y. Chen, B. He, H. Liu, Preparation and Characterization of Palladium Colloidal Nanoparticles by Thermal Decomposition of Palladium Acetate with Microwave Irradiation, J. Mater. Sci. Technol. 21(2) (2005) 187–190.

[41] M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa, T. Tsuji, Microwave-Assisted Synthesis of Metallic Nanostructures in Solution Chem. Eur. J. 11 (2005) 440–452.

[42] Y. Luo, A simple microwave-based route for size-controlled preparation of colloidal Pt nanoparticles, Mater. Lett. 61 (2007) 1873–1875.

[43] H. Wang , L. Gao, W. Li, Q. Li, Preparation of nanoscale α-Al_2O_3 powder by the polyacrylamide gel method, Nanostructure matter 11 (1999) 1263-1267

[44] Herrera G., Chavira E., Jimenez-Mier J., Baños L., Guzmán J., Flores C., Synthesis and structural characterization of YVO_3 prepared by sol–gel acrylamide polymerization and solid state reaction methods, J. Sol-Gel Sci. Technol. 46(1) (2008), 1-10.

[45] Sin A., Odier P., Gelation by Acrylamide, a Quasi-Universal Medium for the Synthesis of Fine Oxide Powders for Electroceramic Applications, Adv. Mater. 12(9) (2000) 649–652.

[46] Cheng-Chuan Wang, Dong-Hwang Chen, Ting-Chia Huang, Synthesis of palladium nanoparticles in water-in-oil microemulsions, Colloids and Surfaces A: Physicochem. Eng. Aspects 189 (2001) 145–154.

[47] Sang-Wook Kim, Jongnam Park, Youngjin Jang, Yunhee Chung, Sujin Hwang, and Taeghwan Hyeon Synthesis of Monodisperse Palladium Nanoparticles Nano Letters 3 (9) (2003) 1289–1291.

Journal of Nano Research Vol. 14
10.4028/www.scientific.net/JNanoR.14

New Synthesis Method to Obtain Pd Nano-Crystals
10.4028/www.scientific.net/JNanoR.14.93

DOI References
[1] Bonnemann, H, Richards, RM, Nanoscopic metal particles- Synthetic methods and potential applications, Eur. J. Inorg. Chem. 10 (2001) 2455-2480.
http://dx.doi.org/10.1002/1099-0682(200109)2001:10<2455::AID-EJIC2455>3.0.CO;2-Z
[3] Prashant V. Kamat, Photophysical, Photochemical and Photocatalytic Aspects of Metal Nanoparticles, J. Phys. Chem. B 106 (2002) 7729–7744.
doi:10.1021/jp0209289
[4] M. -C. Daniel, D. Astruc, Chem. Rev. 104 (2004).
doi:10.1039/b410399h
[5] Karical R. Gopidas, James K. Whitesell, and Marye Anne Fox Synthesis, Characterization, and Catalytic Applications of a Palladium-Nanoparticle-Cored Dendrimer Nano Letters 3 (12) (2003) 1757–1760.
doi:10.1021/nl0348490
[6] D.J. Maxwell, J.R. Taylor, S. Nie, Self-Assembled nanoparticle probes for recognition and detection of biomolecules, J. Am. Chem. Soc. 124 (2002) 9606–9612.
doi:10.1021/ja025814p
[7] M.M. Oliveira, E.G. Castro, C.D. Canestraro, D. Zanchet, D. Ugarte, L.S. Roman A.J.G. Zarbin, A Simple Two-Phase Route to Silver Nanoparticles/Polyaniline Structures J. Phys. Chem. B, 110 (2006) 17063–17069.
doi:10.1021/jp060861f
[8] D.V. Leff, P.C. Ohara, J.R. Heath, W.M. Gelbart, Thermodynamic Control of Gold Nanocrystal Size: Experiment and Theory, J. Phys. Chem. 99-18 (1995), 7036–7041.
doi:10.1021/j100018a041
[10] Z.X. Tang, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, Preparation of manganese ferrite fine particles from aqueous solution, J. Colloid Interf. Sci. 146 (1991) 38-52.
http://dx.doi.org/10.1016/0021-9797(91)90004-R
[11] J.H. Fendler, Atomic and molecular clusters in membrane mimetic chemistry, Chem. Rev. 87 (1987) 877–899.
doi:10.1021/cr00081a002
[12] A. Henglein, Small-particle research: physicochemical properties of extremely small colloidal metal and semiconductor particles, Chem. Rev. 89 (1989) 1861-1873.
doi:10.1021/cr00098a010
[13] K. Osseo-Asare, F.J. Arriagada, Synthesis of nanosize particles in reverse microemulsions, Ceram. Trans. 12 (1990) 3-16.
doi:10.1016/0166-6622(90)80273-7
[14] M.P. Pileni, Reverse micelles as microreactors, J. Phys. Chem. 97 (1993) 6961.
doi:10.1021/j100129a008
[15] Pillai, P. Kumar, M.J. Hou, P. Ayyub, D.O. Shah, Preparation of nanoparticles of silver halides,

superconductors and magnetic materials using water-in-oil microemulsions as nano- reactors, Adv. Colloid Interf. Sci. 55 (1995) 241.
doi:10.1016/0001-8686(94)00227-4
[16] Irina P. Beletskaya, Alexander N. Kashin, Alexander E. Litvinov, Vladimir S. Tyurin, Petr M. Valetsky, and Gerard van Koten Palladium Colloid Stabilized by Block Copolymer Micelles as an Efficient Catalyst for Reactions of C−C and C−Heteroatom Bond Formation, Organometallics 25 (1) (2006).
doi:10.1021/om050562x
[17] P. Fayet, L.Z. Wöste, Atoms, Molecules and Clusters, Phys. D 3 (1986) 177.
doi:10.1007/BF01384819
[18] R.W. Siegel, S. Ramasamy, H. Hahn, L. i Zongquan, L. u Ting, R. Gronsky, Synthesis, Characterization, and Properties of Nanophase TiO2, J. Mater. Res. 3 (1988) 1367.
doi:10.1557/JMR.1988.1367
[19] R. Uyeda, The morphology of fine metal crystallites, J. Cryst. Growth 24 (1974) 69-75.
doi:10.1016/0022-0248(74)90282-6
[21] M. Chen, Y. Feng, L. Wang, L. Zhang, J. -Y. Zhang, Study of palladium nanoparticles prepared from water-in-oil microemulsion, Colloid Surf. A: Physicochem. Eng. Asp. 281 (2006) 119–124.
doi:10.1016/j.colsurfa.2006.02.024
[22] K.R. Gopidas, J.K. Whitesell, M.A. Fox, Synthesis, Characterization, and catalytic applications of a palladium-nanoparticle-cored dendrimer, Nano Lett. 3 (2003) 1757–1760.
doi:10.1021/nl0348490
[23] J. Liu, J. Alvarez, W. Ong, E. Román, A.E. Kaifer, Tuning the catalytic activity of cyclodextrin-modified palladium nanoparticles through host−guest binding interactions, Langmuir 17 (2001) 6762 6764.
doi:10.1021/la015563i
[24] Y. Li, M.A. El-Sayed, The effect of stabilizers on the catalytic activity and stability of Pd colloidal nanoparticles in the Suzuki reactions in aqueous solution, J. Phys. Chem. B 105 (2001) 8938–8943.
doi:10.1021/jp010904m
[26] N.A. Dhas, A. Gedanken, J. Mater. Chem. 8 (1998) 445–450. Sonochemical preparation and properties of nanostructured palladium metallic clusters, N. Arul Dhas and A. Gedanken, J. Mater. Chem. 8 (1998) 445.
doi:10.1039/a706100e
[27] Y. Ozawa, Y. Tochihara, M. Nagai, S. Omi, PdO/Al2O3 in catalytic combustion of methane: stabilization and deactivation, Chem. Eng. Sci. 58 (2003) 671–677.
doi:10.1016/S0009-2509(02)00594-8
[28] J.G. McCarty, Kinetics of PdO combustion catalysis, Catal. Today 26 (1995) 283–293.
doi:10.1016/0920-5861(95)00150-7
[29] T.L. Stuchinskaya, I.V. Kozhevnikov, Liquid-phase oxidation of alcohols with oxygen catalysed by modified palladium(II) oxide, Catal. Commun. 4 (2003) 417–422.
doi:10.1016/S1566-7367(03)00096-7
[30] P. Euzen, J-H.L. Gal, B.R. Rebours, G. Martin, Deactivation of palladium catalyst in catalytic combustion of methane, Catal. Today 47 (1999) 19–27.
doi:10.1016/S0920-5861(98)00280-6
[31] R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, J. Rousell, The use of microwave-ovens for rapid organic-synthesis Tetrahedron Lett. 27 (1986) 279–282.
doi:10.1016/S0040-4039(00)83996-9
[32] X. Xu,W. Yang, J. Liu, L. Lin, Synthesis of a High-Permeance NaA Zeolite Membrane by Microwave

Heating, Adv. Mater. 12 (2000) 195–204.
http://dx.doi.org/10.1002/(SICI)1521-4095(200002)12:3<195::AID-ADMA195>3.0.CO;2-E
[33] W. Yu,W. Tu, H. Liu, Synthesis of Nanoscale Platinum Colloids by Microwave Dielectric Heating, Langmuir 15 (1999) 6–9.
http://dx.doi.org/10.1021/la9806505
[34] Weixia Tu and Hanfan Liu W. Tu, H. Liu, Rapid synthesis of nanoscale colloidal metal clusters by microwave irradiation, J. Mater. Chem. 10 (2000) 2207–2211.
doi:10.1039/b002232m
[35] W. Tu, H. Liu, Continuous Synthesis of Colloidal Metal Nanoclusters by Microwave Irradiation, Chem. Mater. 12 (2000) 564–567.
doi:10.1021/cm990637l
[36] T.C. Deivaraj,W. Chen, J.Y. Lee, T. C Preparation of PtNi nanoparticles for the electrocatalytic oxidation of methanol, J. Mater. Chem. 13 (2003), 2555–2560.
http://dx.doi.org/10.1039/b307040a
[37] F. -K. Liu, Y. -C. Chang, F.H. Ko, T. -C. Chu, Microwave rapid heating for the synthesis of gold nanorods, Mater. Lett. 58 (2004) 373.
doi:10.1016/S0167-577X(03)00504-4
[38] Y. -J. Zhu, X. -L. Hu, Microwave-assisted polythiol reduction method: a new solid–liquid route to fast preparation of silver nanowires, Mater. Lett. 58 (2004) 1517–1519.
doi:10.1016/j.matlet.2003.10.020
[41] M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa, T. Tsuji, Microwave-Assisted Synthesis of Metallic Nanostructures in Solution Chem. Eur. J. 11 (2005) 440–452.
doi:10.1002/chem.200400417
[42] Y. Luo, A simple microwave-based route for size-controlled preparation of colloidal Pt nanoparticles, Mater. Lett. 61 (2007) 1873–1875.
doi:10.1016/j.matlet.2006.07.166
[43] H. Wang , L. Gao, W. Li, Q. Li, Preparation of nanoscale α-Al2O3 powder by the polyacrylamide gel method, Nanostructure matter 11 (1999) 1263-1267.
http://dx.doi.org/10.1016/S0965-9773(99)00417-1
[44] Herrera G., Chavira E., Jimenez-Mier J., Baños L., Guzmán J., Flores C., Synthesis and structural characterization of YVO3 prepared by sol–gel acrylamide polymerization and solid state reaction methods, J. Sol-Gel Sci. Technol. 46(1) (2008).
doi:10.1007/s10971-008-1703-6
[45] Sin A., Odier P., Gelation by Acrylamide, a Quasi-Universal Medium for the Synthesis of Fine Oxide Powders for Electroceramic Applications, Adv. Mater. 12(9) (2000) 649–652.
doi:10.1002/(SICI)1521-4095(200005)12:9<649::AID-ADMA649>3.0.CO;2-K
[46] Cheng-Chuan Wang, Dong-Hwang Chen, Ting-Chia Huang, Synthesis of palladium nanoparticles in water-in-oil microemulsions, Colloids and Surfaces A: Physicochem. Eng. Aspects 189 (2001) 145–154.
doi:10.1016/S0927-7757(01)00576-3