Rev.Adv.Mater.Sci. 18(2008) 685-688

MORPHOLOGY OF DISPERSED AND AGGREGATED PVP-Pd NANOPARTICLES PREPARED BY ULTRASONIC IRRADIATION OF $Pd(NO_3)_2$ SOLUTION IN ETHYLENE GLYCOL

Abderrafik Nemamcha[1] and Jean Luc Rehspringer[2]

[1]Laboratoire d'Analyse Industrielle et Génie des Matériaux, Département de Chimie Industrielle, Faculté des Sciences et de l'Ingénierie, Université 08 Mai 1945 de Guelma, B.P. 401, Guelma 24000, Algérie
[2]Groupe des Matériaux Inorganiques, Institut de Physique et de Chimie des Matériaux de Strasbourg, UMR-ULP 7504, 23 rue de Loess, 67037 Strasbourg cedex, France

Received : March 29, 2008

Abstract. Dispersed and aggregated palladium nanoparticles have been obtained by ultrasonic irradiation of $Pd(NO_3)_2$ solution in presence of ethylene glycol and polyvinylpyrrolidone (PVP). The UV-Visible absorption analyses confirm the dependence of the sonochemical reduction of palladium(II) ions to palladium(0) atoms with increasing sonication time. The transmission electron microscopy micrographs show that, for the high presence of PVP, the sonochemical reduction of palladium ions leads to the formation of monodispersed palladium particles having a rounded shape and a mean diameter of about 5 nm. The use of a low quantity of PVP involves the obtaining of aggregates palladium nanoparticles. The dynamic light scattering measurements reveal that the palladium nanoparticles aggregates have a large size distribution centered at 20 nm.

1. INTRODUCTION

The development of novel metallic nanometer particles has attracted a great attention due to their characteristics which are significantly different to those of the unique atoms and bulk materials [1]. Their special physical and chemical properties depend strongly on their size, shape and stabilizer molecules [2]. In fact, it is assumed that the size and the shape of the particles have an effect on the catalytic reactions due to the changing of the surface/volume ratio [3]. Recently, it is well established that the aggregate of nanoparticles presents several properties which differ to those of dispersed nanoparticles [4]. In this paper, we present a morphologic study of the dispersed and aggregated palladium nanoparticles obtained by ultrasonic irradiation of $Pd(NO_3)_2$ solution in presence of ethylene glycol (EG) and polyvinylpyrrolidone (PVP), as reducing and stabilizing agents, respectively.

2. EXPERIMENTAL

Mixtures of 30 ml of EG and $5 \cdot 10^{-6}$ mol of PVP (K-30, MW 40000 from Aldrich), was mixed under magnetic stirring in a glass vessel during 15 min. After that, different amount of $Pd(NO_3)_2$ solution, 1.5 ml and 2 ml, were added to the mixtures corresponding to $2 \cdot 10^{-3}$ mol $Pd(NO_3)_2$ in sample (a) and $2.66 \cdot 10^{-3}$ mol $Pd(NO_3)_2$ in sample (b), respectively. The obtained mixtures were irradiated into a covered and fixed vial (20 ml) using a multi-wave ultrasonic generator (Hielscher, 30 kHz) equipped with an immersed sonication horn. The sonication was interrupted at different times (30, 60, 90, 120, 150, and 180 min) for the sample taking.

Corresponding author: Abderrafik Nemamcha, e-mail: arnemamcha_dz@yahoo.fr

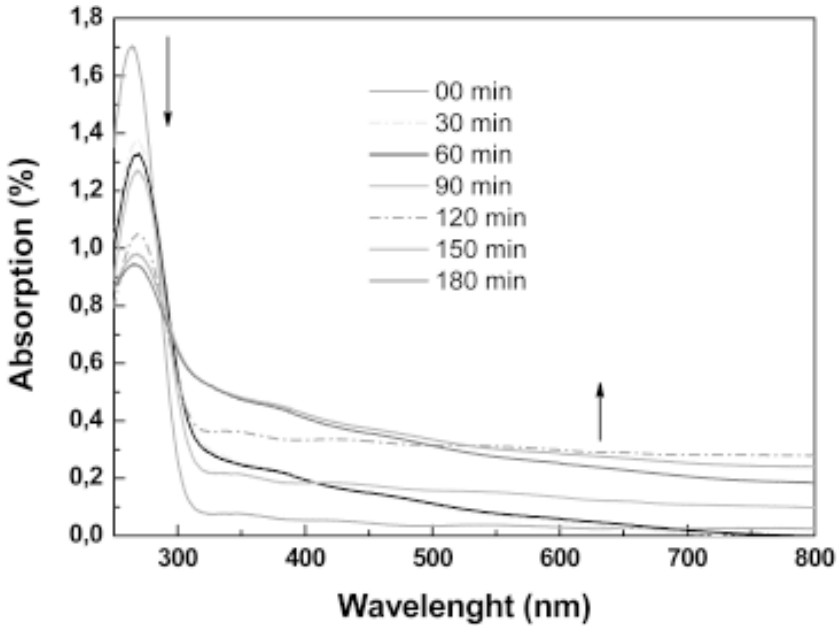

Fig. 1. UV-Visible spectra of Pd colloids after ultrasonic irradiation at different times.

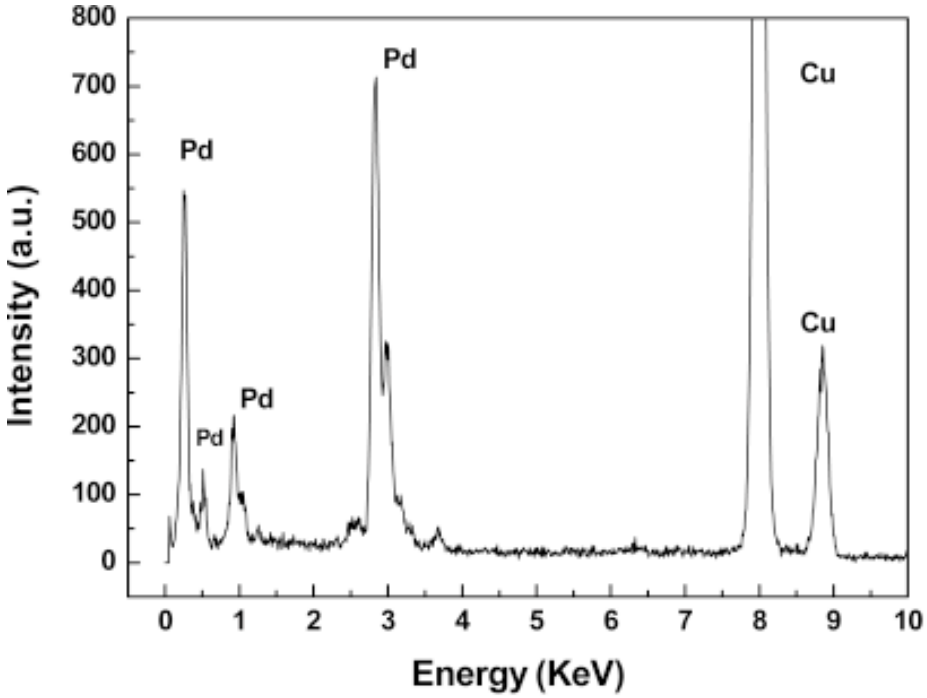

Fig. 2. EDX spectrum of irradiated suspension at 180 min.

The sonochemical process has been followed by UV-Visible absorption spectroscopy (spectrophotometer Hitachi). The particles shape and size were investigated by transmission electron microscopy (TEM, Topcon 002B, at 200 kV) and Electron-dispersive X-ray spectral analysis (EDX) coupled at the TEM microscopy for the identification of palladium nanoparticles. The size of the aggregated particles has been measured by dynamic light scattering (DLS) method using Laser beam in the AutoSizer instrument.

3. RESULTS AND DISCUSSION

The sonochemical reduction of palladium (II) ions, Pd(II), to palladium atoms, Pd(0), can be explained

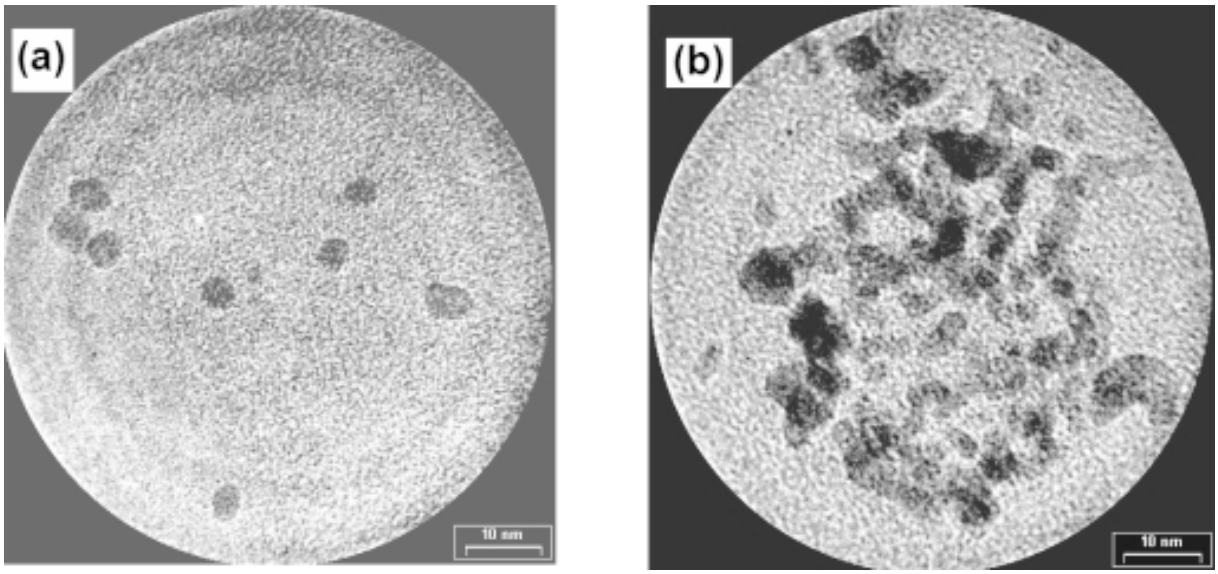

Fig. 3. TEM micrographs of Pd colloids irradiated during 180 min: (a) dispersed Pd nanoparticles, (b) aggregated Pd nanoparticles.

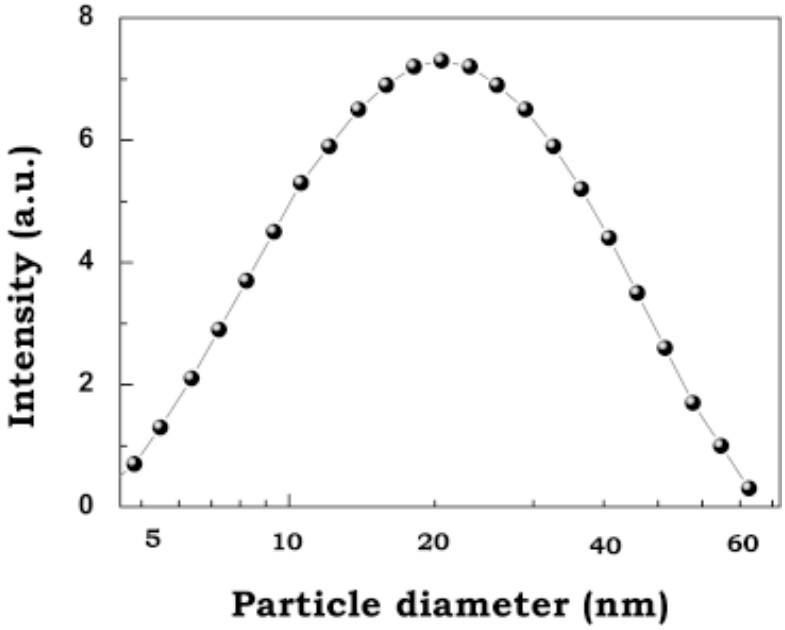

Fig. 4. Size distribution of aggregated Pd nanoparticles.

by considering the intense ultrasonic waves that are strong enough to produce cavitation [5,6]. It is known that during the sonochemical process there are three different regions (the inner, the liquid film surrounding the collapsing cavity and the bulk solution) where the reduction of metallic ions in the aqueous solution can occur [5,7]. In addition, the presence of the shear forces of the polymer (PVP) may also participate at the formation of intermediate radicals such as $^{\bullet}H$, $^{\bullet}CH_3$, $^{\bullet}CH_2R$, *etc*. [7,8]. According to this discussion and on the basis of the previous studies [6,7,9], the sonochemical reduction occurs according to the following steps:

$$\text{Water pyrolyse: } H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}H \quad (1)$$

$$\text{Radical formation: RH (Reducing agent)} + {}^{\bullet}OH({}^{\bullet}H) \rightarrow {}^{\bullet}R + H_2O(H_2) \quad (2)$$

Ions reduction: $Pd(II) + \text{reducing radicals}$

$$\left({}^{\bullet}H,\ {}^{\bullet}R\right) \rightarrow Pd(0) + R^{\bullet}CHO + H^{+} \quad (3)$$

Particle formation: $n\,Pd(0) \rightarrow Pd_n$

dispersed or Pd_n aggregated (4)

Fig. 1 exhibits the UV-Visible absorption spectra of irradiated solutions at different sonication time. The spectrum of the starting solution presents absorption peaks at 540, 340, and 262 nm attributed to the palladium complexes species present in the solution [10,11]. These absorption peaks disappeared with increasing sonication time and the color of irradiated solution turned progressively towards the dark brown indicating the reduction of the Pd(II) ions to Pd(0) [6]. The spectra of irradiated palladium suspensions show a continuous absorption rise in the background towards higher energies. This phenomenon is due to the Mie scattering from palladium nanoparticles in the solution [12].

The identification of palladium nanoparticles can, also, be confirmed by Electron-dispersive X-ray spectral analysis. The EDX spectrum (Fig. 2) of irradiated solution during 180 min indicates clearly the presence of single palladium particles. The Cu peaks originate of scattering from the cooper mesh support grid.

TEM micrographs of the sonicated colloids at 180 min of both samples are presented in Fig. 3. The results analysis show that, for the sample containing $2.0 \cdot 10^{-3}$ mol of $Pd(NO_3)_2$, the sonochemical reduction of Pd(II) leads to the formation of monodispersed palladium particles having a rounded shape and a diameter of about 5 nm (Fig. 3a). However, the use of $2.5\ 10^{-3}$ mol $Pd(NO_3)_2$ involves the obtaining of palladium nanoparticles aggregates (Fig. 3b).

The analysis of the DLS results (Fig. 4) reveals that the palladium nanoparticles, obtained after 180 min of ultrasonic irradiation at low presence of PVP, produce an aggregation of nanoparticles with the size distribution around 20 nm.

4. CONCLUSION

In this study, dispersed and aggregated palladium nanoparticles have been obtained by ultrasonic irradiation of $Pd(NO_3)_2$ solution in presence of EG and PVP. The experimental results analyses show that: (i) The sonochemical reduction of Pd(II) into Pd(0) depends on the sonication time. (ii) The high PVP/Pd(II) molar ratio leads to the formation of monodispersed palladium particles having a rounded shape and a mean diameter of about 5 nm. However, the low PVP/Pd(II) molar ratio involves the obtaining of aggregates palladium nanoparticles with a large size distribution centered at 20 nm.

ACKNOWLEDGEMENTS

This work was supported by the Ministère de l'Enseignement Supérieur et de la Recherche Scientifique Algérie (CNEPRU : B*2401.55.06).

REFERENCES

[1] M.C. Roco // *J. Nanotechnology research* **5** (2003) 181.
[2] R.C. Hoffmann, S. Jia, L.P.H. Jeurgens, J. Bill and F. Aldinger // *Mater. Sci. Eng. C* **26** (2006) 41.
[3] E. Ramirez, S. Jansat, K. Philippot, P. Lecante, M. Gomez, A.M. Masdeu-bulto and B.J. Chaudret // *Org. Met. Chem* **689** (2004) 4601.
[4] Y.X. Jiang and S.G. Sun // *Electrochimica acta* **50** (2006) 3093.
[5] K. S. Suslick, Y. Didenko, M.M. Fang, T. Hyeon, K. J.Kolbeck, W. B. McNamara III, M.M. Mdleleni and M. Wong // *Philos. Trans. R. Soc. A. London* **357** (1999) 335.
[6] K. Okitsu, H. Bandow and Y. Maeda // *Chem. Mater.* **8** (1996) 315.
[7] N. A. Dhas and A.Gedanken // *J. Mater. Chem.* **8** (1998) 445.
[8] J. Rae, M. Ashokkumar, O. Eulaerts, C.V. Sonntag, J. Reisse and F. Grieser // *Ultrason. Sonochem.* **12** (2005) 325.
[9] K. Vinodgopal, Y. He, M. Ashokkumar and F. Grieser // *J. Phys. Chem. B* **110** (2006) 3849.
[10] C. Luo, Y. Zhang and Y. Wang // *J. Molec. Catal. A: Chemical* **229** (2005) 7.
[11] Z. Wang, B. Shen and N. He // *Mater. Lett.* **58** (2004) 3652.
[12] J.A. Creighton and D.G.J. Eadon // *J. Chem. Soc. Farad. Trans.* **87** (1991) 3881.