Spectrochimica Acta Part A 78 (2011) 909–912

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Short communication

A rapid and simple route for the synthesis of lead and palladium nanoparticles in tetrazolium based ionic liquid

Prashant Singh[a,*], Pradeep Kumar[b], Kamlesh Kumari[c], Pankaj Sharma[a], Subho Mozumdar[b], Ramesh Chandra[b]

[a] A. R. S. D. College, University of Delhi, Delhi-110007, India
[b] Department of Chemistry, University of Delhi, Delhi-110007, India
[c] Department of Chemistry, Jamia Hamdard, New Delhi-110062, India

ARTICLE INFO

Article history:
Received 2 June 2010
Received in revised form 28 October 2010
Accepted 30 November 2010

Keywords:
Palladium and lead
Green synthesis
pXRD
TEM and QELS

ABSTRACT

In the present work, we report a novel method for the synthesis of palladium and lead nanoparticles by the reduction method in tetrazolium ring based ionic liquid. Palladium and lead nanoparticles so-prepared were well characterized by powder X-ray diffraction measurements (pXRD), transmission electron microscopy (TEM) and quasi elastic light scattering (QELS) techniques. Powder X-ray diffraction (pXRD) analysis revealed all relevant Bragg's reflection for crystal structure of palladium and lead. Powder X-ray diffraction plots also revealed no oxidized material of palladium and lead nanoparticles. TEM showed nearly uniform distribution of the particles in methanol and confirmed by QELS. Typical applications of palladium nanoparticles include in vitro use and sensor design applications. Palladium nanoparticles is also ideal for spin coating, self-assembly and monolayer formation. Palladium nanoparticles can also be considered as potential new catalysts.

1. Introduction

Over the past few years, research has been directed towards the synthesis and application of metal nanoparticles in view of their unique properties compared to the bulk metals [1,2]. Lead and palladium nanoparticles have received considerable attention because of their unusual properties and potential applications in diverse fields especially chemical reactions [3]. The various synthetic procedures for their synthesis includes micro emulsion, [4] reverse micelles, [5] reduction of aqueous lead and palladium salts, [6] UV-light irradiation, [7–9]. The core–shell particles are of great interest due to their potential applications in diverse fields including catalysis, reductions etc. [7–10]. There is considerable interest in the use of room temperature ionic liquids as promising substitutes for volatile organic solvents. Ionic liquids have been employed as reaction media for several organic reactions, namely alkylation [11], hydrogenation [12], oxidation [13].

Palladium nanostructures have been known as catalysts for the reactions such as oxidation of hydrocarbon in automobiles (three-way catalyst), Heck reaction, Suzuki reaction, Stille coupling and C–N coupling. Also, Pd nanoparticles with preferentially exposed (1 1 1) show high catalytic activity for the hydrogenation of 1,3-butadiene [14–21].

Because of their tunable polarity and hydrophobicity, they can solvate various organic, inorganic, and polymeric compounds, and have been used as green solvents for liquid–liquid separations, extractions, and recycling in homogeneous catalysis. Along with these qualities ionic liquids provides stability to metal nanoparticles and give small size particles. Palladium and lead are widely used materials in the world. It has a great significance in all industries, particularly in the pharmaceutical sector. Palladium and lead nanoparticles have been synthesized and characterized by different methods. Stability and reactivity are the two important factors that impede the use and development of the metal cluster [22–26]. Ionic liquid have very important in the preparation of Pb and Pd nanoparticles as they acts as solvent as well as they provide stability to the nanoparticles. We cannot prepare these nanoparticles in aqueous system because they get oxidized and forms metal oxide.

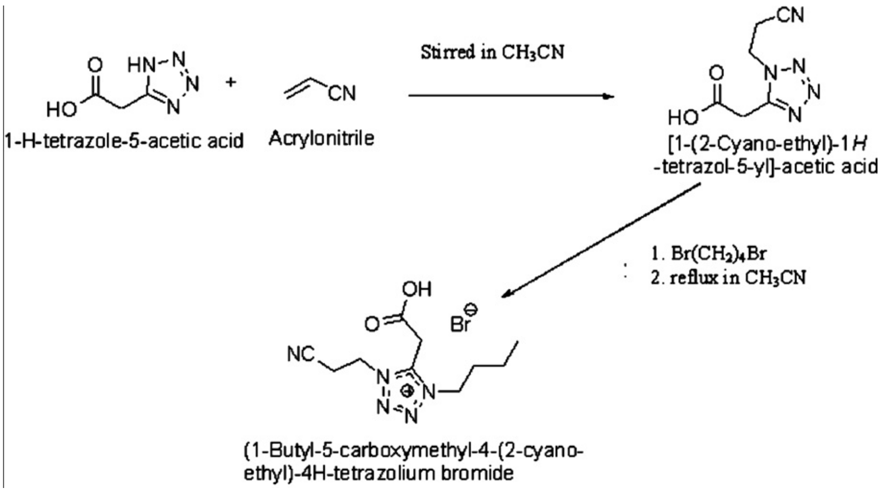
The fields that have recently been greatly impacted by the advancement in nanostructured materials are biology, biophysics, and medicine. The nanobiology toolkit has been greatly enhanced by noble metal nanostructures, which have proven to be highly versatile and tunable materials for a range of bioapplications including biophysical studies, biological sensing, imaging, medical diagnostics, and cancer therapy. In this account, we describe the interesting optical properties of noble metal nanostructures and discuss recent research advances in their bioapplications.

Some of the methods are sonochemical, γ-irradiation, UV-irradiation, microemulsion technique and polyol reduction. However, the facile, cost-effective and large-scale synthetic meth-

---

[*] Corresponding author. Tel.: +91 11 24113436.
E-mail address: arsdchemistry@yahoo.in (P. Singh).

1386-1425/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2010.11.039



Scheme 1. Synthesis of tetrazolium ring based ionic liquid.

ods are still elusive. Herein, we report a simple, rapid and room temperature synthesis of Pd nanoparticles in tetrazolium based ionic liquid and characterized by powder X-ray diffraction, TEM and QELS techniques.

2. Experimental

2.1. Reagents and analysis

All reactions were carried out at ambient temperature in oven-dried glassware. The materials were purchased from Sigma–Aldrich and Merck used. The metal nanoparticles were systematically characterized by powder X-ray diffraction, TEM and QELS techniques. Nanosize and morphology of the palladium and lead nanoparticles were observed under Philips TECNAI-FE12 Transmission Electron Microscope (120 kV). The particles were dispersed in methanol and a drop of it was placed on Formvar-coated copper grid followed by air-drying. The X-ray diffraction patterns were recorded using a RIGAKU ROTAFLEX RAD-B by Rigaku corporation Japan diffractometer using Cu target Cu Kα 1 radiation with tube voltage 40 kV and 60 mA in 2θ ranging from 5° to 60°.

2.2. Synthesis of catalyst

2.2.1. Synthesis of ionic liquid (A)

First Step, in a 50 ml round bottom flask, 10 mmol of ^{1}H-tetrazole-5-acetic acid and 15 mmol of acrylonitrile in 20 ml of acetonitrile was taken. The mixture was stirred for 2 h approximately. Completion of the reaction was checked with thin layer chromatography. Evaporate the solvent and excess of acrylonitrile under reduced pressure. Second step, now 10 mmol of the above compound and 15 mmol of bromobutane were taken in 100 ml round bottom flask having 25 ml of acetonitrile. Reflux the mixture for 6 h and evaporate the solvent and excess of bromobutane under reduced pressure as in Scheme 1 [22–26].

2.2.2. Synthesis of palladium nanoparticles in ionic liquid (A)

In a round bottom flask, 5 ml of the synthesized ionic liquid was taken and 25 mg of palladium acetate was added then excess of methanolic solution of sodium borohydride (20 mg in 10 ml of methanol) was added in the flask. Suddenly a brownish-black color solution was obtained indicates the Pd (0) particles (Scheme 2). The stirring was continued for 3 h. The above solution was taken in

$$\mathrm{Pb\ (CH_3COO)_2} \xrightarrow[\text{Methanolic solution of NaBH}_4]{\text{Ionic liquid}} \mathrm{Pd\ (0)}$$

Scheme 2. Synthesis of palladium nanoparticles in ionic liquid.

$$\mathrm{Pd\ (NO_3)_2} \xrightarrow[\text{Methanolic solution of NaBH}_4]{\text{Ionic liquid}} \mathrm{Pb\ (0)}$$

Scheme 3. Synthesis of lead nanoparticles in ionic liquid.

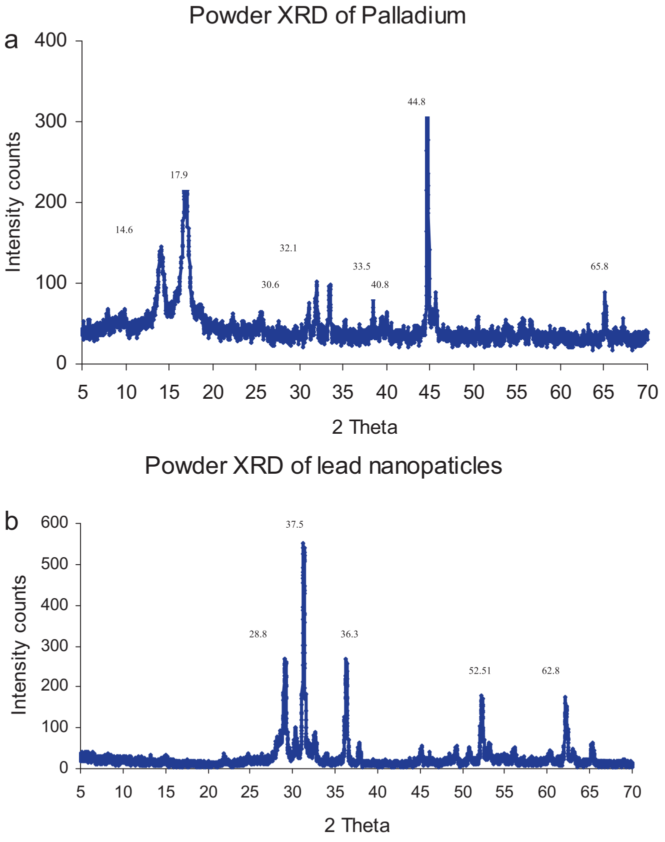


Fig. 1. Powder X-ray diffraction curve of (a) palladium and (b) lead nanoparticles.

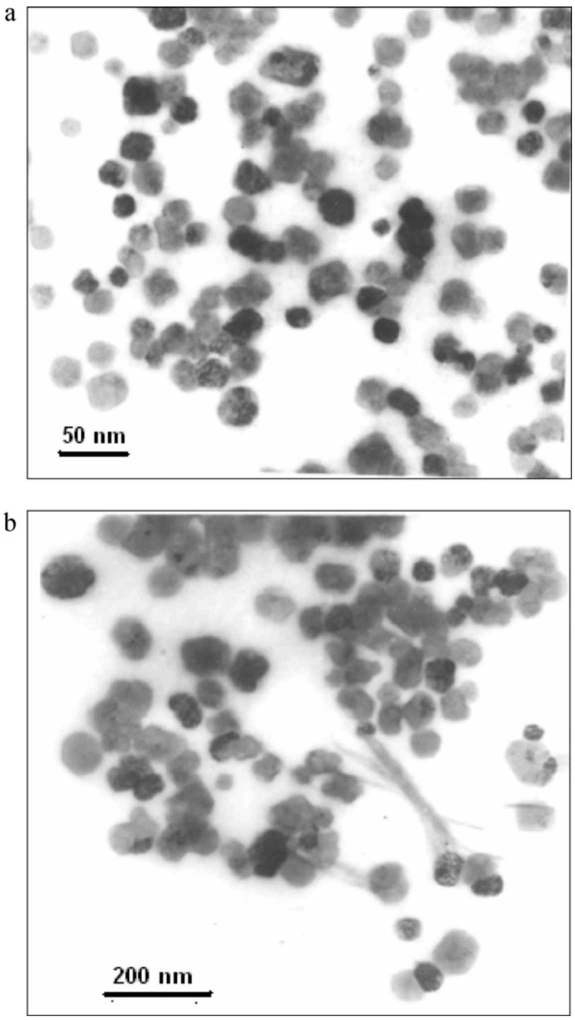


Fig. 2. Transmission electron microscope picture of (a) palladium and (b) lead nanoparticles.

ethanol and then centrifuges the solutions at 6000 rpm for 20 min and decants the supernatant and washed it with ethanol (3×) and dried with nitrogen gas thoroughly. Then the dried material was weighed and analyzed by powder X-ray diffraction, TEM and QELS techniques. (Yield = 10.621 mg)

2.2.3. Synthesis of lead nanoparticles in ionic liquid (A)

In a round bottom flask, 5 ml of the synthesized ionic liquid was taken and 25 mg of lead nitrate was added then excess of methanolic solution of sodium borohydride (15 mg in 10 ml) was added in the flask. Suddenly a white color solution was obtained indicates the lead (0) particles (Scheme 3). The stirring was continued for 2 h. The above solution was taken in ethanol and then centrifuges the solutions at 4000 rpm for 20 min and decants the supernatant and washed it with ethanol (3×) then the left material was dried with nitrogen gas thoroughly. Then the dried material was weighed and analyzed by powder X-ray diffraction, TEM and QELS techniques (Yield = 14.568 mg).

3. Results and discussion

Powder X-ray diffraction pattern of the palladium nanoparticles shows signature for Pd (0) as shown in Fig. 1(a). The peaks at 17.9° and 44.8° indicate the presence of Pd (0) in the sample. High intensity peak in the powder X-ray diffraction indicate the crystalline nature of the sample. Lead nanoparticles were well characterized with powder-X-ray diffraction, TEM and QELS techniques. Powder X-ray diffraction pattern of the lead nanoparticles shows signature for Pb (0) as shown in Fig. 1(b). The peaks at 28.6, 31.2, 36.8, 52.1 and 62.6 in the powder X-ray diffraction plot confirm the presence of Pb (0) in the sample.

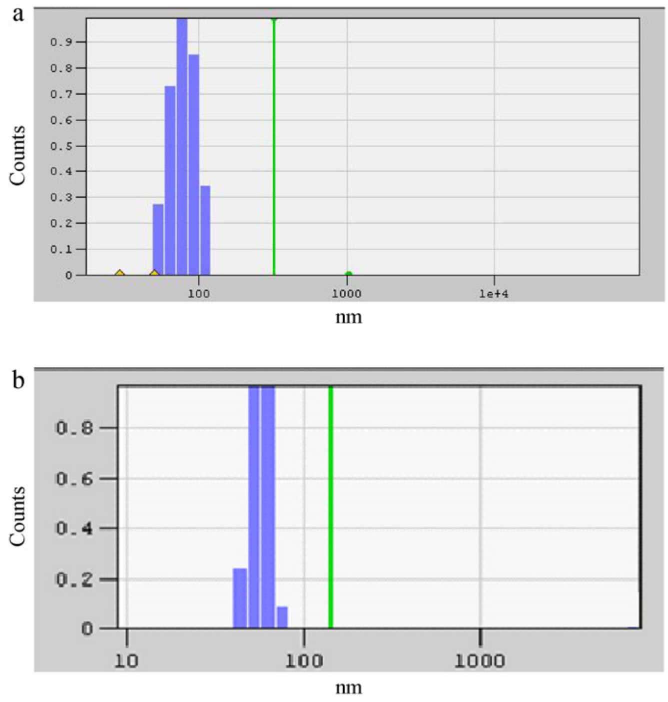


Fig. 3. QELS picture of (a) palladium and (b) lead nanoparticles.

TEM studies of palladium nanoparticles were carried out to understand the shape and size of the particles. Fig. 2(a) shows the transmission electron micrographs of palladium nanoparticles are 35 nm in diameter with spherical shape. TEM studies of lead nanoparticles were carried out to understand the shape and size of the particles. Fig. 2(b) shows the transmission electron micrographs of lead nanoparticles are 70 nm in diameter with spherical shape. The particles size of palladium and lead nanoparticles was confirmed by QELS of palladium and lead nanoparticles as in Fig. 3(a) and (b).**Conclusion**

The present study illustrates simple, convenient and significant methods for the synthesis of palladium and lead nanoparticles through the reduction of palladium and lead respectively in ionic liquid.

Acknowledgement

This work is dedicated to late Dr. N.N. Ghosh (Dr. Prashant Singh).

References

[1] G.G. Ferrier, A.R. Berzins, N.M. Davey, Platinum Met. Rev. 29 (1985) 175–179.
[2] C. Templeton, W.P. Wuelfing, R.W. Murray, Acc. Chem. Res. 33 (2000) 27–36.
[3] L. Lu, M.L. Sui, K. Lu, Science 287 (2000) 1463–1466.
[4] L.M. Qi, J.M. Ma, J.L. Shen, J. Colloid Interface Sci. 186 (1997) 498–500.
[5] M. Lisiecki, L. Biorling, B. Motte, M.P. Ninham, Langmuir 11 (1995) 2385–2392.
[6] X. Ren, D. Chen, F. Tang, J. Phys. Chem. B 109 (2005) 15803–15807.
[7] S. Kapoor, D.K. Palit, T. Mukherjee, Chem. Phys. Lett. 355 (2002) 383–387.
[8] J. Wang, H. Huang, S.V. Kesapragada, D. Gall, Nano Lett. 5 (2005) 2505–2508.
[9] O. Ali, Mater. Sci. Eng. 459 (2007) 294–302.
[10] V.V. Hardikar, E. Matijevic, J. Colloid Interface Sci. 221 (2000) 133–136.
[11] G. Zhou, M. Lu, Z. Yang, Langmuir 22 (2006) 5900–5903.
[12] J.D. Holbrey, K.R. Seddon, Clean Prod. Process B 1 (1999) 232–236.
[13] J. Dupont, R.F.D. Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667–3692.

[14] J.S. Albero, G. Rupprechter, H.J. Freund, J. Catal. 235 (2005) 52–59.
[15] C. Vincenzo, N. Angelo, M. Antonio, D. Antonia, I. Patrizia, Organometallics 22 (2003) 4193–4197.
[16] J.C.G. Martinez, R. Lezutekong, R.M. Crooks, J. Am. Chem. Soc. 127 (2005) 5097–6001.
[17] V. Kogan, Z. Aizenshtat, R. Popovitz-Biro, R. Neumann, Org. Lett. 4 (2002) 3529–3532.
[18] N.A. Dhas, A. Gedanken, J. Mater. Chem. 8 (1998) 445–450.
[19] A.A. Athawale, S.V. Bhagwat, P.P. Katre, A.J. Chandwadkar, P. Karandikar, Mater. Lett. 57 (2003) 3889–3894.
[20] M. Iida, S. Ohkawa, H. Er, N. Asaoka, H. Yoshikawa, Chem. Lett. 10 (2002) 1050–1051.
[21] Y. Xiong, J.M. McLellan, J. Chen, Y. Yin, Z.Y. Li, Y. Xia, J. Am. Chem. Soc. 127 (2005) 17118–17127.
[22] P. Singh, A. Katyal, R. Kalra, R. Chandra, Met. Lett. 62 (2008) 4164–4166.
[23] P. Singh, A. Katyal, R. Kalra, R. Chandra, Tet. Lett. 49 (2008) 727–730.
[24] P. Singh, A. Katyal, R. Kalra, R. Chandra, Catal. Comm. 9 (2008) 1618–1623.
[25] P. Singh, A. Katyal, R. Kalra, R. Chandra, Spectrochim. Acta A: Mol. Biomol. Spect. 73 (2009) 218–220.
[26] P. Singh, A. Katyal, R. Kalra, R. Chandra, Catal. Lett. 127 (2009) 119–124.