Materials Chemistry and Physics 170 (2016) 1–11

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Facile one-pot synthesis of crystalline palladium nanoparticles with exceptional catalytic and antiradical activities

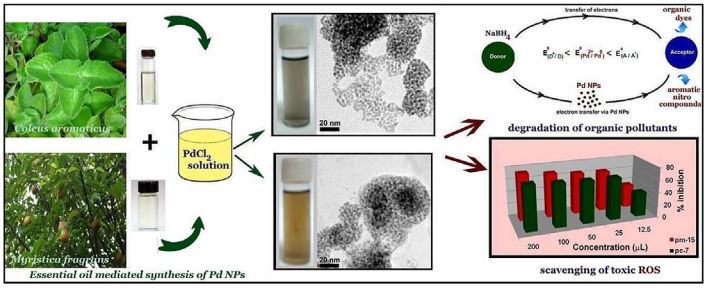
Vidya Vilas [a, b], Daizy Philip [a, *], Joseph Mathew [b]

[a] Department of Physics, Mar Ivanios College, Thiruvananthapuram, 695015, India
[b] Department of Chemistry, Mar Ivanios College, Thiruvananthapuram, 695015, India

HIGHLIGHTS

- Pd nanoparticles are synthesized using essential oil for the first time.
- Terpenoids and phenolic derivatives reduce Pd^{2+} to Pd^{0}.
- Clusters of 2–3 nm sized Pd nanospheroids are formed.
- Pd nanocatalysts efficiently degrade organic dyes and aromatic nitro compounds.
- Biogenic Pd nanoparticles exhibit reducing power and antiradical activities.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form
3 December 2015
Accepted 10 December 2015
Available online 22 December 2015

Keywords:
Biomaterials
Nanostructures
Electron microscopy
Fourier transform infrared spectroscopy

ABSTRACT

It is for the first time that the essential oils of medicinal plants are used for the synthesis of palladium nanoparticles, one of the rarest and precious transition metals known to mankind. In the present study, leaf essential oil of *Coleus aromaticus* and *Myristica fragrans* is used as the bioreductant. The appearance of an absorption continuum in the UV–vis spectrum indicates the formation of palladium nanoparticles. The effect of varying quantities of biomaterial on the synthesis of nanopalladium is studied. TEM micrographs disclose the formation of clusters of well dispersed nanospheroids of size ~2.8 nm. Sharp peaks in the XRD are indexed to Bragg reflections from planes corresponding to face centred cubic crystalline structure. FTIR spectral analyses reveal the participation of terpenoids and phenolic ether derivatives in reduction and capping. The synthesized nanoparticles exhibit significantly high catalytic efficiency in degrading a broad spectrum of organic pollutants including methyl red, methyl orange, eriochrome black T, methylene blue, rhodamine B, ortho-, meta- and para-nitrophenols. The reduction reactions are observed to obey pseudo first order kinetics. Antioxidant potential of the as synthesized palladium nanoparticles is portrayed through DPPH assay, nitric oxide and hydroxyl radical scavenging activities and reducing power activity.

1. Introduction

Over the years, phytosynthesis of precious metallic nanoparticles (NPs) has remained as one of the potential areas of research throughout the world, owing to the eco benign nature of the protocol that restrains from the use of toxic chemicals and aggressive energy conditions. The unique physio-chemical, electronic and magnetic properties of bioinspired metallic NPs have led to their extensive applications in catalysis, electronics, medicine,

* Corresponding author.
E-mail addresses: daizyp@rediffmail.com, philipdaizy@yahoo.co.in (D. Philip).

http://dx.doi.org/10.1016/j.matchemphys.2015.12.011
0254-0584/

agriculture and several other significant areas. The past decade has witnessed extensive research on the biosynthesis of gold and silver NPs [1–3]. However, the synthesis of rare transition metals including Pt, Pd, Rh, Ni and Cu in the nanoregime, by the use of phytochemicals as reducing and capping agents remain unexplored to a certain extent.

Extracts of plant parts have been used as the bioreductant in an attempt to phytosynthesize palladium nanoparticles (Pd NPs). Few prominent works in this field include the use of polyphenols and terpenoids present in the extracts of *Curcuma longer* (tuber) [4], *Terminalia chebula* (seeds) [5], *Pistaria atlantica* (fruit) [6] and *Cinnamom zeylanicum* (bark) [7] to synthesize highly stable Pd nanospheroids. Raut et al. [8] and Baruwati et al. [9] have been successful in synthesizing extremely small Pd nanospheroids of the particle size range of between 1 and 6 nm using aqueous extracts of *Asparagus recemosus* root and red grape pomace respectively under green conditions. Further advancement in this discipline includes the use of a natural polymer (xanthum gum) for the synthesis of catalytically active 2–10 nm sized Pd nanospheroids [10].

Morphology, stability and nature of the surfactants are crucial in determining the possible applications of Pd NPs in distinct fields. In addition to high Fermi potential, small size of the Pd NPs and a consequent elevation in the surface area to volume ratio enhances the availability of a large number of active surface atoms, enabling their use as redox intermediators in reductive degradation reactions, automotive catalytic convertors, catalysts in numerous hydrogenation and coupling reactions, in alcohol oxidation and in low temperature reduction of pollutants in automobile exhaust [11,12].

Herein, we have attempted to synthesize nano Pd through a clean and eco friendly route. Pd NPs have been synthesized using leaf essential oil of *Coleus aromaticus* (C.a) and *Myristica fragrans* (M.f). Focus has also been laid on the possible application of the biogenic Pd NPs as catalyst in the reduction of toxic dyes (methyl red (MR), methyl orange (MO), eriochrome black T (EBT), methylene blue (MB) and rhodamine B (RBB)) and nitro compounds (ortho-(2-np), meta- (3-np) and para-nitrophenols (4-np)) polluting water bodies. Furthermore, the in vitro antioxidant potential of the as synthesized Pd NPs has been exhibited through a series of assays.

2. Materials and methods

The precursor (99.9% pure $PdCl_2$) and sodium borohydride ($NaBH_4$) are procured from Sigma Aldrich. All the chemicals used in the experiment are of analytic grade and are used without further purification. Deionised water is used throughout the experiment.

2.1. Extraction and dilution of essential oil

About 300 g of thoroughly washed, fresh leaves of M.f are subjected to steam distillation for 5 h by employing a Clevenger apparatus. The procedure is repeated with 450 g of fresh leaves of C.a. The % yield of each leaf essential oil with its own characteristic aroma is noted.

Dilution of the extracted oil (using the green solvent, ethanol) is an essential criterion for its adequacy to be used as the bioreductant. The dilution of M.f oil is optimized at oil:ethanol (v/v) = 0.1:25, while that of C.a leaf oil is oil:ethanol (v/v) = 0.05:70. An increase in the concentration of oil in the oil/solvent mixture, resulted in an enhancement in the degree of turbidity of the colloid, indicating an appreciable hindrance in the complete reaction of the reductant added.

2.2. Synthesis of Pd NPs using M.f and C.a leaf oil

To 40 mL of 2.3×10^{-4} M of the precursor solution, set at pH 7 and 373 K, 15 mL of the diluted M.f oil is added slowly with vigorous stirring. The optically transparent pale yellow solution becomes intense brown on addition of the reductant, indicating the formation of Pd NPs. The experiment is repeated using 20 and 25 mL of diluted oil. The colloids so formed are designated as pm-15, pm-20 and pm-25, respectively. Further, to 40 mL of boiling 1.5×10^{-4} M $PdCl_2$ solution, 7 mL of diluted C.a oil is added gradually with constant stirring at pH 7. The experiment is repeated with varying volumes of C.a oil including 15 and 20 mL and the colloids formed are labelled as pc-7, pc-15 and pc-20, respectively.

2.3. Catalytic studies on Pd NPs

To about 1 mL of 1 mM organic dye, 1 mL of 9.9×10^{-2} M $NaBH_4$ (excess) is added. The mixture in 10 mL aqueous solution is vigorously stirred for 10 min. This is followed by the addition of 1 mL of catalytically active nano sized Pd particles with stirring continued for another 5 min for efficient dispersal of the particles. The procedure is repeated with 1 mL of 7.1×10^{-3} M isomers of nitro phenol and 1 mL of 0.25 M $NaBH_4$ in 25 mL aqueous solution. The reduction reactions of the organic pollutants are traced through the UV–vis absorption spectra measured as a function of time.

2.4. Antioxidant activity of Pd NPs

The antiradical activity of the biogenic Pd NPs is ascertained through a series of assays including 2,2-diphenyl-1-pycryl hydrazyl radical (DPPH) assay, Hydroxyl radical (OH) scavenging activity, Nitric oxide (NO) scavenging activity and reducing power activity. The concentration dependant % inhibition values of the Pd NPs are inferred through these assays. Antioxidant assays are primarily based on the generation of toxic radicals and their consequent conversion to complexes with a characteristic absorption in the visible region. Inhibition percentages are calculated based on the efficiency of the antioxidants in scavenging the generated radicals, leading to a subsequent decline in the absorption. Detailed procedures of the assays are presented in the supplementary material.

$$\%\ \boldsymbol{inhibition} = \left\{\frac{\boldsymbol{A_{control}} - \boldsymbol{A_{test}}}{\boldsymbol{A_{control}}}\right\} \times 100 \quad (1)$$

$\boldsymbol{A_{test}}$ and $\boldsymbol{A_{control}}$ being the optical density (measured at λ_{max} depending on the assays) of the solution mixtures with and without the addition of Pd NPs respectively [13].

2.5. Instrumentation

The optical absorption spectra of the colloids are recorded in a quartz cuvette of 1 cm path length using Perkin–Elmer Lambda- 35 UV–visible spectrophotometer at a scan speed of 480 nm/min and a resolution of 1 nm. IR Prestige-21 Shimadzu spectrophotometer is employed to record the FTIR spectra of the bioreductant and the as synthesized Pd NPs in the transmittance mode. The microstructure of the biogenic Pd NPs is determined through TecnaiG^2 30 TEM. Prior to measurement, the samples are drop coated on to carbon coated copper grids followed by vaporization of the solvent. The crystal structure and the crystallite size of the bioinspired Pd NPs are determined by the use of XPERT Pro diffractometer operating at 30 mA and 40 kV using CuKα radiation (λ = 1.5406 A^0).