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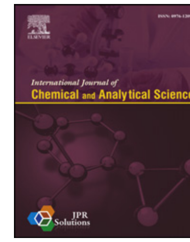

Original Article

Palladium nanoparticles: Single-step plant-mediated green chemical procedure using *Piper betle* leaves broth and their anti-fungal studies

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ABSTRACT

The green synthesis of metal nanoparticles has made broad progress in recent times due to their novel optical, catalytic, hydrogen storage, bio-imaging and electrochemical applications. In recent years, the utilization of phyto-organic moieties from different biological sources has a modern technology for the nanoparticles synthesis. The authors synthesized the palladium nanoparticles (PdNPs) using *Piper betle* leaf extract as reducing and capping material, it can reduce the toxic chemicals, multiple steps in synthesis procedure and environmentally harmless. The surface plasmon resonance of growing PdNPs was investigated by UV–Vis spectroscopy. The particle morphology, distribution and size were estimated by transmission electron microscopy and the particle size is found to be 4 ± 1 nm, phase purity of synthesized PdNPs was characterized by selected area electron diffraction and X-ray diffraction patterns. The presences of the bio-organic moieties, which are responsible for the wrapping around the PdNPs and probable pathway of the synthesis is analyzed with the Fourier transform infrared (FTIR) spectroscopy. We believed that, water soluble flavonoids of *P. betle* are responsible for phyto-reduction of PdNPs. The bioactivity demonstrated by synthesized PdNPs was lead to an excellent clinical use as anti-fungal material.

1. Introduction

Green technology is multi-disciplinary integration of biotechnology, nanotechnology, chemical processing, physical methodology, drug delivery in medicinal and systems engineering into bio-chips and nanobiometerials.[1] The ability to precisely control the synthesis of significant importance not only for fundamental scientific interest but also for

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emerging technology applications such as catalysis, information storage, biological chemical sensing, and optoelectronics due to their electrical, optical and magnetic properties as well as the catalytic activity of these nanoparticles strongly depends on their size and shape. The sizes, crystal structures, controlled mono-dispersion and stabilization are the critical factors due to their applications both heterogenous and homogenous catalysis, due to their high-surface-to- volume ratio and their high-surface energy.[2] The growing interest in the area has led to considerable concern about metal nanoparticles synthetic methods. Chemical reduction in aqueous solution or non-aqueous solution, micro-emulsion method, template method and microwave assisted synthesis are traditional methods. In the last decade, plant-mediated biological synthesis of nanoparticles as an emerging high-light of the intersection of nanotechnology and green nanotechnology has received increasing interest due to grow need to develop environmentally harmless technologies in material synthesis.[3] In particular the widespread use of nanoparticles of platinum group metals in industrial and automotive catalysis is increasing, because they have high corrosion resistance and are stable to oxidation at high temperatures.[4] Palladium belongs to platinum group materials which are widely used in automotive catalytic converters in order to reduce gaseous emission vehicles exhaust for the sake of environment protection. Utilization of inexpensive and nontoxic chemicals, environment friendly solvents and renewable or biodegradable materials of biomolecules is a central tenant in material synthesis and processing when considering green chemical procedures.[5] Driven by growing impetus of naturally motivated green nanoparticles are recently developed new methodologies employing biological sources such as microorganisms and plant extracts.[6,7] In recent years, synthesis of palladium nanoparticles (PdNPs) using biological sources such as *coffee and tea*, *Cinnamom zeylanicum*, *Anacardium occidentale*, *Cinnamomum camphora*, *honey and grape peel* extracts.[8–13] Green synthesis of PdNPs offers many advantages over the corresponding physical and chemical methods. The *Piper betle* leaf extract has a rich source of flavonoids, polyphenols, amides and proteins. Over recent years, flavonoids have been focused interest because of their protective effect on DNA damage, antioxidant, anti-fungal, wound cleaning and their certain kinds of cancer.[14] In many countries herbs and broth are the integral parts of traditional medicine such as Iranian, Unani, Sidda, Ayurvedic and folk medicines. Keeping in the point of the above credentials, in this communication the efforts have been made on synthesis of PdNPs by green chemical method, one-pot aqueous synthesis and characterization and anti-fungal studies of the PdNPs by using *P. betle* leaf extract.

2. Materials and methods

Palladium chloride ($PdCl_2$) was obtained from Sigma–Aldrich (USA) and used without further purification. The fresh *P. betle* leaf extract used for the reduction of palladium ions was prepared by taking 20 g of thoroughly washed, finely cut leaves in a 250 ml Erlenmeyer flask along with 100 ml of Millipore water and then boiling the mixture for 2 min before decanting it. Further, the extract was filtered through Whatman No. 1 filter paper and stored for further experiments.

3. Instrumentation

The process of the reaction between leaf extract and aqueous palladium chloride solution was analyzed by UV–Vis absorption spectroscopy. The UV–Vis absorption spectroscopic analysis was carried out on Thermo Scientific Genesys 10S UV–Vis spectrophotometer with resolution of 1 nm between 200 and 800 nm. The particle size and morphology of the PdNPs were studied with Philips Tecnai FEI 12 model TEM. The TEM grids were prepared by placing a drop of the bio-reduced diluted solution onto a carbon coated copper grid and later dried it under the lamp. An X-ray diffraction (XRD) measurement of a thin film of the bio-reduced colloidal palladium solution was drop coated onto a glass slide and dried it. XRD patterns of the prepared thin film was analyzed by using Inel C120 X-ray diffractometer, which is equipped with a curved position sensitive detector and data were collected using Co–K_α radiation of 1.7889Å. The grain size of the PdNPs are calculated accordingly to the X-ray line broadening method using the Debye–Scherrer's formula $D = 0.9\lambda/\beta\cos\theta$, where D is the average grain size of the particle, λ is the wavelength of the incident X-ray, β is the FWHM of the diffraction peak. The FTIR measurement of the bio-reduced aliquot solution was centrifuged at 10000 rpm per 30 min. The sample was dried and admixed with KBr from Sigma–Aldrich and palletized. The IR spectrum analyzed on Thermo–Nicolet IR 200 spectrophotometer, operated at a resolution of 4 cm^{-1} in the region of 4000–500 cm^{-1}. Q5

4. Results and discussion

4.1. UV–Vis *absorption studies*

The bio-reduction of palladium ions was studied by monitoring changes in color with UV–Vis absorption spectroscopy. The formation of PdNPs was studied as a function of time reaction shown in Fig. 1. The change in color is attributed to the collective oscillation of conduction band electrons induced by the interaction of electromagnetic wave with metallic nanoparticles. Surface plasmon resonance (SPR) can be described as the resonant, collective oscillation of valence electrons in a solid stimulated by incident light. Surface plasmon resonance (SPR) strongly depends upon its size, shape, charge distribution and its dielectric constants of metal and the surrounding medium.[15,16] It is evident that, a small absorption band 600–700 nm was observed which indicates either formation of stable aggregates of the PdNPs in the solution or shape anisotropy in the particles. The SPR peak at 320 nm is well known for the metal nanoparticles in the range of 2–100 nm and this absorption peak corresponds to the real and imaginary parts of dielectric function of metals almost vanish.[13] Thus the phyto-chemicals within *P. betle* leaf broth not only result in effective reduction of Pd^{2+} to stable Pd nanoparticles but also their effective wrapping around the

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