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Phytochemical Synthesis of palladium-gold nanoparticles using in-vitro grown hypericin rich shoot culture of *Hypericum hookerianum*

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Abstract : Green nanobiotechnology pave tremendous attention not only to innovative scientific motto but also an emerging potential area of research, aimed at categorizing compounds of natural origin and establishing economically efficient routes for the production of benign materials that have applicability in environmentally harmless (biodegradable), simple and biocompatible devices. In recent years, the utilization of bio-organic moieties from different biological sources has become a modern technology for the green synthesis of nanoparticles. We synthesized the gold-palladium (Au-Pd) nanoparticles using *Hypericum hookerianum* shoot extract as reducing and capping material. The grown nanoparticles were investigated by UV-Vis, XRD, TEM, SAED and FTIR studies. The morphology, distribution and size of the biomolecule stabilized Au-Pd nanoparticles were carried out by Transmission electron microscopy studies, crystalline nature of the Au-Pd nanoparticles were characterized by SAED and X-ray diffraction analysis. The capping involvement of the water soluble phyto-organic moieties was studied with FT-IR Studies.
Keywords: Phytochemical synthesis***; Hypericum hookerianum;*** Pd-Au Nanoparticles; TEM,

1. Introduction

In recent decade, multi-metallic nanoparticles with alloy or core-shell structures became smart materials because of their compositiondependent optical, catalytic, electronic, and magnetic properties. A number of methods, such as chemical and physical methods have been established to prepare bimetallic nanoparticles[1,2,3]. These methods are quite expensive and dangerous to environment and human health procedures. To overcome these issues, biogenic preparation of nanoparticles is of interest to chemists, physicists, biologists and materials scientists alike, especially in light of efforts to introduce greener methods of inorganic material procedures other than physical and chemical methods[4,5]. Utilization of inexpensive and nontoxic chemicals, eco-friendly solvents and biodegradable materials of biomolecules is a central tenant in material fabrication and processing when considering green and human friendly procedures[6, 7]. Natural environment provides a indication of biomolecules that can be effectively utilized in capping nanostructures. Biological sources such as bacteria, fungus, yeast and plant leaf extracts were used in the synthesis of biomolecules that hosted metal and semiconductor nanoparticles[8,9,10,11,12].

The *Hypericum hookerianum* have high medicinal value and potential applications in medicine such as effective against inflammation, tumors, bacteria, viruses, allergies. Moreover, besides being anti-oxidants they have anti-atherogenic, hyperglycemic and hematological properties and are involved in immune modulating therapies[13,14,15]. In this paper, we present a single step green chemical approach towards the stabilization of gold-palladium nanoparticles using *Hypericum hookerianum* extract. The biomolecules performs the dual action of reducing and capping agent of metallic ions.

2. Materials and methods

$HAuCl_4.3H_2O$ and $PdCl_2$ were obtained from Sigma-Aldrich (USA) and used without further purification. *Hypericum hookerianum* plant was cultivated by using a man-made method, the fresh *Hypericum hookerianum* were raised and maintained in Murashige and Skoog (1962) medium[16] supplemented with 1.0 mg/L kinetin (KIN) and 0.2 mg/L naphthalene acetic acid (NAA) following the procedure described by Padmesh et al. [17, 18]. All the chemicals were procured from Sigma-Aldrich and during whole experiment Milli-Q water was used.

The shoot cultures obtained were thoroughly washed, shade dried and fine powdered. The powdered mass of 10gms was mixed with 100 mL water at $70^{o}C$ for 15 minutes and cooled down to room temperature. The extracts were filtered using Whatman number 1 filter paper. The filtered extract was used as reducing agent for the reduction of 1mM Pd-Au (1:1 ratio) ions.

3. Characterization

The UV-Vis absorption spectroscopic analysis was carried out on Genesys 10 UV-Vis spectrophotometer with resolution of 1nm between 270-1000nm. The particle size and morphology of the prepared samples were measured with Philips Tecnai F 12 model TEM. The TEM grids were prepared by insertion of a drop of the aliquot Pd-Au solution onto a carbon coated copper grid and dried under the lamp. An X-ray diffraction (XRD) measurement of a thin film of the colloidal Pd-Au solution was drop coated onto a glass slide. XRD patterns of the prepared thin film was analyzed by using Inel C120 X-ray diffractometer, equipped with a sensitive detector with curved position and data were collected using Co-Kα radiation of 1.7889Å. The size of the Pd-Au nanoparticles are calculated according 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 size of the particle, λ is the wavelength of the incident X-ray, β is the FWHM of the diffraction peak.

4. Results and discussion

4.1 UV-Vis absorption studies

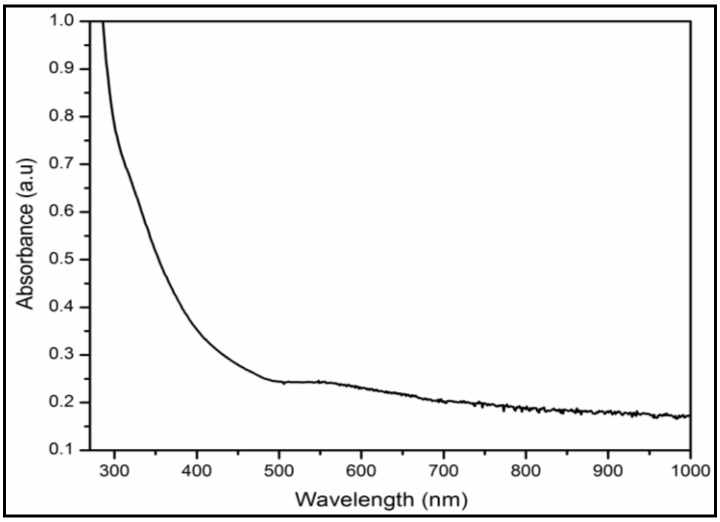

Figure 1.UV-Vis absorption spectrum of palladium-gold nanoparticles.

The reaction between *Hypericum hookerianum* extract and aliquot Pd-Au solution was analyzed by UV-Vis absorption spectroscopy was shown in **Fig. 1**. The absorbance behavior of the bimetallic nanoparticles is found to be different from those of the individual and physical mixture of monometallic nanoparticles. The specific absorbance band of Au nanoparticles that appears at 540 nm is absent in the Au-Pd bimetallic nanoparticles[19, 20]. This clearly suggests that dispersions of Au-Pd nanoparticles systems do not contain single-metallic clusters but contain clusters with bimetallic structure[21].

4.2 XRD analysis

The crystalline nature of the Pd-Au NPs was confirmed from XRD analysis as shown in **Fig. 2**. The number of strong Bragg's diffracted peaks was observed at 44.6º, 52.1º, 76.8º and 93.4º corresponding to the (111), (200), (220) and (311) facets of the face centered cubic (fcc) lattice of gold rich Pd-Au nanoparticles. The calculated average domain size of the Pd-Au NPs was 4 nm using the full width half maximum (FWHM) of the (111) Bragg's reflection, which matches well with the average diameter of nanoparticles determined from TEM.

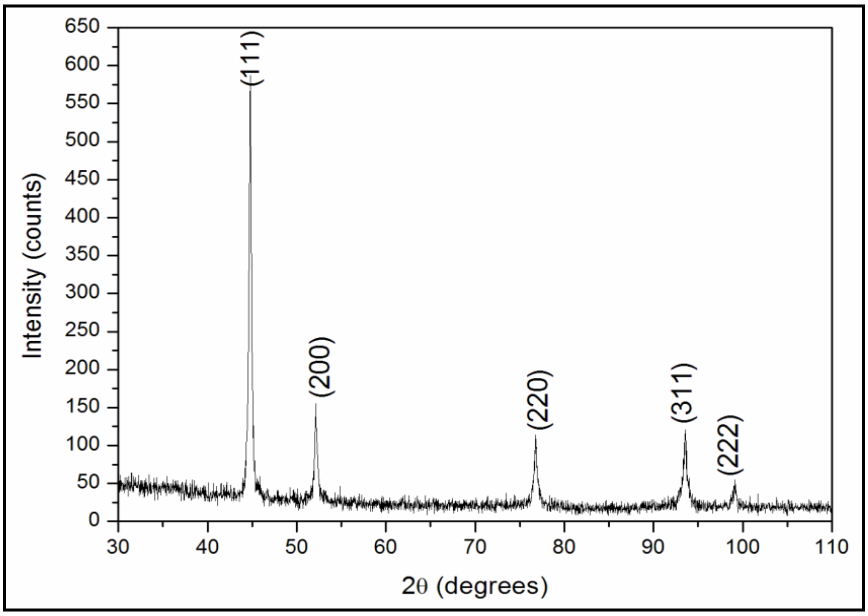

Figure 2.XRD-spectrum of palladium-gold nanoparticles.

4.3 TEM and SAED studies

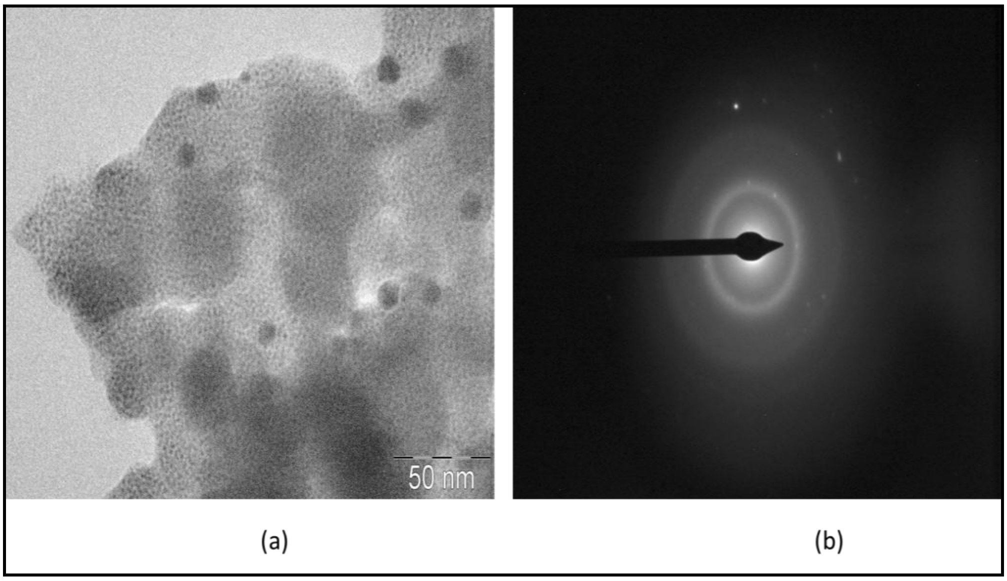

Figure 3 (a).TEM image of palladium-gold nanoparticles. (b) SAED pattern of palladium-gold nanoparticles

The particle morphology, size and crystallinity were studied from TEM, and SAED analysis. **Fig. 3(a)** shows the TEM image of the biosynthesized Pd-Au nanoparticles. From the image, it is interesting to note that particles are not in physical contact and found to be surrounded by a thin layer of biomolecules, which is showing the stabilizing the nanoparticles. The formations of Pd-Au nanoparticles with diameter 2-10 nm were observed. The SAED pattern suggests that the particles are highly crystalline nature as shown in **Fig. 3 (b)**. From the figure, the diffraction rings are from inner to outer, clearly indicating the fcc phases of Pd-Au nanoparticles with (111), (200), (220) and (311) reflections.

4.4 FTIR Analysis

The possible functional groups of adsorbedbio-organic molecules on the exterior of thenanoparticles were studied by FTIR spectroscopy (**Fig. 4**). FTIR peaks identified at 3430, 2925, 2348, 1741, 1627, 1426, 1319, 1043 and 703 cm^{-1}. The band at 3430 cm^{-1}can be associated with stretching vibrations of H in O-H, in alcohols and poly phenols and the peak at 2925 cm^{-1} indicates hydrogen bonded O-H stretch carboxylic acid.The peak 1741 cm^{-1}suggest theC=C vibrationsof aromatic rings.The peaks at 1627, 1319 and 1043 $cm^{-1}$are due to the C=C, C=O and N-H stretching and aromatic stretching vibrations could be attributedto different molecular ratios of carboxylic acid, alkenes and aminecontent of the capping reagents of the nanoparticles reduced in differentplant extracts[22,23]. These interactionsmake simple the gathering of phyto-organic molecules into a protective capping layer on the surface of Pd-Au nanoparticles, which results in both passivations and stabilization of the Pd-Au nanoparticles.

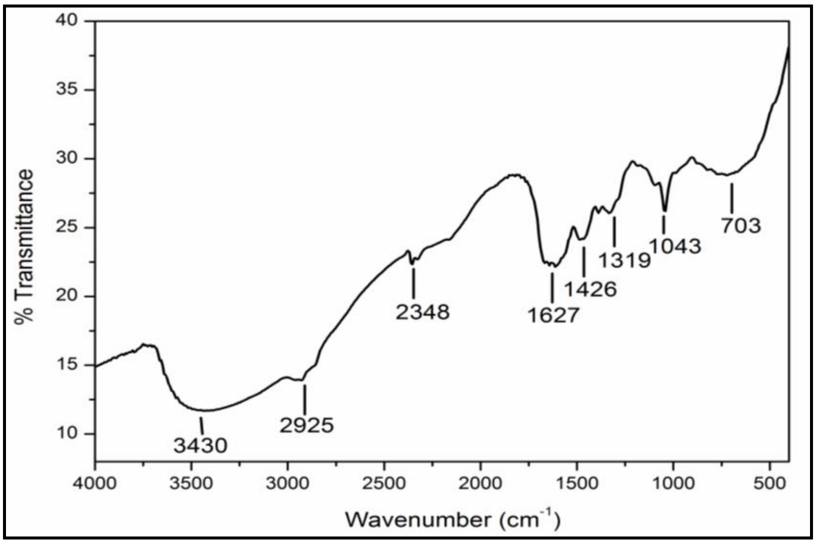

Figure 4.FTIR Spectrumof palladium-gold nanoparticles.

5. Conclusions

Phytochemicals of the shoot cultures of *Hypericum hookerianum* acted as reducing and capping agents for synthesis of Pd-Au nanoparticles. UV-Vis study gives dispersions of Au-Pd nanoparticles systems, which do not contain single-metallic clusters but have clusters with bimetallic structure. TEM image shows the synthesised Pd-Au NPs are spherical shape with size ranging from 2-10nm. FTIR spectrum supports the interactionsthat make simple the gathering of phyto-organic molecules into a protective capping layer on the surface of Pd-Au nanoparticles, which results in both passivations and stabilization of the Pd-Au nanoparticles.

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