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Green Synthesis and Characterization of Platinum Nanoparticles using *Sapindus mukorossi* Gaertn. Fruit Pericarp

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Synthesis of platinum nanoparticles (Pt-NPs) was accomplished by a green procedure employing aqueous solutions of *Sapindus mukorossi* Gaertn. fruit pericarp. The size of nanoparticles obtained are in range of 2-19 nm which is achieved by the reduction of platinum ions with the aqueous extract of *Sapindus mukorossi* Gaertn. fruit pericarp. The resulted platinum nanoparticles are highly crystalline face-centered cubic (fcc) structures. The resulting platinum nanoparticles might be stabilized through the interactions of carboxylic groups in saponins and the carbonyl groups in flavonoids present in the soap-nut shells. TEM, XRD, SEM with EDS were used to study the morphology, distribution, crystallinity and size of the platinum nanoparticles. The results showed that platinum nanoparticles formed with cubic phase. This biogenesis is straight-forward, amenable for big scale industrial production and technical applications.

Keywords: Platinum nanoparticles, *Sapindus mukorossi* Gaertn., Green synthesis.

INTRODUCTION

Recently, research methodologies are implementing to develop easy, amicable and low cost green methods for the production of nanomaterials. Nanoparticles from noble metals are playing a vital role in the fields of bioelectronics, pharmaceuticals and organic catalysis [1-8]. The metal constituted platinum compound *cis*-diamminodichloro-platinum(II) (*cis*-platinum) is a drug for treating cancer [9]. The potential applications of platinum nanoparticles have been developed in the fields of hydrogen storage and fuel cells materials [10,11]. They also showed excellent catalytic activity than bulk materials [12]. Platinum nanoparticles also exhibited efficient catalytic activity in the development of fuel cells as proton-membrane exchangers [13].

Platinum nanoparticles can be prepared by several methods such as reduction of ethanol, water-in-oil microemulsion, polyol synthesis, supercritical fluid, ambient pressure drying method, sputtering methods, sonoelectrochemical method and microwave irradiated method [4-21]. Nevertheless, these conditions are hampering the industrial preparation of platinum nanoparticles in terms of requiring expensive instruments and uses of toxic reagents.

Therefore, the use of biological materials such as plant materials and microorganisms are the best alternative approaches for the above mention approaches for platinum nanoparticles synthesis in industrial preparation procedures. Instead the use of plant materials in place of microorganisms has more advantages including the elimination of elaborative processes and maintenance of cell cultures [22].

In literature, a few methods have been reported for platinum nanoparticles preparation such as Dipyros kaki leaf extract [23], *Cacumen platycladi* extract and herbal *Bidens tripartitus* extract [24,25].

The aqueous extract of Soap nuts (*Sapindus mukorossi* Gaertn. fruit pericarp) mainly constituted with saponins (natural surfactants), flavonoids and carbohydrates. An ancient people of Asia and America have long been using soap nuts for washing [26]. Usually, commercial available detergents release carcinogenic toxins into the environment during production, therefore, the best alternative to avoid this is to use soap nuts for the production of detergents due to its biodegradable properties. Hence, soap nuts are considered and used commercially in detergents, cosmetics, and other products [27]. In addition, soap-nuts have some medicinal characteristic properties such as antiinflammatory and antimicrobial activities [22,26,28]. Recently, green synthesis of nanoparticles [22] using of soap nuts is increasing in the field of nanotechnology to develop cost effective. In order to develop a greener and more economic protocol for the fabrication of platinum nanoparticles, we used an aqueous solution of *Sapindus mukorossi* Gaertn. Fruit pericarp extract as reducing and stabilizing agent.

In view of these facts, herein, we report a biological, eco-friendly and economic procedure for preparation of platinum nanoparticles by thermal treatment in presence of aqueous solution of *Sapindus mukorossi* Gaertn. Fruit pericarp extract as reducing and stabilizing agent. A systematic characterized with UV-visible spectroscopy, transmission electron microscopy and X-ray diffraction techniques. The possible bioreduction of platinum precursor mechanism also has been discussed.

EXPERIMENTAL

Soap nut shells were procured from agricultural fields in India. Hexachloroplatinic acid (H_2PtCl_6) was purchased from Sigma-Aldrich (USA). The organic free water was collected from Marine department, Andhra University, Visakhapatnam, India.

The obtained platinum nanoparticles were characterized by using transmission electron microscope (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). TEM, selected area electron diffraction pattern (SAED) and energy dispersive X-ray (EDX) data were obtained on XPERT-PRO at room temperature, using CuKα radiation λ = 1.5406 Å over a wide range of Bragg angles (30º ≤ 2q ≤ 85º). For TEM analysis, a few drops of platinum nanoparticles samples dispersion onto the carbon coated copper TEM grid and dried overnight. The FT-IR spectra were recorded on Schimadzu FTIR with the samples as KBr pellets.

Procedure: To prepare platinum nanoparticles, 10 mL of 0.01M H_2PtCl_6 solution was added to 10 mL filtrate of 50 % w/v of aqueous extract of *Sapindus mukorossi* Gaertn. fruit pericarp. The tightly sealed bottle was kept in preheated oven at 100 ºC for 10 h. The bio-reduction of H_2PtCl_6 is confirmed by the slow colour change to a stable black blue colour.

RESULTS AND DISCUSSION

The formation of platinum nanoparticles was confirmed by conversion of yellow colour of platinum reduced solutions to black colour colloidal sample. It reveals that an aqueous soap nuts solution reduces Pt(IV) ions into Pt(0) nanoparticles at 100 ºC under the reaction period of 10 h.

UV-visible studies were performed to identify the formation of platinum nanostructures using an aqueous soap nuts solution. Fig. 1 displays the UV-visible spectra of H_2PtCl_6 and reduced platinum sample obtained by an aqueous soap nuts solution. The peaks at 259 nm correspond to H_2PtCl_6 as shown in Fig. 1. Due to thermal treatment in the presence of aqueous soapnuts solution, the peak corresponding to H_2PtCl_6 disappeared, which indicates the reduction of Pt(IV) ions into Pt(0) nanoparticles.

Fig. 2 shows the TEM images of reduced platinum sample treated for 10 h reaction at different magnifications. It can be seen that there are slightly monodispersed, crystalline and spherical nanoparticles. An average particles diameter is 3 nm.

Fig. 3a shows a typical high resolution TEM image of platinum nanoparticles. The oriented and ordered lattice fringes of platinum nanoparticles can be seen in Fig. 3a, the distance between two fringes being 0.23 nm [8]. It revealed that the growth of platinum nanoparticles occurs preferentially on the (111) plane. The SAED image of as-prepared platinum nanoparticles is shown in Fig. 3b. The five rings in SAED patterns

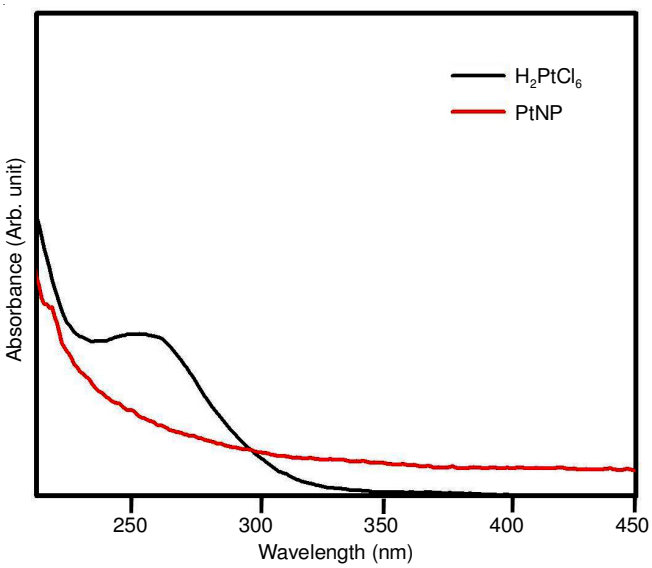

Fig. 1. UV-visible spectra of H_2PtCl_6 and platinum nanoparticles

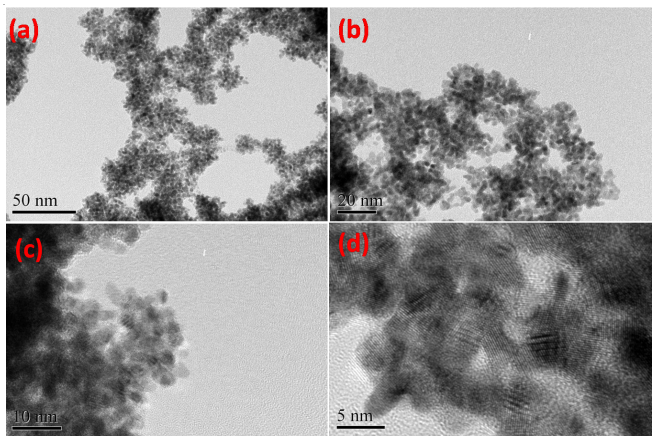

Fig. 2. TEM images of platinum nanoparticles at different magnifications

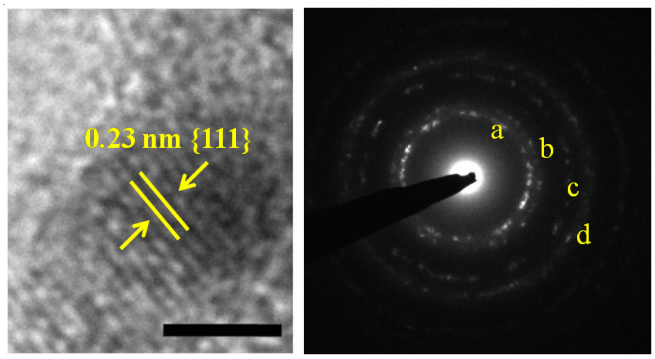

Fig. 3. (a) HR-TEM image and (b) SAED patterns of Pt-NPs. The five rings in (b) "a" to "d" represents to {111}, {200}, {220} and {311} diffraction planes, respectively. The scale bar in (a) is 2 nm

reflect to the (111), (200), (220), (311), and (331) diffraction planes [8], respectively, which corresponds to face-centered cubic (fcc) structure of platinum nanoparticles obtained by means of aqueous soap nuts solution.

As-prepared platinum nanoparticles were verified to contain the platinum according to EDX studies. Fig. 4 represents the EDX spectrum of as-obtained platinum nanoparticles, which confirms the presence of platinum.

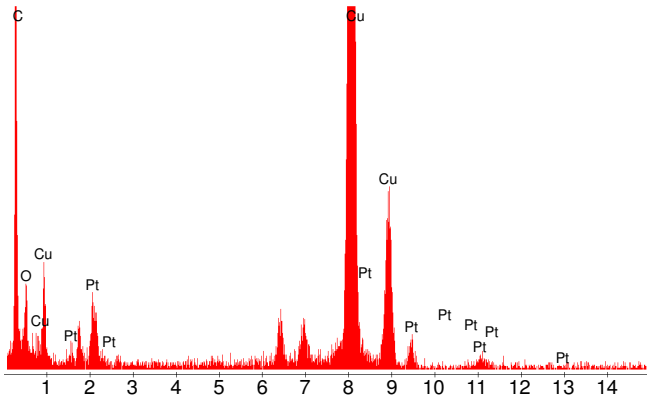

Fig. 4. EDX spectra of as-prepared platinum nanoparticles

The XRD spectrum of as-prepared platinum nanoparticles is shown in Fig. 5. The diffraction peaks at 2θ = 39.9, 46.6, 67.7, 81.6 and 85.9º correspond to the indexed planes (111), (200), (220), (311) and (331), respectively, which were consistent with the fcc structure of platinum [8]. The particle size information of obtained platinum nanoparticles was calculated from Debye-Scherrer equation:

$$L = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, β is the full-width at half maximum of XRD patterns. The estimated crystalline size of as-prepared platinum nanoparticles is 3 nm. These results are in good agreement with results of TEM measurements. SAED patterns, XRD patterns and the HR-TEM image clearly supports the obtained platinum nanoparticles are highly crystalline in nature.

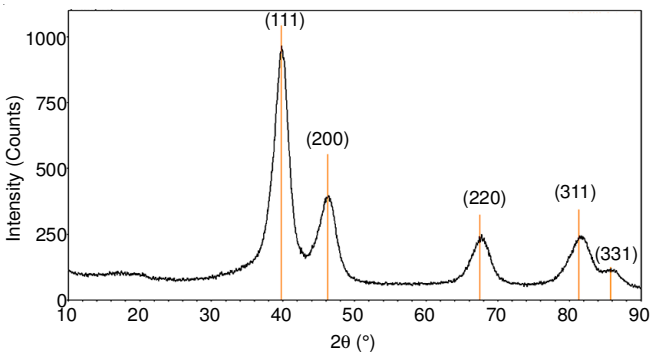

Fig. 5. XRD patterns of as-prepared platinum nanoparticles

It is concluded that the reference explains the mechanism for this bio-reduction (Fig. 6). Soap nut shells have a high content of saponins and flavonoids. The functional groups like hydroxyl groups in saponins and flavonoids could reduces Pt(IV) into Pt(0).

Conclusion

A facile green synthetic method has been developed for the synthesis of platinum nanoparticles by means of *Sapindus mukorossi* Gaertn. fruit pericarp extract. The UV-visible spectroscopy results confirm the formation of platinum nanoparticles by the change of yellow colour of platinum precursor into black colour of platinum nanoparticles. The TEM and XRD studies revealed that the prepared platinum nanoparticles are spherical in shape and highly crystalline nature. The functional

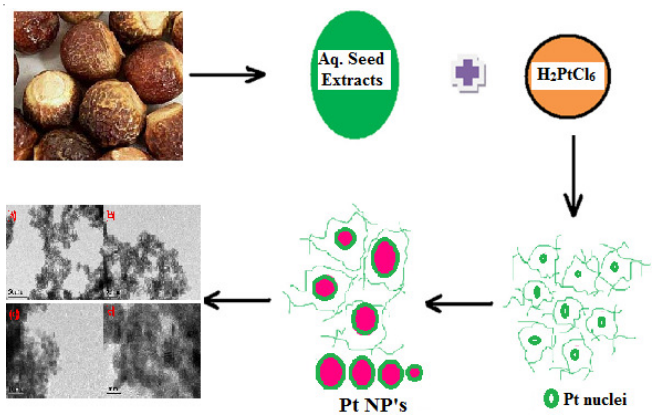

Fig. 6. Plausible mechanism for this bio-reduction

groups like hydroxyl groups in saponins and flavonoids in soap nuts shells could reduces Pt (IV) into Pt(0).

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