Metal nanoparticles prepared by using plant extracts as reducing agents: A review

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The unusual properties of metal nanoparticles make them appropriate for utilization in various areas of optoelectronics, catalysis, pharmaceuticals, etc. They have been synthesized using numerous physical and chemical methods but currently the approach of green synthesis is catching worldwide attention due to being eco-friendlier and economic. In the present study we have prepared Silver (Ag), Iron (Fe), Palladium (Pd) and Zinc (Zn) nanoparticles via the leaves of plants (*Melia azedarach, Urtica dioica and Ziziphus jujuba*). The synthesized nanoparticles were characterized using UV-VIS spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). Heat treatment was provided to the as synthesized Pd nanoparticles at different temperatures. The XRD pattern of Ag nanoparticles displayed formation of face-centered cubic (FCC) structure and those of Zn nanoparticles and as synthesized Pd nanoparticles showed low crystalline nature. Also, presence of oxides of metals along with the metals was found in the Fe, Zn samples, although Fe nanoparticles displayed crystalline behavior. Significant improvement in crystallinity on heating at 280 °C was shown by Pd nanoparticles, however, partial oxidation of the sample was also noticed in the XRD pattern. SEM images of as synthesized Ag, Fe, Pd and Zn nanoparticles revealed agglomeration, whereas SEM images of Pd nanoparticles heated at 280 °C displayed spherical particles clustered together.

Keywords: Metal nanoparticles, Green synthesis, Urtica dioica, Melia azedarach, Ziziphus jujuba, Silver nanoparticles, Iron nanoparticles, Palladium nanoparticles, Zinc nanoparticles.

1 Introduction

The class of materials having at least one dimension within the bracket of 1-100 nm, is generally defined as nanomaterials. These materials show distinctive properties as compared to their bulk because of the great surface area to volume ratio which changes their properties drastically. Nanoparticles (NPs) are a very current topic of interest amongst researchers across the globe. The peculiar properties of NPs make them appropriate for utilization in areas of diagnostic biological probes, catalysis, display devices, and optoelectronics[1]. Metal nanoparticles (MNPs) have attracted huge attention as these find applications in many areas. For example, silver nanoparticles (Ag NPs) possess anti-fungal, anti-viral, anti-bacterial properties and are being employed in cosmetics, food industry etc[2,3]. Palladium nanoparticles (Pd NPs) have remarkable optical, electronic, and chemical properties. They are being studied for use as catalysts and sensors and have huge catalytic potential in various organic reactions, including Suzukicross, Mizoroki-Heck, Stille etc[4]. Iron nanoparticles (Fe NPs) have a variety of applications including site remediation and treatment of water which are the need of the hour[5]. Zinc oxide nanoparticles (ZnO NPs) have numerous technological applications such as gas sensors, transparent conductors, thin-film transistors, biomedical and piezoelectric applications, owing to their outstanding optical and electrical properties[6]. Controlled synthesis of MNPs can be achieved by several techniques, for instance, laser abalation, arc discharge and a wide range of wet chemical processes including, chemical reduction, sonochemical, electrochemical etc.[7]

Green chemistry utilizes some parts of plants/trees e.g. leaves, flowers, fruits etc. or sometimes whole plants for the reduction and/or capping, stabilizing of NPs instead of chemicals, therefore, is an environment friendly and cost effective technique. It is easier to implement as compared to other processes because of the ease of availability of plants. In the report, a brief review of synthesis of MNPs is incorporated along-with the work done in our laboratory. We have prepared Ag, Fe, Pd, Cu, Zn NPs in our lab.

2 Experimental Methodology

Different steps to prepare nanoparticles have been mentioned in Fig. 1.

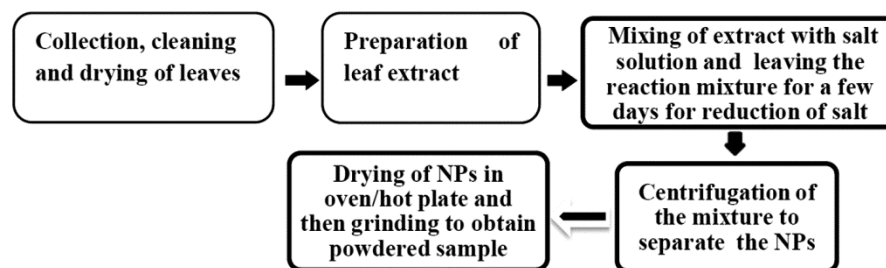*Corresponding author: (E-mail address: shubkala@gmail.com)

Fig. 1 — Schematic diagram showing different steps to prepare nanoparticles.

Table 1 — Green synthesis of Ag NPs using different plants, as reported in literature.

S.No.	Plant	Part(s)	Size (nm)	Application(s)	Ref.
1	*Triphala*	Leaves	59	Antibacterial, antifungal agent	8
2	*Parthenium hysterophorus*	Root	N/A	Mosquito control	2
3	*Azadirachta indica*	Leaves	~21	Antibacterial, antioxidant agent	9
4	*Rosmarinus officinalis*	Leaves	17	Growth of tomato and wheat plants	10
5	*Cinnamon zeylanicum*	Bark	31-40	Bactericidal agent	11
6	*Boerhaavia diffusa*	Plant	25	Antibacterial agent	3
7	*Jatropha curcas*	Seed	15-50	Reducing agent	12
8	*Moringa oleifera*	Leaves	9-11	Antimicrobial agent	13
9	*Vitex negundo*	Leaves	10-30	Antibacterial agent	14
10	*Skimmia laureola*	Leaves	46	Antibacterial agent	15

3 Results and Discussion

3.1 Ag NPs

Ag NPs have been synthesized by using different plants and their parts. Previous reports on Ag NPs are summarized below in the Table 1.

In our study, Ag NPs have been synthesized by using *Melia azedarach* plant leaf extract and $AgNO_3$ salt. Similar steps, as mentioned in the experimental section (Fig. 1), have been followed to prepare Ag NPs. Figure 2 shows the absorption spectrum, X-Ray diffraction pattern (XRD), scanning electron microscope (SEM) image and energy dispersive X-ray (EDX) spectrum of the prepared Ag NPs. The absorption spectrum (Fig. 2 (a)) of the reaction mixture (*Melia* leaf extract and $AgNO_3$ salt mixture) shows a shoulder peak at 420 nm resembling with that of AgNPs.[2] The XRD pattern (Fig. 2 (b)), indicates formation of polycrystalline Ag NPs, exhibiting face-centered cubic (F.C.C.) structure in good agreement with the JCPDS card no. 03-0921, as reported earlier by Farghaly *et al.*[10]The crystallite size was found in the range 17-25 nmby Debye Scherrer formula. The Ag NPs are found as agglomerated structures, as clear from the SEM image (Fig. 2 (c)). EDX spectrum (Fig. 2 (d)) confirms presence of Ag. Some other elements such as C and Ca are also found which could be present in leaf extract.

3.2 Fe NPs

Various plants have been utilized to produce Fe NPs. Table 2 below summarizes the literature of the same.

Green synthesis of Fe NPs has been done in our laboratory by using *Urtica Dioica* leaves and $FeCl_3$ salt by applying the same steps as shown in Fig. 1. The absorption spectrum (Fig. 3 (a) of the leaf extract shows three peaks at 368, 409 and 670 nm, which can be attributed to the polyphenols, alkanes, carbonyl compounds etc., present in the plant.[21] The reaction mixture (*Urtica* leaf extract and $FeCl_3$ mixture) shows complete absence of the 670 nm peak and partial decline of the other two, indicating reduction of salt and hence the formation of Fe NPs. XRD pattern (Fig. 3 (b)) of the Fe NPs shows crystalline nature and presence of different phases of iron and iron oxide. The peaks observed for Fe correspond to hexagonal structure (JCPDS card no. 501275). The crystallite size, calculated by using Debye Scherrer formula, is found between 13-24 nm. SEM image (Fig. 3 (c)) reveals large agglomerated particles. EDX spectrum (Fig. 3 (d)) shows presence of iron (Fe) along with carbon and some other elements such as K, Cl, Ca etc. possibly present in leaf extract.

3.3 Pd NPs

Many plants have been utilized to synthesize Pd NPs. Table 3 below briefly reports some of the studies.

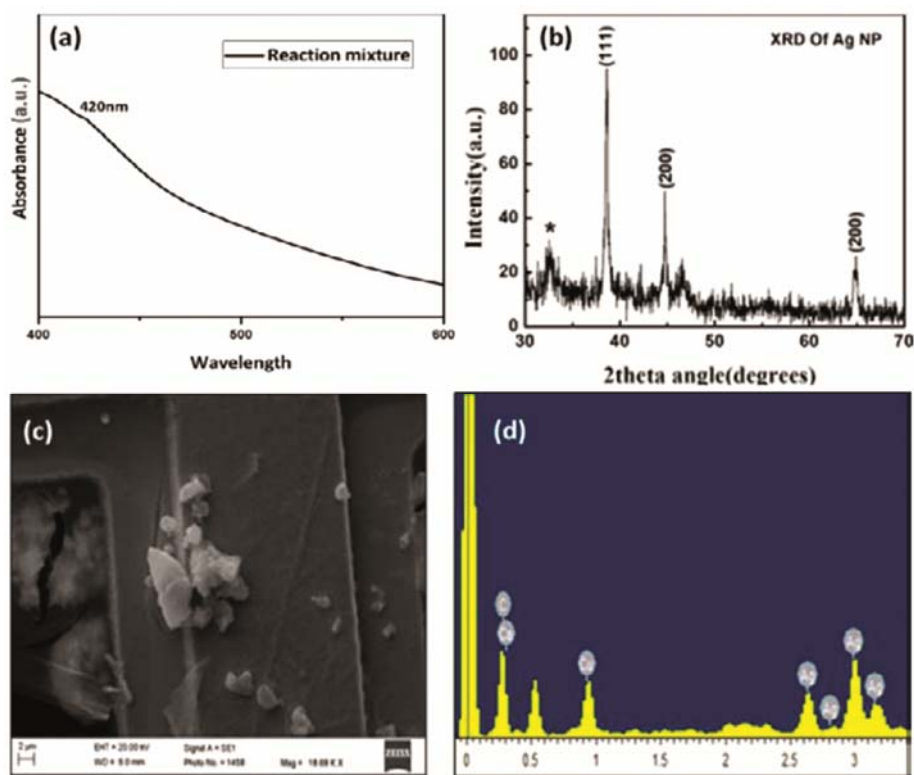Fig. 2 — (a) Absorption spectrum, (b) XRD pattern,(c) SEM image and (d) EDX spectrum, of the Ag NPs synthesized via Melia azedarach leaf extract.
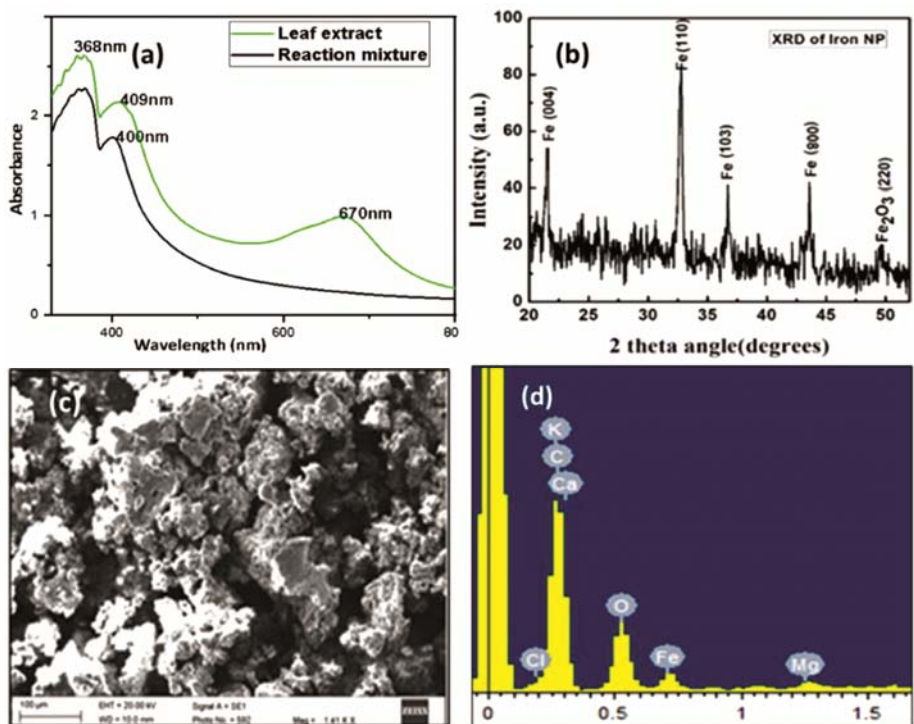

Fig. 3 — (a) Absorption spectra of Urtica leaf extract and reaction mixture, (b) XRD pattern, (c) SEM image and (d) EDX spectrum, of the Fe NPs synthesized via Urtica Dioica leaf extract.

Table 2 — Green synthesis of Fe NPs using different plants.

S.No.	Plant	Part(s)	Size (nm)	Application(s)	Ref.
1	*Eucalyptus*	Leaves	20–80	Treatment of eutrophic wastewater	5
2	*Vaccinium floribundum*	Fruit	5-10	Removal of Petroleum Oil	16
3	*Mentha spicata*	Leaves	20–45	Adsorptive removal of arsenite and arsenate	17
4	*Camillia Sinensis*	Leaves	5-15	Degradation of bromothymolblue	18
5	*Terminalia chebula*	Fruit	<80	N/A	19
6	*Oolong tea*	Leaves	40-50	Degradation of malachite green	20
7	*Lawsonia inermis*	Leaves	21	Antibacterial activity	1
8	*Rosa damascene*	Leaves	100	Removal of 6 Cr(VI)from aqueous solutions	21
9	*Green tea*	Leaves	40-60	Degradation of aqueous cationic & anionic dyes	22
10	*Musa Ornata*	Flower	~44	Antibacterial agent	23

Table 3 — Green synthesis of Pd NPs using different plants.

S.No.	Plant	Part (s)	Size (nm)	Application(s)	Ref.
1	*Camellia sinensis*	Leaves	6–18	Antioxidant, antibacterial, and antiproliferative activities toward the human leukemia (MOlT-4) cell line	4
2	*Artemisia abrotanum*	Plant	20	Suzuki coupling reactions	24
3	*Pulicaria glutinosa*	Plant	20–25	Suzuki coupling reaction	25
4	*Prunus × yedoensis*	Leaves	50–150	Antimicrobial activity	7
5	*Lithodora hispidula*	Leaves	~22	Electrocatalytic reduction of hydrogen peroxide	26
6	*Phoenix dactylifera*	Leaves	5-18	Biomedical and catalytic applications	27
7	*Gardenia jasminoides*	Fruits	3-5	Nanocatalysts for p-nitrotoluene hydrogenation	28
8	*Euphorbia granulate*	Leaves	25–35	Catalytic properties	29
9	*Moringa oleifera*	Peel	27 ± 2	Antibacterial and hemolytic property	30
10	*Piper nigrum*	Pepper	~5	Aryl Halide Cyanation and Hiyama Cross-Coupling Reaction	31

Pd NPs were synthesized in our lab following the steps mentioned in Fig. 1. *Urtica dioica* plant leaf extract and $PdCl_2$ as the precursor were used to prepare Pd NPs.The absorption spectrum (Fig. 4 (a)) of the reaction mixture (mixture of $PdCl_2$ and leaf extract solution) revealed reduction of the two peaks at 430nm, 674 nm which were present in the leaf extract, thus, signifying reduction of salt and hence nucleation of Pd NPs. However, XRD pattern (Fig. 4 (b)) reveals increase in crystallinity of the sample with heating and at 280°C formation of Pd NPs, but also shows partial oxidation of Pd NPs which may be due to oxidation of particles on drying/handling. The Pd NPs heated at 280°C were found to crystallize in cubic structure which is consistent with Inorganic Crystal Structure Database (ICSD) - (01-089-4897) data. The average crystallite size calculated by Debye Scherrer formula was around 10 nm. SEM images of as synthesized sample (Fig. 4 (c)) and sample heated at 100°C (Fig. 4 (d)) revealed agglomeration whereas, roughly spherical Pd NPs clustered together can be observed from the SEM images of Pd NPs heated at 280°C (Fig. 4 (e)). EDX spectra of the samples (Fig. 4 (f,g,h)) reveal presence of Pd along with elements such as C, Cl, P, Mg etc. which may be present in the leaf extract.

3.4 Zn/ZnO NPs

Table 4 below gives a brief summary of various plants which have been used to synthesize Zn/ZnO NPs and their applications.

We synthesized Zn/ZnO NPs using leaf extract of *Ziziphus jujuba* and salt of zinc acetate ($Zn(CH_3CO_2)_2.2H_2O$) as the precursor utilizing the steps as shown in Fig. 1. Absorption spectrum (Fig. 5 (a)) of the reaction mixture (leaf extract and Zinc acetate mixture) shows reduction of the peak at 425 nm present in the plant leaf extract, leaving a shoulder peak at 389 nm, indicating formation of Zn NPs. Presence of different phases of Zn and ZnO is revealed from the XRD (Fig. 5 (b)). The SEM image (Fig. 5 (c)) depicts formation of agglomerated structures. The EDX spectrum (Fig. 5 (d)) shows Zn peaks along-with the peaks of C, Cl, O, Mg, K etc which are possibly due to presence of these elements in plants.
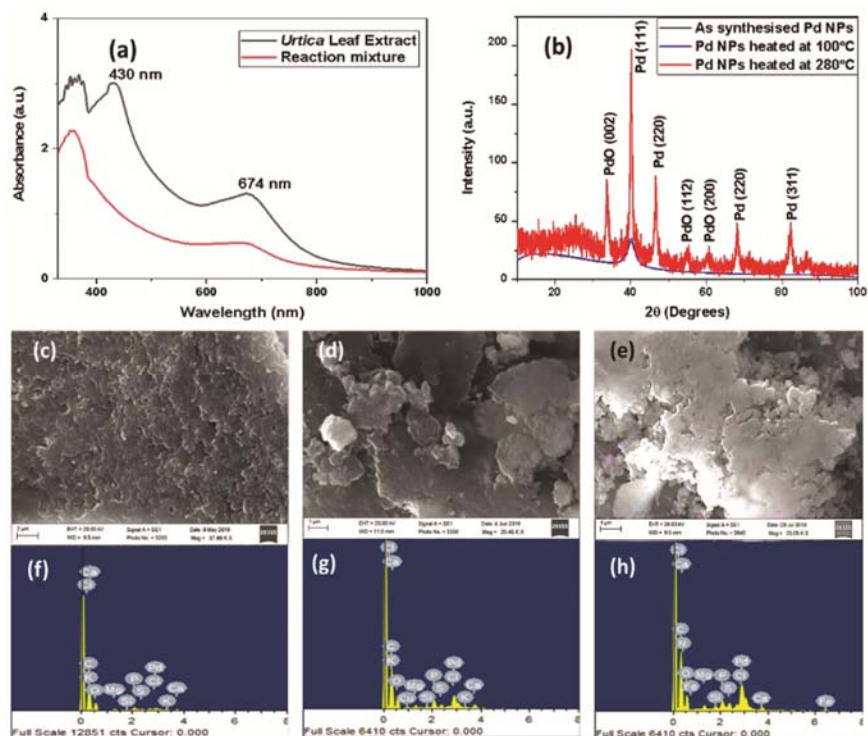
Fig. 4 — (a) Absorption spectra of *Urtica* leaf extract and reaction mixture, (b) XRD patterns of as synthesized, heated at 100°C and heated 280°C Pd NPs; SEM images of (c) as synthesized, (d) heated at 100°C, (e) heated at 280°C Pd NPs; EDX spectra of the (f) as synthesized, (g) heated at 100°C and (h) heated at 280°C Pd NPs, synthesized via *Urtica dioica* leaf extract.
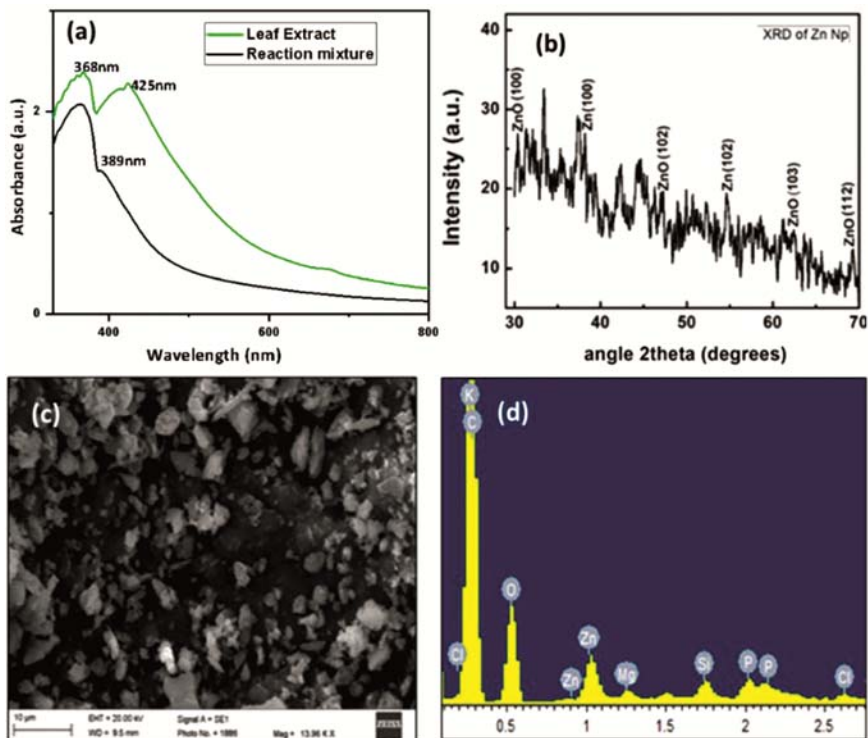

Fig. 5 — (a) Absorption spectra of *ziziphus jujube* leaf extract and reaction mixture, (b) XRD pattern, (c) SEM image and (d) EDX spectrum of the Zn NPs synthesized via *Ziziphus jujuba* leaf extract.

Table 4 — Green synthesis of Zn/ZnO NPs using different plants.

S.No.	Plant	Part(s)	Size (nm)	Application(s)	Ref.
1	*Lycopersicon esculentum*	Fruit	40-100	Photovoltaic application	6
2	*Albizia saman*	Leaves	5-120	Effect on root meristems of Drimiaindica (Roxb.) Jessop	32
3	*Passiflora caerulea*	Leaves	30–50	Treatment of urinary tract infection	33
4	*Aspalathus linearis*	Flowers	1- 8.5	Reducing agent	34
5	*Hibiscus subdariffa*	Leaves	16-60	Anti-bacterial & anti-diabetic agent	35
6	*Punica granatum*	Peel	20±5	Antibacterial agent	36

4 Conclusions

Silver, iron, palladium and zinc nanoparticles were successfully prepared under normal laboratory conditions however the nanoparticles were partially oxidized due to lack of proper vacuum. Using parts of plants/trees instead of other chemicals to act as reducing/stabilizing/capping agent for synthesizing metal/ semiconductor nanoparticles represents a very eco-friendly, cost effective approach and eliminates all the disadvantages associated with using hazardous/ toxic chemicals for the same purpose. However, green chemistry offerslimited control over the size-distribution of synthesized nanoparticles. Besides, sometimes reduction process consumes lots of time.

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