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Review on Green Synthesis of Nanoparticles using Various Strong Electrolytic Metal Solutions Mediated by Various Plant Parts

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ABSTRACT

The present review targets the comparative biogenic synthesis and mechanisms of nanoparticles using various plant-parts extracts and various solutions of strong electrolytic metal salts. The metal salts are AgNO₃, Zn(OAc)₂, Zn(NO₃)₂, ZnSO₄, CuSO₄·5H₂O, Cu(NO₃)₂, Cu(OAc)₂, CuCl₂, H₂UO₄·3H₂O, Mg(NO₃)₂, Mg(OAc)₂, TiO(OH)₂, Fe(NO₃)₂·6H₂O, FeCl₃·6H₂O, FeCl₂·4H₂O, Al(NO₃)₃, BaCl₂·2H₂O, Bi(NO₃)₃, PdCl₂, H₂PtCl₆·6H₂O, NaHSeO₃, Na₂SeO₃, Ca(NO₃)₂·4H₂O, ZrOCl₂·4H₂O, Zr(OAc)₄, NiCl₂·NiSO₄·6H₂O, Ni(NO₃)₂, VCl₃, Co(NO₃)₂·6H₂O, CoCl₂, Hg(OAc)₂, Mn(OAc)₂, (NH₄)₆Mo₇O₂₄, Sr(NO₃)₂, SnCl₂·2H₂O, Na₂S₂O₃·5H₂O, K₂Cr₂O₇, Cr(NO₃)₃·9H₂O and Pb(NO₃)₂. These salts are soluble to produce to highly active positive metal ions in deionised water. These ions are effectively nucleated in the plant constituents. The plant acts akin to a huge “bio-laboratory” comprising of leaves, seeds, stem, root, sprout, fruits, latex, bark, fruits peel, fruits, juices, etc... which are composed of biomolecules and phytoconstituents. These naturally happening biomolecules and phytoconstituents have been recognized to play an energetic role in the formation of nanoparticles with discrete shapes and sizes thus acting as a pouring force for the manipulative of greener, safe and environmentally benign protocols for the synthesis of nanoparticles.

1. Introduction

The development of these ecofriendly methods for the synthesis of nanoparticles is growing into an imperative twig of nanotechnology, which have many applications [1-3]. Biological customs of nanoparticles (NPs) synthesis using microorganisms [4,5], enzymes [6], fungus [7], and plants or plant extracts [8-10]. The strong electrolytic salts are mainly used in the green synthesis of nanoparticles especially nitrate (NO₃⁻) salts are majorly used in this synthesis. It has long been known that plants are able to reduce metal ions both on their surface and in various organs and tissues remote from the ion penetration site. In this regard, plants (especially those which have very strong metal ion hyper accumulating and reductive capacity) have been used for extracting precious metals from land which would be economically unjustifiable to mine; an approach known as phytomining. In this regard, plants and plant part extracts-based biosynthesis has been found to be cost effective and environmentally friendly [11]. The metals accumulated by the plants can be recovered after harvesting via sintering and smelting methods. Interestingly, study of the metal bioaccumulation process in plants has revealed that metals are usually deposited in the form of nanoparticles. Whole plants can obviously be used to produce metal nanoparticles. However, there exist certain limitations that should be taken into account upon industrial application of this technology. Firstly, the size and shape of nanoparticles vary depending on their localization in the plant, which may depend on differences in the contented of metal ions in various tissues and the ensuing likelihood of nanoparticle faction and penetration. These factors could pressure the level of metal deposition around already existing nanoparticles, and also the prospect of new nucleation events (initiation of nanoparticle formation) [12]. The heterogeneity of the size and morphology of nanoparticles produced in whole plants may deter their use in applications where precise, finely tuned sizes and shapes are required; thus, illustrating the incapacity to tailor the whole plant synthesized nanoparticles to market requirements. Moreover, efficient extraction, isolation and purification of nanoparticles from plant material is a difficult and problematic procedure, with a low recovery.

2. Green Synthesis of Nano Particles

“Green synthesis” is required to avoid the production of unwanted or harmful by-products through the build-up of reliable, sustainable and eco-friendly synthesis procedures. The use of ideal solvent systems and natural resources (such as organic systems) is essential to achieve this goal. Green synthesis methodologies based on biological precursors depend on various reaction parameters such as solvent, temperature, pressure, and pH conditions (acidic, basic, or neutral). For the synthesis of metal/metal oxide nanoparticles, plant biodiversity has been broadly considered due to the availability of effective phytochemicals in various plant extracts, especially in leaves such as ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids. These components are capable of reducing metal salts into metal nanoparticles [13]. The basic features of such nanomaterials have been investigated for use in biomedical diagnostics, antimicrobials, catalysis, molecular sensing, optical imaging, and labelling of biological systems [14]. Here, we summarized the current state of research on the green synthesis of metal/metal oxide nanoparticles with their advantages over chemical synthesis methods. In addition, we also discussed the role of solvent systems (synthetic materials), various biological with their advantages over other conventional components/solvents. The main aim of this literature study is to provide detailed mechanisms for green synthesis and their real-world environmental remediation applications. Overall, our goal is to systematically describe “green” synthesis procedures and their related components that will benefit researchers involved in this emerging field [15,16], while serving as a useful guide for readers with a general interest in this topic. Nanotechnology is a deliberate manipulation of matter at size scales of less than 100 nm in at least one dimension meaning at the level of atoms and molecules as compared with other disciplines such as materials science, chemistry, and engineering [17,18]. The green syntheses have actively been developed in recent years, in which plant extracts are used for the bioreduction of metal ions to form nanoparticles. These approaches provide a more flexible control over the size and shape of the nanoparticles (for example, by changing the medium pH and reaction temperature), as well as facilitating easy purification [19]. Significantly, this process occurs much faster than the synthesis of nanoparticles in whole plants, because the reaction proceeds almost instantaneously, without the delay required for the uptake and diffusion

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of metal ions throughout the plant. This *in vitro* approach has been demonstrated using extracts from a variety of different plant species in combination with a variety of acids and salts of metals [20-22], such as silver, copper, zinc, gold, platinum, magnesium, iron, palladium, calcium, zirconium, tin, vanadium, molybdenum, manganese and many others [23-25]. Many researchers have reported, the synthesis of nanoparticles, metal salts of strong electrolyte dissolved in de-ionized water, especially transition metal salts were used in most of the green synthesis method. The colour change of salt solution and extracts is indicated as the formation of nanoparticle. The colour of the nanoparticle formed solution is depends upon the metal ions.

3. Metal Solutions/ Metal Cations

The salt solution of strong electrolyte is widely used in the green synthesis of nanoparticles, because strong electrolytes are easily produced metal cations, radioactive element are not reported till date in green synthesis of nanoparticles. Transition elements are extensively used in the green synthesis of nanoparticles, The usage of alkali metal (Li, Na, K, Rb, Cs, etc.) elements are very low, because alkali metals have shown +1 oxidation state. So, it does not nucleate to long chain phyto-constituents. These metal cations are not easily capping to organic compound of phyto-constituents. Alkaline earth metals of Mg, Ca, Sr and Ba have been reported to the many of the green synthesis of nanoparticles mediated by plant parts extracts. 'd' block elements of transition elements having variable oxidation states, these produce smaller size metal ions and it has high positive charges, so transition metal ions are very efficiently nucleated to long chain organic compounds of phyto-constituents. In the 'p' block elements but radioactive elements and nonmetals are not involved in the green synthesis of nano particles. Inner transition elements of 'f' block elements are not involved in the green synthesis of nanoparticles. The metal salts of nitrates (NO₃⁻), sulphates (SO₄²⁻), acetates (OAc) and chlorides (Cl⁻) are widely used in the green synthesis of nanoparticles. Because metal ions are converted into metal hydroxide [Mⁿ⁺(OH)_n] complexes. The anions like sulphates (SO₄²⁻), nitrates (NO₃⁻) and chlorides (Cl⁻) are non-interfering nature and so they do not interfere the nanoparticles generations. These anions are combined with water molecules to form acids like nitrates (NO₃⁻) to nitric acid (HNO₃), sulphates (SO₄²⁻) to sulphuric acids (H₂SO₄), acetates to acetic acid (CH₃COOH) and chlorides (Cl⁻) to hydrochloric acid (HCl). The acidified filtrate would be washed easily in final filtration process. Some of the interfering anions such as borate (BO₃³⁻), phosphate (PO₃³⁻), oxalate (Ox²⁻), fluorides (F⁻), etc., containing metal salts are very lowly used in green synthesis of nanoparticles. Because, it doesn't produce the highly active metal cations

and anionic parts of the salt is affect the generation of nanoparticles. The crystalline salts are frequently soluble in deionised water and effectively nucleated to phyto-constituents such as poly phenol, amino acid of proteins, alkaloids, steroids, polysaccharides, carbohydrates, tannins, fats and oils forming the nanoparticles. Powder natured salts of carbonates (CO₃²⁻) and sulphides (S²⁻) are not used as the green synthesis of nanoparticles. These salts are not soluble in deionised water, and using the green synthesis process this unionized carbonate part is first hydroxylated then deposited the carbonate parts only, it not yet to form the nanoparticles.

4. Visual Observation

Reduction of metal salts into metal nanoparticles by the biomolecules is always accompanied by the color change of reaction medium. Plant extracts are capping to metal ions turn the solution to different colours, this is a first conformation of nanoparticles generations. The synthesis of silver nanoparticles (AgNPs) using silver nitrate solutions (AgNO₃) have shown brown, brownish yellow and deep brown colours [26-32]. Zinc nanoparticles have been synthesized from zinc acetate, zinc sulphate and zinc nitrate salts. All the zinc salts are colorless because zinc have completely filled '3d' orbitals and it does not contain unpaired electrons but zinc nanoparticles (ZnNPs) have shown yellowish and cream or beige [34-37], brownish green [38], brownish black [39] and even white color also reported [40]. The copper nanoparticles are synthesized from copper sulphate salts such as copper chloride, copper nitrate and copper acetate. All the copper salts are blue and pale blue colour nevertheless the colour of the copper nanoparticle (CuNPs) solutions have been shown green [42], yellowish black [43], yellow [46], green [47] and dark brown black [48] colour. Similarly gold nanoparticles (AuNPs) have shown in violet colour sol [49], ruby red colour [50], magnesium nanoparticles (MgNPs) show brownish, and brownish yellow colour solutions. Titanium nanoparticles (TiNPs) solution show light green colour and the nanoparticles of iron have shown in brown [64], bluish green [65], black [67,68] and dark brown [71]. AlNPs solution have deep yellow coloured paste and BaNPs appeared as white colour in the nanoparticle synthesis. PdNPs were show in yellow [77,78]; platinum nanoparticles sol was shown in dark brownish colour. Selenium (SeNPs) metal ions in nanoparticle were synthesised which gave red and dark pink colour solutions, calcium show white in colour, zirconium reflect black and brown. Nickel nanoparticles have shown pale yellow and green colour, CoNPs provided dark brown in colour, MoNPs as dark grayish brown, HgNPs as dark yellow, CrNPs as green and red dye and PbNPs depict pale orange in colour. This review concluded that colour of the nanoparticle solution is depends upon the metal cations in the strong electrolytic solutions.

Table 1 Green synthesis of various metal nanoparticles mediated by various plant parts

S.No.	Metal solution	Extract of plant part	NPs	Colour	λ_{max} (nm)	FTIR (cm ⁻¹)	Size (nm)	Ref.
1	AgNO ₃	<i>Avicennia marina</i> leaf	AgNPs	Brownish yellow	300-700	3940.57, 3929, 3803.63, 3712.97, 3423.65, 2918.30, 2231.64, 1610.58, 1377.1, 1257.5, 1041.50, 775.38 and 667.37 cm ⁻¹	-	[26]
2	AgNO ₃	Mangosteen leaf extract	AgNPs	Brown	300-700	1619, 1522, 1340 and 1160 cm ⁻¹	6-57	[27]
3	AgNO ₃	<i>Manihot esculenta</i> leaves	AgNPs	Brownish	200-800	-	0.5-1	[28]
4	AgNO ₃	<i>Rhizophora mucronata</i> leaves	AgNPs	Brownish yellow	300-700	3426.89, 2925.49, 2869.56, 2346.95, 1031.73, 1631.49, and 1669.178 cm ⁻¹	60-95	[29]
5	AgNO ₃	<i>Excoecaria agallocha</i> leaves	AgNPs	Brownish yellow	434	-	15-43	[30]
6	AgNO ₃	Olive leaf	AgNPs	Deep brown	441-458	3436, 3395, 1651, 1630, 1520, 1537, 1420 and 1454 cm ⁻¹	8-15	[31]
7	AgNO ₃	<i>O. gratissimum</i> leaves	AgNPs	Brown	415	3435, 1631, 1588, 1452, 1383 and 1349 cm ⁻¹	16-18	[32]
8	AgNO ₃	<i>A. squamosal</i> leaves	AgNPs	Brownish	420	3448, 3424, 1735, 1644.9, 1620, 1636 and 922 cm ⁻¹	-	[33]
9	Zn(OAc) ₂	<i>Hibiscus subdariffa</i> leaf	ZnNPs	Yellowish -cream	377	1381, 2889, 1474, 1576, 1780 and 482 cm ⁻¹	1µm	[34]
10	Zn(NO ₃) ₂	<i>Citrus sinensis</i> (Orange peel)	ZnNPs	Cream or beige	-	1600–800 and 618 cm ⁻¹	12.7-24.3	[35]
11	Zn(OAc) ₂	<i>Aloe vera</i> Leaf	ZnNPs	White	340	437 cm ⁻¹	22.18	[36]
12	Zn(OAc) ₂	<i>Passiflora caerulea</i> fresh leaf	ZnNPs	Yellow cream	380	-	70	[37]
13	ZnSO ₄	<i>Andrographis paniculata</i> leaf	ZnNPs	Brownish green	224	3573,3486, 2926, 2285, 1636, 1153, 1109, 1080, 877, 851, 799, 750 and 699 cm ⁻¹	-	[38]
14	Zn(NO ₃) ₂	Tea leaf	ZnNPs	Brownish black	314	-	20-50	[39]
15	Zn(OAc) ₂	<i>Nyctanthes</i> flowers	ZnNPs	-	200-700	3340.6, 3258.2, 2127.8, 1641.1, 1456.7, 1362.5, 1040, 1026.8, 746.25, And 620.65 cm ⁻¹	74.36	[40]
16	Zn(NO ₃) ₂	<i>Parthenium hysterophorus</i> leaves	ZnNPs	-	300-600	3458, 2451, 2270, 2245 1643 and 424 cm ⁻¹	16-45	[41]
17	CuSO ₄ .5H ₂ O	<i>Ocimum sanctum</i>	CuNPs	Green	-	3373, 1635, 1516, 1376 and 1198 cm ⁻¹	77	[41]
18	CuSO ₄	Tea leaf	CuNPs	Yellowish black	540-570	-	50-100	[42]
19	CuCl ₂ .CuSO ₄ .Cu(NO ₃) ₂	Papaya leaves	CuNPs	Brown black	560	3480 and 617 cm ⁻¹	20	[43]

S.No.	Metal solution	Extract of plant part	NPs	Colour	λ_{max} (nm)	FTIR (cm^{-1})	Size (nm)	Ref.
20	Cu(OAc) ₂	<i>Eclipta prostrata</i> leaves	CuNPs	-	565	3333, 2917, 1615 and 1048 cm^{-1}	41±0.8	[44]
21	CuSO ₄ ·5H ₂ O	Lemongras spieces	CuNPs	Yellow	560-570	3400, 2849, 2939, 1616 1420 and 1054 cm^{-1}	2.90±0.64	[45]
22	CuCl ₂	<i>A. marmelos</i> leaf	CuNPs	Blue to green	-	3355, 1590 and 1430 cm^{-1}	48	[46]
23	CuSO ₄ ·5H ₂ O	<i>Solanum lycopersicum</i> (tomoto juice)	CuNPs	Dark-brown block	-	1674 cm^{-1}	40-70	[48]
24	HAuCl ₄ ·3H ₂ O	Olive leaves	AuNPs	Violet	530-545	1721, 1648, 1624 and 1622 cm^{-1}	50-100	[49]
25	HAuCl ₄ ·3H ₂ O	Salix Alb leaves	AuNPs	Ruby red	540	1635, 1242 and 1296 cm^{-1}	50-80	[50]
26	HAuCl ₄ ·3H ₂ O	<i>Cinnamomum camphora</i> Tree leaves	AuNPs	-	570	1762, 1715, 1622, 1606, 1042, 1384 and 1077 cm^{-1}	10-40	[51]
27	HAuCl ₄ ·3H ₂ O	<i>A. esculentus</i> seed	AuNPs	Ruby red	300-800	3425, 3438, 1643, 321, 1388, 1616, 1064 and 1047 cm^{-1}	45-75	[52]
28	Mg(NO ₃) ₂	<i>Swertia chirayaita</i> leaves	MgNPs	Brownish colloid	200-800	-	<20	[53]
29	Mg(NO ₃) ₂	<i>Saussurea costus</i> root	MgNPs	Yellow-Brown	250	3432, 2918, 1634, 1624, 1462, 1402, 1056 and 594 cm^{-1}	20-50	[54]
30	Mg(OAc) ₂	<i>Maize betel</i> leaf	MgNPs	Brownish	-	3500, 3000, 1750, and 650 cm^{-1}	2 μm	[55]
31	Mg(NO ₃) ₂ ·6H ₂ O	Betel leaf	MgNPs	-	220	1666, 1662, 1124, 1388, 1190 and 850, 800-500 cm^{-1}	-	[56]
32	TiO(OH) ₂	<i>Psidium guajava</i> leaves	TiNPs	Light green	-	3425, 3420, 3410, 2922, 2917, 1659, 1621, 1618, 1368, 1384, 1078 and 1065 cm^{-1}	15-50	[57]
33	TiO(OH) ₂	<i>Nyctanthes arbor-tristis</i>	TiNPs	-	-	-	100-150	[58]
34	TiO(OH) ₂	<i>E. prostrata</i> leaves	TiNPs	-	305	3,420, 2,924, 2,926, 1,618, 1377, 1071 and 649 cm^{-1}	83.22-1.50	[59]
35	TiO(OH) ₂	<i>Syzygium cumini</i> leaves	TiNPs	-	356	3354, 1628, 1024, and 493 cm^{-1}	18	[60]
36	TiO(OH) ₂	<i>Punica granatum</i> peel	TiNPs	-	-	3408.51, 1635.27, 1401.00, 1075.92 and 643.55 cm^{-1}	75-90	[61]
37	TiO(OH) ₂	<i>Psidium guajava</i> leaves	TiNPs	Light green	-	3420, 3410, 3425, 2922, 2917, 1659, 1621, 1618, 1368, 1384, 1078, 1065 cm^{-1}	-	[62]
38	Fe(NO ₃) ₂ ·6H ₂ O	Rambutan fruit peels	FeNPs	-	-	3300-3500, 1353, 545, 445 cm^{-1}	100-200	[63]
39	FeCl ₃ ·6H ₂ O and FeCl ₂ ·4H ₂ O (1:2 molar ratio)	<i>G. mauritiana</i> leaves	FeNPs	Dark brown	404	3334.7, 2115.9, 1632 and 1628.7 cm^{-1}	58-79	[64]
40	FeCl ₃ ·6H ₂ O	<i>Bauhinia tomentosa</i> leaves	FeNPs	Bluish -green	550	3265.49, 2929.87, 1602.85, 1394.53, and 1016.49 cm^{-1}	-	[65]
41	FeCl ₃ ·6H ₂ O	Al- Abbas's (A.S.) Hunt fruit	FeNPs	Redish brown	340	1676 cm^{-1}	45	[66]
42	FeCl ₃ ·6H ₂ O	<i>Cassia fistula</i> leaf	FeNPs	Black	200-800	3375, 3375, 1641, 1545, 1069, 497 and 422 cm^{-1}	20-50	[67]
43	FeCl ₂ ·4H ₂ O	Green tea leaves	FeNPs	Black	505-510	-	-	[68]
44	FeSO ₄ ·4H ₂ O	<i>Musa ornata</i> flower sheath	FeNPs	-	250-350	3438, 3383.42, 1634.15, 480.69 and 472 cm^{-1}	43.69	[69]
45	FeCl ₂ ·4H ₂ O	<i>Camellia sinensis</i> leaves	FeNPs	Black	-	3419, 2923, 1635, 1379 and 1020 cm^{-1}	11.6	[70]
46	FeCl ₃ ·6H ₂ O and FeCl ₂ ·4H ₂ O (1:2 molar ratio)	<i>Azadirachta indica</i> (neem leaves)	FeNPs	Dark brown	230-250	541, 505, 490 and 467 cm^{-1}	9-14	[71]
47	Al(NO ₃) ₂	<i>Aerva lanta</i>	AlNPs	Deep yellow	271	1630, 1385 and 1092 cm^{-1}	50-70	[72]
48	Al(NO ₃) ₂	<i>Terminalia chebula</i>	AlNPs	Deep yellow	271	1633, 1380 and 1080 cm^{-1}	50-100	[72]
49	Al(NO ₃) ₂	Lemon	AlNPs	-	271.50	-	-	[73]
50	BaCl ₂ ·2H ₂ O	kiwifruit, Tomato and carrot leaves	BaSO ₄ NPs	White	-	1635, 1550, 1190-1070, 984 and 849 cm^{-1}	2-8 μm	[74]
51	Bi(NO ₃) ₂	<i>Menthe pulegium</i> leaves	BiNPs	-	290	3363-3414, 2330, 1629 1261 and 542 cm^{-1}	150	[75]
52	PdCl ₂	<i>Pimpinella tirupatiensis</i> leaves	PdNPs	Brown colloidal	200-800	3215.13, 2960.11, 1726.29, 1587.42, 1373.32, 1213.23, 1068.59 cm^{-1}	12.25	[76]
53	PdCl ₂	<i>Camellia sinensis</i>	PdNPs	Yellow	200-800	3345, 2860, 1712, 1667, 1520, 1389, 1124 and 720 cm^{-1}	6-18	[77]
54	PdCl ₂	<i>Origanum vulgare</i>	PdNPs	Yellow	320	~3548, ~3520, ~2950, ~2922, ~2150, ~1680, ~1650, ~1156 and ~1110 cm^{-1}	2.2	[78]
55	PdCl ₂	<i>Cinnamomum camphora</i> leaf	PdNPs	-	300	1730, 1631, 1515, 1459, 1384, 1322, 1267, 1226, 1122, 1079 and 1037 cm^{-1}	3.2 - 6.0	[79]
56	PdCl ₂	<i>Anogeissus latifolia</i> (gum ghatti)	PdNPs	-	300-800	-	4.8 ± 1.6	[80]
57	H ₂ PtCl ₆ ·6H ₂ O	<i>Quercus glauca</i> leaves	PtNPs	Dark brownish	<200	3410, 1732, 1626, 1347, 1226 and 1042 cm^{-1}	5-15	[81]
58	H ₂ PtCl ₆ ·6H ₂ O	<i>Lantana camara</i> (lantana) leaves	PtNPs	Black	-	-	35	[82]
59	H ₂ PtCl ₆ ·6H ₂ O	<i>Jatropha gossypifolia</i> and <i>Jatropha glandulifera</i>	PtNPs	Dark brownish	260	3542, 3451, 2058, 2046, 1637, 1354, 1353, 695 and 607 cm^{-1}	20 & 100	[83]
60	NaHSeO ₃	<i>Petroselinum crispum</i> leaves	SeNPs	Red	270	3280, 2918, 1636, 1530, 1394, 1220, 1050, 668 and 465 cm^{-1}	50-100	[84]
61	Na ₂ SeO ₃	<i>Allium sativum</i>	SeNPs	Dark pink	400	4000, 3400, 3200, 3000, 2300, 2000, 1800, 1500 1200, 1100 and 1000 cm^{-1}	7-45	[85]
62	NaSeO ₃	<i>Aloe vera</i> green fresh leaves	SeNPs	Red	295-340	572.8, 3454.3, 3600- 2400, 2351.1, 2104.1, 2065.6, 1635.5, 1251.7, 1402.2, cm^{-1}	50	[86]
63	NaHSeO ₃ + NaSeO ₃ + Ascorbic acid	Fenugreek seed	SeNPs	-	200-400	2356.2, 1618.7, 1284.7, 2360.1, 1723.2 and 1638 cm^{-1}	50-150	[87]
64	Ca(NO ₃) ₂ · 4H ₂ O	Papaya leaves	CaNPs	White	200-700	3783, 2926, 1796, 1429, 874 and 712 cm^{-1}	86-148	[88]
65	ZrOCl ₂ ·8H ₂ O	<i>Eucalyptus globules</i>	ZrNPs	Black	263	-	9-11	[89]
66	Zr(OAc) ₄	<i>Citrus aurantifolia</i> juice	ZrNPs	Brown gel	200 -600	3420, 1060, 580, and 499 cm^{-1}	21	[90]
67	NiCl ₂	Coriander leaf	NiNPs	Pale yellow	400 -700	3495, 1674, 1565, 1413, 1219, and 500 cm^{-1}	30.71	[91]
68	NiSO ₄	<i>Thespesia populnea</i> leaves	NiNPs	Dark green	362	3700 - 3400, 3448.92, 1385.56, 1020.23, 853.30 and 467.59 cm^{-1}	48.9	[92]
69	NiSO ₄ ·6H ₂ O	Betel leaves	NiNPs	Light green	250-370	3200, 2800, 1627 and 1200 cm^{-1}	< 45	[93]
70	Ni(NO ₃) ₂	<i>Ocimum sanctum</i> leaves	NiNPs	-	374 -422	3163, 2348, 2282, 1638, 1401, 1122 and 723 cm^{-1}	12-36	[94]
71	VCl ₂	Moringao leaves	VNPs	-	200-800	3333 - 3155, 1689- 1620, 1242 - 1219, 1026 - 987 cm^{-1}	-	[95]

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S.No.	Metal solution	Extract of plant part	NPs	Colour	λ_{max} (nm)	FTIR (cm^{-1})	Size (nm)	Ref.
72	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	<i>Punica granatum</i> peel	CoNPs	-	350 -550	3225, 1569, 1313, 1049 cm^{-1}	40-50	[96]
73	CoCl_2	<i>Ocimum sanctum</i> leaves	CoNPs	Dark green	646	1640-1650, cm^{-1} , 1050-1080 cm^{-1} , 1100-1150 cm^{-1}	-	[97]
74	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	<i>Populus ciliate</i> leaves	CoNPs	Dark brown	-	3458, 1622, 1381, 1082, and 533 cm^{-1}	40-50	[98]
75	$\text{Hg}(\text{OAc})_2$	<i>Callistemon viminalis</i> Flower	HgNPs	Dark yellow	243	3200-3550, 1730, 1640, 1414, 1021 and 650 cm^{-1}	2-4	[99 - 100]
76	$\text{Mn}(\text{OAc})_2$	Lemon juice	MnNPs	Pale yellow	360	3650, 2935, 1704, 1625, 1574-1515, 1393, 1160, 1026, 901 and 730 cm^{-1}	50	[101]
77	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	<i>Syzygium aromaticum</i> flower buds	MoNPs	-	252	3302.2, 2932.93, 1725.71, 1327.7, 853.7, and 779.6 cm^{-1}	19.47	[102]
78	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	<i>Citrus limetta</i> pith	MoNPs	Dark grayish brown	257	2924.1, 2355.5, 1747.5, 1383, 1155.4 and 486 cm^{-1}	24-50	[103]
79	$\text{Sr}(\text{NO}_3)_2$	<i>Ocimum sanctum</i> leaf	SrNPs	-	274	856.39, 810.10, 732.95 and 428.20 cm^{-1}	75±2.5	[104]
80	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	<i>Ficus carica</i> leaves	SnNPs	-	-	2360, 2340, 1555, 1335, 1001, 890 and 400 - 500 cm^{-1}	132	[105]
81	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	<i>F. benghalensis</i> leaves	SNPs	-	200 - 700	3737, 3606, 2357, 1539, 1513, 1369, 1056, 1052, 880.6, 876, 667.9 and 656 cm^{-1}	5.1	[106]
82	$\text{K}_2\text{Cr}_2\text{O}_7$	<i>Allium sativum</i> (Garlic)	CrNPs	Green	200 - 700	3620, 3202, 2597, 1528, 1103, 700, 690, 643 and 599 cm^{-1}	60-80	[107]
83	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	<i>Callistemon viminalis</i> flower	CrNPs	Red dye	-	2100 -2700, 643, 558, and 418 cm^{-1}	~92.2	[108]
84	$\text{Pb}(\text{NO}_3)_2$	<i>Cuminum cyminum</i> seed	PbNPs	Pale Orange	350-500	-	40-150	[109]

5. Mechanism

A mechanism as discussed above could be operating during green synthesis of MNPs by plant extracts in vitro. Fig. 1 schematically describes the formation of metallic MNPs from the corresponding metal ions. When metallic salt dissociates into cation and anion, cations (M^{n+}) will be saturated to form hydroxyl complexes $[\text{M}(\text{OH})_n]$. Instantaneously after the super saturation of hydroxyl complexes, crystallite growth of metal with oxygen species starts to originate. This results in the formation of crystalline planes with different energy levels. Heat plays a key role in providing energy to the reaction system. The route continues until activation of the capping agent from the plant-parts extracts, which will ultimately arrest the growth of high-energy atomic growth planes. This results in the formation of precise type MNPs.

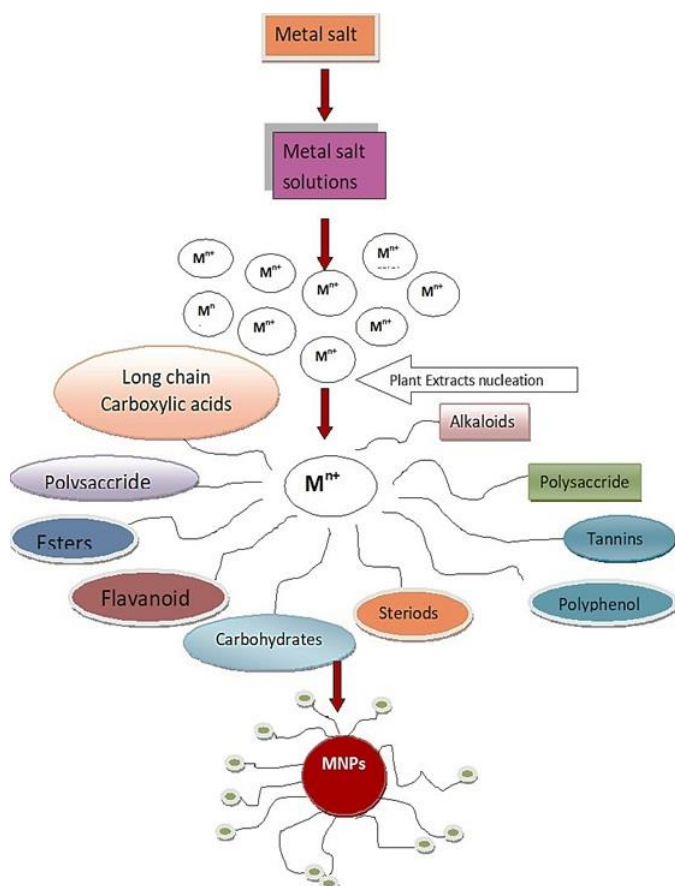


Fig. 1 Nucleation of metal cation with phyto-constituents

Generally, during the synthesis, the reducing agents bestow electrons to the metal ions and adapt them to MNPs. These MNPs exist at a high-surface energy state and tend to convert to their low-surface energy conformations by aggregating against each other. Thus, the presence of

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higher amounts of reducing agents and stabilizing agents prevents the aggregation of nanoparticles and promotes production of smaller MNPs. Additionally, amine group containing proteins can ensnare metal ions on their surface and convert them to their corresponding nuclei, which could further aggregate and, consequently, form MNPs. Amine groups of proteins ($\sim\text{NH}_2$), hydroxyl ($\sim\text{OH}$) and carboxyl groups ($\sim\text{COOH}$) of polyphenols ($\sim\text{Ph-OH}$) and amino acids, hydroxyl groups of polysaccharides, and carboxyl groups of organic acids chelate metal ions and suppress the superoxide-driven Fenton reaction (which is believed to be the most important source of ROS), catalyzing the formation of metallic NPs. Although it is indispensable to form a protein-metal ion complex for the vacuolar impounding of metal ions during in vivo accrual of MNPs, the role of proteins upon in vitro green synthesis is not clear. Interestingly, plant-parts extracts possess the capacity to reduce metal ions and produce MNPs even after boiling [110–113]. Although boiling could denature proteins by altering their secondary and tertiary structures, the peptide bonds of the primary structure between the amino acids are left intact. Because all structural levels of the protein establish its function, the denatured protein can no longer be fully functional. It has been stated that the protein can bind to Au NPs, either through free amino groups or cysteine residues; the surface-bound protein led to the stabilization of the MNPs [114].

Capping agents engage in recreation a very pivotal and resourceful role in the MNPs synthesis. MNPs can be functionalized and stabilized using capping agents (amine groups of proteins ($\sim\text{NH}_2$), hydroxyl ($\sim\text{OH}$) and carboxyl groups ($\sim\text{COOH}$) of polyphenols ($\sim\text{Ph-OH}$) and amino acids, hydroxyl groups of polysaccharides, and carboxyl groups of organic acids) to pass on useful properties by controlling morphology, size and defensive the surface thereby preventing aggregation. Many surfactants have been reported to be used as capping agents for varying the desired shape and size of the MNPs but these are thorny to remove and do not simply disgrace. Thus, the profitable surfactants are hazardous to the environment [115,116]. In the view of the limitation possessed by these chemicals, there is an urgent need to use environment-friendly capping agents and intend green biochemical routes at laboratory and industrial level for the MNPs synthesis. There are different types of molecules that could act or be used as capping agents but some of the broadly classified green capping agents have been discussed below with their potential role.

6. Characterization of Nanoparticles

The UV-Visible spectral characterization is one of the vital techniques to find out the reduced metal NPs in solution. Most of the researchers using UV spectroscopy finding range of the absorption. Some researchers indicated absorption maximum (λ_{max} , nm) of the nanoparticle solutions with blue shift. Few researchers tested UV-vis spectrophotometry with various time interval [117] of the nanoparticle formation after adding the extracts in metal salt solutions and various concentrated solutions of extracts added to the metal salt solution [118]. The Fourier transform infra-red (FTIR) spectroscopy characterizations are reported to demonstrate the contribution of plant metabolites such as sugars, terpenoids, polyphenols, flavonoids, tannins, alkaloids, phenolic acids, and proteins in the nanoparticle synthesis [119–121]. They play an important role in the reduction of metal ions into nanoparticles and in supporting their subsequent stability [122–124]. The morphologies of the

nanoparticles are measured by X-ray diffraction studies (XRD), scanning electron microscope (SEM) and tunneling electron microscope (TEM) analysis. These studies help to identify the magnetization, morphology, size and shape of the synthesized nanoparticles.

7. Conclusion

Obviously, the positive metal cations and plant extracts are having lot of applications. The metal cations are capped with phyto-constituents in green synthesis of nanoparticles, increases the pharmacological and industrial applications have been shown in metal as well as plant extracts containing phyto-constituents. In the case of “green” synthesis, the bulk of the costs will be determined only by the cost of the metal salts. At no cost, plant parts extracts from plant leaf, root, latex, seed and stem have also been used for the synthesis of NPs as they act as stabilizing or reducing agents. This fact further emphasizes the environmental advantages of “green” synthesis over traditional methods of nanoparticle production. This review will be very useful for the pursuing nanoparticle researchers and can give the idea about the selection of metal ions and plant resources in the green synthesis of nanoparticles.

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