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REVIEW

Biogenic synthesis of metallic nanoparticles and prospects toward green chemistry

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Abstract: The immense importance of nanoparticles and their applications is a strong motiviation for exploring new synthetic techniques. However, due to strict regulations to manage potential environmental impacts, greener alternatives to conventional synthesis are the focus of intense research. In the scope of this perspective, a concise discussion about the use of green reducing and stabilizing agents toward the preparation of metal nanoparticles is presented. Reports on the sysnthesis of noble metal nanoparticles using plant extracts, ascorbic acid and sodium citrate as green reagents are summarized and discussed, pointing toward an urgent need of understanding the mechanistic aspects of the involved reactions.

Introduction

Nanomaterials were used by humans in ancient times, without actually knowing about it. Some examples can be found in churches across Europe, where gold nanoparticles (NPs) of different sizes and compositions gave bright colours to stained glasses.[1] With the availability of advanced microscopy techniques, scientists were able to perceive the arrangement of particles and the different shapes and sizes in the nanometer scale that were actually affecting the performance of many substances. These studies revealed that nanomaterials with dimensions below 100 nm, exhibit new and often superior size-dependent properties, as compared to their bulk counterparts.[2] Among various materials, metallic nanoparticles have contributed more than any other material in human life.[3] Therefore, these nanomaterials have been the subject of extensive research over several decades.[4] Noble metallic NPs, such as Ag, Au, Pd, have enticed tremendous interest of the scientific community.[5] These materials have given rise to a busy area of research, due to a wide variety of applications in fields such as biomedicine, catalysis, preparation of nanocomposites with tunable electrical conductivity, thermal conductivity, tensile strength, superior rigidity, hardness and erosion resistance, which can be used for manufacturing of satellite components, aircraft spares, industry parts and electronic segments such as microchips processors, etc.[6 7 8]

Owing to such remarkable applications and many others that are yet to be explored, a large portion of the research on nanoparticles has focused on the rational synthesis of these nanoparticles, from which the desired functionality could be derived. The emphasis has been on synthesizing nanoparticles of well defined size and shape, aiming at studying the effect of morphological changes on various physical and chemical properties.[9] A variety of experimental approaches, often categorized as physical and chemical methods or top-down and bottom-up approaches, have been used for the synthesis of nanomaterials. The physical methods comprise mechanical attrition, melt mixing, physical vapour deposition (PVD), laser ablation, sputter deposition, electric deposition, among others, while a wide

variety of chemical methods have been employed, including metal salt reduction, sol-gel chemistry, co-precipitation, photoreduction, thermolysis, spray pyrolysis, microemulsion-confined reaction, etc.[10][11][12][13] These methods frequently involve the use of capping agents such as thiols and amines, various types of surfactants, and in some cases also organic solvents.

However, growing environmental concerns have motivated researchers to avoid the use of harmful chemicals that may pose a significant ecological threat to the environment. Consequently, researchers have started to search for innovative alternatives, with a focus on green approaches, which will be more eco-friendly and environmentally viable. It has been reported that the shape control of inorganic materials found in biological systems is achieved either by growth in constrained environments such as membrane vesicles,[14] or through functional molecules such as polypeptides that bind specifically to inorganic surfaces.[15] Based on this approach various attempts were made to prepare inorganic nanomaterials using functional phyto molecules of plant extract. One such example is the preparation of triangular gold nanoprisms using the extract of the plant lemongrass (*Cymbopogon flexuosus*).[16] Green approaches mainly consist of using phytochemicals such as proteins, amino acids, vitamins, polysaccharides, polyphenols, terpenoids, and organic acids such as citric acid, which often play a dual role of reducing agents as well as stabilizing agents, while being eco-friendly and environmentally viable natural products. Special attention is given to chemicals derived from plant extracts. This perspective article intends to present a compilation of examples of green approaches that have been devised during recent years, toward the synthesis of metal nanoparticles. We briefly discuss some chemical methods and their potential adverse effects on the environment, should large scale production be implemented. We then discuss synthesis methods using environmentally friendly approaches.

Chemical Nanoparticle Synthesis

Among the most commonly utilized chemicals in the synthesis of metal nanoparticles we find sodium borohydride, thiols and amines, which are not considered green chemical reagents due to their potential adverse effect on the environment.

Sodium borohydride is a well-known reducing agent with wide applications in the area of organic synthesis. For this reason, it has also been extensively used to reduce metal salts into nanoparticles.

One of the most popular nanoparticle synthesis methods is the so-called Brust-Schiffrin two-phase process,[17] in which chemical reduction takes place at an oil–water interface, immediately followed by adsorption of thiolated molecules and stabilization in the organic phase. The simplicity and efficiency of this method has been crucial to expand the knowledge and applications on gold and silver nanoparticles,[18] and therefore it has been widely employed. The use of borohydride typically requires the addition of capping molecules for colloidal stabilization. Although sometimes rather mild molecules are used, such as β-cyclodextrin derivatives[19] or clays,[20] such stabilizing agents are most often thiols and amines, including alkanethiolates,[21] dodecanethiol[22] or dodecylamine.[23] Occasionally, thiols and amines have been reported to induce metal ion reduction, oleylamine being one of the most popular choices.[24] Another extremely popular method for the synthesis of spherical gold and silver nanoparticles is based on the use of citrate ions as both reducing and stabilizing agents.[25,26] For the synthesis of metal nanoparticles with other morphologies, a wide variety of capping molecules and reductants have been reported, including surfactants, polymers, carboxylic acids, and even aromatic and halogenated organic compounds.[27,28]

However, the use of these chemicals for nanoparticle synthesis has raised certain controversy related to potential harm to the environment. For example, $NaBH_4$ is reported to be corrosive and to lead to the generation of hydrogen and diborane, which are highly flammable. Similarly, many thiols and amines may be toxic, even in moderate concentrations. Aliphatic and aromatic thiols are responsible for producing haemolytic effects in animals, while aminothiols have been found to induce *in vitro* cytotoxic effects, and thiyl radicals are responsible for initiating tissue damage provoked by thiols and disulphides. Amines on the other hand are caustic and are cause severe irritation to skin, eyes and mucous membranes.

Although such adverse effects are of little relevance when the use of these chemicals is restricted to the research laboratory, large scale production may pose additional environmental risks that can be minimized if alternative approaches are implemented, which are more ecologically friendly and less environmentally hazardous. This challenge has led to the development of green nanoparticle synthesis methods based on mild and environmentally friendly bio-reductants and capping agents derived from natural products.

Plant Extracts for Nanoparticle Synthesis

A straightforward approach toward green synthesis of nanomaterials is the use of plant-derived reagents, e.g. phytochemicals as reducing agents for metal salts, since these are environmentally friendly. Much research has been carried out in this direction and extracts have been obtained from different parts of the plants, such as leaves, stems, bark, pods, flowers, fruits, etc. Although numerous reports describe the use of plant extracts for the synthesis of nanoparticles, this perspective is restricted to the synthesis of noble metal nanoparticles, specifically silver, gold, palladium, and platinum.

Silver Nanoparticles

Silver nanoparticles are particularly attractive because of their remarkable physico-chemical properties. For example, their plasmonic response is extremely efficient because interband transitions are restricted to the UV, resulting in huge absorption coefficients and can generate intense electromagnetic fields, which are useful for surface-enhanced spectroscopy.[29] Additionally, Ag NPs also display high electrical and thermal conductivity,[30] catalytic activity,[31] and non-linear optical behavior.[32] They also possess strong bactericidal and fungicidal activity,[33] which has been extensively exploited in a range of consumer and pharmaceutical products such as soaps, pastes, food, textiles, water filtration systems, antimicrobial paints, ointments and gels for topical use, packiging paper for food preservation, fabrics for clinical clothing, bandages, cotton swabs, and anticancer drugs.[34] Such a broad range of applications require the implementation of large scale synthesis methods and greener techniques, which we discuss in this section.

Similar to other chemical methods, the use of different plant extracts has been found to yield nanoparticles of diverse sizes due to the wide variety of phytochemicals that they contain, which are responsible for reducing and stabilizing the nanoparticles. Silver nanoparticles in the size range below 20 nm were obtained by using various plant extracts as reducing and stabilizing agents. According to the literature reports, the smallest Ag NPs obtained with plant extracts had a size of 2.2 nm, when root extract of *Delphinium denudatum* was employed as both reducing and stabilizing agent. The nanoparticles were found to possess face-centred cubic (fcc) crystalline structure and cube-like morphology, which was confirmed by X-ray diffraction.[35] Spherical nanoparticles with an average size of 7.3 nm were obtained using the leaf extract of *Melia dubia*,[36] whereas when either water extract of *Vitex negundo* L or kiwifruit juice were employed, the average sizes of the obtained

nanoparticles were found to be in the range of 4-10 nm and 5–25 nm respectively.[37,38] Particles in the size range of 10-20 nm were formed when aqueous extract of *Myrmecodia pendan* (Sarang Semut plant) and latex of *Jatropha curcas*, were used as bioreductants. It was revealed that the cyclic octapeptide, *i.e.* curcacycline A and the cyclic nonapeptide, *i.e.* curcacycline B, present in the latex of *Jatropha curcas*, which are likely to act as capping agents, were responsible for the formation of small nanoparticles. On the other hand, larger particles with uneven shapes were mainly stabilized by curcain, an enzyme present within the latex.[39,40] Aqueous leaf extract of *Ficus benghalensis* was used as reducing and capping agent for the efficient synthesis of 16 nm Ag NPs.[41] On the other hand, aqueous extract of *Salicornia brachiata* yielded NPs with high colloidal stability but diverse shapes like spherical, rod-like, prism, triangular, pentagonal and hexagonal, whereas the extract obtained from dried fruit of *Tribulus terrestris* yielded Ag NPs within the size range of 16–28 nm. It should be taken into account that the *S. brachiata* extract contains a diverse range of chemical constituents with different interactions and adsorption energies, The obtained NPs were found to be stable up to 3 and 6 months, respectively.[42,43] The high colloidal stability could be due to the oligosaccharides, triterpenoids and saponins, which are the major components present in the extracts.[44,45]

An interesting contribution compared the use of extracts of various plants such as *Ocimum tenuiflorum*, *Solanum tricobatum* (traditionally used for treating cold and cough), *Centella asiatica* (traditionally used for improving memory), and *Citrus sinensis* (commonly known as Orange) *vs.* commercially available powders of the same plants. Whereas the plant extracts yielded average NP sizes around 25 nm,[46] the particles obtained from commercial powders were in the 40-50 nm range.[47] The observed variation in size highlights the role of phytochemicals from extracts as efficient reducing and stabilizing agents, which may not be accessible to the metal salts in the powders.

Ag NPs with triangular shapes and 30-50 nm particle sizes were obtained by employing leaf extract of *Artemisia annua*, which is different than the spherical shaped particles, which are obtained from most extracts.[48] The aqueous extracts of various parts of the pernicious aquatic weed ipomoea (*Ipomoea carnea*) yielded spherical Ag NPs with sizes varying from 20 to 40 nm from the leaf extract, while 30-50 nm NPs were obtained using the extract from the stem.[49] Again, Ag NPs of diverse shapes such as spherical, rod-

like, prism, triangular, pentagonal and hexagonal, in the 28–33 nm range, were obtained using the aqueous extract of *Salicornia brachiate*.[50] Apart from extracts, fruit juices from lingonberry, cranberry and lemon were also employed for the green synthesis of Ag NPs. Lingonberry and cranberry juices resulted in the formation of NPs with mainly spherical and triangular shapes, in size range from 6 to 60 nm, whereas lemon juice yielded spherical shaped particles with below 50 nm. The juices were found to contain phenolics, anthocyanins and benzoic acid as the major constituent, which acts as reducing agent.[51,52] Particles in the size range of 40–50 nm were obtained when aqueous rinds extract of *Brucea javanica* (L.) Merr, *Hoveniadulcis* and *Piper longum* fruit extracts were used.[53,54,55] Similarly, spherical Ag NPs of ca. 30 nm resulted from *Gossypium hirsutum* (cotton) extract,[56] whereas more polydisperse (18–60 nm) spherical NPs formed using Saponin isolated from *Trianthemadecandra* L.[57]

Larger Ag NPs (20-100 nm) with different shapes were obtained when using phytochemicals from extracts of *Elaeocarpus ganitrus* Roxb., *Terminalia arjuna* Roxb., *Pseudotsuga menzietii*, *Prosopis spicigera, Ficus religiosa, Ocimum sanctum (also known as Holy Basil), Curcuma longa*.[58] Related works used pods extract of *Acacia auriculiformis*, yielding spherical NPs ranging from 20 to 150 nm, with the reaction pH playing a determining role in the final particle size.[59] Rod shaped Ag NPs (25–80 nm) were obtained from aqueous leaf extracts of *Euphorbia prostrate*, and gas chromatography–mass spectrometry analysis revealed that the major chemical constituent of the extract is 2-phenylethanol, which is probably responsible for both Ag reduction and NP capping.[60] An interesting finding was reported when using *Caesalpinia coriaria* leaf extracts, which yielded highly stable Ag NPs in triangular, hexagonal and spherical shapes, with sizes of 78- 98 nm, whereas only triangular Ag NPs around 40-50 nm were obtained when the boiled leaf extract was used, indicating that extraction temperature plays an important role.[61] *Alternanthera dentata* and *Artemisia nilagirica* were used for the biosynthesis of Ag NPs, resulting in size ranges of 50-100 nm and 70–90 nm, respectively.[62,63] Using *mangrove* plant extract yielded 60-95 nm spherical NPs,[64] while methanolic leaf extracts of *Eucalyptus chapmaniana* and *Psidium guajava* L led to stable and spherical particles with a mean diameter of ~60 nm.[65,66] However, aqueous extract from *Manilkara zapota* yielded spherical and oval shaped nanoparticles of 70–140 nm,[67] and the bark aqueous extract of *Ficus racemosa* led to formation of uniform Ag NPs with cylindrical shape and average size of 250 nm.[68]

Some of us synthesized metal nanoparticles using chemical methods[69,70] and evaluated their catalytic performance in selective oxidation reactions.[71,72,73] Additionally, we explored green methods based on extracts from locally available plants such as *Pulicaria Glutinosa* for the synthesis of AgNPs, which yielded spherical NPs with 40-60 nm in size (**Figure 1**),[74] displaying remarkable antibacterial properties.[75]
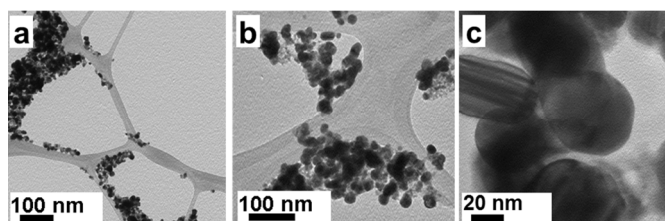
Figure 1. (A–C) TEM images of Ag NPs synthesized by green chemistry, at different scales. Reproduced from Ref. 74 with permission. Copyright Dove Press, 2013.

Gold Nanoparticles

Green synthesis of Au NPs has also been widely studied using various extracts from either full plants or various components. Similar to Ag NPs, Au NPs with different sizes and shapes resulted from the use of various plant extracts as bioreductants. A few recent reports are described below.

Green synthesis of AuNPs using *Galaxaura elongate* has been reported to yield a wide range of NP sizes from 4 to 77 nm, which were mostly spherical but also contained rod-like, triangular and hexagonal nanoparticles.[76] When agricultural waste of mango peel extract was employed, the obtained particle size was found to be around 6 and 18 nm at pH 9.0 and 2.0, respectively, indicating that pH can affect the relevant chemicals in the plant extract.[77] Au NPs were also obtained using leaf extract of *Sesbania grandiflora*, which yielded predominantly spherical, well-dispersed nanoparticles of 7–34 nm.[78] Aqueous root extract of *Morinda citrifolia* L. resulted in the formation of spherical and triangular Au NPs, with sizes ranging from 12 to 38 nm. From FT-IR analysis it was concluded that the proteins present in the extract play an important role in both the reduction and the stabilization of the nanoparticles.[79] Polyphenolic compounds such as catechin, epicatechin, anthocyanidin, proanthocyanidin and condensed tannins, which are present in grape seed, skin and stalk are thought to be responsible for reducing and stabilizing 20 nm Au NPs.[80] The fruit of date palm may also be used,

as indicated by the formation of spherical Au NPs (32-45 nm) using the aqueous extract *Phoenix dactylifera*.[81] Remarkably, the particle size was found to decrease with increasing plant extract concentration, while FT-IR analysis revealed that hydroxyl and carbonyl groups in carbohydrates, flavonoids, tannins and phenolic acids present in *P. dactylifera* are involved in the stabilization of the NPs.[82] In an important contribution, essential oils extracted from fresh leaves of *Anacardium occidentale* resulted in the formation of monodisperse hexagonal Au NPs with average size of 36 nm.[83] AuNPs of ~50 nm were obtained by using the potent antidiabetic *Gymnema sylvestre* and leaf extract of *Solanum nigrum*.[84,85] Similar sizes were obtained from *Stachys lavandulifolia* extracts, which contain flavonoids and terpenes. Interestingly, these NPs were found to be stable under physiological conditions, meaning that they can be useful for biomedical applications.[86]

Palladium and Platinum Nanoparticles

Very small Pt nanoparticles (2.4±0.8 nm) were obtained using plant extracts derived from *Cacumen Platycladi*. The sugars and flavonoids present in this extract play an important role in the bioreduction of Pt(II) ions.[87] Dried leaf powder of *Anacardium occidentale* was also used to synthesize Pd and Pt NPs, where biomolecules containing polyols were identified as the reducing agents while carboxylate ions and proteins served to stabilize the NPs, which was confirmed by FT-IR analysis. Interestingly, whereas Pd NPs were spherical (2.5 – 4.5 nm), irregular rod shaped Pt NPs were obtained.[88] Similar extract of *Piper betle* was used along with PdCl$_2$ to produce spherical Pd NPs with average size of 4±1 nm. FTIR spectra revealed that flavonoids were responsible for both reduction of Pd(II) ions and stabilization of the NPs.[89]

Besides leaf extracts, Pd and Pt NPs were also synthesized using aqueous peel extract of *Annona squamosa* L, which was reported to possess acaricidal, insecticidal and larvicidal efficacy, which yielded larger spherical Pd NPs, with sizes above 80 nm.[90] Pd NPs of a similar size range but with triangular and pentagonal shapes were obtained using aqueous fruit extract of *Terminalia chebula*, which is a rich source polyphenolic compounds.[91] Interestingly, Pd NPs obtained using *Pulicaria Glutinosa* (**Figure 2**) were found to display excellent cataltalytic activity for Suzuki C-C coupling reaction.[92]
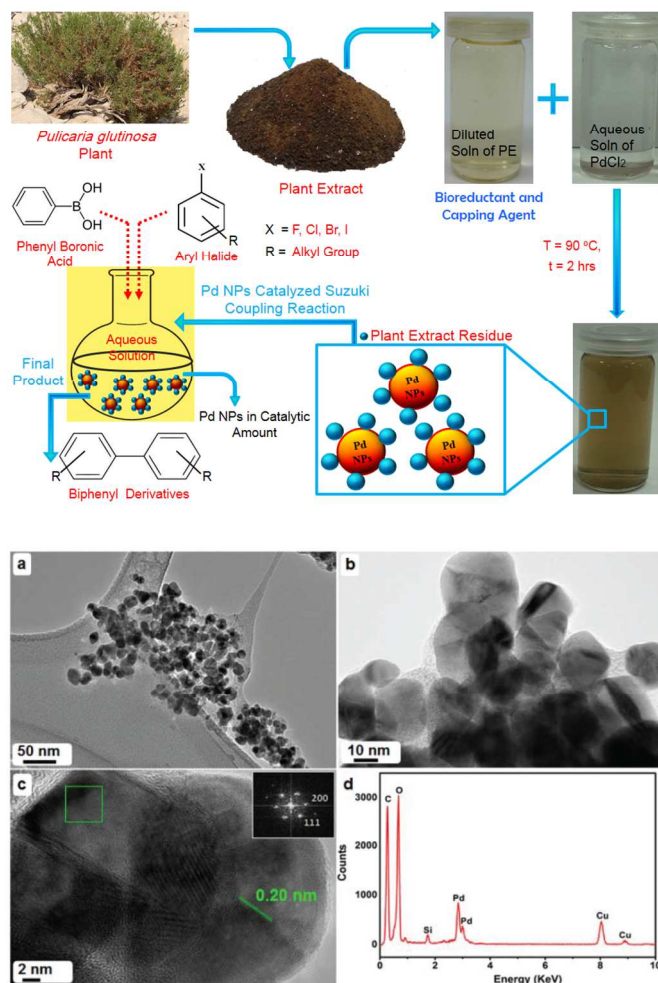
Figure 2. Upper panel: Schematic represntaion of the preparation of Pd nanoparticles using plant extract. Lower panel: Representative TEM and HRTEM images of the obtained particles. Reproduced from Ref. 92 with permission. Copyright 2014, Royal Society of Chemistry.

From the above-mentioned reports, it can be concluded that various plant extracts can be used to produce metallic nanoparticles. Phytomolecules such as polyphenolic compounds, flavonoids, carbohydrates, etc. are responsible for the reduction of metal salts and stabilization of the formed nanoparticles. However, the pH of the reaction and the extraction temperature also play important roles in determining the size and shape of the nanoparticles. A wide range of NP sizes were obtained from ~2 nm to 250 nm. In the case of Ag NPs, quasi-spherical morphology was typically obtained, but rod-like, triangular and hexagonal shapes were also formed. In the case of Au NPs, particles in the size range of 3.8-56 nm have been reported, and it was found that the phytochemicals present in the extract were crucial toward NP formation. Fewer studies are

available on Pd and Pt NPs but sizes ranging from 2 up to100 nm were reported for mostly spherical nanoparticles.

In order to facilitate a general overview of the data presented in the previous sections, tables are included as Electronic Supplementary Information. Researchers interested in employing plant extracts as bioreductants have two basic choices: l) utilizing a plant that has not been previously reported in the literature, meaning that the plant extract is first used to study its bioreduction efficiency and then investigation is carried out at a later stage to identify the biomolecular entities that are responsible for the reduction of metal salts and the stabilization of the nanoparticles. 2) if extracts of a known plant are to be employed then the biomolecular composition of the various parts of the plant can be first identified to predict an expected outcome. From the literature it can be concluded that if the phytochemical composition consists of polyphenols, flavonoids, tannins, carbohydrates and phenolic acids , there is a high probability of achieving spherical nanoparticles. However, further studies are needed to understand which biomolecules are responsible for the growth of other shapes and morphologyies.

Ascorbic Acid Mediated Nanoparticle Synthesis

We have seen in the previous sections that plant extracts are effcient bioreducing and stabilizing agents. However, the related methods are still inefficient in terms of morphology control, mainly because the reactions are entirely dependent of the specific phytochemical(s) involved. Much progress and refinement is still required if well-defined nanoparticles of different shapes are to be obtained. Notwithstanding, some of the commonly used reducing agents for nanoparticle synthesis can also be considered as "green reagents". A distinguished example is ascorbic acid, also known as L-hexuronic acid, which is a form of vitamin C, a naturally occurring organic compound with antioxidant properties. Ascorbic acid has been extensively used as both reducing and stabilizing agent and can be considered as a green reagent due to its environmentally friendly and non-toxic character.

Although ascorbic acid is a rather weak reducing agent, it can efficiently reduce Ag^+ ions under basic pH conditions. For example, a combination of ascorbic acid and citrate at room temperature has been shown to lead to the formation of quasi-spherical Ag NPs with sizes between 31 and 73 nm, for pH values between 10.5 and 6. The quality of the spherical NPs was improved by heating the reaction mixture at 100 ºC for 2h, which facilitated intraparticle ripening,[93]

but probably also increased the reducing ability of citrate ions present in solution. Ascorbic acid has also been used along with poly(vinylpyrrolidone) PVP, with the interesting result that the relative amount of ascorbic acid influenced the morphology of the formed NPs. Whereas at lower ascorbic acid concentration spherical particles were the main reaction product, when the concentration was increased overgrowth was found to lead to the formation of nanorods displaying five-fold symmetry, as well as multiply-twinned decahedral particles. When the concentration of ascorbic acid was as high as 0.1 M, the reduction rate increased, leading to formation of larger Ag micro-rods up to 23 μm in length and diameters between 150 and 500 nm.[94] Silver nanoparticles with high optical quality were prepared by using ascorbic acid to reduce silver ions within sodium dioctylsulfosuccinate (AOT) reverse micelles. The obtained nanoparticles were in the range 5.7–8.3 nm.[95] Reduction with ascorbic acid was also used for the synthesis of positively charged silver and copper nanoparticles under microwave heating, using chitosan to maintain the colloidal stability of the particles and prevent agglomeration. Although the obtained silver nanoparticles were typically of 200 nm, the size was found to vary with variations of the concentration of silver nitrate.[96]

The mild reducing power of ascorbic acid has been largely exploited in the so-called seeded growth methods, which involve the formation of small nanoparticle seeds, on which further growth is induced by selective reduction on the seeds surface. The most representative example is the synthesis of gold nanorods.[97] Both twinned and single crystal nanorods were synthesized in high yields, by exploiting the reducing ability of ascorbic acid, in combination with the templating effects of cationic surfactants, mainly cetyltrimethylammonium bromide (CTAB) and other additives. Variations of this widely employed prodecure have been reported to lead to a variety of morphologies, including Ag-coated Au nanoparticles.[98] Similar compositions were also used for the direct synthesis of gold nanoparticles, using mixtures of a strong (sodium borohydride) and a weak (ascorbic acid) reducing agent, which may also lead to nanorod formation in a single step.[99] Formation of well-defined spheres was also reported by reduction of $AuCl_4$–CTAB complex by ascorbic acid. The particle sizes obtained by this method could be varied between 24 and 42 nm.[100] Unfortunately, the need to include CTAB in these preparation methods severely hinders their green nature, since it has been shown that CTAB is highly cytotoxic.[101] Therefore, alternative capping molecules should be developed to improve the biocompatibility and environmental friendliness of the process.

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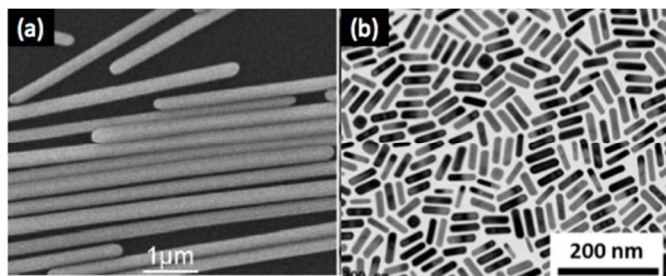
Figure 3. Elongated NPs formed by seeded growth using ascorbic acid. (a) SEM image of Ag nanowires (Reproduced with permission from ref. 94, copyright 2013 IOP). (b) TEM image of single crystal Au nanorods.

Citrate as a Green Reducing Agent

One of the first and still widely used methods for the preparation of gold and silver nanoparticles comprises reduction of the respective metallic salts with citrate ions, which are also responsible of the stabilization of the formed nanoparticles in aqueous solution. Although this has been largely overseen, citrate is a green reagent and thus can be safely used for large-scale production. Trisodium citrate is the sodium salt of citric acid, a naturally occurring compound that is mainly found in citrus fruits. It can thus be found in high abundance and can be considered as ecologically safe and biodegradable. Although the method was initially reported in the 1950's,[25] much refinement has been carried out to improve the outcome and to expand even further the scope of application of the resulting biocompatible nanoparticles.

One of the challenges in the citrate-based synthesis of AgNPs has been a suitable control over particle size. Recently, some reports have been published in this direction. For example, the combined effect of trisodium citrate with starch, a naturally abundant polymer, allowed the preparation of Ag NPs ranging from 30 to 110 nm, with average particle sizes around 50–90 nm.[102] An alternative method for a more uniform growth and monodispersity was based on citrate-induced seeded growth of Ag on Au NPs. Monodisperse colloids with average sizes ranging between 30 and 110 nm and with high optical quality were reported by using this method.[103] Further refinement with no need to use gold seeds, but simply controlling the kinetics of particle growth was reported to lead to monodisperse citrate-capped Ag colloids with sizes up to 200 nm.[104] Interestingly, formation of silver nanowires by sodium citrate reduction and stabilization has also been reported. Under optimum conditions, a high yield of nanowires was obtained using a 1:1 molar ratio of Ag^+ to citrate and pH 7.1, at 130 °C. However, when the pH was

increased, spheres were obtained.[105] Other morphologies were also obtained, through the reconstruction of citrate-stabilized silver sols by irradiation of the colloid with visible light.[106,107] Similar shape conversion of AgNPs in citrate solution has been recently reported to occur upon laser ablation.[108]

Although the mechanism of formation of Au NPs by citrate reduction has been studied in detail,[109,110,111] it has been remarkably difficult to improve the quality of the particles and to expand the size range and access non-spherical geometries. Improvements in the monodispersity and sphericity of the NPs have been recently reported through minor variations in the reaction conditions.[112] On a related systematic study, Au NPs with with narrow size distribution and sizes up to 200 nm could be readily obtained through kinetic control of nanoparticle growth. The growth was controlled by reaction conditions such as temperature, gold precursor to seed particle concentration ratio, and pH, leading to fine tuning the desired AuNPs.[113] Another variation was achieved by applying a cryogenic process, in the presence of a mixture of tannic acid and sodium citrate, which led to a reduction in particle size from 17 to 4 nm and no signs of agglomeration, which was ascribed to the role of sodium citrate.[114] In one of the few reports regarding shape control in citrate-mediated nanoparticle growth, it was found that initially dot-shaped NPs gradually grew into tadpole-like, dumbbell-shaped and rod-like particles.[115] Still, anisotropic growth with high yield remains to be demonstrated in the absence of other additives.
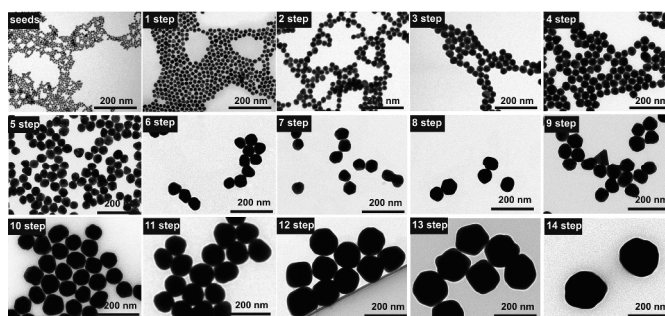
Figure 4. TEM images of Au particles formed by seeded growth reaction with citrate. The particle size increases from 8.4±1.0 to 180.5±10.7 nm. Reproduced with permission from ref. 113. Copyright 2011, American Chemical Society.

Apart from Ag and Au NPs, other noble metals such as Pd and Pt have also been prepared using citrate as reducing and stabilizing agent. Early work indicated that the resulting particle sizes for Pt

were significantly smaller than for Au or Ag,[116] which has been recently refined to prepare 2 nm Pt NPs for applications in electrocatalysis.[117] An alternative strategy is based on the adsorption of the formed NPs on various types of supports, depending on the targeted application. For example, carbon (XC-72) was used to support ~2 nm Pt nanoparticles for direct methanol fuel cells,[118] while citrate-reduced Pt NPs supported on graphene sheets displayed excellent electrochemical activity.[119] Formation and assembly of 5 nm Pd NPs onto ZnO nanorods was achieved in a one-pot reaction, using citrate as stabilizer, and the resulting composite nanostructures were used as catalysts for CO sensing.[120]

Conclusions

As metal nanoparticles acquire increasing interest, not only from the academic point of view but also toward industrial applications, environmentally friendly processes based on non-toxic reagents become an urgent need. Therefore, a huge effort is being made toward exploiting natural resources and implementing green nanoparticle synthesis methods. Most of these methods are based on direct application of extracts from either whole plants or different parts of the plants, such as leafs, roots, etc. However, the identification of the chemical components that are actually responsible for nanoparticle formation and stabilization is still at early stages and therefore much research is needed in this direction. Additionally, the currently available methods have not provided reliable means to direct or control the shape of the nanoparticles and a remaining challenge is thus related to obtaining anisotropic particles while avoiding the use of toxic chemicals. It is however important to realize that, some of the standard reductants, such as sodium citrate and ascorbic acid, can also be considered as green chemicals and therefore such popular methods should acquire even higher relevance in the near future.

Acknowledgements
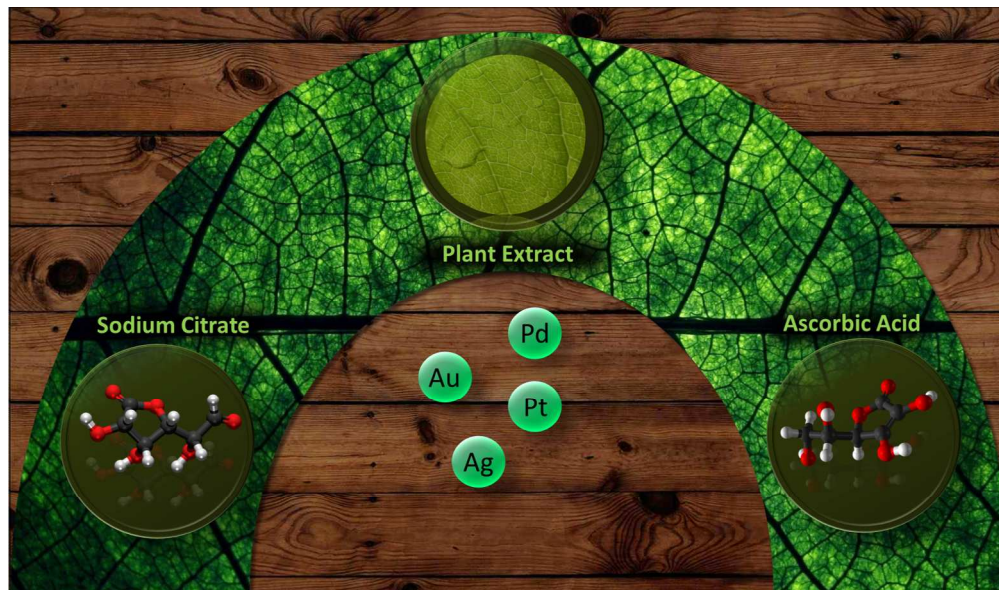
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