A Review on Green Synthesis of Sulfur Nanoparticles via Plant Extract, Characterization and its Applications

Suresh Ghotekar¹, Trupti Pagar², Shreyas Pansambal³, Rajeshwari Oza³

¹ Department of Chemistry, Sanjivani Arts, Commerce and Science College, Kopargaon 423 603, Savitribai Phule Pune University, Maharashtra, India
² Department of Chemistry, G.M.D Arts, B.W Commerce and Science College, Sinnar, 422 103, Savitribai Phule Pune University, Maharashtra, India
³ Department of Chemistry, S.N. Arts, D.J.M. Commerce and B.N.S. Science College, Sangamner 422 605, Savitribai Phule Pune University, Maharashtra, India

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ABSTRACT

Among diverse non-metal nanoparticles (NPs), sulfur nanoparticles (SNPs) are one of the most significant and intriguing nanomaterials. An important concern about the synthesis of SNPs is the formation of hazardous wastes, noxious by-products and ruinous pollutants. The best solution to mitigate and/or exclude these noxious substances are plant mediated biosynthesis of SNPs. Eco-benevolent SNPs from plant extracts have been identified as precious nanomaterial in various agricultural, biomedical and catalytic applications including lithium-sulfur batteries, pesticides, fungicides, carbon nanotube modification, gas sensor and neutron capture in cancer therapy because of their splendid performance and selectivity. They have captured the consideration of researchers owing to their sustainable, economical, non-noxious, convenient, green and eco-benevolent nature. This review attempts to cover the recent advancements in the biosynthesis, characterization techniques and applications of biogenic SNPs in environmental and biomedical systems. Furthermore, the stability of biosynthesized SNPs and mechanism of their formation are briefly discussed.

GRAPHICAL ABSTRACT

* Corresponding author: Suresh Ghotekar
E-mail: ghotekarsuresh7@gmail.com
Tel number: +918698255427
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Introduction

In recent times, scientists have found the gigantic capability behind nanotechnology and since it has played an overriding role in this era. Nanotechnology is definitely receiving in popularity owing to the advantages and prospects it can provide to human being. Therefore, day by day nanomaterials display eclectic and novel biological and physicochemical properties in the domain of nanotechnology. They have miraculous applications of diverse fields; namely, agriculture, pharmaceutics, catalysis, transportations, bioengineering, water purification, biosensors, textiles, food technology, electronics, optoelectronics, ceramics, health care, information storage, fuel, solar energy, medicine, sensing, and automobiles [1-30].

The non-metal sulfur has numerous uses for pharmaceutics and agriculture industry [31-32]. Also, sulfur used as a component of fertilizers such as calcium sulphate which is the most common fertilizer in agriculture used to improve the nutritious quality of phosphorous and nitrogen fertilizers [33]. Therefore, SNPs have significant applications (Fig. 1) in several fields of modern technology including, lithium-sulfur batteries [34], pesticides [35], fungicides [36], carbon nanotube modification [37], gas sensor [38], catalysis [39] and neutron capture in cancer therapy [40]. Moreover, SNPs generated significant roles in the arena of biomedical concerns such as antibacterial and pharmacokinetic purpose [41], anticancer activity [42], antitumor and antioxidant activity [43] and wound healing activity [44].

Till date, several approaches were applied into production of SNPs such as microemulsion method [46], surfactant assisted method [47], solvent free method [48], precipitation method [49], electrochemical method [50], egg shell membrane assisted method [51], liquid phase chemical precipitation method [52], heating sulfur powder with polyethylene glycol PEG-600 [53], supersaturated solvent method [54], ultrasonic method [54], membrane-assisted precipitation method [55] and sodium polysulphide hydrolysis method [56]. However, aforesaid approaches have a high yield capacity, but at the same time they have lacks such as the raise energy cost, requires complicated, tedious, time-consuming and pernicious processes. Therefore, need to enhance of reliable and efficient synthetic approaches to avoid and/or mitigate the limitations through “green nanotechnology”. Indeed, parts of plant extract assisted NPs syntheses have become predominant due to the sustainable, safer, affordable, non-noxious rapid synthesis and simplicity in protocols [5-10]. Also, plant extracts assisted NPs generates an excellent route for SNPs synthesis as they provide herbal reductants and stabilizing agents [2-3]. This review presents current advancements in the eco-benign, sustainable, facile, non-noxious, clean, reliable and green synthesis of SNPs. Besides, the diverse and significant applications of SNPs in agriculture, biomedicine and environmental remediation have been investigated in this review. In addition, the probable reaction mechanisms using bio-reducing/stabilizing compounds in plant broths involved in the green synthesis of SNPs are discussed.

Fig. 1. Diverse applications of SNPs.
Green Synthesis of SNPs

Nowadays, researchers have established it economical to synthesize bio-NPs (Fig. 2) from plants, yeasts, algae and fungus as they are reliable, cost-effective, capable, straightforward and readily accessible. In accomplishing this prowess, scientists have explored various approaches to developing efficient nanomaterials. Hence, the green synthesis route utilizing biological specimens has emerged as a facile, affordable and environmentally benevolent. The green methodologies are the preferred route for NPs synthesis because of its viability, non-noxious, ecological friendliness, and well-being to human health and environment when compared with known physical and chemical approaches. In recent times, plant assisted NPs production using plant part extracts and/or living plant has been mentioned in literatures [2-3].

The usage of plant materials in the fabrication of NPs engages the secondary phytochemical/metabolites such as flavonoids, alkaloids, saponins, proteins, phenols, carbohydrates, quinine, glycosides and tannins [5-6]. Biological constituents played a key role as herbal reducers and/or stabilizers in the procedure of forming NPs [7-8]. Although the precise mechanism involved in NPs biosynthesis using extracts from various plants is dubious, it has been noticed that the biomolecules in plant extract such as protein, phenol, flavonoids and vitamins play essential roles in the reduction and capping the biosynthesized NPs [9-10]. The biogenic synthesis of plant assisted SNPs have been carried out by several scientists using typical plants (Table 1). Afterwards, the fabricated SNPs need to be explored using known characterization techniques.

Protocol for Green Synthesis of SNPs

Biogenic synthesis of SNPs is an effortless, convenient, efficient, one pot synthesis and eco-accommodating approach without intervention of any noxious and perilous additives. SNPs are prepared to use typical parts of plants such as pods, leaves, peels, barks and fruits (Table 1). A wholly sustainable and procurable approach is applied for their complete biosynthesis (Fig. 3). In plant extract assisted approaches to SNPs production utilizing fresh and/or dried plant materials such as pods, leaves, peels, barks and fruits are washed with distilled water, cut into fine pieces using kitchen blenders and boiled in double distilled water to acquired plant broth. The plant extract may additionally be purified by certain procedures like centrifugation and/or filtration. Different concentrations of sodium thiosulfate or sodium sulfide and extract of plant at various pH, pressure, temperature and time interval can be used for preparation of SNPs. The extract from plants is completely mixed with the diverse concentrations of sodium thiosulfate or sodium sulfide solution and their conversion into SNPs take place within minutes in safe, efficient, convenient, one pot, rapid, sustainable and eco-benevolent manners. Due to multifarious phytoconstituents are already present in the plant extract and behaves as herbal reducing, capping and/or stabilizing agents, therefore there is no requirement to involve external pernicious stabilizing/capping substances.
Table 1. Biosynthesis of SNPs using different plant source with morphology and size

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Name of Plants</th>
<th>Part</th>
<th>Precursors</th>
<th>Shape</th>
<th>Size</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acanthe phylum bracteatum</td>
<td>-</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>-</td>
<td>40 nm</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>Alianthus altissima</td>
<td>Leaves</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>-</td>
<td>5-80 nm</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>Albizia julibrissin</td>
<td>Fruits</td>
<td>Na₂S₂O₃</td>
<td>Spherical</td>
<td>20 nm</td>
<td>59</td>
</tr>
<tr>
<td>4</td>
<td>Allium sativum</td>
<td>-</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>Spherical</td>
<td>56.61 nm</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>Azadirachta indica</td>
<td>Leaves</td>
<td>Na₂S</td>
<td>Spherical</td>
<td>89 nm</td>
<td>61</td>
</tr>
<tr>
<td>6</td>
<td>Catharanthus roseus</td>
<td>Leaves</td>
<td>Na₂S</td>
<td>Spherical</td>
<td>86 nm</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>Mangifera indica</td>
<td>Leaves</td>
<td>Na₂S</td>
<td>Spherical</td>
<td>95 nm</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>Polyalthia longifolia</td>
<td>Leaves</td>
<td>Na₂S</td>
<td>Spherical</td>
<td>62 nm</td>
<td>61</td>
</tr>
<tr>
<td>9</td>
<td>Ficus benghalensis</td>
<td>Leaf</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>Random shape</td>
<td>2-15 nm</td>
<td>62</td>
</tr>
<tr>
<td>10</td>
<td>Cinnamomum zeylanicum</td>
<td>Barks</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>63</td>
</tr>
<tr>
<td>11</td>
<td>Melia azedarach</td>
<td>Leaves</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>-</td>
<td>20 ±4 nm</td>
<td>64</td>
</tr>
<tr>
<td>12</td>
<td>Oscimum basilicum</td>
<td>Leaves</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>Spherical</td>
<td>23 nm</td>
<td>65</td>
</tr>
<tr>
<td>13</td>
<td>Punica granatum</td>
<td>Peels</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>Spherical</td>
<td>20 nm</td>
<td>66</td>
</tr>
<tr>
<td>14</td>
<td>Rosmarinus officinalis</td>
<td>Leaves</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>Spherical</td>
<td>20 nm</td>
<td>67</td>
</tr>
<tr>
<td>15</td>
<td>Rosmarinus officinalis</td>
<td>Leaves</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>Spherical</td>
<td>40 nm</td>
<td>68</td>
</tr>
<tr>
<td>16</td>
<td>Sophora japonica</td>
<td>Pods</td>
<td>Na₂S₂O₃</td>
<td>Spherical</td>
<td>60 nm</td>
<td>69</td>
</tr>
</tbody>
</table>

The brief procedure of biogenic syntheses of SNPs by Punica granatum peels extract is described by authors demonstrated in [66]. A fine SNPs powder is obtained and collected for further application as well as characterization purposes.

Plausible mechanism for biogenic synthesis of SNPs

Recently, there have been few published reports on the green synthesis of SNPs using plant extracts. Nevertheless, only a few attempts have been made to investigate the reaction mechanism. Plant extracts are complex mixtures...
of active reducing biomolecules such as antioxidant, coumarins, flavonoids, saponins, polyphenols, steroids, and phenolic acids.

Tripathi and co-workers synthesized SNPs by using *Ficus benghalensis* leaves extract. He demonstrated in his studies that the proteins and phytochemicals present in the leaves extract behaves as reducing/stabilizing agents who led to the formation of stable SNPs via disproportionation reaction.

When these proteins/phytochemicals and citric acids are mixed with thiosulfate solutions, instantaneous reduction of $S^{6+}$ to $S^{0}$ by proteins/phytochemicals and oxidation of $S^{2-}$ to $S^{0}$ by citric acid occur simultaneously through the disproportionation process. Then $S^{0}$ undergoes a nucleation process to reach its optimum size and shape that is influenced by various parameters such as the nature of reducing and/or capping agents, pH and temperature. He beautifully depicted the probable mechanism of formation of SNPs (Fig. 3).

Awad and co-workers synthesized SNPs using pods extract of *Sophora japonica*. He reported on his studies that sodium thiosulfate solutions mixed with pods extract of *Sophora japonica*. Further, addition of hydrochloric acid into the solution, which releases sulfur ion in the solution, which dispersed and capped by pods extract from *Sophora japonica*. The plausible reaction and mechanism is described in Fig. 4.

![Fig. 3. Possible mechanism of green synthesis of SNPs by using *Ficus benghalensis* leaves extract]("https://example.com/fig3.png")

[Reproduced from ref. 62].
Moreover, Khairan and co-workers described green synthesis of SNPs using *Allium sativum*. He reported to his studies that the sulfur ions bind to the garlic metabolites and stabilizing agents and then reduce to sulfur atoms into complex forms of metabolites and sulfur atoms, which form SNPs through a nucleation process. This process continued until the SNPs assumed a stable shape and size. The plausible mechanisms of SNPs formation are depicted in Fig. 5.

**Characterization Techniques for SNPs**

NPs are mostly characterized by their topography, size, dispersity and surface area. The known techniques are analyzing NPs characteristics. These approaches involve a range of several techniques like, UV–vis spectroscopy, X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and dynamic light scattering (DLS). SNPs characteristics can be examined using the techniques that in turn, are helpful to resolve diverse parameters such as particle size, crystallinity, morphology, pores size, surface area, and purity and fractal dimensions.
Fig. 5. Plausible mechanism of green synthesis of SNPs by using *Allium sativum* extract [Reproduced from ref. 60].

**UV–vis spectrophotometry**

UV-vis spectroscopy mentions to absorption spectroscopy in the region of UV-vis spectrum. Light frequencies of the 200–800 nm are commonly used for portraying different metal NPs in the size range of 2 nm to 100 nms. UV-vis spectroscopy is a crucial technique to ascertain the stability and formation of SNPs. UV-vis absorption measurement of the wavelength ranging from 250-400 nm is utilized to characterize SNPs (Fig. 6) [61, 65].

Fig. 6. UV-Vis absorption spectrum of biogenically synthesized SNPs [Reproduced from ref. 62].
XRD

XRD is a helpful tool for receiving information about the atomic and crystal structure of nanomaterials. XRD is a precious characterization technique to confirm the formation of SNPs, analyze the crystal structure, crystal planes and calculate the crystalline NPs size [70]. The standard JCPDS (Joint Committee on Powder Diffraction Standards) cards were used as a reference for confirmation of SNPs.

FT-IR

FT-IR is a molecular spectroscopy that analyses multifarious chemical functional groups in the regions between 400 and 4000 cm\(^{-1}\). FT-IR tools are carried out to find out the possible biomolecules accountable for reduction, capping and efficacious stabilization of SNPs.

SEM

SEM is an essential analysis method that utilizes electrons instead of light to form a micro-image as an output. The SEM investigation is utilized to describe the shape, size, morphology and distribution of biosynthesized SNPs (Fig. 7). The SEM microphotographs also evince the polydispersity and purity of resulting SNPs.

TEM

TEM is a valuable characterization technique and assists to examine the particle size of a material in nano-scale and to scrutiny the crystal structure carefully with high resolution. TEM assessments are proceeded in order to estimate the average NPs size and size distribution of the biosynthesized SNPs (Fig. 8).

Fig. 7. SEM images of synthesized SNPs [Reproduced from ref. 69].

Fig. 8. TEM images of synthesized SNPs [Reproduced from ref. 62].
EDS

EDS is an analytical method used for the chemical characterization or elemental analysis of SNPs. EDS provided the information about chemical composition, phase identification and purity of the biosynthesized SNPs.

AFM

The size, topography and surface area of the biosynthesized SNPs are examined using AFM. The advantage of AFM over ordinary microscopes such as TEM and SEM is that AFM technique makes three-dimensional (3D) images so that NPs volume and height and can be intended.

DLS

DLS method as a characteristic tool for particle size distribution (PSD) profiles of SNPs in solutions and/or colloidal suspensions has been broadly utilized in industry and scientific laboratory. DLS is characterized as a procedure by changing the dispersing light intensity fluctuation to procure the average diameter of SNPs. Real-time monitoring NPs size can be acknowledged by DLS because the assessment procedure of DLS is speedy and susceptible detection. Currently, DLS have been applied to identify cancer biomarkers and metal particles.

Apart from the aforesaid characterization tools, scientists also have utilized various precious characterization techniques for the affirmation of the NPs [71-76] (Fig. 9).

Applications of biogenically synthesized SNPs

SNPs have lots of stupendous applications for multifarious discipline of agriculture and biomedical. Nevertheless, the agricultural, biomedical and catalytic applications of the green synthesized SNPs are very prominent nowadays.

Accordingly, we have investigated in brief their eclectic and stupendous applications as guidance to new researchers for upcoming prospects (Table 2).

Salem et al. synthesized SNPs using Alianthus altissima leaves extract and reported to the seed germination study against tomato [58]. This study revealed that, the concentration dependent SNPs have the ability to enhance shoots and root growth of tomato. Khairan et al. synthesized spherical shaped SNPs using Allium sativum extract and studied the antifungal activity of as-prepared NPs. They carried out the antifungal activity of SNPs against Candida albicans [60].

Paralkar et al. reported the bio-inspired synthesis of spherical SNPs using Azadirachta indica, Catharanthus roseus, Mangifera indica, and Polyalthia longifolia leaves extract and reported their antibacterial activity using disk diffusion method. This antibacterial activity revealed that the synthesized SNPs showed better bactericidal efficacy against Escherichia coli and Staphylococcus aureus [61].

Najafi et al. reported the green synthesis of SNPs using Cinnamomum zeylanicum barks extracts and examined their effects on physiological and biochemical factors of Lactuca sativa [63].
Tripathi et al. synthesized random shaped SNPs using the leaf extract from *Ficus benghalensis* in the size of 2-15 nm and studied their catalytic detoxification of hexavalent chromium in water. They showed that the conversion rate of Cr(VI) into less toxic Cr(III) up to 88.7% in the presence of SNPs in 80 min. The optimal concentration ratios were maintained between SNPs and formic acid (10 ppm: 480 mM) [62].

Salem et al. described the green synthesis of SNPs using leaves extract from *Melia azedarach* were in the size of 5-80 nm and evaluated their seed germination activity against *Cucurbita pepo* [64]. Ragab et al. described the synthesis of spherical SNPs using *Oscum basilicum* leaves extracts and reported its effect on manganese stressed *Helianthus annuus* seedlings. They showed that the seed presoaking with medium doses of SNPs enhanced sunflower tolerance against Mn toxicity, balanced mineral uptake and photosynthetic pigments levels as well as maintaining of membrane stability [65].

Salem et al. reported the green synthesis of spherical shaped SNPs using *Punica granatum* peels extract and employed in agricultural application. This study evinced that the 200 ppm SNPs containing foliar spraying on tomato leaves are very advantageous to plant growth and generated healthy plant with high quality of tomato fruits and greener leaves compared with control [66].

**Table 2.** Applications of SNPs as-synthesized using various plants extracts

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of Plants</th>
<th>Applications</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><em>Alianthus altissima</em></td>
<td>Seed germination study</td>
<td>58</td>
</tr>
<tr>
<td>2.</td>
<td><em>Allium sativum</em></td>
<td>Antifungal activity</td>
<td>60</td>
</tr>
<tr>
<td>3.</td>
<td><em>Azadirachta indica</em></td>
<td>Antibacterial activity</td>
<td>61</td>
</tr>
<tr>
<td>4.</td>
<td><em>Catharanthus roseus</em></td>
<td>Antibacterial activity</td>
<td>61</td>
</tr>
<tr>
<td>5.</td>
<td><em>Mangifera indica</em></td>
<td>Antibacterial activity</td>
<td>61</td>
</tr>
<tr>
<td>6.</td>
<td><em>Polyalthia longifolia</em></td>
<td>Antibacterial activity</td>
<td>61</td>
</tr>
<tr>
<td>7.</td>
<td><em>Ficus benghalensis</em></td>
<td>Catalytic activity</td>
<td>62</td>
</tr>
<tr>
<td>8.</td>
<td><em>Cinnamomum zeylanicum</em></td>
<td>Agricultural application</td>
<td>63</td>
</tr>
<tr>
<td>9.</td>
<td><em>Melia azedarach</em></td>
<td>Seed germination study</td>
<td>64</td>
</tr>
<tr>
<td>10.</td>
<td><em>Oscum basilicum</em></td>
<td>Seed germination study</td>
<td>65</td>
</tr>
<tr>
<td>11.</td>
<td><em>Punica granatum</em></td>
<td>Foliar spray</td>
<td>66</td>
</tr>
<tr>
<td>12.</td>
<td><em>Rosmarinus officinalis</em></td>
<td>Seed germination study</td>
<td>67</td>
</tr>
<tr>
<td>13.</td>
<td><em>Rosmarinus officinalis</em></td>
<td>Nematicidal activity</td>
<td>68</td>
</tr>
</tbody>
</table>
Moreover, a same author has described biosynthesis of SNPs using leaves extract of *Rosmarinus officinalis*. They also studied the seed germination activities of as-synthesized SNPs on *Cucumis sativus*. This study showed that the increased seed germination and seedling growth of *Cucumis sativus* significantly, when increase to concentration of synthesized SNPs [67].

Banna *et al.* synthesized spherical shaped SNPs using *Rasmarinus officinalis* leaves extracts and studied their nematicidal activity against *Meloidogyne javanica*. This nematicidal activity revealed that the SNPs synthesized using *Rasmarinus officinalis* leaves aqueous extracts could be used as nematicidal to manage *Meloidogyne javanica* infestation [68].

**Conclusion**

This review has presented the recent advancements in the discipline of green syntheses of SNPs by using plants. It also critically discusses precise mechanisms behind the green synthesis of SNPs. Plant broths may act as herbal reducing and/or stabilizing additives in the production of NPs. Syntheses of SNPs using plant extract have several merits over the other known physical routes as it is sustainable, safer, affordable, non-noxious rapid synthesis and simplicity in protocols as well as simple to use. Plants have vast ability for the production of SNPs of wide range of stupendous applications for selective shapes and size. Further study needs to highlight the lucid mechanism behind the facile synthesis of SNPs, although few reports are existed in literature about this but just hypothesis. Therefore, further research needs to highlight the precise mechanism behind the fabrication of SNPs and improve their applications in diverse sectors.

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**Conflict of interest**

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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