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MINI-REVIEWS

Green and sustainable synthesis of silica nanoparticles

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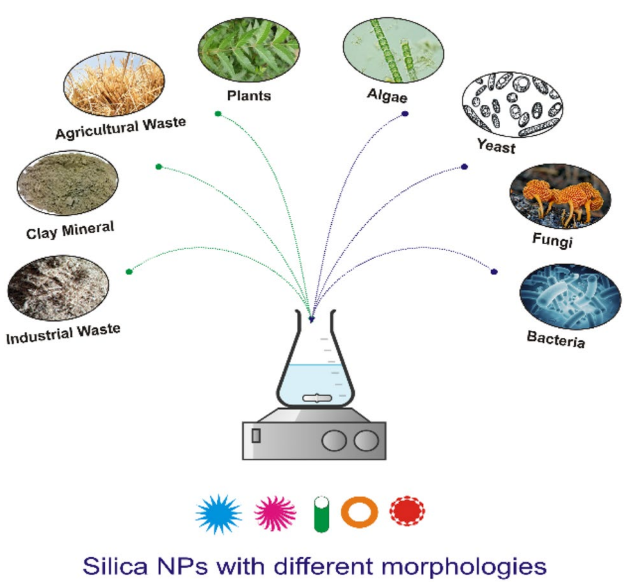
Abstract

Silica nanoparticles (SiNPs) have shown a wide range of applications in various technological fields. It is due to their unique properties such as biocompatibility, stability, tunable pore size, high surface area and surface reactivity. The ease of surface functionalization of SiNPs further extends their applications in biomedicine, targeted drug delivery and biosensing applications. Most of the works on SiNPs are focused on their synthesis by chemical methods for different applications. However, SiNPs can be prepared by green synthetic protocols that utilize plants, agriculture waste, industrial waste, fungi, bacteria, yeast, clay/mineral, worms, actinomycetes, etc. The green and sustainable methods offer distinctive encouraging features to produce nanomaterials with desired properties. The green synthesis of silica nanoparticles is an important area of research having considerable potential for further future developments. In this mini review, collective information on current green approaches for the synthesis of SiNPs is presented. The various green methods of synthesis for SiNPs are discussed with examples from the literature. The future challenges and expected advances are also pointed out which will decide the direction of research in this field.

Graphic abstract



Keywords Silica nanoparticles · Silicon dioxide · Green synthesis · Plant extracts · Microorganisms

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Introduction

Silica nanoparticles (SiNPs) and porous SiNPs have shown wide range of applications in various technological fields ranging from nanocomposites and ceramics to diagnosis tools and drug delivery [1]. Stöber et al. synthesized silica nanoparticles in 1962 by using tetraethyl orthosilicate (TEOS) as the silica precursor, ethyl alcohol and water as solvents and ammonia as an alkaline catalyst [2]. The scheme of synthesis of SiNPs by Stöber's method using TEOS as silica source is shown, in Fig. 1. Then onwards, there are several reports in the literature about the synthesis of SiNPs. The synthesis was done by modifying the reaction conditions, varying the base or catalyst and by using different precursors [3, 4]. The nanoparticles can be synthesized by "top-down" and "bottom-up" approaches [5]. The bottom-up methods use various hazardous chemicals and expensive processes that can cause potential environmental and biological hazards [6]. The SiNPs can also be synthesized by different physical and chemical methods, such as sol–gel synthesis [7], chemical vapour condensation [8], flame synthesis [9], laser ablation [10], reverse microemulsion synthesis, etc. [11].

However, these methods have some disadvantages. For instance, sol–gel and hydrothermal synthesis methods need costly raw materials and they also need very high-temperature furnace or heating devices [12]. The chemical vapour condensation method needs high temperatures, it has slower growth rates and it uses toxic reagents like $Ni(CO)_4$, B_2H_6, $SiCl_4$, etc. Some of these reagents are explosive and are also corrosive in nature [13]. The main disadvantage of flame synthesis is control over the particle size, morphology and phase composition [14]. The laser ablation method has a limitation in wavelength of laser impinging metallic target, duration of laser pulses, laser fluency, duration of ablation and an effective liquid medium with or without the presence of surfactants [15]. Reverse microemulsion methods are costly and the removal of surfactants from final products is a difficult task [5].

The green methods for synthesis of SiNPs offer several advantages and they can also overcome some of the drawbacks of other synthesis techniques mentioned above [16]. Importantly, the SiNPs synthesized by green methods are of similar quality as prepared by the chemical methods. The SiNPs produced by green methods can be used in medicine, pharmaceuticals, electrical, paints, cosmetics and in many other technical applications. In green synthesis methods, eco-friendly reagents replace the harmful chemical regents. Hence, the particles are less toxic and reasonably pure than those prepared by the chemical techniques. In the case of green synthesis of SiNPs, natural precursors of silica and sustainable bases are used. Many minerals, rocks, clays; agricultural wastes like rice husk, hull, straw; industrial waste like sugarcane bagasse and some plants are good sources of silica in various forms for the synthesis of nanoparticles. The leaf extracts, fruit pulps as well as aqueous extracts of ash of some plant parts can be used as alkaline catalysts for the synthesis of SiNPs. The green synthesis of SiNPs by using natural resources is an efficient, economical, time saving and sustainable process [7]. Recently, there are many reports about chemical and green synthesis of various nanoparticles [17] such as silicon oxide [18], calcium oxides [19], copper oxides [20, 21], gold [22], iron oxides [23–25], silver [15], zinc oxides [26–30] and titanium oxides [31, 32] for various applications. Instead, a very little investigation

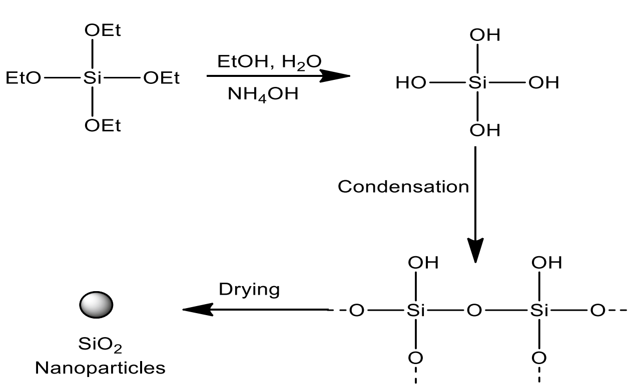

Fig. 1 Basic scheme of synthesis of silica nanoparticles

has been carried out on the eco-friendly green synthesis of SiNPs. The different types of natural resources that can be used for the green synthesis of silica nanoparticles are shown in Fig. 2.

Due to the wide range of applications of SiNPs in various technological fields, their demand in coming days is going to increase. The applications in fields such as biomedicine, food, catalysis, smart pesticides and in the agriculture (as mineral carrier for plants) demand large quantities of SiNPs. In addition, SiNPs also show applications as an additive for the manufacture of rubber and plastics, as strengthening filler for concrete and other construction composites. These fields also demand huge quantities of SiNPs. The large-scale production of SiNPs by chemical routes may cause considerable harmful effects to the environment. In this review, collective information about different green methods for the synthesis of SiNPs is discussed with examples from the literature. Almost all green methods that can be used to synthesize SiNPs are covered in the discussion. Some future prospects and challenges are also pointed out and discussed.

Green methods for the synthesis of SiNPs

Agricultural waste

Agricultural waste products are utilized for the preparation of green fertilizers, as fuel and in some cases for the extraction of useful chemicals. The agricultural waste is used as precursor for synthesis of SiNPs. The main advantage of using agricultural waste is its availability in abundance at the end of each harvesting season. Hence, the nanoparticle synthesis methods that utilize agricultural wastes are always economical compared to other methods. Rice hull is a waste product of agriculture, which contains bulk of silica. There are many reports in the literature about use of this material to produce SiNPs with good quality. For instance, Jansomboon et al. synthesized silica micro- and nanoparticles by using rice hull for first time [33]. Lu et al. used rice straw as a source of silica and synthesized highly pure amorphous silica nano-discs [34]. Figure 3a, b shows SEM and TEM images of SiNPs obtained from rice straw ash. Figure 3c shows distribution of diameter of SiNPs obtained by using rice straw ash, which was determined from more than 200 particles in their TEM images. Sugarcane bagasse is a major waste product produced in the sugar industry. Mohd et al. reported the production of SiNPs from sugarcane bagasse [35]. This green approach gives a way for agricultural waste utilization by economical route. G Falk et al. used sugarcane bagasse ash to synthesize SiNPs and nano-silicon by magnesiothermic reactions [36]. Sankar et al. used sticky, red and brown rice husk ash and synthesized biogenerated SiNPs [37]. Vaibhav et al. synthesized SiNPs from agricultural

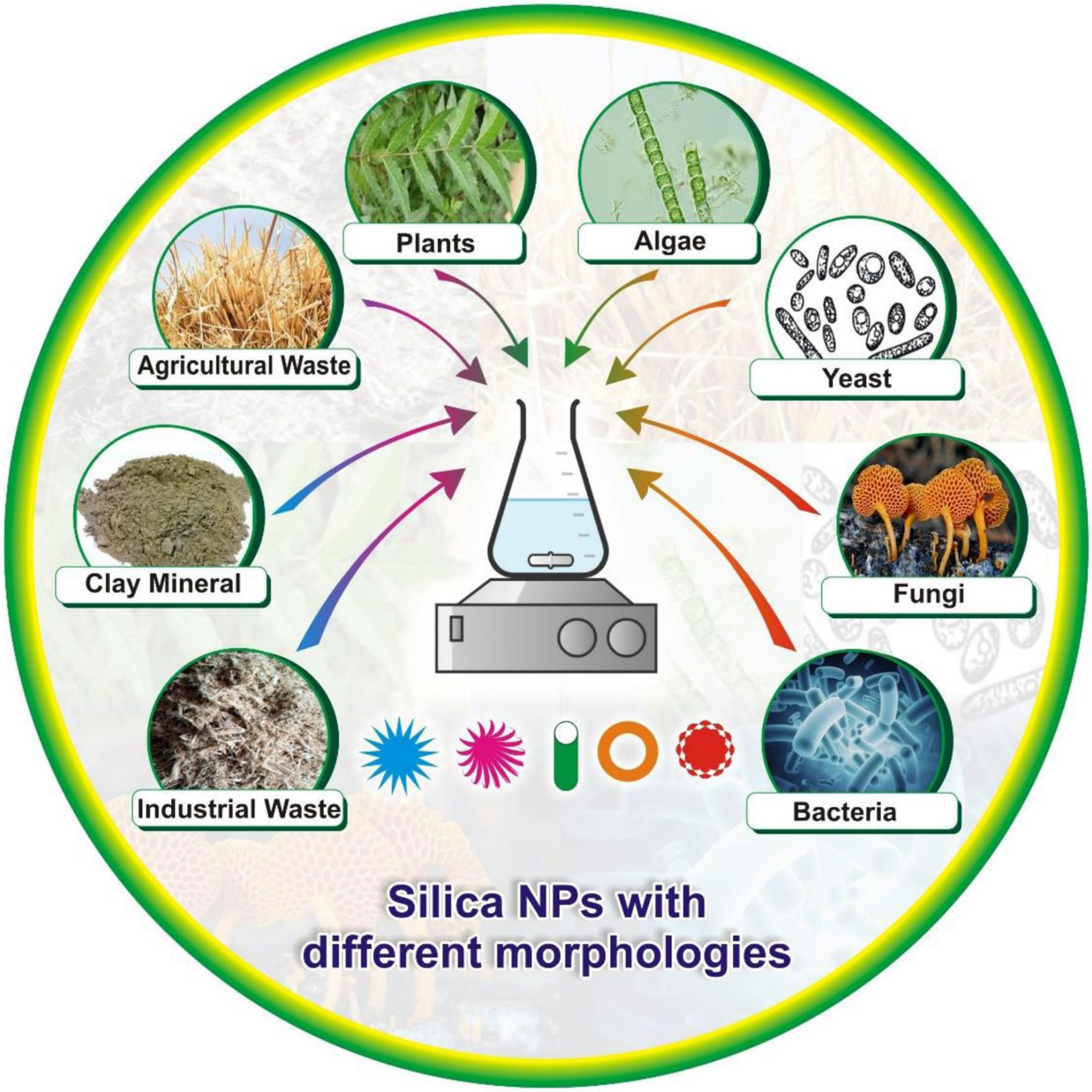

Fig. 2 Resources for the green synthesis of silica nanoparticles

waste like rice husk, bamboo leaves, sugarcane bagasse and groundnut shell and recovered 52–78% silica from respective wastes [38]. Gonzalez et al. synthesized crystalline SiNPs via Annelid bioprocessing of agricultural waste. These agro-wastes were subjected to Annelid treatment by using *Eisenia foetida* species to produce humus and then SiNPs were obtained by calcination and acid treatment [39]. Gurbani et al. reported a novel method to synthesize silica nanoparticles by using sedge. The sedge *Carex riparia* is a weed which produces large amount of agro-waste. The synthesis of SiNPs from it provided an excellent way to obtain useful nanomaterials from waste [40]. Sorghum bicolor also produces agricultural residue, but these agricultural residues were not disposed properly hence they create pollution. Sorghum residues consist high amount of silica, so it can be used as precursor for the synthesis of SiNPs. Athinarayan et al. synthesized silica nanoparticles using leaves of *Sorghum bicolor* for various applications in food industry [41]. Nanosilica was also synthesized by using *Sorghum vulgare* seed head by Balamurugan et al. [42]. Sivakumar et al. synthesized pure silica from waste material like cow-dung ash by using sol–gel process. They obtained SiNPs of 100% purity having spherical shape [43]. Teff straw is an agricultural residue available in high amount in Ethiopia. Wassie et al. reported the synthesis of nanosilica by using Teff straw. They extracted nano-silica by using heat and acid treatment [44]. Therefore, by looking at all above examples from the literature, it can be concluded that agricultural waste emerges as a good source for the synthesis of SiNPs.

Industrial waste

Some of the industrial waste products were turned to be useful materials for synthesis of SiNPs with minimum efforts. A classic example is the conversion of fly ash into nanosilica. The coal fly ash is a waste or by-product of coal-fired power plants. Yadav et al. reported the synthesis of amorphous silica nanoparticles from fly ash which is rich in silica. This is an efficient and economical method for synthesis of SiNPs [45]. Yan et al. derived a green method in which silica nanoparticles were obtained from coal fly ash [46]. This green protocol gave a new way to reduce the industrial waste which can harm the nature. The nanosilica derived from the fly ash was tested for its CO_2 capturing ability and it showed excellent results. The SEM and TEM images of the obtained particles are shown in Fig. 4. Figure 4a, b is obtained at magnification ×10,000 and ×50,000, respectively. This report also proves that the nanosilica obtained from waste products by green approach shows excellent properties compared to that of SiNPs synthesized from chemical methods.

Clay/minerals

The clay and minerals have been also used to prepare nanosilica. Malatya Pyrophyllite is a clay mineral that contains a significant amount of silica. Sarikoya et al. used Malatya Pyrophyllite and synthesized nano-amorphous silica nanoparticles [47]. Zulfiqar et al. synthesized silica nanoparticles by using bentonite clay [48]. Silica-rich clay was prepared from bentonite by a sequence of acid and thermal processes. It was later treated with sodium hydroxide solution to prepare sodium silicate. Silica particles were obtained by hydrolysing sodium silicate solution with nitric acid in the presence of ethanol. In this report, effect of acid concentration on particle size was also studied which shows that particle

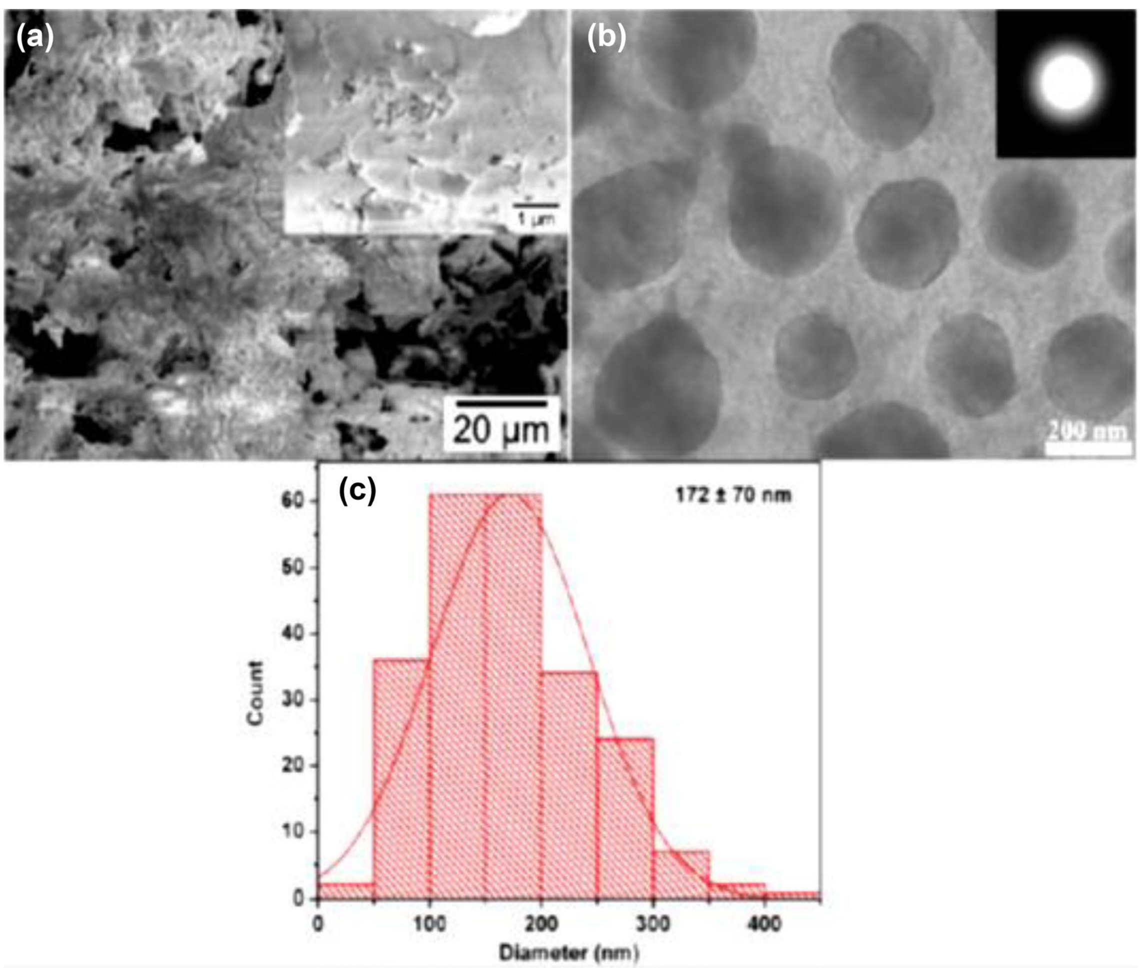

Fig. 3 SEM (**a**) and TEM (**b**) micrographs of silica from rice straw ash. The inset in (**a**) is a higher-magnification SEM image and the one in (**b**) is the selected area electron diffraction (SAED) pattern of silica. The diameter distribution (**c**) of silica particles was determined from more than 200 individual particles in TEM images. Reproduced with permission from Lu et al. © 2012 Elsevier

size can be tuned by varying the concentration of the acid used. Mourhly et al. synthesize mesoporous silica nanoparticles from Pumice rock, which is a silica-rich material [49]. Many researchers obtained nanosilica from different types of minerals. Stopic et al. derived silica nanoparticles from olivine mineral through carbonation under high pressure in autoclave [50]. Figure 5 shows the TEM analysis of the obtained SiNPs. The results confirmed that the particles have a spherical shape. The diameters of the particles were approximately 400–500 nm and the particles were amorphous in nature.

Plants

Recently, there are a huge number of reports in the literature about the green synthesis of nanoparticles by using different plants. As pointed out earlier, nanoparticles of different materials and from various categories can be synthesized by using various parts of the plants. The synthetic methods have used the extracts of various parts of plants from different origins as reducing or hydrolysing agents for the synthesis of nanomaterials. This eco-friendly approach is helpful to avoid use of chemicals needed for the synthesis of various nanomaterials. Some classic examples of green synthesis of SiNPs using plants are as follows. Babu et al. used *Cynodon dactylon* plant as source of silica and produced SiNPs for antimicrobial study [51]. Sethy et al. used bamboo leaf ash to synthesize silica nanoparticles and incorporate in polydimethylsiloxane (PDMS) membrane to enhance its separation properties [52]. Most of the studies have used extract of plant parts as a base in the synthesis of SiNPs in the alkaline hydrolysis step (refer to Fig. 1). Durairaj et al. produced silica nanoparticles by well-known sol–gel method using *Bambusa vulgaris* leaves ash and used it for environmental applications [53]. Jabeen et al. reported the synthesis of silica nanoparticles using *Azadirachta indica* (Neem) leaves extract which acts as an effective chelating agent [54]. Azawi et al. prepared silica nanoparticles by using hot aqueous extract of *Thuja orientalis* leaves and study its effect on biofilm formation [55]. Irzaman

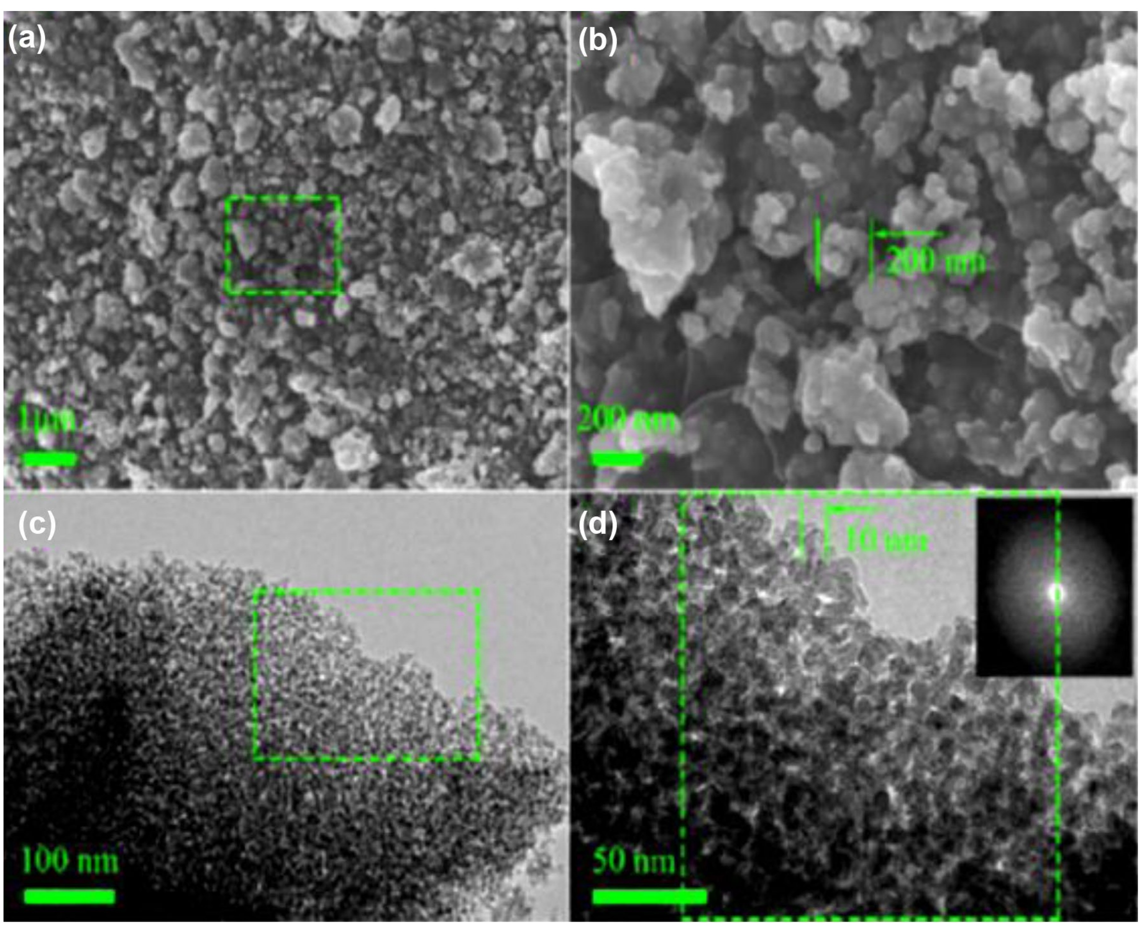

Fig. 4 **a**, **b** SEM images, **c** TEM image and **d** HR-TEM image of "nano-SiO_2-2%". Magnification factor: ×10,000 for (**a**) and ×50,000 for (**b**). Reproduced with permission from Yan et al. © 2017 American Chemical Society

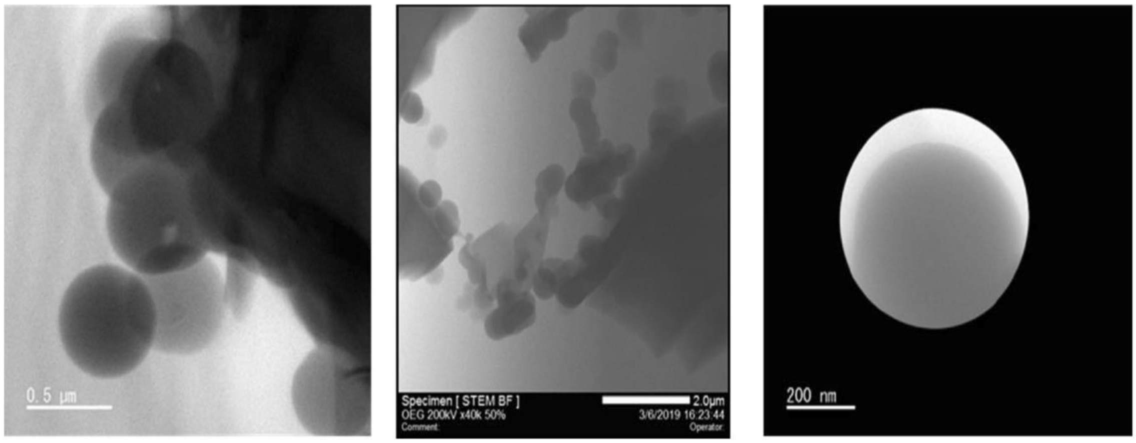

Fig. 5 The TEM and STEM images of nanosilica obtained by olivine mineral carbonation under high pressure in an autoclave. Reproduced with permission from Stopic et al. © 2019 MDPI

et al. used bamboo leaves to synthesize SiO_2 with 99.9%* purity [56]. Yusaldi et al. extracted silica from banana stem by using acid leaching method [57]. San et al. synthesized silica nanoparticles from sugarbeet bagasse by novel one-step method using laser ablation and reported environmental benign procedure to produce SiNPs [10]. Their results

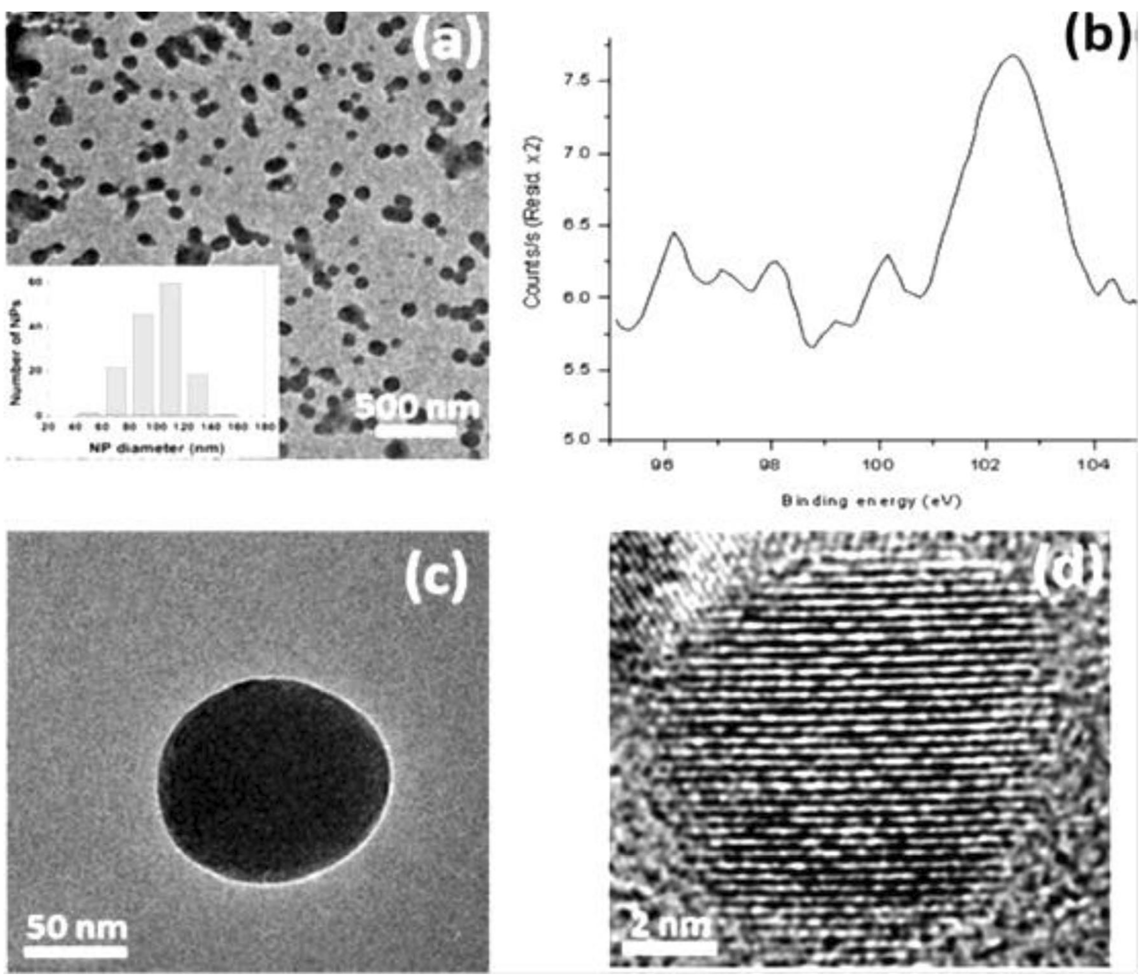

Fig. 6 **a** TEM image of SiNPs, inset: size distribution, **b** XPS analysis recorded from SiNPs, **c** amorphous structure of SiNPs and **d** nanocrystal (NC) structure of SiNPs. Reproduced with permission from San et al. © 2014 Elsevier

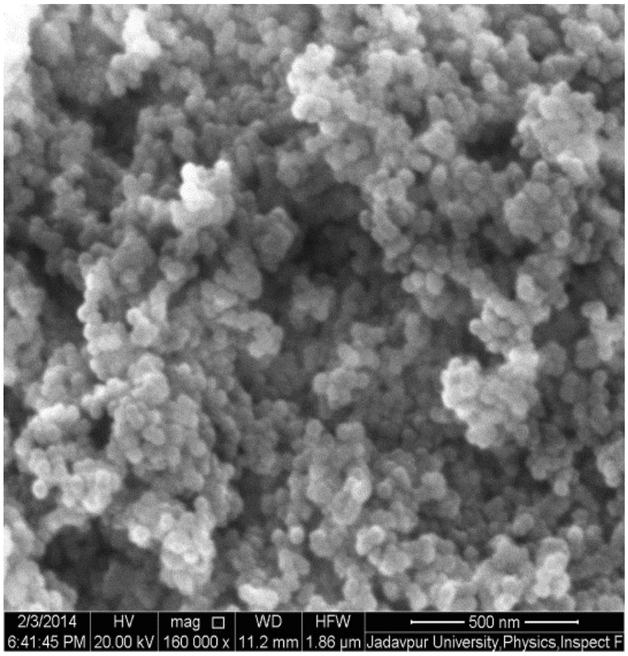

Fig. 7 FE-SEM image of SiO_2-NPs formed by the interaction of BKH1 cell with magnesium trisilicate hydrates solution

showed that the SiNPs obtained by laser ablation are significantly smaller (38–190 nm) or comparable to those prepared using chemical routes. The analysis results of the particles are shown in Fig. 6. Agunsoye et al. in their work investigated the utilization of Cassava periderm as new source of silica. They recovered silica nanoparticles from Cassava periderm by reduction method [58]. Fahmi et al. explored coconut husk waste as raw material for silica synthesis. They extract silica from coconut husk by chemical extraction method [59]. Subramanian et al. synthesized silica nanoparticles from coconut shell [60]. All these examples prove the worth of various plants in the green synthesis of SiNPs.

Bacteria and yeast

The handling and genetic manipulation of various bacteria is possible due to recently invented techniques hence they can be used in the synthesis of useful nanomaterials. In fact, they are considered as the most potent eco-friendly nanofactories [61]. There are some reports about bacteria-assisted synthesis of SiNPs. Vetchinkina et al. used bacterial culture liquids to synthesize silicon nanospheres having a size ranging from 5 to 250 nm [62]. Silicon/silica nanocomposites were produced by Singh et al. by using bacterium *Actinobacter* species. In this report, silica precursor K_2SiF_6 and bacteria were exposed together. The reductase and oxidase enzymes secreted by the bacteria led to the synthesis of silica nanoparticles [63]. Show et al. derived a green protocol to produce SiNPs by using thermophilic bacteria BKH1 and inorganic magnesium trisilicate precursor and organic tetraethyl orthosilicate precursor [64]. Figure 7 shows the SEM image of the particles obtained. The EDS analysis of the particles showed the presence of only two major peaks of Si and O which confirmed the high purity of the particles obtained. Yeasts are simple eukaryotic organisms which can be used for production of nanoparticles. Liu et al. synthesize silica nanoparticles by a photochemical method using diphenyl iodonium hexafluorophosphate as a super acid generator and TEOS as silicon source [65]. The generated acid was responsible for the initial hydrolysis of the silica source (TEOS) which subsequently led to the particle formation. Zamani et al. used *Saccharomyces cerevisiae* yeast for the biochemical synthesis of silica nanoparticles for its application in enhanced oil recovery [66].

Fungi, worms and actinomycetes

Recently, fungi have gained more attention as nanofactories for the biosynthesis of various nanoparticles. The use of fungi for synthesis of nanoparticles is potentially exciting since they secrete large amounts of enzymes and are simpler to deal with in the laboratory. Studies indicate that the genera *Fusarium*, *Aspergillus* and *Penicillium* have promising potential for the extracellular bio-production of different metal nanoparticles and *Verticillium Sp*. could be harvested for intracellular synthesis of nanoparticles. There are considerable numbers of reports in the literature about synthesis of SiNPs using fungi. For instance, Aleksandra Pieta et al. obtained the silica nanoparticles of defined size and morphology from bioconversion of corn cob husk using fungus of the *Fusarium culmorum* [67]. Bansal et al. derived a novel method to produce silica nanoparticles by bioleaching of sand using fungus *Fusarium oxysporum*. This Bioleaching method is quite rapid and takes place within one day of reaction of the Biomass with sand [68]. In another report, Bansal et al. biosynthesized silica nanoparticles from fungus *Fusarium oxysporum* using aqueous and anionic complex of SiF_6^{-2}. The detailed study showed that the exposure of fungus to silicon complex induce secretions of proteins which are capable of hydrolysing SiF_6^{-2} to produce SiNPs [69]. Bansal et al. derived a new way to synthesize nanosilica from rice husk. In this report, fungus *Fusarium oxysporum* is used to bioleach silica from rice husk. This fungal species is capable of rapid biotransformation of the naturally occurring biosilica from rice husk into crystalline silica nanoparticles [70]. Figure 8 shows TEM images of SiNPs produced by using fungus *Fusarium oxysporum* upon exposure to rice husk. Many research reports suggest agro-waste rice husk as a better natural source of silica. In one of the reports from Rohtagi et al., they have synthesized SiNPs from rice husk by microbial fermentation using white rot fungus Python [71]. Zielonka et al. produced silica nanoparticles from agro-waste rice

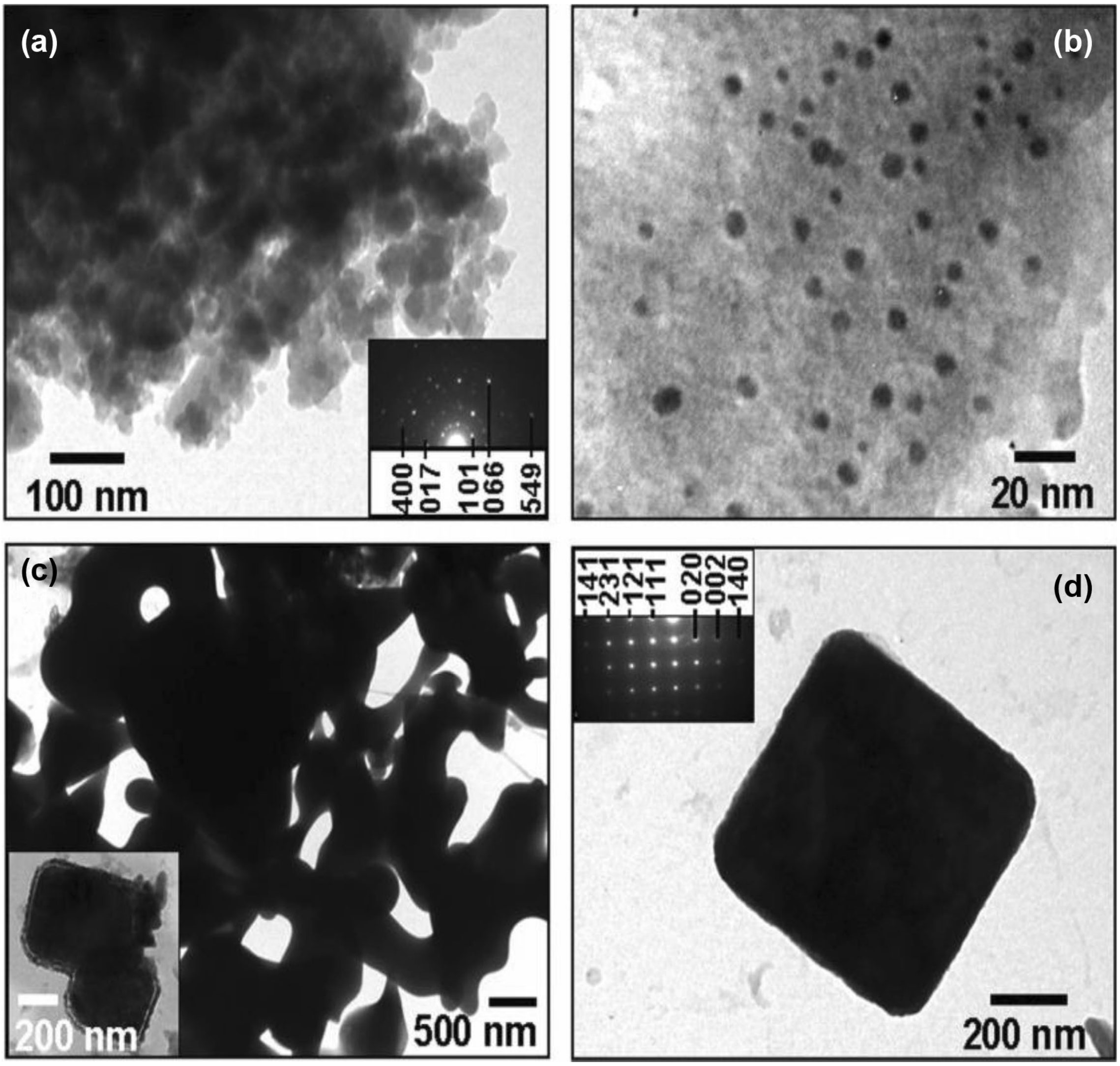

Fig. 8 TEM micrographs at different magnifications of silica nanoparticles synthesized by the exposure of rice husk to the fungus *Fusarium oxysporum* before (**a** and **b**; text for details) and after calcination at 400 °C for 2 h (**c** and **d**). Reproduced with permission from Bansal et al. © 206 American Chemical Society

husk by fungal mediated biotransformation using *Aspergillus parasiticus* species, which gives SiNPs having size 3–400 nm [72]. In an interesting report, Estevez et al. produced silica nanoparticles through biodigestion of rice husk using Californian red worm. The worms are fed with rice husk and water which produce humus. After different treatments, silica nanoparticles are obtained within the range 55–250 nm [73].

Actinomycetes are gram-positive, anaerobic, mycelial bacteria. They can be also harvested for the synthesis of nanoparticles. Biosilification is economically beneficial, energy-saving and eco-friendly method for commercial synthesis of oxide nanomaterials. Kaur et al. synthesized SiO_2 nanocomposites from rice husk and wheat bran by using various eukaryotic micro-organisms such as *Actinomycetes, Fusarium oxysporum, Aspergillus niger, Trichoderma* species and *Penicillium* species. All of these micro-organisms biotransform amorphous silica from natural source to crystalline silica within 24 h in the size range of 232 to 250 nm [74]. The brief comparative analysis of all the methods discussed above with their advantages and disadvantages is given in Table 1. Table 2 shows the role of various green sources or reagents in synthesis of SiNPs. The SiNPs obtained by use of micro-organisms are pure. Their separation and purification can be done by performing unit operations on the crude products. The separation of biomass and other impurities can be done by filtration, centrifugation and drying. The purity of the SiNPs obtained by various green methods mentioned above is considerably high compared to the SiNPs obtained by chemical methods, as there is no any

Table 1 Comparative analysis of green synthesis methods for SiNPs

Method/source	Advantages	Disadvantages
Agricultural waste	Low cost or free availability of raw materials at the end of each harvesting season. Superior quality of SiNPs can be obtained	There is a potential to synthesize SiNPs on large scale by this method but scale-up issues need to be addressed. The papers report mostly laboratory-scale synthesis
Industrial waste	Low cost of the raw materials. Reduction of industrial waste and transformation into useful products is possible	There is a potential to synthesize SiNPs on large scale by this method. Quantitative information about amount of particles obtained per unit mass of waste is not reported
Clay/minerals	Superior quality SiNPs can be obtained and also hybrid (other metal/metal oxide embedded) SiNPs can be obtained. Low cost at the site of availability of the clay or minerals	Availability of the raw materials is at specific locations where the minerals used are abundant
Plants	This green method guarantees the production of high-quality, pure and safe SiNPs. The natural resource used is available in abundance	The yield may be an issue. The stability of the SiNPs obtained by this technique must be compared with the particles obtained by chemical methods
Bacteria and yeast	Highly pure SiNPs can be obtained. Due to it SiNPs obtained by this method can be used in biomedical applications	The quantitative yields and cost of productions are not reported for such approached so far
Fungi, worms and actinomycetes	Highly pure SiNPs can be obtained. The biosilification is economically beneficial, energy-saving and eco-friendly method	There is a potential to synthesize SiNPs on large scale by this method but scale-up issues needs to be addressed

possibility of formation of toxic by-products during their synthesis.

Expected future advances

Recently, there is an increased interest in the synthesis of various nanoparticles including SiNPs using advanced synthetic techniques such as continuous flow synthesis in microfluidic devices (laboratory on chip concept) [75–78], by laser ablation [79] and microwave-assisted synthesis methods [80]. In these methods, the particle size and morphology can be controlled via parameters such as temperature, residence time, process chemistry, flow rates, irradiation times and precursor concentrations. These methods yield monodisperse nanoparticles and offer great control over the size of the particles. Additionally, the large-scale production of nanoparticles is also possible by using these methods. In particular, the continuous flow microfluidic chemistry has demonstrated relatively superior process performance over conventional nanoparticle synthesis technologies. At present, these modern nanoparticle synthesis methods are using the same chemicals used in the synthesis of the nanoparticles by other conventional techniques. As a future advancement in this field, it is possible to replace the harmful chemicals used in these modern techniques with green alternatives. Natural precursors, precursors derived from wastes and green catalysts can be used. The bases used in the hydrolysis of silica precursors to produce SiNPs can be easily replaced with plant extracts mentioned before. Some microfluidic devices can also be invented for biological synthesis of nanoparticles where micro-organisms (nanofactories) can flow through the channels easily, survive the conditions and produce nanoparticles. Such sustainable modern synthetic technique with the capability of large-scale production that utilizes green precursors, solvents and catalysts is the demand of future.

Conclusions and future outlook

The green methods for synthesis of nanoparticles eliminate use of unsafe chemicals and reduce the risks to the environment. All the examples of green synthesis of SiNPs discussed above show that variously shaped nanoparticles of silica can be prepared by simple biological and eco-friendly methods by using green resources. Many natural resources such as plants and minerals, micro-organisms and waste products from agriculture and industries can be used to prepare SiNPs. The green synthetic methods do not produce any hazardous by-products, provide better control over shape, size and morphology of the particles prepared. Further, in the case of micro-organism-assisted synthesis, the purity of the nanoparticles obtained is very high and there is no need for purification of the obtained nanoparticles by complex

Table 2 Role of different sources in green synthesis of SiNPs

Waste or green source	Used as source of Si or base	Product
Agricultural waste	Source	
	1. Rice hull	Silica micro- and nanoparticles
	2. Rice straw	Silica nano-discs
	3. Sugarcane bagasse	Silica nanoparticles
	4. Rice husk ash	Silica nanoparticles
	5. Bamboo leaves	Silica nanoparticles
	6. Groundnut shell	Silica nanoparticles
	7. Sedge *Carex riparia*	Silica nanoparticles
	8. *Sorghum bicolor*	Silica nanoparticles
	9. Cow-dung ash	Silica nanoparticles
	10. Teff straw	Silica nanoparticles
Industrial waste	Source	
	1. Fly ash	Silica nanoparticles
	2. Coal fly ash	Silica nanoparticles
Clay/mineral	Source	
	1. Malatya pyrophyllite	Amorphous silica
	2. Bentonite clay	Silica nanoparticles
	3. Pumice rock	Mesoporous Silica nanoparticles
	4. Olivine mineral	Amorphous Silica nanoparticles
Plants	Source	
	1. *Cynodon dactylon*	Silica nanoparticles
	2. Bamboo leaf ash	Silica nanoparticles
	3. Banana stem	Silica nanoparticles
	4. Sugarbeet bagasse	Silica nanoparticles
	5. Cassava periderm	Silica nanoparticles
	6. Coconut husk	Silica nanoparticles
	7. Coconut shell	Silica nanoparticles
	8. Corn cob husk	Silica nanoparticles
	Base	
	1. *Bambusa vulgaris* leaves ash	Silica nanoparticles
	2. *Azadirachta indica* leaves extract	Silica nanoparticles
	3. Aqueous extract of *Thuja orientalis* leaves	Silica nanoparticles
Bacteria and yeast	Biocatalyst	
	1. Bacterial culture	Silicon nanospheres
	2. *Actinobacter* sp.	Silicon/silica nanocomposites
	3. BHK1 bacteria	Silica nanoparticles
	4. *Saccharomyces cerevisiae* yeast	Silica nanoparticles
Fungi, worms and actinomycetes	Biocatalyst	
	1. *Fusarium culmorum*	Silica nanoparticles
	2. *Fusarium oxysporum*	Silica nanoparticles
	3. White rot fungus Python	Silica nanoparticles
	4. *Aspergillus parasiticus*	Silica nanoparticles
	5. Californian red worm	Silica nanoparticles
	6. Actinomycetes	Crystalline silica
	7. *Eisenia foetida*	Silica nanoparticles

operations. The purification step is rather time-consuming and requires costly solvents in the chemical methods of synthesis of nanoparticles. This eliminates the use of large amounts of hazardous organic solvents used for the purification of the nanomaterials. In spite of the good progress in the field of green synthesis of SiNPs, several issues are still needed to be sorted out in near future. There is a need to develop even more "green" synthesis protocols for the synthesis of SiNPs than existing methods which can utilize various other available agricultural and industrial wastes. The demand of SiNPs is going increase in future; therefore, large-scale production of SiNPs will be needed. Presently, the large-scale production of SiNPs is done mostly by chemical routes due to high yields and industrial feasibility of the technology. There is still a lot of scope to develop and further modify presently invented green synthesis methods for the large-scale production of SiNPs. Thus, despite the current research, new innovations and further research is needed to upgrade the current green methods and processes to prepare SiNPs in future.

Author contributions SAJ and SDK developed the idea and performed literature search and complied the manuscript. All other co-authors contributed towards final completion of the paper.

Declaration

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Jadhav SA (2014) Incredible pace of research on mesoporous silica nanoparticles. Inorg Chem Front 1:735–739. https://doi.org/10.1039/C4QI00118D
2. Stöber W, Fink A, Bohn E (1968) Controlled growth of monodisperse silica spheres in the micron size range. J Colloid Interf Sci 26(1):62–69. https://doi.org/10.1016/0021-9797(68)90272-5
3. Singh L, Agarwal S, Bhattacharyya S et al (2011) Preparation of silica nanoparticles and its beneficial role in cementitious materials. Nanomater Nanotechnol 1:9. https://doi.org/10.5772/2F50950
4. Azlina H, Hasnidawani J, Norita H, Surip S (2016) Synthesis of sio_2 nanostructures using sol-gel method. Acta Phys Pol A 129:842–844
5. Rahman I, Padavettan V (2012) Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites—a review. J Nanomater 2012:1–15. https://doi.org/10.1155/2012/132424
6. Yugandhar P, Haribabu R, Savithramma N (2015) Synthesis, characterization and antimicrobial properties of green-synthesised silver nanoparticles from stem bark extract of *Syzygium alternifolium* (Wt.) Walp. 3 Biotech 5:1031–1039. https://doi.org/10.1007/s13205-015-0307-4
7. Jadhav SA, Garud HB, Thoravat SS, Patil VS, Shinde PS, Burungale SH, Patil PS. Synthesis and testing of functional mesoporous silica nanoparticles for removal of Cr(VI) ions from water (2021) Biointerface Res Appl Chem 11:8599–8607. https://doi.org/10.33263/BRIAC112.85998607
8. Ji-Hun Y, Chang-Wu L, Sung-Soon I, Jai-Sung L (2003) Structure and magnetic properties of SiO_2 coated Fe_2O_3 nanoparticles synthesized by chemical vapor condensation process. Adv Mater 15:55–59. https://doi.org/10.1007/BF02700020
9. Yue R, Meng D, Ni Y, Jia Y, Liu G, Yang J, Liu H, Wu X, Chen Y (2013) One-step flame synthesis of hydrophobic silica nanoparticles. Powder Technol 235:909–913. https://doi.org/10.1016/j.powtec.2012.10.021
10. San N, Kurşungöz C, Tümtaş T, Yaşa O, Ortaç B, Tekinay T (2014) Novel one-step synthesis of silica nanoparticles from sugarbeet bagasse by laser ablation and their effects on the growth of freshwater algae culture. Particuology 17:29–35. https://doi.org/10.1016/j.partic.2013.11.003
11. Lin C, Chang J, Yeh Y, Wu S, Liu Y, Mou C (2015) Formation of hollow silica nanospheres by reverse microemulsion. Nanoscale 7:9614–9626. https://doi.org/10.1039/C5NR01395J
12. Barry Carter C, Grant Norton M (2013) Ceramic materials-science and engineering, Foreward by David R. Clarke. Springer, New York
13. Creighton JR, Ho P (2001) Introduction to chemical vapor deposition (CVD). ASM International 2001. ASM International, Materials Park
14. Klabaunde Kenneth J, Richards Ryan M (2001) Nanoscale materials in chemistry. Wiley. https://doi.org/10.1002/0471220620
15. Iravani S, Korbekandi H, Mirmohammadi SV, Zolfaghari B (2014) Synthesis of silver nanoparticles: chemical, physical and biological methods. Res Pharm Sci 9:385–406
16. Sharma D, Kanchi S, Bisetty K (2019) Biogenic synthesis of nanoparticles: a review. Arab J Chem 12:3576–3600. https://doi.org/10.1016/j.arabjc.2015.11.002
17. Das R, Pachapur V, Lonappan L, Naghdi M, Pulicharla R, Maiti S et al (2017) Biological synthesis of metallic nanoparticles: plants, animals and microbial aspects. Nanotechnol Environ Eng. https://doi.org/10.1007/s41204-017-0029-4
18. Shwokat A, Kim M, Gopalan A, Reddy K, Lee K (2007) Analysis of heavy metal toxic ions by adsorption onto amino-functionalized ordered Mesoporous silica. Bull Korean Chem Soc 28(11):1985–1992. https://doi.org/10.5012/bkcs.2007.28.11.1985
19. Yugandhar P, Savithramma N (2013) Green synthesis of calcium carbonate nanoparticles and their effects on seed germination and seedling growth of *Vigna mungo* (L.) Hepper. Int J Adv Res 1:89–103
20. Shende S, Ingle A, Gade A, Rai M (2015) Green synthesis of copper nanoparticles by *Citrus medica* Linn. (Idilimbu) juice and its antimicrobial activity. World J Microb Biot 31:865–873. https://doi.org/10.1007/s11274-015-1840-3
21. Bukkitgar S, Kumar S, Pratibha XX, Singh S, Singh V, Raghava Reddy K et al (2020) Functional nanostructured metal oxides and its hybrid electrodes—recent advancements in electrochemical biosensing applications. Microchemical J 159:102. https://doi.org/10.1016/j.microc.2020.105522
22. Gopinath K, Gowri S, Karthika V, Arumugam A (2014) Green synthesis of gold nanoparticles from fruit extract of Terminalia Arjuna, for the enhanced seed germination activity of Gloriosa superba. J Nanostructure Chem 4:115. https://doi.org/10.1007/s40097-014-0115-0
23. Naseem T, Farrukh M (2015) Antibacterial activity of green synthesis of iron nanoparticles using *Lawsonia inermis* and *Gardenia jasminoides* leaves extract. J Chem 2015:1–7. https://doi.org/10.1155/2015/912342
24. Reddy K, Lee K, Gopalan A, Kang H (2007) Organosilane modified magnetite nanoparticles/poly(aniline-co-o/m-aminobenzenesulfonic acid) composites: synthesis and characterization. React

Funct Polym 67(10):943–954. https://doi.org/10.1016/j.reactfunctpolym.2007.05.023
25. Shetti N, Malode S, Nayak D, Naik R, Kuchinad G, Reddy K et al (2020) Hetero-nanostructured iron oxide and bentonite clay composite assembly for the determination of an antiviral drug acyclovir. Microchem J 155:104727. https://doi.org/10.1016/j.microc.2020.104727
26. Bala N, Saha S, Chakraborty M, Maiti M, Das S, Basu R, Nandy P (2015) Green synthesis of zinc oxide nanoparticles using Hibiscus subdariffa leaf extract: effect of temperature on synthesis, anti-bacterial activity and anti-diabetic activity. RSC Adv 5:4993–5003. https://doi.org/10.1039/C4RA12784F
27. Bukkitgar S, Shetti N, Malladi R, Reddy K, Kalanur S, Aminabhavi T (2020) Novel ruthenium doped TiO2/reduced graphene oxide hybrid as highly selective sensor for the determination of ambroxol. J Mol Liq 300:112368. https://doi.org/10.1016/j.molliq.2019.112368
28. Ilager D, Shetti N, Malladi R, Shetty N, Reddy K, Aminabhavi T (2021) Synthesis of Ca-doped ZnO nanoparticles and its application as highly efficient electrochemical sensor for the determination of anti-viral drug, acyclovir. J Mol Liq 322:114552. https://doi.org/10.1016/j.molliq.2020.114552
29. Koutavarapu R, Reddy C, Syed K, Reddy K, Shetti N, Aminabhavi T, Shim J (2021) Ultra-small zinc oxide nanosheets anchored onto sodium bismuth sulfide nanoribbons as solar-driven photocatalysts for removal of toxic pollutants and phtotoelectrocatalytic water oxidation. Chemosphere 267:128559. https://doi.org/10.1016/j.chemosphere.2020.128559
30. Koutavarapu R, Babu B, Reddy C, Reddy I, Reddy K, Rao M et al (2020) ZnO nanosheets-decorated Bi2WO6 nanolayers as efficient photocatalysts for the removal of toxic environmental pollutants and photoelectrochemical solar water oxidation. J Environ Manag 265:110504. https://doi.org/10.1016/j.jenvman.2020.110504
31. Shetti N, Malode S, Ilager D, Raghava Reddy K, Shukla S, Aminabhavi T (2019) A novel electrochemical sensor for detection of molinate using ZnO nanoparticles loaded carbon electrode. Electroanalysis 31(6):1040–1049. https://doi.org/10.1002/elan.201800775
32. Shetti N, Malode S, Nayak D, Reddy K (2019) Novel heterostructured Ru-doped TiO2/CNTs hybrids with enhanced electrochemical sensing performance for cetirizine. Mater Res Express 6(11):115085. https://doi.org/10.1088/2053-1591/ab4b92
33. Jansomboon W, Boonmaloet K, Sukaros S, Prapainainar P (2016) Rice hull micro and nanosilica: synthesis and characterization. Key Eng Mater 718:77–80. https://doi.org/10.4028/www.scientific.net/KEM.718.77
34. Lu P, Hsieh Y (2012) Highly pure amorphous silica nano-disks from rice straw. Powder Technol 225:149–155. https://doi.org/10.1016/j.powtec.2012.04.002
35. Mohd N, Wee N, Azmi A (2017) Green synthesis of silica nanoparticles using sugarcane bagasse. AIP Conf Proc 1885:1–7. https://doi.org/10.1063/1.5002317
36. Falk G, Shinde G, Teixeira L, Moraes E, de Oliveira A (2019) Synthesis of silica nanoparticles from sugarcane bagasse ash and nano-silicon via magnesiothermic reactions. Ceram Int 45:21618–21624. https://doi.org/10.1016/j.ceramint.2019.07.157
37. Sankar S, Sharma S, Kaur N, Lee B, Kim D, Lee S, Jung H (2016) Biogenerated silica nanoparticles synthesized from sticky, red, and brown rice husk ashes by a chemical method. Ceram Int 42:4875–4885. https://doi.org/10.1016/j.ceramint.2015.11.172
38. Vaibhav V, Vijayalakshmi U, Roopan S (2015) Agricultural waste as a source for the production of silica nanoparticles. Spectrochim Acta A 139:515–520. https://doi.org/10.1016/j.saa.2014.12.083
39. Espíndola-Gonzalez A, Martinez-Hernández A, Angeles-Chávez C, Castaño V, Velasco-Santos C (2010) Novel crystalline SiO_2 nanoparticles via annelids bioprocessing of agro-industrial wastes. Nanoscale Res Lett 5:1408–1417. https://doi.org/10.1007/s11671-010-9654-6
40. Ghorbani F, Younesi H, Mehraban Z, Çelik M, Ghoreyshi A, Anbia M (2013) Preparation and characterization of highly pure silica from sedge as agricultural waste and its utilization in the synthesis of mesoporous silica MCM-41. J Taiwan Inst Chem Eng 44:821–828. https://doi.org/10.1016/j.jtice.2013.01.019
41. Athinarayanan J, Jaafari S, Periasamy V, Almanaa T, Alshatwi A (2020) Fabrication of biogenic silica nanostructures from sorghum bicolor leaves for food industry applications. SILICON 12:2829–2836. https://doi.org/10.1007/s12633-020-00379-4
42. Balamurugan M, Saravanan S (2012) Producing nanosilica from *Sorghum vulgare* seed heads. Powder Technol 224:345–350. https://doi.org/10.1016/j.powtec.2012.03.017
43. Sivakumar G, Amutha K (2012) Studies on silica obtained from cow dung ash. Adv Mater Res 584:470–473. https://doi.org/10.4028/www.scientific.net/AMR.584.470
44. Wassie A, Srivastava V (2017) Synthesis and characterization of nano-silica from Teff straw. J Nano Res 46:64–72. https://doi.org/10.4028/www.scientific.net/JNanoR.46.64
45. Yadav V, Fulekar M (2019) Green synthesis and characterization of amorphous silica nanoparticles from fly ash. Materials Today: Proceedings 18:4351–4359. https://doi.org/10.1016/j.matpr.2019.07.395
46. Yan F, Jiang J, Li K, Liu N, Chen X, Gao Y, Tian S (2017) Green synthesis of Nanosilica from coal fly ash and its stabilizing effect on CaO sorbents for CO_2 capture. Environ Sci Technol 51:7606–7615. https://doi.org/10.1021/acs.est.7b00320
47. Sarikaya M, Depci T, Aydogmus R, Yucel A, Kizilkaya N (2016) Production of nano amorphous SiO_2 from Malatya pyrophyllite. IOP Conf Ser Earth Environ Sci 44:052004
48. Zulfiqar U, Subhani T, Husain S (2016) Synthesis and characterization of silica nanoparticles from clay. J Asian Ceram Soc 4:91–96. https://doi.org/10.1016/j.jascer.2015.12.001
49. Mourhly A, Khachani M, Hamidi A, Kacimi M, Halim M, Arsalane S (2015) The synthesis and characterization of low-cost mesoporous silica SiO_2 from local Pumice rock. Nanomater Nanotechnol 5:35. https://doi.org/10.5772/2F62033
50. Stopic S, Dertmann C, Koiwa I, Kremer D, Wotruba H, Etzold S, Telle R, Knops P, Friedrich B (2019) Synthesis of nanosilica via Olivine mineral carbonation under high pressure in an autoclave. Metals 9:708. https://doi.org/10.3390/met9060708
51. Babu R, Yugandhar P, Savithramma N (2018) Synthesis, characterization and antimicrobial studies of bio silica nanoparticles prepared from *Cynodon dactylon* L.: a green approach. Bull Mater Sci 41:65. https://doi.org/10.1007/s12034-018-1584-4
52. Sethy N, Arif Z, Mishra P, Kumar P (2019) Synthesis of SiO2 nanoparticle from bamboo leaf and its incorporation in PDMS membrane to enhance its separation properties. J Polym Eng 39:679–687. https://doi.org/10.1515/polyeng-2019-0120
53. Durairaj K, Senthilkumar P, Velmurugan P, Dhamodaran K, Kadirvelu K, Kumaran S (2019) Sol-gel mediated synthesis of silica nanoparticle from *Bambusa vulgaris* leaves and its environmental applications: kinetics and isotherms studies. J Sol-Gel Sci Technol 90:653–664. https://doi.org/10.1007/s10971-019-04922-7
54. Jabeen N, Maqbool Q, Sajjad S, Minhas A, Younas U, Anwaar S, Nazar M, Kausar R, Hussain S (2017) Biosynthesis and characterisation of nano-silica as potential system for carrying streptomycin at nano-scale drug delivery. IET Nanobiotechnol 11:557. https://doi.org/10.1049/iet-nbt.2016.0106
55. Al-Azawi MT, Hadi SM, Mohammed CH (2019) Synthesis of silica nanoparticles via green approach by using hot aqueous extract of *Thuja orientalis* leaf and their effect on biofilm formation. Iraqi J Agric Sci 50:245–255. https://doi.org/10.36103/ijas.v50iSpecial.196

56. Irzaman XX, Oktaviani N, Irmansyah XX (2018) Ampel bamboo leaves silicon dioxide (SiO_2) extraction. IOP Conf Ser Earth Environ Sci 141:012014
57. Yusaidi N, Abdullah S, Zarib N (2019) Structural analysis of silica extract from banana stems via acid leaching under different reaction time. Int J Eng Adv Technol 9:5858–5862
58. Agunsoye JO, Adebisi JA, Bello SA, Haris M, Agboola JB, Hassan SB (2018) Synthesis of silicon nanoparticles from *Cassava periderm* by reduction method. Contributed papers from materials science and technology, pp 701–709
59. Anuar M, Fen Y, Zaid M, Matori K, Khaidir R (2018) Synthesis and structural properties of coconut husk as potential silica source. Results Phys 11:1–4. https://doi.org/10.1016/j.rinp.2018.08.018
60. Pal S, Tak Y, Song J (2007) Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticle? A study of the gram-negative bacterium *Escherichia coli*. Appl Environ Microbiol 73:1712–1720
61. Pugazhenthiran N, Anandan S, Kathiravan G, Udaya Prakash N, Crawford S, Ashok kumar M, (2009) Microbial synthesis of silver nanoparticles by *Bacillus* sp. J Nanopart Res 11:1811–1815. https://doi.org/10.1007/s11051-009-9621-2
62. Vetchinkina E, Loshchinina E, Kupryashina M, Burov A, Nikitina V (2019) Shape and size diversity of gold, silver, selenium and silica nanoparticles prepared by green synthesis using fungi and bacteria. Ind Eng Chem Res 58:17207–17218. https://doi.org/10.1021/acs.iecr.9b03345
63. Singh S, Bhatta U, Satyam P, Dhawan A, Sastry M, Prasad B (2008) Bacterial synthesis of silicon/silica nanocomposites. J Mater Chem 18:2601–2606. https://doi.org/10.1039/B719528A
64. Show S, Tamang A, Chowdhury T, Mandal D, Chattopadhyay B (2014) Bacterial (BKH1) assisted silica nanoparticles from silica rich substrates: a facile and green approach for biotechnological applications. Colloids Surf B 126:245–250. https://doi.org/10.1016/j.colsurfb.2014.12.039
65. Liu F, Yang W, Wang Y, Xue X, Yang H (2014) Photochemical synthesis of silica nanoparticles. Chem Lett 43:720–722. https://doi.org/10.1246/cl.131133
66. Zamani H, Jafari A, Mousavi S, Darezereshki E (2020) Biosynthesis of silica nanoparticle using *Saccharomyces cervisiae* and its application on enhanced oil recovery. J Petrol Sci Eng 190:107002. https://doi.org/10.1016/j.petrol.2020.107002
67. Pieła A, Żymańczyk-Duda E, Brzezińska-Rodak M, Duda M, Grzesiak J, Saeid A, Mironiuk M, Klimek-Ochab M (2020) Biogenic synthesis of silica nanoparticles from corn cobs husks. Dependence of the productivity on the method of raw material processing. Bioorg Chem 99:1073. https://doi.org/10.1016/j.bioorg.2020.103773
68. Bansal V, Rautaray D, Bharde A, Ahire K, Sanyal A, Ahmad A, Sastry M (2005) Fungus-mediated biosynthesis of silica and titania particles. J Mater Chem 15:2583–2589. https://doi.org/10.1039/B503008K
69. Bansal V, Sanyal A, Rautaray D, Ahmad A, Sastry M (2005) Bioleaching of Sand by the fungus *Fusarium oxysporum* as a means of producing extracellular silica nanoparticles. Adv Mater 17:889–892. https://doi.org/10.1002/adma.200401176
70. Bansal V, Ahmad A, Sastry M (2006) Fungus-mediated biotransformation of amorphous silica in rice husk to nanocrystalline silica. J Am Chem Soc 128:14059–14066. https://doi.org/10.1021/ja062113+
71. Rohatgi K, Prasad S, Rohatgi P (1987) Release of silica-rich particles from rice husk by microbial fermentation. J Mater Sci Lett 6:829–831. https://doi.org/10.1007/BF01729027
72. Zielonka A, Żymańczyk-Duda E, Brzezińska-Rodak M, Duda M, Grzesiak J, Klimek-Ochab M (2018) Nanosilica synthesis mediated by *Aspergillus parasiticus* strain. Fungal Biol 122:333–344. https://doi.org/10.1016/j.funbio.2018.02.004
73. Estevez M, Vargas S, Castaño V, Rodriguez R (2009) Silica nanoparticles produced by worms through a bio-digestion process of rice husk. J Non-Cryst Solids 355:844–850. https://doi.org/10.1016/j.jnoncrysol.2009.04.011
74. Kaur T, Singh G, Kaur G, Kaur S, Gill P (2016) Synthesis of biogenic silicon/silica (Si/SiO_2) nanocomposites from rice husks and wheat bran through various microorganisms. Mater Res Express 3:085026
75. Yepez A, Prinsen P, Pineda A, Balu AM, Garcia A, Lam FLY, Luque R (2018) A comprehensive study on the continuous flow synthesis of supported iron oxide nanoparticles on porous silicates and their catalytic applications. Reac Chem Eng 3:757–768. https://doi.org/10.1039/C8RE00063H
76. Jundale R, Bari A, Thara C, Kulkarni A (2018) Continuous flow synthesis of micron size silica nanoparticles: parametric study and effect of dosing strategy. J Flow Chem 8:59–67. https://doi.org/10.1007/s41981-018-0008-3
77. Liu Z, Zhu J, Peng C, Wakihara T, Okubo T (2019) Continuous flow synthesis of ordered porous materials: from zeolites to metal-organic frameworks and mesoporous silica. React Chem Eng 4:1699–1720. https://doi.org/10.1039/C9RE00142E
78. Wacker JB, Lignos I, Parashar VK, Gijs MAM (2012) Controlled synthesis of fluorescent silica nanoparticles inside microfluidic droplets. Lab Chip 12:3111. https://doi.org/10.1039/C2LC40300E
79. Al-Kattan A, Nirwan VP, Popov A, Ryabchikov YV, Tselikov G, Sentis M, Fahmi A, Kabashin AV (2018) Recent advances in laser- ablative synthesis of bare Au and Si nanoparticles and assessment of their prospects for tissue engineering applications. Int J Mol Sci 19:1563. https://doi.org/10.3390/ijms19061563
80. Díaz de Greñu B, de Reyes R, Costero AM, Amorós P, Ros-Lis JV (2020) Recent progress of microwave-assisted synthesis of silica materials. Nanomaterials 10:1092. https://doi.org/10.3390/nano10061092

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