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REVIEW ARTICLE

Cyanobacteria as biochemical energy source for the synthesis of inorganic nanoparticles, mechanism and potential applications: a review

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Abstract

Green synthesis of nanoparticles (NPs) has gained great concern among researchers due to their unique properties, excellent applications and efficient route of synthesis. From the last decades, the number biologicals such as plants, fungus, bacteria, yeast, algae, and cyanobacteria and their products are using by various researchers for the synthesis of different NPs. However, the pillar of green chemistry keeps touching new heights to improve the performance. This review paper unveils almost recent cyanobacteria-assisted greener NP synthesis technique, characterization and application. The enormous potency of cyanobacteria in NP synthesis (silver, gold, copper, zinc, palladium, titanium, cadmium sulfide, and selenium) and significance of reducing enzymes were summarized. The extracellular and intracellular entity such as metabolites, enzyme, protein, pigments in cyanobacteria play a significant role in the conversion of metal ions to metal NPs with unique properties discussed briefly. The green synthesis of nanomaterials is valuable because of their cost-effective, nontoxic and eco-friendly prospects as well as the potential application metal NPs such as antibacterial, antifungal, anticancerous, catalytic, drug delivery, bioimaging, nanopesticide, nanofertilizer, sensing properties, etc. Therefore, in the present review, we have systematically discussed the mechanisms of synthesis and applications of cyanobacteria-assisted green synthesis of NPs.

Keywords Cyanobacteria · Green synthesis · Extracellular NPs · Intracellular NPs · Application of NPs

Abbreviations

AAS	Atomic absorbance spectrometry
AFM	Atomic force microscopy
Ag	Silver
AgNPs	Silver nanoparticles
Au	Gold
BET	Brunauer–Emmett–Teller
BGA	Blue Green algae
CdS	Cadmium sulfide
CFU	Colony forming unit
C-PE	C-phycoerythrin
Cu	Copper
CuO	Copper oxide
DLS	Dynamic light scattering
DNA	Deoxyribonucleic acid
EDX	Energy-dispersive X-ray spectroscopy
EELS	Electron energy-loss spectroscopy
ESBL	Spectrum beta lactamases
FTIR	Fourier-transform infrared spectroscopy
IC-50	Inhibitory concentration
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively couple plasma optical emission spectrometry
MB	Methylene blue
MBC	Minimum bactericidal concentration
MIC	Minimum inhibitory concentration
NAD^+	Nicotinamide adenine dinucleotide
NMs	Nanomaterials
NPs	Nanoparticles
Pd	Palladium
Pt	Platinum
ROS	Reactive oxygen species
Se	Selenium
SEM	Scanning electron microscope
TEM	Transmission electron microscopy

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TiO_2	Titanium dioxide
XRD	X-ray diffraction
Zn	Zinc
ZnO	Zinc Oxide

Introduction

Nanotechnology is the emerging and multiperspective field holding study, design, manipulation and synthesis of ultrafine nanomaterials (NMs) for multipurpose applications for the human welfare. The term "nano" has been derived from a Greek word factually means the dwarf or small, ranging from 1 to 100 nm dimensions (Bhardwaj et al. 2021a; Khan et al. 2019). NPs have attracted considerable attention from the past few decades, owing to their unique physical and chemical properties related to optical, electrical, catalytic and biomedical efficiencies (Bhardwaj et al. 2018; Burda et al. 2005; Liz-Marzán 2004). In current age, NPs consider as a potential solution for several technological and environmental confront in the field of bio-sensing, medical, clinical, solar energy harnessing and water treatment strategies of human benefits (Cohen-Karni et al. 2012). These potential applications of NPs are considerably possible due to their exclusive characteristics of high surface volume ratio and nanoscale dimensions (Brayner et al. 2010). Generally, NPs may develop and exist in several forms of nanostructures with diverse dimensions such as 0D, 1D, 2D and 3D arrays in a controlled manner (Bhardwaj et al. 2021b; Sengupta et al. 2015).

Owing to the broader range of novel applications, NPs are experimentally synthesized via different techniques of physical, chemical and biochemical routes (Bhardwaj et al. 2021a). Various methods for the synthesis of nanomaterials (NMs) include laser ablation, co-precipitation, microwave-assisted, photochemical, hydrothermal, etc., which are broadly categorized into a top down and bottom-up approaches based on the origin of NMs (Bhardwaj et al. 2017b; Singh et al. 2012; Singh et al. 2018a, b). Such methods employed for the synthesis and stabilization of different kind NPs are executed using physical, chemical and biological processes (Bhardwaj et al. 2019a; Maurya et al. 2016). The laser ablation and evaporation condensations of the physical method of synthesis are the most preferably used. However, they have several drawbacks such as expensive production, lower yields, energy consuming and time-consuming synthesis (Bhardwaj et al. 2019b; Singh et al. 2010). Similarly, the direct involvement of noxious chemicals during chemical synthesis of nanomaterials is damaging to the environment and living creatures, which can never be part of the eco-friendly policy. Therefore, keeping view of the above-mentioned concerns, the research has been oriented towards the wide consideration of biogenic or biological approaches using microorganisms including algae, bacteria, fungi, yeast, etc., different parts of higher plants and animals for the green synthesis of NPs (Bhardwaj et al. 2018; Katas et al. 2019; Sanjivkumar et al. 2019; Tomer et al. 2019). These synthesis approaches are non-toxic, economical, biocompatible, environmentally benign and uncomplicated establishing green synthesis (Naraian and Bhardwaj 2020). Earlier reports showed that among the prospective of several methods; green synthesis of NPs with the exploitation of cyanobacteria is inadequate that has not yet been furnished surprisingly. Whereas, the cyanobacteria are the potential bioactive compounds can regard full considered as prospective of unique bio-factories exerting the biosynthesis of metal NPs (Elsayed et al. 2018; Gowramma et al. 2015). Several cyanobacterial species and their culture extracts exhibiting enzymes and unusual biomolecules have strong potency to react for the reduction of desired precursors (metal ions) and consequently synthesizing the green NPs (Li et al. 2021). The cyanobacteria-assisted synthesis of NPs can be performed both through extracellularly and intracellularly reducing metals (gold, silver, copper, platinum, palladium, zinc, selenium, etc.) have reported by several scientists (Mahdieh et al. 2012; Ramkumar et al. 2017; Pathak et al. 2019). Primarily synthesis of gold nanoparticles using extracellular enzymes extracted from marine algae *Sargassum wightii* and *Kappaphycus alvarezii* have been reported Singaravelu et al. 2007; Rajasulochana et al. 2010). Similarly, *Tetraselmis kochinensis* and *Spirulina platensis*, the potent species of algae, were reported for the intracellular synthesis of gold NPs and silver NPs, respectively (Senapati et al. 2012; Sudha et al. 2013). The culture extract too can convert and reduce the metal ion (M^+) to a zero-valent ion (M^0) using a reductase, the electron is shuttled to quinine in an extracellular environment (Durán et al. 2005). Besides the organism also has the potential to bio-transform metals in the presence of an enzyme NADH-dependent reductase in intracellular circumstances (Kumar et al. 2007). Therefore, the present review article is fully devoted to the detailed account related to the use of different cyanobacteria in the biosynthesis of various NPs and their effective applications for the eco-friendly benefits to human beings.

The potency of cyanobacteria for the green synthesis of nanoparticles

Cyanobacteria are the most primitive photosynthesizing prokaryotic autotrophs ubiquitous in nature found distributed in different parts of the globe including oceans, rivers, estuaries, lakes, swamps, tropical rain forests, hot springs, deserts, glaciers and dry valleys of Antarctica (Durall and Lindblad 2015). It is also believed that cyanobacteria primarily played a very significant role in the phenomenon of the transformation of the Earth's atmosphere from its initial anaerobic state into current aerobic conditions. They exhibit variable shape, size, and unique cell morphology along with unique diversity of pigments as well as a highly noticeable vast variety of metabolic pathways (Heidorn et al. 2011). Their biochemical processes and specific adaptations such as their resistance to drying and potential of nitrogen fixation make them very elastic and enable them to survive under diversified habitats; therefore, they have great advantages over other organisms.

Moreover, cyanobacteria also have a peculiar capacity to shift towards mixotrophic nutrition depending on the ingredients available in the surrounding nutrient medium (Dale and Sanders 2020). In the meantime, cyanobacteria as mixotrophs metabolizes both organic and inorganic substances and the reducing power of protoplasmic enzymes may lead synthesis of desired NPs intracellularly. Additionally, cyanobacterial culture extracts contain several pigments like phycocyanin, C-phycoerythrin as well as several polysaccharides and proteins with the inherent capability to reduce metal ions to zero-valent metal and metal oxide NPs (El-Naggar et al. 2017). Patel et al. (2015) synthesized spherical and spherically elongated silver NPs employing the phycocyanin extracted, respectively, from two cyanobacteria *Limnothix* sp. and *Spirulina* sp. Similarly, CdS NPs were also synthesized using isolated pigment C-phycoerythrin (C-PE) from a marine cyanobacterium, *Phormidium tenue* NTDM05.

For NP synthesis, researchers use cyanobacterial culture in the required volume of grown in appropriate media such as BG-11, Zarrouk growth medium (Stanier et al. 1971) and followed by illuminated with about 2000 lx, for 12 h day and night cycles (Rippka et al. 1979). For large-scale biomass production further, sub-culturing is performed and produced cyanobacterial biomass is subjected to proper washings with demineralized water before freeze-drying (lyophilization) storage. These certain amounts of dried mass crushed using mortar and pestle and finally mixed with distilled water in the required amount to store for a few hours at below 45 °C. Thereafter, the extract is filtered through Whatman filter No. 4. The culture filtrate (extract) thus obtained now become ready to use in the synthesis process of various kind of metal-based NPs.

Green synthesis of NPs

Synthesis of cyanobacteria-assisted silver NPs

Biosynthesis of silver nanoparticles using *Westiellopsis* sp. (A15), a filamentous cyanobacterium belonging to the family *Fischerellaceae*, has been demonstrated (Lakshmi et al. 2015). Aqueous silver ions (Ag^{+}), when exposed to the culture filtrate of Westiellopsis, were reduced in the solution, which was characterized by biophysical techniques employing the UV–Vis spectroscopy, scanning electron microscopy (SEM), and FTIR. The nanoparticles exhibited the maximum absorbance at 420 nm in UV–Vis spectroscopy, while the SEM micrograph revealed that the aggregated nanoparticles vary in size between 20 nm and 5 µm. However, the FTIR analysis provided evidence for the presence of proteins in the filtrate to be involved in the reduction of silver ions (Lakshmi et al. 2015). Recently, Husain et al. (2021a) synthesized silver NPs with average size 30 nm using *Nostoc muscorum* NCCU 442 and further employed for antibacterial and antioxidant activity against *Staphylococcus aureus* MTCC 902. Again, Husain et al. (2021b) reported synthesis of silverNPs with smaller sive 7 nm using aqueous extract of cyanobacteria *Microchaete* which further suggested as antioxidant, anti-proliferative, and apoptotic activities against HepG2 and MCF-7 cell lines, the IC50 of the AgNPs reported as 75 µg/ml and 79.41 µg/ml. Several other reports of silver NPs synthesized from different strain of cyanobacteria mentioned in Table 2

Synthesis of cyanobacteria-assisted Gold NPs

The synthesis of gold nanoparticles employing cyanobacterial culture has been also attempted by Parial et al. (2016). They used freshly collected culture several cyanobacterial samples, washed them and treated with 15 ppm solution of hydrogen tetrachloroaurate under suitable conditions with different levels of pH (pH 5, pH 7 and pH 9) and incubation at 20˚C 72 h. They found that the color of few screened cyanobacteria (*Phormidium valderianum*, *Phormidium tenue* and *Microcoleus chthonoplastes*), thallus changed from green to purple, which is characteristic of intracellular synthesis of gold NPs. Finally, gold NPs extracted from biomass through sonicating with 7.5 nM sodium citrate for a half hour Parial et al. (2016). Recently, cyanobacterial strain of *Synechocystis* sp. PCC 6803 used for the intracellular synthesis of gold NPs via bioelectrochemical reduction (Liu and Choi 2021). This intracellular synthesis of gold NPs behaves as cyanobacterial biophotovoltaics which able to enhance the maximum power density up to 33.6 times in compare control or normal *Synechocystis* sp. PCC 6803 cells. Various intracellular and extracellular gold NPs synthesized from different strain of cyanobacteria are mentioned in Table 2.

Synthesis of cyanobacteria-assisted some other metal NPs

Except for silver and gold synthesis using cyanobacteria, several other NPs came in considerable attraction over the few years; however, several workers attempted to synthesize NPs employing cyanobacterial cultures, which can reduce several metal ions and form NPs. Most of the available reports are focused to synthesize silver- and gold-assisted NPs but these sections discuss the studies other than silver and gold such as zinc oxide, selenium, platinum, cadmium, copper and palladium. Recently, Davaeifar et al. (2019) isolated bioactive compound C-Phycocyanin pigment from native cyanobacterium *Limnothrix* sp. KO05 strain and utilized it for the synthesis of the rod-shaped zinc oxide NPs. The pigment-based reduction of ZnO NPs have a small size, surface feature and can efficiently penetrate, which shows moderate toxicity to extended-spectrum beta lactamases (ESBL) producing bacteria *E. coli, P.aeruginosa,* and methicillin-resistant bacterium *Staphylococcus aureus*. Furthermore, Zinicovscaia et al. (2016) reported that cyanobacterium *Arthrospira platensis* applied for the removal of selenium from water (with 21 mg/l and 210 mg/l) with maximum absorption within 5 min and as a result, the selenium ions were reduced inside the cyanobacterial cell in the form of NPs. MubarakAli et al. (2012) reported that the C-phycoerythrin extracted from the marine cyanobacterium, *Phormidium tenue* NTDM05 was used to synthesize cadmium sulfide (CdS) NPs. The extracellular synthesis and stabilizing of copper oxide NPs (with particle size ranges10–40 nm) using *Phormidium cyanobacterium* was effectively performed by (Rahman et al. 2009a, b). Moreover, the intracellular synthesis of platinum spherical (Pt) NPs with cyanobacterial (*Plectonema boryanum* UTEX 485) cells under appropriate conditions of 25 – 100 °C for 28 days and 180 °C for 1 day has been promptly performed (Lengke et al. 2006). Likewise, palladium (Pd)-based NPs were intracellularly prepared to exhibit spherical and elongate shape with size ≤ 30 nm inside the cells (Lengke et al. 2007b). Brayner et al. (2007) attempted with *Calothrix* for the intracellular synthesis of Pt and Pd NPs. They also used *Anabaena, Leptolyngbya* for the synthesis of gold and silver NPs and advocated that the nitrogenase enzyme was responsible for this reduction.

Mechanism of cyanobacteria mediated nanoparticles biosynthesis

Extracellular synthesis mechanism of nanoparticles

During the extracellular synthesis of NPs, the extracellular secretions (culture filtrate) of the cyanobacterial population collects and use for synthesis of NMs. Cells typically exhibit resistance to metal ions and generally tend to produce metal NPs efficiently. The toxic characteristics of individual metals vary from organism to organism and different cyanobacterial strain. Lengke et al. (2007a) reported that *Plectonema boryanum UTEX 485* culture was used for the reduction of Ag^+ into Ag^0 extracellular (1–200 nm diameter) and intracellular (< 10 nm diameter).

Though the actual mechanism of cyanobacteria-assisted synthesis of NPs is unclear, it is proposed that the reduction of Ag^+ ions takes place through a combination of biomolecules such as enzymes, proteins, amino acids, polysaccharides, vitamins, etc. particularly found in culture extracts (Bhardwaj et al. 2017a, b; Roychoudhury et al. 2016). Cyanobacteria usually intake nitrate as the main source of nitrogen content (Suzuki et al. 1995) to carry out the use of nitrate for three different purposes, including growth, generation of metabolic energy and redox equilibrium (Moreno-Vivián et al. 1999). Ionic dissociation of silver ions and nitrate allows entry inside cyanobacterial cells through transport system mentioned as below:

$$AgNO_3 \rightarrow Ag^+ + NO_3^- \tag{1}$$

According to Lengke et al. (2007a) initially, the cyanobacterial metabolic process produces nitrite from the reduction of nitrate (NO_2^-) and then form ammonium (NH_4^+), as represented by the following reactions:

$$NO_3^- + 2H^+ + 2e^- \leftrightarrow NO_2^- + H_2O \tag{2}$$

$$NO_2^- + 8H^+ + 6e^- \leftrightarrow NH_4^+ + 2H_2O \tag{3}$$

Consequently, ammonium is fixed as the amide group of glutamine; which factually means that the nitrate is metabolically assimilated by the cells during glutamine formation Suzuki et al. (1995), while Nies and Silver (1995) explained that silver ions are reduced by intracellular electron donors or exported by a membrane transporter system. The schematic diagram of the mechanism is represented in Fig. 1.

Intracellular synthesis mechanism of nanoparticles

Cyanobacteria significantly stand as a promising green source for the synthesis of a different kind of metal-based NPs. As it is obvious that all organisms do not exhibit the ability to convert metals into nanoforms, some members of cyanobacteria have excellent potential for the synthesis of metal NPs both under intracellular or extracellular modes. During intracellular synthesis, the metal ions enter and accumulate inside to the cyanobacterial cells, where they are nucleated through a reduction system while cell growth runs normally. The intracellular reduction of metal ions comprises a multistep including (a) capture of ions on the cell surface (b) entry and arrest of ions inside the cells (c) reduction of ions with the action of reducing enzyme. Sneha et al. (2010) discussed the mechanism of silver and gold-based NPs employing an algal *verticillum* sp. They hypothesized very remarkable and essential step as; (a) capture of

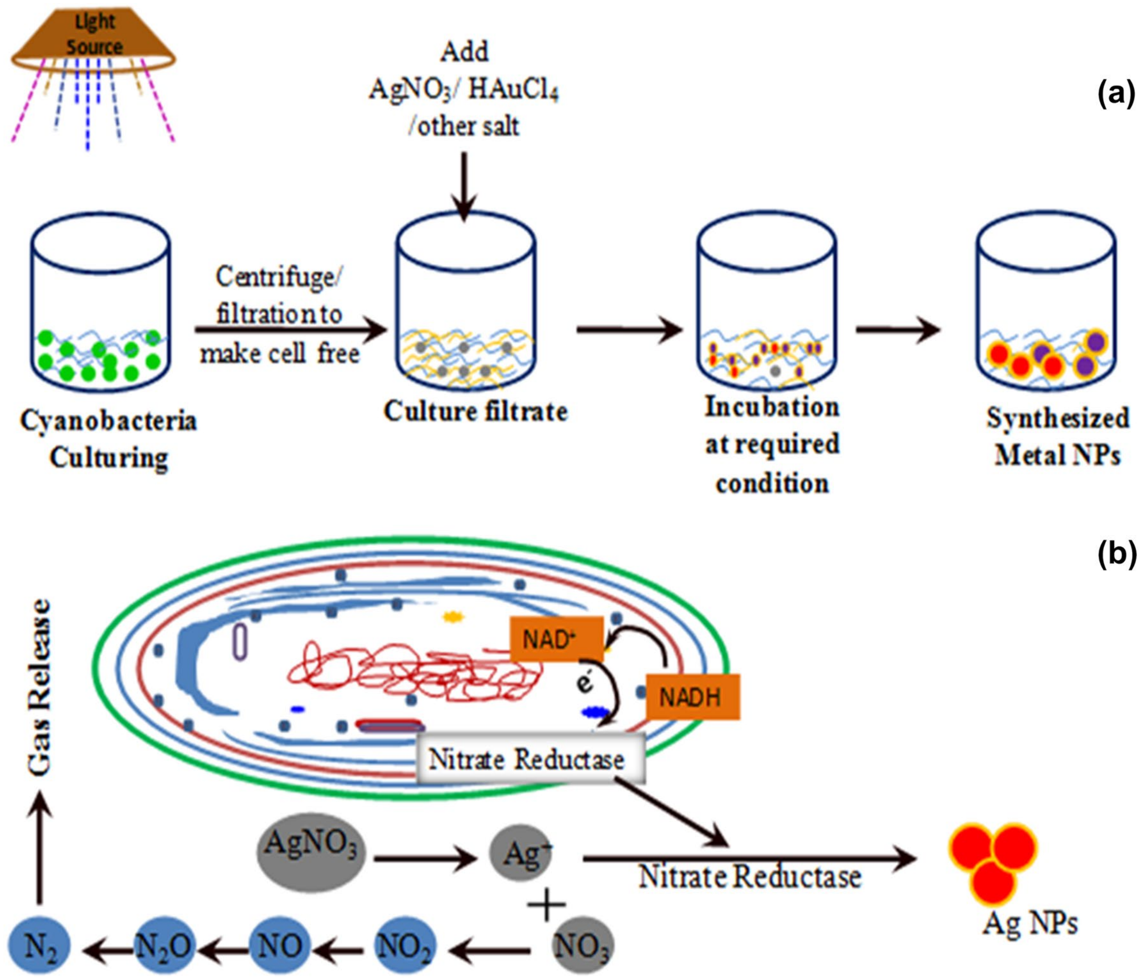

Fig. 1 Cyanobacteria-assisted **a** extracellular synthesis of NPs with the help of enzyme in aqueous medium where it react with respected salt, **b** mechanism of NPs (gold and silver) synthesis in presence of nitrate reductase

silver or gold ions on the cell surface through electrostatic interaction between ions and negatively charged cell wall (b) Bioreduction of silver and gold ions with the key role of NADH- and NADH-dependent nitrate reductase enzyme (Singh et al. 2018a, b). Thereafter, NPs with living cells are harvested after the optimal time for growth. The harvested cells require special treatment to release the intracellularly synthesized NPs. Several authors have made significant attempts to synthesize the verity of NPs with the employment of cyanobacterial cultures of versatile utility.

Bakir et al. (2018), Chakraborty et al. (2009) recovered gold from Batch laboratory experiments, indicating that gold (III) ions with rapid and metabolic intake are observed into the *S. Subsala* and *L. majuscule* cells and actively converted in the form of gold NPs resulting in the turn of color purple. The intracellular synthesis of NPs happens due to presence of various intracellular metabolites inside the cynobacterial cells of *Spirulina subsalsa* and *Lyngbya majuscule*. Similarly, Focsan et al. (2011) also reported the synthesis of gold NPs (size 13 ± 2 nm) inside the cyanobacterium *Synechocystis* sp. PCC 6803. The NPs were seen in the cyanobacterial cell wall, plasma membrane, and into the cytoplasm. Recently, has been observed that the biologically selective uptake and intracellular synthesis of gold NPs (10 nm) when the equal concentration of gold, iridium, and rhodium (0.1 mM each) was treated to cyanobacteria *A. cylindrical* at nontoxic level (Rochert et al. 2017). The intracellular synthesis of metal NPs (silver, gold, platinum, etc.) is not fully understood, while few workers speculated that electrons generated through photosynthesis and respiration might be the reason for the conversion of metal ions into zero-valent ions**.** Cyanobacteria can utilize photosynthesis and respiration of several redox-active ingredients like $NADPH_2$- (nicotinamide adenine dinucleotide phosphate) and NADH-dependent reductase in thylakoids (Mahdieh et al. 2012). The reduced cofactor is oxidized during the reduction process and re-circulated by the energy generation reaction. Photosynthetic electron transport, respiratory electrons are an important factor in the synthesis of MNPs which have already proposed for the synthesis of gold NPs using cyanobacteria *Synechocystis* sp. (Focsan et al. 2011), bacteria *Rhodopseudomonas capsulate* (He et al. 2007) and fungi *Fusarium oxysporum* (Senapati et al. 2005). Metal NPs can also accumulate over cyanobacterial cell wall due to (a) the affinity of formed metal NPs for sulfur atom in cysteine or methionine compound present in the outer membrane (b) presence of a carboxyl group, polyphosphates and polysaccharides in the cyanobacterial cell membrane, which may lead to participating in the reduction of metal ion (Fig. 2).

Characterization of biosynthesized NPs

The multidimensional characterization becomes essential to understand the composition, dimension and surface nature of cyanobacterial assisted synthesis of NPs to determine suitability to an appropriate application in multidisciplinary sector. Therefore, the synthesis of NMs is followed by characterizations of NMs to evaluate variable aspect such as size distribution and aggregation (aggregate structure, mechanism and kinetics of nanostructure), surface (charge, chemistry, specific area etc.), morphology (shape, crystal structure and purity), solubility, dissolution rate and leaching are represented in Table 1. Since the particle size is inversely proportional to surface area and volume ratio, it allows tunable interaction between the materials and its surroundings (Bhardwaj et al. 2019a). Thus, the size and surface area of NMs are primary and highly influential characteristics of NMs. The size, shape, surface and structural characteristics of the materials are important factors because these provide important information for properly understanding the behavior of NPs, which helps to decide their appropriate applications. Several spectroscopic, microscopic, chromatographic, and separation techniques are necessarily used to

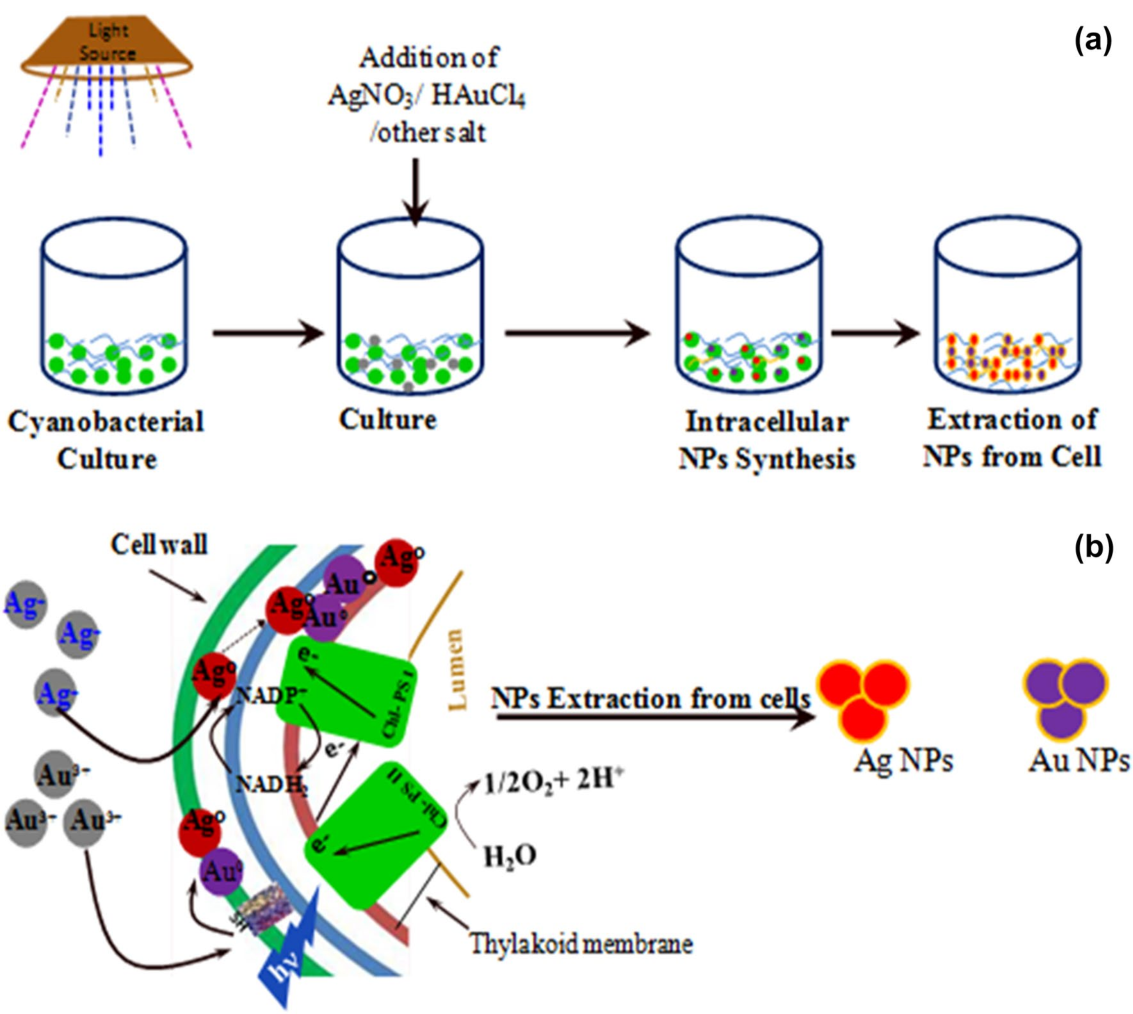

Fig. 2 Cyanobacteria-assisted **a** intracellular synthesis of NPs after uptake of respected salt precursor, **b** mechanism of NPs (gold and silver) synthesis within a cyanobacterial cell

Table 1 Efficient techniques for the characterization of cyanobacteria-assisted synthesized nanomaterials reported in numerous recent studies

Techniques	Variants and method	Expected observations with different parameter analyzed	References
Spectroscopy	UV–VIS Spectroscopy	Size and surface plasmon resonance explains the expected NPs size distribution, orientation and surface plasmon resonance range	Haiss et al. (2007), Bhardwaj et al. (2018)
	FTIR	Surface moiety of prepared NPs are detected the presence of functional group over the surface of NPs	Alvarez et al. (2000)
	ICP-MS, ICP-OES, AAS	Concentration of NPs and their ions leaching in drinking water calculates total elemental composition of nanomaterials	Bojdi et al. (2014)
	EDX	Semi-quantitative elemental composition and mapping for single particles with accurate and fast. Single particle elemental information	Shukla et al. (2017), Lewis et al. (2014)
	XPS	Chemical composition of NPs recognizes the biomolecules that bound specifically on the gold surface	Xie et al. (2007)
	EELS	Elemental and chemical information of NPs can observe single particle chemical information	Koh et al. (2009)
Microscopy	SEM	Size, shape and surface structure of NPs with high resolution. 3D images	Mallikarjuna and Varma (2007)
	TEM	Size, shape and internal structure of NPs with high resolution 2D images	Bhardwaj et al. (2018)
	AFM	Surface area and surface relief suggests thickness of gold nanoplates and surface area	Xie et al. (2007)
Others	DLS	Hydrodynamic diameter measures the particles distribution in solution phase	Khan et al. (2019)
	BET	Specific surface area/porosity explains direct measure of surface area high with precision	Grassian (2008)
	XRD	Crystal structure and crystallite size states the detailed crystallographic information	Shukla et al. (2018)

characterize the NMs to collect morphological, structural, quantitative and qualitative information that can help to further exploitation in the field of energy, medical, clinical and environment. Such techniques are also helping to understand enzymatic systems of cyanobacteria that act over the ions (precursor) for the conversion of stabilized NPs and their stabilization (El-Naggar et al. 2017).

Potential applications of cyanobacteria-assisted NPs

Scientists working in the field of nanotechnology have a great opportunity toward the green synthesis of nanomaterials exploiting several cyanobacterial strains. The account of cyanobacteria-assisted synthesis of various NPs and their studied application shown in Table 2. Since the nanostructures have unique properties, they permit regeneration of new and advanced perspectives such as drug delivery, optoelectronics, bio-sensing, bio-labeling, antibacterial along the development of biomedical devices, storage of food and beverages shown in Fig. 3 (Bhardwaj et al. 2018; MubarakAli et al. 2012).

As an antibacterial agent

The cyanobacteria-assisted synthesis of metal NPs has achieved a landmark in the progress of antibacterial prospects in the form of NMs. This could have been possible due to the large surface area of NMs that provide better adherence with microbial cells in comparison to the larger (bulk) particles of the same parent material. Several workers have been attempted NPs confirming their potent antibacterial nature. The particle size of silver NPs dependent bacterial killing efficacy was proved by Patel et al. (2015). The AgNPs synthesized using different strains of cyanobacteria (*Anabaena* sp. 66-2, *Cylindropermopsis* sp. USC-CRB3, *Limnothrix* sp.15-2, *Synechococcus* sp. 145-6, Lyngbya sp. 48-3, Synechocystis) showed that the antibacterial activity was found inhibitory to many bacterial strains viz., *B. megaterium, B. subtilis, E, coli, M. luteus, P. aeruginosa, S. aureus.* However, a cyanobacterium Limnothrix assisted synthesized silver nanoparticles (Ag NPs) found ineffective against all bacterial strain. Silver NPs synthesized using the culture extract of cyanobacteria *Nostoc* sp. strain HKAR-2 employed for complete inhibition of bacterial cells of *Ralstonia solanacearum* and *Xanthomonas campestris* besides it was also inhibitory for two fungal sp. *Aspergillus niger*

Table 2 Recent studies of different cyanobacteria-assisted extracellular and intracellular synthesis of various NPs and their unique applications

SN	Cyanobacterial strains	Nanoparticles	Size of NPs (nm)	Applications	References
1	*Synechocystis* sp. PCC 6803	Gold	–	Effective light-absorber to increase photo-excited electrons which help to electron transfer through the cell membrane	Liu and Choi (2021)
2	*Cylindrospermum stagnale*	CuO	12.21 nm	Antimicrobial activity against pathogens *Candida albicans*, *Klebsiella pneumoniae*, *Enterobacter cloacae*, *Pseudomonas aeruginosa*, *Escherichia coli*, as MICs of 1.5, 2.4, 1.7, 2.5, and 0.6 mM respectively Cytotoxic against HepG2 cell line and effective against larvae of *Aedes ageypti*, *Anopheles subpictus* Grassi and *Culex quinquefasciatus* also observed	Sonbol et al. (2021)
3	*Nostoc muscorum NCCU 442*	Silver	30 nm	Biological activities of as Antioxidant and antibacterial potential of purified AgNPs found the highest antibacterial activity against *Staphylococcus aureus MTCC 902*	Husain et al. (2021a)
4	*Microchaete*	Silver	7 nm	Anticancer activity (IC50 of the AgNPs) against HepG2 and MCF-7 cell lines reported as 75 µg/ml and 79.41 µg/ml	Husain et al. (2021b)
5	*Desertifilium* sp. EAZ03	ZnO	88 nm (rod shape)	Synthesized ZnO employed for antimicrobial antibiofilm and anticancer against *S. aureus*, *E. coli* and *P. aeruginosa* and also as anticancer against normal lung (MRC-5) cells	Ebadi et al. (2021)
6	*Spirulina platensis*	Silver	13 nm	The bactericidal activity against seven different species of bacterial pathogens present in respiratory tract	Ameen et al. (2020)
7	*Anabaena variabilis* and *Spirulina platensis*	Silver	17.9 and 26.4 nm	Malachite green dye removal 93% for *S. platensis* and 82% for *A. variabilis* AgNPs	Ismail et al. (2020)
8	*Desertifilum IPPAS B-1220*	Silver	Size ranges from 4.5 to 26 nm	Suppressed the growth of five pathogenic bacteria, and exerted cytotoxic effects against MCF-7, HepG2, and Caco-2 cancer cells with IC_{50} values of 58, 32, and 90 µg/ml, respectively	Hamida et al. (2020)
9	*Chroococcus minutus*	Silver	–-	Bactericidal capability with lowest dose, 100 mg against pathogenic strains of *E. coli* and *S. pyogenes* (responsible for upper respiratory tract infection)	Sahoo et al. (2020)
10	*Anabaena flos-aquae*	Silver	Ranges from 5 to 25 nm	T47D cell for 24 h with AgNPs leading to an increase in apoptosis and necrosis by 6.21 and 28%, respectively	Ebrahimzadeh et al. (2020)
11	*Haloleptolyngbya alcalis KR2005/106*	Silver	< 50	Ammonia sensing for water quality	Tomer et al. (2019)
12	*Limnothrix* sp. *KO05*	ZnO	33	Biocompatible (PHY-ZnO NPs had a less cytotoxicity on fibroblast L929 compared to the ZnONPs-treated cells)	Davaeifar et al. (2019)
13	*Spirulina platensis*	TiO_2	17.3	Strong antioxidant capacity	Hifney and Abdel-Wahab (2009)
14	*Lyngbya majuscule*	Gold	41	Antioxidant and anti-myocardial infarction activities	Bakir et al. (2018)
15	*Phormidium* sp.	Silver	–	Antibacterial against *S. aureus*, *E. coli* and *P. aeruginosa*	Al Rashed et al. (2018)
16	*Spirulina plantensis*	Palladium	10–20	Adsorption of lead up to 90% of 10 mg/l	Sayadi et al. (2018)

Table 2 (continued)

SN	Cyanobacterial strains	Nanoparticles	Size of NPs (nm)	Applications	References
17	*Phycocyanin extracted from Nostoc linckia*	Silver	9–26	Antibacterial against (*S. aureus, Pseudomonas aeruginosa, E. coli and Klebsiella pneumonia*) and cytotoxicity test against breast cancer MCF-7 cell in vitro and in vivo	El-Naggar et al. (2017)
18	*Anabaena cylindrica*	Gold	< 10	Bioselective nature of cyanobacteria	Rochert et al. (2017)
19	*Anabaena laxa*	Gold		Biocatalyst	Lenartowicz et al. (2017)
20	*Nostoc* sp. strain HKAR-2	Silver	51–100	Cytotoxic activity against human breast cancer MCF-7 cells with IC50- 27.5 µg/ml, also antibacterial and antifungal properties were found	Sonker et al. (2017)
21	*Lyngbya majuscule*	Silver	20–50	Antibacterial and antileukemic	Roychoudhury et al. (2016)
22	*Arthrospira (Spirulina) platensis*	Selenium	100–550	Antioxidant Activity	Zinicovscaia et al. (2016)
23	*Synechococcus* sp.	Silver	430–450	Methylene blue degradation and antibacterial test against *B. subtilis, E. coli* and *S. aureus*	Keskin et al. (2016)
24	*Spirulina platensis*	Silver		Thermostable silver NPs use in therapeutics	Kaliamurthi et al. (2016)
25	*Leptolyngbya tenuis, Coleofasciculus chthonoplastes, and Nostoc ellipsosporum*	Gold	40	Found biocompatible when Bio-safety evaluation of gold were done	Parial et al. (2016)
26	*Nostoc commune*	Silver	15–54	Surface sterilization, Antibacterial and antibacterial	Morsy et al. (2014)
27	*Anabaena* sp. L31	ZnO	80	Conjugation UV-B absorbing ZnO NPs with compound shinorine	Singh et al. (2014)
28	*Microcoleus* sp.	Silver	44–64	Antibacterial against *P. vulgaris, S. typhi, V. cholera, Streptococcus* sp., *B. subtilis, S. aureus, E. coli*)	Sudha et al. (2013)
29	*Phormidium willei*	Gold	25	Antioxidant properties, Biolabeling (interaction with DNA and gold	MubarakAli et al. (2013)
30	*Phormidium tenue*	CdS	5	Bio-labeling	MubarakAli et al. (2012)
31	*Synechocystis* sp. PCC 6803	Gold	13 ± 2	Raman base biomolecule sensing	Focsan et al. (2011)
32	*Spirulina subsalsa*	Gold	< 20	Bio-recovery of gold	Chakraborty et al. (2009)

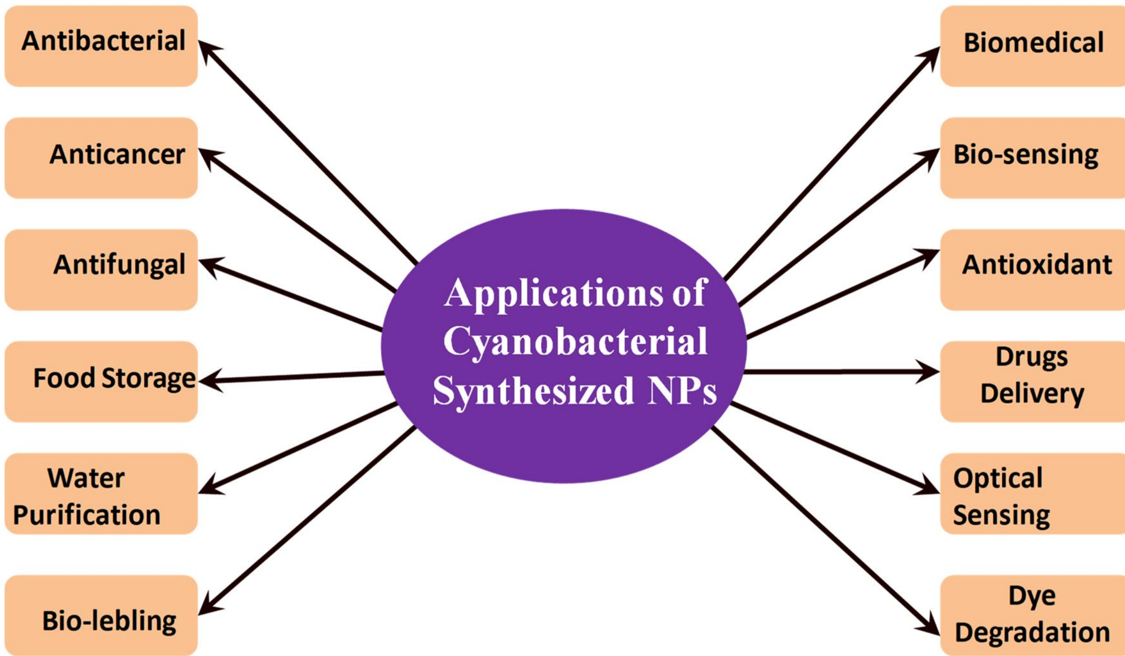

Fig. 3 Multiple application of cyanobacteria-assisted synthesized NPs

and *Trichoderma harzianum* (Sonker et al. 2017). Moreover, cyanobacteria *Nostoc* sp., *Scytonema* sp. and *Phormidium* sp. were used for the preparation of silver NPs and attempted for testing its antibacterial activity against *S. aureus, E. coli* and *P. aeruginosa* have resulted remarkable zone of inhibition by killing bacteria (Al Rashed et al. 2018). *Lyngbya majuscula*-based preparation of silver NPs (20–50 nm) represented antibacterial nature against Gram-negative bacterium (*P. aeruginosa*) with a concentration of 0.1 mg/ml can form around 4 mm zone of inhibition (Roychoudhury et al. 2016). The cyanobacterial extract was utilized synthesis of silver NPs and finally employed as an antibacterial agent against *Bacillus subtilis* (ATCC-6653), *Staphylococcus aureus* (ATCC-25923) and *Escherichia coli* (ATCC-10536). The growth of *Bacillus subtilis* was greatly reduced after the treatment of silver NPs (2 mg/ml) for 24 h in comparison to standard growth (Keskin et al 2016).

The extracellular polysaccharide of a cyanobacterium (*Nostoc* sp.) was utilized for the synthesis of silver NPs and tested against the growth of *E. coli* bacteria, with the MIC and MBC of 0.012 and 0.016 mg/l, respectively. Furthermore, two different types of pre-water soaked seeds (sorghum and broad bean) were treated with a five-fold higher concentration of silver NPs on *E. coli* (~0.08 mg/l) did not cause any adverse effect on the seed germination. The protection of seed growth from the unwanted bacteria and fungus infection employed by silver synthesized cyanobacteria. Hence, this protective approach might be potentially harnessed in the field of agriculture, which can be utilized for the sterilization of any surface (Morsy et al. 2014). Therefore, such antibacterial properties of cyanobacteria-assisted metal NPs shown in Fig. 4. It can be employed with medical supplements, catheters, wound dressings and implants to routinely inhibit the pathogen growth, besides can also be exploited as a preservative in cosmetics to eliminate clinical microbes.

As an anticancer agent

The ultrafine metal NPs have been suggested for various promising applications in the biomedical field due to their high solubility, stability, low toxicity and better cellular uptake (Huang et al. 2011). The cyanobacteria (*Nostoc* sp.) assisted synthesized silver NPs have strong anticancer properties (Sonker et al. 2017). The dose-dependent cytotoxic effect also studied against human breast cancer MCF-7 cells that recorded as IC_{50} around 27.5 µg/ml. Preparation of silver NPs (20–50 nm) based on *Lyngbya majuscula* were tested for anti-proliferative activity against three leukemic cell lines (K562, MOLT-3, REH) through MTT assay and the effect of silver NPs (100–1000 µg/ml) was determined at 24 and 48 h where REH strain was more sensitive than other two (Roychoudhury et al. 2016). The C-Phycocyanin pigment-based preparation of low-cost and eco-friendly phycocyanin-zinc oxide conjugates NPs (PHY-ZnO NPs). It had found a less cytotoxic effect against fibroblast L929 compared to the ZnO NP-treated cells. Consequently, a remarkable increase in ROS level was investigated in cells treated with ZnO with

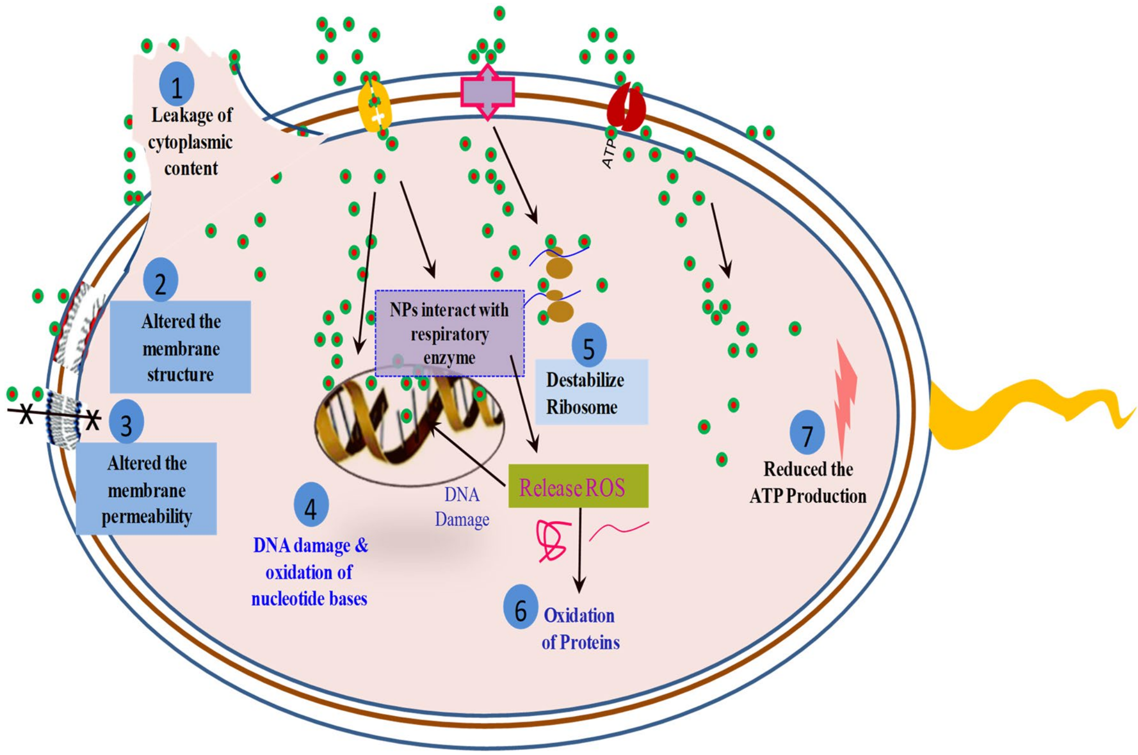

Fig. 4 Mode of action of bacterial killing against bacteria with given ways (1) leakage of cytoplasmic content, (2) alteration of membrane permeability, (3) alteration in membrane structure, (4) DNA damage and oxidation of nucleotide bases, (5) destabilization of ribosomes, (6) oxidation of proteins, (7) reduction in the ATP production

variable concentrations of 100, 200 and 500 μg/ml (78 ± 7, 99 ± 8 and 116 ± 11, respectively). They observed that in PHY-ZnO, phycocyanin has a protective effect responsible for to decline of the ROS content confirmed by fluorescent microscopy (Davaeifar et al. 2019). A face-centered central composite of silver NPs (1100.025 μg/ml) synthesized using cyanobacterium *Nostoc linckia* was optimized with four variables of isolated phycocyanin pigment concentrations (1 mg/ml) and incubation period (24 h). These NPs showed effective cytotoxic activity against MCF-7 and their IC_{50} was recorded as 27.79 ± 2.3 μg/ml (El-Naggar et al. 2017).

In the various works of literature, the anticancer potential of biosynthesized metal nanoparticles is underestimated, however, the cyanobacterial assisted synthesized Ag NPs have been also proved as anticancerous. This schematic representation is demonstrated in Fig. 5. Silver NPs uptake by tumor cells is catabolized and produce silver ions. The absorption of nanoparticles by cancerous cells results in the capture of free electrons, which enhances the synthesis and accumulation of reactive oxygen species (ROS), which reacts with proteins and generates oxidative stress to cancer cells (Rahman et al. 2009b). This process results in partial or permanent loss of the structure and function of cellular proteins. It further reduces the production of adenosine triphosphate (ATP) (AshaRani et al. 2009; Park et al. 2011). The cytotoxicity of NPs is due to silver ions that interact with intracellular macromolecules of the cells including protein and DNA. DNA damage and increased mitochondrial membrane permeability have observed against the nanoparticles (Almofti et al 2003). Nanoparticles have also been shown to negatively regulate the activity of DNA-dependent protein kinases, which are key enzymes involved in DNA damage repair through non-homologous end-joining. Damage to cells by silver nanoparticles may be due to cell membrane integrity, loss of apoptosis and oxidative stress (Dos Santos et al 2014). Apoptosis can be activated through mitochondrial dysfunction, which may inhibit cancer cell proliferation. Nanoparticles with different sizes and surface properties have a great effect on cell membranes (Souza et al 2016). Note that the phase transition temperature of the lipid membrane is increased by increasing the surface roughness of the NPs (Lin and Gu 2014).

Degradation of carcinogenic dyes

The cyanobacterial extract was utilized for the green synthesis of Ag NPs and finally employed for the photocatalytic degradation of the dye methylene blue (MB). Where silver NPs work as catalysts during UV light-assisted degradation of methylene blue dye with a concentration of 20 mg/L by

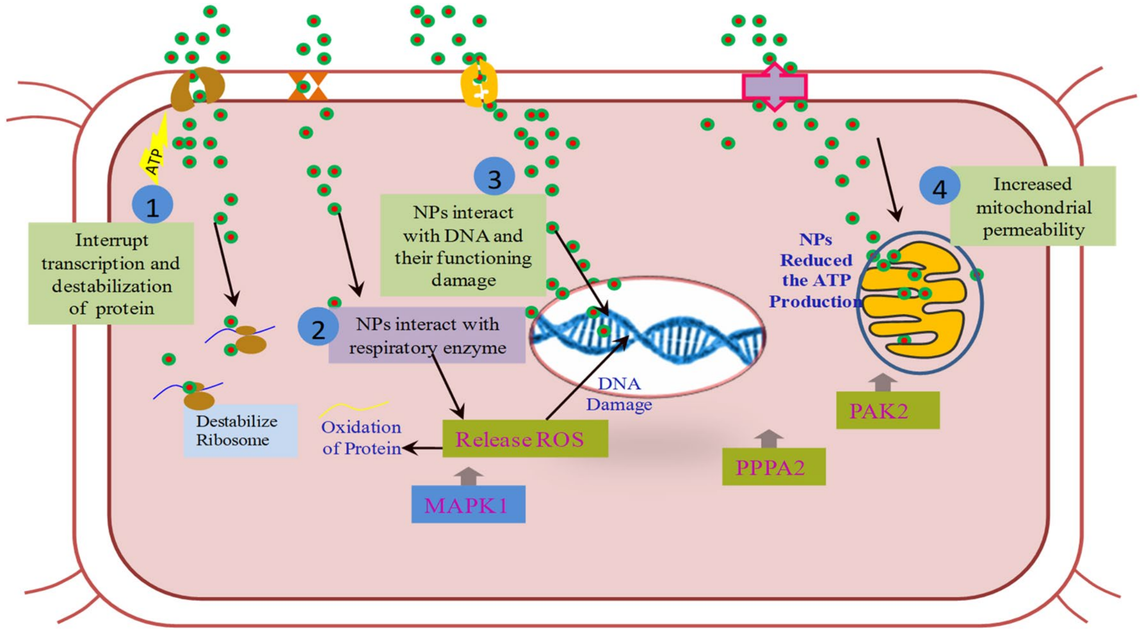

Fig. 5 Mode of action of NPs against cancerous cells; (1) interruption of transcription and destabilization of proteins, (2) NPs interact with respiratory enzymes, (3) NPs interact with DNA and their functioning damage (4) increase in mitochondrial permeability

yielding dye removal efficiency of almost 18% within the time of 4 h (Keskin et al 2016). *Anabaena variabilis* and *Spirulina platensis* were used to synthesize silver NPs and employed as the bio-sorbent for the removal of dye (malachite green). It was observed that the dye concentration decreased with the removal efficiency increased to reach 93% for *S. platensis* and 82% for *A. variabilis* Ag NPs. Results also indicate the smaller particle diameter and larger specific surface area of *S. platensis* Ag NPs enabled boosted catalytic activity for dye removal than those of *A. variabilis*. The Ag NPs after the treatment of dye, effluent of NPs again apply in the growth of seedlings *Triticum aestivum* L (Giza 171) to prove nontoxic nature in environment and safety for cultivation practices (Ismail et al. 2020). Husain et al. (2019) synthesized silver NPs using cell free aqueous cyanobacterial (Microchaete NCCU-342) and employed for the ago dye Methyl Red (MR) degradation. The MR dye 50 mg/l decolorization rate has been reported 84.60% within 2 h while only extract (without NPs) found 49.80% removal of dye (Sayadi et al 2018).

Ammonia sensing

Recently cyanobacterium *Haloleptolyngbya alkalis* KR2005/106 has been reported for the photo-biochemical synthesis of silver NPs (~50 nm). These cyanobacterial isolates obtain from saline-alkaline habitat (soda lake). The biosynthesized silver NPs employed for sensing of dissolved ammonia in water. It has been also clearly observed that the strong blue shift in the absorbance with the interaction of silver NPs and ammonia. The high sensitivity of such a shift was recorded between 50 and 500 ppm of ammonia (Tomer et al. 2019).

Heavy metal removal

Spherical palladium NPs with a size range 10–20 nm produced using *Spirulina platensis* employed for the removal of lead from water. This adsorption experiment was performed under the batch culture system where consequences of certain parameters such as pH, contact time, adsorbent dose, and initial concentration of lead were studied. The highest adsorption efficiency was reported around 90% under optimal conditions such as at pH 6, contact time 60 min, adsorbent dose 0.5 g/l, and lead concentration 10 mg/l. It was also reported that the increase in the initial concentration of lead from 10 to 150 mg/l, resulted in a decrease of the lead removal percentage from 87 to 32%, while the adsorbent dose increased from 0.02 to 0.5 g/l, with the removal percentage increased from 12 to 90% (Sayadi et al 2018).

Challenges and future remarks

The green synthesis of nanomaterial is consider as promising area in current scinario to development of new science and technology. In order to researchers are trying to open a new edge of safe, economical, green synthesis methods of various functional nanomaterial steadily. This synthesis methods are consume less energy, inexpensive, eco-friendly and produce high yield. Number of green material is used in the production of metal NPs such as different part of plants, grass, green waste, fungi, bacteria, yeast and cyanobacteria. However, several species of cyanobacteria and their isolated pigments and metablits is still not explored in the synthesis of nanomaterials. Therefore, extensive study is needed and explore more diversified cyanobacteria to obtain better performance of synthesis and application. The nanomaterial synthesis mathod is simple and fast but the bioconversion and biotransformation of metal ions into the NPs is highly intricate due to the presence of varsatile metabolite (enzymes, proteins, pigments, etc.) within the cayanobactrial cells. It is also need to short out how diverse morphological structure of NPs formed by the different strain with same species of cyanobacteria. Even though several hypothesis and mechanism of NPs synthesis has been anticipated, the clear cut mechanism of green NPs preparation has not yet been stablished. The emergence of various human health issues would be encorage to find new vista in the field of clinical and medical domain such as anticancerous, antimicrobial, antiinflammatory and antioxidant. Therefore, the author of this review recommend to research over the understanding the nature of different biomolecules of cyanobacteria and precursors (metal ions) during the synthesis of metal NPs and explore the research for the biomolecule stability over the surface of nanomaterials.

Conclusion

In this review, synthesized metal NPs and their applications have been reported, the cyanobacteria-assisted synthesis of NPs are reported lesser in number than other green synthesis however, this review proves that the cyanobacteria have good NPs synthesis efficacy. It is also found that there are two prominent candidates: first silver NPs and second gold NPs were synthesized by several researchers while comparatively lesser articles have been found, which synthesized copper, zinc, palladium, selenium titanium and cadmium sulfide using a range of extracellular and intracellular enzyme of cyanobacteria. These synthesized materials also utilized in the range of applications in the field of various medical and environments such as sensing, bio-recovery, bactericidal, bio-leveling, dye degradation, cancer treatment and antioxidant. This is possible because of the unique biomolecules of cyanobacteria responsible to make the NPs synthesis process is environmentally benign, rapid, safe, one step and does not produce any toxic chemicals. The interest of the range of cyanobacteria is attracted because of the continuous exploration of the synthesis of newer advanced NPs. This review tried to discuss the mechanism of extracellular and intracellular synthesis of NPs. Therefore, the cyanobacteria can be understood as the nanobiofactory for the synthesis for advanced materials which will be explored in the many more application of detection, diagnostics, therapeutics, pharmaceuticals, photonics, optics, forensic and catalysis.

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