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Microbial Biomanufacturing for Metal/Metallic Nanomaterials and Metabolic Engineering: Design Strategies, Fundamental Mechanisms, and Future Opportunities

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Abstract

Biomanufacturing of metal/metallic nanomaterials with the ordered micro/nanostructures and controllable functions is of great importance in both fundamental studies and practical applications, due to their low toxicity, less pollution production, and energy conservation. Microorganism as efficient biofactories, have significant ability to biomineralize and bioreduce metal ions that can be obtained as nanocrystals of varying morphologies and sizes. The development of nanoparticle biosynthesis maximizes the safety and sustainability of the nanoparticle preparation. Great efforts and progress have been made to develop new green and environmentally friendly methods for biocompatible metal/metallic nanomaterials. In this review, we mainly focus on the microbial biomanufacturing of different metal/metallic nanomaterials due to their unique advantages of wide availability, environmental acceptability, low cost, and circular sustainability. Specifically, we summarize recent and important advances in the synthesis strategies and mechanisms for different types of metal/metallic nanomaterials using different microorganisms. Finally, we highlight current challenges and future research directions in this growing multidisciplinary field of biomaterial science, nanoscience, and nanobiotechnology.

Keywords: Microorganism; Biomanufacturing; Metal nanomaterials; Metallic compound; Nanobiotechnolgy

1. Introduction

Nanoparticles (NPs) with a size range of 1-100 nm have unique structure-property characteristics of small particle size, large surface area, and high reactivity, which bridge macroscopic performance and atomic structures. Among different NPs, metal/metallic compound nanomaterials (MNMs/MCNMs) are a special class of NPs [1] due to its unique optical, catalytic, magnetic, and chemical properties, making them as promising materials for many applications in optics, catalysis and pollutant degradation[2, 3]. In addition, MNMs/MCNMs are the most widely used in environmental remediation, drug transportation [4-6], and construction materials [7], so the demand for types and performance requirements have increased. As the continuous increase of severe environmental issues caused by the material synthesis process and accumulation of material waste, the development of environmentally friendly MNMs/MCNMs is fundamentally and practically important for environmental and materials science.

Preparation of MNMs/MCNMs mainly adopts physical and chemical methods [8]. The physical methods include evaporation and condensation, ion sputtering, and high-energy mechanical ball milling [9]. MNMs/MCNMs as produced by physical methods often have high activity and high purity, but they suffer from wide size distribution and undesirable agglomeration [10]. Also, physical methods require large-scale equipment and high operation cost. Chemical methods include electrochemical reduction, photochemical reduction, and molecular self-assembly [11], which produce MNMs/MCNMs with the better dispersibility, narrow particle size distribution, and relatively uniform morphology. However, an additional concern is paid to surface impurities of MNMs/MCNMs [12]. Also, physical and chemical methods often require rigorous synthesis conditions and complex processes, making it more difficult for saving energy and materials consumption [13].

Apart from conventional chemical and physical methods, microbial biomanufacturing has been developed for the synthesis of MNMs/MCNMs [14]. Microbial synthesis of nanomaterials can be traced back to 1989, the biosynthesis method of *Candida glabrata* was used to synthesize intracellular CdSe nanomaterials [15]. Then, the mineralization and synthesis of magnetic NPs in magnetotactic bacteria were reported in 1993 [16]. In 2001, the biosynthesis method of Ag nanoparticles (AgNPs) by *Fusarium oxysporum* was reported, which successfully demonstrate the concept of biosynthesis technology for the first time [17]. Microorganisms widely exist on the earth, with rapid growth and reproduction, strong environmental adaptability, and diverse

metabolic types, all of which allow them to first capture target ions from the environment and then use the enzymes, proteins, and other active substances for carrying out a series of bioprocessing to synthesize NPs. Microorganisms are also recognized as "nanomaterials processing plants" [18]. Use of microorganisms to synthesize MNMs/MCNMs has several environmentally friendly advantages, including reduction of chemical consumption, decrease of secondary pollution, and mass production at low cost[19]. Meanwhile, the synthesis process does not require harsh conditions, instead can occur at room temperature and neutral pH, thus making the whole process in a safe, economical, and productive way. Secondly, biological modifications of the surface of MNMs/MCNMs by microorganisms enable to achieve the higher biocompatibility and structurally stability. On the other hand, microbial synthesis of MNMs/MCNMs also has some limits for controlling cell stability, separating and purifying products, and bioaccessibility of some types of microorganisms. From a mechanistic viewpoint, while significant efforts have been made for the synthesis of MNMs/MCNMs, molecular mechanisms that mediates this synthesis still remain under investigation[20]. Furthermore, few reviews have been reported on the development of functional microorganisms and the practical application of synthetic materials[21, 22].

Here, this review aims to summarize, categorize, and analyze the recent and important findings on the microbial biomanufacturing for MNMs/MCNMs metabolic engineering. Specifically, this review mainly covers fundamental principles of microbial biosynthesis from intracellular and extracellular and other environments, selectively highlight some typical and interesting microbial-induced MNMs/MCNMs systems, and finally presents some personal opinions about current challenges and future directions in microbial biomanufacturing for MNMs/MCNMs. Hopefully, this review will stimulate more research efforts to develop new, green microorganisms for MNMs/MCNMs productions, which will offer a better mechanistic understanding of synthesis strategies, processes, and mechanisms.

2. General biomanufacturing process of metal/metallic compound nanomaterials

MNMs/MCNMs can generally be synthesized by either "top-down" or "bottom-up" methods[23], in which most of microbial synthesis is driven by bottom-up methods. The top-down methods are often developed for the breakdown of the larger compounds into nanoscale ones through an external physical and/or chemical forces. Such physical or chemical top-down synthesis processes allows to prepare various structures of

MNMs/MCNMs, but often suffers from the relatively large expense of raw materials. Differently, bottom-up methods often involve the self-assembly of atoms and molecules into larger nanoscale compounds. In this way, the morphology and size of MNMs/MCNMs can be well controlled, but the self-assembly methods are often limited by some microbial systems for synthesis.

Since the microbial synthesis of MNMs/MCNMs is accompanied by microbial growth and enzyme catalysis, its synthesis conditions are mild and can be carried out at room temperature and neutral pH conditions, as compared with physical and chemical methods [24]. Generally speaking, there are two typical microbial synthesis methods, i.e., intracellular and extracellular synthesis processes. Firstly, since microorganisms contain rich biological components such as proteins, lipids, and polysaccharides, they often endow synthetic NPs with unique biological properties, such as better biocompatibility and stability, which differ from MNMs/MCNMs as synthesized by physical and chemical methods [25]. Secondly, microorganisms can biologically modify the surface of MNMs/MCNMs to achieve the better biocompatibility, dispersion, and stability, which will expand their uses to biomedical and materials applications. Third, microorganisms can synthesize MNMs/MCNMs with specific shapes and morphologies (e.g., spherical, hexagonal, triangular, rod-shaped, flat, dendritic, decahedron, icosahedron, and some irregular shapes) in a controllable and programmable way [26]. Moreover, the composition and crystallinity of MNMs/MCNMs can also be well controlled by microorganisms [27]. As a result, a wide range of MNMs/MCNMs are synthesized by microorganisms, including iron oxide, nano-gold (AuNPs), AgNPs, quantum dots (QDs) and barium titanate. More importantly, different types of microorganisms can synthesize not only single MNMs, but also composite MCNMs, such as $BaTiO_3$, CdTe, and CdSe [28], which possess more physicochemical properties and functions (stronger Raman and Rayleigh scatterings, higher catalytic activity, and better optical properties) than ordinary NPs.

3. Biomanufacturing strategies of metal/metallic compound nanomaterials

Thank to natural evolution, microorganisms have strong vitality, wide adaptability, and different metabolisms in response to environmental changes, so they are the first biological groups being considered for biosynthesis techniques [29]. Bacteria, fungi, and yeasts [30] are the most common microorganisms used to synthesize MNMs/MCNMs to date. Microbial synthesis is generally classified into intracellular and extracellular synthesis. For instance, intracellular synthesis produces

MNMs/MCNMs in cell walls, which requires sonic degradation or special reactions to extract these NPs. Different from intracellular synthesis, extracellular synthesis does not require such a particle extraction process, so it is more convenient for synthesizing MNMs/MCNMs [31, 32].

3.1. Bacteria

Among the microorganisms, prokaryotic bacteria have received the most attention in the area of biosynthesis of NPs. Bacterial synthetic NPs are considered as the main biosynthetic nanomaterials due to their advantages of short cultivation time and simple operation. Bacteria not normally exposed to large concentrations of metal ions may also be used to grow NPs. When living bacteria are incubated with metal ions, the electronegative surface of cells induces strong adsorption and absorption capacity for metal cations, followed by the self-assembly of metal cations into NPs by different active molecules inside and outside cells[24].

Table 1 presents dozens of bacteria for NPs synthesis, including *Pseudomonas* sp, *Shewanella* sp, *Bacillus* sp, *Lactobacillus* sp, and *Sulfate-reducing* bacteria [33]. NPs synthesized by bacteria have several common features. Firstly, bacteria can use different synthetic metal materials, including Au, Ag, Pd, Fe_3O_4, ZnS, CdS, CdTe, TiO_2. As shown in Figure 1, Xiong et al. proposed to use *Shewanella oneidensis* to produce Pd NPs via a reduction of $PdCl_4^{2-}$ for pollutants removal[34]. They observed that the activated Pd NPs were synthesized via the contacting-production mechanism, in which *Shewanella oneidensis* acted as reducing, capping, and stabilizing agents to produce Pd NPs of different shapes and compositions by activating KOH at elevated temperatures. The resultant Pd NPs showed an enhanced catalytic reduction by converting 4-nitrophenol to 4-aminophenol, as evidenced by a remarkable apparent kinetic constant of 5.0×10^{-3} s^{-1}, which was 12 times greater than that of the raw biogenic Pd NPs.

Although many aspects of magnetite biomineralization in magnetotactic bacteria are still unclear. The study found that magnetotactic bacteria can biomineralize the magnetosomes and form magnetite [35]. In addition, *Pichia postoris* can also synthesize gold nanowires [36]. The above examples prove the specificity and diversity of bacteria when synthesizing materials. Secondly, synthetic MNMs/MCNMs have a wide range of spherical-like particle sizes ranging from 0.1-300 nm. Also, different bacteria

synthesize different MNMs/MCNMs. For instance, *Escherichia coli*, *Pseudomonas, Aeruginosa* favor synthesizing AuNPs, while *Bacillus brevis*, *Lactobacillus casei*, *Klebsiella pneumonia*, *Serratia nematodiphila*, *Enterobacter cloacae*, *Escherichia coli*, and *Corynebacterium* sp. prefer to synthesize AgNPs [37]. As shown in Fig. 2(a), *Lactobacillus* sp. can synthesize not only single AgNPs MNMs, but also bimetallic AgNPs via a series of intracellular biochemical reactions in cheese [38]. Another example, De Corte et al. [39] reported that using hydrogen as an electron supply, *Shewanella oneidensis* can simultaneously reduce the two metal ions of Pd^{2+} (II) and Au^{3+} into Pd-Au NPs. Among these bacteria, *Escherichia coli* is not only recognized as a strong synthetic ability, but also further genetically engineered to improve its synthesis performance. As shown in Fig. 2(b) and Fig. 2(c), recombinant *Escherichia coli* can secrete metal binding proteins and can synthesize CdSe QDs.

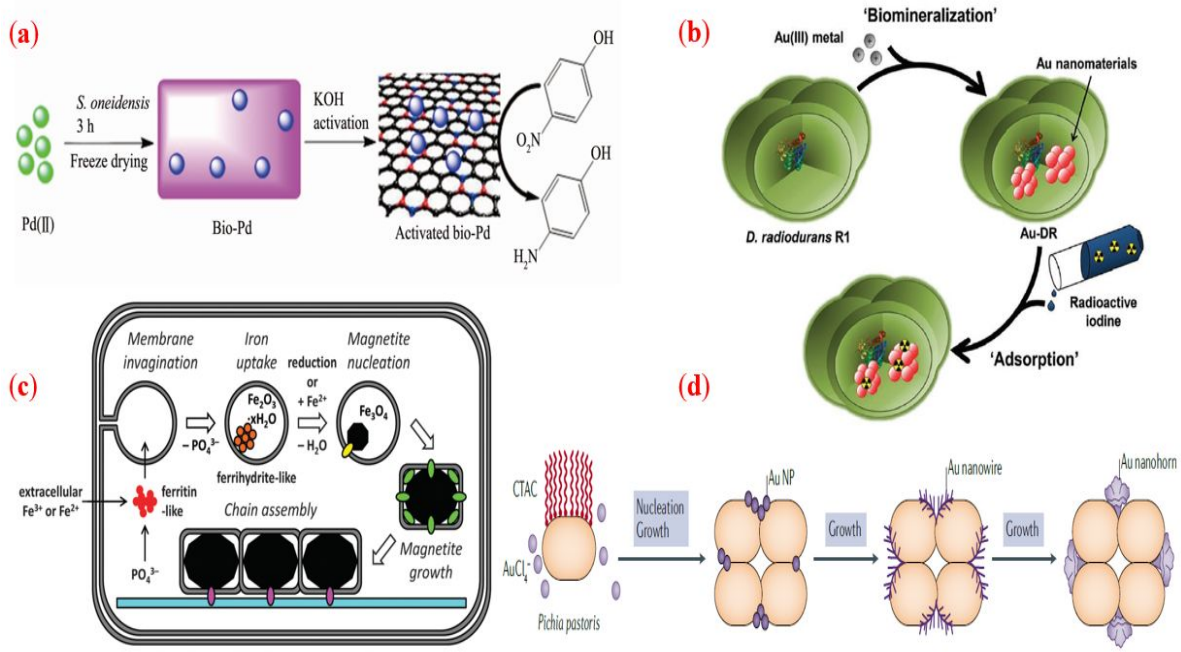

Figure 1. (a) Preparation of heteroatom-doped porous carbon materials with Pd nanopartieles synthesized by Shewanella oneidensis [34]. (b) Schematic illustration of the bioremediation procedure of radioactive iodine anions using Au-DR. (c) Model of the biomineralization of magnetite in the magnetosomes of magnetotactic bacteria [35]. (d) Biosynthesis of Au nanohorns between the surfaces of Pichia pastoris cells in the presence of cetyltrimethylammonium chloride [36].

Bacteria-based microbial synthesis has many advantages in synthesizing MNMs/MCNMs. Bacteria are easier to isolate, survive, and cultivate due to natural evolution, have already pre- or co-existence with metal ions under different environmental conditions, and can be mass-produced in a short time with low cost, all

of which lead to the rapid synthesis of a wide range of MNMs/MCNMs. Bacteria have fewer enzymes, non-enzyme proteins and peptides involved, so the bioreduction process in bacteria is slower than in other microbial cells such as fungi. Thus, to enhance bioreduction of inorganic ions in bacteria, we can amplify the homologous or heterologous genes encoding proteins responsible for bioreduction [40].

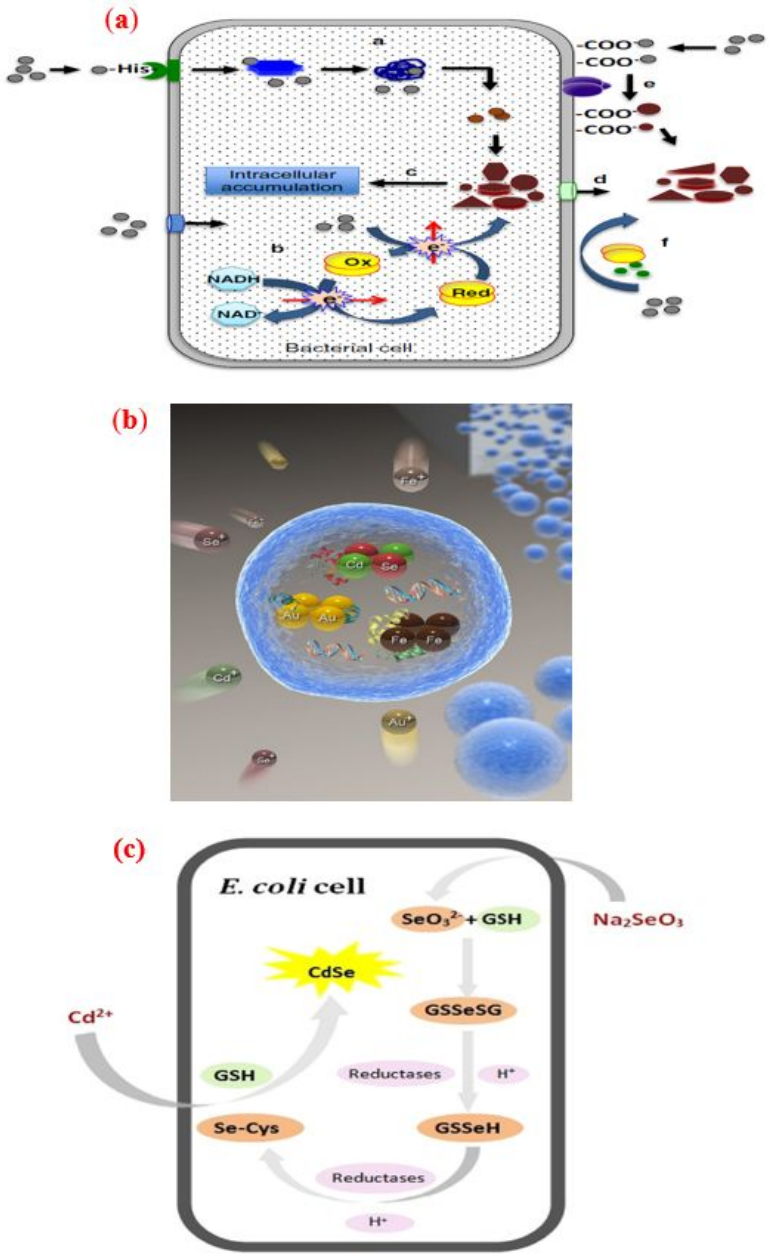

Figure 2. (a) Intracellular synthesis and metabolic pathways of AgNPs by bacteria [41]. (b) Biosynthesis schematic for in vitro synthesis of MNMs/MCNMs by recombinant *Escherichia coli* expressing metal-binding proteins [42]. (c) Scheme of biosynthesis of fluorescent CdSe QDs by *Escherichia coli* [28].

Table 1. Summary of metal/metallic compound nanomaterials as synthesized by bacteria

Bacteria	Nanoparticle	Localization/morphology	Size (nm)	Reference
Rhizopus oryzane	Au	Spherical	10	43
Plectonema boryanum	Au	Cubic	25	44
Bacillus subtilis 168	Au	Octahedral inside cell wall	5 -25	45
Sulfate-reducing bacteria	Au	Cell envelope	<10	46
Shewanella algae	Au	Periplasmic space, bacterial envelope	10-20	47
Plectonema boryanum UTEX485	Au	Membrane vesicles/Cubic	10	44
Escherichia coli DH5c	Au	Cell surface/Spherical	ND	30
Rhodobacter capsulatus	Au	Plasma membrane	ND	48
Lactobacillus sp.	Au, Ag, Au-Ag	Hexagonal/Contour	20- 50	49
Rhodopseudomonas capsulata	Au	Spherical	10-20	50
Pseudomonas aeruginosa	Au	ND	15-30	51
Corynebacterium sp. SH09	Ag	Cell wall	10-15	52
Enterobacter aerogenes	Ag	Spherical	25-35	53
Morganella. sp.	Ag	Spherical	20	54
P.aeruginosa	Ag	Spherical	13	54
Bacillus amybolique faciens	Ag	ND	14.6	55
Bacillus sp.	Ag	Periplasmic space	5- 15	56
Morganella sp.	Ag	Spherical	20	57
Pseudomonas aeruginosa	Se	Spherical/Contour	ND	58
Shewanella algae	Pt	ND	5	59
Plectonema boryanum UTEX 485	Pt	Spherical, Chains, Dendritic	30	60
Magnetospirillum magnetotacticum	Fe_3O_4	Membrane-bound/Cubo octohedrons	47.1	61
M. magnetotacticum (MS-1)	Fe_3O_4	Inside the cell/Cuboctahedral	50	62
Clostridium	CdS	Cell surface	ND	63
Escherichia coli	CdS	Spherical, lliptical	2-5	64
Rhodopseudomonas	CdS	Spherical	8.0	65

palustris				
Gluconoacetobacter xylinus	CdS	Cellulose fibre	30	[66]
Sulfate-reducing bacteria	ZnS	spherical	2-5	[67]
Rhodobacter sphaeroides	ZnS	Spherical	8	[68]
Lactobacillus sp.	Ti	Spherical	40-60	[69]
Plectonema boryanum UTEX 485	Pt	Spherical, Chains, Dendritic	30	[60]
Geobacter metalireducens GS-15	Magnetite	ND	10- 50	[70]
Thermophilic bacteria TOR-39	Magnetite	Octahedral	<12	[71]
Actinobacter sp.	Magnetite	Quasi-spherical	10-40	[72]
Thermoanaerobacter ethanolicus (TOR-39)	Co, Cr, Ni-substituted-Co_3O_4	Octahedral	ND	[73]
Brevibacterium casei		ND	5-7	[74]
Rhodobacter sphaeroides	PbS	Spherical	10.5	[75]

3.2. Fungi

Fungi have thousands of different species that have made a significant contribution to the materials cycle in nature. The use of fungi in the synthesis of NPs is a relatively recent addition to the list of microorganisms. The use of fungi is potentially exciting. However, the genetic manipulation of eukaryotic organisms as a means of overexpressing specific enzymes identified in nanomaterial synthesis would be much more difficult than that in prokaryotes [76]. Fungi including *Aspergillus flavus*, *Trichoderma asperellum*, *Coriolus versicolor*, *Cladosporium*, *Fusarium oxysporum*, *Penicillium fellutanum* have their own merits to synthesize MNMs/MCNMs [77-81], including strong resistance to high environmental external stress, general growth and colonialization on most inorganic substrates, and high enzyme and protein secretion capabilities, all of which enable to produce nucleation-rich centers for synthesizing highly dispersed NPs by slowing down particle aggregation and forming mucus media. And also, since the nanoparticles precipitated outside the cell is devoid of unnecessary cellular components, it can be directly used in various applications. The fungi-synthesized MNMs/MCNMs mainly include Au, Ag, and metal oxides and adopt spherical and quasi-spherical shapes, with an average size of 2-400 nm (Table 2) [82].

Fungi also have great potentials in the synthesis of AuNPs. Liang et al.[83] developed the fastest approach, as reported so far, to synthesize spherical AuNPs with controllable sizes of 45 nm within 1 minute using the cell filtrate of *Penicillium* to react with $AuCl_7$. The resultant AuNPs can be well dispersed in cells and cell walls. Bhainsa et al.[84] were the first to apply *Aspergillus fumigatus* to synthesize AgNPs of 5-25 nm at an extracellular environment. This extracellular reduction synthesis was very efficient to produce AgNPs within several minutes upon bringing silver ions to contact with the cell filtrate.

Apart from AgNPs and AuNPs, the fungus also demonstrates their ability to synthesize magnetic NPs and metal sulfide NPs. For instance, *Candida glabrata* can produce CdS and PbS when culturing with Cd^{2+} and Pb^{2+} [85]. Different fungi have different selectivity and specificity to synthesize different NPs. Future efforts should be devoted to discovering more fungi for synthesizing different MNMs/MCNMs.

Table 2. Summary of metal/metallic compound nanomaterials as synthesized by fungi.

Fungi	Nanoparticle	Localization/morphology	Size (nm)	Reference
Verticillium (AAT-TS-4)	Ag	Spherical	13-37	77
Veticllium sp.	Au	Cell wall/spherical	20	78
Colletotrichum sp.	Au	Spherical	20-40	79
Trichothecium sp.	Au	Triangle, hexagonal	5- 200	86
Verticillium sp.	Ag	Cell wall, cytoplasmic membrane/	25	78
Aspergillus flavus	Ag	Cell wall	8.9	87
Trichoderma asperellum	Ag	ND	13-18	88
Phaenerochaete chrysosporium	Ag	Pyramidal	5-200	89
Fusarium solani USM 3799	Ag	Spherical	16.23	90
Fusarium semitectum	Ag	Spherical	10-60	91
Aspergillus fumigatus	Ag	Spherical, triangular	5- 25	87
Coriolus versicolor	Ag	Spherical	25-75	92
Aspergillus niger	Ag	Spherical	20	93
Phoma glomerata	Ag	Spherical	60-80	94
Penicillium brevicompactum	Ag	ND	58-95	95
Cladosporium	Ag	Spherical	10-100	96

cladosporioides				
Penicillium fellutanum	Ag	Spherical	5-25	[97]
Volvariella volvacea	Au, Ag, Au-Ag	Spherical	20-150	[98]
Fusarium oxysporum	Zr	Quasi-spherical	3-11	[99]
Fusarium oxysporum	Pt	Triangle, hexagons, square, rectangles	10-50	[100]
Fusarium oxysporum	$BaTiO_3$	Quasi-Spherical	4-5	[101]
Fusarium oxysporum	Bi_2O_3	Quasi-Spherical	5-8	[102]

3.3. Yeast

Yeast is considered as the first domestic microorganism of human beings. Yeast as a single-cell fungus not only has a strong detoxification ability, but also can accumulate a large number of heavy metal ions. Yeasts are rich in biomolecules such as glutathione, metallothionein, and phytochelatins. On the one hand, active molecules in yeast cells enhance the resistance of cells, on the other hand, they also improve the detoxification ability of cells [103, 104]. Yeasts including *Extremophilic*, *Candida guilliermondii*, *Pcihia capsulata*, *Rhodosporidium*, *diobovatum*, *Rhodotorula mucilaginosa*, *Saccharomyces cerevisiae* have been found to synthesize NPs [104-106]. Since phytochelatins in yeast cells can efficiently chelate highly toxic, heavy metal ions (e.g., Cd^{2+}), Yeast is amenable to the synthesis of semiconductor nanomaterials. Besides, phytochelatins also improve the stability and dispersion of NPs, so the yeast can easily synthesize small-sized semi-conductive QDs in the cells [107]. For instance, *Candida glubrata* detoxified metal ions by generating metal-thiolate complexes with phytochelatins to produce the intracellular spherical and mono-dispersed quantum crystallites of CdS [108]. Yeast can also synthesize CdTe NPs outside the cells. Bao et al. reported that when adding $CdCl_2$ and $NaTeO_3$ to the yeast cell culture medium, it produced CdTe NPs outside the cell under mild conditions, with a particle size of 2.0-3.6 nm [109]. Apart from quantum dot nanomaterials, yeast is also reported to synthesize AuNPs and AgNPs. Pimprikar et al. used *Tropical marine* yeasts to synthesize AuNPs by changing the number of cells and the concentration of gold salts to control the morphology and size of AuNPs [103]. Later, Kowshik et al. used silver-tolerant yeast strain MKY3 to synthesize AgNPs of 2-5 nm outside the cells [110].

In general, yeast-based biosynthesis processes were mainly due to enzymatic reduction, and chelation with extracellular peptides/polysaccharides resulted in different sizes, morphologies, and sites of NPs synthesis. Table 3 presents a variety of nanomaterials as synthesized by different yeast. It has long been recognized that among the eukaryotes, yeasts are explored mostly in the biosynthesis of the semiconductor NPs. Studies have shown that the hydroxyl groups of polysaccharides and the carboxyl groups of amino acids in the yeast cell wall are the adsorption sites for metal ions, thus yeast is prone to form NPs on cell walls [111]. Besides, the reduction synthesis of MNMs/MCNMs is related to the reductase and protease present in the yeast, so the yield of the synthesized NPs is directly related to the performance of the yeast secretase.

Table 3. Summary of metal/metallic compound nanomaterials as synthesized by yeasts.

Yeasts	Nanoparticle	Localization/morphology	Size (nm)	Reference
Yeast strain MKY3	Ag	Hexagonal	25	[105]
Fluorescing	CdSe	Spherical	3	[106]
Fluorescing	CdTe	Cubic	2-3	[112]
Yeast	$CaCO_3$	ND	4-6	[113]
Yarrowia lipolytica	Au	Intracellular/ Spherical	7.5-23	[114]
Schizosaccharomyces pombe	CdS	hexagon	1-1.5	[115]
Moanaero bacter sp.	Fe_3O_4	Spherical	13-14	[116]
Extremophilic Yeast	Ag	Spherical	20	[117]
Candida guilliermondii	Ag	Face-centered cube	10-20	[118]
Pichia capsulate	Ag	Intracellular/ Spherical	1-100	[119]

4. Microbial synthesis of metal/metallic compounds

4.1. Precious metals

Precious MNMs/MCNMs have high catalytic and bactericidal properties. It successfully combines the excellent physical and chemical properties of metals with the special properties of nanomaterials [120]. AuNPs and AgNPs are typical precious metal NPs, which have been well synthesized and studied by a large number of microorganisms. As early as 1980, Beveridge et al. used *Bacillus subtilis* 168 to synthesize AuNPs on the cell wall, and proved carboxyl groups provide the major site of metal deposition in the cell wall [121]. He et al. [32] later confirmed that *Rhodopseudomonas capsulata* can synthesize nanospheres, nanosheets, and nanowires by using this method. In addition to AuNPs, many types of microorganisms synthesize

AgNPs. Due to the high Ag^+ tolerance of *Pseudomonas stttzeri* AG259, Klaus et al. used it to synthesize AgNPs in the periplasm for the first time in 1999 [122]. Shi et al. used *Shewanella oneidensisl* to synthesize AgNPs. Saifuddin et al. [123] used the supernatant of *Bacillus subtilis* to synthesize AgNPs under microwave irradiation. Shahverdi et al. [124] proved that various compounds released by bacteria have a reducing effect on Ag^+, and it is nitrate reductase that plays a major role in the synthesis process. It is generally accepted that biosynthetic AgNPs are formed by the reduction of Ag^+ by nitrate reductase. Alternatively, MNMs/MCNMs containing Pt and Pd are synthesized by *Shewanella*, *Escherichia coli*, and others. Since the total amount of precious metals in nature is limited, it is very important to recycle these metals and resources through new transformation and synthesis methods [125]. Microorganisms have demonstrated their ability to successfully recover precious metals from smelting wastewater and precious metal catalysts.

4.2. Metal oxides

Metal oxide nanomaterials synthesized by microorganisms mainly include Fe_3O_4, Fe_2O_3, and Co_3O_4 [126]. The synthesis of magnetic NPs was the first and widely studied, and it is now mass-produced [127]. High-throughput screen and identification of magnetotactic bacteria for magnetic NPs is of great importance for drug delivery, immunoassay, and medical imaging [116]. In addition to magnetic NPs, microorganisms can also synthesize Ag_2O, CeO_2, CuO, Bi_2O_3, and ZnO. Raliya et al. discovered *Aspergillus flavus* for synthesizing TiO_2 NPs from its cells [128]. *Bacillus mycoides* isolated from the soil sample can also use $TiO(OH)_2$ to produceTiO_2 NPs with an average particle size of 40-60 nm at room temperature [129]. In addition to synthesizing nano-sized metal oxides, microorganisms can also synthesize MNMs/MCNMs in different shapes of sphere, hexagon, triangle, and rod. Tripathi et al. [130] used *Bacillus licheniformis* to synthesize ZnO nanoflowers with strong photocatalytic properties. Microbial synthesis of oxide nanomaterials usually requires high redox potential conditions. Microorganisms can adapt to the environment and resist extreme conditions, which promote MNMs/MCNMs synthesis. As compared to ultrasonic, microwave radiation, and alternating current electrodeposition technologies, microbial synthesis is the most promising method for preparing high-purity, small particle size, and uniformly dispersed NPs.

4.3. Metal sulfides

Nanomaterials have unique properties after vulcanization. It has been proved that NPs vulcanization increases the utilization of electrons, thereby improving the removal efficiency of target pollutants [131]. Metal sulfide NPs can be formed directly from their precursor ions or indirectly by sulfide ion-assisted transformation of the corresponding metal oxides under anaerobic conditions. Numerous studies have also shown that the ability of microorganisms to synthesize sulfide NPs usually comes from the adaptation and resistance to heavy metals [132, 133]. The synthesis of sulfide NPs by microorganisms requires a lower redox potential condition, so it usually requires to add metal ion precursors and sulfur-containing compounds. Sulfur ions are often combined with metal ions and reduced by specific reductases in microbial cells to produce metal sulfide NPs [134]. Co-culture of *Fusarium oxysporum* with different metal sulfides can generate different PbS, ZnS, NiS, MnS, and CdS NPs through an enzyme-catalyzed process [135]. In other cases, the synthesis of sulfide NPs by microorganisms also requires the participation of amino acids and peptides. Yeast can use cysteine and peptides in cells to synthesize CdS and ZnS NPs, while other microorganisms can synthesize Ag_2S, HgS, Bi_2S_3, CuS particles, as well as transition VS_4 and MoS_2 with different crystal structures and particle sizes[136]. For example, *Stenotrophomonas maltophilia* SMCD1 uses the amino acid L-cysteine as a sulfur source to synthesize CdS NPs at 37°C, with an average particle size of 2-4 nm [137]. Liu et al. used the newly isolated *Clostridium* family to synthesize high-purity, uniform, and dense MnS nanocrystals with hexagonal shapes [138]. Seshadri et al. isolated bacteria to synthesize PbS from contaminated industrial soils [139]. Metal sulfur compound nanomaterials have unique physical and chemical properties such as semiconductors, catalysis, electromagnetics, and optics, making them proposing in broad applications for electronic nanodevices, petroleum hydrodesulfurization processes, and hydrogenation of unsaturated carbon compounds. Current research mainly focuses on the discovery of bacteria, fungi, and yeasts to synthesize sulfide nanomaterials, however, less efforts have been made to discover other functional microorganisms for synthesizing sulfide nanomaterials [140].

4.4. Other metal compounds

Apart from precious metals, metal sulfides, and metal oxides, microbes can also synthesize other types of nanomaterials. When microorganisms produce CO_2, they can synthesize $PbCO_3$, $CdCO_3$, and $SrCO_3$ [141]. In the presence of phosphate, yeast can synthesize $Zn_3(PO_4)_2$ NPs with a micro butterfly-like structure [142]. More importantly, microorganisms not only synthesize single MNMs, but also bimetal or multi MCNMs.

As shown in Fig. 3(a), Liu et al. used *Shewanella oneidensis* MR-1 to first synthesize Fe_3O_4 NPs outside the cells, followed by the second synthesis of Pd/Fe_3O_4, Au/Fe_3O_4, and PdAu/Fe_3O_4 NPs on the surface of Fe_3O_4 via a biological reduction process [143]. As shown in Fig. 3(b), A carbon-coated lithium iron phosphate (LiFePO4@C) cathode materials were synthesized by biomineralization. In the process of synthesizing materials, yeast acts as a template and biological carbon source, playing a role of biological reduction [144]. The synthesized NPs can not only catalyze the degradation of pollutants, but can be recycled by a magnetic field. Park et al. [145] expressed *PCS* and *MT* genes through recombinant *Escherichia.coli* and used them to synthesize tri-metal (CdSeZn, FeCoNi, FeCoMn) and multi-metal (CdSeZnTe, Au(CdSeZn)) NPs, which provided a new possibility for microorganisms to generate alloy NPs. Taken together, microorganisms demonstrate their ability to synthesize different MNMs/MCNMs.

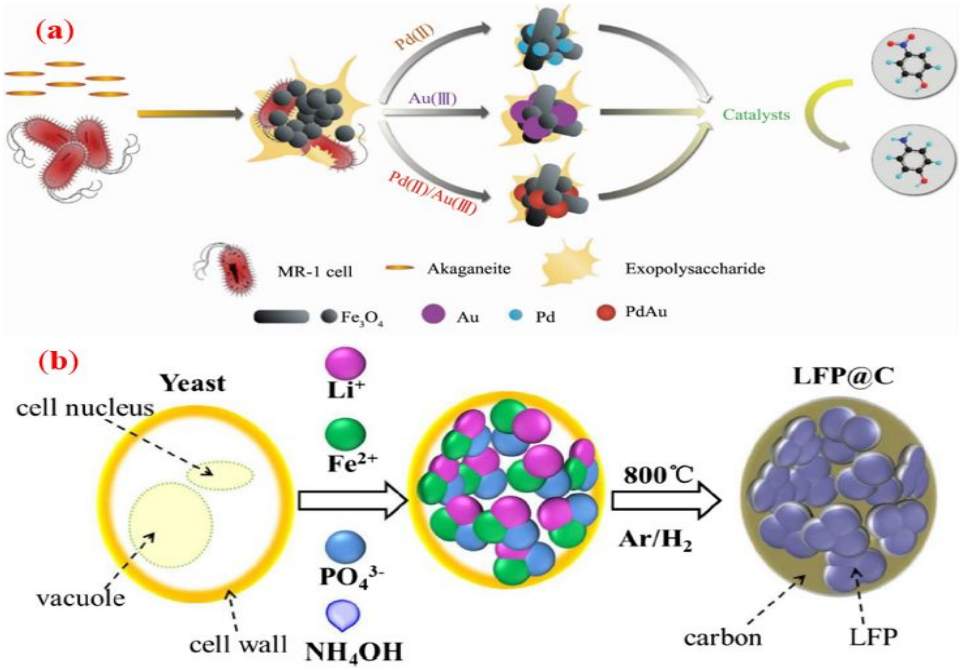

Figure 3. (a) Biosynthesis of Pd/Fe_3O_4, Au/Fe_3O_4, and PdAu/Fe_3O_4 composites by *Shewanella oneidensis* MR-1[143]. (b) Schematic illustrating the preparation process of LFP@C[144].

5. Separation and purification of microbial synthesis of metal nanomaterials

Fermentation broth for MNMs/MCNMs synthesis is a complex multiphase system containing target products, cells, metabolites, and unused culture media. Since the density and viscosity of solid and colloidal substances are similar to that of bulk media liquid [146], it makes difficult to separate the target MNMs/MCNMs from the precursor media. In addition, low concentration and high impurity of target MNMs/MCNMs also

increase the difficulty for MNMs/MCNMs purification. To address this issue, the commonly used strategies for separation and purification of MNMs/MCNMs after microbial synthesis include magnetic separation, chromatographic separation, centrifugation, membrane filtration, extraction, all of which involve the four stages of pretreatment of culture broth and solid-liquid separation, preliminary purification, high-level purification, and final product processing.

Among different separation technologies, magnetic fields separate MNMs/MCNMs based on their magnetic susceptibilities or sizes. Theoretical calculations predict that the limiting size for the separation of iron oxide NPs in the low magnetic field gradients (< 100 T/m) is ~50 nm [147]. For even smaller NPs, thermal diffusion and Brownian motions will be dominated forces against magnetic forces acting on the nanoparticles, thus making fractionation less effective. For chromatographic separations where a mobile phase containing a mixture to be separated passes through a stationary phase, the separation is based on the differences in the partition coefficients between mobile and stationary phases for all components of the mixture. While several examples of the use of HPLC for NP separation have been reported [148], size exclusion chromatography is considered as the most cost-effective chromatographic technique for NP fractionation. Centrifugation is another simple separation technique used widely for separating colloid-like nanoparticles (even non-spherical particles) using the gravity, but this process is usually time-consuming and less sensitive to separate different nanoparticles of similar mass[149]. Sharma et al.[150] have recently reported the centrifugation separation of AuNRs and AuNPs. Both spherical and cubic sediments at the bottom were well segregated from high-purity rods on the side wall. Moreover, membrane filtration as alternative purification and size-fractionation of NPs has the greatest advantages of industrial-level scalability[151]. Separation efficiency for the retention and elution of an analyte strongly depend on the size, structure, and chemistry of membrane pores. In generally, the more uniform pore sizes lead to the better the quality of NP separation. Use of extraction to separate compounds is based on their relative solubilities in two different, immiscible liquid phases, often involving water and organic solvent phases. Considering that microbial

metabolites, such as extracellular polymers and proteins, often increase the difficulty for product separation and purification, synthetic materials engineering is a necessary tool for controlling the metabolic process of microorganisms by optimizing temperature, pH, and substrate concentration[152]. More recently, wet "nanosynthetic" procedures are considered as applicable, high-throughput, and inexpensive methods for separating polydisperse particles and worthy for further development.

6. Key factors to control microbial synthesis

MNMs/MCNMs by microbial synthesis are affected by many factors to control their size, shape, and synthesis conditions, including microorganism types, metal ion concentrations, medium compositions, microorganism or protein concentrations, and all-relevant synthesis conditions (pH, temperature, ionic strength, incubation time)[153]. Undoubtedly, microorganisms [154] as the most important factor have different genes, proteins, and metabolic processes, all of which will contribute differently to synthesis and biomineralization of MNMs/MCNMs[155, 156]. Further, a large number of studies have shown that pH can significantly affect the morphology and synthesis rate of MNMs/MCNMs[157]. For instance, *Rhodopseudomonas capsulatus* can synthesize gold nanosheets of larger than 200 nm extracellularly at pH=4, but 10-20 nm NPs at pH=7 [158]. pH value also has different effects on the synthesis of MNMs/MCNMs by different microorganisms. Using the synthesis process of AuNPs as an example, the lower pH value will lead to the higher proton concentration, which in turn easily produces the amino, sulfhydryl, carboxyl, and other groups involved in the reduction process and thus the decrease of their reduction ability and reduction rate to from AuNPs[159]. Collective results also showed that an overly acidic and alkaline environment not only is unfavorable for the reduction process, but also causes the instability of the surface charge of MNMs/MCNMs, leading to agglomeration[160]. Similarly, microorganisms as a complex biochemical reaction system are also very sensitive to temperature. Generally speaking, the rate of microbial synthesis of MNMs/MCNMs increases as temperature[161]. As an example, the synthesis rate of AgNPs increased at a temperature range of 4-25℃ [162]. On the other hand, too high temperature will not only denature biomolecules and inactivate enzymes on the surface of MNMs/MCNMs, but also cause NP agglomeration, both of which decrease or even halt the synthesis[163]. Finally, metal ion concentration (i.e., substrate concentration) is another critical factor for

microorganisms. While microorganisms always have a certain degree of metal tolerance, it is inevitable that a large amount of metal ions will destroy the function and structure of microorganisms[164]. The higher metal ion concentrations usually lead to a significant increase in the initial microbial synthesis rate. However, excessive metal ions will also cause the death of microorganisms and the dysfunction of biomolecules[165]. It was reported that when co-incubation of *Verticillium luteoalbum* with $HAuCl_4$ of 250-500 mg/L, gold nanoparticles of ~20 nm can be synthesized successfully. But, as $HAuCl_4$ concentration increased to 2500 mg/L, gold nanosheets with irregular shapes of ~200 nm were synthesized at the expense of *Verticillium luteoalbum*[166].

7. Biomanufacturing mechanism of metal/metallic compounds

Microbial synthesis of nanomaterials is a complex biochemical process, including the following steps: (1) Metal ions are adsorbed on the cell surface by electrostatic interactions; (2) Various reductases reduce metal ions inside or outside the cells; (3) After microbial cells consume energy, active substances such as proteins and polysaccharides are wrapped on the surface of the nanocrystals and a coating layer is produced to increase the stability of the NPs; (4) Cells secrete specific enzymes, reducing assistants and protective agents to accelerate the synthesis and secretion of NPs. Generally, the main synthesis mechanism is explained by biological reduction and abiotic reduction.

7.1. Biological reduction

Biological reduction almost involves in the entire process of microbial synthesis of MNMs/MCNMs. As shown in Fig. 4, NPs are produced from small atoms and molecules and reduction/oxidation reactions. The biological reduction/oxidation process of NPs is relatively complicated because it is accompanied by the growth and reproduction of microorganisms, the nucleation, aggregation, and stabilization of NPs, as well as electron transfer and heavy metal ion transformation [102].During biological reduction, biological molecules including reducing coenzyme I, reductive coenzyme II, nitrate reductase, hydrogenase are used as electron donors to reduce metal ions under the catalysis of enzymes or proteins, producing elemental or low-priced substances with poor water solubility or toxic metals [167, 168].

As shown in Fig. 5(a), the location of microbial reduction synthesis is related to the distribution of active molecules, depending on intracellular and extracellular synthesis. For intracellular synthesis, metal ions are first transported to the cytoplasm by the membrane transport molecules and then reduced by biologically active

molecules. For extracellular synthesis, there are two common scenarios. The first scenario is that metal ions are directly reduced by biologically active molecules outside the cell. The second one occurs by first adsorbing metal ions on the surface of cells through electrostatic attraction, followed by the reduction of metal ions using bioactive molecules on the cell wall or cell membrane [93]. As shown in Figure 5(b) ions are reduced by proteins, enzymes and organic molecules in the medium or by cell wall components. Extracellular reduction appears to be more favorable than intracellular reduction, due to its lower cost, simpler extraction and higher efficiency. However, in the intracellular process, carboxyl groups located on the cell wall attract metal and metalloid ions by electrostatic interactions. Then, the ions enter the cells and interact with intracellular proteins and cofactors to produce NPs.

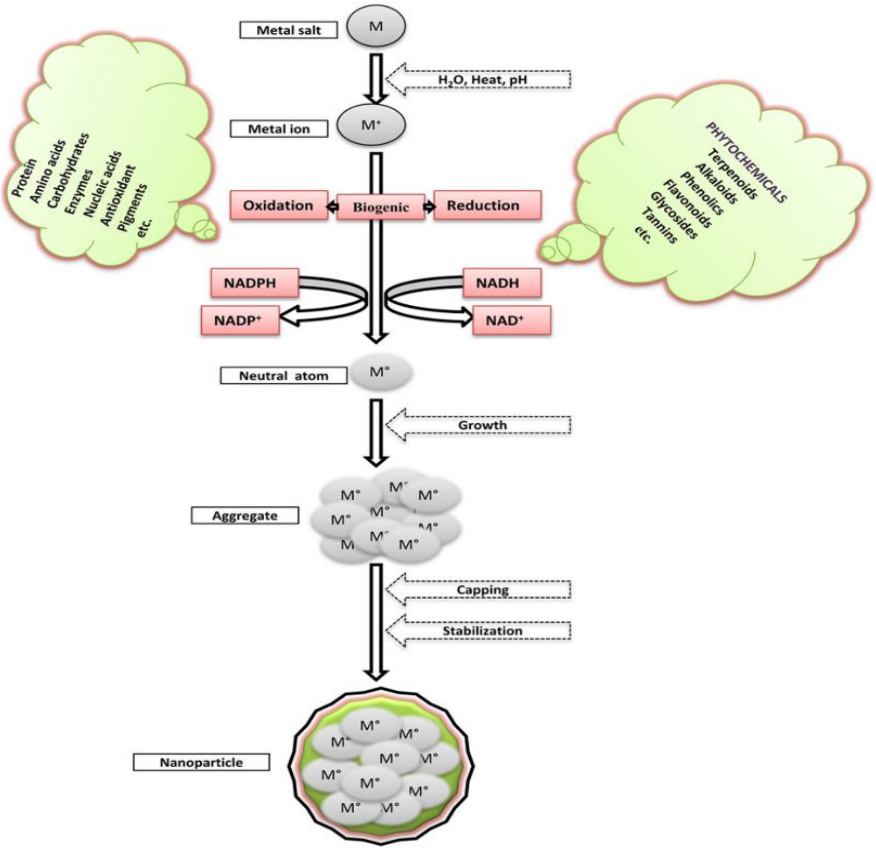

Figure 4. Scheme of the possible pathways to synthesize NPs by microorganisms. M: metal salt, M^+: Metal ion, Mo: neutral atom [102].

It is well known that microorganisms can synthesize nanomaterials simultaneously at multiple locations. *Rhizopus oryzae* can use intracellular and extracellular proteins to synthesize AuNPs [169]. Some Au atoms are reduced to AuNPs by proteins on the cell surface, while the other Au^{3+} penetrate the cytoplasm, are covalently bound to proteins, and are reduced to AuNPs by metal reductase. Also, many extracellular biological

reduction processes involve complex electron transport pathways for respiration. As shown in Fig. 5(c), Das et al. [170] think that when *Rhizopus oryzae* synthesizes AuNPs. A part of Au^{3+} is reduced to AuNPs by protein on the cell surface. In addition, another part of Au^{3+} penetrates into the cytoplasm and is covalently bound to proteins and reduced to AuNPs by metal reductase. Zhi et.al found that cytochrome C played an important role in electron transport in the synthesis of AgNPs by *Escherichia* coli. As shown in Fig. 5(d) , when silver-tolerant *Escherichia coli* reacts with the $AgNO_3$ solution, it happens simultaneously for the oxidization of respiratory substrates by cells and the reduction of silver ions in the periplasmic space by cytochrome C [171]. Since microorganism synthesis often requires a variety of enzymes and intracellular/extracellular substances to work together for the synthesis of metal nanomaterials, it is a challenging task to precisely determine the combinatorial effects of growth and reproduction, metabolic activities, and cell configuration on material production. In addition, due to the super-fast generation time of a single cell, the cell not only enters the decay stage after completing the material synthesis in a short time, but also is quickly removed by separation and purification, all of which imposes a great road blocker to sufficiently sample synthesis time and cycle for better understanding microbial synthesis mechanisms[172].

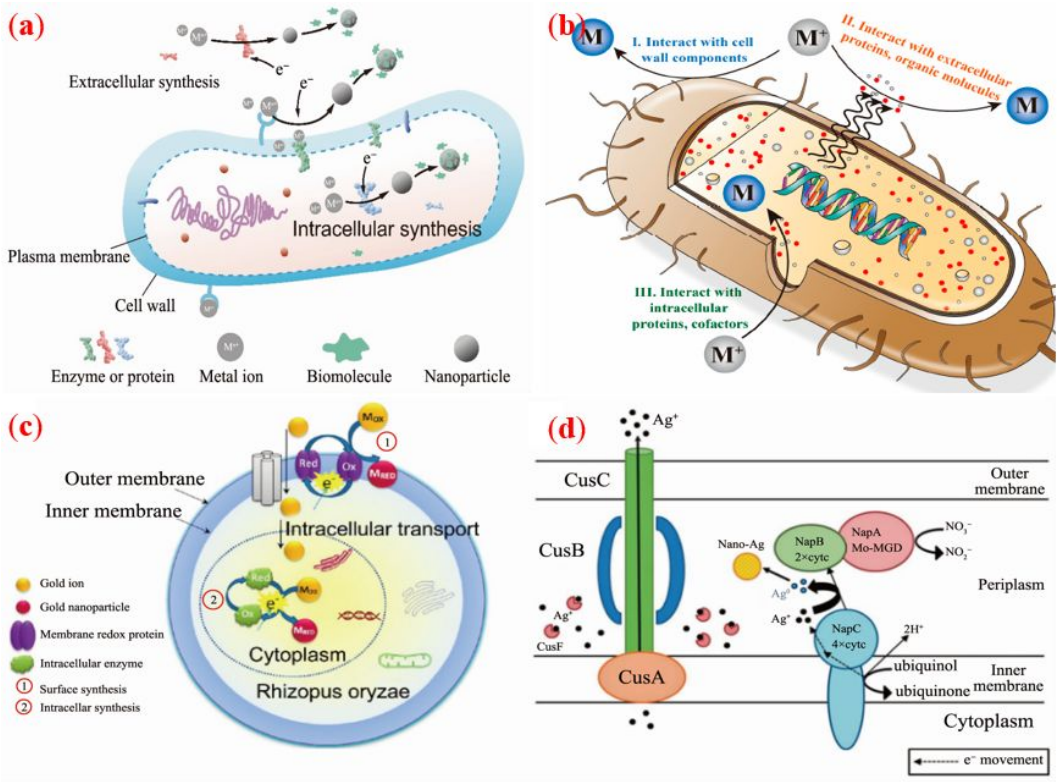

Figure 5. (a) Biosynthesis of metal nanomaterials by a bioreduction process [93]. (b) Schematic representation of bacteria synthesis of NPs; both intracellular and extracellular process are included [37]. (c) Proposed mechanism of AuNPs biosynthesis by fungi *Rhizopus oryzae* [170]. (d) Biosynthesis mechanism of AgNPs by cytochrome subunit NapC in *Escherichia coli* [171].

7.2. Abiotic reduction

In some cases, it is difficult for microorganisms to precipitate metal ions in a stable oxidation state through a biological reduction process. To address this issue, microorganisms develop more complicated mechanisms to synthesize MNMs/MCNMs via intracellular or extracellular abiotic reduction, similar to the biological reduction process. While the exact mechanism of abiotic reduction remains unclear, it is likely accepted that the synthesis of some oxides mainly stems from the hydrolysis process as mediated by microorganisms. Microbial synthesis of TiO_2 comes from the biologically induced hydrolysis of TiF_6. Viruses can also synthesize oxide nanomaterial coatings through hydrolysis [173]. The microbial synthesis of NPs is also related to chelation. The synthesis of semiconductor materials containing highly toxic heavy metals such as CdS and PbS is usually related to the chelation of polypeptides [107]. Among them, phytochelatins and metallothionein are very common chelating agents for stabilizing heavy metal ions in microorganisms [174]. Studies have shown that glutathione in the phytochelatins and the cysteine group in the metallothionein can effectively chelate metal ions. These biological chelating agents will express rapidly under toxic conditions to achieve detoxification. It was reported that glutathione and phytochelatins in yeast were highly expressed to enrich Cd^{2+} and Pb^{2+}, then cysteineprovides a sulfur source to synthesize CdS and PbS NPs [175]. In addition to hydrolysis and chelation mechanisms, some MNMs/MCNMs could be obtained as by-products of microorganism metabolic processes. Additional mechanisms of microbial synthesis of MNMs/MCNMs also include (i) the protein metabolism pathway, in which proteins on the surface of bacteria promote the nucleation of calcite fine-grained minerals; (ii) the sulfur metabolism pathway, in which sulfate-reducing bacteria promote the formation of sulfur-based NPs [176].

8. Environmental applications of microbial synthesis of metal nanomaterials

MNMs/MCNMs as synthesized by microorganisms have realized both merits of metals and nanomaterials, enabling them to expand their applications in the environmental field. Among them, MNMs/MCNMs have been widely used in the

removal of organic pollutants, nutrients, heavy metals, sterilization, and disinfection of water sources. AuNPs are widely used for the removal of organic pollutants. Shi et al. used *Pycnoporus sanguineus* to synthesize AuNPs that further catalyze the degradation of nitroaniline. The resultant AuNPs at optimal conditions can rapidly degrade 12.5 μmol of nitroaniline within 6 minutes [177]. Compared with traditional Au and Ag-based NPs, PdNPs synthesized by microorganisms exhibited more efficient catalytic reduction, dehalogenation, and hydrogenation[178], while MNMs/MCNMs play an important role in the removal of nutrients from water sources[179]. Briefly, nano-zero-valent iron has a small size, large surface area, superior adsorption capacity, and high reduction activity, thus being suitable for removing nitrate pollutants from groundwater[180]. Last but not least, MNMs/MCNMs can use for heavy metal removal, e.g. use of *Geobacter sulfurreducens* to reduce the carcinogenic Cr(Ⅵ) to low-toxic Cr(Ⅲ) [157]; AgNPs as traditional fungicides are often used for disinfection and sterilization due to their high efficiency and stability, e.g., AgNPs of 2-11 nm by microorganisms exhibited the better sterilization effect on *Bacillus subtilis* effect than colloidal Ag by chemical methods[163]. Despite environmental promising of MNMs/MCNMs, additional efforts should be made to investigate the environmental risks of MNMs/MCNMs, as well as to expand their uses in the soil and atmospheric environmental management.

9. Conclusion and perspectives

Microbial biomanufacturing of MNMs/MCNMs has been emerging over the past decades, which not only discovers and develops new nanomaterials, microbial systems, and applicable products in a greener, safer, and more efficient way, but also demonstrates a new biosynthesis strategy to fabricate NPs with controllable shapes, sizes, and structural hierarchy. As compared to conventional physical preparation and chemical synthesis strategies, microbial biomanufacturing of MNMs/MCNMs using living microorganisms (i.e. bacteria, fungi, and yeast) as small and efficient bio-factories has great advantages of cost-effectiveness, eco-friendliness, energy sustainability, and industrial scalability. More importantly, microorganisms can be applied to remove and recycle toxic heavy metals from wastes and pollutants, and then convert them into biogenic NPs with controlled sizes and morphologies. Microorganism-assisted NPs synthesis and the associated parameters can be further optimized to maximize the productivity and safety of NPs.

Despite great progress for microbial biomanufacturing of MNMs/MCNMs, some critical challenges remain to be addressed for increasing its impacts across different fields of biomaterial science, nanoscience, and nanobiotechnology. microorganisms-synthesized MNMs/MCNMs of different compositions are still rather limited. Rational design or discovery of new microorganisms via advanced genetic, molecular, cellular engineering is another promising strategy for not only synthesizing new NPs with controllable morphologies and desirable functions, but also imposing the new functionality of microorganisms with high environmental adaptability and metabolic activity. The specific ways include: 1) Improve the performance of microorganisms through domestication, separation, and genetic engineering, so as to isolate and obtain highly active functional microorganisms. 2) Through the control of the size and shape of the microbial product, the stability, biocompatibility and other properties of the microbial product can be controlled. 3) Make full use of multi-omics sequencing technology, comprehensively analyze the characteristic enzymes and functional genes of microorganisms, and further clarify its synthesis mechanism.

In addition, it is equally important for developing a new biomanufacturing process with optimized operating parameters to isolate, purify, and stabilize the produced MNMs/MCNMs from microorganisms, particularly on an industrial scale, all of which will improve low yield, poor quality, and emanating biotoxicity of MNMs/MCNMs; Finally, parallel to experimental efforts, it is critical to developing multiscale modeling and simulations for a better understanding of the complex interactions between enzymes and metal ions at molecular, cellular, and multicellular scales. The proposed computational models and simulations allow revealing different key aspects of the biomanufacturing process, including mechanism explanation models for elucidating microbial metabolism and pathways, production optimization models for optimizing operating parameters to achieve the maximal yield, economic analysis models for predicting the commercial value of synthetic products, and molecular simulation models for determining crystal structures and formation of NPs. In conclusion, Microbial biomanufacturing of MNMs/MCNMs awaits innovations from interdisciplinary research to catalyze breakthroughs ranging from developing effective microorganisms to controllable NPs synthesis.

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References

1. P. Mondal, A. Anweshan and M. K. Purkait, *Chemosphere*, 2020, **259**, 127509.
2. D. G. Barnes, M. Vidiassov, B. Ruthensteiner, C. J. Fluke, M. R. Quayle and C. R. McHenry, *PLoS One*, 2013, **8**, e69446.
3. T. Wang, J. Lin, Z. Chen, M. Megharaj and R. Naidu, *J. Cleaner Prod.*, 2014, **83**, 413-419.
4. K. Woo and J. Hong, *IEEE*, 2005, **41**, 4137-4139.
5. S. Angaiah, S. Arunachalam, V. Murugadoss and G. Vijayakumar, *ES Energy Environ.*, 2019, **4**, 50-65.
6. N. Li, F. Zhang, H. Wang and S. Hou, *Eng. Sci.*, 2019, **7**, 72-79.
7. S. Ghahari, E. Ghafari, P. Hou and N. Lu, *ES Mater. Manuf.*, 2018, **2**, 51-59.
8. L. Sintubin, W. De Windt, J. Dick, J. Mast, D. van der Ha, W. Verstraete and N. Boon, *Appl Microbiol Biotechnol*, 2009, **84**, 741-749.
9. R. D. Finlay, S. Mahmood, N. Rosenstock, E. B. Bolou-Bi, S. J. Köhler, Z. Fahad, A. Rosling, H. Wallander, S. Belyazid, K. Bishop and B. Lian, *Biogeosciences*, 2020, **17**, 1507-1533.
10. M. Darroudi, S. J. Hoseini, R. K. Oskuee, H. A. Hosseini, L. Gholami and S. Gerayli, *Ceram. Int.*, 2014, **40**, 7425-7430.
11. X. Ren, D. Philo, Y. Li, L. Shi, K. Chang and J. Ye, *Coord. Chem. Rev.*, 2020, **424**, 213516.
12. B. Dey, M. W. Ahmad, A. Almezeni, G. Sarkhel, D. S. Bag and A. Choudhury, *Bull. Mater. Sci*, 2020, **43**, 207.
13. F. Huang, Z. Li, A. Yan, H. Dong, Q. Li, M. Hu, X. Xiong and Q. Gao, *Nanotechnology*, 2020, **31**, 185201.
14. J. Ali, S. Zainab and N. Ali, *J. Nanoanalysis*, 2015, **2**, 32-38.
15. C. T. Dameron, R. N. Reese, R. K. Mehra, A. R. Kortan, P. J. Carroll, M. L. Steigerwald, L. E. Brus and D. R. Winge, *Nature*, 1989, **338**, 596-597.
16. E. F. Delong, R. B. Frankel and D. A. Bazylinski, *Science*, 1993, **259**, 803-806.
17. P. Mukherjee, A. Ahmad, D. Mandal, S. Senapati, S. R. Sainkar, M. I. Khan, R. Parishcha, P. V. Ajaykumar, M. Alam, R. Kumar and M. Sastry, *Nano Lett*, 2001, **1**, 515-519.
18. A. Ahmad, P. Mukherjee, S. Senapati, D. Mandal, M. I. Khan, R. Kumar and M. *Colloids Surf. B Biointerfaces*, 2003, **28**, 313-318.
19. X. Q. Li, H. Z. Xu, Z. S. Chen and G. F. Chen, *J. Nanomater.*, 2011, **2011**, 1-16.
20. S. Iravani and R. S. Varma, *Environ. Chem. Lett.*, 2020, ***18,*** 703-727.
21. S. Iravani and R. S. Varma, *Green Chemistry*, 2019, **21**, 4583-4603.
22. S. Iravani and R. S. Varma, *ACS Sustainable Chem. Eng.*, 2020, **8**, 5395-5409.
23. D. G. Sullivan, M. Cruz-Romero, T. Collins, E. Cummins, J. P. Kerry and M. A.Morris, *Food Hydrocoll.*, 2018, **83**, 355-364.
24. P. Mohanpuria, N. K. Rana and S. K. Yadav, *J. Nanopart. Res.*, 2008, **10**, 507-517.
25. A. Taniguchi, D. Sasaki, A. Shiohara, T. Iwatsubo, T. Tomita, Y. Sohma and M. Kanai, *Angew. Chem. Int. Ed.*, 2014, **53**, 1382-1385.
26. G. Wang, F. Qian, C. W. Saltikov, Y. Jiao and Y. Li, *Nano Res.*, 2011, **4**, 563-570.
27. P. Tartaj, M. P. Morales, T. González-Carre?O, S. Veintemillas-Verdaguer and C. J. Serna, *J. Magn. Magn. Mater.*, 2005, **290-291**, 28-34.
28. Z. Yan, J. Qian, Y. Gu, Y. Su, X. Ai and S. Wu, *Mater. Res. Express*, 2014, **1**, 015401.
29. R. Singh, U. U. Shedbalkar, S. A. Wadhwani and B. A. Chopade, *Appl. Microbiol. Biotechnol.*, 2015, **99**, 4579-4593.

30. L. Du, H. Jiang, X. Liu and E. J. E. C. Wang, *Electrochem. Commun.*, 2007, **9**, 1165-1170.

31. X. Zhang, X. He, K. Wang, Y. Wang, H. Li and W. Tan, *J. Nanosci. Nanotechnol.*, 2009, **9**, 5738-5744.

32. S. He, Z. Yu, Z. Guo and G. Ning, *Biotechnol. Progr.*, 2010, **24**, 476-480.

33. M. Alavi and M. Rai, *Expert Rev. Anti-Infect. Ther.*, 2019, **17**, 419-428.

34. L. Xiong, X. Zhang, Y.-X. Huang, W.-J. Liu, Y.-L. Chen, S.-S. Yu, X. Hu, L. Cheng, D.-F. Liu and H.-Q. Yu, *ACS Appl. Nano Mater.*, 2018, **1**, 1467-1475.

35. G. Mirabello, J. J. Lenders and N. A. Sommerdijk, *Chem. Soc. Rev.*, 2016, **45**, 5085-5106.

36. M. Wang, T. Odoom-Wubah, H. Chen, X. Jing, T. Kong, D. Sun, J. Huang and Q. Li, *Nanoscale*, 2013, **5**, 6599-6606.

37. X. Fang, Y. Wang, Z. Wang, Z. Jiang and M. Dong, *Energies*, 2019, **12**, 190.

38. L. Wen, Z. Lin, P. Gu, J. Zhou, B. Yao, G. Chen and J. Fu, *J. Nanopart. Res.*, 2009, **11**, 279-288.

39. S. D. Corte, T. Hennebel, J. P. Fitts, T. Sabbe, V. Bliznuk, S. Verschuere, D. V. D. Lelie, W. Verstraete and N. Boon, Environ. *Sci. Technol.*, 2011, **45**, 8506-8513.

40. X. Xie, X. Ma, X. Ru, Y. Chang and L. Yang, *Process. Chem.,* 2018, **30**, 1511-1523.

41. C. Liao, Y. Li and S. C. Tjong, *Int. J. Mol. Sci.*, 2019, **20**, 449.

42. K. G. Lee, J. Hong, K. W. Wang, N. S. Heo, D. H. Kim, S. Y. Lee, S. J. Lee and T. J. Park, *Acs. Nano.*, 2012, **6**, 6998-7008.

43. S. K. Das, A. R. Das and A. K. Guha, *Langmuir*, 2009, **25**, 8192-8199.

44. M. F. Lengke, M. E. Fleet and G. Southam, *Langmuir*, 2006, **22**, 2780-2787.

45. T. J. Beveridge and R. G. Murray, *J. Bacteriol.*, 1980, **141**, 876-887.

46. M. Lengke and G. Southam, *Geochim. Cosmochim. Acta*, 2006, **70**, 3646-3661.

47. Y. Konishi, T. Tsukiyama, T. Tachimi, N. Saitoh, T. Nomura and S. Nagamine, *Electrochim. Acta*, 2008, **53**, 186-192.

48. Y. Feng, Y. Yu, Y. Wang and X. Lin, *Curr. Microbiol.*, 2007, **55**, 402.

49. B. Nair and T. Pradeep, *Cryst. Growth Des.*, 2002, **2**, 293-298.

50. S. He, Z. Guo, Y. Zhang, S. Zhang, J. Wang and N. Gu, *Mater. Lett.*, 2007, **61**, 3984-3987.

51. M. I. Husseiny, M. A. El-Aziz, Y. Badr and M. A. Mahmoud, *Acta, Part A: Mol. Biomol. Spectrosc.*, 2007, **67**, 1003-1006.

52. H. Zhang, Q. Li, Y. Lu, D. Sun, X. Lin, D. Xu, H. Ning and S. Zheng, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 285-290.

53. M. Fayaz, C. S. Tiwary, P. T. Kalaichelvan, R. J. C. Venkatesan and S. B. Biointerfaces, *Colloids Surf. B Biointerfaces*, 2010, **75**, 175-178.

54. R. Vaidyanathan, S. Gopalram, K. Kalishwaralal, V. Deepak, S. R. K. Pandian and S. Gurunathan, *Colloids Surf. B Biointerfaces*, 2010, **75**, 335-341.

55. A. Nanda and M. Saravanan, *Nanomedicine*, 2009, **5**, 452-456.

56. N. Pugazhenthiran, S. Anandan, G. Kathiravan, N. K. U. Prakash, S. Crawford and M. Ashokkumar, *J. Nanopart. Res.*, 2009, **11**, 1811.

57. R. Y. Parikh, S. Singh, B. L. V. Prasad, M. S. Patole, M. Sastry and Y. S. Shouche, *Chembiochem*, 2008, **9**, 1415-1422.

58. R. S. Oremland, M. J. Herbel, J. S. Blum, S. Langley, S. J. A. Curran and E. Microbiology, *Appl. Environ. Microbiol.*, 2004, **70**, 52-60.

59. Y. Konishi, K. Ohno, N. Saitoh, T. Nomura, S. Nagamine, H. Hishida, Y. Takahashi and T. Uruga, *J. Biotechnol.*, 2007, **128**, 648-653.

60. M. F. Lengke, M. E. Fleet and G. Southam, *Langmuir*, 2006, **22**, 7318-7323.

61. A. P. Philipse and D. Maas, *Langmuir*, 2002, **18**, 9977-9984.

62. H. Lee, A. M. Purdon, V. Chu and R. M. Westervelt, *Nano Lett.*, 2004, **4**, 995-998.

63. D. P. Cunningham and L. L. Lundie, *Appl. Environ. Microbiol.*, 1993, **59**, 7-14.

64. R.Y. Sweeney, C. B. Mao, X. X. Gao, J. L. Burt, A. M, Belcher, G. Georgiou and B. L. Iverson, *Chem. Biol.*, 2004, **11**, 1553-1559.

65. D. R. Lovley, E. J. P. Phillips, Y. A. Gorby and E. R. Landa, *Nature*, 1991, **350**, 413-416.

66. L. Xin, S. Chen, W. Hu, S. Shi, S. Wei, Z. Xiang and H. Wang, *Carbohydr. Polym.*, 2009, **76**, 509-512.

67. M. Labrenz, G. K. Druschel, T. Thomsen-Ebert, B. Gilbert, S. A. Welch, K. M. Kemner, G. A. Logan, R. E. Summons, G. D. Stasio and P. L. Bond, *Science*, 2000, **290**, 1744-1747.

68. H. J. Bai, Z. M. Zhang and J. Gong, *Biotechnol. Lett.*, 2006, **28**, 1135-1139.

69. K. Prasad, A. K. Jha and A. R. Kulkarni, *Nanoscale. Res. Lett.*, 2007, **2**, 248-250.

70. D. R. Lovley, J. F. Stolz, G. L. Nord and E. J. P. Phillips, *Nature*, 1987, **330**, 252-254.

71. C. Zhang, H. Vali, C. S. Romanek, T. J. Phelps and S. V. Liu, *Am. Mineral.*, 1998, **83**, 1409-1418.

72. S.-H. Yu, *Biomineralization II*, 2007, 79-118.

73. Y. Roh, R. J. Lauf, A. D. Mcmillan, C. Zhang, C. J. Rawn, J. Bai and T. J. Phelps, *Solid State Commun.* 2001, **118**, 529-534.

74. U. Kumar, A. Shete, A. S. Harle, O. Kasyutich, W. Schwarzacher, A. Pundle and P. Poddar, *Chem. Mater.*, 2008, **20**, 590-593.

75. H. J. Bai, Z. M. Zhang, Y. Guo and G. E. Yang, *Colloids Surf. B Biointerfaces*, 2009, **70**, 142-146.

76. R. G. Saratale, I. Karuppusamy, G. D. Saratale, A. Pugazhendhi, G. Kumar, Y. Park, G. S. Ghodake, R. N. Bhargava, J. R. Banu, H. S. Shin, *Colloids Surf., B*, 2018, **170**, 20-35.

77. A. Tripathy, A. M. Raichur, N. Chandrasekaran, T. C. Prathna and A. J. Mukherjee, *J. Nanopart. Res.*, 2010, **12**, 237-246.

78. P. Mukherjee, A. Ahmad, D. Mandal, S. Senapati, S. R. Sainkar, M. I. Khan, R. Ramani, R. Parischa, P. V. Ajayakumar and M. Alam, *Chem. Int. Ed.*, 2001, **40**, 3585-3588.

79. P. Mukherjee, S. Senapati and D. Mandal, *Chembiochem*. 2002, **3**, 461-463.

80. R. G. Saratale, I. Karuppusamy, G. D. Saratale, A. Pugazhendhi, G. Kumar, Y. Park, G. S. Ghodake, R. N. Bharagava, J. R. Banu and H. S. Shin, *Colloids Surf. B Biointerfaces*, 2018, **170**, 20-35.

81. G. S. Dhillon, S. K. Brar, S. Kaur and M. Verma, *Crit. Rev. Biotechnol.*, 2012, **32**, 49-73.

82. G. Grasso, D. Zane and R. Dragone, *Nanomaterials (Basel)*, 2019, **10**, 11.

83. L. Du, L. Xian and J. X. Feng, *J. Nanopart. Res.*, 2011, **13**, 921-930.

84. A. N. Mishra, S. Bhadauria, M. S. Gaur and R. Pasricha, *JOM*, 2010, **62**, 45-48.

85. J. M. Jacob, P. N. L. Lens and R. M. Balakrishnan, *Microb. Biotechnol*, 2016, **9**, 11-12.

86. A. Ahmad, S. Senapati, M. I. Khan, R. Kumar and M. J. Sastry, *J. Biomed. Nanotechnol.*, 2005, **1**, 47-53.

87. V. Verma, S. Singh, R. SolankiSatya and P. Letters, *Nanoscale Res. Lett.*, 2011, **6,** 261.

88. P. Mukherjee, M. Roy, B. P. Mandal, G. K. Dey, P. K. Mukherjee, J. Ghatak, A. K. Tyagi and S. P. Kale, *Nanotechnology*, 2008, **19**, 075103.

89. N. Vigneshwaran, A. A. Kathe, P. V. Varadarajan, R. P. Nachane and R. H. Balasubramanya, *Colloids Surf. B Biointerfaces*, 2006, **53**, 55-59.

90. A. Ingle, M. Rai, A. Gade and M. Bawaskar, *J. Nanopart. Res.*, 2009, **11**, 2079-2085.

91. S. Basavaraja, S. D. Balaji, A. Lagashetty, A. H. Rajasab and A. Venkataraman, *Mater. Res. Bull.*, 2008, **43**, 1164-1170.

92. R. Sanghi and P. Verma, *Bioresour. Technol.*, 2009, **100**, 501-504.

93. A. K. Gade, P. Bonde, A. P. Ingle, P. D. Marcato, N. Durán and M. K. Rai, *Colloids Surf. B Biointerfaces*, 2008, **2**, 243-247.

94. S. S. Birla, V. V. Tiwari, A. K. Gade, A. P. Ingle, A. P. Yadav and M. K. Rai, *Appl. Microbiol.*, 2010, **48**, 173-179.

95. N. S. Shaligram, M. Bule, R. Bhambure, R. S. Singhal, S. K. Singh, G. Szakacs and A. Pandey, *Process Biochem.*, 2009, **44**, 939-943.

96. D. S. Balaji, S. Basavaraja, R. Deshpande, D. B. Mahesh, B. K. Prabhakar and A. Venkataraman, *Colloids Surf. B Biointerfaces*, 2009, **68**, 88-92.

97. K. Kathiresan, S. Manivannan, M. A. Nabeel, B. J. C. Dhivya and S. B. Biointerfaces, *Colloids Surf. B Biointerfaces*, 2009, **71**, 133-137.

98. D. Philip, *Spectrochim. Acta, Part A*, 2009, **73**, 374-381.

99. V. Bansal, D. Rautaray, A. Ahmad and M. Sastry, *J. Mater. Chem.*, 2004, **14**, 3303-3305.

100. T. L. Riddin, M. Gericke and C. G. Whiteley, *Nanotechnology*, 2006, **17**, 3482-3489.

101. V. Bansal, P. Poddar, A. Ahmad and M. Sastry, *J. Am. Chem.*, *Soc.*, 2006, **128**, 11958-11963.

102. I. Uddin, S. Adyanthaya, A. Syed, K. Selvaraj and P. Poddar, *J. Nanosci. Nanotechnol.*, 2008, **8**, 3909-3913.

103. P. S. Pimprikar, S. S. Joshi, A. R. Kumar, S. S. Zinjarde and S. K. Kulkarni,*Colloids Surf. B Biointerfaces,* 2009, **74**, 309-316.

104. S. K. Das, A. R. Das and A. K. Guha, *Small*, 2010, **6**, 1012-1021.

105. M. Kowshik, S. Ashtaputre, S. Kharrazi, W. Vogel, J. Urban, S. K. Kulkarni and K. M. Paknikar, *Nanotechnology*, 2003, **14**, 95-100.

106. R. Cui, H. H. Liu, H. Y. Xie, Z. L. Zhang, Y. R. Yang, D. W. Pang, Z. X. Xie, B. B. Chen, B. Hu and P. Shen, *Adv. Funct. Mater.*, 2009, **19**, 2359-2364.

107. S. K. Das, A. R. Das and A. K. Guha, *Langmuir,* 2009, **25**, 360-366.

108. K. B. Narayanan and N. Sakthivel, *Adv. Colloid Interface Sci.*,2010, **156**, 1-13.

109. H. F. Bao, N. Hao, Y. X. Yang and D. Y. Zhao, *Nano Res.*, 2010, **3**, 481-489.

110. M. Kowshik, W. Vogel, J. Urban, S. K. Kulkarni and K. M. Paknikar, *Adv. Mater.,* 2010, **14**, 815-818.

111. A. Rahman, J. Lin, F. E. Jaramillo, D. A. Bazylinski, C. Jeffryes, and S. A. Dahoumane, *Molecules*, 2020, **25**, 3246.

112. H. Bao, N. Hao, Y. Yang and D. Zhao, *Nano Res.*, 2010, **3**, 481-489.

113. X. Ma, H. Chen, L. Yang, K. Wang and L. Yuan, *Angew. Chem. Int. Ed.*, 2011, **50**, 7414-7417.

114. P. S. Pimprikar, S. S. Joshi, A. R. Kumar, S. S. Zinjarde and S. K. Kulkarni, *Colloids Surf. B Biointerfaces*, 2009, **74**, 309-316.

115. P. Mohanpuria, N. K. Rana and S. K. Yadav, *J. Nanopart. Res.*, 2007, **10**, 507-517.

116. J. W. Moon, C. J. Rawn, A. J. Rondinone, L. J. Love, Y. Roh, S. M. Everett and R. J. Lauf, *J. Ind. Microbiol. Biotechnol.*, 2010, **37**, 1023-1031.

117. A. Mourato, M. Gadanho, A. R. Lino and R. Tenreiro, *Bioinorg. Chem. Appl.*, 2011, **2011**, 546074.

118. A. Mishra, S. K. Tripathy, S. I. Yun, *J. Nanosci. Nanotechnol.*, 2011, **11**, 243-248.

119. M. Subramanian, N. M. Alikunhi and K. Kandasamy, *J. Nanosci. Nanotechnol.*, 2010, **3**, 428-433.

120. M. Wang, Q. Tan, J. F. Chiang, J. Li, *Front. Env. Sci. Eng.*, 2017, **11**, 1.

121. T. J. Beveridge and R. G. Murray, *J. Bacteriol.*, 1980, **141**, 876-887.

122. T. Klaus, R. Joerger, E. Olsson and C. G. Granqvist, *Proc. Natl. Acad. Sci. U. S. A*, 1999, **96**, 13611-13614.

123. N. Saifuddin, C. W. Wong and Y. A. A. Nur, *J. Chem.*, 2009, 6, 61-70.

124. A. R. Shahverdi, S. Minaeian, H. R. Shahverdi, H. Jamalifar and A. A. Nohi, *Process Biochem.*, 2007, **42**, 919-923.

125. G. Wang, B. G. Zhang, S. Li, M. Yang, and C. C. Yin, *Bioresour. Technol.*, 2017, **227**, 353-358.

126. Y. Dessie, S. Tadesse, R. Eswaramoorthy and B. Abebe, *J. Sci.: Adv. Mater. Devices*, 2019, **4**, 353-369.

127. I. Ali, C. Peng, Z. M. Khan and I. Naz, *J. Basic Microb.*, 2017, **57**, 643-652.

128. R. Raliya. *Biotechnol. Rep.*, 2015, **5**, 22-26.

129. J. P. Monrás, B. Collao, R. C. Molina-Quiroz, G. A. Pradenas, L. A. Saona, V. Durán-Toro, N. órdenes-Aenishanslins, F. A. Venegas, D. E. Loyola and D. Bravo, *BMC Genomics*, 2014, **15**, 1099.

130. R. M. Tripathi, A. S. Bhadwal, R. K. Gupta, P. Singh, A. Shrivastav and B. R. Shrivastav, *J. Photochem. Photobiol.*, 2014, **141**, 288-295.

131. Y. Gu, B. Wang, F. He, M. J. Bradley and P. G. Tratnyek, *Environ. Sci. Technol.*, 2017, **51**, 12653-12662.

132. V. K. Sharma, J. Filip, R. Zboril and R. S. Varma, *Chem. Soc. Rev.*, 2015, **44**, 8410-8423.

133. D. O’Connor, D. Hou, Q. Liu, M. R. Palmer and R. S. Varma, *ACS Sustainable Chem. Eng.*, 2020, **8**, 15791-15808.

134. S. Senapati, A. Syed, S. Khan, R. Pasricha, M. I. Khan, R. Kumar, A. Ahmad, *Curr. Nanosci*., 2014, **10**, 588-595.

135. A. Ahmad, P. Mukherjee, D. Mandal, S. Senapati, M. I. Khan, R. Kumar and M. Sastry, *J. Am. Ceram. Soc.*, 2002, **124**, 12108-12109.

136. R. Cai, B. Zhang, J. Shi, M. Li and Z. He, *ACS Sustainable Chem. Eng.,* 2017, **5**, 7690-7699.

137. Z. Chen, H. Chen, H. Meng, G. Xing, X. Gao, B. Sun, X. Shi, H. Yuan, C. Zhang and R. Liu, *Toxicol. Appl. Pharmacol.*, 2008, **230**, 364-371.

138. X. Liu, J. Wang, L. Yue, B.P. Xin, S. Chen, J. L. Dai, W. Q. Wang and Y. T. Wang, *Bioproc. Biosyst. Eng.*, 2015, **38**, 219-227.

139. S. Qi, M. Zhang, X. Guo, L. Yue and J. Wang, Z. Q. Shao and B. Q. Xin, *J. Nanopart. Res.* 2017, **19**, 212.

140. S. Sharma, V. Dutta, P. Raizada, A. Hosseini-Bandegharaei, P. Singh and V. H. Nguyen, *Environ. Chem. Lett.*, 2020, **19**, 271-306.

141. A. Sanyal, D. Rautaray, V. Bansal, A. Ahmad and M. Sastry, *Langmuir*, 2005, **21**, 7220-7224.

142. S. Yan, W. He, C. Sun, X. Zhang, H. Zhao, Z. Li, W. Zhou, X. Tian, X. Sun and X. Han, *Dyes Pigm.,* 2009, **80**, 254-258.

143. C. Lin, W. Yu-Ling, L. Qing-Yan and Y. Yang, *Chinese J. Struct. Chem.,* 2016, **35***,* 615-620.

144. L. J. Chen, W. J. Feng, Z. S. Pu, X. Wang and C. K. Song, *Ionics*, 2019, **25**, 5625-5632.

145. T. J. Park, S. Y. Lee, N. S. Heo and T. S. Seo, *Angew. Chem. Int. Ed.*, 2010, **122**, 7173-7178.

146. B. Kowalczyk, I. Lagzi and B. A.Grzybowski, *Curr. Opin. Colloid Interface Sci.*, 2011, **16**, 135-148.

147. D. Fletcher, *IEEE Trans. Magn.*, 1991, **27**, 3655-3677.

148. V. L. Jimenez, M. C. Leopold, C. Mazzitelli, J. W. Jorgenson and R. W. Murray, *Anal. Chem.*, 2003, **75**, 199-206.

149. J. P. Wilcoxon，J. E. Martin and P. Provencio, *Langmuir*, 2000, **16**, 9912-9920.

150. V. Sharma, K. Park and M. Srinivasarao, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 4981-4985.

151. A. Akthakul, A. I. Hochbaum, F. Stellacci and A. M. Mayes, *Adv. Mater.*, 2005, **17**, 532-535.

152. O. M. Wilson, R. W. J. Scott, J. C. Garcia-Martinez and R. M. Crooks, *Chem. Mater.*, 2004, **16**, 4202-4204.

153. S. A. Dahoumane, M. Mechouet, K. Wijesekera, C. D. M. Filipe, C. Sicard, D. A. Bazylinskie and C. Jeffryes*, *Green chem.*, 2017, **19**, 552-587.

154. R. Singh, U. U. Shedbalkar, S. A. Wadhwani and B. A. Chopade, *Appl. Microbiol. Biotechnol.*, 2015, **99**, 4579-4593.

155. K. B. Narayanan, and N. Sakthivel, *Colloid Interface Sci.*, 2010, **156**, 1-13.

156. P. L. Kashyap, S. Kumar, A. K. Srivastava and A. K. Sharma, *Microbiol. Biotechnol.*, 2013, **29**, 191-207.

157. G. Gahlawat and A. R. Choudhury, *RSC Adv.*, 2019, **9**, 12944-12967.

158. S. Y. He, Z. R. Guo, Y. Zhang, S. Zhang, J. Wang and N. Gu, *Mater. Lett.*, 2007, **61**, 3984-3987.

159. Y. M. Li, Y. M. Li, Li Qiang and B. Jie, *J. Nanomater.*, 2017, **2017**, 9703614.

160. S. K. Srikar, D. D. Giri, D. B. Pal, P. K. Mishra and S. N. Upadhyay, *Green Sustainable Chem.*, 2016, **6**, 34-56.

161. R. Ramanathan, A. P. O’ Mullane, R. Y. Parikh, P. M. Smooker, S. K. Bhargava and V. Bansal, *Chemosphere*, *Langmuir*, 2011, **27**, 714-719.

162. G. S. Dhillon, S. K. Brar, S. Kaur and M. Verma, *Crit. Rev. Biotechnol.*, 2012, **32**, 49-73.

163. B. Liu, J. Xie, J. Y. Lee, Y. P Ting, and J. P. Chen, *J. Phys. Chem. B*, 2005, **109**, 15256-15263.

164. J. P. Xie, J. Y. Lee, D. I. C. Wang, and Y. P. Ting, *J. Phys. Chem. C*, 2007, **111**, 16858-16865.

165. K. Kathiresan, S. Manivannan, M. A. Nabeel and B. Dhivya, *Colloids Surf. B*, 2009, **71**, 133-137.

166. M. Gericke and A. Pinches, *Gold Bull.*, 2006, **39**, 22-28.

167. T. J. Park, S. Y. Lee, N. S. Heo and T. S. Seo, *Angew. Chem. Int. Ed.*, 2010, **49**, 7019-7024.

168. K. Deplanche, I. Caldelari, I. P. Mikheenko, F. Sargent and L. E. Macaskie, *Microbiology*, 2010, **156**, 2630-2640.

169. Y. L. Chen, H. Y. Tuan, C. W. Tien, W. H. Lo and Y. C. Hu, *Biotechnol. Progr.*, 2010, **25**, 1260-1266.

171. S. He, Z. Yu, Z. Guo and G. Ning, *Biotechnol. Progr.*, 2008, **24**, 476-480.

172. D. Wc. Davies, K. T. Butler, A. J. Jackson, A. Morris, J. M. Frost, J. M. Skelton and A. Walsh, Chem, 2016, 1, 617-627.

173. Y. Amemiya, A. Arakaki, S. S. Staniland, T. Tanaka and T. Matsunaga, *Biomaterials*, 2007, **28**, 5381-5389.

174. N. Krumov, I. Perner-Nochta, S. Oder, V. Gotcheva, A. Angelov and C. Posten, *Chem. Eng. Technol.*, 2010, **32**, 1026-1035.

175. M. R. Lisy, A. Hartung, C. Lang, D. Schüler, W. Richter, J. R. R. Reichenbach, W. A. Kaiser and I. Hilger, *Invest*, 2007, **42**, 235.

176. D. Mandal, M. E. Bolander, D. Mukhopadhyay, G. Sarkar and P. Mukherjee, *Appl. Microbiol. Biotechnol.*, 2006, **69**, 485-492.

177. H. Shi, N. W. Zhu, Y. L. Cao and P. X. Wu, *Nanoscale Res. Lett.*, 2015, **10**, 147-155.

178. S. De Corte, T. Hennebel, J. P. Fitts, T. Sabbe, V. Bliznuk, S. Verschuere, D. van der Lelie, W. Verstraete and N. Boon, *Environ. Sci. Technol.*, 2011, **45**, 8506-8513.

179. Y. Tuo, G. f. Liu, B. Dong, H. L. Yu, J. T. Zhou, J. Wang and R. F. Jin, *Environ. Sci. Pollut. Res.*, 2017, **24**, 5249-5258.

180. Y. Zhang, Y. M. Li, J. F. Li, L. J. Hu and X. M. Zheng, *Chem. Eng. J.*, 2011, **2**, 526-531.