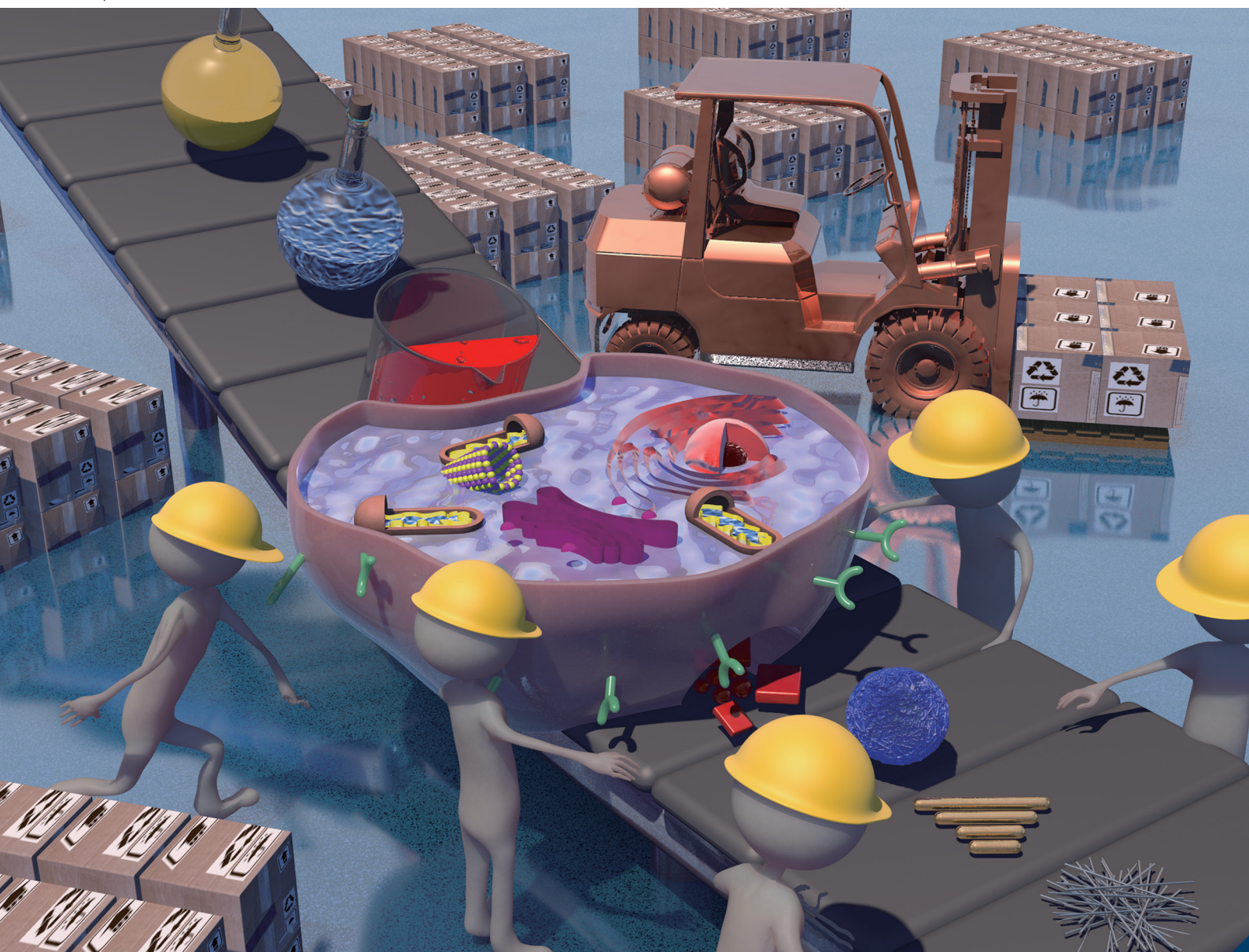


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Microbial biomanufacture of metal/metallic nanomaterials and metabolic engineering: design strategies, fundamental mechanisms, and future opportunities

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Biomanufacturing metal/metallic nanomaterials with ordered micro/nanostructures and controllable functions is of great importance in both fundamental studies and practical applications due to their low toxicity, lower pollution production, and energy conservation. Microorganisms, as efficient biofactories, have a 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. Significant 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 biomanufacture 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 the current challenges and future research directions in this growing multidisciplinary field of biomaterials science, nanoscience, and nanobiotechnology.

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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 structure. Among different NPs, metal/metallic compound nanomaterials (MNM/MCNM) are a special class of NPs¹ due to their unique optical, catalytic, magnetic, and chemical properties, making them promising materials for many applications in optics, catalysis and pollutant degradation.^{2,3} In addition, MNMs/MCNMs are most widely used in environmental remediation, drug transportation,^{4–6} and construction materials,⁷ so the demand for different types and performance requirements has increased. With the continuous increase of severe environmental issues caused by materials-synthesis processes and the accumulation of material waste, the development of environmentally friendly MNMs/MCNMs is fundamentally and practically important for environmental and materials science.

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

Apart from conventional chemical and physical methods, microbial biomanufacturing has been developed for the synthesis of MNMs/MCNMs.¹⁴ The microbial synthesis of



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nanomaterials can be traced back to 1989: a biosynthesis method using *Candida glabrata* was used to synthesize intracellular CdSe nanomaterials.¹⁵ Then, the mineralization and synthesis of magnetic NPs in magnetotactic bacteria was reported in 1993.¹⁶ In 2001, the biosynthesis of Ag nanoparticles (AgNPs) by *Fusarium oxysporum* was reported, which successfully demonstrated the concept of biosynthesis technology for the first time.¹⁷ Microorganisms exist ubiquitously on Earth. Their rapid growth and reproduction, strong environmental adaptability, and diverse metabolic types allow them first to capture target ions from the environment and then to use enzymes, proteins, and other active substances for carrying out a series of bioprocessing steps to synthesize NPs. Microorganisms are also recognized as “nanomaterial processing plants”.¹⁸ The use of microorganisms to synthesize MNMs/MCNMs has several environmentally friendly advantages, including a reduction in chemical consumption, a decrease in secondary pollution, and mass production at low cost.¹⁹ Meanwhile, the synthesis process does not require harsh conditions, but instead can occur at room temperature and neutral pH, thus making the whole process safe, economical, and productive. Second, biological modifications of the surface of MNMs/MCNMs by microorganisms enable a higher biocompatibility and structural stability to be achieved. On the other hand, the microbial synthesis of MNMs/MCNMs also has some limits for controlling the cell stability, the separation and purification of products, and the bioaccessibility of some types of microorganisms. From a mechanistic view point, while significant efforts have been made for the synthesis of MNMs/MCNMs, molecular mechanisms that mediate 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}

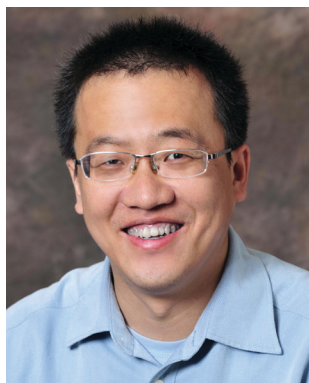
Here, this review aims to summarize, categorize, and analyze the recent and important findings on the microbial biomanufacture of MNMs/MCNMs and metabolic engineering. Specifically, this review mainly covers the fundamental principles of microbial

biosynthesis from intracellular, extracellular and other environments, selectively highlights some typical and interesting microbial-induced MNM/MCNM systems, and finally presents some personal opinions about the current challenges and future directions of the microbial biomanufacture of MNMs/MCNMs. Hopefully, this review will stimulate more research efforts to develop new, green microorganisms for MNMs/MCNMs production, which will offer a better mechanistic understanding of synthesis strategies, processes, and mechanisms.

2. General biomanufacturing process of metal/metallic compound nanomaterials

Generally, MNMs/MCNMs can be synthesized by either “top-down” or “bottom-up” methods,²³ although most microbial synthesis is driven by bottom-up methods. The top-down methods are often developed for the breakdown of larger compounds into nanoscale compounds through external physical and/or chemical forces. These physical or chemical top-down synthesis processes enable the preparation of various MNM/MCNM structures, but they often suffer from the relatively large cost of the 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 the MNMs/MCNMs can be well controlled, although 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 under neutral pH conditions compared with physical and chemical methods.²⁴ Generally, there are two typical microbial synthesis methods, *i.e.*, intracellular and extracellular processes. First, 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 synthesized using physical and chemical methods.²⁵ Second, microorganisms can biologically modify the surface of MNMs/MCNMs to achieve 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-like, flat, dendritic, decahedral, icosahedral, 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 BaTiO₃, CdTe, and CdSe,²⁸ which possess more physicochemical properties and functions



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(stronger Raman and Rayleigh scatterings, higher catalytic activity, and better optical properties) than ordinary NPs.

3. Biomanufacture strategies of metal/metallic compound nanomaterials

Due 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 So far, bacteria, fungi, and yeasts³⁰ are the most common microorganisms used to synthesize MNMs/MCNMs. Microbial synthesis is generally classified into intracellular and extracellular syntheses. For instance, intracellular synthesis produces MNMs/MCNMs in cell walls, which requires sonic degradation or special reactions to extract the 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 microorganisms, prokaryotic bacteria have received the most attention in the area of NP biosynthesis. 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 the cells induces a strong adsorption and absorption capacity for the metal cations, followed by the self-assembly of metal cations into NPs by different active molecules inside and outside the cells.²⁴

Table 1 presents dozens of bacteria for NP synthesis, including *Pseudomonas* sp., *Shewanella* sp., *Bacillus* sp., *Lactobacillus* sp., and sulfate-reducing bacteria.³³ NPs synthesized by bacteria have several common features. First, bacteria can use different synthetic metal materials, including Au, Ag, Pd, Fe₃O₄, ZnS, CdS, CdTe, and TiO₂. As shown in Fig. 1, Xiong *et al.* proposed the use of *Shewanella oneidensis* to produce Pd NPs via the reduction of PdCl₄²⁻ for the removal of pollutants.³⁴ They observed that the activated Pd NPs were synthesized via a contact-production mechanism in which *Shewanella oneidensis* acted as a reducing, capping, and stabilizing agent to produce Pd NPs of different shapes and compositions by activating KOH at elevated temperature. The resultant Pd NPs showed enhanced catalytic reduction by converting 4-nitrophenol to 4-aminophenol,

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

Bacteria	Nanoparticle	Localization/morphology	Size (nm)	Ref.
<i>Rhizopus oryzae</i>	Au	Spherical	10	43
<i>Plectonema boryanum</i>	Au	Cubic	25	44
<i>Bacillus subtilis</i> 168	Au	Octahedral inside cell wall	5–25	45
Sulfate-reducing bacteria	Au	Cell envelope	<10	46
<i>Shewanella algae</i>	Au	Periplasmic space and bacterial envelope	10–20	47
<i>Plectonema boryanum</i> UTEX485	Au	Membrane vesicles/cubic	10	44
<i>Escherichia coli</i> DH5c	Au	Cell surface/spherical	ND	30
<i>Rhodobacter capsulatus</i>	Au	Plasma membrane	ND	48
<i>Lactobacillus</i> sp.	Au, Ag, Au–Ag	Hexagonal/contour	20–50	49
<i>Rhodospseudomonas capsulata</i>	Au	Spherical	10–20	50
<i>Pseudomonas aeruginosa</i>	Au	ND	15–30	51
<i>Corynebacterium</i> sp. SH09	Ag	Cell wall	10–15	52
<i>Enterobacter aerogenes</i>	Ag	Spherical	25–35	53
<i>Morganella</i> sp.	Ag	Spherical	20	54
<i>P. aeruginosa</i>	Ag	Spherical	13	54
<i>Bacillus amyloliquefaciens</i>	Ag	ND	14.6	55
<i>Bacillus</i> sp.	Ag	Periplasmic space	5–15	56
<i>Morganella</i> sp.	Ag	Spherical	20	57
<i>Pseudomonas aeruginosa</i>	Se	Spherical/contour	ND	58
<i>Shewanella algae</i>	Pt	ND	5	59
<i>Plectonema boryanum</i> UTEX 485	Pt	Spherical, chains, and dendritic	30	60
<i>Magnetospirillum magnetotacticum</i>	Fe ₃ O ₄	Membrane-bound/cuboctahedrons	47.1	61
<i>M. magnetotacticum</i> (MS-1)	Fe ₃ O ₄	Inside the cell/cuboctahedron	50	62
<i>Clostridium</i>	CdS	Cell surface	ND	63
<i>Escherichia coli</i>	CdS	Spherical and elliptical	2–5	64
<i>Rhodospseudomonas palustris</i>	CdS	Spherical	8.0	65
<i>Gluconacetobacter xylinus</i>	CdS	Cellulose fibre	30	66
Sulfate-reducing bacteria	ZnS	Spherical	2–5	67
<i>Rhodobacter sphaeroides</i>	ZnS	Spherical	8	68
<i>Lactobacillus</i> sp.	Ti	Spherical	40–60	69
<i>Plectonema boryanum</i> UTEX 485	Pt	Spherical, chains, and dendritic	30	60
<i>Geobacter metalireducens</i> GS-15	Magnetite	ND	10–50	70
Thermophilic bacteria TOR-39	Magnetite	Octahedral	<12	71
<i>Actinobacter</i> sp.	Magnetite	Quasi-spherical	10–40	72
<i>Thermoanaerobacter ethanolicus</i> (TOR-39)	Co, Cr, Ni-substituted-	Octahedral	ND	73
<i>Brevibacterium casei</i>	Co ₃ O ₄	ND	5–7	74
<i>Rhodobacter sphaeroides</i>	PbS	Spherical	10.5	75

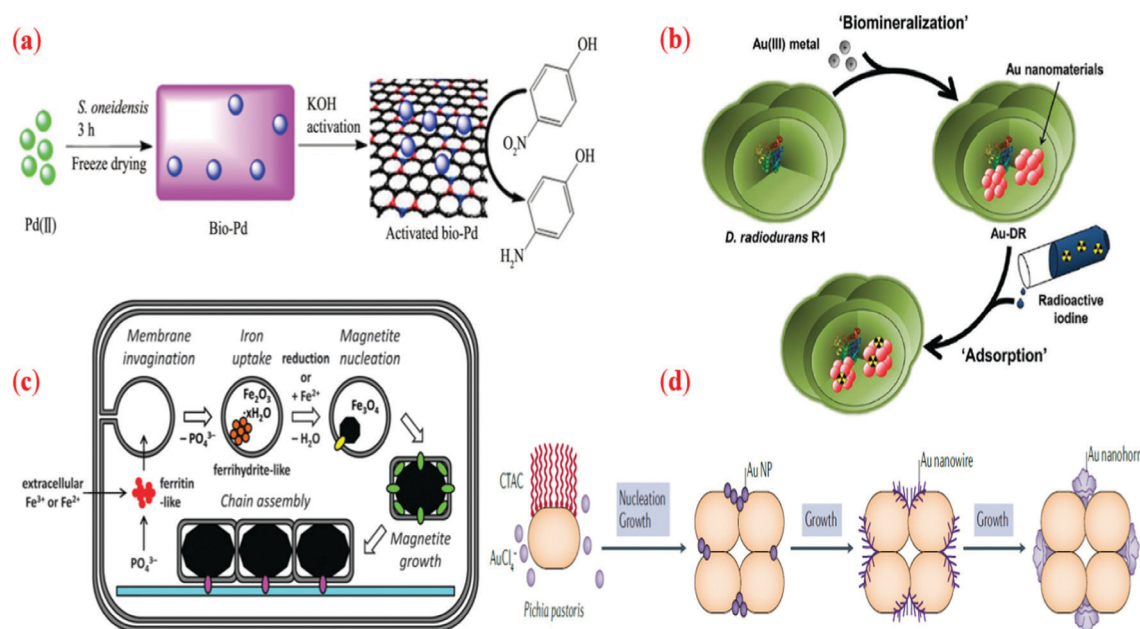


Fig. 1 (a) Preparation of heteroatom-doped porous carbon materials with Pd NPs synthesized by *Shewanella oneidensis*.³⁴ (b) Schematic illustration of the bioremediation procedure of radioactive iodine anions using Au-*Deinococcus radiodurans*. (c) Model of the biomineralization of magnetite in the magnetosomes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

as confirmed by a remarkable apparent kinetic constant of $5.0 \times 10^{-3} \text{ s}^{-1}$, which was 12 times greater than that of the raw biogenic Pd NPs.

However, many aspects of magnetite biomineralization in magnetotactic bacteria are still unclear. A study found that magnetotactic bacteria can biomineralize magnetosomes and form magnetite.³⁵ In addition, *Pichia pastoris* can also synthesize gold nanowires.³⁶ The above examples confirm the specificity and diversity of bacteria when synthesizing materials. Second, synthetic MNMs/MCNMs have a wide range of spherical-like particle sizes ranging from 0.1 to 300 nm. Also, different bacteria synthesize different MNMs/MCNMs. For instance, *Escherichia coli* and *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 In another example, De Corte *et al.*³⁹ reported that using hydrogen as an electron supply, *Shewanella oneidensis* can simultaneously reduce Pd^{2+} and Au^{3+} metal ions into bimetallic Pd-Au NPs. Among these bacteria, *Escherichia coli* is not only recognized as having a strong synthetic ability but was also further genetically engineered to improve its synthesis performance. As shown in Fig. 2(b) and (c), recombinant *Escherichia coli* can secrete metal-binding proteins and synthesize CdSe QDs.

Bacteria-based microbial synthesis has many advantages for the synthesis of MNMs/MCNMs. Bacteria are easier to isolate, survive, and cultivate due to natural evolution, the already have

a pre- or co-existence with metal ions under different environmental conditions, and they can be mass-produced in a short time at 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 the bioreduction of inorganic ions in bacteria, we can amplify the homologous or heterologous gene-encoding proteins that are responsible for bioreduction.⁴⁰

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 is much more difficult than that of prokaryotes.⁷⁶ Fungi including *Aspergillus flavus*, *Trichoderma asperellum*, *Coriolus versicolor*, *Cladosporium*, *Fusarium oxysporum*, and *Penicillium fellutanum* have their own merits for the synthesis of 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 them to produce nucleation-rich centers for synthesizing highly dispersed NPs by slowing down particle aggregation and the formation of mucus media. In addition, since the nanoparticles precipitated outside the cell are devoid of unnecessary cellular components, they can be used directly in various applications.

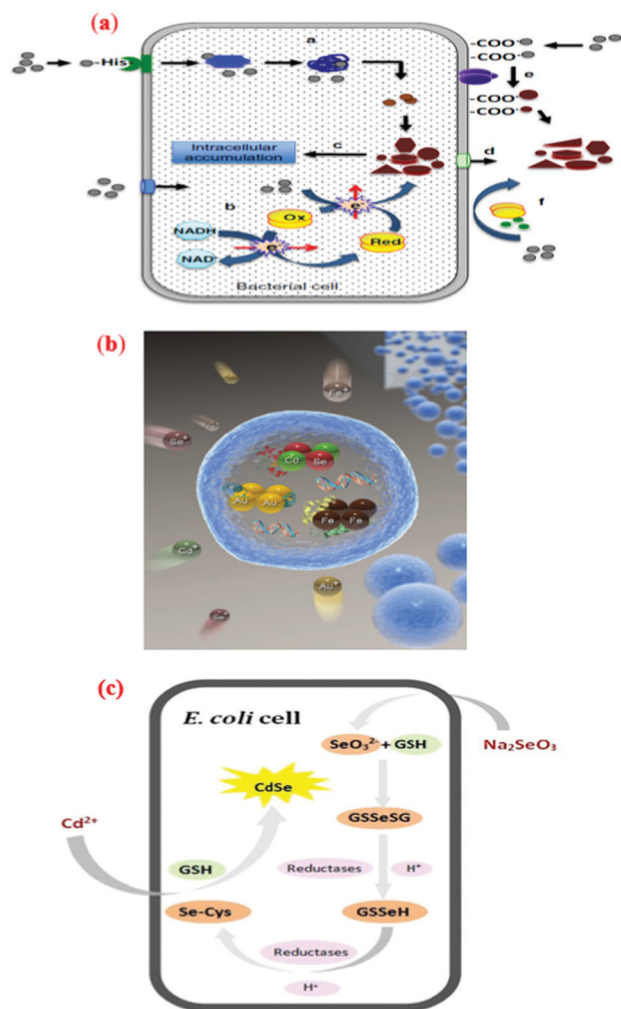


Fig. 2 (a) Intracellular synthesis and metabolic pathways of AgNPs by bacteria.⁴¹ (b) Biosynthesis schematic for the *in vitro* synthesis of MNMs/MCNMs by recombinant *Escherichia coli* expressing metal-binding proteins.⁴² (c) Scheme of the biosynthesis of fluorescent CdSe QDs by *Escherichia coli*.²⁸

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 potential in the synthesis of AuNPs. Liang *et al.*⁸³ developed the fastest approach, as reported so far, to synthesize spherical AuNPs with a controllable size of 45 nm within 1 minute using the cell filtrate of *Penicillium* to react with AuCl₃. 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 in an extracellular environment. This extracellular reduction synthesis was very efficient for the production of AgNPs within several minutes upon bringing silver ions into contact with the cell filtrate.

Apart from AgNPs and AuNPs, fungi also demonstrate an ability to synthesize magnetic NPs and metal sulfide NPs. For instance, *Candida glabrata* can produce CdS and PbS when culturing with Cd²⁺ and Pb²⁺.⁸⁵ Different fungi have different selectivity and specificity for the synthesis of different NPs.

Future efforts should be devoted to discovering more fungi for synthesizing different MNMs/MCNMs.

3.3. Yeasts

Yeasts are considered as the first domestic microorganism of human beings. As a single-cell fungus, yeasts not only have a strong detoxification ability but can also accumulate a large number of heavy metal ions. Yeasts are rich in biomolecules such as glutathione, metallothioneins, and phytochelatins. On the one hand, active molecules in yeast cells enhance the resistance of cells, and on the other hand, they improve the detoxification ability of cells.^{103,104} Yeasts including *Extremophilic*, *Candida guilliermondii*, *Pichia capsulata*, *Rhodospiridium diobovatum*, *Rhodotorula mucilaginosa*, and *Saccharomyces cerevisiae* have been found to synthesize NPs.^{104–106} Since phytochelatins in the yeast cells can efficiently chelate highly toxic, heavy metal ions (e.g., Cd²⁺), yeasts are 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 glabrata* detoxified metal ions by generating metal-thiolate complexes with phytochelatins to produce the intracellular spherical and mono-dispersed quantum crystallites of CdS.¹⁰⁸ Yeast cells can also synthesize CdTe NPs *via* extracellular growth. Bao *et al.* reported that when adding CdCl₂ and NaTeO₃ 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, yeasts are also reported to synthesize AuNPs and AgNPs. Pimprikar *et al.* used tropical marine yeast strains to synthesize AuNPs by changing the number of cells and the concentration of gold salts to control the morphology and size of the AuNPs.¹⁰³ Later, Kowshik *et al.* used a silver-tolerant yeast strain MKY3 to synthesize AgNPs of 2–5 nm outside the cells.¹¹⁰

In general, yeast-based biosynthesis processes are mainly due to enzymatic reduction and chelation with extracellular peptides/polysaccharides, resulting in different sizes, morphologies, and sites of NPs synthesis. Table 3 presents a variety of nanomaterials as synthesized by different yeasts. It has long been recognized that among the eukaryotes, yeasts are mostly investigated in the biosynthesis of 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, and thus yeasts are prone to forming NPs on the cell walls.¹¹¹ Besides, the reduction synthesis of MNMs/MCNMs is related to the reductases and proteases present in the yeast, so the yield of the synthesized NPs is directly related to the performance of the yeast secretase.

4. Microbial synthesis of metal/metallic compounds

4.1. Precious metals

Precious MNMs/MCNMs have high catalytic and bactericidal properties. They successfully combines the excellent physical and chemical properties of metals with the special properties of

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

Fungi	Nanoparticle	Localization/morphology	Size (nm)	Ref.
<i>Verticillium</i> (AAT-TS-4)	Ag	Spherical	13–37	77
<i>Verticillium</i> sp.	Au	Cell wall/spherical	20	78
<i>Colletotrichum</i> sp.	Au	Spherical	20–40	79
<i>Trichothecium</i> sp.	Au	Triangular and hexagonal	5–200	86
<i>Verticillium</i> sp.	Ag	Cell wall and cytoplasmic membrane	25	78
<i>Aspergillus flavus</i>	Ag	Cell wall	8.9	87
<i>Trichoderma asperellum</i>	Ag	ND	13–18	88
<i>Phanerochaete chrysosporium</i>	Ag	Pyramidal	5–200	89
<i>Fusarium solani</i> USM 3799	Ag	Spherical	16.23	90
<i>Fusarium semitectum</i>	Ag	Spherical	10–60	91
<i>Aspergillus fumigatus</i>	Ag	Spherical and triangular	5–25	87
<i>Coriolus versicolor</i>	Ag	Spherical	25–75	92
<i>Aspergillus niger</i>	Ag	Spherical	20	93
<i>Phoma glomerata</i>	Ag	Spherical	60–80	94
<i>Penicillium brevicompactum</i>	Ag	ND	58–95	95
<i>Cladosporium cladosporioides</i>	Ag	Spherical	10–100	96
<i>Penicillium fellutanum</i>	Ag	Spherical	5–25	97
<i>Volvariella volvacea</i>	Au, Ag, Au–Ag	Spherical	20–150	98
<i>Fusarium oxysporum</i>	Zr	Quasi-spherical	3–11	99
<i>Fusarium oxysporum</i>	Pt	Triangular, hexagonal, square, and rectangular	10–50	100
<i>Fusarium oxysporum</i>	BaTiO ₃	Quasi-spherical	4–5	101
<i>Fusarium oxysporum</i>	Bi ₂ O ₃	Quasi-spherical	5–8	102

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

Yeasts	Nanoparticle	Localization/morphology	Size (nm)	Ref.
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
<i>Yarrowia lipolytica</i>	Au	Intracellular/spherical	7.5–23	114
<i>Schizosaccharomyces pombe</i>	CdS	Hexagonal	1–1.5	115
<i>Thermoanaerobacter</i> sp.	Fe ₃ O ₄	Spherical	13–14	116
<i>Extremophilic yeast</i>	Ag	Spherical	20	117
<i>Candida guilliermondii</i>	Ag	Face-centered cubic	10–20	118
<i>Pichia capsulata</i>	Ag	Intracellular/spherical	1–100	119

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 that carboxyl groups provide the major site of metal deposition in the cell wall.¹²¹ Later, He *et al.*³² confirmed that *Rhodopseudomonas capsulata* can synthesize nanospheres, nanosheets, and nanowires using this method. In addition to AuNPs, many types of microorganisms synthesize AgNPs. Due to the high Ag⁺ tolerance of *Pseudomonas stutzeri* AG259, Klaus *et al.* used it to synthesize AgNPs in the periplasm for the first time in 1999.¹²² Shi *et al.* used *Shewanella oneidensis* 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 Fe₃O₄, Fe₂O₃, and Co₃O₄.¹²⁶ The synthesis of magnetic NPs was the first (and most widely) studied, and magnetic NPs are now mass-produced.¹²⁷ The high-throughput screening and identification of magnetotactic bacteria for magnetic NPs is of great importance for drug delivery, immunoassays, and medical imaging.¹¹⁶ In addition to magnetic NPs, microorganisms can synthesize Ag₂O, CeO₂, CuO, Bi₂O₃, and ZnO. Raliya *et al.* discovered *Aspergillus flavus* for synthesizing TiO₂ NPs from its cells.¹²⁸ *Bacillus mycoides* isolated from soil samples can also use TiO(OH)₂ to produce TiO₂ NPs with an average particle size of 40–60 nm at room temperature.¹²⁹ In addition to synthesizing nano-sized metal oxides, microorganisms can synthesize MNMs/MCNMs in different shapes of spheres, hexagons, triangles, and rods. Tripathi *et al.*¹³⁰ used *Bacillus licheniformis* to synthesize ZnO nanoflowers with strong photocatalytic properties. The microbial synthesis of oxide nanomaterials usually requires high redox potential conditions. Microorganisms can adapt to the environment and resist extreme conditions to promote MNMs/MCNMs synthesis. As compared with ultrasonic and microwave radiation, and alternating-current electrodeposition technologies, microbial synthesis is the most promising method for preparing NPs of high-purity, small particle size, and uniform dispersion.

4.3. Metal sulfides

Nanomaterials have unique properties after vulcanization. It has been proved that the vulcanization of NPs 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 their adaptation and resistance to heavy metals.^{132,133} The synthesis of sulfide NPs by microorganisms requires lower redox potential conditions, so the addition of metal ion precursors and sulfur-containing compounds is usually required. Sulfur ions are often combined with metal ions and reduced by specific reductases in microbial cells to produce metal sulfide NPs.¹³⁴ The 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. Yeasts can use cysteine and peptides in the cells to synthesize CdS and ZnS NPs, while other microorganisms can synthesize Ag₂S, HgS, Bi₂S₃, and CuS particles, as well as transition metal chalcogenides VS₄ and MoS₂ 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 characteristics such as semiconducting, catalytic, electromagnetic, and optical properties, making them promising for broad applications in electronic nanodevices, petroleum hydrodesulfurization processes, and the hydrogenation of unsaturated carbon compounds. Current research is mainly focused on the discovery of bacteria, fungi, and yeasts for the synthesis of sulfide nanomaterials; however, fewer efforts have been devoted to the discovery of 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 CO₂, they can synthesize PbCO₃, CdCO₃, and SrCO₃.¹⁴¹ In the presence of phosphate, yeasts can synthesize Zn₃(PO₄)₂ NPs with a micro butterfly-like structure.¹⁴² More importantly, microorganisms synthesize not only 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 Fe₃O₄ NPs outside the cells, followed by the second synthesis of Pd/Fe₃O₄, Au/Fe₃O₄, and PdAu/Fe₃O₄ NPs on the surface of Fe₃O₄ via a biological reduction process.¹⁴³ As shown in Fig. 3(b), carbon-coated lithium iron phosphate (LiFePO₄@C) cathode materials were synthesized by biomineralization. In the process of synthesizing materials, yeasts act as a template and biological carbon source, playing the role of biological reduction.¹⁴⁴ Not only can synthesized NPs catalyze the degradation of pollutants, but they can also be recycled using a magnetic field.

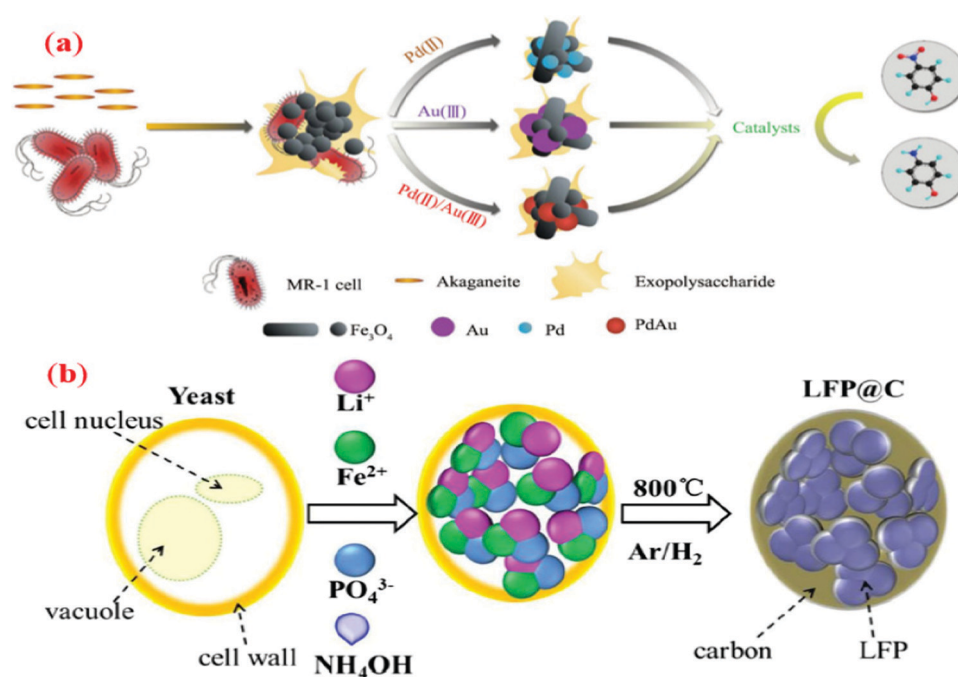


Fig. 3 (a) Biosynthesis of Pd/Fe₃O₄, Au/Fe₃O₄, and PdAu/Fe₃O₄ composites by *Shewanella oneidensis* MR-1.¹⁴³ (b) Schematic illustration of the preparation process of LFP@C.¹⁴⁴

Park *et al.*¹⁴⁵ expressed PCS and MT genes through recombinant *Escherichia coli* and used them to synthesize tri-metal (CdSeZn, FeCoNi, and FeCoMn) and multi-metal (CdSeZnTe and 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.

5. Separation and purification of the microbial synthesis of metal nanomaterials

The fermentation broth for MNM/MCNM synthesis is a complex multiphase system that contains target products, cells, metabolites, and unused culture medium. Since the density and viscosity of solid and colloidal substances are similar to those of the bulk media liquid,¹⁴⁶ it is difficult to separate the target MNMs/MCNMs from the precursor medium. In addition, the low concentration and high impurity of the target MNMs/MCNMs also increase the difficulty of MNM/MCNM purification. To address this issue, commonly used strategies for the separation and purification of MNMs/MCNMs after microbial synthesis include magnetic separation, chromatographic separation, centrifugation, membrane filtration, and extraction, all of which involve the four stages of the 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 low magnetic field gradients ($<100 \text{ T m}^{-1}$) is $\sim 50 \text{ nm}$.¹⁴⁷ For even smaller NPs, thermal diffusion and Brownian motions will be the dominating forces against magnetic forces acting on the nanoparticles, thus making fractionation less effective. For chromatographic separations where the mobile phase containing a mixture to be separated passes through a stationary phase, the separation is based on the differences in partition coefficients between the 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 to be the most cost-effective chromatographic technique for NP fractionation. Centrifugation is another simple separation technique that is used widely for separating colloid-like nanoparticles (even non-spherical particles) *via* the use of gravity, but this process is usually time-consuming and is less sensitive for the separation of different nanoparticles of similar mass.¹⁴⁹ Recently, Sharma *et al.*¹⁵⁰ reported the separation of AuNRs and AuNPs by centrifugation. Both the spherical and cubic sediments at the bottom were well segregated from the high-purity rods on the side wall. Moreover, membrane filtration as an alternative to the purification and size-fractionation of NPs has the greatest advantage of industrial-level scalability.¹⁵¹ The separation efficiency for the retention and elution of an analyte depends strongly on the size, structure, and chemistry of the membrane

pores. Generally, the more uniform the pore sizes, the better the quality of NP separation. The use of extraction to separate compounds is based on their relative solubility 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 of product separation and purification, synthetic materials engineering is a necessary tool for controlling the metabolic process of microorganisms by optimizing the temperature, pH, and substrate concentration.¹⁵² More recently, wet “nanosynthetic” procedures have been considered as applicable, high-throughput, and inexpensive methods for separating polydisperse particles, and they are worthy of further development.

6. Key factors to control microbial synthesis

MNMs/MCNMs by microbial synthesis are affected by many factors that control their size, shape, and synthesis conditions, including the microorganism type, metal ion concentration, medium composition, microorganism or protein concentration, and all relevant synthesis conditions (*i.e.*, pH, temperature, ionic strength, and incubation time).¹⁵³ Undoubtedly, microorganisms¹⁵⁴ as the most important factor have different genes, proteins, and metabolic processes, all of which will contribute differently to the synthesis and biomineralization of MNMs/MCNMs.^{155,156} Further, a large number of studies have shown that the pH can significantly affect the morphology and synthesis rate of MNMs/MCNMs.¹⁵⁷ For instance, *Rhodospseudomonas capsulatus* can extracellularly synthesize gold nanosheets of larger than 200 nm at pH 4, but NPs of 10–20 nm at pH = 7.¹⁵⁸ The pH value also has different effects on the synthesis of MNMs/MCNMs by different microorganisms. Using the synthesis process of AuNPs as an example, a lower pH value will lead to a higher proton concentration, which in turn easily produces the amino, sulfhydryl, carboxyl and other groups involved in the reduction process, and thus a decrease in their reduction ability and reduction rate to form AuNPs.¹⁵⁹ Collective results also showed that an overly acidic or alkaline environment is not only unfavorable for the reduction process, but also causes 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 with temperature.¹⁶¹ As an example, the synthesis rate of AgNPs increased over a temperature range of 4–25 °C.¹⁶² On the other hand, too high a temperature will not only denature the biomolecules and inactivate the enzymes on the surface of the MNMs/MCNMs, but it will also cause agglomeration of the NPs, both of which decrease or even halt the synthesis.¹⁶³ Finally, the 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 the microorganisms.¹⁶⁴

Higher metal ion concentrations usually lead to a significant increase in the initial microbial synthesis rate. However, an excess of metal ions will also cause the death of the microorganisms and dysfunction of the biomolecules.¹⁶⁵ It was reported that for co-incubation of *Verticillium luteoalbum* with 250–500 mg L⁻¹ HAuCl₄, gold nanoparticles of ~20 nm size were synthesized successfully. But, as the HAuCl₄ concentration was increased to 2500 mg L⁻¹, gold nanosheets with irregular shapes of ~200 nm were synthesized at the expense of *Verticillium luteoalbum*.¹⁶⁶

7. Biomanufacture mechanism of metal/metallic compounds

Microbial synthesis of nanomaterials is a complex biochemical process that includes 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 enclose the surface of the nanocrystals, producing a coating layer that increases the stability of the NPs; and (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 is involved in almost the entire process for the microbial synthesis of MNMs/MCNMs. As shown in Fig. 4, NPs are produced from small atoms and molecules *via* reduction/oxidation reactions. The biological reduction/oxidation process for 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, and 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 whether synthesis is intracellular or extracellular. For intracellular synthesis, the 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 the metal ions are directly reduced by biologically active molecules outside the cell. The second one occurs by first adsorbing the metal ions on the surface of the cells through an electrostatic attraction, followed by reduction of the metal ions using bioactive molecules on the cell wall or cell

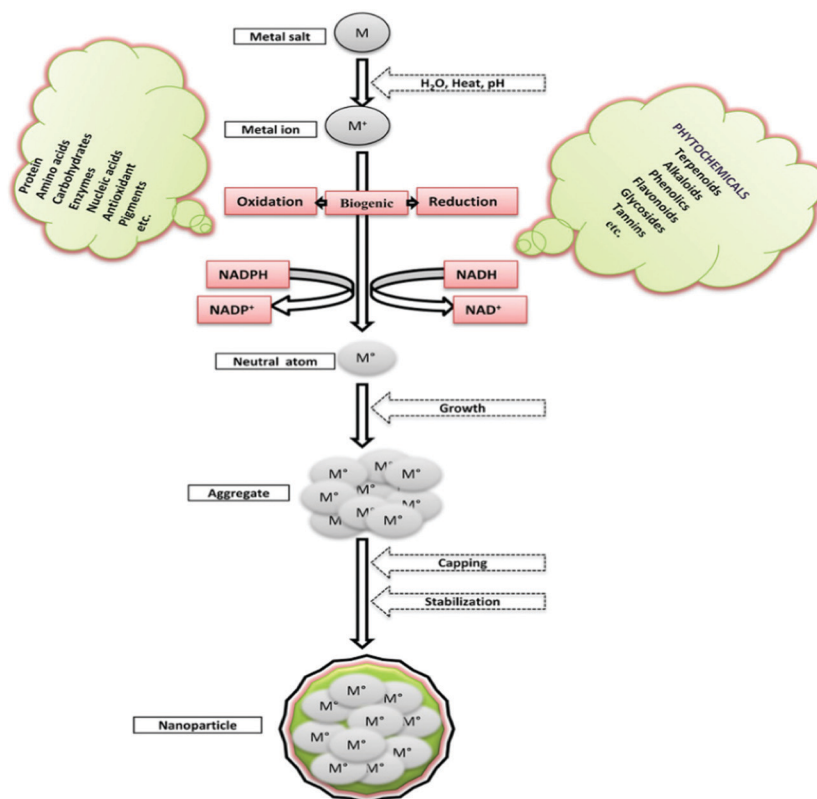


Fig. 4 Schematic of the possible pathways to synthesize NPs by microorganisms. M: metal salt, M⁺: metal ion, and M⁰: neutral atom.¹⁰²

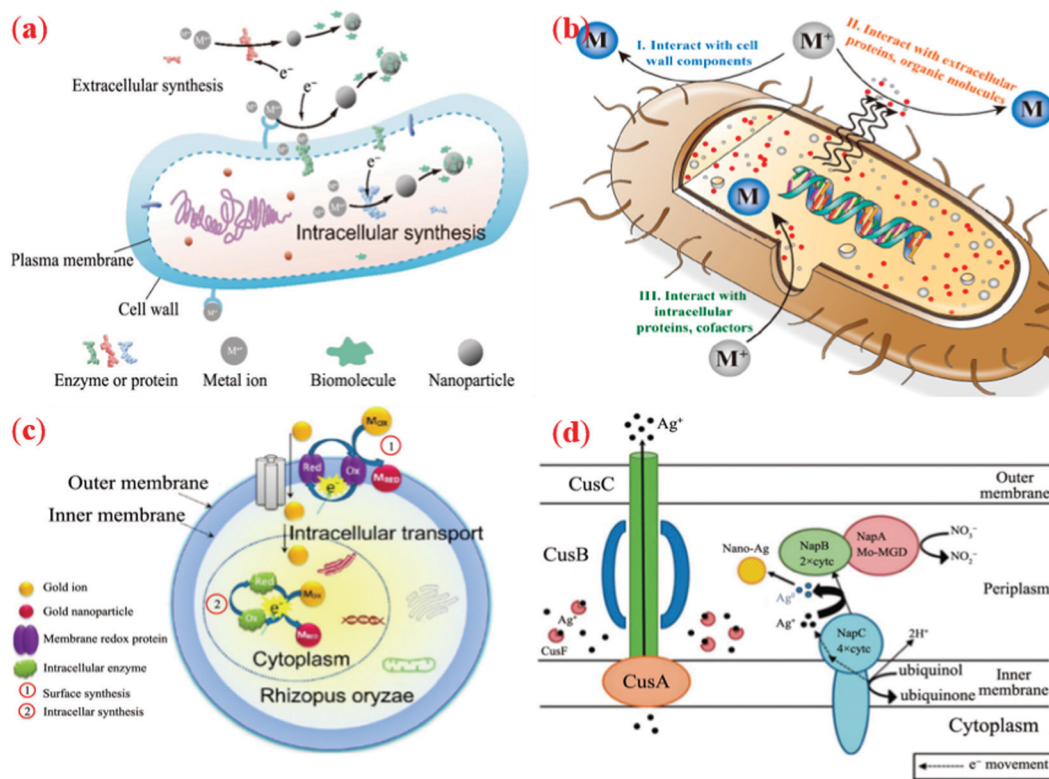


Fig. 5 (a) Biosynthesis of metal nanomaterials by the bioreduction process.⁹³ (b) Schematic representation of the bacterial synthesis of NPs; both intracellular and extracellular processes are included.³⁷ (c) Proposed mechanism of AuNP biosynthesis by the fungus *Rhizopus oryzae*.¹⁷⁰ (d) Biosynthesis mechanism of AgNPs by a cytochrome subunit NapC in *Escherichia coli*.¹⁷¹

membrane.⁹³ As shown in Fig. 5(b), metal ions are reduced by proteins, enzymes and organic molecules in the medium or by the 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 co-factors to produce NPs.

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 Au³⁺ penetrates into the cytoplasm, is covalently bound to proteins, and is 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 found that when *Rhizopus oryzae* synthesizes AuNPs, some Au³⁺ ions are reduced to AuNPs by proteins on the cell surface, and some Au³⁺ ions penetrate into the cytoplasm and are covalently bound to proteins and reduced to AuNPs by metal reductase. Zhi *et al.* found that cytochrome C plays 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 AgNO₃ 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 the 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 impose a great barrier to sufficiently sample the synthesis time and cycle for better understanding of the microbial synthesis mechanisms.¹⁷²

7.2. Abiotic reduction

In some cases, it is difficult for microorganisms to precipitate metal ions in a stable oxidation state through the biological reduction process. To address this issue, microorganisms have developed 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 probably accepted that the synthesis of some oxides mainly stems from the hydrolysis process as mediated by microorganisms. The microbial synthesis of TiO₂ comes from the biologically induced hydrolysis of TiF₆. 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 such as CdS and PbS that contain highly toxic heavy metals is usually related to the chelation of polypeptides.¹⁰⁷ Among them, phytochelatins and metallothioneins are very common chelating agents for stabilizing heavy metal ions in microorganisms.¹⁷⁴ Studies have shown that glutathione in phytochelatins and the cysteine group in the metallothioneins can effectively chelate the metal ions. These biological chelating agents will express rapidly under toxic conditions to achieve detoxification. It has been reported that glutathione and phytochelatins in yeasts are highly expressed to enrich Cd²⁺ and Pb²⁺, before cysteine provides a sulfur source to synthesize CdS and PbS NPs.¹⁷⁵ In addition to hydrolysis and chelation mechanisms, some MNMs/MCNMs can be obtained as by-products of microorganism metabolic processes. Additional mechanisms of the microbial synthesis of MNMs/MCNMs include (i) the protein metabolism pathway in which proteins on the surface of bacteria promote the nucleation of calcite fine-grained minerals, and (ii) the sulfur metabolism pathway in which sulfate-reducing bacteria promote the formation of sulfur-based NPs.¹⁷⁶

8. Environmental applications of the microbial synthesis of metal nanomaterials

MNMs/MCNMs as synthesized by microorganisms have the benefits of both metals and nanomaterials, enabling them to expand their applications to 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 under optimal conditions can rapidly degrade 12.5 μmol of nitroaniline within 6 minutes.¹⁷⁷ Compared with traditional Au- and Ag-based NPs, Pd NPs synthesized by microorganisms exhibit 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 the removal of nitrate pollutants from groundwater.¹⁸⁰ Last but not least, MNMs/MCNMs can be used for heavy metal removal, *e.g.* the use of *Geobacter sulfurreducens* to reduce carcinogenic Cr(VI) to low-toxic Cr(III);¹⁵⁷ in addition, 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 synthesized by microorganisms exhibited better sterilization effect on *Bacillus subtilis* than colloidal Ag by chemical methods.¹⁶³ Despite the environmental promise of MNMs/MCNMs, additional efforts should be made to investigate the environmental risks of MNMs/MCNMs and to expand their use in the soil and atmospheric environmental management.

9. Conclusion and perspectives

Microbial biomanufacture of MNMs/MCNMs has been emerging over the past few decades, and has not only discovered and developed new nanomaterials, microbial systems, and applicable products in a greener, safer, and more efficient way, but has also demonstrated a new biosynthesis strategy for the fabrication of NPs with controllable shapes, sizes, and structural hierarchy. Compared with conventional physical preparation and chemical synthesis strategies, the microbial biomanufacture of MNMs/MCNMs using living microorganisms (*i.e.* bacteria, fungi, and yeasts) as small and efficient biofactories has the 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 waste and pollutants and then convert them to biogenic NPs with controlled sizes and morphologies. Microorganism-assisted NP synthesis and the associated parameters can be further optimized to maximize the productivity and safety of NPs.

Despite great progress in the microbial biomanufacture of MNMs/MCNMs, some critical challenges remain to be addressed for increasing its impact across different fields, such as biomaterials science, nanoscience, and nanobiotechnology. Microorganism-synthesized MNMs/MCNMs of different compositions are still rather limited. The rational design or discovery of new microorganisms *via* advanced genetic, molecular, and 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 control over 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 the synthesis mechanism.

In addition, it is equally important when 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 the low yield, poor quality, and emanating biotoxicity of MNMs/MCNMs. Finally, parallel to experimental efforts, it is critical to develop multiscale modeling and simulations for a better understanding of the complex interactions between enzymes and metal ions at the molecular, cellular, and multicellular scales. The proposed computational models and simulations will enable the different key aspects of the biomanufacturing process to be revealed, including mechanism explanation models for elucidating microbial metabolism and pathways, the production of models for optimizing the operating parameters so as to achieve maximal yields, the production of economic analysis models for predicting the commercial value of synthetic products, and developing

molecular simulation models for determining the crystal structures and the formation of NPs. In conclusion, the microbial biomanufacture of MNMs/MCNMs awaits innovations from interdisciplinary research to catalyze breakthroughs ranging from the development of effective microorganisms to controllable NP synthesis.

Conflicts of interest

There are no conflicts to declare.

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