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Nanoparticle and nanomineral production by fungi

Qianwei LI^{a,b}, Feixue LIU^c, Min LI^b, Chunmao CHEN^b,
Geoffrey Michael GADD^{b,c,*}

^aState Key Laboratory of Petroleum Pollution Control, China University of Petroleum, Beijing 102249, China

^bState Key Laboratory of Heavy Oil Processing, Beijing Key Laboratory of Oil and Gas Pollution Control, China University of Petroleum, Beijing 102249, China

^cGeomicrobiology Group, School of Life Sciences, University of Dundee, DD1 5EH, Scotland, UK

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ABSTRACT

Fungi show a variety of abilities in affecting metal speciation, toxicity, and mobility and mineral formation, dissolution or deterioration through several interacting biomechanical and biochemical mechanisms. A consequence of many metal-mineral interactions is the production of nanoparticles which may be in elemental, mineral or compound forms. Organisms may benefit from such nanomaterial formation through removal of metal toxicity, protection from environmental stress, and their redox properties since certain mycogenic nanoparticles can act as nanozymes mimicking enzymes such as peroxidase. With the development of nanotechnology, there is growing interest in the application of biological systems for nanomaterial production which may provide economic benefits and a lower damaging environmental effect than conventional chemical synthesis. Fungi offer some advantages since most are easily cultured under controlled conditions and well known for the secretion of metabolites and enzymes related to nanoparticle or nanomineral formation. Nanoparticles can be formed intracellularly or extracellularly, the latter being favourable for easy harvest, while the cell wall also provides abundant nucleation sites for their formation. In this article, we focus on the synthesis of nanoparticles and nanominerals by fungi, emphasizing the mechanisms involved, and highlight some possible applications of fungal nanomaterials in environmental biotechnology.

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1. Introduction

The word “nano” refers to one billionth of a meter or 10^{-9} m. The concept of nanotechnology was first developed by Richard P. Feynman in his lecture entitled ‘There’s plenty of room at the bottom’ and the term nanotechnology was introduced by

Norio Taniguchi in 1974 (Rai *et al.*, 2009). Nanoparticles and nanominerals are widely found throughout the atmosphere, oceans, soils and in most living organisms, and their formation always occurs when nanoparticle nucleation rate is high while their growth rate is slow, or where their growth as mineral aggregates is not a dominant process (Hochella

* Corresponding author. Geomicrobiology Group, School of Life Sciences, University of Dundee, DD1 5EH, Scotland, UK.

E-mail address: g.m.gadd@dundee.ac.uk (G. M. Gadd).

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et al., 2008). The size range of nanoparticles and nanominerals may vary from 1 nm to several tens of nanometres in at least one dimension. Compared with conventional materials, particles and minerals in the nanoscale exhibit unique catalytic, electronic, magnetic, chemical, photoelectrochemical and optical properties and much research has been carried out on the synthesis and properties of nanomaterials including chemical composition, size and monodispersity (Mandal et al., 2006).

Microorganisms show a variety of abilities in affecting metal speciation, toxicity, and mobility and mineral formation, dissolution or deterioration through direct and indirect mechanical and biochemical mechanisms (Gadd, 2010, 2013). A frequent consequence of many metal-mineral microbial interactions is the production of nanoparticles and fungi are no exception to this. Such production may be a direct or indirect consequence of metabolism and/or the reactivity of structural components, or a component of a metal resistance mechanism, an example of the latter being the formation of CdS crystallites in certain yeasts (Dameron et al., 1989; Dameron and Winge, 1990; Jacob et al., 2016). Organisms may benefit through metal detoxification and protection from environmental stress, while certain nanoparticles can act as nanozymes, mediating redox reactions and catalysis, affecting iron speciation and organic matter degradation, and providing protection from reactive oxygen species (Yu et al., 2019, 2020; Meng et al., 2020; Chi et al., 2021). Nanozymes are inorganic nanoparticles that mimic enzyme-like properties in redox reactions and include metals and metal oxides. Most of the catalytic reactions mediated by nanozymes involve oxidase (OXD), peroxidase (POD), catalase (CAT) and superoxide dismutase (SOD) activities (Meng et al., 2020). Since fungi can mediate formation of reactive nanoparticles, including metal oxides, these biomaterials are receiving deserved attention. Of the nanozymic minerals, ferrihydrite ($\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$) is of particular interest because of its ubiquity in the Earth's surface and its known catalytical properties which imitate natural peroxidase (Yu et al., 2020). This antioxidant enzyme removes excess reactive oxygen species (ROS), such as superoxide (O_2^-) and hydrogen peroxide (H_2O_2), to combat oxidative stress and maintain redox balance. Ferrihydrite nanoparticles produced by fungal transformation of hematite indeed possess peroxidase activity, scavenge hydrogen peroxide for mitigation of cytotoxicity, and ensure the acquisition of essential iron (Yu et al., 2019, 2020). This has also been shown for mycogenic magnetite nanoparticles which also exhibit peroxidase-like activity (Chi et al., 2021). This raises intriguing questions about the roles of biogenic nanomaterials in co-evolution of the lithosphere and biosphere (Yu et al., 2020).

With growing interest in biological routes for sustainable and environmentally-friendly means of nanoparticle production, the application of fungi for synthesis of nanomaterials seems to offer advantages (Bharde et al., 2006; Bansal et al., 2011; Gade et al., 2010). Fungal hyphae grow, branch and fuse to form a filamentous explorative mycelium which possesses a high surface area to mass ratio (Gadd, 2007; Gadd and Raven, 2010) and nutrient translocation properties, while the hydrated mucilaginous sheath that often surrounds hyphae provides a matrix beneficial for geochemical reactions. The branching network provides an efficient template for nanoparticle or nanomineral formation because of the large number of

metal-binding functional groups in the cell wall and associated extracellular polymeric substances (EPS) that act as nucleation sites. Moreover, many fungi are excellent candidates for metal immobilization, mineral dissolution and formation, and many can flourish in the presence of high metal concentrations due to various active and incidental mechanisms to combat metal toxicity (Dhillon et al., 2012; Gadd and Raven, 2010).

2. Mycogenic nanoparticles and nanominerals

The list of nanoparticles and nanominerals known to be synthesized by fungi has expanded greatly in recent years and they include about 30 elements of the Periodic table. These include alkaline earth metals (Sr, Mg, Ba), transition metals (Ti, Mn, Fe, Co, Ni, Cu, Zr, Ag, Pt, Au), post-transition metals (Al, Zn, Cd, Bi), metalloids (Si, Te), non-metals (H, C, N, O, P, S, Se), lanthanides (La, Ce) and an actinide (U) (Table 1). Nanoscale elemental particles of gold (reduction of Au(III) to Au(0)), silver (reduction of Ag(I) to Ag(0)), palladium (reduction of Pd(IV, II) to Pd(0)) and metalloids such as selenium and tellurium, produced by reduction of Se/Te oxyanions (Se(IV, VI)/Te(IV, VI) to Se(0)/Te(0)), can be produced by a range of fungal species. Nanominerals include oxides, carbonates, phosphates, selenides, tellurides and sulfides that may incorporate metal(loid)s including Cu, Cd, Zn, Mn, Ni, Ba, Zr, Fe, Pb, Sr, Se, Te and Ti. Other elements are likely to be added to this list in view of the large numbers of nanoparticle-forming fungal species and susceptible elements, compounds and minerals. Mineral and elemental nanoparticles can be formed intracellularly, associated with cell walls and EPS, and/or be released into the external medium, and can also form on dead biomass. It should be noted that some of the processes that lead to nanomineral formation might be the same as those involved more generally in production of secondary minerals above the nanoscale, differences in scale depending on chemical and biological conditions, protein and metabolite excretion, proximity to substrate etc. Some nanoparticles appear only to be synthesised at the nanoscale, particularly elemental forms such as Ag(0), Au(0), Se(0), and Te(0) perhaps reflecting differences in their mode of production (see later).

Among the different nanomaterials, silver nanoparticles have drawn much attention due to their antimicrobial properties (Rai et al., 2009; Zhao et al., 2018). Many fungi can mediate the synthesis of Ag(0) nanoparticles (Table 1). An early study discovered that the yeasts *Debaryomyces hansenii*, *Candida albicans*, *Saccharomyces cerevisiae*, and *Rhodotorula rubra*, and the polymorphic fungus *Aureobasidium pullulans* were capable of growth in silver-containing media which resulted in blackening of colonies and the external medium. Transmission electron microscopy and elemental analysis showed that elemental silver particles of nanoscale dimensions were deposited within and around cell walls, and in the external medium (Kierans et al., 1991). Reduction of Ag^+ to Ag^0 was proposed as the mechanism of formation (Kierans et al., 1991). The focus of this research was silver removal and recovery from photographic waste waters, and later developments in nanoscience regarding the antimicrobial properties of Ag

Table 1 – Nanoparticles produced by different fungal species.

Nanoparticles	Size (nm)	Shape	Species	Reference
Ag	–	Granular	<i>A. pullulans</i> , <i>D. hansenii</i> , <i>C. albicans</i> , <i>R. rubra</i>	Kierans et al. (1991)
Ag	2.0–13.8	Spherical	<i>A. terreus</i>	Velhal et al. (2016)
Ag	50–200	Spherical	<i>Phanerochaete chrysosporium</i>	Vigneshwaran et al. (2007)
Ag	3.4–26.8	-	<i>F. oxysporum</i>	Ishida et al. (2014)
Ag	2–20	-	<i>S. cerevisiae</i>	Korbekandi et al. (2016)
Ag	5–25	Monodispersed	<i>A. fumigatus</i>	Basavaraja et al. (2008)
Ag	5–200	Pyramidal	<i>Cladosporium cladosporioides</i>	Balaji et al. (2009)
Ag	8.92	-	<i>A. flavus</i>	Sanghi and Verma (2009a)
Ag	20	Spherical	<i>A. niger</i>	Gade et al. (2008)
Ag	10–60	Spherical	<i>F. semitectum</i>	Ingle et al. (2008)
Ag	15	Spherical	<i>Vovariella volvacea</i>	Shaligram et al. (2009)
Ag	16 ± 6	Spherical	<i>P. cyclopium</i>	Wanarska and Maliszewska (2019)
Ag	20–60	Polydisperse spherical	<i>Alternaria alternata</i>	Bansal et al. (2005)
Au	20 ± 2.0	Spherical	<i>Rhizopus oryzae</i>	Das et al. (2012a)
Au	43–63		<i>A. niger</i>	
Au	20		<i>A. niger</i>	
Au	8.7 ± 6		<i>A. niger</i>	
Au	6–37		<i>A. oryzae</i>	
Au	3.5 ± 3		<i>A. tamarii</i>	
Au	5		<i>F. oxysporum</i>	
Au	7.7 ± 4.3		<i>Penicillium ochro-chloron</i>	
Au	75	Heterogeneous	<i>Penicillium sp.</i>	
Au	15–20	Spherical	<i>S. cerevisiae</i>	Sen et al. (2011)
BaTiO ₃	20–30	Spherical	<i>F. oxysporum</i>	Riddin et al. (2006)
Bi ₂ O ₃	5–8	Spherical	<i>F. oxysporum</i>	Uddin et al. (2008)
BiMnO ₃	50	Spherical	<i>Humicola sp.</i>	Mazumder et al. (2007)
CdCO ₃	55–870	Granular	<i>Neurospora crassa</i>	Li et al. (2014)
CdS	5–20	Monodisperse	<i>F. oxysporum</i>	Sanghi and Verma (2009b)
CdTe	15–20	Spherical	<i>F. oxysporum</i>	Syed and Ahmad (2013)
CeO ₂	5–20	Spherical	<i>A. niger</i>	Gopinath et al. (2015)
CeO ₂	12–20	Spherical	<i>Humicola sp.</i>	Khan and Ahmad (2013)
CePO ₄	100–200, 500	Needles, spherical	<i>S. cerevisiae</i>	Jiang et al. (2010)
CoCO ₃	30–80	Granular	<i>Neurospora crassa</i>	Li et al. (unpublished)
Co ₃ O ₄	54.85	Spherical	<i>S. cerevisiae</i>	Li et al. (2018)
Cu ₂ CO ₃ (OH) ₂ , Cu ₃ (OH) ₂ (CO ₃) ₂	10–20	Granular	<i>Neurospora crassa</i>	Li and Gadd (2017a)
Cu, CuO	5–20	Spherical	<i>Stereum hirsutum</i>	Cuevas et al. (2015)
CuS	2–5	Irregular	<i>F. oxysporum</i>	Hosseini et al. (2012)
CuS	10–40	Irregular	<i>F. oxysporum</i>	Schaffie and Hosseini (2014)
CuAlO ₂	5	Spherical	<i>Humicola sp.</i>	Ahmad et al. (2007)
FeCO ₃ , Fe	~80	Granular	<i>Neurospora crassa</i>	Li et al. (2020)
Fe ₃ O ₄	20–50	Quasi-spherical	<i>F. oxysporum</i>	Vainshtein et al. (2014)
FePO ₄	50–200	Amorphous	<i>S. cerevisiae</i>	He et al. (2009)
Hydronium-jarosite jarosite	–	Spherical	<i>Purpureocillium lilacinum</i>	Oggerin et al. (2013)
	–	–	<i>P. lilacinum</i> Y3	Xia et al. (2020)
LaCO ₃	~80	Needles	<i>Neurospora crassa</i>	Li and Gadd (2017b)
LiFePO ₄	–	Blocky	<i>S. cerevisiae</i>	Cao et al. (2018)
LiFePO ₄	–	Spherical	<i>S. cerevisiae</i>	Zhang et al. (2012)
LiFePO ₄	–	Amorphous	<i>S. cerevisiae</i>	Zhang et al. (2013)
MgO	45.12–95.37	Heterogeneous	<i>Trichoderma viride</i>	Alrabadi et al. (2017)
MnCO ₃ /Mn ₂ O ₃	20	Lamellar	<i>Neurospora crassa</i>	Li et al. (2016)
NiCO ₃	60	Granular	<i>Neurospora crassa</i>	Li et al. (2019)
Ni oxide	1.25–3.8	Spherical	<i>Hypoxea lixii</i>	Salvadori et al. (2015)
PbSe	20–160	Rods	<i>A. terreus</i>	Jacob et al. (2014)

(continued on next page)

Table 1 (continued)

Nanoparticles	Size (nm)	Shape	Species	Reference
Pt	10–100	Hexagonal, Pentagonal, Spherical, Cuboid	<i>F. oxysporum</i>	Riddin et al. (2006)
Pd	10–14	Spherical	<i>P. chrysosporium</i>	Tarver et al. (2019)
Pd	10–20	Spherical	<i>S. cerevisiae</i>	Saitoh et al. (2020)
Se	70–90	Spherical	<i>Magnusiomyces ingens</i>	Lian et al. (2019)
Se, Te	48–78	Granular	<i>Aureobasidium pullulans</i> , <i>Mortierella humilis</i> , <i>Trichoderma harzianum</i> , <i>Phoma glomerata</i>	Liang et al. (2019)
Se–Te	50–600	–	<i>P. chrysosporium</i>	Espinosa-Ortiz et al. (2017)
SiO ₂ /TiO ₂	5–15	Spherical	<i>F. oxysporum</i>	Bansal et al. (2005)
SmPO ₄	50–200	–	<i>S. cerevisiae</i>	Jiang et al. (2018)
SrCO ₃	10–50	Needles	<i>Fusarium oxysporum</i>	Rautaray et al. (2004)
Te	20–465	Needles	<i>P. chrysosporium</i>	Espinosa-Ortiz et al. (2017)
Ti/TiO ₂	2–16	Spherical	<i>Trichoderma harzianum</i>	Jayaseelan et al. (2013)
TiO ₂	6.7 ± 2.2	Spherical, oval	<i>S. cerevisiae</i>	Peiris et al. (2018)
TiO ₂	4.7, 11.3	Spherical	<i>S. cerevisiae</i>	Cui et al. (2009)
TiO ₂	10	Oval	<i>S. cerevisiae</i>	He et al. (2011a)
U(VI)	50–100	Needles	<i>Geotrichum</i> sp.	Zhao et al. (2016)
ZnCO ₃	~50	Honeycombed, granular	<i>Neurospora crassa</i>	Li et al. (unpublished)
ZnO	–	Cuboid	<i>Pichia fermentans</i>	Chauhan et al. (2015)
ZnS	42	Spherical	<i>F. oxysporum</i>	Mirzadeh et al. (2013)
Zn ₃ (PO ₄) ₂	10–80 nm in width and 80–200 nm in length	Butterfly-like	<i>S. cerevisiae</i>	Yan et al. (2009)
ZrO ₂	7–8	Spherical	<i>F. oxysporum</i>	Bansal et al. (2004)

nanoparticles led to renewed interest in fungal silver transformations.

Fusarium oxysporum and *Verticillium* sp. are capable of extracellular or intracellular synthesis of Ag and gold (Au(0)) nanoparticles as they produce significant amounts of extracellular proteins and secondary metabolites which act as a reductase and stabilization agent for the produced nanoparticles. Several strains of *Fusarium oxysporum* exhibited extracellular Ag nanoparticle synthesis with a size range of 20–50 nm, their formation being dependent on the reductase/electron shuttle relationship (Durán et al., 2005). Mukherjee et al. (2001) demonstrated that AuCl₄⁻ could be reduced to Au⁰ nanoparticles (~20 nm) by a *Verticillium* sp. and particles were located on the cell wall as well as the cytoplasmic membrane. Of note is that a much larger number of Au nanoparticles were assembled in the fungal system in comparison with a bacterial system where often no more than 10–15 nanoparticles were associated with one bacterial cell (Mukherjee et al., 2001). Many other fungal genera have been explored for the synthesis of nanoparticles and nanominerals, including *Aspergillus*, *Penicillium* and *Neurospora*. Gopinath et al. (2015) demonstrated a simple method for the biosynthesis of cerium oxide (CeO₂) nanoparticles using *Aspergillus niger* culture filtrate, with various functional groups present on molecules in the filtrate being responsible for their production. In a urea-containing medium, *Neurospora crassa* was tested for the bioprecipitation of metal ions (e.g. Ni²⁺, Co²⁺, Cu²⁺, Fe²⁺, Zn²⁺, Mn²⁺) and the results showed that

most of these metals were precipitated as nanoscale carbonates or oxides (Li et al., 2014; Li and Gadd, 2017a, b; Li et al., 2016; Li et al., 2020; Liu et al., 2021). *Penicillium* is one of the most common fungal genera in the environment and several species have been viewed as potential “nanofactories” for nanoparticle biosynthesis including Ag, Au, and Se (Barabadi et al., 2019; Salem et al., 2021). Polymorphic, crystalline and stable titanium dioxide (TiO₂) nanoparticles with a size range of 10–400 nm were synthesised using an extract of *Trichoderma citrinoviride* as a reducing agent (Arya et al., 2021).

3. Physico-chemical characteristics of nanoparticles

Nanoparticles provide excellent performance in a variety of technological applications owing to distinctive physicochemical characteristics, including elemental composition, stability, crystallinity, size, shape, surface area, surface energy, and reactivity (Hochella et al., 2008; Choi and Lee, 2020).

The biosynthesis of nanoparticles can be predicted with geochemical models (e.g. Phreeq, Geochemist’s workbench (GWB), RokGeM) which include the equilibrium distribution of different chemical species, and the dominance and stability of minerals under specific reaction conditions such as concentration, temperature, pH and pressure (Charlton and Parkhurst, 2011; Colbourn et al., 2013; Li and Gadd, 2017a). GWB is a useful geochemical modelling software which can

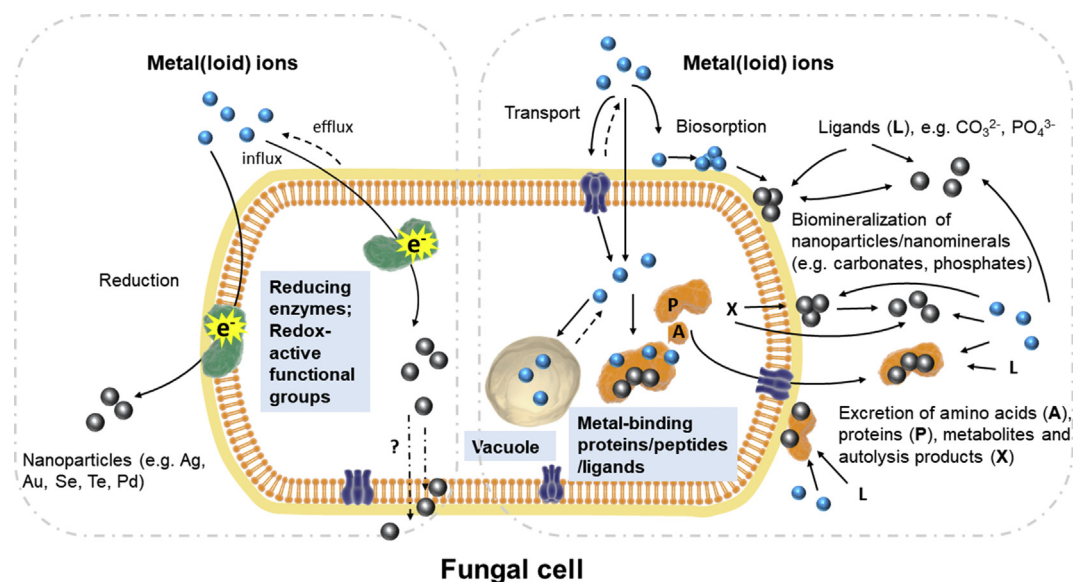


Fig. 1 – Some of the main mechanisms involved in the formation of nanoparticles and nanominerals by fungi. Nanomaterials may be formed extracellularly, intracellularly, associated with cell walls and surface materials, and can also form on dead biomass and in biomass-free reactive culture filtrates. Metal(loid) species may be sorbed to cell walls and EPS providing nucleation sites for subsequent mineral formation. Redox reactions and the availability of ligands, metabolites and organic molecules can determine the nature of the nanomaterials produced. Secreted amino acids, proteins, and autolysis products can influence growth and size of formed nanomaterials. Some ligands, e.g. phosphate, carbonate, sulfide, may themselves be a result of fungal metabolism and mineral dissolution. Metal(loid) transport across the plasma membrane can result in intracellular vacuolar compartmentation, sequestration by intracellular macromolecules, e.g. metallothionein, phytochelatins, and redox transformations of accumulated metal(loid) species. Intracellular movement of nanoparticles to the cell membrane or cell wall, or exocytotic expulsion to the exterior is indicated by “?” in view of the lack of detailed information.

calculate and plot activity–activity diagrams, and the equilibrium state of natural fluids and theoretical systems. For example, GWB was applied to simulate the formation of copper/nickel carbonate nanoparticles in a biomass-free carbonate-laden fungal culture supernatant (the carbonate resulting from urea hydrolysis by the fungus) which agreed closely with experimental results (Li and Gadd, 2017a; Li et al., 2019).

The morphology of Ag⁰ nanoparticles was highly variable and these could be spherical and triangular (Ahmad et al., 2003). Transmission electron microscopy (TEM) showed that the nanoparticles (5–50 nm) were not in direct contact, even within aggregates, and exceptionally stable which was related to the proteins secreted by the experimental fungus, *F. oxysporum* (Ahmad et al., 2003). Compared with bulk minerals, nanoscale biominerals have a much greater surface area to volume ratio which will result in superior advantages in any industrial applications.

A urease-positive fungal cultivation system, where urea hydrolysis results in carbonate release, provides a facile method for biomineralization of metal carbonates, especially those in the nanoscale. To further understand physical differences of mycogenic CdCO₃ in nanoscale and microscale dimensions, a capsular geometric model was devised to calculate the surface area (Li et al., 2014). The surface area of particles with a maximum diameter (~870 nm) was almost 250 times that of those of minimum diameter (~55 nm) but for the same unit volume of particles, the total surface area

of the smallest particles was about 17 times greater than that of the largest particles (Li et al., 2014).

Physical parameters including precursor concentration, pH, temperature and reaction time can affect the size and shape of fungal nanoparticles. Various sizes of Au nanoparticles ranging from 2 to 500 nm were obtained using *Trichoderma viride* filtrate and the resulting shapes were found to include nanospheres, nanotriangles, nanopentagons, nanohexagons and nanosheets when changing parameters such as pH, temperature, time, substrate and filtrate concentration (Kumari et al., 2016). The reaction time and temperature affect the size, morphology and crystallinity of fungal nanoparticles as these parameters influence the rate of nucleation and crystal growth. *Aspergillus oryzae* was utilized for the synthesis of Ag nanoparticles and their size decreased from 14 to 7 nm when the temperature increased from 30 to 90 °C (Phanjom and Ahmed, 2017).

4. Mechanisms of nanoparticle and nanomineral production

Although the exact mechanisms involved in the fungal synthesis of nanoparticles and nanominerals are often unclear, much research has demonstrated that the formation of nanoparticles can be related to reducing enzymes (e.g. NADH-dependent or NADPH-dependent reductases, nitrate (NO₃⁻) and nitrite (NO₂⁻) reductases), and non-enzyme proteins and

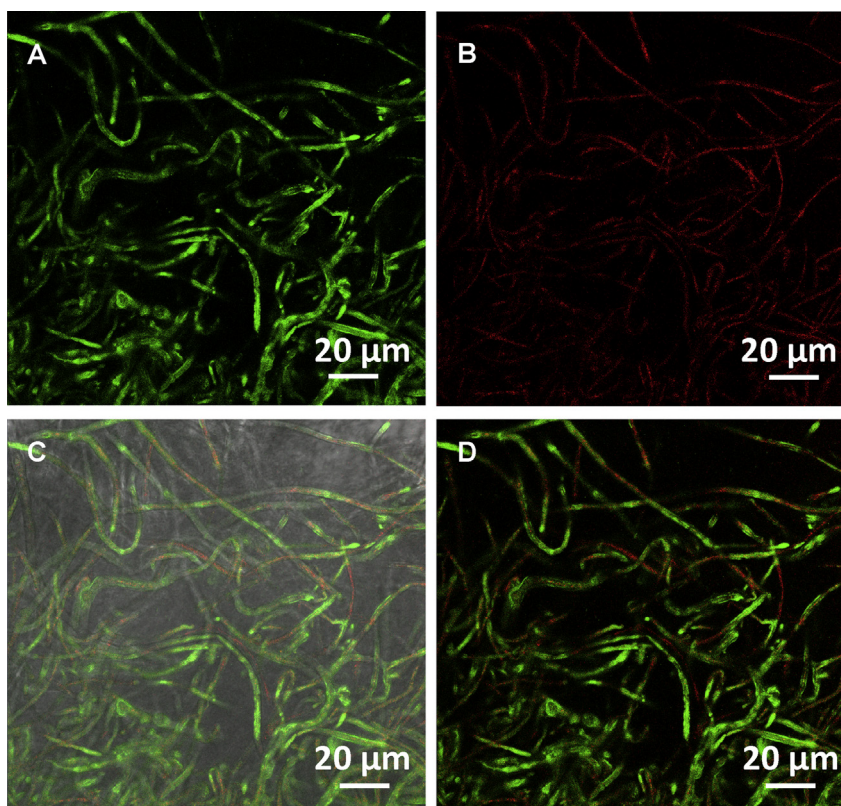


Fig. 2 – Confocal microscope images of *Neurospora crassa* hyphae grown in AP1 medium with 50 mM CaCl_2 . (A) Distribution of calcium carbonate formed along the fungi hyphae stained using Fura-2 AM (green); (B) fungal extracellular proteinaceous matrix stained using FilmTracer™ SYPRO® Ruby Biofilm Matrix Stain (red); (C) overlay of Ca and protein channels including bright field and (D) overlay of Ca and protein channels. The scale bars are 20 μm and representative images are shown from several determinations (Liu and Gadd, unpublished data, see also Liu et al., 2021).

peptides, capable of non-specific and specific metal interactions, present in cell walls, cytoplasmic membranes or intracellularly (e.g. metallothionein, phytochelatins) (Choi and Lee, 2020; Dhillon et al., 2012) (Fig. 1). Dhillon et al. (2012) proposed a hypothetical model for the biosynthesis of nanoparticles by fungi which included electrostatic interactions between the metal ion and an enzyme associated with the cell wall, and subsequent enzymic reduction of M^{n+} to M^0 resulting in intracellular or extracellular production of nanoparticles.

Enzymes can therefore be important agents responsible for the reduction of metal(loid)s and reported reductases include NAD(P)H-dependent reductase, nitrate and nitrite reductase, and sulfate (SO_4^{2-}) and sulfite (SO_3^{2-}) reductases (Choi and Lee, 2020). Ahmad et al. (2002) proposed that the extracellular secretion of sulfate reductase by *F. oxysporum* could be applied for the synthesis of CdS nanoparticles in aqueous solution, which was subsequently extended to the formation of PbS, ZnS and MoS_2 nanoparticles. It was found that an NADH-dependent reductase was the major protein related to the reduction of Ag^+ and subsequent Ag^0 nanoparticle formation, and that the secondary structure of the protein was not affected by reaction with Ag^+ or binding with Ag nanoparticles (Ahmad et al., 2003). This reductase appeared specific to the *F. oxysporum* strain used as Ag nanoparticles were not produced

by *Fusarium moniliforme* under the same experimental conditions. Nitrate reductase was purified from *F. oxysporum* culture supernatant for synthesis of Ag nanoparticles (~50 nm) using gelatine as a capping agent to avoid aggregation. The purified NADPH-dependent nitrate reductase showed a molecular weight of 214 kDa with three subunits of 125, 60 and 25 kDa (Gholami-Shabani et al., 2014). Electrostatic attractions between free amine groups or cysteine residues in fungal proteins resulted in stabilization of the nanoparticles. Apart from reductases, quinine derivatives of naphthoquinones and anthraquinones can also be redox centres for metal reduction and nanoparticle formation (Zhao et al., 2018).

Biomining refers to the formation of minerals by organisms and the process may be considered to be biologically-induced mineralization (BIM) or biologically-controlled mineralization (BCM). In BIM, the activities and structures of organisms alter the local microenvironment and create appropriate conditions for the precipitation of minerals. BCM refers to the process of forming minerals that is directly controlled by the organism, including mineral nucleation, growth, and morphology, as well as the final location. NiCO_3 nanominerals were precipitated by biomass-free spent urease-positive fungal culture media as a result of urea degradation. The precipitation of NiCO_3 was the result of BIM where urea was degraded to release NH_4^+ and CO_3^{2-} , the latter

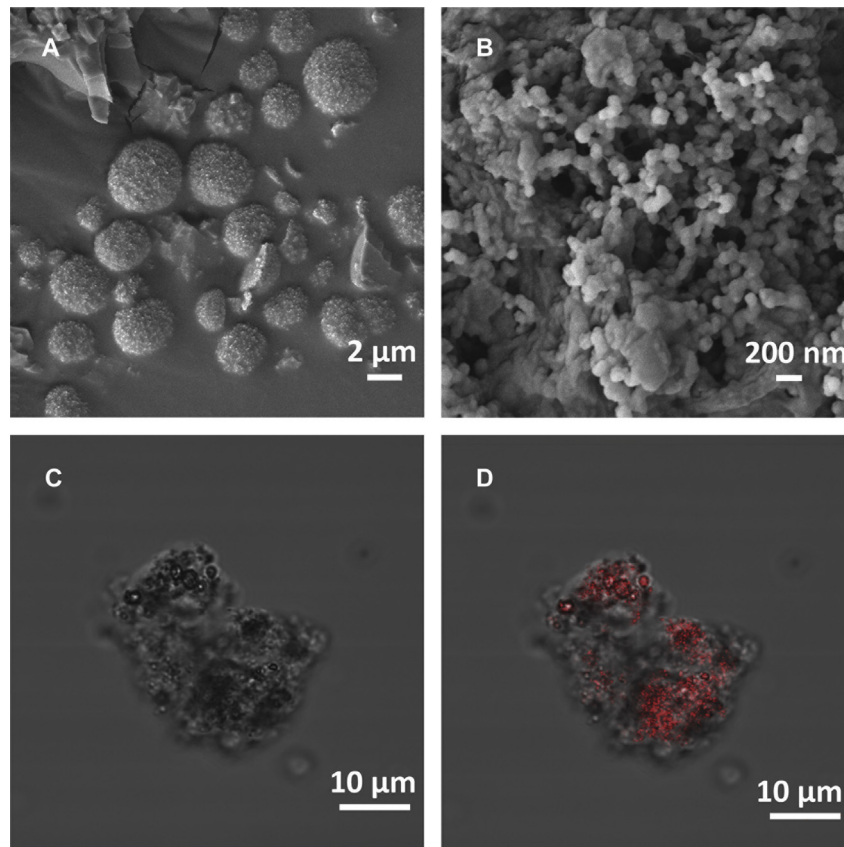


Fig. 3 – Scanning electron microscope and confocal microscope images showing the impact of protein on mineral morphologies. (A) Copper carbonate synthesized from abiotic mixing of 20 mM $(\text{NH}_4)_2\text{CO}_3$ and 2 mM CuCl_2 after a 14 d reaction time; (B) Copper carbonate nanoparticles (CuNPs) synthesized from mixing 20 mM $(\text{NH}_4)_2\text{CO}_3$ and 2 mM CuCl_2 in the presence of 0.1 mg/mL purified *N. crassa* triosephosphate isomerase (TPI) after a 14 d reaction time; (C) confocal microscope images of the protein-CuNP cluster under bright field and (D) an overlay of the bright-field and protein channel (red) images. Representative images are shown from several determinations (Liu and Gadd, unpublished data, see also Liu et al., 2021).

precipitating available Ni. Further study demonstrated that the precipitation of nanoparticles was related to the secretion of extracellular proteins (Li et al., 2019). Using a carbonate-laden fungal culture supernatant, various other metal carbonate/oxide biominerals in the nanoscale were synthesised, including capsular CdCO_3 (55–870 nm) (Li et al., 2014), lamellar MnO_x (~20 nm) (Li et al., 2016), granular malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$, 10–20 nm) and azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$, 10–20 nm) (Li and Gadd, 2017a), granular FeCO_3 (~80 nm) (Li et al., 2020), honeycombed and granular ZnCO_3 (~50 nm) (Li et al. unpublished) and granule al. unpublished)– from the text or else advise what needs to be done exactly to proceed further.→lar CoCO_3 (30–80 nm) (Li et al. unpublished). Moreover, the contribution of extracellular amino acids in biomass-free ureolytic fungal supernatant to nanomineral formation is also likely. Many amino acids show pronounced metal chelating abilities, e.g. cysteine (Choi and Lee, 2020). Ten different extracellular amino acids were detected in urease-positive fungal growth supernatants (*Neurospora crassa*, *Pestalotiopsis* sp. and *Myrothecium gramineum*), including glutamine, glycine, cysteine, threonine, aspartic acid, alanine and glutamic acid. Three types of Zn-containing minerals were obtained when produced with different amino acids:

rod-shaped in the nanoscale, spherical minerals around 100 nm and porous minerals. When produced with L-glutamic acid, Cu-containing minerals were nanoscale and around 30 nm (Li et al., unpublished). It has also been demonstrated that glutathione, a tripeptide of L-glutamic acid, L-cysteine and L-glycine, can effectively bind with metal(oids) (e.g. As^{5+} , As^{3+} , Cd^{2+} , Hg^{2+} and Pb^{2+}) and thiol groups, such as those present in cysteine, can reduce metal ions in the formation of nanoparticles (Choi and Lee, 2020).

5. Role of protein in nanoparticle formation

The formation of nanoparticles involves two processes: nucleation of nanoparticles followed by a stabilization step. Small metal-containing nanoparticles are highly reactive and unstable and tend to aggregate which may alter their physicochemical properties and reactivity. With analogy to the organic stabilizers used in the fabrication of synthetic nanoparticles with controlled size and shape, proteins can act as capping agents as well as crystal growth regulators to minimize nanoparticle aggregation and regulate their development (Kröger et al., 1999; Douglas et al., 2002; Naik et al.,

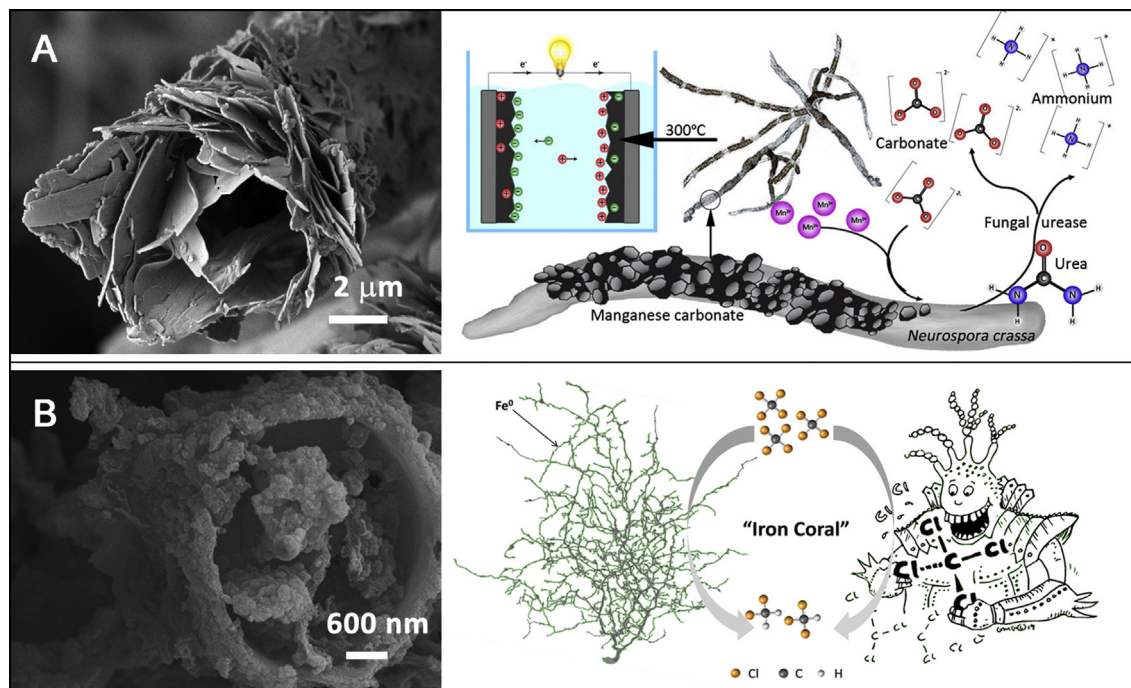


Fig. 4 – Application of fungal biomineralization of metal carbonates in (A) electronic materials and (B) pollutant degradation. (A) left hand panel is a scanning electron microscopy image of a transverse view of a *Neurospora crassa* hypha that was encrusted with manganese carbonate, as result of urea hydrolysis in the presence of $MnCl_2$, and carbonized ($300^\circ C$, 4 h) to produce a manganese oxide/C composite material. The lamellar MnO_x minerals sheathing the carbonized hyphae are ~ 20 nm in thickness. Scale bar = 2 μm . (A) right hand panel is an outline scheme for the preparation of the electrochemically-reactive MnO_x/C nanomaterial using fungal-induced carbonate precipitation through urea hydrolysis (see Li et al., 2016). (B) left hand panel is a scanning electron microscopy image of a transverse view of a *N. crassa* hypha that was encrusted with iron carbonate, as result of urea hydrolysis in the presence of $FeSO_4$, and carbonized ($900^\circ C$, 1 h) to produce a C composite encrusted with nanoscale zerovalent iron (nZVI) particles, “iron coral”, individual nanoparticles being ~ 50 nm in diameter. Scale bar = 600 nm (B) right hand panel is an outline scheme for preparation of the catalytically-active iron coral by mycogenic carbonate biomineralization through urea hydrolysis, and application in xenobiotic degradation (see Li et al., 2020).

2002). Full control of the synthesis of nanoparticles with a narrow size and shape distribution profile is desirable so that nanoparticles can be produced to meet the specific needs of different applications. The study of protein-nanoparticle interactions therefore builds a bridge between nature-inspired biomineralization and protein-mediated inorganic nanoparticle synthesis.

The involvement of organic molecules such as proteins, glycolipids, polysaccharides, and amino acids in biomineral formation has been reported in previous studies (Fig. 2) (Evans, 2019; Liu et al., 2019; Suzuki, 2020). Fungi can produce large amounts of extracellular proteins associated with various metabolic functions, although limited knowledge exists about the specific composition of proteins that fungi can produce, and their impact on nanoparticle formation (Kitching et al., 2015). However, several studies have reported the association of specific proteins with nanoparticles produced by fungal biomineralization. Zhang et al. (2011) described the formation of gold nanoparticles by *Fusarium oxysporum* and detected three proteins, including plasma membrane ATPase, 3-glucan-binding protein and glyceraldehyde-3-phosphatedehydrogenase, which were involved in the synthesis of AuNPs. Triosephosphate isomerase (TPI), a key

enzyme in sugar catabolism, was found to have a strong affinity with copper carbonate nanoparticles (CuNPs), produced using biomass-free spent ureolytic culture medium after growth of *Neurospora crassa*, and played an important role in controlling the morphology and structure of the produced CuNPs (Fig. 3) (Liu et al., 2021). A detailed proteomic study on the protein composition of spent *N. crassa* growth medium showed the secretion of extracellular proteins, for example, laccase and putative rhamnogalacturonase, but also suggested a wide suite of intracellular proteins were also released by the fungus, probably a result of autolysis (Liu et al., 2021). During fungal growth, particularly with increasing culture age, the growth medium can be markedly enriched by compounds released as a result of autolysis, which describes the ‘self-destruction’ of aged mycelial cultures and intracellular constituents. Cell wall degradation by glucanases and chitinases can cause the cell wall to become porous and, together with lysis of the plasma membrane, intracellular proteins can leak into the external medium (White et al., 2002), and participate in later biomineralization events (Liu et al., 2021).

Proteins can coordinate or chelate with metals and form metal-protein complexes, through the interaction of amino groups, carboxylate groups and some amino acid side chains.

For instance, histidine and cysteine residues have a strong affinity to chelate with metals (Janairo, 2016). It has been proposed that fungal extracellular proteins might reduce the nucleation barrier by providing nucleation sites and promoting nanoparticle crystallization (Li and Gadd, 2017a,b; Li et al., 2019). Some proteins with reducing amino acids such as tyrosine can participate in metal reduction and promote the formation of zero-valent metal nanoparticles such as those of Au and Ag (Selvakannan et al., 2004). A study of the synthesis of Ag nanoparticles by several *Fusarium oxysporum* strains verified the reduction of metal ions by a nitrate-dependent reductase and an extracellular quinone shuttle (Durán et al., 2005). The final stage of nanoparticle synthesis involves the capping of proteins onto the nanoparticle surface. The amino acid sequence, secondary structure, metal co-factors and position of specific amino acids can influence such attachment of proteins to the inorganic mineral surface. Proteins can prevent further growth of the nanocrystals through binding to the particle surface, and this can be an important feature of how biogenic molecules can control the size and morphology of the formed nanominerals during biomineralization. The stabilization of Ag nanoparticles by fungal proteins synthesized by *F. oxysporum* was confirmed by transmission electron microscopy (TEM)-electron spectroscopic imaging, which showed the association of N and S atoms around the Ag nanoparticles (Durán et al., 2007). Fourier-transform infrared spectroscopy (FTIR) is one of the most commonly used methods to detect the attachment of proteins to nanoparticle surfaces, and can reveal the presence of amide I, II and III groups and other functional moieties such as carboxylic, aromatic and phenolic groups (Mukherjee et al., 2008; Das et al., 2009; Sanghi and Verma, 2009a,b). After adsorption onto mineral surfaces, the unfolding of proteins has been reported in several previous studies (Shang et al., 2007; Pan et al., 2012; Saptarshi et al., 2013). A detailed analysis revealed that the secondary structure of the extracellular proteins changed from α -helix to β -sheets when nanoscale nickel carbonates were precipitated (Li et al., 2019b). FTIR and circular dichroism (CD) spectroscopy can be used to examine the conformational changes of the proteins, as their conformation determines how the proteins can bind to the material surface which, in turn, determines the resultant morphology of the nanostructures (Janairo, 2016).

6. Applications in environmental nanobiotechnology

Nanoparticles and nanominerals synthesised by fungi are considered to have diverse potential applications as catalysts, antimicrobial agents, and electrochemical materials, and in processes such as pollutant degradation, bioremediation and element biorecovery.

(1) Electrochemical materials

With the increasing consumption of fossil fuels, much attention has focused on the development of eco-friendly and high energy storage devices such as lithium, sodium, and zinc ion batteries, supercapacitors and fuel cells. To improve the

electrochemical performance of such energy storage devices, the use of suitable electronic materials is necessary in determining the specific capacitance, cycling stability, safety, and highly-efficient use (Li and Gadd, 2017b; Zhang and Zhao, 2009; Zhang et al., 2017). Transition metal oxides and hydroxides (e.g. Fe_3O_4 , MnO_2 , $\text{Ni}(\text{OH})_2$) are good electrode materials. Compared with microscale materials, nanomaterials with controlled morphologies and structure exhibit advantages, including a high specific surface area which represents a high number of reactive sites, a small particle size which contributes to better penetration of electrolyte and reduces electrolyte diffusion, and a controlled structure which provides stable channels for electron transfer and ensures cycling stability (Zhang et al., 2017). Fungal biomineralization of metal carbonates was applied for the synthesis of electrode materials and the electrochemical properties of a carbonized fungal biomass-manganese oxide mineral composite (MycMnO_x/C) were investigated in a supercapacitor and a lithium ion battery (Li et al., 2016) (Fig. 4A). After carbonization, the MnO_x minerals were lamellar shaped with a thickness of around 20 nm. Compared with MnO_x synthesised by other methods, the MnO_x/C composite showed a very favourable specific capacitance (362 F g^{-1}) when used as an electrode material in a supercapacitor and an outstanding cycling stability when used in a lithium ion battery. Compared with manganese oxide synthesised by other methods, the biogenic MnO_x/C exhibited excellent energy storage in comparison with other abiotic supercapacitor materials, with a specific capacitance of 208 F g^{-1} at a current density of 1 A g^{-1} . In comparison with other reported MnO_x materials used in lithium ion batteries, the biogenic MnO_x/C showed a capacity of $\sim 400 \text{ mAh g}^{-1}$ at a current density of 100 mA g^{-1} with 91% capacity retention after 200 cycles (see Tables 1 and 2 in Supplemental Information, Li et al., 2016).

(2) Pollutant degradation

Chlorinated pollutants with volatility, carcinogenic effects and bioaccumulation potential in groundwater can cause serious environmental problems and threaten human health. Nanoscale zerovalent (nZVI) iron has been used as an effective material for contaminant removal due to a large specific surface area, high reactivity and mobility. However, conventional nZVI tends to aggregate which limits reaction efficiency and practical applications. Li et al. (2020) demonstrated that *Neurospora crassa* could be used for the synthesis of nZVI with a unique N-doped branching structure originating from the fungal hyphae. The biosynthesised nZVI (termed 'iron coral') showed high degradation of carbon tetrachloride (CCl_4) and excellent stability (Fig. 4B). The iron coral composites showed a porous branching structure which could improve the dispersion of nZVI and the capture efficiency for CCl_4 while the N-doped sites may accelerate electron transfer between nZVI and CCl_4 . Further studies have shown that the iron coral composites exhibited excellent degradation ability for other organic pollutants, e.g. chlorobenzene, dichloroethane, carbon trichloride and perchloroethylene (Li et al., unpublished). Various shapes (spheres, triangles, penta/hexagons and sheets) and sizes of gold nanoparticles were synthesised using a *Trichoderma viride* culture filtrate capable of differing degradation abilities for 4-nitrophenol (Kumari et al., 2016). Spherical

gold nanoparticles of the smallest sizes (3–10 nm) were better catalytic agents for degradation of 4-nitrophenol into less toxic 4-aminophenol. Moreover, biosynthesised nanoparticles, such as SnO₂, ZnO, TiO₂, TiO₂/SiO₂ and Fe₃O₄, are excellent catalysts for the degradation of dyes in wastewater, such as methylene blue, methyl orange, methyl red, methyl violet, acid red 14 and rhodamine B (Choi and Lee, 2020; Priyadarshini et al., 2021). ZnO nanoparticles (~10 nm) were prepared by a co-precipitation method with *Cordyceps militaris* and these could degrade >95% of supplied methylene blue after 180 min UV irradiation (Li et al., 2019).

(3) Element biorecovery

With the increasing consumption of renewable resources, valuable metals and mineral resources are increasingly over-exploited, including cobalt, platinum group metals, rare earth elements and metalloids such as selenium and tellurium (Liang and Gadd, 2017; Nancharaiah et al., 2016). Compared with conventional methods, biorecovery of these valuable metal(loids) could provide advantages in low energy consumption, low environmental perturbations, and low carbon emissions (Pollmann et al., 2016). Selenium and tellurium have drawn significant attention due to their wide applications in solar cells, thermoelectric elements, specialised glass, semi-conductors, and other electronics (Liang et al., 2019; Nancharaiah et al., 2016). Four fungal species (*Aureobasidium pullulans*, *Mortierella humilis*, *Trichoderma harzianum* and *Phoma glomerata*) were incubated in Se- and Te-containing medium for the synthesis of Se or Te nanoparticles (Liang et al., 2019). The fungal hyphae provided sites for the deposition of Se or Te nanoparticles while extracellular protein and polymeric substances influenced the final location. Das et al. (2012b) described a biorecovery process using production of gold nanoparticles by *Rhizopus oryzae*, the reduction of AuCl₄⁻ to Au⁰ nanoparticles occurring in the cell wall as well as in the cytoplasm. The formation of the Au⁰ nanoparticles comprised four steps: ion adsorption, initial reduction to Au(I), formation of Au(I) complexes and final reduction to Au(0), where two proteins (45 and 42 kDa) participated in the reduction process and an 80 kDa protein acted as a capping agent for the Au nanoparticles.

(4) Mesoporous nanomaterials

One area of nanobiotechnology investigates the application of fungi, particularly yeasts, as templates for synthesis of nanoparticles, nano-structures and mineral “shells”, including mesoporous materials (He et al., 2011a,b; Chen et al., 2014; Wang et al., 2018). These have applications as drug, enzyme and cell carriers, adsorbents, catalysts, chemical sensors, and in fuel cells and other electronic and optical devices. Mesoporous inorganic materials synthesised using yeast templates include anatase (TiO₂), silica (SiO₂), hydroxyapatite, Zn₃(PO₄)₂, Mg₃(PO₄)₂, titanium phosphate, FePO₄, Ag₃PO₄, and zirconium phosphate (Wang et al., 2018). Synthesis of mesoporous Ca-, Zn-, Mg-, and Ti-phosphate-protein nanocomposites has also been reported, while mesoporous Na₃V₂(PO₄)₃/C or LiFePO₄/C nanocomposites (the carbon arising from fungal biomass), exhibit enhanced

electrochemical properties as battery materials (He et al., 2011a,b; Cao et al., 2018; Chang et al., 2020).

7. Conclusions

Nanoparticles and nanominerals have shown great potential in different fields, including medicine, environmental biotechnology, electronics and chemical engineering. However, it is still a challenge to develop sustainable methods for synthesis of these nanomaterials. Compared with conventional physico-chemical methods, biological systems may provide a sustainable, resource efficient and economical method of synthesis. However, most demonstrations to date are at the laboratory scale and future progress in this area depends on industrial involvement and full assessment of economic and environmental implications, as well as optimization of upscaled microbial fermentations for adequate bulk production. Fungal mediated synthesis of nanoparticles and nanominerals possesses several advantages although there are still unsolved problems during the formation process, including the role of fungal metabolites in size and morphology control, the biorecovery or pollutant degradation efficiencies in practical applications, and potential toxicity within the producing system. Application of enzymic catalysis or use of biomass-free reactive culture supernatants may be useful in minimizing toxic effects and enabling easier harvest although the spectrum of metabolites and reactive substances released by fungi in liquid media make precise control difficult.

Conflict of interest statement

None declared.

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freely-available images and videos of fungal growth and morphogenesis are widely used by many of us for informing students and researchers of the intricacies of the fungal organism. He is greatly missed by his colleagues in the British Mycological Society, his worldwide network of friends and collaborators, and of course the generations of his own post-graduate and postdoctoral researchers he taught and inspired in Edinburgh and Manchester.

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