Chapter 3
Biosynthesis of Gold Nanoparticles: A Review

Maggy F. Lengke, Charoen Sanpawanitchakit, and Gordon Southam

3.1 Introduction

Gold is one of the rarest metals on earth, and its importance has been acknowledged since antiquity. Gold is not only used in jewelry industry but also in a diverse range of industrial applications covering the field of biology and medicine, environment, and technology (e.g., Oldenburg et al. 1998; Vieira and Volesky 2000; Salata 2004; Sperling et al. 2008; Cai et al. 2008; Chen et al. 2008; Mohanpuria et al. 2008). Because of the increased demand of gold in many industrial applications, there is a growing need for cost effectiveness as well as to implement green chemistry in the development of new nanoparticles. Although various chemical and physical synthesis methods successfully produce pure and well-defined nanoparticles, these methods remain expensive and involve the use of hazardous chemicals. In consequence, biological processes that lead to the formation of nanoscale inorganic materials are appealing as possible environmentally friendly nanofactories.

The synthesis of gold nanoparticles of different sizes, ranging from <1 to several hundred nanometers, and shapes has been conducted in both aqueous and nonpolar organic solutions (Brust et al. 1994; Handley 1989; Selvakannan et al. 2003; Daniel and Astruc 2004). The usual synthetic route to prepare gold nanoparticles involves the reduction of a gold salt (usually a halide) in solution by various reducing agents in the presence of a stabilizer (Brust et al. 1994; Handley 1989; Selvakannan et al. 2003; Daniel and Astruc 2004; Masala and Seshadri 2004). The use of rapid reductants (e.g., white phosphorus, tannic acid, formamide, *o*-anisidine) results in bigger and generally spherical nanoparticles, while weak reducing agents (e.g., citrate, tartarate)

M.F. Lengke (✉)
Geomega Inc, 2525 28th Street, Suite 200, Boulder, CO 80301, USA
e-mail: maggylengke@yahoo.com

C. Sanpawanitchakit
EnviroGroup Limited, 3561 Stagecoach Road, Suite 205, Longmont, CO 80504, USA

G. Southam
Department of Earth Sciences, University of Western Ontario, London, ON, N6A 5B7, Canada

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results in a slow reaction generating small nanoparticles (Handley 1989; Daniel and Astruc 2004). Sulfur-containing ligands (e.g., xanthates, disulfides, dithiols or trithiols), phosphanes, phosphines, amines, chalcogenides, carboxylates, and polymers have all been used to stabilize gold nanoparticles (Brust et al. 1994; Daniel and Astruc 2004).

Biological methods using organisms, such as bacteria and fungi (e.g., Southam and Beveridge 1994, 1996; Canizal et al. 2001; Kashefi et al. 2001; Mukherjee et al. 2001, 2002; Shankar et al. 2003; Keim and Farina 2005; Nair and Pradeep 2002; Ahmad et al. 2005; Lengke and Southam 2005, 2006, 2007; Lengke et al. 2006a, b, c, 2007), plants (e.g., Gardea-Torresdey et al. 2002), plant extracts (e.g., Shankar et al. 2003, 2004), and dead plant biomass (e.g., Gardea-Torresdey et al. 1999, 2000), for the synthesis of gold nanoparticles are relatively new areas, and are currently being explored. Although the biosynthesis of gold nanoparticles is relatively new, the interactions between bacteria and metals have been well documented (e.g., Heath 1981; Nash et al. 1981; Ehrlich 2002) and the ability of bacteria to accumulate metals has been recognized in the bioremediation field (e.g., Lloyd 2002; Dermont et al. 2008). Previous studies of the biosynthesis of gold nanoparticles have been focused on the use of gold (III)–chloride [$AuCl_4^-$] and gold(I)–thiosulfate [$Au(S_2O_3)_2^{3-}$] complexes. Therefore, the objective of this chapter is to review the current state of knowledge concerning the biosynthesis of gold nanoparticles by bacteria, cyanobacteria, and algae using these two gold complexes, based on the existing literature.

3.2 Gold Chemistry

Gold can occur in one of the six oxidation states, from -1 to $+5$ (Puddephatt and Vittal 1994), which can be related to its relatively high electronegativity. The most common form of gold complexes is in aurous [Au(I)] and auric [Au(III)] oxidation states (Emery and Leddicotte 1961). The dissolution of gold in aqueous solution is a combination process of oxidation and complexation. In the presence of a complexing ligand, Au(I) and Au(III) can form stable complexes, otherwise they can be reduced in solution to metallic gold (Nicol et al. 1987). The stability of gold complexes is related not only to the properties of the complexing ligand, but also more specifically to the donor atom of the ligand that is bonded directly to the gold atom. According to Nicol et al. (1987), the first rule is that the stability of gold complexes tends to decrease when the electronegativity of the donor atom increases. For example, the stability of gold halide complexes in solution follows the order $I^- > Br^- > Cl^- > F^-$. The second rule is that Au(III) is generally favored over Au(I) with hard ligands and Au(I) over Au(III) with soft ligands. The soft ligands containing less electronegative donor atoms such as S, C, P, and I form more stable complexes with Au(I), whereas the hard electron donor ligands such as F, Cl, O, and N prefer Au(III). The preferred co-ordination number of Au(I)

is 2, tending to form linear complexes, and that of Au(III) is 4, tending to form square planar complexes.

The review of gold complexes below is limited for the gold(III)–chloride and gold(I)–thiosulfate because the published biosynthesis of gold nanoparticles by bacteria, cyanobacteria, and algae mainly utilized these two gold complexes.

3.2.1 Gold(I)–Thiosulfate Complex

Gold(I)–thiosulfate complex is a predominant species at a wide range of pH (acidic to alkaline) and moderate oxidizing to reducing conditions (Senanayake et al. 2003). Sodium thiosulfate is one component of an alternative lixiviant to cyanide for extraction of gold (Aylmore and Muir 2001), and it forms a strong complex with Au(I). The advantage of this approach is that thiosulfate is essentially non-toxic, and ore types that are refractory to gold cyanidation (e.g., carbonaceous or Carlin type ores) can be leached by thiosulfate. Some problems with this alternative process include the high consumption of thiosulfate, and the lack of a suitable recovery technique, because gold(I)–thiosulfate does not adsorb to activated carbon, a standard technique used in gold cyanidation to separate the gold complex from the ore slurry.

3.2.2 Gold(III)–Chloride Complex

Gold (III)–chloride complex is stable under oxidizing and acidic conditions (Ran et al. 2002). It decomposes above 160°C or in light. Many studies of biosynthesis gold nanoparticles had utilized the gold(III)–chloride acid solid as a starting material to form gold(III)–chloride complex (e.g., Nair and Pradeep 2002; Lengke et al. 2006a, b, c, 2007). Gold(III)–chloride acid solid ($HAuC1_4 \cdot xH_2O$) can be produced by dissolving gold in aqua regia and then evaporating nitric acid (HNO_3) with hydrochloric acid (HCl). This solid is also referred to as acid gold trichloride or gold(III)–chloride trihydrate (Emery and Leddicotte 1961; http://en.wikipedia.org/wiki/Gold(III)_chloride). Gold(III)–chloride acid – appearing as long, bright yellow, needle-like crystals – is very hygroscopic and highly soluble in water and ethanol.

3.3 Biosynthesis of Gold Nanoparticles

The interactions between bacteria/cyanobacteria/algae and gold have been well documented since 1986 for biosorption and biorecovery of gold. Our review includes 46 published papers, utilizing bacteria (24), cyanobacteria (8), and algae

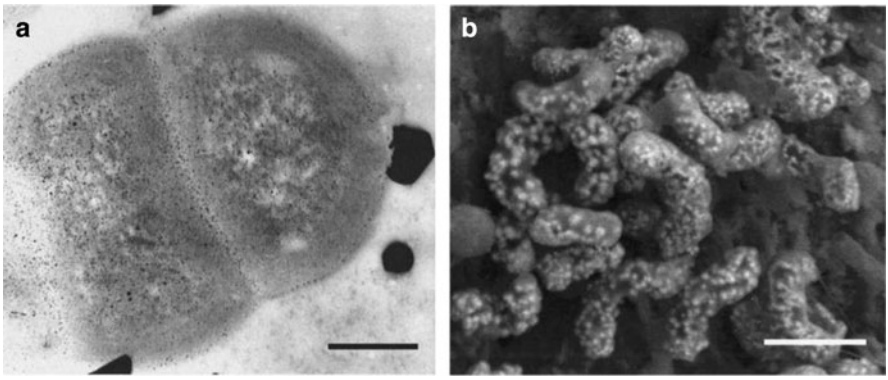

Fig. 3.1 (**a**) A TEM micrograph of a thin section of cyanobacteria cell with the gold nanoparticles inside the cell, (**b**) a SEM micrograph of gold nanoparticles on the surface of sulfate-reducing bacteria (*Desulfovibrio* sp). *Scale bars* in (**a**) and (**b**) are 0.5 and 1.5 μm, respectively

(14) to determine whether gold can be accumulated from gold(I)–thiosulfate and gold(III)–chloride solutions. Because of purposes other than the biosynthesis of gold particles, some studies of biosorption and biorecovery neither included details of the shape and size of gold particles (e.g., Kashefi et al. 2001; Nakajima 2003) nor described the experimental conditions such as pH, temperature, duration, initial gold concentrations, or bacterial population (e.g., Ting et al. 1995; Kashefi et al. 2001). In general, gold nanoparticles were precipitated intracellularly and/or extracellularly depending on the species (Fig. 3.1). The shape of gold particles precipitated by bacteria/cyanobacteria/algae includes spherical, oval, spongy clots, mushroom, irregular, triangular, tetragonal, hexagonal, octahedral, rod, cubic, docahedral, icosahedral, coil or wire, plate, and thin foil, with size ranging from 1 nm to several mm (Fig. 3.2), as discussed below.

3.3.1 Gold(I)–Thiosulfate Complex

The interactions between bacteria and cyanobacteria with a gold–thiosulfate complex have been studied by Lengke and Southam (2005, 2006, 2007) and Lengke et al. (2006a), and are summarized in Table 3.1. *Acidithiobacillus thiooxidans* isolated from the Driefontein Consolidated gold mine in Witwatersrand Basin, Republic of South Africa was able to produce gold particles in the presence of up to 0.26 mmol/L gold at pH ~ 1.9–2.2 and 25°C within a period of 35–75 days (Lengke and Southam 2005). In the presence of dead bacterial cells and in the chemical abiotic experiments, gold was not precipitated under similar experimental conditions and duration. The bacterial system was able to precipitate 87–100% of the gold under diurnal light exposure, while only 11–69% of the gold was precipitated in the dark. The gold nanoparticles were precipitated inside the bacterial cells with the size <10 nm,

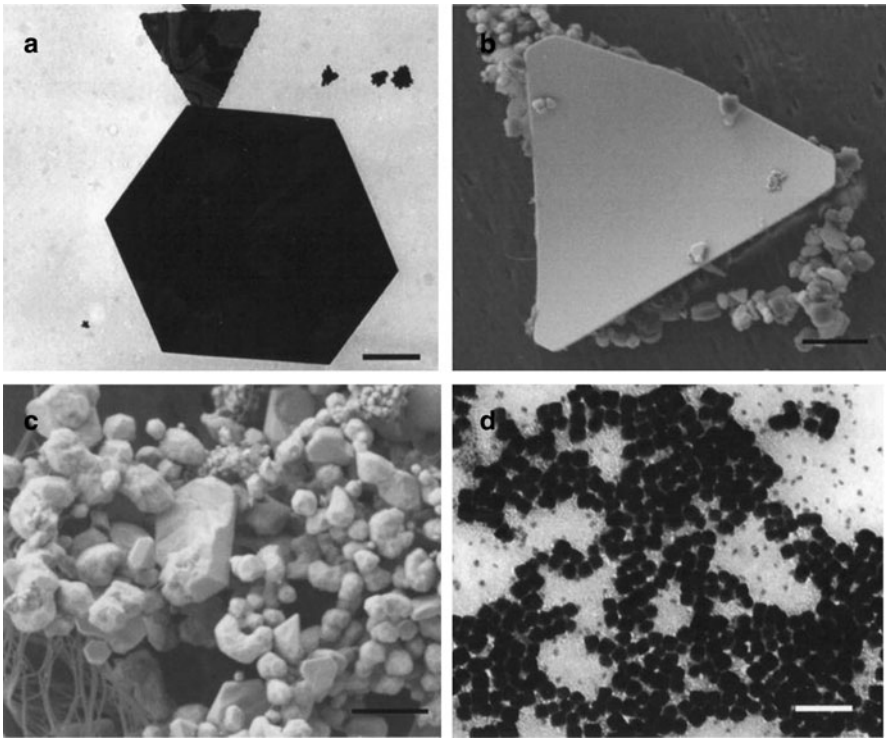

Fig. 3.2 TEM and SEM micrographs of selected gold nanoparticles formed by cyanobacterial interactions with gold(III)–chloride and gold(I)–thiosulfate complexes. *Scale bars* in (**a**), (**b**), (**c**), and (**d**) are 0.5, 2, 1, and 0.1 μm, respectively

forming a spherical shape. Outside the bacterial cells, the gold had formed coiled or wire, irregular, and rounded structures with an approximate size of 0.5–5 μm, and a crystalline octahedral shape.

Heterotrophic sulfate-reducing bacteria (SRB) isolated from the Driefontein Consolidated gold mine in Witwatersrand Basin, Republic of South Africa was able to produce gold particles in the presence of up to 2.6 mmol/L gold at pH ~ 7.4–7.9 and 23–25°C within a period of 6–53 days, in the presence or absence of iron (Lengke and Southam 2006). Only in the presence of live bacterial cells, gold was precipitated from solution. The gold nanoparticles were precipitated inside and at the bacterial cells with the size <10 nm, forming a spherical shape. In bulk solution, the gold had formed spherical, sub-octahedral to octahedral shape with size ranging from 0.5 to 6 μm (Lengke and Southam 2006). The role of SRB in the precipitation of gold was also investigated through column experiments in the presence of up to 2.6 mmol/L gold at pH ~ 7.4–8.5 and 23–25°C within a period of 148 days, in the presence or absence of iron (Lengke and Southam 2007). In the bacterial systems, SRB precipitated gold inside and at the cells, forming spherical nanoparticles (<10 nm). In bulk solution, the formation of octahedral gold crystals,

Table 3.1 A summary of bacterial and cyanobacterial interactions with a gold(I)–thiosulfate complex

No	Bacteria Name	Shape	Extracellular/ Intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
Bacteria											
1	*Acidithiobacillus thiooxidans*	Spherical, irregular, coil or wire, octahedral	Extracellular and intracellular	<10 nm (intracellular); 0.5–5 μm (extracellular)	1.9 and 2.2	25	35 days	(0–0.26) × 10^{-3}	10^7–10^8	Bacteria stationary growth phase	Lengke and Southam (2005)
		Spherical, irregular, coil or wire, octahedral	Extracellular and intracellular	<10 nm (intracellular); 0.5–5 μm (extracellular)	5.4–1.9	25	75 days	(0–0.26) × 10^{-3}	10^6–10^8	Inoculate with bacteria	
			No precipitation		1.9	25	75 days	(0–0.26) × 10^{-3}		Dead cells (autoclaved)	
			No precipitation		1.9 and 5.4	25	75 days	(0–0.26) × 10^{-3}		Abiotic	
2	Heterotrophic sulfate-reducing bacteria (SRB)	Octahedral, spherical	Extracellular and intracellular	<10 nm (intracellular); 0.5–6 μm (extracellular)	7.4–7.9	23–25	53 days	(0–2.55) × 10^{-3}	7×10^6 to 3.5×10^7	Bacteria stationary growth phase	Lengke and Southam (2006)
		Octahedral, spherical	Extracellular and intracellular	<10 nm (intracellular); 0.5–6 μm (extracellular)	7.4–7.9	23–25	6 days	(0–1.14) × 10^{-3}	5×10^3 to 10^6	Inoculate with bacteria	
			No precipitation		7.7	23–25	53 days	(0–1.14) × 10^{-3}		Dead cells (autoclaved)	
			No precipitation		7.4–7.7	23–25	53 days	(0–2.55) × 10^{-3}		Abiotic	

3	Heterotrophic sulfate-reducing bacteria (SRB)	Spherical, octahedral, foil	Extracellular and intracellular	<10 nm (intracellular); 1 μm to several mm (extracellular)	7.4–8.5	23–25	148 days	(0–2.55) × 10^{-3}	4.5 × 10^{8} to 1.4 × 10^{9}	Bacteria	Lengke and Southam (2007)
		Spherical		1 μm	7.4–9.1	23–25	148 days	(0–2.55) × 10^{-3}		Abiotic	
Cyanobacteria											
1	*Plectonema boryanum* UTEX 485	Irregular-thin	Extracellular		5.3	25	28 days	(2–2.8) × 10^{-3}	3.8 × 10^{8}	Cyanobacteria stationary growth phase	Lengke et al. (2006a)
		Irregular, cubic	Extracellular and intracellular	<10 nm (intracellular); 10–25 nm (extracellular)	5.3	60	28 days	(2–2.8) × 10^{-3}	3.8 × 10^{8}	Cyanobacteria stationary growth phase	
		Cubic	Extracellular and intracellular	<10 nm (intracellular); 10–25 nm (extracellular)	5.3–3.9	100	28 days	(2–2.8) × 10^{-3}	3.8 × 10^{8}	Cyanobacteria stationary growth phase	
		Irregular	Extracellular and intracellular	<10 nm (intracellular); 10–25 nm (extracellular)	5.3–3.0	200	1 day	(2–2.8) × 10^{-3}	3.8 × 10^{8}	Cyanobacteria stationary growth phase	
			No precipitation		5	25	28 days	(2–2.8) × 10^{-3}		Abiotic	
		Cuboctahedral	Precipitation	25 nm	5–3.9	60	28 days	(2–2.8) × 10^{-3}		Abiotic	
		Cuboctahedral	Precipitation	25 nm	5–2.2	100	28 days	(2–2.8) × 10^{-3}		Abiotic	
		Cuboctahedral	Precipitation	25 nm	5–1.9	200	1 day	(2–2.8) × 10^{-3}		Abiotic	

framboid-like structures (~1.5 μm), and gold foil (mm-scale) was observed in the bacterial systems, while only a spherical shape with a size ~1 μm was observed in the chemical abiotic systems.

Plectonema boryanum UTEX 485, a filamentous cyanobacterium, had been reacted with a gold–thiosulfate complex (up to 2.8 mmol/L gold) at 25–100°C for up to 1 month and at 200°C for 1 day (Lengke et al. 2006a). The interaction of cyanobacteria with a gold–thiosulfate complex caused the separation of filaments into their constituent cells and released membrane vesicles after 14 days at 25°C. The precipitation of irregular gold particles on the surface of membrane vesicles was observed. At 60–200°C, nanoparticles of gold and gold sulfide were deposited inside the cells (<10 nm) and on the outer surface of the sheaths (~10–25 nm). The larger nanoparticles of gold (~20–25 nm) were distinctly cubic in shape. In the chemical abiotic systems, the gold–thiosulfate were stable for 1 month at 25°C, whereas gold nanoparticles (~25 nm) with a cubohedral habit were precipitated at 60–200°C.

3.3.2 Gold(III)–Chloride Complex

The interactions between bacteria, cyanobacteria, and algae with a gold(III)–chloride complex have been studied using different species, and the results of these studies are summarized in Tables 3.2, 3.3, and 3.4. The first published laboratory study to understand the interaction of a mixed bacteria (*Bacillus mesentericus niger*, *Bacillus oligonitrophilus*, and *Bacterium nitrificans*) with initial elemental gold was conducted by Korobushkina and Korobuskhin (1986). The objective of their study was to determine whether gold can be biologically re-deposited. The elemental gold was dissolved into solution, presumably as gold(III)–chloride or gold–organic complexes, and a reduction process occurred simultaneously, forming spherical/oval (1–2 μm), spongy clots/clusters/nodules (0.1–20 μm), and mushroom (0.1–0.5 μm) shapes. Southam and Beveridge (1994, 1996) employed *Bacillus subtilis* 168 in their experiments at 4, 23–25, 60, and 90°C within 1 week to 8 months. Gold nanoparticles were initially precipitated inside the bacterial cells (5–50 nm) and were released into solution, forming spherical (20 nm) and hexagonal–octahedral (4–20 μm) gold. The formation of crystalline octahedral gold was enhanced by an increase in the experimental duration and temperature. The potential of 14 hyperthermophilic and mesophilic dissimilatory iron(III) reducing bacteria to precipitate elemental gold from solutions was investigated by Kashefi et al. (2001) using hydrogen (H_2), lactate, or acetate electron donor at neutral pH. Of 14 species, 6 were able to precipitate elemental gold only in the presence of H_2 electron donor at 100°C. Most of the six bacteria precipitated gold at the cell surfaces (nm scale), except for *Geovibrio ferrireducens* (ATCC 51996). However, a closer inspection of the thin sections of several species [e.g., *Geobacter sulfurreducens* (ATCC 51573), *Pyrobaculum islandicum* (DSM 4184), *Thermotoga maritima* (DSM 3109)] indicated that gold was also precipitated intracellularly.

Table 3.2 A summary of bacterial interactions with a gold(III)–chloride complex

No	Bacteria name	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
1	*Bacillus mesentericus niger*	Spherical, oval	Extracellular	1–2 μm (Extracellular)	7.5	25	360 days	2.5×10^{-3}		Nutrient medium	Korobushkina and Korobuskhin (1986)
	Bacillus oligonitrophilus	Spongy clots/ clusters/ nodules	Extracellular	0.1–20 μm (Extracellular)							
	Bacterium nitrificans	Mushroom	Extracellular	0.1–0.5 μm (extracellular)							
2	*Bacillus subtilis* 168	Irregular, spherical	Extracellular and intracellular	5–50 nm (Intracellular)	2.69	60	7–224 days	2.5×10^{-3}	20 mg/mL dry cell weight	Bacteria late stationary phase	Southam and Beveridge (1994)
		Hexagonal, octahedral		20 μm (Extracellular)							
			No precipitation			60	7–224 days	5×10^{-3}		Abiotic	
3	*Bacillus subtilis* 168	Spherical, irregular, octahedral	Extracellular and intracellular	<20 nm (intracellular)	2.6	4	7–28 days	2.5×10^{-3}	20 mg/mL dry cell weight	Bacteria late stationary phase	Southam and Beveridge (1996)
			Extracellular and intracellular	20 nm(1 h), 4–10 μm (4 weeks) – extracellular	2.6	21–23		2.5×10^{-3}		Bacteria late stationary phase	
			Extracellular and intracellular		2.6	60		2.5×10^{-3}		Bacteria late stationary phase	
			Extracellular and intracellular		2.6	90		2.5×10^{-3}		Bacteria late stationary phase	
			No precipitation		2.6	4		5×10^{-3}		Abiotic	
			No precipitation		2.6	21–23		5×10^{-3}		Abiotic	
			No precipitation		2.6	60		5×10^{-3}		Abiotic	
			No precipitation		2.6	90		5×10^{-3}		Abiotic	
4	*Pyrobaculum islandicum* (DSM 4184)		Extracellular	few nm	6–6.2	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol) or N_2-CO_2 (80:20 vol/vol) with lactate or acetate	Kashefi et al. (2001)

(*continued*)

Table 3.2 (continued)

No	Bacteria name	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
				No precipitation	6–6.2	100	0.5–3 h		0.025 mg/mL	No electron donor	
				No precipitation	6–6.2	30	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol) or N_2–CO_2 (80:20 vol/vol) with lactate or acetate	
	Pyrobaculum aerophilum (DSM 7523)			No precipitation	7	100	0.5–3 h		0.025 mg/mL		
	Pyrococcus furiosus (DSM 3638)		Extracellular		7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol)	
	Archaeoglobus fulgidus (DSM 4304)			No precipitation	7	100	0.5–3 h		0.025 mg/mL		
	Ferroglobus placidus (DSM 10642)			No precipitation	7	100	0.5–3 h		0.025 mg/mL		
	Shewanella algae strain BRY (ATCC 51181)		Extracellular (also intracellular)		7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol)	
				No precipitation	7	100	0.5–3 h		0.025 mg/mL	N_2–CO_2 (80:20 vol/vol) with lactate	
	Desulfuromonas vulgaris (ATCC 35115)		Extracellular		7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol)	
				No precipitation	7	100	0.5–3 h		0.025 mg/mL	N_2–CO_2 (80:20 vol/vol) with lactate	
	Desulfuromonas palmitatis (ATCC 51701)			No precipitation	7	100	0.5–3 h		0.025 mg/mL	N_2–CO_2 (80:20 vol/vol) with lactate or acetate	
	Geothrix fermentans (ATCC 700665)			No precipitation	7	100	0.5–3 h		0.025 mg/mL	N_2–CO_2 (80:20 vol/vol) with	

										lactate or acetate	
	Geobacter metallireducens (ATCC 53774)			No precipitation	7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol) or N_2–CO_2 (80:20 vol/vol) with acetate	
	Thermotoga maritima (DSM 3109)		Extracellular (also intracellular)		7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol)	
				No precipitation	7	30	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol)	
	Geovibrio ferrireducens (ATCC 51996)		Intracellular		7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol)	
	Desulfitobacterium metallireducens			No precipitation	7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol) or N_2-CO_2 (80:20 vol/vol) with lactate	
	Geobacter sulfurreducens (ATCC 51573)			No precipitation	7	100	0.5–3 h		0.025 mg/mL	H_2–CO_2 (80:20 vol/vol) or N_2-CO_2 (80:20 vol/vol) with acetate	
5	*Pseudomonas aeruginosa* PAO1 biofilm		Extracellular and intracellular	<10 nm (intracellular); 1–2 mm within biofilm	acid	20	0.5 h	1×10^{-5} to 5×10^{-3}			Karthikeyan and Beveridge (2002)
6	*Lactobacillus* sp.	Spherical, triangular, hexagonal	Extracellular and intracellular	20–50 nm and >100 nm	4.4	25	3 days	1×10^{-3}			Nair and Pradeep (2002)
		Spherical	Extracellular and intracellular	100–300 nm	4.4	25	3 days	Au + Ag (equimolar)			
7	*Arthrobacter tumescens* IAM 1447 *Bacillus subtilis* IAM 1026				3	30	1 h	5×10^{-5}	15 mg/100 mL cell weight		Nakajima (2003)

(*continued*)

Table 3.2 (continued)

No	Bacteria name	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
	Brevibacterium helovolum IAM 1637										
	Corynebacterium equi IAM 1038										
	Deinococcus proteolyticus IAM 1214										
	Escherichia coli IAM 1264										
	Pseudomonas maltophilia IAM 1554										
	Zooglea ramigera IAM 12136										
8	*Acinetobacter calcoaceticus* IAM 12087				3	25	1 h	5×10^{-5}	15 mg/100 mL dry cell weight	Batch test	Tsuruta (2004)
	Arthrobacter simplex IAM 1660				3	25		5×10^{-5}	0.66 g cell weight/g dry weight polyacrylamide	Column tests	
	Arthrobacter tumesseus IAM 1447										
	Bacillus cereus IAM 1656										
	Bacillus licheniformis IAM 11054										
	Bacillus megaterium IAM 1166										
	Bacillus subtilis IAM 1026										
	Bacillus subtilis IAM 1633										
	Bacillus subtilis IAM 11060										

Brevibacterium helovolum IAM 1637
Corynebacterium equi IAM 1038
Enterobacter aerogenes IAM 1183
Erwinia herbicola IAM 1562
Escherichia coli IAM 1264
Micrococcus luteus IAM 1056
Nocardia corallina IAM 12121
Nocardia erythropolis IAM 1399
Nocardia rugosa kccA0193
Pseudomonas aeruginosa IAM 1054
Pseudomonas aeruginosa IAM 1095
Pseudomonas fluorescens IAM 12022
Pseudomonas maltophilia IAM 1554
Pseudomonas putida IAM 1506
Serratia marcescens IAM 1022
Thiobacillus novelus IFO 12443

(*continued*)

Table 3.2 (continued)

No	Bacteria name	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
9	Magnetotactic bacteria (cocci, bacilli and multicellular)	Irregular	Extracellular and intracellular	few nm		25	1 day	0.1×10^{-3}		Uncultured bacteria	Keim and Farina (2005)
							>1 day	0.4×10^{-3} (Au) + 12.8×10^{-3} (Ag)			
10	*Ralstonia metallidurans*		Extracellular and intracellular	few nm (intracellular)		30	3 days	5×10^{-2}	10^3 to 1.8×10^7	Inoculate with bacteria in a gold containing growth medim	Reith et al. (2006)
						30	2 days		4.2×10^4 to 1.5×10^8	Inoculate with bacteria in a growth medium without gold	
			Extracellular			30	5 days	5×10^{-2}		Dead cells (lysed)	
11	*Pseudomonas stutzeri* NCIMB 13420 *Bacillus subtilis* DSM 10	Spherical, irregular	Extracellular and intracellular	<10 nm and above	5–6	28	1–3 days	$1.3–10^{-3}$		(1) Sceening process	Gericke and Pinches (2006a) Gericke and Pinches (2006b)
	Pseudomonas putida DSM 291	Spherical	Intracellular	<10 nm	3	28	1–3 days	1.3×10^{-3}		(2) Determine the effect of pH	
		Spherical	Intracellular	<10 nm	5						
		Spherical, irregular	Extracellular and intracellular	<10 nm and above	7						
		spherical, irregular	Extracellular and intracellular	<10 nm and above	9						
		Spherical, irregular	Extracellular and intracellular	<10 nm and above	5	25, 35, and 50	1 day	1.3×10^{-3}	10 mg cells/mL	(3) Determine the effect of temperature	

		Spherical, irregular	Extracellular and intracellular	<10 nm and above		28	1 day	1.3×10^{-3}, 2.5×10^{-3}, and 1.3×10^{-2}		(4) Determine the effect of gold concentrations	
12	*Shewanella algae* ATCC 51181	Irregular	Intracellular	10–20 nm	7	25	1–2 h	1×10^{-4} to 1×10^{-3}	$0.3–4 \times 10^{9}$	H_2-CO_2 (80:20 vol/vol)	Konishi et al. (2006)
				No precipitation	7	25	1–2 h	1×10^{-4} to 1×10^{-3}	$0.3–4 \times 10^{9}$	N_2–CO_2 (80:20 vol/vol) with lactate	
						60	1 h	1.4×10^{-3}		Chemical reaction with citric acid (0.02 mol/L)	
13	*Escherichia coli* DH5α	Mostly spherical, with triangular and quasi-hexagonal	Extracellular	25 ± 8 nm		25	5 days	1×10^{-3}			Du et al. (2007)
14	*Escherichia coli*	Spherical, irregular	Extracellular and intracellular	<10 nm (intracellular), 20–50 nm (extracellular)	7	25	2 h	2×10^{-3}	0.5 mg dry weight/mL	Live bacteria (H_2 and lactate electron donor)	Deplanche and Macaskie (2007)
	Desulfovibrio desulfuricans ATCC 29577				7	25	2 h	2×10^{-3}	0.5 mg dry weight/mL	Live bacteria + copper	
				Negligible precipitation	7	25	2 h			Dead cells (heat-killed)	
				No precipitation	7					Abiotic	
				Red suspension	2	25	2 h	2×10^{-3}	0.5 mg dry weight/mL	Determine the effect of pH	
				Purple suspension	6						
				Dark blue suspension	9						
15	*Rhodopseudomonas capsulata*	Plate, spherical, triangular, hexagonal	Extracellular	10–50 nm (spherical); 50–400 nm (triangular and plate)	4	25	2 days	1×10^{-3}	1 g wet weight/20 mL		He et al. (2007)
					5	25	2 days				
					6	25	2 days				
		Spherical	Extracellular	10–20 nm	7	25	2 days				

(*continued*)

Table 3.2 (continued)

No	Bacteria name	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
16	*Pseudomonas aeruginosa* with fluorescent pigment pyoverdin	Spherical	Extracellular	15 ± 5 nm		37	1 day	1×10^{-3}		Live bacteria	Husseiny et al. (2007)
	Pseudomonas aeruginosa with blue pigment pyocyanin			25 ± 15 nm							
	Pseudomonas aeruginosa ATCC 90271			40 ± 10 nm							
				No precipitation		37	1 day	1×10^{-3}		Abiotic	
17	*Rhodobacter capsulatus* (purple non-sulfur bacteria)	Spherical, irregular	Extracellular and intracellular			25	20 h	2×10^{-4}	1×10^{9}	Live bacteria with N_2 gas and lactate	Feng et al. (2008)
				10 nm				4×10^{-4}			
				20–48 nm				8×10^{-4}			
18	*Bacillus licheniformis*	Cubes	Extracellular	10–100 nm		25	2 days	1×10^{-3}	1 g wet weight/ 100 mL	Live bacteria	Kalishwaralal et al. (2009)
19	*Bacillus megatherium* D01	Spherical, irregular, hexagonal, triangular, anisotrophic	Extracellular	<2.5 nm (10–30 min); 1–8 nm (1 h); 1–30 nm (>6 h)	3.2	26	9 h	0.5×10^{-6}	100 mg dry weight/ 100 mL	Live bacteria	Wen et al. (2009)
		Spherical	Extracellular	1–3 nm	3.2	26	9 h	0.5×10^{-6}	100 mg dry weight/ 100 mL	Live bacteria and dodecanethiol as the capping ligand	
		Spherical	Extracellular	1.5–2.5 nm; average 1.9 ± 0.8 nm	3.2	26	4 h	0.5×10^{-6}	1 g dry weight/L	Dried biomass and dodecanethiol as the capping ligand	
20	*Stenotrophomonas maltophilia*	Spherical, irregular	Intracellular	40 nm		25	8 h	1×10^{-3}			Nangia et al. (2009)

Table 3.3 A summary of cyanobacterial interactions with a gold(III)–chloride complex

No	Bacteria name	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
1	*Nostoc punctiforme* *Microcystis aeruginosa* *Spirulina platensis* *Phormidium inundatum* *Anabaena cylindrica* *Anacystis nidulans* *Synechococcus elongatus* *Synechococus parvulus* *Phormidium boryanum*					25	0.5 h	3×10^{-5}	0.1–0.12 mg/mL dry cell weight	Live cyanobacteria	Karamushka et al. (1991a, b)
2	*Plectonema terebrans*		Extracellular and intracellular			25	14 days	1×10^{-2}		Live cyanobacteria	Dyer et al. (1994)
			Extracellular and intracellular			25	14 days	1×10^{-2}		Dead cells (autoclaved)	
3	*Plectonema boryanum* UTEX 485	Irregular, spherical, octahedral	Extracellular and intracellular	<10 nm (intracellular); 1 μm (extracellular)	1.6–2.2	25	28 days	(2–2.8) $\times 10^{-3}$	8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	Lengke et al. (2006a)
			Extracellular and intracellular	<10 nm (intracellular);	1.6–2.2	60	28 days	(2–2.8) $\times 10^{-3}$			

(*continued*)

Table 3.3 (continued)

No	Bacteria name	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Bacterial population (cells/mL)	Experimental condition	References
		Irregular, spherical, octahedral		1 μm (extracellular)					8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	
		Irregular, spherical, octahedral	Extracellular and intracellular	<10 nm (intracellular); 1–10 μm (extracellular)	1.6–2.2	100	28 days	(2–2.8) $\times 10^{-3}$	8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	
		Irregular, spherical, octahedral	Extracellular and intracellular	<10 nm (intracellular); 1–10 μm (extracellular)	1.6–2.2	200	1 day	(2–2.8) $\times 10^{-3}$	8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	
				No precipitation		25	28 days	(2–2.8) $\times 10^{-3}$		Abiotic	
				No precipitation		60	28 days	(2–2.8) $\times 10^{-3}$		Abiotic	
		Irregular		25 nm		100	28 days	(2–2.8) $\times 10^{-3}$		Abiotic	
		Irregular		25 nm		200	1 day	(2–2.8) $\times 10^{-3}$		Abiotic	
4	*Plectonema boryanum* UTEX 485	Irregular, spherical, octahedral	Extracellular and intracellular	<10 nm (intracellular); 1.5 μm (extracellular)	1.6–2.2	25	28 days	2×10^{-3}	8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	Lengke et al. (2006b)
		Irregular, spherical, octahedral		<10 nm (intracellular); 1.5 μm (extracellular)	1.6–1.9	60	28 days	2×10^{-3}	8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	
		Irregular, spherical, octahedral		<10 nm (intracellular); 1–10 μm (extracellular)	1.6–1.9	100	28 days	2×10^{-3}	8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	
		Irregular, spherical, octahedral		<10 nm (intracellular); 1–10 μm (extracellular)	1.9–2.2	200	1 day	2×10^{-3}	8 mg/10 mL dry weight	Cyanobacteria stationary growth phase	

		Irregular, spherical, octahedral	Extracellular and intracellular		2.2	25	28 days	2×10^{-3}		Dead cells (autoclaved)	
			No precipitation		2.2	25	28 days	2×10^{-3}		Abiotic	
			No precipitation		2.2	60	28 days	2×10^{-3}		Abiotic	
		Cubic	Precipitation	25 nm	2.2–1.9	100	28 days	2×10^{-3}		Abiotic	
		Cubic	Precipitation	25 nm	2.2–1.6	200	1 day	2×10^{-3}		Abiotic	
5	*Plectonema boryanum* UTEX 485	Irregular, spherical, octahedral	Extracellular and intracellular	<20 nm to 6 μm	1.9–2.2	25	1 day	(0.8–7.6) $\times 10^{-3}$	20 mg/mL dry weight	Cyanobacteria stationary growth phase	Lengke et al. (2006c)
6	*Plectonema boryanum* UTEX 485	Irregular, octahedral	Extracellular and intracellular	<10 nm to 6 μm	1.9	25	2 days	7.6×10^{-3}	20 mg/mL dry weight	Cyanobacteria stationary growth phase	Lengke et al. (2007)
		Irregular, octahedral	Extracellular and intracellular	<10 nm to 6 μm	1.9	60	2 days	7.6×10^{-3}	20 mg/mL dry weight	Cyanobacteria stationary growth phase	
		Irregular, octahedral	Extracellular and intracellular	<10 nm to 6 μm	1.9	80	1 day	7.6×10^{-3}	20 mg/mL dry weight	Cyanobacteria stationary growth phase	
				No precipitation	1.9	25	2 days	7.6×10^{-3}		Abiotic	
				No precipitation	1.9	60	2 days	7.6×10^{-3}		Abiotic	
				No precipitation	1.9	80	1 day	7.6×10^{-3}		Abiotic	

Table 3.4 A summary of algae interactions with a gold(III)–chloride complex

No	Algae	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Algae concentration	Experimental condition	References
1	*Chlorella vulgaris* biomass				2–7	25	2 h	1×10^{-4} (equimolar of Au^{3+}, Hg^{2+}, Pb^{2+}, Al^{3+}, Zn^{2+}, and Cu^{2+})		Batch experiment with dead cells (lyophilized)	Darnall et al. (1986)
					2–6	25		1×10^{-4} (equimolar of Au^{3+}, Hg^{2+}, Pb^{2+}, Al^{3+}, Zn^{2+}, and Cu^{2+})		Column experiment with dead cells (lyophilized) and polyacrylamide matrix	
2	*Chlorella vulgaris* biomass	Tetrahedral crystals, decahedral, icosahedral structures	Extracellular and intracellular	few nm		25	0.25 h	$(0.1–0.8) \times 10^{-3}$	2 mg/mL	Dead cells (lyophilized)	Hosea et al. (1986)
3	*Chlorella vulgaris* biomass				2–3	25	1 h	1×10^{-4}	5 mg/mL	Dead cells	Greene et al. (1986)
					1–8	25	1 h	1×10^{-4}	5 mg/mL	Dead cells	
4	*Chlorella vulgaris* biomass				3	25	0.5 h			Dead cells (lyophilized)	Watkins et al. (1987)
5	*Sargassum natans* biomass *Sargassum fluitans* biomass *Macrocystis pyrifera* biomass	Spherical, irregular	Extracellular		1–6.3	4–60	0.5–4 h	$0.05–5 \times 10^{-3}$		Dead cells	Kuyucak and Volesky (1989a, b)

	Undaria sp. biomass *Laminaria sp.* biomass *Ascophyllum nodosum* biomass *Cosium taylori* biomass *Halimeda opuntia* biomass *Chondrus crispus* biomass *Palmaria palmata* biomass *Porphyra tenera* biomass						
6	*Cyanidium caldarium* biomass *Eisenia bicyclis* biomass *Laminaria japonica* biomass *Spirulina platensis* biomass *Chlorella pyrenoidosa* biomass	5	25	2 days	4.06 $\times 10^{-6}$ and 6.6 $\times 10^{-4}$	Dead cells	Gardea-Torresdey et al. (1990)

(*continued*)

Table 3.4 (continued)

No	Algae	Shape	Extracellular/ intracellular	Size	pH	Temperature (°C)	Period	Initial gold concentrations (mol/L)	Algae concentration	Experimental condition	References
7	*Chlorella vulgaris* YA-1-1				4–10	25	up to 1 h	3×10^{-5}	0.02–0.08 mg/mL dry weight	Live algae	Karamushka et al. (1991a)
8	*Chlorella vulgaris* LARG-1 *Chlorella vulgaris* LARG-3 *Chlorella vulgaris* N 875 *Chlorella vulgaris* YA-1-1 *Scenedesmus obliquus* *Porphyridium sordidum* *Porphyridium cruentum* *Porphyridium purpureum*				4–10	25	up to 1 h	3×10^{-5}	0.02–0.08 mg/mL dry weight	Live algae	Karamushka et al. (1991b)
9	*Chlorella vulgaris*							0.05 or 0.1×10^{-3}		Live algae, and different treatment applied	Ting et al. (1995)
10	Dealginated seaweed waste	Hexagonal, tetrahedral, rod, irregular, docahedral	Extracellular	20 nm to 5 μm	2–10	25	1 day	5×10^{-6} to 3.8×10^{-3}	3 g/L dry weight	Dead cells	Romero-Gonzãlez et al. (2003)

11	*Saccharomyces cerevisiae* biomass		Extracellular		3	20–60	1 h	5×10^{-4}	2.5 mg/mL dry weight	Dead cells	Lin et al. (2005)
12	*Sargassum wightii* biomass	Spherical	Extracellular	8–12 nm			15 h	1×10^{-3}	0.1 g/L dry weight	Dead cells	Singaravelu et al. (2007)
13	*Fucus vesiculosus* biomass	Irregular, spherical	Extracellular		2–11	23	up to 24 h	5×10^{-4}	1 g/L dry weight	Dead cells	Mata et al. (2009)

The interaction of *Pseudomonas aeruginosa* PAO1 biofilm and a gold(III)–chloride complex resulted in the formation of both extracellular and intracellular gold (Karthikeyan and Beveridge 2002). Most gold particles were precipitated at the cell surfaces with lesser amounts inside the cells and little throughout the exopolymeric substances (EPS). Nair and Pradeep (2002) used *Lactobacillus* sp. to assist the precipitation of gold, silver, and gold–silver alloy. Gold particles were precipitated both within and outside the cells in the range of 20–50 nm and >100 nm forming spherical, triangular, and hexagonal shapes. In the system containing both silver and gold, gold–silver alloy precipitated inside the bacterial cells, forming 100–300 nm crystals within 3 days. Nakajima (2003) and Tsuruta (2004) conducted gold biosorption to determine maximum gold accumulation using 8 and 25 bacterial species, respectively. However, the size and shape of gold accumulation were not described in their studies. *Escherichia coli* and *Pseudomonas maltophilia* have extremely high ability to accumulate gold from a gold(III)–chloride solution at pH 3 and 30°C (Nakajima 2003). Tsuruta (2004) found that some gram-negative bacterial species (e.g., *Acinetobacter calcoaceticus*, *Erwinia herbicola*, *Pseudomonas aeruginosa*, and *Pseudomonas maltophilia*) have high ability to sorb gold at pH 3 and 25°C. Uncultured magnetotactic cocci bacteria, collected from Itaipu lagoon, Rio de Janeiro, Brazil were able to precipitate gold in the capsule and granules (Keim and Farina 2005). 16S ribosomal DNA clones from bacterial biofilms of the secondary gold grains from two sites in Australia (Tomakin Park Gold Mine, New South Wales and the Hit and Miss Gold Mine, Queensland) displayed 99% similarity to *Ralstonia metallidurans* (Reith et al. 2006). The laboratory experiments using the same bacteria confirmed that elemental gold was precipitated during the interaction with a gold(III)–chloride solution with both viable and dead cells. Gericke and Pinches (2006a, b) conducted laboratory experiments using three bacterial species (*Pseudomonas stutzeri* NCIMB 13420, *Bacillus subtilis* DSM 10, and *Pseudomonas putida* DSM 291) to determine the effect of pH (3–9), temperature (25–50°C), and gold concentrations (1.3–13 mol/L) on the size and shape of gold particles. In all cases, gold was precipitated uniformly inside the cells as spherical shapes (<10 nm) at all pH values, but larger particles with irregular, undefined shapes formed at pH 7 and 9. The size and rate of gold precipitation increased with increasing temperature and gold concentrations. Konishi et al. (2006) investigated the reduction and precipitation of gold using *Shewanella algae* ATCC 51181. The results showed that elemental gold was only formed in the presence of bacteria with H_2 electron donor, forming 10–20 nm irregular shape. The biosynthesis of gold nanoparticles was investigated using *Escherichia coli* DH5α by Du et al. (2007). The gold nanoparticles formed on the bacterial surfaces, mostly as spherical with triangular and quasi-hexagonal shapes. Deplanche and Macaskie (2007) achieved gold precipitation intracellularly (<10 nm) and extracellularly (20–50 nm) using both *Escherichia coli* and *Desulfovibrio desulfuricans* with H_2 as the electron donor. Gold particles were not precipitated in the abiotic conditions or the presence of heat-killed cells, and the presence of copper in solution inhibited gold precipitation. At pH 2, red suspension was observed, indicating the formation of smaller gold particles, and at pH 9, dark blue suspension was formed, presumably

containing larger gold particles. *Rhodopseudomonas capsulata* was able to precipitate gold from a gold(III)–chloride solution at pH 4–7, forming spherical, plate, triangular, and hexagonal gold with size ranging from 10 to 400 nm (He et al. 2007). Biosynthesis of gold nanoparticles using *Pseudomonas aeruginosa* was achieved and formed extracellular spherical gold with size ranging from 15 to 40 nm (Husseiny et al. 2007). Feng et al. (2008) discovered that *Rhodobacter capsulatus* were able to precipitate gold nanoparticles within and outside the bacterial cells, forming spherical and irregular gold with average size ranging from 10 to 48 nm. *Bacillus licheniformis* precipitated gold nanocubes (10–100 nm) within 2 days at 25°C (Kalishwaralal et al. 2009). Monodispersed gold nanoparticles capped with dodecanethiol were biosynthesized extracellularly by *Bacillus megatherium* D01 at 26°C (Wen et al. 2009). The presence of thiol capping ligand induced the formation of spherical gold nanoparticles with size <2.5 nm. Nangia et al. (2009) reported the biosynthesis of gold nanoparticles by *Stenotrophomonas maltophilia* forming ~40 nm spherical and irregular shapes at 25°C for 8 h.

In the cyanobacterial system, Karamushka et al. (1991a, b) investigated gold biosorption using nine different species, and all of them were able to accumulate gold. Dyer et al. (1994) found that live and dead cells of *Plectonema terebrans* were able to precipitate and accumulate elemental gold. The studies by Karamushka et al. (1991a, b) and Dyer et al. (1994) did not describe the size and shape of the gold formed. *Plectonema boryanum* UTEX 485, a filamentous cyanobacterium, had been reacted with a gold(III)–chloride complex (up to 2.8 mmol/L gold) at 25–100°C for up to ~1 month and at 200°C for 1 day (Lengke et al. 2006a, b, c, 2007). On the addition of a gold(III)–chloride solution to the cyanobacteria, all cyanobacteria were killed within several minutes at all temperatures investigated. A significant increase in the precipitation of gold occurred with increasing temperature from 25 to 60–200°C. Gold nanoparticles were precipitated inside the cells (<10 nm) and also formed octahedral shape in the bulk solution from 1 μm at 25°C to 10 μm at 100°C. For abiotic experiments using a gold(III)–chloride solution, total soluble gold was stable in solution at 25–80°C, but it decreased with time at 100 and 200°C, forming irregular or cubic gold (~25 nm).

In the algae system, most of the published literature focused on the biosorption and biorecovery of gold from solution (e.g., Darnall et al. 1986; Hosea et al. 1986; Watkins et al. 1987); therefore, the size and shape of gold particles were not described in their published papers. Darnall et al. (1986) conducted the biosorption and biorecovery experiments of Au, Hg, Pb, Al, Zn, and Cu on *Chlorella vulgaris* biomass at pH 2–7. Between pH 5 and 7, these metals bound strongly to the cell surfaces, but most of these algae-bound metals were desorbed back into solution by lowering the pH to 2, except for Au, Hg, and Ag. Hosea et al. (1986) also conducted the biosorption and biorecovery experiments of gold using *Chlorella vulgaris* biomass. Elemental gold was precipitated inside and outside the cells forming nanometer-scale of irregular and spherical gold. Biosorption of gold by *Chlorella vulgaris* biomass reached maximum binding at pH 3 (Greene et al. 1986). Inhibition and reversal of gold binding by strong ligands were pH dependent, with the order of effectiveness: thiourea > cyanide > mercaptoethanol > bromide. Watkins et al. (1987)

confirmed that *Chlorella vulgaris* biomass has high affinity for a gold(III)–chloride solution. Eleven species of brown, green, and red algae were tested for their ability to sorb gold from a gold(III)–chloride solution, and the maximum gold sorption was shown by *Sargassum natans* at pH 2.5 (Kuyucak and Volesky 1989a, b). The rates of gold biosorption increased at higher temperature from 4 to 60°C. The presence of other cations such as U, Fe, Zn, Ni, Ca, Ag, and Co did not affect the gold biosorption of *Sargassum natans* biomass at pH 2.5; however, anions such as sulfate, nitrate, and phosphate affected the biosorption ability. Gardea-Torresdey et al. (1990) showed that the gold binding capacity of five alga biomass increased as the algal carboxyl groups were esterified. Karamushka et al. (1991a, b) investigated gold biosorption using nine different species of algae and all of them were able to accumulate gold. The uptake of gold (III)–chloride solution was enhanced by several treatments such as acid, alkali, heat, and formaldehyde over the live/pristine cells (Ting et al. 1995). Gold precipitation by dealginated seaweed waste has been studied to elucidate the mechanisms of gold uptake from solution at pH 2–9 by Romero-Gonzãlez et al. (2003). In this study, gold was precipitated as hexagonal, tetrahedral, rod, irregular, and decahedral shapes with size ranging from ~20 nm to 5 μm. Lin et al. (2005) conducted a study of gold biosorption by *Saccharomyces cerevisiae* and determined that the gold bound on the cell wall had been reduced to elemental gold. Biosynthesis of gold nanoparticles was performed using *Sargassum wightii* biomass, collected from Mandapam Camp, Tamil Nadu, India (Singaravelu et al. 2007). The gold particles were precipitated as monodisperse spherical gold with size ranging from 8 to 12 nm. Mata et al. (2009) investigated gold biosorption and bioreduction using *Fucus vesiculosus* and reported that the maximum gold uptake occurred between pH 4 and 9, with optimum uptake at pH 7. The precipitated gold formed irregular or spherical shapes.

3.4 Mechanisms of Biosynthesis of Gold Nanoparticles

The mechanisms for the biosynthesis of gold particles by bacteria, cyanobacteria, and algae from two gold complexes have been tested using several methods including laboratory-based experiments, microscopy technique [transmission electron microcopy (TEM) or scanning electron microscopy (SEM)], Fourier transform infrared spectroscopy (FT-IR), and/or X-ray absorption spectroscopy (XAS), as discussed below.

3.4.1 Gold(I)–Thiosulfate Complex

The mechanisms of gold precipitation from a gold(I)–thiosulfate complex by *Acidithiobacillus thiooxidans*, SRB, and *Plectonema boryanum* UTEX 485 are summarized here. Gold(I)–thiosulfate was entered into the cell of *Acidithiobacillus*

thiooxidans as part of a metabolic process (Lengke and Southam 2005). This gold complex was initially decomplexed to Au(I) and thiosulfate ($S_2O_3^{2-}$) ions. Thiosulfate was used as energy source and Au(I) was presumably reduced to elemental gold within the bacterial cells. During the late stationary growth phase, the gold nanoparticles that were initially precipitated inside the cells were released from the cells, resulting in the formation of gold particles at the cell surface. Finally, the gold particles in the bulk solution were grown into micrometer-scale wire and octahedral gold.

The precipitation of gold(I)–thiosulfate complex by SRB was caused by three possible mechanisms: (1) iron sulfide formation, (2) localized reducing conditions, and (3) a metabolic process (Lengke and Southam 2006, 2007). In the iron system, the formation of iron sulfide generated by SRB could have adsorbed a gold(I)–thiosulfate complex onto freshly forming surfaces, leading to the precipitation of elemental gold. The localized reducing conditions generated by SRB were associated with metabolism. Thiosulfate ion from a gold(I)–thiosulfate complex was initially reduced to hydrogen sulfide (HS^-), as the end product of metabolism. The release of hydrogen sulfide through the outer membrane pores decreased redox conditions around the cells and caused the precipitation of elemental gold. The precipitation of elemental gold by SRB through metabolic process was initiated when a gold(I)–thiosulfate entered the bacterial cells and was decomplexed to Au(I) and thiosulfate ($S_2O_3^{2-}$) ions. Thiosulfate was used as energy source and Au(I) was presumably reduced to elemental gold within the bacterial cells. During the late stationary growth phase or death phase, the gold nanoparticles that were initially precipitated inside the cells were released into the bulk solution and formed sub-octahedral to octahedral, sub-spherical to spherical aggregates resembling framboids, and ultimately millimeter-thick gold foil at longer experimental duration.

In the cyanobacterial system (*Plectonema boryanum* UTEX 485) with the addition of gold(I)–thiosulfate complex, gold was precipitated as thin nanoparticles associated with the surfaces of membrane vesicles at 25°C (Lengke et al. 2006a). *Plectonema boryanum* UTEX 485 exhibits the characteristics of gram-negative bacteria which can produce membrane vesicles. When the cyanobacteria interacted with relatively high concentrations of gold(I)–thiosulfate complex, the cells released membrane vesicle as a protective shield to prevent the uptake of gold (I)–thiosulfate from solutions and to keep gold(I)–thiosulfate away from sensitive cellular components. The interaction of gold(I)–thiosulfate complex with membrane vesicle caused the precipitation of elemental gold, possibly through the reaction with phosphorus, sulfur, or nitrogen ligands of outer membrane proteins, lipopolysaccharide, periplasmic proteins, phospholipids, DNA, and RNA. In the experiments at 60–200°C, gold nanoparticles were precipitated both intracellularly (<10 nm) and extracellularly (~10–25 nm), the latter with a distinct cubic shape and admixed with gold sulfide from 60 to 100°C. The stress on cyanobacteria caused by increasing temperature presumably decreased the cell sensitivity to receiving gold(I)–thiosulfate, and this gold complex was then reduced to gold sulfide and gold inside the cells. During the death of cyanobacteria, nanoparticles of gold sulfide and

gold produced inside the cells were released through the cell membrane into solutions, as indicated by the precipitation of gold nanoparticles around the cells.

3.4.2 Gold(III)–Chloride Complex

In the bacterial system using a gold(III)–chloride solution, gold was precipitated intracellularly (<10 nm) and extracellularly (~1 to 10 μm) (e.g., Southam and Beveridge 1994, 1996; Karthikeyan and Beveridge 2002; Nair and Pradeep 2002; Reith et al. 2006; Gericke and Pinches 2006a, b; Deplanche and Macaskie 2007; Feng et al. 2008). The presence of intracellular gold nanoparticles suggests that gold entered the cells as a gold(III)–chloride complex and was then reduced to elemental gold. These bacteria were killed and the resulting release of organics caused further precipitation of gold (Southam and Beveridge 1996). A role of sulfur and phosphorus has been linked to the precipitation of octahedral gold at acidic pH by *Bacillus subtilis* 168 (Southam and Beveridge 1996). The precipitation of gold by magnetotactic cocci bacteria occurred in the Phosphorus–Sulfur–Iron (PSFe) granules which suggests the association of gold with these elements (Keim and Farina 2005). The reduction and precipitation of gold by dissimilatory iron(III) reducing bacteria were catalyzed by H_2 electron donor and not by lactate, indicating the involvement of hydrogenase (Kashefi et al. 2001). Deplanche and Macaskie (2007) further investigated the hydrogenase enzyme on the role of gold precipitation by *Escherichia coli* and *Desulfovibrio desulfuricans* ATCC 29577. They suggested that the periplasmic hydrogenases were involved in the gold precipitation but were not essential; however, the cytoplasmic hydrogenases and/or cytochrome c3 could be a complementary mechanism of gold reduction.

In the cyanobacterial system, the mechanisms of gold reduction by *Plectonema boryanum* UTEX 485 from gold(III)–chloride solutions have been studied at several gold concentrations (0.8–7.6 mmol/L) and at 25–80°C, using both fixed-time laboratory and real-time synchrotron radiation XAS experiments (Lengke et al. 2006c, 2007). The XAS results showed that Au(III) was reduced to Au(I) in a very fast reaction (within minutes), and Au(I) was immediately coordinated with sulfur atoms from cyanobacteria forming gold(I)–sulfide for all gold concentrations and temperatures. Within the cyanobacteria, sulfur presumably was present as cysteine or methionine groups of the outer membrane or periplasmic proteins. Sulfur from the cysteine or methionine groups was released into the bulk solutions through the outer membrane and immediately bound with the reduced gold forming gold(I)–sulfide on the cells or at the cell walls. The fast reduction of Au(III) to Au(I) and the fast release of organic sulfur from the dying and dead cyanobacteria at the higher temperatures investigated (60 and 80°C) resulted in the presence of gold (I)–sulfide as a major phase at the initial stage in the reaction. The reduction of gold (I)–sulfide to elemental gold was slower at 25°C than at 60 and 80°C. The cysteine or methionine within the outer membrane or periplasmic proteins also contained carbon and nitrogen, and this may explain indirect relationship between nitrogen

and gold. The steps of mechanism of gold reduction and precipitation by cyanobacteria are deduced:

$$\text{gold(III)} - \text{chloride}(AuCl_4^-) \rightarrow \text{gold(I)} - \text{sulfide}(Au_2S) \rightarrow \text{gold(Au)} \quad (3.1)$$

In the algae system, the mechanisms of gold reduction by *Chlorella vulgaris* biomass from gold(III)–chloride solutions have been studied using XAS (Watkins et al. 1987). The XAS results showed that Au(III) was partly reduced to Au(I) and Au(I) was coordinated with sulfur atoms from free sulfhydryl residues and also to a light-atom element, probably nitrogen. Kuyucak and Volesky (1989b) showed that elemental gold was mostly precipitated on the cell wall of *Sargassum natans* biomass and suggested that the carbonyl (C ≡ O) groups of the cellulosic materials were the main functional group in the gold binding with N-containing groups involved in a lesser degree. Lin et al. (2005) suggested that the hydroxyl group of saccharides, the carboxylate anion of amino-acid residues, from the peptidoglycan layer on the cell wall appeared to be the sites for gold binding. However, the gold uptake by algal biomass increased after esterification, suggesting that carboxyl groups played a minor role in gold binding (Gardea-Torresdey et al. 1990). Romero-Gonzãlez et al. (2003) studied the mechanisms of gold biosorption by dealginated seaweed biomass using FT-IR and XAS. Although FT-IR showed the presence of carboxylate groups on the surface of the biomass, XAS showed that the reduction of gold species occurred on the biomass surfaces to form gold nanoparticles and was followed by retention of Au(I) at the sulfur containing sites. Therefore, the steps of mechanism of gold reduction and precipitation by algae are similar to cyanobacteria (Reaction 3.1).

3.5 Application of Gold Nanoparticles

The properties of gold nanoparticles remarkably differ from the bulk gold because of quantum size confinement imposed by nano-size regimen (Link et al. 1999; Reddy 2006). The electronic, magnetic, and catalytic properties of gold nanoparticles depend mainly on their size and shape (Link et al. 1999). For example, spherical gold nanoparticles show a strong absorption band in the visible region of electromagnetic field (~520 nm) but is absent for very small particles (≤2 nm) as well as in the bulk gold. With a variety of unique properties, when gold nanoparticles are manipulated effectively, it can be applied to many different applications across the field of biology and medicine, environment, and technology (e.g., Oldenburg et al. 1998; Vieira and Volesky 2000; Salata 2004; Sperling et al. 2008; Chen et al. 2008; Cai et al. 2008).

Ancient cultures in Egypt, India, and China have used gold to treat diseases such as smallpox, skin ulcers, syphilis, and measles (Huaizhi and Yuantao 2001; Richards et al. 2002; Gielen and Tiekink 2005; Kumar 2007; Chen et al. 2008). Gold is currently used for medical devices including pacemakers

and gold plated stents (Edelman et al. 2001; Svedman et al. 2005), for the management of heart disease, middle ear gold implants, and gold alloys in dental restoration (Svedman et al. 2006). Organogold compounds are widely used for the treatment of rheumatoid arthritis but at high doses, side effects such as proteinuria and skin reactions have been observed (Sun et al. 2007; Chen et al. 2008).

3.5.1 Biology and Medicine

Gold nanoparticles have been primarily used for labeling and bioimaging applications (Sperling et al. 2008; Chen et al. 2008). The gold nanoparticles are directed and enriched at the region of interest, providing contrast for observation and visualization. With the characteristic of strongly absorption and scattering visible light, the light energy excites the free electrons in the gold nanoparticles to a collective oscillation, known as surface plasmon. The excited electron gas relaxes thermally by transferring the energy to the gold lattice, and finally the light absorption leads to heating of the gold nanoparticles. The interaction of gold nanoparticles with light can be used for the visualization of particles using optical microscopy, fluorescence microscopy, photothermal, and photoacoustic imaging. In addition, the interaction of gold nanoparticles with both electron waves and X-rays can also be used for visualization, e.g., using TEM. Other noninvasive diagnostic tools such as magnetic resonance imaging (MRI) and X-ray computed tomography (X-ray CT) have also utilized gold nanoparticles as contrasting agent due to the ease of surface modification and higher X-ray absorption coefficient, respectively (Debouttiére et al. 2006; Kim et al. 2007).

Gold nanoparticles have been used for a long time for delivery of molecules into cells (Sperling et al. 2008; Chen et al. 2008). The molecules are adsorbed on the surface of gold nanoparticles and then are introduced into the cells using gene guns or particle ingestion. Inside the cells, these molecules will eventually detach themselves from the gold nanoparticles. Gene guns have been used for the introduction of plasmic DNA into plant cells and animal cells, which result in expression of the corresponding proteins inside the cells.

Gold nanoparticles can also be used as a heat source (Sperling et al. 2008; Cai et al. 2008). When gold particles absorb light, the free electrons in the gold particles are excited. Excitation at the plasmon resonance frequency causes a collective oscillation of the free electrons. During the interaction between the electrons and the crystal lattice of the gold nanoparticles, the electrons relax and the thermal energy is transferred to the lattice. The heat from the gold particles can be used for manipulating the surrounding tissues, e.g., hyperthermia, optically triggered opening of bonds, and opening of containers. Cells are sensitive to small increases in temperature and an increase of a few degrees can lead to cell death. If gold nanoparticles can be directed to the localized cancer tissue and is then heated

by external stimuli, the cells in the vicinity of the gold particles can be selectively killed. Photo-induced heating of gold nanoparticles can also be used for the opening of chemical bonds (e.g., melting double stranded DNA and disassembling protein aggregates). Finally, photo-induced heating of gold nanoparticles can also be used for remotely controlled release of cargo molecules from capsules inside living cells. A newly functionalized gold nanoparticle (dendrimers) has been designed for not only targeting and killing tumors but also to fight cancer (Nam et al. 2009; Escosura-Muńiz et al. 2009). Gold nanoparticle is engineered not only to identify, target, and kill tumors but also to carry the additional drug to slow down the growth of cancer cells or kill the cancer cells. Dendrimers acts as an arm to the gold nanoparticles so that different molecules are attached to the arms. Once the cancer cells are surrounded by gold nanoparticles, lasers or infrared light heats the gold particles and the dendrimers release the various molecules to kill the tumors.

Gold nanoparticles can also be used for active sensor applications (Sperling et al. 2008). The objectives for sensor applications are to determine the presence of analyte and to provide its concentration. The plasmon resonance frequency is a reliable feature of gold nanoparticles that can be used for sensing. The binding of molecules to the particle surface can change the plasmon frequency directly. On the other hand, the plasmon resonance frequency is changed when the average distance among gold nanoparticles is reduced by forming small aggregates. The effect of plasmon coupling can be used for colorimetric detection of the analyte, known as a gold-based sensor. In the presence of target sequence, the gold nanoparticles bind to the target by hybridization of complementary strands of DNA which lead to a change in the plasmon resonance and the solution appears to be a violet/blue color. When the sample is heated, single sequence mismatches result in a different melting temperature of the aggregates and cause color change. The same concept applied for DNA assays can also be used for RNA- and peptide-based sequences and enzyme. The color changes can also be used to measure lengths, known as “rulers on the nanometer scale”. The fluorescence quenching occurs when many fluorophores are in close proximity to gold surfaces and this effect can be used for several sensor strategies. Raman scattering is enhanced if the analyte is close to a gold surface, called as surface-enhanced Raman scattering. Gold nanoparticles modified with Raman-active reporter molecules have been used for the detection of DNA (Krug et al. 1999), protein (Ni et al. 1999), and two-photon excitation (Kneipp et al. 2006). Gold nanoparticles can also be used for the transfer of electrons in redox reactions (Willner et al. 2006). The enzyme is conjugated to the surface of the gold particles and is immobilized on the surface of an electrode (Xiao et al. 2003). An electrode covered with a layer of gold nanoparticles has a much higher surface roughness and larger surface area which lead to higher currents. In addition, due to the presence of small gold particles, the contact of the gold nanoparticles with the enzyme can be more intimate, i.e., located in a close proximity to the reactive center, which can facilitate the electron transport.

3.5.2 Environment

Gold nanoparticle based technologies are currently being developed for the environmental applications to pollution control and water purification (Das et al. 2009). Bimetallic gold–palladium nanoparticles provide an active catalyst to degrade trichloroethene (TCE), one of the major pollutants in groundwater to a non-toxic form (Wong et al. 2009). Palladium catalyst has been shown to degrade TCE in water but the cost is significant to be widely adopted. Although gold is more expensive than palladium, a combination of gold–palladium nanoparticles is much more reactive to remove TCE, resulting in more cost-effective application. Gold nanoparticles incorporated in a water purification device can effectively capture and remove halocarbon-based pesticides from drinking water (Das et al. 2009) and can also enhance the oxidation of mercury generated from coal power plants (Pradeep and Anshup 2009). A mixture of gold nanoparticles as well as the traditional platinum and palladium has been developed for automotive catalysts in diesel engines to increase hydrocarbon oxidation activity by U.S. Nanostellar (http://www.nanostellar.com). The use of gold nanoparticles as a catalyst has a major role to play in green chemistry (Dahl et al. 2007; Herzing et al. 2008). Most industrial oxidation processes tend to use chlorine or organic peroxides which result in large amounts of chloride salts and chlorinated organic byproducts. Gold nanoparticles supported on carbon active molecular oxygen in air are able to convert alkenes to partial oxidation products such as epoxides at atmospheric pressure and at 60–80°C (Hughes et al. 2005). Gold nanoparticles have been developed for selective oxidation of the biomass-derived chemicals, furfural and hydroxymethylfurfural, to form methyl esters. These chemicals are used for flavor and fragrance applications, in plastics and industrial solvents (Taarning et al. 2008).

3.5.3 Technology

Gold nanoparticles have been designed to improve computer memory (Lee et al. 2007). A three-dimensional computer memory device composed of layers of gold nanoparticles has been developed to increase the memory capacity of a single chip. The device is built on a base of silicon that is coated with hafnium oxide. Then, alternating layers of 16-nm sized gold nanoparticles and insulating polymers are formed on top. Another development of computer memory using gold nanoparticles is an organic nonvolatile bistable memory, which is a mixture of plastic and gold (Lin et al. 2007). Organic nonvolatile memories have been developed using plastic and other carbon-based chemicals but the organic memory devices tend to break down in air and under the stress of many read–write cycles. Therefore, a new memory consisting of gold nanoparticles mixed into a polymer and sandwiched between two aluminum electrodes is considered essential to be implemented in flexible electronics, such as radio-frequency identification, smart cards, e-paper, and flexible displays.

3.6 Future Directions

During the past two decades, the interaction of a variety of bacteria and two gold solutions [gold(I)–thiosulfate and gold(III)–chloride] have been well investigated, although the focus of these studies is not necessarily on the biosynthesis of gold nanoparticles. Living and dead bacteria/cyanobacteria/algae have huge potential for the production of gold nanoparticles; however, the previous studies are still largely in the discovery phase. Given the anticipated wide application of gold nanoparticles for commercial applications, consideration of the material design, processes, and applications using bacteria/cyanobacteria/algae that minimize hazard and waste will be essential for the transition of nanoscience discoveries to commercial products of nanotechnology. Future work should implement systematic experiments which include development of gold nanoparticles of well-defined size and shape. Better understanding of the mechanisms of gold biosynthesis will enable us to achieve better control over size, shape, and monodispersivity which will lead to the development of high precision in the production level and the application of nanoparticles for commercial scale applications.

3.7 Conclusions

We provide a comprehensive review of research conducted on the biosynthesis of gold nanoparticles by bacteria, cyanobacteria, and algae using gold(I)–thiosulfate [$Au(S_2O_3)_2^{3-}$] and gold(III)–chloride [$AuCl_4^-$] complexes. In general, many bacteria, cyanobacteria, and algae have the ability to produce gold nanoparticles with properties similar to chemically synthesised materials. Intracellular synthesis of gold nanoparticles, as well as extracellular formation of nanoparticles in the presence of these microorganisms has been successfully demonstrated. The shape of gold particles precipitated by bacteria/cyanobacteria/algae includes spherical, oval, spongy clots, mushroom, irregular, triangular, tetragonal, hexagonal, octahedral, rod, cubic, docahedral, icosahedral, coil or wire, plate, and thin foil, with size ranging from 1 nm to several millimeters. The mechanisms of gold precipitation from a gold(I)–thiosulfate complex by *Acidithiobacillus thiooxidans* and SRB are directly or indirectly associated with metabolism. For the dissimilatory iron(III) reducing bacteria using gold(III)–chloride complex, the involvement of cytoplasmic hydrogenases and/or cytochrome c3 could be a complementary mechanism of gold reduction. For the cyanobacteria and algae using gold(III)–chloride complex, Au(III) was reduced to Au(I), and Au(I) was immediately coordinated with sulfur atoms from the cysteine or methionine groups, forming gold(I)–sulfide. The reduction of gold(I)–sulfide to elemental gold was a slower step mechanism than the formation of gold(I)–sulfide.

Previous work on the biosynthesis of gold nanoparticles is still largely in the discovery phase. Given the anticipated wide application of gold nanoparticles for

commercial applications, continuing work is recommended to focus on the mechanisms of the biosynthesis of gold nanoparticles and the development of gold nanoparticles of well-defined size and shape.

References

Ahmad A, Senapati S, Khan MI, Kumar R, Sastry M (2005) Extra-/intracellular biosynthesis of gold nanoparticles by alkalotolerant fungus, *Trichothecium* sp. J Biomed Nanotechnol 1 (1):47–53

Aylmore MG, Muir DM (2001) Thiosulfate leaching of gold – a review. Miner Eng 14(2):135–174

Brust M, Walker M, Bethell D, Schiffrin DJ and Whyman R (1994) Synthesis of thiol derivatised gold nanoparticles in a two-phase liquid/liquid system. Chem Commun: 801–802

Cai W, Gao T, Hong H, Sun J (2008) Applications of gold nanoparticles in cancer nanotechnology. Nanotechnol Sci Appl 1:17–32

Canizal G, Ascencio JA, Gardea-Torresday J, Jose-Yacaman M (2001) Multiple twinned gold nanorods grown by bio-reduction techniques. J Nanopart Res 3:475–481

Chen PC, Mwakwari SC, Oyelere AK (2008) Gold nanoparticles: from nanomedicine to nanosensing. Nanotechnol Sci Appl 1:45–66

Dahl JA, Maddux BLS, Hutchison JE (2007) Toward greener nanosynthesis. Chem Rev 107:2228–2269

Daniel M-C, Astruc D (2004) Gold nanoparticles: assembly, supramolecular chemistry, quantum size-related properties, and applications toward biology, catalysis and nanotechnology. Chem Rev 104:293–346

Darnall DW, Greene B, Henzl MT, Hosea JM, McPherson RA, Sneddon J, Alexander MD (1986) Selective recovery of gold and other metal ions from an algal biomass. Environ Sci Technol 20 (2):206–208

Das SK, Das AR, Guha AK (2009) Gold nanoparticles: microbial synthesis and application in water hygiene management. Langmuir 25(14):8192–8199

Debouttiére P-J, Roux S, Vocanson F, Billotey C, Beuf O, Favre-Réguillon A, Lin Y, Pellet-Rostaing S, Lamartine R, Perriat P, Tillement O (2006) Design of gold nanoparticles for magnetic resonance imaging. Adv Funct Mater 16(18):2330–2339

Deplanche K, Macaskie LE (2007) Biorecovery of gold by *Escherichia coli* and *Desulfovibrio desulfuricans*. Biotechnol Bioeng 99(5):1055–1064

Dermont G, Bergeron M, Mercier G, Richer-Lafléche M (2008) Metal-contaminated soils: remediation practices and treatment technologies. Pract Periodical Hazard Toxic Radioactive Waste Manage 12(3):188–209

Du L, Jiang H, Liu X, Wang E (2007) Biosynthesis of gold nanoparticles assisted by *Escherichia coli* DH5α and its application on direct electrochemistry of hemoglobin. Electrochem Commun 9:1165–1170

Dyer BD, Krumbein WE, Mossman DJ (1994) Accumulation of gold in the sheath of *Plectonema terebrans* (filamentous marine cyanobacteria). Geomicrobiol J 12:91–98

Edelman ER, Seifert P, Groothuis A, Morss A, Bornstein D, Rogers C (2001) Gold-coated NIR stents in porcine coronary arteries. Circulation 103:429–34

Ehrlich HL (2002) Geomicrobiology, 4th edn. New York, Marcel Dekker, p 800

Emery JF, Leddicotte GW (1961) The radiochemistry of gold. National Academy of Sciences - National Research Council, Washington DC, p 34

Escosura-Muñiz ADL, Sánchez-Espinel C, Díaz-Freitas B, González-Fernández A, Costa MM, Merkoci A (2009) Rapid identification and quantification of tumor cells using an electrocatalytic method based on gold nanoparticles. Anal Chem 81:10268–10274

Feng Y, Lin X, Wang Y, Wang Y, Hua J (2008) Diversity of aurum bioreduction by *Rhodobacter capsulatus*. Mater Lett 62:4299–4302

Gardea-Torresdey JL, Becker-Hapak MK, Hosea JM, Darnall DW (1990) Effect of chemical modification of algal carboxyl groups on metal ion binding. Environ Sci Technol 24(9):1372–1378
Gardea-Torresdey JL, Tiemann KJ, Gamez G, Dokken K, Tehuacanero S, Jose-Yacaman M (1999) Gold nanoparticles obtained by bio-precipitation from gold(III) solutions. J Nanoparticles Res 1:397–404
Gardea-Torresdey JL, Tiemann KJ, Gamez G, Dokken K, Cano-Aguilera I, Furenlid LR, Renner MW (2000) Reduction and accumulation of gold(III) by *Medicago sativa* alfalfa biomass: X-ray absorption spectroscopy, pH, and temperature dependence. Environ Sci Technol 34:4392–4396
Gardea-Torresdey JL, Parsons JG, Gomez E, Peralta-Videa J, Troini HE, Santiago P, Jose-Yacaman M (2002) Formation and growth of Au nanoparticles inside live alfalfa plants. Nano Lett 2(4):397–401
Gericke M, Pinches A (2006a) Microbial production of gold nanoparticles. Gold Bull 39(1):22–28
Gericke M, Pinches A (2006b) Biological synthesis of metal nanoparticles. Hydrometallurgy 83:132–140
Gielen M, Tiekink ERT (2005) Metallotherapeutic drugs and metal-based diagnostic agents. The use of metals in medicine. Wiley, Hoboken, New York
Greene B, Hosea M, McPherson R, Henzl M, Alexander MD, Darnall DW (1986) Interaction of gold(I) and gold(III) complexes with algal biomass. Environ Sci Technol 20(6):627–632
Handley DA (1989) Methods for synthesis of colloidal gold, Chap. 2. In: Hayat MA (ed) Colloidal gold: principles, methods and application, vol 1. Academic, San Diego, pp 13–33
He S, Guo Z, Zhang Y, Zhang S, Wang J, Gu N (2007) Biosynthesis of gold nanoparticles using the bacteria *Rhodopseudomonas capsulata*. Mater Lett 61:3984–3987
Heath GR (1981) Ferromanganese nodules of the deep sea. Economic Geology 75th Anniversary Volume, 735–765.
Herzing AA, Kiely CJ, Carley AF, Landon P, Hutchings GJ (2008) Identification of active gold nanoclusters on iron oxide supports for CO oxidation. Science 321:1331–1335
Hosea M, Greene B, McPherson R, Henzl M, Alexander MD, Darnall DW (1986) Accumulation of elemental gold on the alga *Chlorella vulgaris*. Inorg Chim Acta 123:161–165
Huaizhi Z, Yuantao N (2001) China's ancient gold drugs. Gold Bull 34:24–9
Hughes MD, Xu YJ, Jenkins P, McMorn P, Landon P, Enache DI, Carley AF, Attard GA, Hutchings GJ, King F, Stitt EH, Johnston P, Griffin K, Kiely CJ (2005) Tunable gold catalysts for selective hydrocarbon oxidation under mild conditions. Nature 437:1132–1135
Husseiny MI, El-Aziz MA, Badr Y, Mahmond MA (2007) Biosynthesis of gold nanoparticles using *Pseudomonas aeruginosa*. Spectrochim Acta A 67:1003–1006
Kalishwaralal K, Deepak V, Pandian SRK, Gurunathan S (2009) Biological synthesis of gold nanocubes from *Bacillus licheniformis*. Biosource Technol 100:5356–5358
Karamushka VI, Ul'berg ZR, Gruzina TG, Sukhovii NV, Tsarenko PM (1991a) Characteristics of the concentration of trivalent gold by microalgal cells in an energized state. Biotekhnologiya 2:65–68
Karamushka VI, Ulberg ZR, Gruzina TG, Dukhin AS (1991b) ATP-dependent gold accumulation by living chlorella cells. Acta Biotechnol 11(3):197–203
Karthikeyan S, Beveridge TJ (2002) *Pseudomonas aeruginosa* biofilms react with and precipitate toxic soluble gold. Environ Microbiol 4(11):667–675
Kashefi K, Tor JM, Nevin KP, Lovley DR (2001) Reductive precipitation of gold by dissimilatory Fe(III)-reducing bacteria and archaea. Appl Environ Microbiol 67(7):3275–3279
Keim CN, Farina M (2005) Gold and silver trapping by uncultured magnetotactic cocci. Geomicrobiol J 22:55–63
Kim D, Park S, Lee JH, Jeong YY, Jon S (2007) Antibiofouling polymer-coated gold nanoparticles as a contrast agent for in vivo X-ray computed tomography imaging. J Am Chem Soc 129 (24):7661–7665
Kneipp J, Kneipp H, Kneipp K (2006) Two-photon vibrational spectroscopy for biosciences based on surface-enhanced hyper-Raman scattering. Proc Natl Acad Sci USA 103(46):17149–17153

Konishi Y, Tsukiyama T, Ohno K, Saitoh N, Nomura T, Nagamine S (2006) Intracellular recovery of gold by microbial reduction of $AuCl_4^-$ ions using the anaerobic bacterium *Shewanella algae*. Hydrometallurgy 81:24–29

Korobushkina YeD, Korobuskhin IM (1986) Interaction of gold with bacteria and the generation of new gold. Dokl Akad Nauk SSSR 287(4):978–980

Krug JT, Wang GD, Emory SR, Nie S (1999) Efficient Raman enhancement and intermittent light emission observed in single gold nanocrystals. J Am Chem Soc 121(39):9208–9214

Kumar CSSR (2007) Nanomaterials for cancer diagnosis. Wiley, Weinheim, Germany

Kuyucak N, Volesky B (1989a) Accumulation of gold by algal biosorbent. Biorecovery 1:189–204

Kuyucak N, Volesky B (1989b) The mechanism of gold biosorption. Biorecovery 1:219–235

Lee JS, Cho J, Lee C, Kim I, Park J, Kim YM, Shin H, Lee J, Caruso F (2007) Layer-by-layer assembled charge-trap memory devices with adjustable electronic properties. Nat Nanotechnol 2:790–795

Lengke MF, Southam G (2005) The effect of thiosulfate-oxidizing bacteria on the stability of the gold-thiosulfate complex. Geochim Cosmochim Acta 69(15):3759–3772

Lengke MF, Southam G (2006) Bioaccumulation of gold by sulfate-reducing bacteria cultured in the presence of gold(I)-thiosulfate complex. Geochim Cosmochim Acta 70:3646–3661

Lengke MF, Southam G (2007) The deposition of elemental gold from gold(I)-thiosulfate complex mediated by sulfate-reducing bacterial conditions. Econ Geol 102(1):109–126

Lengke MF, Fleet ME, Southam G (2006a) Morphology of gold nanoparticles synthesized by filamentous cyanobacteria from gold(I)-thiosulfate and gold(III)-chloride complexes. Langmuir 22(6):2780–2787

Lengke MF, Fleet ME, Southam G (2006b) Bioaccumulation of gold by filamentous cyanobacteria between 25 and 200°C. Geomicrobiol J 23:591–597

Lengke MF, Ravel B, Fleet ME, Wanger G, Gordon RA, Southam G (2006c) Mechanisms of gold bioaccumulation by filamentous cyanobacteria from gold(III)-chloride complex. Environ Sci Technol 40(20):6304–6309

Lengke MF, Ravel B, Fleet ME, Wanger G, Gordon RA, Southam G (2007) Precipitation of gold by the reaction of aqueous gold(III) chloride with cyanobacteria at 25–80°C – studied by x-ray absorption spectroscopy. Can J Chem 85(10):651–659

Lin Z, Wu J, Xue R, Yang Y (2005) Spectroscopic characterization of Au^{3+} biosorption by waste biomass of *Saccharomyces cerevisiae*. Spectrochim Acta A 61:761–765

Lin HT, Pei Z, Chen JR, Hwang GW, Fan JF, Chan YJ (2007) A new nonvolatile bistable polymer-nanoparticle memory device. IEEE Electron Device Lett 28(11):951–953

Link S, Mohamed MB, El-Sayed MA (1999) Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant. J Phys Chem B 103:3073–3077

Lloyd JR (2002) Bioremediation of metals; the application of micro-organisms that make and break minerals. Microbiol Today 29:67–69

Masala O, Seshadri R (2004) Synthesis routes for large volumes of nanoparticles. Annu Rev Mater Res 34:41–81

Mata YN, Torres E, Blāzquez ML, Ballester A, Gonzālez F, Muńoz JA (2009) Gold(III) biosorption and bioreduction with the brown alga *Fucus vesiculosus*. J Hazard Mater 166:612–618

Mohanpuria P, Rana NK, Yadav SK (2008) Biosynthesis of nanoparticles: technological concepts and future applications. J Nanopart Res 10:507–517

Mukherjee P, Ahmad D, Mandal D, Senapati S, Saikar SR, Khan MI, Ramani R, Parischa R, Ajaykumar PV, Alam M, Sastry M, Kumar R (2001) Bioreduction of $AuCl_4^-$ ions by the fungus, *Verticillium* sp. surface trapping gold nanoparticles formed. Angew Chem Int Ed 40 (19):3585–3588

Mukherjee P, Senapati S, Mandal D, Ahmad A, Khan MI, Kumar R, Sastry M (2002) Extracellular synthesis of gold nanoparticles by the fungus *Fusarium oxysporum*. Chembiochem 5:461–463

Nair B, Pradeep T (2002) Coalescence of nanoclusters and formation of submicron crystallites assisted by *Lactobacillus* strains. Cryst Growth Des 2(4):293–298

Nakajima A (2003) Accumulation of gold by microorganisms. World J Microbiol Biotechnol 19:369–374
Nam J, Won N, Jin H, Chung H, Kim S (2009) pH-induced aggregation of gold nanoparticles for photothermal cancer therapy. J Am Chem Soc 131:13639–13645
Nangia Y, Wangoo N, Sharma S, Wu J, Dravid V, Shekhawat GS, Suri CR (2009) Facile biosynthesis of phosphate capped gold nanoparticles by a bacterial isolate *Stenotrophomonas maltophilia*. Appl Phys Lett 94(23):1–3
Nash JT, Granger HC, and Adams SS (1981) Geology and concepts of genesis of important types of uranium deposits. Economic Geology 75th Anniversary Volume, 63–116.
Ni J, Lipert RJ, Dawson GB, Porter MD (1999) Immunoassay readout method using extrinsic Raman labels adsorbed on immonogold colloids. Anal Chem 71:4903–4908
Nicol MJ, Fleming CA, Paul RL (1987) The chemistry of the extraction of gold. In: Stanley GG (ed) The extractive metallurgy of gold in South Africa, vol 2. South Africa Institute of Mining and Metallurgy, Johannesburg, South Africa, pp 831–905
Oldenburg SJ, Averitt RD, Westcott SL, Halas NJ (1998) Nanoengineering of optical resonances. Chem Phys Lett 288:243–247
Pradeep T, Anshup (2009) Noble metal nanoparticles for water purification: a critical review. Thin Solid Films 517(24):6441–6478
Puddephatt RJ, Vittal JJ (1994) Gold: inorganic and coordination chemistry. In: King RB (ed) Encyclopedia of inorganic chemistry. Wiley, Chichester, UK, pp 1320–1331
Ran Y, Fu J, Rate AW, Gikes RJ (2002) Adsorption of Au(I, III) complexes on Fe, Mn oxides and humic acid. Chem Geol 185:33–49
Reddy VR (2006) Gold nanoparticles: synthesis and applications. Synlett 11:1791–1792
Reith F, Rogers SL, McPhail DC, Webb D (2006) Biomineralization of gold: biofilms on bacterioform gold. Science 313:233–236
Richards DG, McMillin DL, Mein EA, Nelson CD (2002) Gold and its relationship to neurological/glandular conditions. Int J Neurosci 112(1):31–53
Romero-Gonzãlez ME, Williams CJ, Gardiner PHE, Gurman SJ, Habesh S (2003) Spectroscopic studies of the biosorption of gold(III) by dealginated seaweed waste. Environ Sci Technol 37 (18):4163–4169
Salata OV (2004) Application of nanoparticles in biology and medicine. J Nanobiotechnol 2:3–9
Selvakannan PR, Mandal S, Phadtare R, Pasricha R, Sastry M (2003) Capping of gold nanoparticles by the amino acid lysine renders them water-dispersible. Langmuir 19:3545–3549
Senanayake G, Perera WN, Nicol MJ (2003) Thermodynamic studies of the gold(III)/(I)/(0) redoc system in ammonia-thiosulfate solutions at 25°C. In: Yong CA, Alfantazi AM, Anderson CG, Dreisinger DB, Harris B, James A (eds) Hydrometallurgy 2003 - Fifth International Conference in Honor of Professo Ian Ritchie, Vancouver, vol 1. TMS, Warrendale, Pennsylvania, pp 155–168
Shankar SS, Ahmad A, Pasricha R, Sastry MJ (2003) Bioreduction of chloroaurate ions by geranium leaves and its endophytic fungus yields gold nanoparticles of different shapes. J Mater Chem 13:1822–1826
Shankar SS, Rai A, Ankamwar B, Singh A, Ahmad A, Sastry M (2004) Biological synthesis of triangular gold nanoprisms. Nature 3:482–488
Singaravelu G, Arockiamary JS, Ganesh Kumar V, Govindaraju K (2007) A novel extracellular synthesis of mondisperse gold nanoparticles using marine alga, *Sargassum wightii* Greville. Colloids Surf, B 57:97–101
Southam G, Beveridge TJ (1994) The in vitro formation of placer gold by bacteria. Geochim Cosmochim Acta 58(20):4527–4530
Southam G, Beveridge TJ (1996) The occurrence of sulfur and phosphorus within bacterially derived crystalline and pseudocrystalline octahedral gold formed in vitro. Geochim Cosmochim Acta 60(22):4369–4376
Sperling RA, Gil PR, Zhang F, Zanella M, Parak WJ (2008) Biological application of gold nanoparticles. Chem Soc Rev 37:1896–1908

Sun RW-Y, Ma D-L, Wong EL-M, Che C-M (2007) Some uses of transition metal complexes as anti-cancer and anti-HIV agents. Dalton Trans 43:4884–4892

Svedman C, Tillman C, Gustavsson CG, Moller H, Frennby B, Bruze M (2005) Contact allergy to gold in patients with gold-plated intracoronary stents. Contact Dermat 52(4):192–196

Svedman C, Dunér K, Kehler M, Moller H, Gruvberger B, Bruze M (2006) Lichenoid reactions to gold from dental restorations and exposure to gold through intracoronary implant of a gold-plated stent. Clin Res Cardiol 95:689–91

Taarning E, Nielsen IS, Egeblad K, Madsen R, Christensen CH (2008) Chemicals from renewables: aerobic oxidation of furfural and hydroxymethylfurfural over gold catalysts. ChemSusChem 1:75–78

Ting YP, Teo WK, Soh CY (1995) Gold uptake by *Chlorella vulgaris*. J Appl Phycol 7:97–100

Tsuruta T (2004) Biosorption and recycling of gold using various microorganisms. J Gen Appl Microbiol 50:221–228

Vieira RHSF, Volesky B (2000) Biosorption: a solution to pollution. Int Microbiol 3:17–24

Watkins JW II, Elder RC, Greene B, Darnall D (1987) Determination of gold binding in an algal biomass using EXAFS and XANES spectroscopies. Inorg Chem 26(7):1147–1151

Wen L, Lin Z, Gu P, Zhou J, Yao B, Chen G, Fu J (2009) Extracellularbiosynthesis of monodispersed gold nanoparticles by a SAM capping route. J Nanopart Res 11:279–288

Willner B, Katz E, Willner I (2006) Electrical contacting of redox proteins by nanotechnological means. Curr Opin Biotechnol 17:589–596

Wong MS, Alvarez PJJ, Fang YL, Akcin N, Nutt MO, Miller JT, Heck KN (2009) Cleaner water using bimetallic nanoparticle catalysts. J Chem Technol Biotechnol 84:158–166

Xiao Y, Patolsky F, Katz E, Hainfeld JF, Willner I (2003) Plugging into enzymes: nanowiring of redox enzymes by a gold nanoparticle. Science 299(5614):1877–1881