

Bionanoparticles, a green nanochemistry approach

Ana Cauerhff¹ · Guillermo R. Castro¹ ✉

¹ Universidad Nacional de La Plata, Facultad de Ciencias Exactas, Instituto de Biotecnología Aplicada, Laboratorio de Nanobiomateriales, La Plata, Argentina

✉ Corresponding author: grcastro@gmail.com

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Abstract

Background: In the past decade, considerable attention has been paid for the development of novel strategies for the synthesis of different kind of nano-objects. Most of the current strategies are usually working by the use physical or chemical principles to develop a myriad of nano-objects with multiple applications. Main fields of nanotechnology applications range from catalysis, micro- and nano-electronics (semiconductors, single electrons transistors), non-linear optic devices, photo-electrochemistry to biomedicine, diagnostics, foods and environment, chemical analysis and others.

Results: Two main avenues for nanoparticles synthesis: cell-free extract and cell cultivation have been reported. The state of art of both biotechnological approaches for different type nanoparticles are reviewed in this work.

Conclusions: Nanotechnology is a revolutionary field just at its onset, the trend in the next decades being its integration with the green chemistry approach. Several strategies involving exhaustive strain selection, cultivation modes, recombinant gene expression, metabolic engineering, protein re-design and re-engineering, and predictive modeling will allow to create nanobioreactors, a new nanobiotechnology arena with a high potential impact in many fields.

Keywords: bacteria, bionanoparticles, fermentation, fungi green chemistry, plant extracts.

INTRODUCTION

Nanotechnology is becoming a new area of increasing research and industrial interest since the 1980's. Nanotechnology can be defined as the manipulation of atom by atom from the material world by the combination of engineering, chemical and biological approaches. In the past decade, considerable attention has been paid for the development of novel strategies for the synthesis of different kind of nano-objects. Most of the current strategies are usually working by the use physical or chemical principles to develop a myriad of nano-objects with multiple applications. Main fields of nanotechnology applications range from catalysis, micro- and nano-electronics (semiconductors, single electrons transistors), non-linear optic devices, photo-electrochemistry to biomedicine, diagnostics, foods and environment, chemical analysis and others (Contescu and Putyera, 2009).

In general, the nano-objects properties depend on chemical composition, but also on size, shape, composition and their environment including their spatial distribution. It is clear that synthesis techniques can affect considerably the properties of the nano-objects. The synthesis techniques can be categorized into top-down and bottom-up strategies. The top-down techniques work with the material in its bulk form, and the size reduction to the nanoscale is made via specialized ablations (e.g. lithography, thermal decomposition, laser ablation) (Contescu and Putyera, 2009).

SYNTHESIS OF NANOPARTICLES

In the case of nanoparticle (NPs) synthesis, bottom-up (or self-assembly) procedures involve a homogeneous system wherein catalysts (e.g. reducing agents, enzymes) are producing nanostructures affected by catalyst properties, reaction media and conditions (e.g. solvents, stabilizers, temperature). For example, the chemical reduction method is the most commonly employed synthetic route for metallic particles synthesis (Contescu and Putyera, 2009). In the case of silver nanoparticles, the chemical reduction technique is based on the reduction of metal salts like silver nitrate in an appropriate medium using reducing agents like citrate, or branched polyethyleneimine. However, citrate produces negatively charged silver nanoparticles while branched polyethyleneimine produces the positively charged ones (Tan et al. 2007). Particularly, intermediates and by-products are playing a crucial role in NP synthesis. Indeed, NP physicochemical properties, surface and morphological characteristics will influence their fate, activity, transport and toxicity (Contescu and Putyera, 2009).

Toxicological aspects of NP synthesis

Chemical and physical NP synthesis cannot be expanded easily to large-scale production because of many drawbacks such as the presence of toxic organic solvents, production of hazardous by-products and intermediary compounds, and high energy consumption (Figure 1). Aqueous media are prevalent in the synthesis of metal nanoparticles, but because of the presence of attractive forces, e.g. van der Waal's, those particles may produce aggregates. Some synthetic molecules, named "capping agents" were added in the steric stabilizers to prevent particle aggregation and to control nanoparticle morphology. Besides, other problems are found in NP synthesis such as toxicity, reduced rate of particle synthesis, structural particle deformation, and inhibition of particle growth. Additionally, chemical NP synthesis included in nanocomposites or metallic NPs are composed by more than one chemical species or molecules which could increase the particle reactivity and toxicity and might harm human health and the environment due to the composition ambiguity and lack of predictability. Based on the high number of molecules and species combinations used during NP chemical synthesis, it is required to take into account all the details of the reaction conditions. This fact should be a prerequisite to track the molecular species involved along the reaction kinetics.

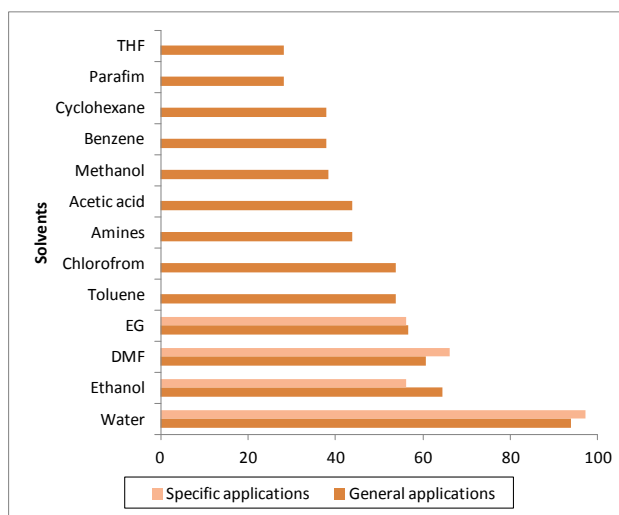


Fig. 1 Solvents used for metal nanoparticle synthesis (modified from Tolaymat et al. 2010).

Biochemical synthesis of NPs

Alternatively, the biochemical NP (bioNP) synthesis, beyond being environmentally friendly, is simple, cost-effective, more reproducible and with defined physicochemical properties. BioNPs can be classified into organic, inorganic, and hybrid. Among the bioNPs, most of macromolecules and cellular substructures are able to form NPs based on environmental conditions and sample treatment. The

ability of biological structures to produce NPs was reported in many living organisms ranging from yeast, fungi, plants, algae, to bacteria (eubacteria, cyanobacteria), as recently reviewed (Durán et al. 2007; Mohanpuria et al. 2008; Narayanan and Sakthivel, 2010; Rodriguez-Carmona and Villaverde, 2010; Durán et al. 2011; Lloyd et al. 2011; Narayanan and Sakthivel, 2011; Durán and Marcato, 2012). BioNPs can be synthesized from carbohydrates, lipids, DNA, proteins and also complex molecular mixtures. After cell lysis, sample treatments could involve many strategies commonly used for cell fractioning including solvents, salts, homogenization in the presence of surfactants, chaotropic agents, differential precipitation, and so on.

Inorganic bioNPs can be classified into oxides and metallic. The synthesis of inorganic bioNPs is carried out by unspecific reducing agents present in the medium and/or as the result of triggering the SOS system in the cell to reduce toxicity.

In the case of hybrid bioNPs, the synthesis can be driven by molecular precursors in the presence of biological templates (e.g. DNA, proteins) (Contescu and Putyera, 2009). The advantage of using biological templates is the huge diversity of tridimensional biostructures available as templates that can be used to create NPs with many different characteristics and properties.

Two main strategies were developed for bioNPs production by means of the use of biological extracts or specific molecules, named as *in-vitro* biosynthesis, and using living cells, named as *in-vivo* biosynthesis. However, in some cases it is difficult to determine if the synthesis mechanism is specific or not, namely biosynthetic or unspecific like the biomimetic approach.

***In vitro* mechanisms of synthesis**

The main *in vitro* mechanisms have been recently reviewed (Durán et al. 2011; Durán and Seabra, 2012).

In-vitro bio-strategies were developed using microbial extracts which are more extensively used because of the simplicity of the method. The technical procedure involves the addition of molecular precursors to crude or partially purified bioextracts obtained from cell-free supernatants or cell cultures lysates containing the reactants.

In the case of algae, the syntheses of metallic NPs were made by collecting, washing and drying the biomass. Later, the grinded algal biomass was placed in a solution containing the metal precursors, an organic or inorganic salt (e.g. HAuCl₄, AgNO₃, Pb-acetate, etc.) in defined experimental conditions to interact with redox agents (oxygen) and/or energy sources (microwave, oven) at specified time intervals until the presence of NPs is detected by the analytical techniques (Merin et al. 2010; Arockiya et al. 2012; Singh et al. 2013).

In the last decades, many procedures and some biomimetic mechanisms to synthesize metallic NPs by plants have been described (Schabes-Retchkiman et al. 2006; Jha et al. 2009; Vijayaraghavan et al. 2012). Most of the publications reported the use of dried leaves or buds cut into pieces and extracted with solvents, generally using aqueous or ethanolic fractions. The extracts were exposed to metal salts under determined experimental conditions. The reducing conditions of ion metals were attributed to the presence of polyphenolic antioxidant compounds found in the plant extracts such as flavonoids, and acids like 3,4-dihydroxy benzoic, p-hydroxy benzoic, caffeic, capryllic, p-coumeric, ferulic, gadoleic, lauric, sinapic, syringic and vainillic, among other compounds (Zhou et al. 2010; Shen et al. 2011; Aromal et al. 2012). However, the presence of many reducing compounds seasonally synthesized by the plants does not allow predicting the main properties of the bioNPs. For example, full width at half maximum (FWHM) of bioNPs can fluctuate from 55 to 102 nm (about 54%) just by changing the plant extract content (Aromal et al. 2012). Furthermore, bio-NPs chemical composition synthesized by plant extracts cannot be specifically determined. For example, FTIR analysis of Au- and Ag-NPs showed the presence of proteins, aromatic amines and polyphenols in the NPs (Schabes-Retchkiman et al. 2006; Shen et al. 2011). Additionally, in some cases the NPs synthesized by plants extracts were reported spherical but also hexagonal and triangular which depends on the extract chemical compositions, concentration, and pH of media (Chandran et al. 2006; Aromal et al. 2012; Khalil et al. 2012).

Biomimetic NP syntheses were reported also in many microorganisms, from cyanobacteria (Mubarakali et al. 2012) to sporulating bacteria (e.g. *Bacillus* and related genus), actinomycetes, and several fungi. NP syntheses can be classified based on the change of the oxidation state of the element making the particle:

1. When the element oxidation state is changing, NPs resulted from metal reduction by classical redox processes, e.g. Ag, Au, Pt NPs.
2. When NPs are produced by insoluble salt formation with no change in oxidation state of the element, it is most properly mentioned as nanocrystals. The NPs formation is a result of low Kps of the salt in the medium. Typical examples are sulphate reducing bacteria, where sulphate ions are reduced to sulphide by a mechanism mediated by a sulphate reductase. Addition of Cd^{2+} ions to media containing sulphide anion induces CdS precipitation because the Kps is 1.0×10^{-27} . However, the mechanism is not restricted to a sulphate reducing bacteria; other microorganisms with different evolutionary pathways are also able to produce CdS NPs ranging from the cyanobacterium *Phormidium tenue*, to *Lactobacillus* sp., *Fusarium oxysporum* and *Sachharomyces cerevisiae* with average nanoparticle diameters from 2.5 to 5.5 nm (Prasad and Jha, 2010; Mubarakali et al. 2012).

In both types of syntheses, they were described as intra- and/or extracellular in many microorganisms. The main concern in *in-vitro* strategies is how to develop the control of NP synthesis.

Biosynthesis of metal NPs

In vitro biosynthesis of Ag-NPs was studied in several microorganisms, showing different NP profiles and properties (Shahverdi et al. 2007). These authors reported the synthesis of Ag-NPs using 24 hrs to 3 days old microbial supernatants of *Bacillus cereus*, *Bacillus subtilis*, *Escherichia coli*, *Enterobacter cloacae*, *Klebsiella pneumoniae*, *Lactobacillus acidophilus*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*, *Candida albicans* and *Aspergillus niger*. The Ag-NPs ranged from 28.2 to 122 nm in diameter with an average of 52.5 nm (Shahverdi et al. 2007). The general mechanism was described as non-specific and based on the presence of hydroquinones, molecules with high redox properties, which could act as electron shuttles in metal reductions (Durán et al. 2005). The largest plasmon resonance peak was observed in the supernatant of *K. pneumoniae* after 5 min of incubation in the presence of AgNO_3 . Besides, energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) analysis demonstrated the presence of Ag-NPs but also nanocrystals, which can be attributed to the insoluble salt formation in the presence of several anions in the medium (e.g. Cl^{-1} , SO_4^{-2} and MoO_4^{-2}). In addition, EDS spectra showed the presence of sodium, calcium, iron, and chloride in the Ag-NPs (Shahverdi et al. 2007). Additionally, the NP size dispersion increases by the presence of impurities in the solution. Both, contamination of NPs by other elements and changes in the NP size are serious limitations for specific therapeutic applications.

In the case of *in vitro* biosynthesis of Au-NPs, the suggested mechanism was catalyzed by extracellular NADH-dependent enzymes from *Rhodopseudomonas capsulata*. The authors found pH to be a relevant factor to determine the shape of the Au NPs: at pH 7.0 most of the Au-NPs were spherical with diameters between 10 and 20 nm as determined by TEM, but when the pH was decreased to 4.0 the shape changed to 60% triangular NPs and also the size increased from 50 to 400 nm bisectors (He et al. 2007). Recently, the biomimetic synthesis spherical Ag-NPs from 10 to 100 nm in diameter was reported by the extremophile *Ureibacillus thermosphaericus*. The diameter of Ag-NPs showed strong dependence with temperature in the 60 to 80°C range and with silver concentration in the 1 to 10 mM range (Juibari et al. 2011). The increase from 60 to 80°C reduced the Ag-NPs diameters from 57 at 60°C, to 29 at 70°C and to 13 nm at 80°C when 1 mM AgNO_3 was supplemented to the microbial culture. On the contrary, the diameter trend of the Ag-NPs was reversed from 51 at 60°C, to 67 at 70°C and to 75 nm at 80°C when the AgNO_3 was increased to 10 mM. The variation of Ag-NP diameter associated with the changes in AgNO_3 concentration and temperature is considered by the authors to be related to the activation/deactivation of secondary reduction mechanisms (Juibari et al. 2011), which is probable because died and lysed cells are predominant in the microbial stationary phase. However, the mechanisms of synthesis could be not only extracellular, as the authors claimed, since most Ag-NPs synthesis occurs in the stationary growth phase which is currently associated with the differentiation process of sporulation in microorganisms.

In the classical biosynthetic strategy, the NPs can be generally grouped based on their molecular structures as: organic (biopolymeric) NPs, metallic NPs, and salt NPs.

Biosynthesis of polymeric NPs

Synthesis of polymers by bacteria was reported long time ago. However, its application for the synthesis of nanobiomaterials used in many fields has been observed only in recent years. Organic NPs are included in intracellular granules generally used as carbon, nitrogen and/or energy sources and accumulated during exponential bacterial growth phase under some nutrient starvation condition. During the last decade, lipid accumulation, including polyhydroxy alkanoates (PHAs), triacylglycerols, wax esters, polyphosphates, and glycogen-like intracellular polymers have been reported in many bacteria (Hamilton, 1968; Alvarez et al. 1997; Kalscheuer et al. 2001; Tobin et al. 2007). Some biopolymer NPs of potential use are summarized in Figure 2.

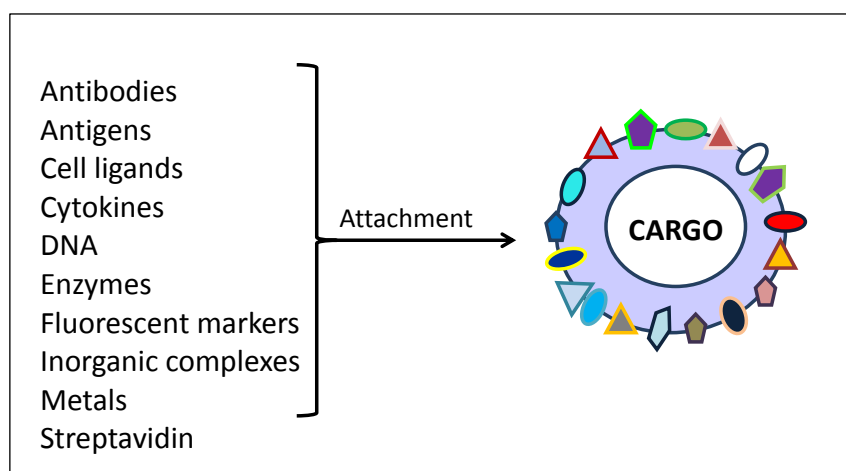


Fig. 2 Potential uses of nanoparticle biopolymers.

Acinetobacter sp. strain 211 cultivated in the presence of olive oil as carbon source has about 25% of fatty acids on dry cell weight basis. Analysis of NPs lipid content revealed the presence of fatty acids with chain length between 12 to 18 carbon atoms, and also the presence of a 39 kDa protein predominant in the NPs as a template (Alvarez et al. 1997). The result suggests specific biosynthetic mechanism able to be monitored and controlled by metabolic engineering tools.

In the case of metal NPs, a selected wild-type *Bacillus licheniformis* Ag-resistant was grown in the presence of AgNO_3 in the medium. Silver NPs were detected intracellularly and the proposed mechanism involved the cytoplasmatic NADH-dependant nitrate reductase and Ag^0 formation followed by the nucleation into Ag-NPs of 50 nm average size (Kalimuthu et al. 2008). In a further work, the presence of NADH- dependant nitrate reductase was confirmed and optimized for the production of Ag-NPs (Vaidyanathan et al. 2010).

Also, intracellular biosynthesis of manganese oxide NPs was described in batch culture of *Bacillus* sp. (Sinha et al. 2011). The maximum oxidation rate of Mn^{+2} was reached at stationary growth phase, and the NP was characterized as MnO_2 . The manganese transport into the bacterial cells is still unknown, but the authors speculated with the induction of cellular mechanism during the exponential growth phase to reduce the toxicity of manganese forming less toxic molecules intracellularly. The MnO_2 -NPs had an average size of 6 nm at $10 \text{ mg} \times \text{L}^{-1} \text{ Mn}^{+2}$ and were homogeneously distributed in the cytoplasm; however, when Mn^{+2} was increased to $200 \text{ mg} \times \text{L}^{-1}$ the oxide NPs were located close to the cell wall and its size decreased to 4.6 nm. These results are indicative of a detoxification mechanism triggered by the presence of manganese at toxic concentrations.

Cytoplasmatic biosynthesis of CdS-NPs by the photosynthetic bacterium *Rhodospseudomonas palustris* was reported by Bai et al. (2009). The starting materials were soluble cadmium salts and sodium sulphate, and the mechanism of NP biosynthesis was attributed to the presence of inducible cytoplasmatic cysteine desulphhydrase isoenzymes able to convert sulphate to sulphide mainly at the stationary growth phase. The CdS colloidal NPs showed an average size of about 8 nm (with a range of 6 to 11 nm), and no aggregation in aqueous solutions was observed when the NPs were exported by the cell (Bai et al. 2009). Similar results of CdS NPs biosynthesis were reported in yeasts and fungi (Dameron et al. 1989; Kowshik et al. 2002).

Also, the biosynthesis of Hg salt NPs was described in *Enterobacter* spp. (Sinha and Khare, 2011). The authors reported a lag growth phase extension for more than 48 hrs in the presence of HgCl_2 in the medium. Analysis of the particles revealed the presence of an average size of 2 and 5 nm in diameter monodispersed spherical nanoparticles of $\text{Hg}_3(\text{PO}_4)_2$. The Hg-NPs were located inside the cell, both bound to the cellular membrane and uniformly dispersed in the cytoplasm. Besides, pH affected NPs morphology and abundance: at pH 6.0, the Hg-NPs were of irregular shape, but at pH 7.0 became spherical and higher NPs density was found at pH 8.0; at pH 9.0, density was even higher and smaller Hg-NPs were observed. The mechanisms of NP synthesis are still speculative but it can be generally considered as based on SOS cell response mediated by enhanced polyphosphate synthesis *de novo*, as it was suggested previously for cell cultures under stress conditions (Haakenson, 2007).

In the case of polyesters, like PHAs and their derivatives, they were synthesized inside the cytoplasm with an average particle diameter of 200 to 500 nm, and more than 80 PHAs components were reported in numerous bacteria. The great diversity of monomers and templates allows creating from crystalline structures to elastic rubber cytoplasmatic granules depending of the components which can be manipulated to obtain also unnatural PHAs (Lütke-Eversloh et al. 2001; Aldor and Keasling, 2003). However, the main limitation of the present approach is related to the biosynthetic pathway control of the polymerization process carried out by the promiscuous PHA synthase, who determines the dimensions and characteristics of the particles (Rehm, 2006).

Glycogen and amylopectin-like polymers as inclusion bodies were reported in bacteria more than 50 years ago. Both biopolymers were synthesized and accumulated in the cytoplasm during the stationary phase of growth under excess of carbon source and at some nutrient starvation, reaching in some cases up to 50% of the microbial cell dry weight. The mechanisms of glycogen synthesis and accumulation are well understood in Gram-negative microorganisms such as *E. coli* and *S. typhimurium* (Preiss and Romeo, 1990). Besides, glycogen granules of 30 to 500 nm in diameter are widespread in the microbial world from archeobacteria and eubacteria to yeast and fungi (Schimz and Overhoff, 1987; Preiss and Romeo, 1990). However, a positive correlation between infectivity and biopolymer content in pathogenic bacteria was found, which is restricting their use in animals (Bonafonte et al. 2000).

Additionally, microorganisms capable to produce extracellular carbohydrate polymers are well known, but the research on this area is still moving on (Zhu et al. 2001; Castro et al. 2006; Díaz-Barrera et al. 2010). Extracellular colloidal biopolymers can be used as template or adsorbent for the nanoparticles. Extracellular bacterial cellulose produced by fermentation of *Gluconacetobacter xylinum* was used as a nanoparticle adsorbent of Fe_3O_4 nanoparticles. The resulting magnetic nanoparticles with 15 nm average in diameter were uniformly dispersed in the cellulose matrix reaching a composition of 33% Fe_3O_4 on cellulose (Zhu et al. 2001).

Cultivation strategies, like repetitive batches, fed-batch and continuous culture were used to study the polymer synthesis and degradation which are allowing to tailor the biopolymer quantities and composition. The options for different cultivation strategies depend on many considerations, like the mode of culture, the microorganism, the selection pressure, and the level of gene expression among others (Linton and Cripps, 1978; Talebnia and Taherzadeh, 2007; Díaz-Barrera et al. 2010; Vargas et al. 2013).

A mixed approach between biomimetic and fermentative strategies was developed using genetically modified *E. coli* to produce micro- or nano-particles (Jahns et al. 2008). PHAs biosynthesis and accumulation in cytoplasmatic granules by bacteria was used as a template for the synthesis of micro- and nano-particles in transformed *E. coli* (Jahns et al. 2008). PHAs are biodegradable polyesters accumulated in the stationary growth phase of many microorganisms, and their biosynthesis and

molecular weight can be modulated by culture conditions (nitrogen, phosphorous and carbon source starvation) and by fermentation methodology (e.g. fed-batch). The PHAs genes were cloned and co-expressed with a fusion protein in *E. coli* (Figure 3). The biosynthetic PHA-particle contained gold, silica and antibody binding domains (Jahns et al. 2008).

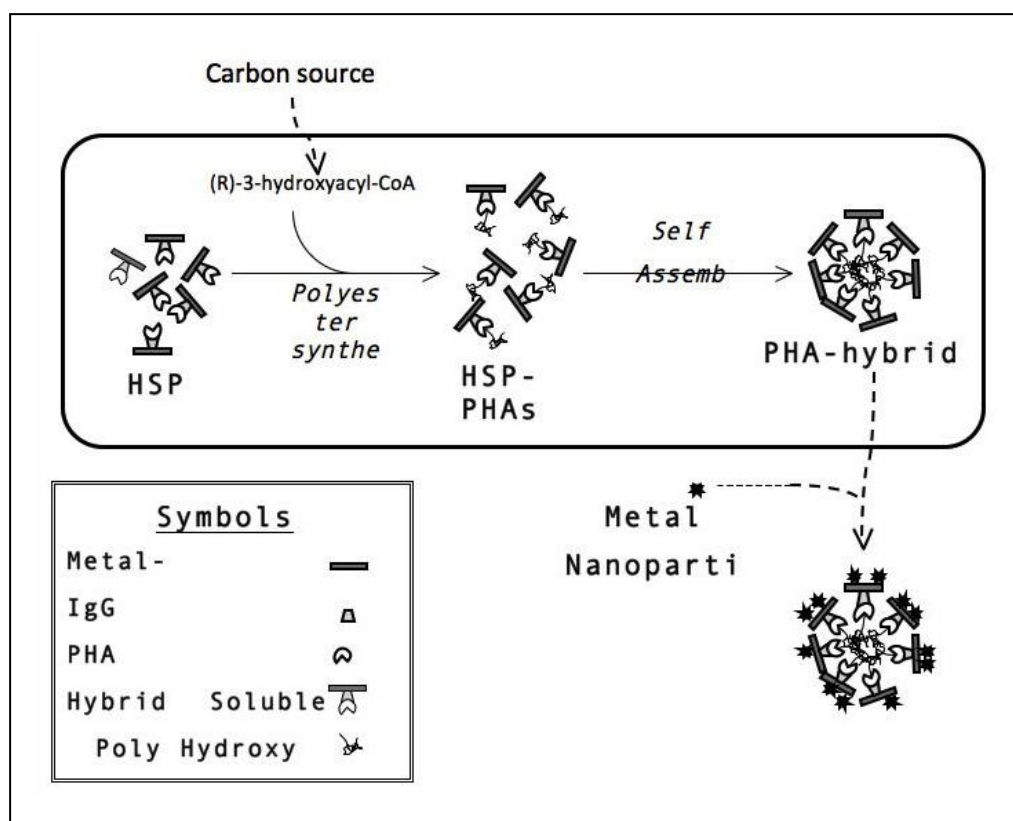


Fig. 3 Biosynthetic particles containing multidomains produced by recombinant *E. coli* (modified from Jahns et al. 2008).

CONCLUDING REMARKS

Nanotechnology is a revolutionary field just at its onset, the trend in the next decades being its integration with the green chemistry approach. Several strategies involving exhaustive strain selection, cultivation modes, recombinant gene expression, metabolic engineering, protein re-design and re-engineering, and predictive modeling will allow to create nanobioreactors, a new nanobiotechnology arena with a high potential impact in many fields.

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