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Biosynthesis of gold nanoparticles by the living freshwater diatom *Eolimna minima*, a species developed in river biofilms

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Abstract Testing biotransformation capacities of living aquatic microalgae diatoms to naturally synthesize gold nanoparticles (AuNP) from gold salts and assessing aftereffects on their viability by microscope observations is a great challenge. In this work, a laboratory experiment was conducted, which aimed to observe (i) directly by transmission electronic and light microscopy and (ii) through indirect measurements (UV-visible spectroscopy) the periphytic freshwater diatom *Eolimna minima* exposed to gold salts. This work revealed the capacity of *E. minima* to intracellularly biosynthesize AuNP and to tolerate it. AuNP synthesis appears as a mechanism of detoxification to protect diatom from gold salt contamination. We also pointed out the risks associated with the spread of diatoms full of AuNP, through the trophic web of freshwater ecosystems. The preponderant part of the diatoms in natural biofilms associated with their position at the basis of the trophic webs in rivers could then make them responsible for the contamination of their consumers (grazer animals) and consequently for the potential release of AuNP through the entire food web.

Keywords Periphytic microalgae · Diatom · Aquatic environment · Biomineralization of gold salts · Gold nanoparticles · Contamination · Microscopy · Laboratory experiment

Introduction

For more than 30 years, nanosciences and technologies have explored the fields of the infinitely small, and the technological developments here are concomitant with an increasing demand by biotech industries looking for new products from electronic components to medical applications in biomaterials, automobiles, and a great diversity of consumer products (cosmetology, paint...). However, the industrial synthesis of nano-objects, as for chemical synthesis, is a source of environmental pollution via the numerous chemicals used in their synthesis. Development of new and clean nanotechnology manufacturing approaches which minimize potential environmental and human health risks is a challenge which motivates the scientific community (Guowu et al. 2011; Narayanan and Sakthivel 2011; Korbekandi et al. 2009).

The use of microorganisms as nanofactories has been recently considered (Thakkar et al. 2010; Zhang et al. 2011; He et al. 2008; Mohanpuria et al. 2007; Gericke and Pinches 2006; Mandal et al. 2006). In aquatic environments, Singaravelu et al. (2007) then Govindaraju et al. (2009) took an interest in the capacity of the marine alga, *Sargassum*, to synthesize gold nanoparticles (NP) by an extracellular path, but few studies have focused on synthesis in living organisms (Gong et al. 2011; Schröfel et al. 2011; Brayner et al. 2007; Gardea-Torresdey et al. 2002). Identification of such a biological model, able to live, thrive, and reproduce while producing nanoparticles, could be a great help in promoting green NP synthesis. Terrestrial organisms exposed to very high metal concentrations (Moradi et al. 2010; Barbaroux et al. 2009) are known to highly concentrate the metal in their tissues, all the while prospering. Similar behavior might exist in organisms exposed to nanoparticles. Additionally, there is increasing evidence that engineered particles could pose an important risk to the environment and human life. Gold particles have widespread uses; they are one of the six major nanomaterials

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included in traded products (massive use in cosmetics, paint, coatings...) thanks to their optical and optoelectronic properties (Corti et al. 2007). They are the topic of numerous fundamental research studies in nanosciences, especially in plasmonics, photonics, metamaterials, or catalysis (Liz-Marzan 2004). In more applied fields, they have proven to be very useful in genomics, as biomedical imaging contrast agents in tomography X-rays, as a platform of vectorization of drug molecules, as well as in radiotherapy (Berbeco et al. 2011). And owing to the strong electron density of gold, detection of gold nanoparticles is possible by transmission electronic microscopy (TEM) (Xu et al. 2006), making them thus very useful in cellular imaging. On the other hand, there is very little work on the impact of gold nanoparticles (AuNP) on human beings or aquatic organisms (Von Moos et al. 2014; Tedesco et al. 2010, 2008).

Thus, progress in nanotechnologies must be accompanied by awareness of the potential environmental and toxic impact of nanomaterials (Oberdörster et al. 2005), which may end up in natural aquatic environments via industrial effluents or consumer use, and there interfere with the dynamics among the trophic levels of natural ecosystems. For example Renault et al. (2008) showed the toxic effect of AuNP in two species (the green microalga *Scenedesmus subspicatus* and the bivalve *Corbicula fluminea*) and the trophic transfer of AuNP between these two species.

Work concerning nanomaterial synthesis and work focused on the potential risks incurred by NP dispersion in the environment are almost always tackled separately. In order to jointly consider both of these aspects of nanomaterials, and to pursue research into nanomaterials which are more environmentally friendly throughout their lifecycle, this work has a double objective: (i) testing the biotransformation capacities of living microalgae diatoms to naturally synthesize AuNP from gold salts, and (ii) assessing the aftereffects of this biotransformation on the viability of these diatoms. In this work, we conclude that living diatoms have a good capacity to biosynthesize AuNP inside their cellular milieu. Possible detoxification mechanisms by diatoms are evoked to explain this synthesis, which might occur as a protection reaction to the presence of gold salts. We also point out the potential risks associated with the spread of diatoms full of AuNP through the trophic web of freshwater ecosystems.

Material and methods

Diatom species studied

The biological model is a freshwater microalga (*E. minima*, length 5–18 μm) of the diatom group (Pennales, Biraphidae), well known for the architecture and nanometric ornamentation of their two siliceous valves called frustule protecting their

inner cellular content (Fig. 1). Diatoms generate their cell walls by silica biomineralization. The cell walls are composed of silica and organic macromolecules and different atomic force microscopy (AFM) techniques show a complex microscopic structure with a nanostructured granular surface (Noll et al. 2002). Diatoms produce exudates through their frustule which constitute a coating of extracellular polymeric substances (Gélabert et al. 2004, 2007; Pokrovsky et al. 2010) and agglomerate to bacteria, fungi, protozoa, and other microalgae, to form cohesive biofilms on any support immersed in running waters and are consumed by various trophic levels of the aquatic ecosystem. They are responsible for a large proportion of vegetal primary production in upstream watercourses because of their short development cycles (a few hours to a few days by mainly asexual reproduction) and their ubiquity. *E. minima* development is therefore the basis of the functioning of aquatic food webs. This is a cosmopolite species, recorded all over the world but particularly in organic rich and/or polluted aquatic environments, and is therefore considered a resistant species. It develops by adhering to the substrate and is one of the pioneer species involved in the elaboration of a biofilm. Its selection in this study appears therefore justified to answer our double objective of looking for AuNP biosynthesis in living diatoms and looking for effects of AuNP in the aquatic food web.

Exposure of the diatom *E. minima* to contaminant solution

An axenic strain of *E. minima* was obtained from the Culture Collection of Algae (UTEX, Austin, USA), and it was cultured in suspension in 3 L Erlenmeyer flasks in the laboratory at 20 °C in sterile Dauta culture medium (Dauta 1982) modified by the addition of siliceous (10 mg L⁻¹), at pH~7.7. Flasks were kept in a thermoregulated chamber under a light intensity of 160 $\mu\text{mol photon m}^{-2} \text{s}^{-1}$ and 12:12 light/dark cycle to favor diatom growth.

E. minima diatom suspensions were exposed in 50 mL polypropylene tubes under axenic conditions to potassium gold (III) chloride (KAuCl₄, 99.995 %, Sigma Aldrich) at three concentrations (20 $\mu\text{g/mL}$: NP20; 50 $\mu\text{g/mL}$: NP50;

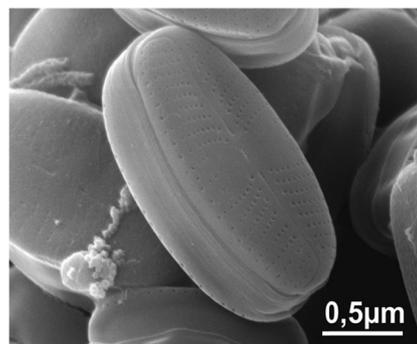


Fig. 1 SEM image of *Eolimna minima*

100 $\mu\text{g/mL}$: NP100) and were sampled twice (one day after t_0 contamination: t_1 , then 7 days: t_7) looking for AuNP. pH was checked in all the samples at the start and end of the experiment.

Control tubes (Control20, Control50, and Control100) contained only culture medium and KAuCl_4 solution at the three concentrations. During the experiment, each tube contained 1.2×10^6 cells/mL of diatoms, in suspension in Dauta culture medium solution, exposed under a light intensity of $40 \mu\text{mol photon m}^{-2} \text{s}^{-1}$, a temperature of 20°C , and a photoperiod of 12L/12D. AuNP production was verified after 7 days by UV-visible spectroscopy measurements between 400 and 800 nm with a UV-Schimadzu spectrophotometer (resolution 1 nm) to detect AuNP peaks at 520 nm. At both sampling times, whole diatoms were observed by light microscopy (Leitz Wetzlar). At sampling time (t_7), histological diatom preparations obtained from 50–70 nm ultra thin cuts were prepared for observation by transmission electronic microscopy (TEM, Technai 12, Phillips).

Results

pH during exposure

pH was checked in all the samples at the start and end of the experiment (Table 1). After 7 days of exposure, pH values did not change in control tubes without diatoms, but increased in the tubes containing diatoms in suspension while remaining in a pH range acceptable for them, *E. minima* being considered as an alkalophil diatom (Kovacs et al. 2006).

Evolution of the absorption spectra of the contaminant solutions to the different conditions of exposure

Diatom solutions from NP50 presented an absorption spectrum with a peak between 520 and 585 nm, corresponding to the surface plasmon resonance of AuNP in formation (Fig. 2a). This peak signaled AuNP biosynthesis within the diatom solution, and was corroborated by visual observation of coloration (from light to red purple) at t_7 ; control and t_0 samples were uncolored. These observed surface plasmon

Table 1 pH values at the beginning (t_0) and at the end (t_7) of the experiment

pH	Ctrl 20	NP20	Ctrl 50	NP50	Ctrl 100	NP100
t_0	7.7	7.7	7.0	7.0	5.8	5.8
t_7	7.6	9.7	7.1	7.9	5.7	7.3

Control (Ctrl) 20, 50, and 100 (respectively 20, 50, 100 $\mu\text{g KAuCl}_4/\text{mL}$) correspond to Dauta culture medium with KAuCl_4 and no diatoms. NP10, 50, and 100 (respectively 20, 50, 100 $\mu\text{g KAuCl}_4/\text{mL}$) correspond to KAuCl_4 solutions in Dauta medium with diatom suspensions

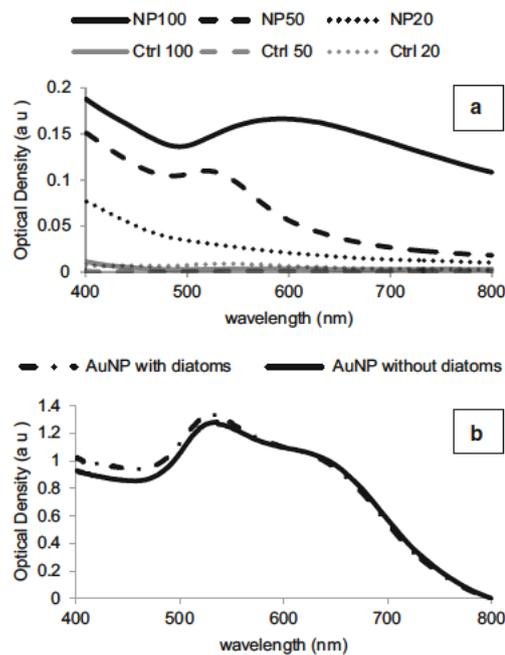


Fig. 2 Absorption spectra (between 400 and 800 nm) a of the KAuCl_4 solutions tested during the 7 day experiment: Control (*Ctrl*) 20, 50, and 100 (respectively 20, 50, 100 $\mu\text{g KAuCl}_4/\text{mL}$) corresponding to Dauta culture medium with KAuCl_4 and no diatoms; and NP10, 50, and 100 solutions (respectively 20, 50, 100 $\mu\text{g KAuCl}_4/\text{mL}$) corresponding to KAuCl_4 solutions in Dauta medium with diatom suspensions; b of an artificially prepared mixture of AuNP with or without diatoms

band are due to the interaction of the light with surface conduction electron of the gold nanoparticles. This band which appears for small particles with sizes from around 5 nm to tens of nanometers is red shifted to the near IR domain and broadened when the size increases. The wide plasmon band with a maximum of around 585 nm confirms the presence of large particles of gold with magnitude order of 100 nm or particles aggregates.

Microscopic observations of *E. minima*

Microscopic observations complemented the optical density (O.D.) values supporting AuNP biosynthesis in diatom solutions in the presence of KAuCl_4 . After 7 days, light microscopy revealed a pronounced color within the diatom cells, with light pinkish-colored cells still showing their green chloroplasts at NP20 to uniformly dark pink cells at NP100 (Fig. 3). This gradient of color corresponds to the different aggregation stages and sizes of AuNP in formation, as confirmed by the red shift of the broad plasmon band at NP100. Transmission electron microscopy confirmed the presence of AuNP inside (and outside) the cells with AuNP size not quite homogeneous and ranging from a few nanometers to around 100 nm (Fig. 4). At the two lower concentrations (NP20 and NP50), AuNP were preferentially confined between the siliceous frustule and the plasma membrane with a more marked



Fig. 3 *Eolimna minima* cells observed by light microscopy (scale bar 10 µm) after 7 days of exposure to **a** NP10, **b** NP50, and **c** NP100 solutions (respectively 20, 50, 100 µg KAuCl₄/mL) corresponding to KAuCl₄ solutions in Dauta medium with diatom suspensions

accumulation at NP50 on the inside edges of the wall. At these concentrations, diatom organelles such as the nucleus and chloroplasts were clearly visible and the cells appeared viable with well separated and structured organelles. For diatoms at NP100, AuNP uniformly occupied all of the intracellular space including within vital organelles such as the chloroplasts, causing the form of both cells and organelles to appear impaired with destructured content. Finally, no AuNP was detected in control tubes (Control20, Control50, and Control100) containing only culture medium and KAuCl₄ solution.

Discussion

Several studies have shown that gold salts affect intracellular metabolism (Robinson et al. 1996; Hosea et al. 1986) and that KAuCl₄-treated cells show a loss of chlorophyll fluorescence accompanied by a fall in carbon sequestration. These observations may be linked to the presence of AuNP in the chloroplasts, as seen here at the highest concentration. Thus, the reduction of Au (III) to non toxic Au (0) in nanoparticle form, would be a mechanism for cell detoxification (active or passive), but surprisingly no AuNP was detected within the vacuole, a storage organelle often involved in detoxification

processes (Brembu et al. 2011; Nassiri et al. 1997). Yet, we must consider that the AuNP was made in the cell and then somehow released since no AuNP was detected in control tubes containing only culture medium and KAuCl₄ solution. For low gold salt concentration (under 50 µg/mL), the observed plasmon bands in Fig. 2a around 510–550 nm attest to the presence of gold in colloidal form with sizes in the range of 5–80 nm (Perrault and Chan 2009; Njoki et al. 2007). These colloidal dispersions are stabilized by electrostatic or steric forces which would be provided by ligands or macromolecules such as extracellular polymer substances present in the microenvironment. For high concentration (up to 100 µg/mL), all the gold atoms would not be taken in charge and bigger particles and aggregates would be then formed. Indeed, the absorption spectra obtained with AuNP solely in Dauta medium or in the presence of diatoms are quite different. In addition to the maximum at 520 nm, these broad bands display a secondary maximum around 620 nm from multipolar dielectric interactions traducing an aggregated state of gold colloids. Despite the large amounts of AuNP and the misshapen cells and organelles at the highest concentration, cells remained alive at all three salt concentrations, as indicated by the increase in pH after 7 days which attests to respiratory algal activity and thus diatom vitality. Indeed, it is known that during culture, pH tends to increase with the growth of algal

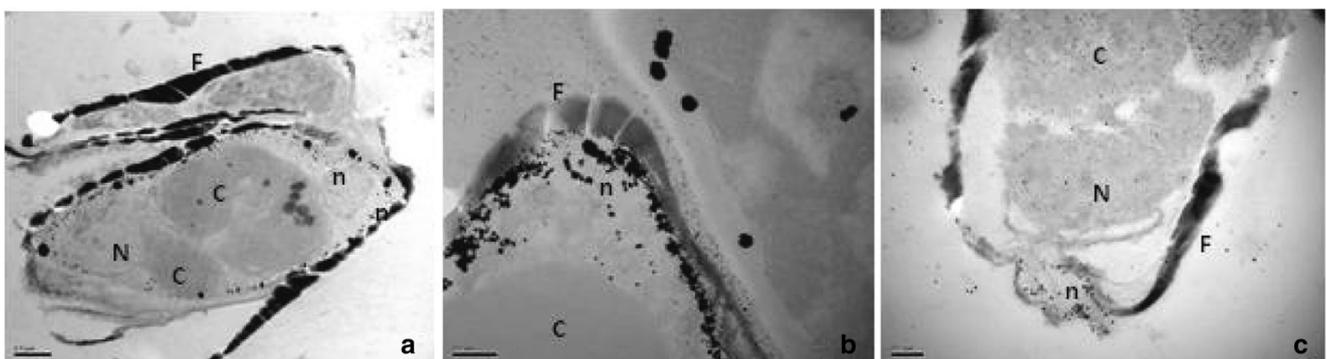


Fig. 4 TEM images of *Eolimna minima* (scale bar: respectively 0.5, 0.2, and 10 µm) after 7 days of exposure to **a** NP10, **b** NP50, and **c** NP100 solutions (respectively 20, 50, 100 µg KAuCl₄/mL) corresponding to

KAuCl₄ solutions in Dauta medium with diatom suspensions. Details of cellular organelles (*F* frustule, *C* chloroplast, *N* noyau) and location of nanoparticles (*n*)

population that depletes the carbon oxide from the culture medium to perform photosynthesis processes. pH in culture medium may then reach values of 9 (Barsanti and Gualtieri 2014) that do not optimize the algal growth, but do not endanger its viability.

AuNP synthesis is not tolerated at the highest concentration but at the two lowest concentrations, it seems that AuNP are coated with biomolecules (sugars, proteins) which create a stable organic matrix around the particles and prevent their flocculation in the medium (which would be indicated by a blue color). At NP20, the small amount of AuNP synthesized by the cell and adsorbed on the plasma membrane did not appear sufficient to induce AuNP expulsion from the diatom cell. It appears different at NP50, as AuNP began to be visible outside the diatom cell. This could have resulted from AuNP being expelled/rejected through the pores of the diatom siliceous frustules or at the junction area between the two valves.

From a chemical point of view, we can suspect that within the cells, there is a reduction of the KAuCl_4 solution by membrane proteins, not yet clearly identified (Gericke and Pinches 2006), to explain the observed AuNP biosynthesis. Recently, Schröfel et al. (2011) suggested various mechanisms of nanoparticle formation by living cells via the interaction of metallic salt with cellular organic compounds such as carbohydrates or proteins to reduce Au^{3+} to Au^0 : (i) by oxidation of hydroxyl groups (abundant in polysaccharides of the algal cell wall) to carbonyl groups, (ii) by algal pigments rich in hydroxyl groups (fucoxanthins) or other highly reactive functional groups such as sulfhydryl present in the polysaccharides of the cell wall (fucoidans), and (iii) through the role of silaffin polypeptides. Although nitrogenase is recognized as able to reduce gold in cyanobacteria (Brayner et al. 2007), few enzymes or biomolecules have been identified as responsible for AuNP synthesis in algal extracts. Xie and co-workers (2007) reported synthesis of gold nanoplates in an algal extract and identified proteins as the primary reducing and shape-directing agents. These single-crystalline gold nanoplates were produced by treating an aqueous solution of chloroauric acid with an extract of the unicellular green algae *Chlorella vulgaris*. A protein with a molecular weight of approximately 28 kDa was isolated and purified by reversed-phase HPLC; it tested positive for the reduction of chloroauric acid in aqueous solution, and is suspected of performing the dual function of Au^{3+} reduction and size- and shape-controlled synthesis of gold nanocrystals. The isolated protein (named gold shape-directing protein, GSP) was used to produce gold nanoplates with distinctive triangular and hexagonal shapes in high yields (~90 %).

This work highlights the capacity of diatoms to synthesize AuNP while maintaining a state of cellular viability. Their ability to store AuNP raises questions concerning environmental impacts in freshwaters: e.g., the potential to stock AuNP intracellularly over time and its possible release into

the aquatic environment. Indeed, diatoms have shown during this experience their potential to act as a bioreactor by synthesizing gold nanoparticles from gold salts. In case of even low gold salts contamination in natural freshwater environment, they could be suspected of playing the same role. The preponderant part of the diatoms in natural biofilms associated with their position at the basis of the trophic webs in rivers could then make them responsible for the contamination of their consumers (grazer animals) and consequently for the potential release of AuNP through the entire food web. Yet no data are currently available on AuNP quantification in aquatic ecosystems. To respond to these questions, further investigations are needed and these should first assess the quantification of AuNP bioaccumulation by diatoms for a concentration gradient of gold salts.

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