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Silver, gold and bimetallic nanoparticles production using single-cell protein (*Spirulina platensis*) Geitler

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Abstract Interaction of single-cell protein of *Spirulina platensis* with aqueous $AgNO_3$ and $HAuCl_4$ was investigated for the synthesis of Ag, Au and Au core—Ag shell nanoparticles. Biological reduction and extracellular synthesis of nanoparticles were achieved in 120 h at 37 °C at pH 5.6. The nanometallic dispersions were characterized by surface plasmon absorbance measuring at 424 and 530 nm for Ag and Au nanoparticles, respectively. For bimetallic nanoparticles, absorption peak was observed at 509, 486 and 464 nm at 75:25, 50:50 and 25:75 (Au:Ag) mol concentrations, respectively. High-resolution transmission electron microscopy showed formation of nanoparticles in the range of 7–16 (silver), 6–10 (gold) and 17–25 nm (bimetallic 50:50 ratio). XRD analysis of the silver and gold nanoparticles confirmed the formation of metallic silver and gold. Fourier transform infrared spectroscopic measurements revealed the fact that the protein is the possible biomolecule responsible for the reduction and capping of the biosynthesized nanoparticles.

Introduction

One of the major developments in nanotechnology is the production and application of nanoparticles in biology. New methods to produce nanoparticles are constantly being studied and developed. Various physical and chemical synthesis methods, aimed at controlling the physical properties of the particles, are currently employed in the production of metal nanoparticles. Most of the methods are still in the developmental stage and various problems are often experienced with the stability of the nanoparticle preparations, control of the crystals growth and aggregation of the particles [1–4]. Nanoparticles of free metals have been extensively researched because of their unique physical properties, chemical reactivity and potential applications in catalysis [5], biological labelling [6], biosensing [7], drug delivery [8], antibacterial activity [9], antiviral activity [10], detection of genetic disorders [11, 12], gene therapy and DNA sequencing [13].

Concerning the biological application of nanoparticles it has been emphasized that methods of synthesis through biological systems viz, microorganisms including bacteria, yeasts, fungi [14, 15] and diatoms [16–18] synthesizing inorganic materials either intra or extracellularly would make the nanoparticles more biocompatible [19]. Plants used for synthesis of gold [20–24], silver [21–24] and bimetallic nanoparticles [19] have also been reported. Formation of phytochelation-coated CdS nanocrystallites in a marine phytoplanktonic alga *Phaeodactylum tricornutum* has been reported in response to Cd [25]. Konishi et al. [26] observed that Fe (III) reducing bacteria *Shewanella algae* can reduce Au (III) ions in anaerobic environments. Recently, there is a study on the extracellular biosynthesis of monodisperse gold nanoparticles using the marine alga, *Sargassum wightii* [27].

Various species of cyanobacteria and algae have been known to adsorb and take up heavy metal ions [28–31]. The carboxyl groups of dead algae (algae biomass) apparently bind to various metal ions [32], while intracellular polyphosphates as well as extracellular polysaccharides of live

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algae appear to participate in metal sequestrations [33, 34]. In this paper, we report the use of the highly structured physical algal cells of *Spirulina platensis* for the biosynthesis of pure metallic silver, gold and Au core/Ag shell nanoparticles by simultaneous reduction of aqueous $AgNO_3$ and $HAuCl_4$.

Spirulina is gaining more attention in the field of medical science because of its nutraceutical and pharmaceutical importance [35]. It has been demonstrated that small amounts of *Spirulina* reduced HIV-1 replication while higher concentration totally stopped its reproduction. Thus, the *Spirulina* mediated synthesis of Au, Ag and bimetallic nanoparticles communicated in this work gains its importance in its medical application.

Experimental procedure

Spirulina platensis was collected from a fresh water lake of Vellore in South India. Before experimentation, the biomass was washed thrice in deionized water to remove the unwanted materials. For the synthesis of silver nanoparticles, silver nitrate ($AgNO_3$) (Qualigens) and for gold nanoparticles, chloroauric acid ($HAuCl_4$) (Sd fine) were used as received. Double-distilled deionized water was used for all the experiments. Silver, gold and bimetallic nanoparticles formations were carried out by taking 500 mg of dry *S. platensis* (blue green alga) in a 250 mL Erlenmeyer flask with 10^{-3} M aqueous $AgNO_3$, $HAuCl_4$ and $HAuCl_4$:$AgNO_3$ with different molar concentrations (100, 25:75, 50:50, 75:25 and 100%) and incubated at room temperature. The pH was checked during the course of reaction and it was found to be 5.6. The bioreduction of pure $AgNO_3$, $HAuCl_4$ and $HAuCl_4$:$AgNO_3$ mixtures was monitored using UV–Vis spectroscopy at regular intervals. UV–Vis spectra were recorded as a function of time of reaction on a UV–Vis 1601 Schimadzu spectrophotometer operated at a resolution of 1 nm. The silver and gold nanoparticles synthesized using *S. platensis* were subjected to Fourier transform infrared (FT-IR) spectrum analysis to identify (if possible) whether the biomolecules are stabilizing and reducing agents. The complete reduction of Ag^+ and $AuCl_4^-$ ions by *S. platensis* was monitored using UV–Vis spectrum. The metal nanoparticles were centrifuged at 6,000 rpm for 15 min separately to isolate the silver and gold nanoparticles from free proteins. The silver and gold nanoparticle pellets obtained after centrifugation were redisperesed in water prior to FT-IR analysis. For FT-IR data, spectroscopy measurements were done on a Termo nicolet arater 300 instrument in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets. X-ray diffraction (XRD) measurements of the bioreduced silver and gold solutions drop-coated onto glass substrates were done on a Siefert X-diffractometer instrument operating at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. Samples for high-resolution transmission electron microcopy (HR-TEM) analysis were prepared by drop-coating Ag, Au and Au–Ag nanoparticles solutions on to carbon-coated copper TEM grids. The films on the TEM grids were allowed to stand for 2 min, following which, the extra solution was removed using a blotting paper and the grid was allowed to dry prior to measurement. HR-TEM analysis was performed using a JEOL 3010 instrument operated at an accelerating voltage of 120 kV.

Results and discussion

Addition of *S. platensis* biomass to 10^{-3} M aqueous $AgNO_3$ and $HAuCl_4$ solutions led to the appearance of yellowish brown and ruby red colour in solutions after 120 h of reaction, indicating the formation of silver and gold nanoparticles, respectively. These colours arise due to excitation of surface plasmon vibrations in the metal nanoparticles [36]. Figures 1 and 2 show the UV–Vis spectra recorded from the aqueous silver nitrate—*S. platensis* and auric chloride—*S. platensis* reaction medium, as a function of time of reaction. The silver surface plasmon resonance (SPR) band occurred at 424 nm and steadily

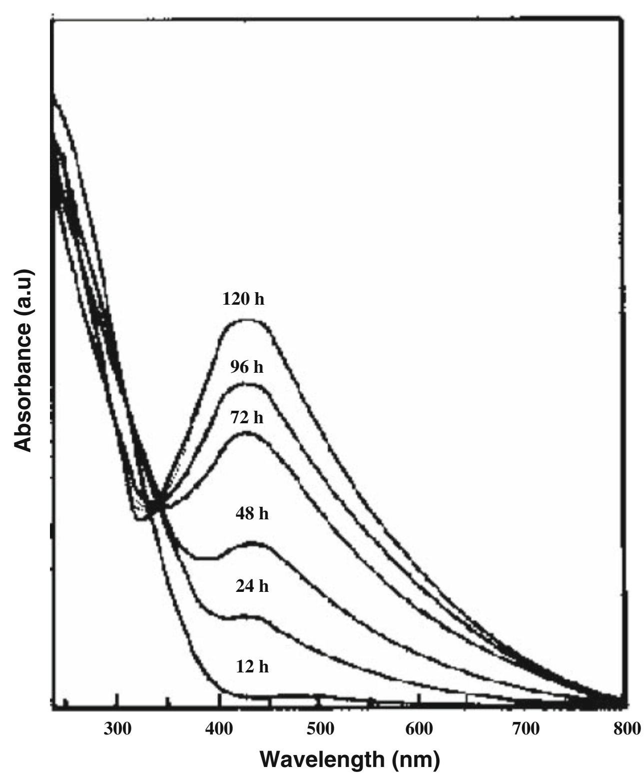

Fig. 1 UV–Vis spectra recorded as a function of time of reaction of aqueous solution of silver nitrate with *S. platensis*

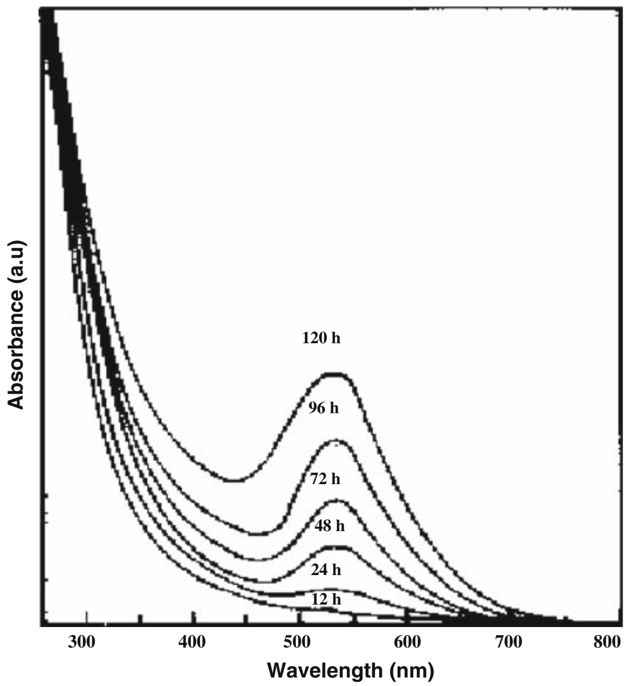

Fig. 2 UV–Vis spectra recorded as a function of time of reaction of aqueous solution of chloroauric acid with *S. platensis*

increased in intensity as a function of time of reaction without any shift in the peak wavelength. In gold ion reduction, the SPR band occurred at 530 nm. The *S. platensis* mediated syntheses of metal nanoparticles (silver and gold) were observed to be stable in solution even 3 months after their synthesis.

The silver nanoparticles synthesized using *S. platensis* showed strong bands at 1,651, 1,545 and 1,241 cm^{-1} (Fig. 3a). In gold nanoparticles, strong bands at 1,653, 1,541 and 1,242 cm^{-1} were observed (Fig. 3b). These bands correspond to the amide I–III bands of polypeptide/proteins, respectively. Curve (C) of Fig. 3 represents the FT-IR spectrum of the plain *S. platensis* showed peaks indicating the presence of proteins and which might have diffused from *S. platensis* in water and agree with those reported in the literature [37, 38]. The overall observation confirms the presence of protein in the samples of silver and gold nanoparticles. Reports on various species of cyanobacteria and algae having the ability to adsorb and take up heavy metal ions [28–31] can be accounted here. Interactions of transition metals appear due to be carboxyl groups, polyphosphate and amino acids of algae [28, 32, 39] and indeed polysaccharides in the cyanobacterial cells and water soluble polymer around the cells facilitate binding of metal ions [40]. It has been reported that possible metal binding site in cyanobacteria is through the formation of metallothioneins or metal binding proteins that bind metal ions as metal thiolate [28, 41]. Gole et al. [42] have stated that either through free amine groups or

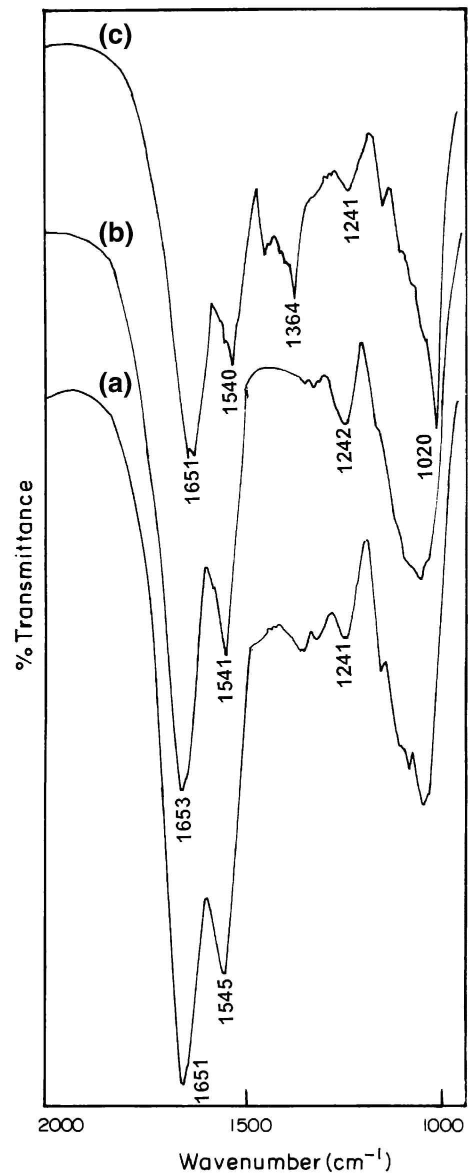

Fig. 3 FT-IR spectra of (**a**) silver nanoparticles synthesized by reduction of Ag^{+} ions by *S. platensis* (**b**) gold nanoparticles synthesized by reduction of $AuCl_4^{-}$ ions by *S. platensis* (**c**) plain *S. platensis*

cysteine residues, the protein can bind to gold nanoparticles that lead to the stabilization of gold nanoparticles by surface bound protein. It is therefore inferable that the bioreduction property of *S. platensis* lies in its protein.

Figure 4a, b shows the XRD patterns obtained for the silver and gold nanoparticles synthesized by single cell protein *S. platensis*. The presence of intense peaks of nanoparticles (111), (200) and (211) appeared which are indexed as crystalline silver and gold face centered cubic phase. The XRD pattern thus clearly shows that the silver and gold nanoparticles formed by the reduction of Ag^{+} and $AuCl_4^{-}$ ions by *S. platensis* are crystalline in nature.

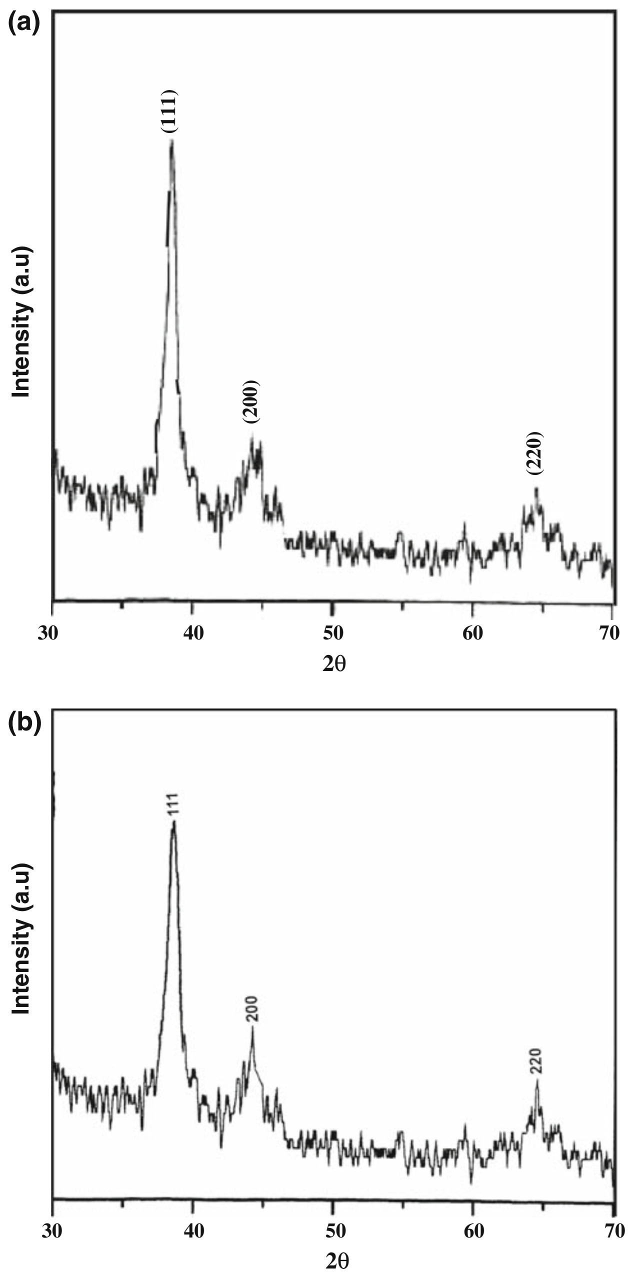

Fig. 4 XRD patterns of (**a**) silver and (**b**) gold nanoparticles synthesized by treating *S. platensis* with silver nitrate and chloroauric acid aqueous solution

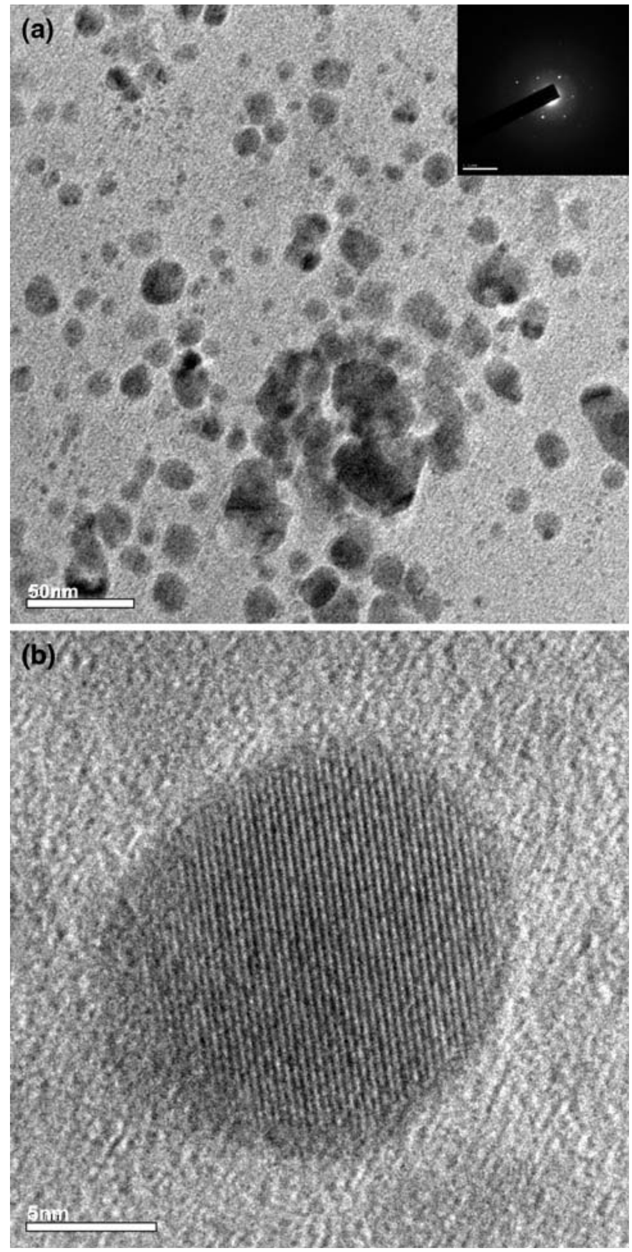

Fig. 5 (**a**, **b**) HR-TEM images of silver nanoparticles formed by reduction of Ag ions using *S. platensis*. The inset shows a typical SAED pattern of a silver nanoparticle

HR-TEM has provided further insight into the morphology and size details of the silver and gold nanoparticles. The HR-TEM images recorded from silver and gold nanoparticle solutions are shown in Figs. 5a, b and 6a, b. The silver and gold nanoparticles formed were predominantly spherical with diameters ranging from 7 to 16 and 6 to 10 nm, respectively.

Present observation lends support to a previous study where formation of spherical silver and triangular gold nanoparticles was reported using the *Aloe vera* plant extract [23]. Shiv et al. [22] demonstrated the neem leaf mediated synthesis of Ag, Au and bimetallic Au core–Ag shell nanoparticles. Further, silver and gold nanoparticles have been synthesized using bacteria, fungi, yeasts [14, 15] and amino acids [43]. There are also reports on the microbes-mediated synthesis of alloy nanoparticles, both extra and intracellularly [44, 45]. Recently, cyanobacterium-mediated platinum nanoparticles' synthesis by the reaction of filamentous *Plectonema boryamum* with platinum (IV) chloride complex has also been reported.

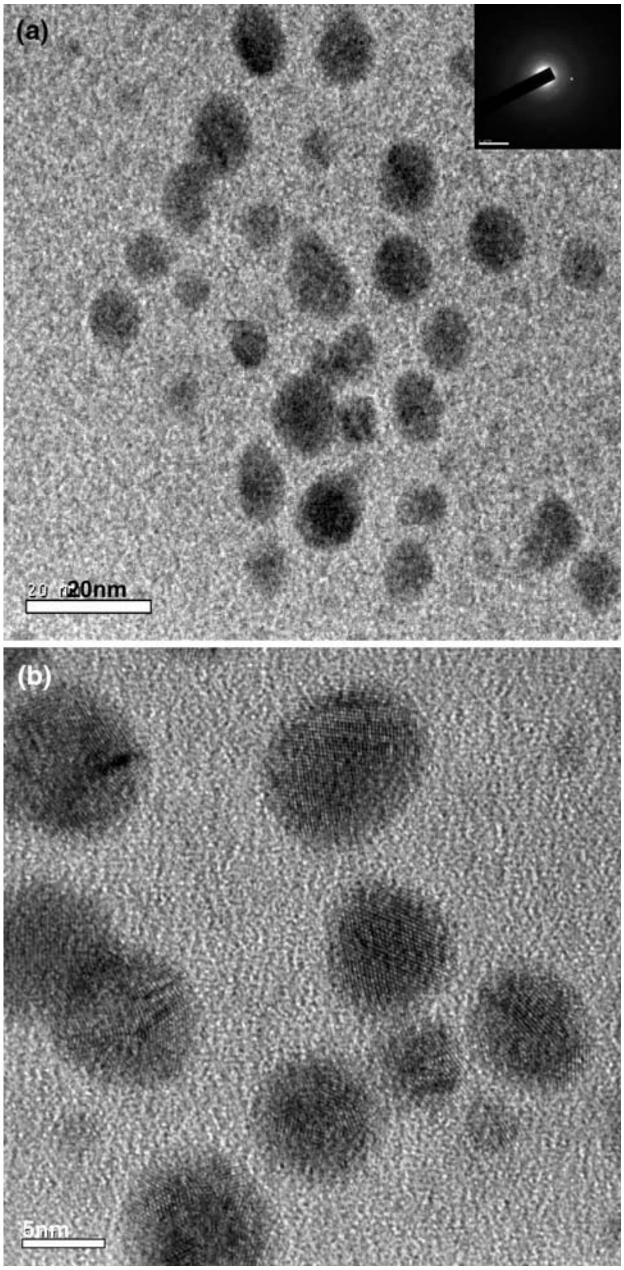

Fig. 6 (**a**, **b**) HR-TEM images of gold nanoparticles synthesized by reduction of $AuCl_4^-$ ions using *S. platensis*. The inset shows a typical SAED pattern of a gold nanoparticle

Biosynthesis of Au core–Ag shell nanoparticles using *S. platensis* was monitored in the UV–Vis spectra. When the $AuCl_4$ and $AgNO_3$ of different molar ratios (100, 25:75, 50:50, 75:25 and 100%) were exposed to *S. platensis* biomass, a gradual shift of the plasmon resonance was observed at 530, 509, 486, 464 and 424 nm, respectively, after the reaction for 120 h. Change of colour from purple to deep brown clearly indicated the formation of Au core–Ag shell nanoparticles. The gradual change of colour was found to be dependent on the rate of reduction of Ag^+ ions

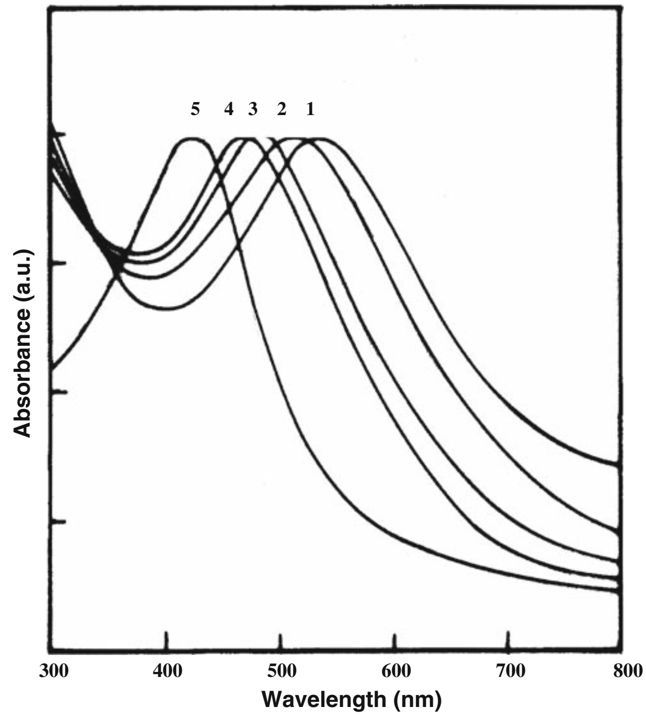

Fig. 7 UV–Vis absorption spectra of Au core–Ag shell nanoparticles with varying mole ratios with metal ions concentration 10^{-3} M. All the spectra have been normalized at their maxima (1) 100% Au, (2) 75:25% Au:Ag, (3) 50:50% Au:Ag, (4) 25:75% Au:Ag and (5) 100% Ag

by *S. platensis*. Figure 7 shows the corresponding UV–Vis absorption spectra. The observed gradual shift of SPR from 530 to 424 nm commensurated with the increasing Ag mole fraction. This can be seen in Fig. 8, in which the UV–Vis absorption peak position is plotted with respect to the amount of Au content in the prepared samples. Bimetallic nanoparticles synthesized by a simultaneous reduction of two different metal salts are usually claimed to possess a structure in which one of the two metals occupies the core of the particles and the other forms a surrounding shell [46]. Due to the difference in the reduction rate of the two different metal ions, composite bimetallic nanoparticles are assumed to have a core–shell structure, rather than forming a homogenous mixture [47].

FT-IR spectrum recorded from plain *S. platensis* (Fig. 9a) and bimetallic Au/Ag nanoparticles (Fig. 9b) are shown. The peaks observed at 1,653 and 1,546 cm^{-1} are identified as the amide I, II bands and are due to carbonyl stretch and –N–H stretch vibrations in the amide linkages of the proteins, respectively [42, 48–51]. The positions of these bands are close to that reported for native proteins [42, 48–51] and are in excellent agreement with that observed in gold colloid: pepsin bioconjucates [42]. The FT-IR results thus show that the secondary structure of the proteins is not affected as a consequence of reacting with the $AuCl_4^-$ ions or binding with the bimetallic nanoparticles. The band at

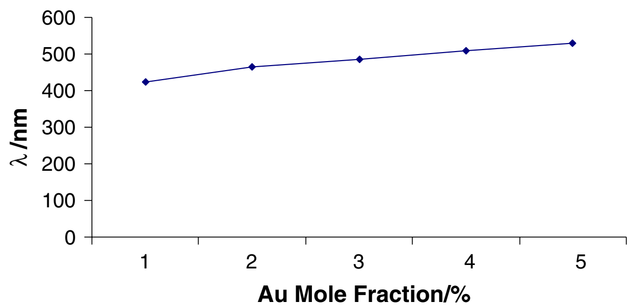

Fig. 8 Positions of surface plasmon bands plotted with respect to the mole fraction of Au atoms in bimetallic nanoparticles

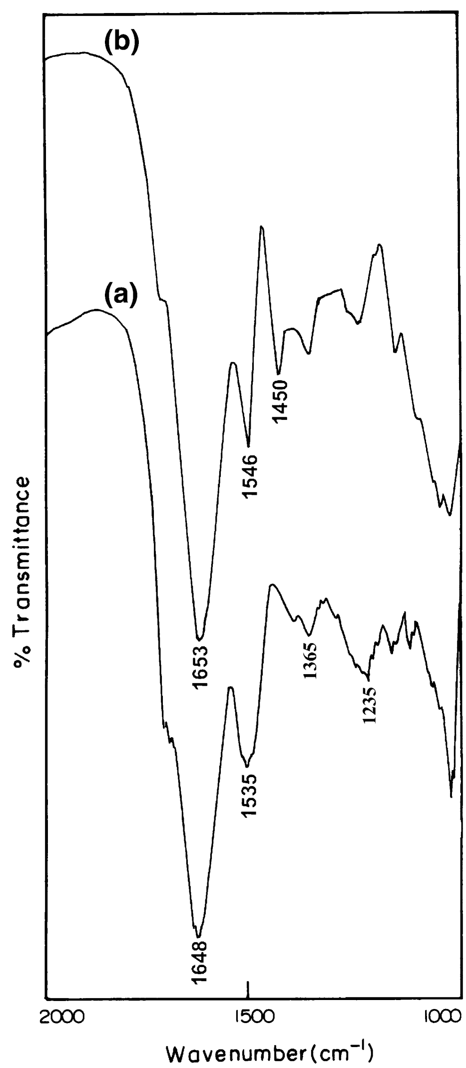

Fig. 9 FT-IR spectra of (**a**) plain *S. platensis* (**b**) bimetallic Au/Ag nanoparticles synthesized by simultaneous of Ag^+ and $AuCl_4^-$ ions by *S. platensis*

approximately 1,450 cm^{-1} assigned to methylene scissoring vibrations from the proteins in the solution [52]. Figure 10a-c shows HR-TEM images of bimetallic Au/Ag nanoparticles in the range of 17–25 nm, which were predominantly spherical. The rate of formation of gold nanoparticles was very much faster when compared with the silver nanoparticles formation, suggesting that the gold nanoparticles are formed first and the silver nanoparticles are formed later. It was interesting to note that the silver nanoparticles formed after the equilibration of the gold nanoparticles assembled on to the surface of the larger gold nanoparticles as evidenced by the formation of peculiar Au core–Ag shell structures. Several material scientists have synthesized various types of core–shell nanoparticles through physical and chemical methods [46, 53, 54]. Bimetallic nanoparticles, either as alloys or as core–shell structures, exhibit unique electronic, optical and catalytic properties [55–59] and have important biological applications in DNA sequencing [60]. Core–shell nanoparticles in particular have attracted significant topical interest since the addition of the second metal in the form of a shell provides control over the physical and chemical properties of the nanoparticles [61–63]. Various groups have demonstrated that properties such as SPR [64] and surface-enhanced Raman scattering associated with gold and silver nanoparticles [65, 66] can be tailored by synthesizing these nanoparticles in the core–shell configuration. The deposition of one metal on the preformed monometallic nanoparticle surface of other metals appears to be very effective and is desirable from the application point of view [67]. Senapati et al. [45] envisaged that chemical synthesis may still lead to the presence of some toxic chemical species adsorbed on the surface that may have adverse effects in medical applications. On this basis, the present study has its importance. Although therapeutic potential of *S. platensis* is promising, its bioreduction property of inorganic materials is yet to be exploited. There are good possibilities for the biomedical and biotechnological applications of bimetallic nanoparticles since they are synthesized extracellularly, quite stable and eco friendly in nature.

Conclusion

In this study, we have demonstrated the extracellular biosynthesis of silver, gold and bimetallic nanoparticles using *S. platensis*. The formation of these nanoparticles is aided by the polypeptide/proteins of the above alga. The characterization of Ag, Au and Au/Ag 1:1 ratio exposed to this blue green alga by UV, FT-IR, XRD and HR-TEM analyses to confirm the reduction and it is believed that protein might have played an important role in the stabilization of Ag, Au and Au/Ag bimetallic nanoparticles. The use of blue green alga offers a means of developing 'nanofactories' for production of metal nanoparticles and it is clear

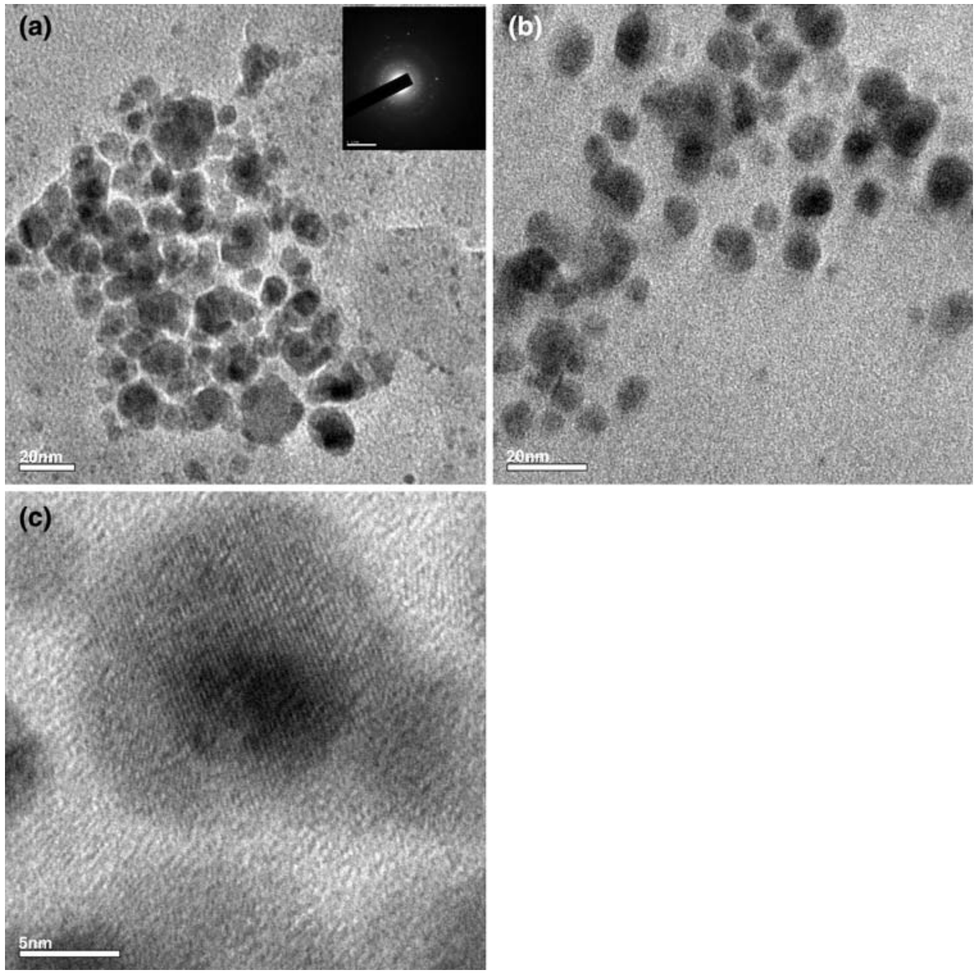

Fig. 10 (**a–c**) HR-TEM images of bimetallic Au/Ag nanoparticles synthesized by simultaneous reduction of Ag^{+} and $AuCl_4^{-}$ ions from an aqueous bimetallic solution of 1:1 molar ratio $AgNO_3$ and $HAuCl_4$. The inset shows a typical SAED pattern of a bimetallic Au core–Ag shell nanoparticle

that interaction of single-cell protein (*S. platensis*) with inorganic materials can benefit much from effectively interfacing nanoparticles and biology.

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