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RESEARCH PAPER

Extracellular biosynthesis of monodispersed gold nanoparticles by a SAM capping route

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Abstract Monodispersed gold nanoparticles capped with a self-assembled monolayer of dodecanethiol were biosynthesized extracellularly by an efficient, simple, and environmental friendly procedure, which involved the use of *Bacillus megatherium* D01 as the reducing agent and the use of dodecanethiol as the capping ligand at 26 °C. The kinetics of gold nanoparticle formation was followed by transmission electron microscope (TEM) and UV-vis spectroscopy. It was shown that reaction time was an important parameter in controlling the morphology of gold nanoparticles. The effect of thiol on the shape, size, and dispersity of gold nanoparticles was also studied. The results showed that the presence of thiol during the biosynthesis could induce the formation of small size gold nanoparticles (<2.5 nm), hold the shape of spherical nanoparticles, and promote the monodispersity of nanoparticles. Through the modulation of reaction time and the use of thiol, monodispersed spherical gold nanoparticles capped with thiol of 1.9 ± 0.8 nm size were formed by using *Bacillus megatherium* D01.

Keywords Gold nanoparticles · Extracellular biosynthesis · Monodispersity · Control of particle size · Self-assembled monolayer · Nanobiotechnology

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Introduction

In the past two decades, gold nanoparticles have potential applications in catalysis, chemical sensing, biosensing, and photonics areas, owing to their unique chemical, optical, and physical properties (Novak et al. 2000; Olofsson et al. 2003; Zayats et al. 2003; Comotti et al. 2006). Various particle morphologies of gold have been routinely synthesized by chemical and physical methods (Brust et al. 1994; Bethell et al. 1996; Carotenuto and Nicolais 2003; Schaaff et al. 1997; Schulz-Dobrick et al. 2005). The classic citrate reduction has been utilized extensively to generate water-soluble gold nanoparticles (Frens 1973). However, the nanoparticles are much larger in size (≥10 nm) with high polydispersity. One of the most popular methods for the preparation of gold nanopartilces capped with a self-assembled monolayer (≤5 nm) is a two-phase synthesis reported by Brust et al. (1994), which involves the use of tetraoctylammonium bromide as the phase transfer agent to transfer

tetrachloroaurate ($AuCl_4^-$) ions from aqueous solution to toluene, and subsequent reduction with aqueous sodium borohydride in the presence of alkanethiols. Recently, Xu et al. (2002) have developed a method, in which tetrabutylammonium bromide is used as the phase transfer agent and tetrahydrofuran is used as solvent. However, these two methods usually cause environment pollution due to the toxicity of the reagents used. As far as the synthesis of nanoparticles are concerned, there is a great and growing need to develop clean, nontoxic, and environmental friendly synthetic procedure. Biological methods have recently been considered as a possible environmental friendly nanofactories.

Gold nanoparticles of different sizes, ranging from 1 nm to 8 μm, and shapes, including spherical, octahedral, sub-octahedral, decahedral multiple twinned, icosahedral multiple twinned, irregular shape, nanotriangles/nanoprims, tetrahedral, hexagonal platelets, and nanorods (Gardea-Torresdey et al. 1999; Canizal et al. 2001; Karthikeyan and Beveridge 2002; Ahmad et al. 2003a, b; Senapati et al. 2005; Chandran et al. 2006; Lengke et al. 2006; Lengke and Southam 2006), have been synthesized either intra- or extra-cellularly by using microorganisms such as bacteria and fungi (Mukherjee et al. 2001; Mukherjee et al. 2002; Nair and Pradeep 2002; Ahmad et al. 2003b; Shankar et al. 2003), algae (Greene et al. 1986), yeasts (Slocik et al. 2005), and plant extracts (Shankar et al. 2004). Unfortunately, greater control over size, shape, and monodispersity of gold nanoparticles formed by using microorganisms has hitherto remained little successful. Furthermore, that the nanoparticles can directly be synthesized extracellularly in the aqueous medium has greater commercial application. Recently, Ahmad et al. (2003b) has shown that fairly monodispersed gold nanoparticles capped with proteins ($\sim$8 nm) may be synthesized extracellularly by reaction of aqueous chloroaurate ions with the alkalothermophilic actinomycete, *Thermomonospora* sp. Shankar et al. (2004) have reported the synthesis of a high percentage of thin, flat, single-crystalline gold nanotriangles by using the lemongrass plant. Very recently, Rai et al. (2006) have demonstrated that the presence of halide ions and the modulation of temperature can control the morphology of biologically synthesized gold nanotriangles using lemongrass leaf extract.

In previous studies on the recovery of precious metals, we have screened *Bacillus megatherium* D01 from the soil of mining area. The properties of Au^{3+} adsorption and reduction by *Bacillus megatherium* biomass have been investigated. Complete reduction of aqueous $AuCl_4^-$ ions occur after nearly 2 h of reaction, indicating that it is a fast process, and *Bacillus megatherium* biomass has a relatively strong ability of adsorbing and reducing Au^{3+} (Fu et al. 1999). It has been reported that the mechanism of colloidal gold fixation by bacillus cells is dependent on the cell surface and involves a number of functional groups (provided by proteins and carbohydrates) (Savvaidis et al. 1998). We speculate that the possible mechanism of Au^{3+} adsorption and reduction by *Bacillus megatherium* biomass involves the hydroxyl group of saccharides and the ionized carboxyl group of amino acid residues on the cell wall as the sites for Au^{3+} binding, and the hydrolysates of the polysaccharides, serving as the electron donor, in situ reducing the Au^{3+} to Au^0 (Lin et al. 2004).

In this article, we extend our previous study on bioaccumulation of gold using *Bacillus megatherium*, and describe an extracellular synthetic method for the preparation of monodispersed gold nanoparticles capped with a self-assembled monolayer (SAM) of dodecanethiol, via chemical reaction of the biomass with aqueous $AuCl_4^-$ ions. A detailed description of the biomass contacted with aqueous $AuCl_4^-$ ions for different intervals of time is given in the absence and presence of thiol. We believe that the modulation of reaction time and the use of thiol plays an important role in controlling the size, shape, and dispersity of gold nanoparticles.

Experimental

Chemicals

Dodecanethiol ($C_{12}S$, $\geq$98%, Alfa Aesar). All other reagents were acquired from standard sources and used as received. Water was purified with a Milli-Q water system instrumentation.

Bacterial cultivation and biomass preparation

The *Bacillus megatherium* biomass, isolated from the soil of mining areas, was cultured in a water solution containing beef gels, peptone, and salt etc. The cultures were harvested by centrifugation (3500 rpm/

min, 15 min). The cell pellets were subsequently washed 3 times with ultrapure water, dried at 60 °C and then ground in a mortar and pestle. The dried dead biomass was stored in capped bottles in a dryer.

Bacterial experiments

The effect of reaction time on the morphology of gold nanoparticles was investigated by carrying out the reaction of 100 mg of the *Bacillus megatherium* biomass (dry weight) with 100 mL of aqueous solution containing 200 μg/mL $HAuCl_4$. The experiment was conducted on a rotary shaker at 200 rpm/min, pH 3.2 and 26 °C for a period of 9 h. The bioreduction of the $AuCl_4^-$ ions in solution was measured with time by transmission electron microscopy (TEM) and UV-vis spectroscopy.

To study the effect of dodecanethiol on size, shape, and dispersity of gold nanoparticles, 100 mg of the biomass was added to 100 mL of ethanol solution containing 0.05 M dodecanethiol, sonicated for 30 min at 26 °C. Then, 2 mL of aqueous solution containing 10 mg/mL $HAuCl_4$ was added to the above mixture, followed by continuously shaking on a rotary shaker (200 rpm/min) at 26 °C. The biotransformation was monitored by the TEM analysis of the reaction mixture as a function of time.

For the synthesis of monodispersed gold nanoparticles, the dried biomass was mixed with a solution of $HAuCl_4$ in ultrapure water. The mixture containing 100 mg Au^{3+}/L and 1 g dried biomass/L was incubated on a rotary shaker at 200 rpm/min, pH 3.2 and 26 °C for 10 min, centrifuged at 3000 rpm/min and 26 °C for 10 min. The mixture was filtered through a 0.22 μm pore-size cellulose acetate filter membrane to block the passage of the biomass and adsorbed Au^{3+} ions, and the filtrate was assayed using atomic absorption spectroscopy (AAS) for the determination of the residual Au^{3+} concentration, the calculation of the efficiency (%) and the capacity (mg/g) of Au^{3+} biosorption. Subsequently, 30 mL of ethanol solution containing 0.135 M dodecanethiol was quickly added to the biomass containing adsorbed Au^{3+} ions. The mixture was shaked at 200 rpm/min at 26 °C for 4 h. The bio-transformed product was collected by separating the *Bacillus megatherium* biomass from the reaction mixture by filtration, and then characterized using TEM, UV-vis spectroscopy and X-ray photoelectron spectroscopy (XPS).

Characterization techniques

Transmission electron microscopic (TEM) measurement of the gold nanoparticles synthesized by using the *Bacillus megatherium* biomass was carried out using a JEM-2100HC electron microscope (JEOL, Japan) operated at 120 kV. Samples for the TEM measurement were prepared by drop coating the nanoparticles onto standard carbon-coated (200–300 Å) Formvar films on copper grids (400 mesh) placed on a clean Teflon piece, and the grids were allowed to dry prior to measurement. Size distributions of gold nanoparticles were measured from enlarged TEM image photographs for 150 individual nanoparticle images.

UV/vis spectroscopic measurement of the gold nanoparticles synthesized was carried out on a Cary 5000 spectrometer (Varian, USA) operated at a resolution of 1 nm.

X-ray photoelectron spectroscopy (XPS) measurement was preformed using a Quantum 2000 XPS spectrometer (Physical Electronics, USA) with monochromatic Al-Kα (1486.6 eV) radiation. The binding energy scale was corrected for surface charging by considering the C 1s peak as a reference at 285.0 eV.

The residual Au^{3+} concentration without adsorption by the biomass was determined by a SOLAAR

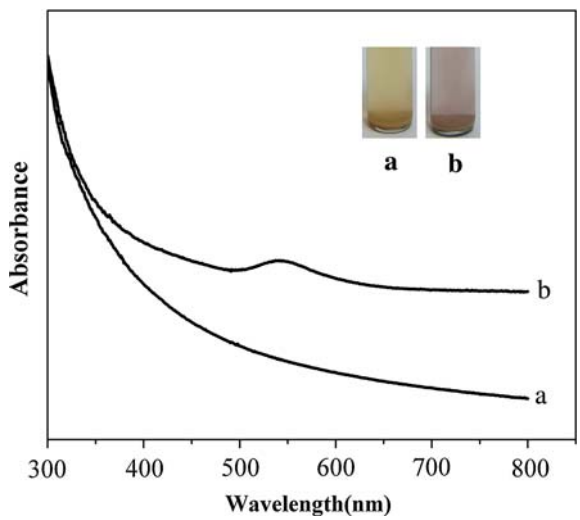

Fig. 1 UV/vis spectra recorded from the solution of the *Bacillus megatherium* biomass before (curve a) and after (curve b) exposure to aqueous $AuCl_4^-$ ions for 9 h. The inset shows two bottles with the *Bacillus megatherium* biomass before (**a**) and after (**b**) reaction with $AuCl_4^-$ ions for 9 h. A color version of the inset can be seen

M6 atomic absorption spectroscopy (AAS, Thermo Electron, England).

Results and discussion

The inset of Fig. 1 shows two bottles with the *Bacillus megatherium* biomass before (a) and after (b) reaction with $AuCl_4^-$ ions for 9 h. The biomass has a yellow color before reaction with the $AuCl_4^-$ ions (a). After the *Bacillus megatherium* biomass is exposed to the aqueous solution of $HAuCl_4$ for 9 h, the solution changes color from yellow to vivid pink (b). The appearance of the pink color clearly indicates the formation of gold nanoparticles in the reaction mixture. Upon filtration, it is observed that the biomass is

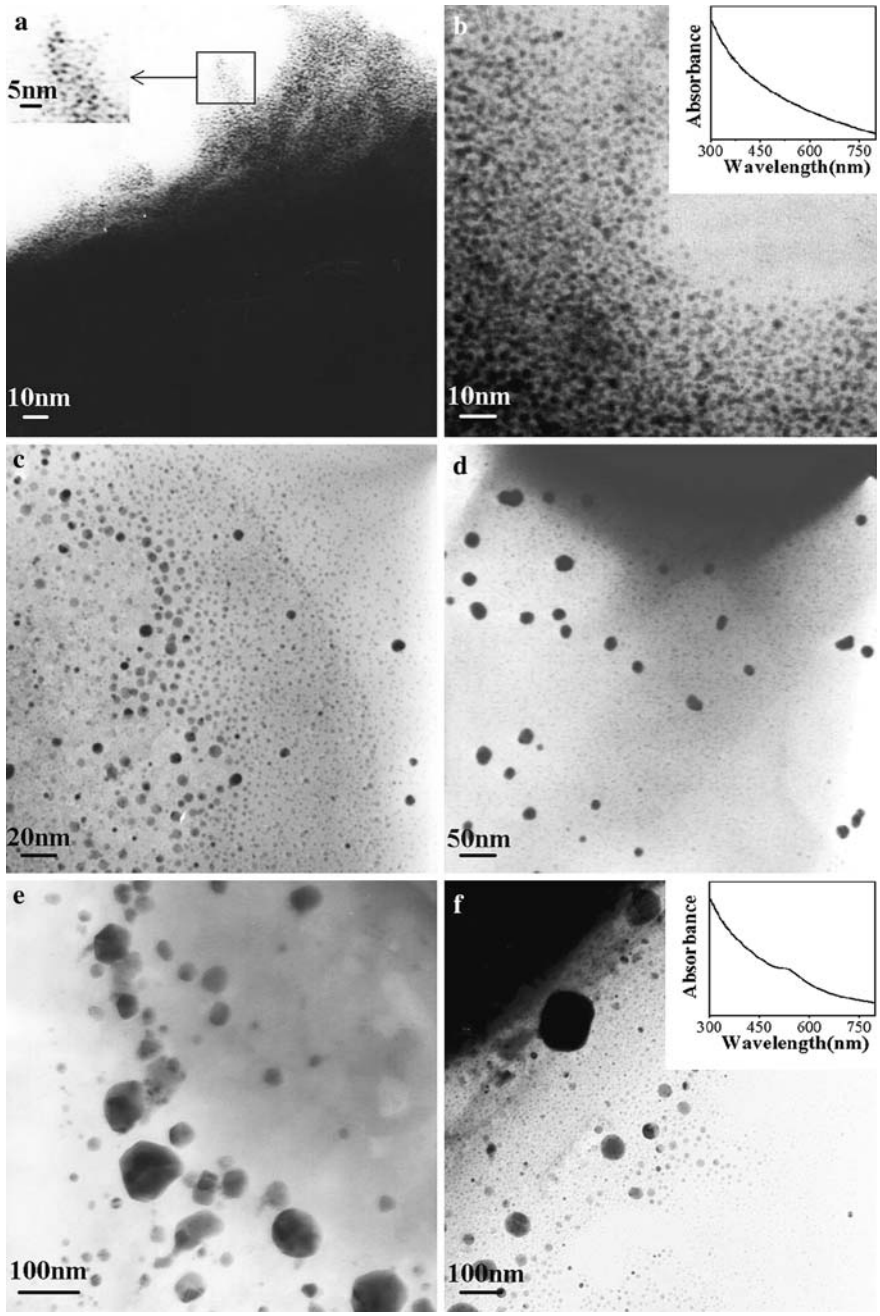

Fig. 2 TEM images recorded from aqueous $AuCl_4^-$ ions—*Bacillus megatherium* D01 reaction solution as a function of reaction time in the absence of thiol. The inset in b shows the UV-vis spectrum recorded from the reaction solution after 30 min of reaction. The inset in f shows the UV-vis spectrum recorded from the reaction solution after 6 h of reaction. (**a**) 10 min; (**b**) 30 min; (**c**) 1 h; (**d**) 3 h; (**e**, **f**) 6 h

still yellow and the aqueous solution is pink. This indicates that the aqueous solution contains the gold nanoparticles, and the reduction of the $AuCl_4^-$ ions occurs extracellularly. The corresponding UV/vis absorption spectra are shown in Fig. 1. The UV/vis spectrum shows no evidence of absorption in the range 300–800 nm for the as-harvested *Bacillus megatherium* biomass (curve a). After the *Bacillus megatherium* biomass is exposed to the aqueous solution of $HAuCl_4$ for 9 h, the reaction solution shows a distinct broad absorption at ~540 nm (curve b). The presence of the broad resonance indicates the aggregation of the gold nanoparticles in the solution.

The TEM images of the *Bacillus megatherium* biomass contacted with aqueous $AuCl_4^-$ ions in the absence of dodecanethiol for different intervals of time are shown in Fig. 2. At a very early stage of reaction (10 min, Fig. 2a), small spherical gold nanoparticles are observed on the cell wall and at the interface between the cell wall and the bulk solution. The particle size distribution of the gold particles show that the average size of the spherical particles are smaller than 2 nm at the early stage of reaction (Fig. 3a). After 30 min reaction time, the particle size and shape of the gold nanoparticles have not obviously changed, and well-separated

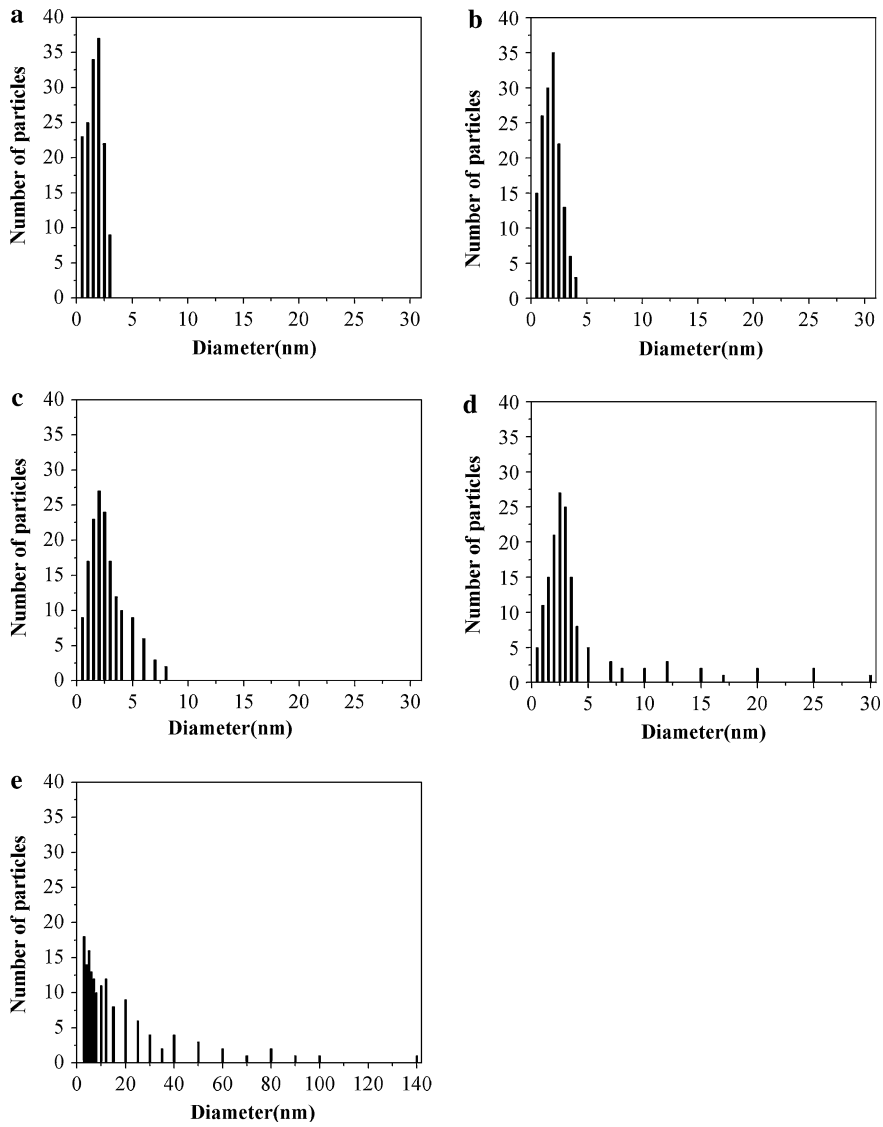

Fig. 3 Gold size distributions corresponding to Fig. 2, panels **a**–**e**, respectively

nanoparticles with occasional aggregation (<2.5 nm) can clearly be seen in the bulk solution (Figs. 2b, 3b). The UV-vis spectrum recorded from the reaction solution shows no discernible absorption in the range 300–800 nm (inset in Fig. 2b). After 1 h of reaction, there are small amounts of larger spherical gold particles (~5–8 nm) in the bulk solution (Fig. 2c). The gold nanoparticles do not have a uniform size, but instead exhibit a broad distribution (~0.5–8 nm) (Fig. 3c). After 3 h of reaction, the gold particles formed are mostly spherical and irregular in shape (Fig. 2d). The size distribution of gold nanoparticles (Fig. 3d) show that the majority of the gold nanoparticles are in a relatively narrow size range of ~1–3 nm, and some larger nanoparticles (~9–30 nm) are also found. The particles show a much broader size distribution. After 6 h of reaction, the gold nanoparticles are formed both on the cell wall and in the solution as well as in the cytoplasmic membrane, and the number of gold nanoparticles are clearly higher in the cell wall than in the cytoplasmic membrane (Fig. 2e, f). Some larger hexagonal, triangular, spherical, and anisotropic gold particles are observed in addition to some smaller spherical particles. The UV-vis spectrum for the gold nanoparticles synthesized by using the *Bacillus megatherium* biomass shows a broad absorption at ~540 nm (inset in Fig. 2f). The broad absorption band indicates the aggregation of the gold nanoparticles. The size distribution histogram of the gold particles is shown in Fig. 3e. It can be clearly seen that the size distribution apparently shifts to a larger value (~3–140 nm), and no particles with diameter below 3 nm are seen after 6 h of reaction. Based on data presented above, it can be found that in the initial time of 1 h reaction time, the particle size and shape of the gold nanoparticles do not seem to undergo any noticeable change. After 1 h reaction time, with increasing reaction time, the percentage of spherical particles goes down and is accompanied by an increase in the number of hexagonal, triangular, and anisotropic particles. Furthermore, the particle size goes up with increasing

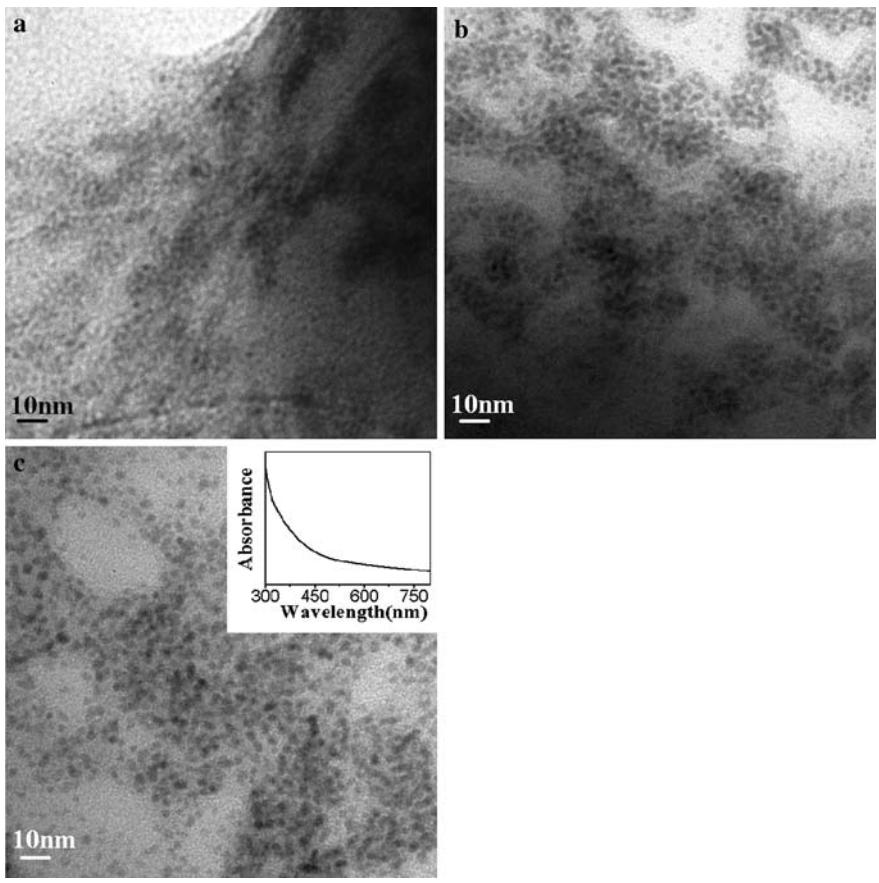

Fig. 4 TEM images recorded from aqueous $AuCl_4^-$ ions—*Bacillus megatherium* D01 reaction solution as a function of reaction time in the presence of thiol. The inset in c shows the UV-vis spectrum recorded from the reaction solution after 6 h of reaction. (**a**) 10 min; (**b**) 1 h; (**c**) 6 h

reaction time. Thus, it is clear that reaction time is an important parameter in controlling the morphology of the gold nanoparticles formed by reduction of the $AuCl_4^-$ ions with the *Bacillus megatherium* biomass. In consequence, spherical gold nanoparticles (<2.5 nm) could be obtained via the modulation of reaction time.

The TEM measurements of gold nanoparticles as a function of reaction time of aqueous $AuCl_4^-$ ions with the *Bacillus megatherium* biomass in the presence of dodecanethiol were carried out. At a very initial stage of reaction (after 10 min, Figs. 4a, 5a), the spherical nanoparticles of gold ranging in size from 0.5 nm to 2.5 nm are seen on the cell wall and at the interface between the cell wall and the bulk solution. After 1 h of reaction, a large population of the spherical gold particles with occasional aggregation is formed on the cell wall and in the solution (Fig. 4b). A relatively narrow size range of approximately 1–3 nm is observed for the gold nanoparticles, as shown in Fig. 5b. The particle size of the gold nanoparticles obviously decreases in comparison with that of the nanoparticles formed by reaction of $AuCl_4^-$ with the *Bacillus megatherium* biomass in the absence of thiol for 1 h (Figs. 2c, 3c). After 6 h of reaction, the gold nanoparticles remain to be predominantly spherical in shape, densely populating both the cell wall and the solution (Fig. 4c). Some discrete nanoparticles can clearly be discerned in the bulk solution. The UV-vis spectrum reveals that the surface plasmon (SP) resonance band of the gold nanoparticles is not seen (inset in Fig. 4c). This indicates that the size of the gold nanoparticles synthesized by using the *Bacillus megatherium* biomass in the presence of thiol is still very small after 6 h of reaction. The size distribution of particles is shown in the histogram in Fig. 5c. It can be seen that the diameter of the majority of the gold particles is in the range of ~1–3 nm. The gold nanoparticles obtained have much smaller size compared to those synthesized using the biomass in the absence of thiol for 6 h (Fig. 2e, 3e). Furthermore, a much higher population of the spherical nanoparticles with moderate monodispersity is observed. Thus, a significant improvement on size, shape, and monodispersity has been achieved using dodecanethiol as the capping ligand. Consequently, it can be concluded that by addition of thiol into the reaction medium, small size and spherical gold nanoparticles with moderate monodispersity can be formed by using the *Bacillus megatherium* biomass.

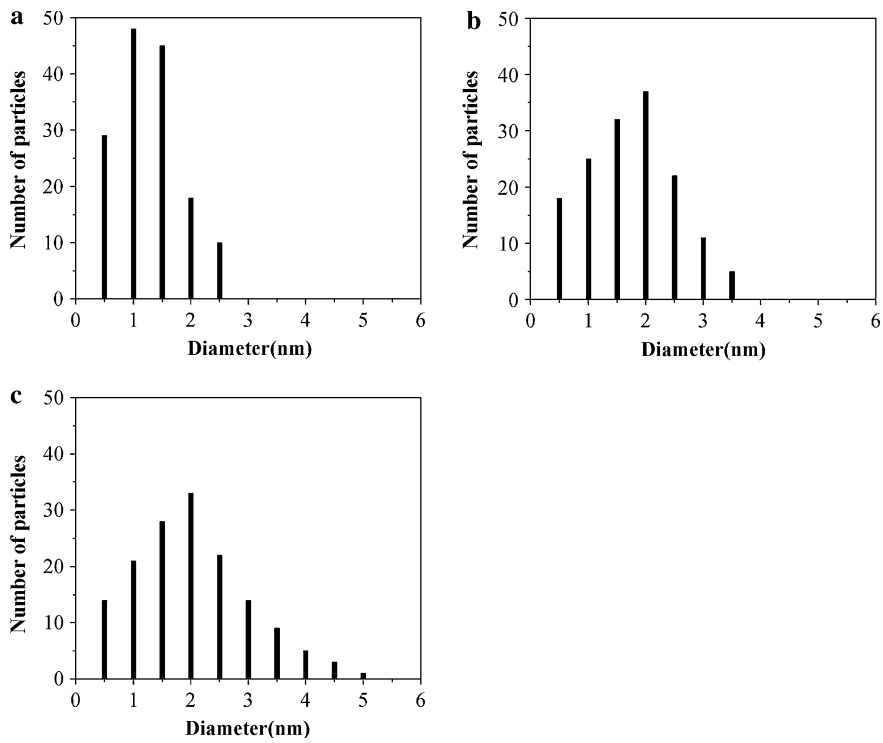

Fig. 5 Gold size distributions corresponding to Fig. 4, panels **a**–**c**, respectively

As noted in the *Introduction*, although other studies have described gold nanoparticles biosynthesized by using microorganisms, fabrication of monodispersed gold nanoparitlces (<5 nm) has so far been unsuccessful. If biological processes are a viable alternative to the current chemical methods for the production of gold nanoparticles, then greater control over particle size, shape, and monodispersity would be required. Previous studies by Schaaff et al. (1997) and Brust et al. (1994) have demonstrated that alkanethiols are effective capping agents to restrict the growth of the nanoparticles by effectively passivating their surfaces, and the addition of alkanethiols to aqueous $HAuCl_4$ solution ultimately results in the formation of the polymeric AuSR compounds by a reaction of the type

$$AuCl_4^- + 3RSH \rightarrow AuSR + RSSR + (acid + salt) \quad (1)$$

In the present study, the gold nanoparticles were formed by reaction of aqueous $AuCl_4^-$ ions with the *Bacillus megatherium* biomass for 4 h in the presence of dodecanethiol, and then were separated from the reaction mixture by filtration. Figure 6a shows a representative TEM image of the separated gold nanoparticles capped with a dodecanethiolate monolayer shell. It can be seen that the shape of the gold nanoparticles is almost spherical and there is no aggregation of the nanoparticles. The particle size histogram derived from the nanoparticles is shown in Fig. 6b. A relatively narrow size range of approximate 1.5–2.5 nm is observed, confirming that the gold nanoparticles biosynthesized by using the *Bacillus megatherium* biomass are well monodispersed. The average size of the gold nanoparticles is 1.9 ± 0.8 nm. Figure 7 shows a UV/vis absorption spectrum of the gold nanoparticles synthesized by using the *Bacillus megatherium* biomass in the presence of thiol. The SP band intensity of gold nanoparticles is undetectable. The loss of the SP band for sufficiently small gold core is attributed to "quantum size effect" (Hostetler et al. 1998). It is observed that the gold nanoparticles are stable and do not show signs of aggregation over a period of several weeks (as determined by TEM, data not shown). The binding energy and the valence state of gold in the nanoparticles were determined by XPS. The binding energies of the doublet for Au $4f_{7/2}$ (84.0 eV) and Au $4f_{5/2}$ (87.7 eV) shown in Fig. 8 are characteristic of Au^0.

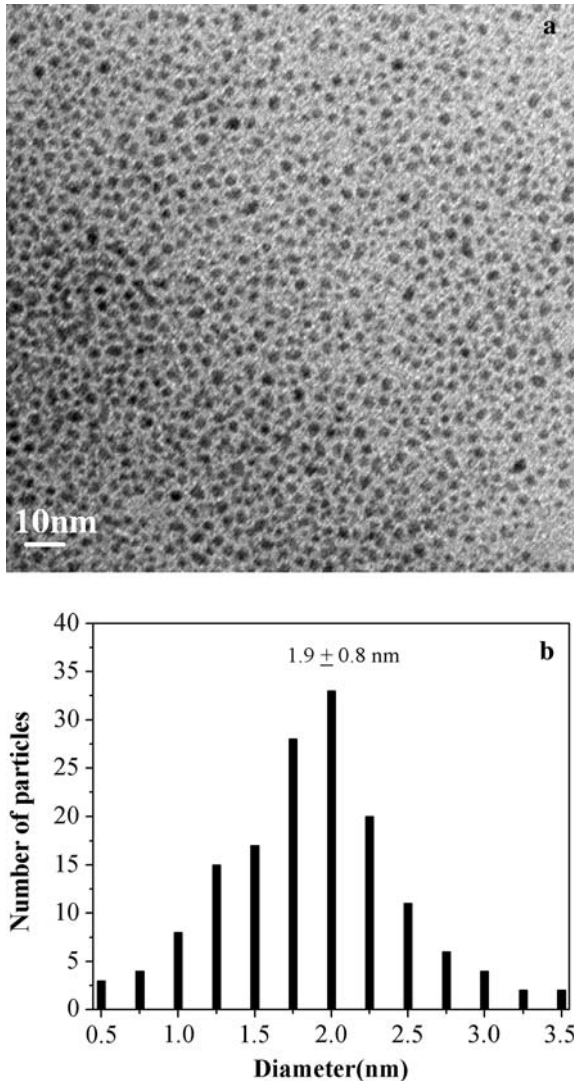

Fig. 6 A TEM image (**a**) and a size distribution histogram (**b**) of gold nanoparticles capped with a dodecanethiolate monolayer shell synthesized by using the *Bacillus megatherium* D01

Finally, in the process of monodispersed gold nanoparticles synthesized, the residual Au^{3+} concentration without biosorption by the biomass was determined by AAS. When the initial concentration of Au^{3+} is 100 mg/L, the efficiency and the capacity of biosorption of Au^{3+} by the biomass reach as high as 99.6% and 111.7 mg Au^{3+}/g dry biomass, respectively. The residual amount of Au^{3+} in the solution is 0.4 mg/L. This indicates that the *Bacillus megatherium* biomass has a relatively strong ability of adsorbing Au^{3+}.

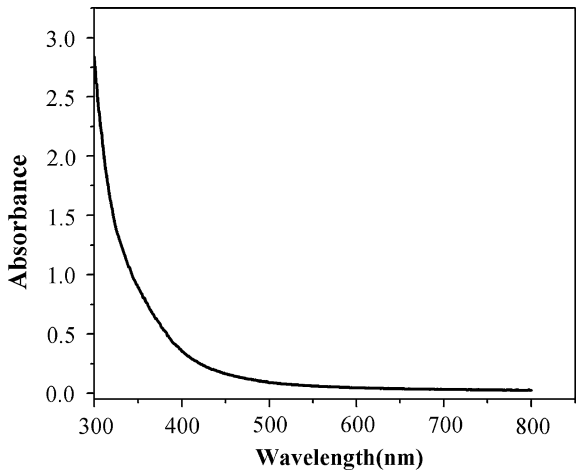

Fig. 7 The UV/vis spectrum of gold nanoparticles capped with a dodecanethiolate monolayer shell synthesized by using the *Bacillus megatherium* D01

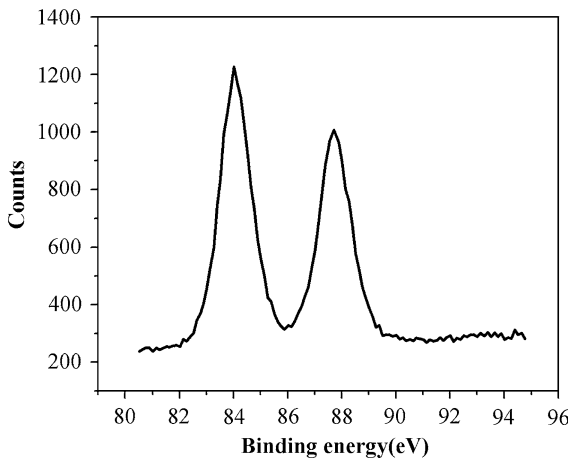

Fig. 8 Au 4f XPS spectrum of gold nanoparticles synthesized by using the *Bacillus megatherium* D01

Conclusion

In conclusion, monodispersed spherical gold nanoparticles capped with a SAM of thiol of 1.9 ± 0.8 nm size have been synthesized extracellularly by reaction of aqueous $AuCl_4^-$ ions with *Bacillus megatherium* D01. The size, shape, and monodispersity of gold nanoparticles can be easily controlled by the modulation of reaction time and the use of thiol. The advantages of this route lie in its simplicity, the low toxicity of the reagents used, the preparation of small size nanoparticles with good monodispersity, and the high purity of the products. In addition, it has been shown that other noble metals, such as Ag, Pt, Pd, could be synthesized using the biomass. Consequently, this procedure can further be extended for the synthesis of composite nanoparticles with different ligands such as Au–Ag, Ag–Pt, Au–Pt.

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