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A sunlight-induced method for rapid biosynthesis of silver nanoparticles using an *Andrachnea chordifolia* ethanol extract

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Abstract In this study a sunlight-induced method for rapid synthesis of silver nanoparticles using an ethanol extract of *Andrachnea chordifolia* is described. The silver nitrate solutions (1 mM) containing the ethanol extract of *Andrachnea chordifolia* were irradiated by both sunlight radiation and by sunlight radiation passed through different colored filters (red, yellow or green). The smallest size of silver nanoparticles was obtained when a silver ion solution was irradiated for 5 minutes by direct sunlight radiation. Further examination of the shape and size and of the surface chemistry of these biogenic silver nanoparticles, which were prepared under sunlight radiation, was carried out using transmission electron microscopy and infrared spectroscopy, respectively. Transmission electron microscopy images show spherical particles with an average size of 3.4 nm. Hydroxyl residues were also detected on the surface of these biogenic silver nanoparticles fabricated using plant extract of *Andrachnea chordifolia* under sunlight radiation. Our study on the reduction of silver ions by this plant extract in darkness shows that the synthesis process can take place under dark conditions at much longer incubations (48 hours). Larger silver polydispersed nanoparticles ranging in size from 3 to 30 nm were obtained when the silver ions were treated with the ethanol extract of *Andrachnea chordifolia* under dark conditions for 48 hours.

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1 Introduction

Among the different fabrication methods, green synthesis of metal nanoparticles (NPs) is preferred due to its cost effectiveness and environmental compatibility [1–6]. There are many different reports on the biogenesis of silver NPs using plant extracts or their fractions [7–10]. Some reducing ingredients, such as polyphenolic compounds, have been known to reduce metal ions into their corresponding NP forms [11, 12]. However, the synthesis of silver nanoparticles using plant extracts usually takes a significantly longer time [13, 14]. Recently, we showed that visible light radiation can significantly prompt the synthesis of silver NPs using a culture supernatant of the *Klebsiella pneumonia* bacterium [15]. During our screening program on the various Pakistani plant extracts for synthesis of silver NPs, we found that a plant extract prepared from *Andrachnea chordifolia* (Euphorbiaceae) can be used for rapid synthesis of silver NPs under bright conditions. In this paper, a sunlight photobiochemical method for rapid synthesis of silver NPs using an ethanol extract of *Andrachnea chordifolia* has been investigated.

2 Materials and methods

2.1 Plant extracts

The aerial parts of *Andrachnea chordifolia* were collected from Kaghan valley, Shogran, K.P.K., Pakistan at 6000 ft

above sea level on 6th September 2007. Taxonomic identification of the plant was done by Mr. Shahid Farooq, Principal Scientific Officer, Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratories, K.P.K., Peshawar. A voucher specimen (No. PES7852) was deposited at the herbarium of PCSIR Laboratories, Peshawar. The plant material was dried in shade under controlled conditions. The dried plant was ground into powder with a heavy-duty grinding machine. The powdered plant material (100 g) was exhaustively extracted at room temperature with 95% ethanol using the percolation method. The extract obtained was evaporated by a vacuum rotary evaporator while keeping the temperature below 40°C. A gummy residue (6.4 g, 6.4%) was obtained as the crude extractive. A stock solution (10 mg ml^{-1}) was prepared in ethanol for further tests. All experiments were performed on the basis of the dry mass of the concentrated extracts.

2.2 Rapid light-induced synthesis and characterization of silver nanoparticles

Silver nitrate was purchased from Merck, Darmstadt, Germany. Aqueous silver nitrate solution (10^{-3} M) was added separately to the reaction vessel containing the ethanol extract of *A. chordifolia* (1.5% v/v), and the resulting mixture was separately allowed to stand for 5 min under bright conditions of sunlight radiation (1800 µmol m^{-2} s^{-1}) and under dark conditions in a sealed cabinet. The irradiated sunlight mixtures' densities were recorded using a DO9721K Datalogger Photo Radiometer. Other reaction samples were also produced using the above-mentioned protocol and incubated for 5 min under artificial bright conditions with sunlight radiation passed through one of three different colored photography filters (red, yellow or green). The free plant extract silver nitrate solution (1 mM) was used as a control sample and placed under light conditions. The photoreduction of the Ag^{+3} ions in the presence of the ethanol extract of *A. chordifolia* in the solutions was monitored after 5 minutes by sampling the aqueous component (2 ml) and measuring the UV–visible spectrum of the solutions. All samples were diluted three times with distilled water and the UV–visible spectra of these samples were measured on a Labomed Model UVD-2950 UV–VIS Double Beam PC Scanning Spectrophotometer, operated at a resolution of 2 nm. Furthermore, particle-size distributions and surface zeta potentials of the prepared silver NPs were obtained using a Zetasizer Nano ZS (Malvern Instruments, Southborough, UK). Also, the shapes and sizes of the silver NPs in selected colloids were further studied with transmission electron microscopy (model EM 208 Philips).

2.3 The surface chemistry of silver nanoparticles prepared under sunlight radiation

An aliquot of the prepared silver colloid (10 ml), which was fabricated from the ethanol extract of *A. chordifolia* under bright conditions of sunlight radiation, was centrifuged for 30 min at 22000 × g and the produced pellet was washed with distilled water. The process of centrifugation and redispersion in distilled water was repeated three times to ensure better separation of any free entities from the metal NPs. The washing procedure was repeated with acetone and the purified pellets were then dried at room temperature under vacuum conditions and subjected to Fourier transform infrared spectroscopy (FTIR, Nicolet 550).

3 Results and discussion

3.1 Synthesis of silver nanoparticles

This study reports a sunlight-induced biogenic method for rapid preparation of silver NPs. An ethanol extract prepared from *A. chordifolia* was used for the first time for rapid biosynthesis of silver NPs under bright conditions with direct sunlight radiation or filtered sunlight irradiation. All prepared silver colloids were characterized by UV–visible spectroscopy. The technique outlined above proved to be very useful for the analysis of the NPs [16–18]. The inset in Fig. 1 shows test tubes containing the prepared silver colloids after irradiation by direct sunlight (A), and green (B), yellow (C) and red (D) filtered light radiations. No yellowish-brown color change in the reaction vessel nor a strong plasmon resonance peak were observed for the silver nitrate solution, which was mixed with the ethanol extract of *A. chordifolia* and irradiated by red light radiation for 5 min (test tube D). In contrast, as illustrated in Fig. 1, strong broad absorption bands with maxima located at 415 nm, 416 nm and 485 nm were observed for the biogenic silver colloids prepared using the ethanol extract of *A. chordifolia* and irradiated by direct sunlight, green and yellow filtered light radiations, respectively. These peaks are assigned to a surface plasmon; a phenomenon that is well documented for various metal NPs with sizes ranging from 2 nm to 100 nm [16–18].

The particle sizes and surface zeta potentials of these prepared silver colloids were studied by the Malvern Instruments Zetasizer. Figure 2 shows different representative particle-size histograms of biogenic silver NPs synthesized under different light radiations. The particle-size histogram of the synthesized silver NPs under direct sunlight radiation shows the particles to have an average size of 12 nm (Fig. 2a). Furthermore Figs. 2b and 2c show particle-size

histograms of silver colloids prepared under green and yellow filtered light radiations and represent the formation of silver NPs with average sizes of 81 and 133 nm, respectively.

Table 1 shows the average size of biogenic silver NPs prepared under different light irradiations and their surface zeta potentials determined by the Malvern Instruments Zetasizer. The surface zeta potential of generated silver NPs using direct sunlight, yellow and green filtered lights were −28, −26 and −32, respectively. As can be seen in Figs. 2b and 2c, the larger biogenic silver NPs have been obtained by photoirradiation with yellow and green filtered light radiations (corresponding to visible light with a wavelength of 495–566 nm). On the other hand, smaller sized biogenic silver NPs were fabricated under direct sunlight radiation and, therefore, sunlight radiation was used for further study and rapid synthesis of smaller biogenic silver NPs. Also, no plasmon resonance peaks were observed in the absence of the plant extract (curve not shown). Moreover, we could not observe any plasmon peak resonance when the reaction took place for 5 min in the dark (curve not shown) or under red light radiation (Fig. 1).

In the next step, different sunlight intensities (800, 1300, 1500 and 1800 $\mu mol\, m^{-2}\, s^{-1}$) during the afternoon of a sunny day (12 July 2009) were used for preparation of silver colloids from the previously mentioned silver nitrate solution containing the ethanol extract of *A. chordifolia*. Fabrication of silver NPs was monitored by measuring the UV–visible spectrum of the solutions. The left-hand picture in Fig. 3 demonstrates the plot of the intensity of surface plasmon resonance of sunlight-induced biogenic silver NPs at 416 nm (λ_{max}) against different sunlight intensities (800, 1300, 1500 and 1800 $\mu mol\, m^{-2}\, s^{-1}$). The right-hand illustration in this figure shows photographs (A–D) of test tubes containing biogenic silver colloids that were prepared under sunlight radiation with different intensities of 800 (A), 1300 (B), 1500 (C) and 1800 (D) $\mu mol\, m^{-2}\, s^{-1}$.

The highest optical density of biogenic silver colloid was obtained at higher luminous emittance (1800 $\mu mol\, m^{-2}\, s^{-1}$) (left-hand illustration in Fig. 3). The optical densities of biogenic silver colloids, which were prepared under the highest sunlight emittance (1800 $\mu mol\, m^{-2}\, s^{-1}$), were further monitored at its λ_{max} (416 nm) by UV–visible spectroscopy at different irradiation times (1, 2, 3, 4, 5, 6 and 7 minutes). In the left-hand illustration in Fig. 4, the development of NPs for different sunlight irradiation times was shown for

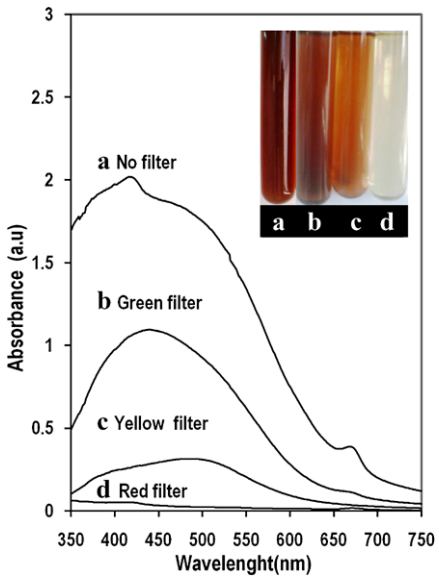

Fig. 1 Ultraviolet–visible spectra of mixtures of silver nitrate and ethanol extract of *Andrachnea chordifolia* after 5 min of photoirradiation by direct sunlight (A) and filtered green (B), yellow (C) and red (D) light radiations. Measurements were done immediately after the photoirradiation against a blank solution. The *inset* in this figure shows a photograph from test tubes containing different prepared colloids designated as A, B, C and D

Table 1 Average sizes and zeta potentials of silver nanoparticles prepared during photoirradiation of silver nitrate solution (1 mM) containing an ethanol extract of *Andrachnea chordifolia* (1.5% v/v) obtained by the Zetasizer Nano ZS (Malvern Instruments, Southborough, UK)

Irradiation light	Average particle size (nm)	Zeta potential (mV)
Sunlight (a)	12	−28
Green filter (b)	81	−32
Yellow filter (c)	133	−26

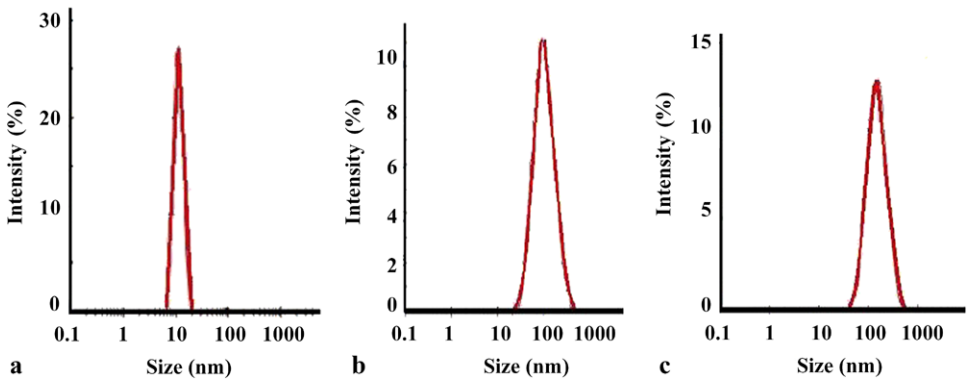

Fig. 2 Distribution of particle sizes of silver NPs fabricated under photoirradiation of silver nitrate solution (1 mM) containing an ethanol extract of *Andrachnea chordifolia* (1.5% v/v) measured by Zetasizer instruments

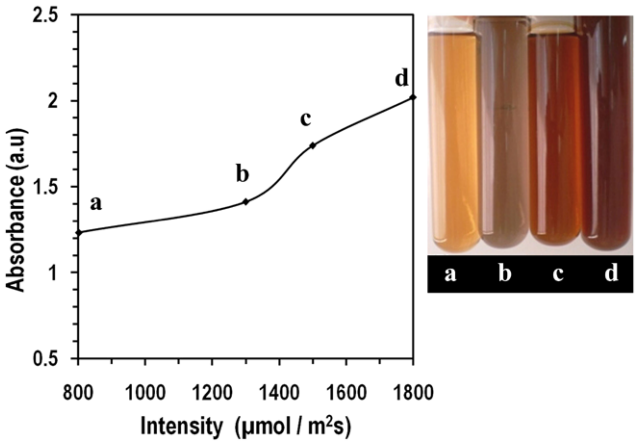

Fig. 3 The absorbance of silver NP colloids, which were prepared under bright conditions with different sunlight radiation intensities. Measurements were done at the maximum absorption band (416 nm)

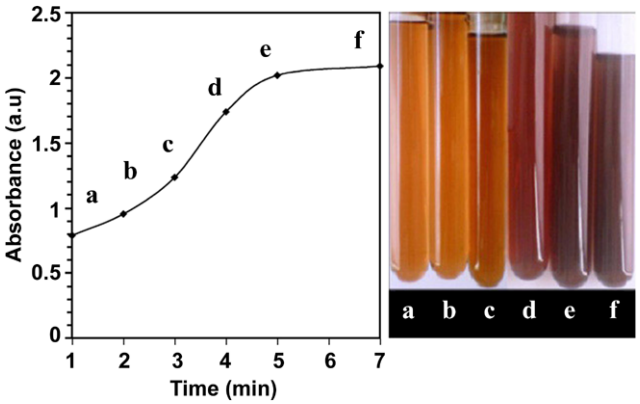

Fig. 4 Variation of absorbance at the colloidal maximum absorption band of silver NPs prepared by sunlight radiation with different irradiation times

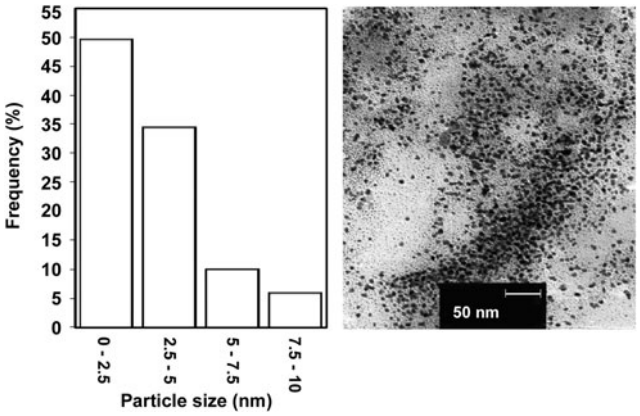

Fig. 5 Transmission electron micrograph of silver NPs formed by reducing Ag^{+} ions using the ethanol extract of *Andrachnea chordifolia* under sunlight irradiation (1800 µmol m^{-2} s^{-1}). *Scale bars* correspond to 50 nm. The particle-size histogram of the silver particles is shown in the *left-hand* picture

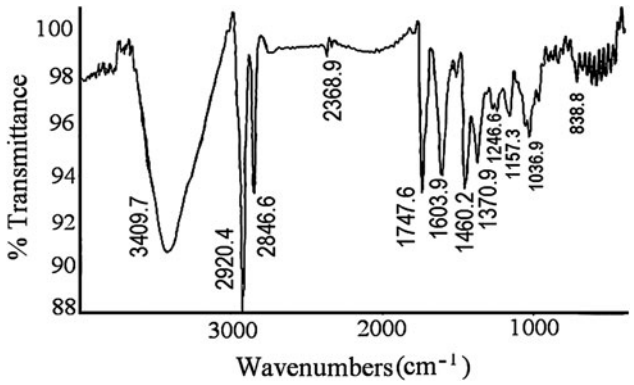

Fig. 6 Infrared spectrum of biogenic silver NPs obtained using the sunlight irradiation process

the silver nitrate solution containing the ethanol extract of *A. chordifolia*. The optical density of the silver ion solution containing the ethanol extract of *A. chordifolia* (1.5% v/v) was increased during the 5-minute post-sunlight irradiation period (1800 µmol m^{-2} s^{-1}) and remained constant after this irradiation period. The right-hand illustration in Fig. 4 shows pictures of test tubes (A–F) photographed after different developing times (1, 2, 3, 4, 5, 6 and 7 minutes) containing biogenic silver colloids that were prepared using sunlight radiation with the highest luminous emittance (1800 µmol m^{-2} s^{-1}).

The right-hand illustration in Fig. 5 shows a representative TEM image recorded from the drop-coated film of the biogenic silver NPs synthesized by treating the silver nitrate solution with plant extracts of *A. chordifolia* and irradiating by direct sunlight (1800 µmol m^{-2} s^{-1}) for 5 minutes. The particle-size histogram of the prepared silver particles shows that the particles range in size from 2 nm to 10 nm and possess an average size of 3.4 nm (left-hand illustration in Fig. 5). The surface chemistry of the prepared biogenic silver NPs under this condition was studied using infrared spectroscopy (IR) and the IR peaks centered at 3410 cm^{-1} and 2920 cm^{-1} confirming the presence of an OH and CH group on the surface of the silver NPs prepared from the ethanol extract of *A. chordifolia* with sunlight photoirradiation (Fig. 6).

As mentioned earlier, our experience showed that the silver NPs cannot be synthesized in darkness during short incubation times (5 minutes). However, the biosynthesis of silver NPs by plant extracts has been reported to take place over longer time periods [13, 14]. Therefore, in this investigation we further monitored the reduction of silver ions by using an ethanol extract of *A. chordifolia* at room temperature for an additional incubation time of 24 and 48 hours in darkness. The results show that the silver ions can be reduced to silver NPs after 48 hours (left-hand illustration in Fig. 7). Under UV–visible spectroscopy examination, the silver NPs which were prepared using these plant extracts in darkness show a maximum absorbance at 414 nm. The inset in the left-hand

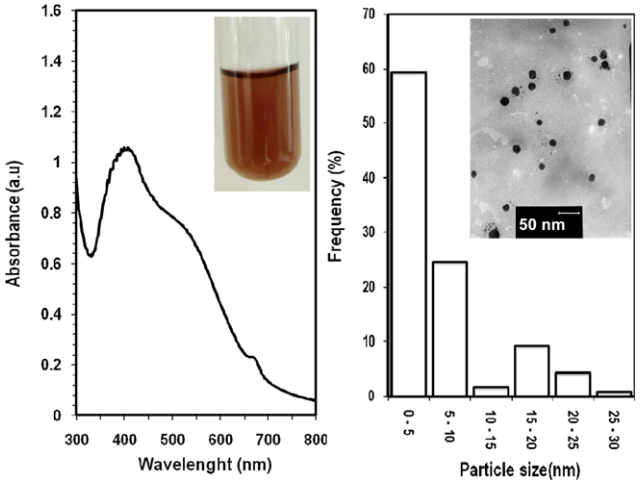

Fig. 7 *Left-hand* picture: ultraviolet-visible spectra of silver NPs formed by reducing Ag^+ ions using the ethanol extract of *Andrachnea chordifolia* after 48 hours in darkness. The *inset* in this picture shows a photograph from a test tube containing silver colloid prepared in dark conditions after 48 hours. The particle-size histogram of the silver particles is shown in the *right-hand* illustration and the *inset* in this figure demonstrated its corresponding transmission electron micrograph recorded from a drop-coated film of an aqueous silver nitrate solution (1 mM) mixed with plant extract and incubated for 48 hours in darkness

illustration of Fig. 7 shows a photograph from a test tube containing silver colloid prepared using the ethanol extract of *A. chordifolia* incubated for 48 hours in darkness. Asymmetric and broad peaks at 414 nm, which were observed after 48 hours, can be attributed to a wide size distribution of the particles with different shapes formed in the solution (right-hand illustration in Fig. 7). Representative TEM images of biogenic silver NPs fabricated in darkness for 48 hours are shown in the inset of the right-hand picture of Fig. 7. Moreover, this illustration shows the particle-size histogram of the silver NPs fabricated in darkness and demonstrates that the polydispersed particles varied in size from 2.5 to 28 nm.

4 Conclusion

In this investigation the ethanol extract of a Pakistani plant (*A. chordifolia*) was successfully used for rapid or slow biosynthesis of hydroxyl surface-coated silver NPs. The irradiation of silver ion solutions containing an ethanol extract of *A. chordifolia* by direct sunlight radiation can drastically reduce the time required for biosynthesis of small silver NPs. On the other hand, this indicated that, in the absence of sunlight photoirradiation, the reduction by the above-mentioned plant extract is possible but the process is very slow. This clearly indicates that a sunlight irradiation step is of prime importance in this biosynthesis procedure for the rapid fabrication of small silver nanoparticles. Also, we showed that the silver nitrate reduction in the presence of an ethanol extract of *A. chordifolia* cannot take place in a reaction vessel irradiated by red light for 5 minutes, which confirms that some visible light with wavelengths of 627 to 770 nm (corresponding to the red light spectrum) may not promote the biosynthesis of silver NPs in the presence of an ethanol extract of *A. chordifolia*.

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References

1. K.N. Thakkar, S.S. Mhatre, R.Y. Parikh, Nanomedicine **6**, 257 (2010)
2. R. Vaidyanathan, K. Kalishwaralal, S. Gopalram, S. Gurunathan, Biotechnol. Adv. **27**, 924 (2009)
3. V.K. Sharma, R.A. Yngard, Y. Lin, Adv. Colloid Interface Sci. **145**, 83 (2009)
4. A. Nabikhan, K. Kandasamy, A. Raj, N.M. Alikunhi, Colloids Surf. B, Biointerfaces **79**, 488 (2010)
5. K.N. Thakkar, S.S. Mhatre, R.Y. Parikh, Nanomedicine **6**, 257 (2010)
6. S.P. Dubey, M. Lahtinen, M. Sillanpää, Process Biochem. **45**, 1065 (2010)
7. C. Krishnaraj, E.G. Jagan, S. Rajasekar, P. Selvakumar, P.T. Kalaichelvan, N. Mohan, Colloids Surf. B, Biointerfaces **76**, 50 (2010)
8. A.K. Jha, K. Prasad, K. Prasad, A.R. Kulkarni, Colloids Surf. B, Biointerfaces **73**, 219 (2009)
9. J. Kasthuria, S. Veerapandianb, N. Rajendiranb, Colloids Surf. B, Biointerfaces **68**, 55 (2009)
10. S. Li, Y. Shen, A. Xie, X. Yu, L. Qiu, L. Zhang, Q. Zhang, Green. Chem. **9**, 852 (2007)
11. V. Kumar, S.K. Yadav, J. Chem. Technol. Biotechnol. **84**, 151 (2009)
12. J. Huang, Q. Li, D. Sun, Y. Lu, Y. Su, X. Yang, Nanotechnology **18**, 105104 (2007)
13. R. Sathyavathi, M.B. Krishna, S.V. Rao, R. Saritha, D.N. Rao, Adv. Sci. Lett. **3**, 1 (2010)
14. N.A. Begum, S. Mondal, S. Basu, R.A. Laskar, D. Mandal, Colloids Surf. B, Biointerfaces **71**, 113 (2009)
15. N. Mokhtari, S. Daneshpajouh, S. Seyedbagheri, R. Atashdehghan, K. Abdi, S. Sarkar, S. Minaian, H.R. Shahverdi, A.R. Shahverdi, Mater. Res. Bull. **44**, 1415 (2009)
16. P. Mulvany, Langmuir **12**, 788 (1996)
17. A. Henglein, J. Phys. Chem. B **97**, 5457 (1993)
18. M. Sastry, K.S. Mayya, K. Bandyopadhyay, Colloids Surf. A, Physicochem. Eng. Asp. **127**, 221 (1997)