

# Biosynthesis of high concentration, stable aqueous dispersions of silver nanoparticles using *Citrus limon* extract

Bandita Mohapatra<sup>1</sup>, Reena Kaintura<sup>1</sup>, Jaspal Singh<sup>1,2</sup>, Sini Kuriakose<sup>1,2</sup>, Satyabrata Mohapatra<sup>1,2\*</sup>

<sup>1</sup>Multifunctional Nanomaterials Laboratory, School of Basic and Applied Sciences, Guru Gobind Singh Indraprastha University, Dwarka, New Delhi 110078, India

<sup>2</sup>School of Basic and Applied Sciences, Guru Gobind Singh Indraprastha University, Dwarka, New Delhi 110078, India

\*Corresponding author. Tel: (+91) 11 25302414; E-mail: [smiuac@gmail.com](mailto:smiuac@gmail.com)

Received: 30 August 2014, Revised: 28 November 2014 and Accepted: 12 December 2014

## ABSTRACT

Stable aqueous dispersions with high concentration of silver nanoparticles were synthesized by a facile and green synthetic route by treating silver ions with aqueous *Citrus limon* extract, used as a reducing and capping agent. The formation and growth of silver nanoparticles, prepared by this simple and convenient method, was monitored using UV-visible absorption spectroscopy. The effects of Ag concentration, *Citrus limon* extract concentration, in-situ and ex-situ pH variations upon NaOH addition on the structural, optical and plasmonic properties of the synthesized Ag nanoparticles were investigated. X-ray diffraction studies revealed the formation of Ag nanoparticles, whose morphology was studied using atomic force microscopy. UV-visible absorption studies revealed surface plasmon resonance (SPR) peak around 465 nm, confirming the presence of Ag nanoparticles. The SPR peak blue shifted along with significant enhancement in intensity with increase in Ag concentration and pH, due to the growth and increased aggregation of Ag nanoparticles. We have shown that addition of NaOH is a key to rapid biosynthesis of stable aqueous dispersions of high concentration of silver nanoparticles. This green synthetic route provides faster synthesis of silver nanoparticles with improved colloidal stability, which can be used in foods, cosmetics and biomedical applications. Copyright © 2015 VBRI press.

**Keywords:** Biosynthesis; silver nanoparticles; surface plasmon resonance.



**Bandita Mohapatra** is working as a visiting researcher in Multifunctional Nanomaterials Laboratory at Guru Gobind Singh Indraprastha University, New Delhi, India. She completed M.Sc. in Applied Microbiology from Utkal University, Bhubaneswar, India in 2007. Her main area of research is biosynthesis of nanostructured materials for environmental remediation and biomedical applications.



**Reena Kaintura** completed M.Tech. in Nanoscience and Technology from Guru Gobind Singh Indraprastha University, New Delhi, India and B.Tech. in Instrumentation Engineering from HNB Garhwal University, Uttarakhand, India. Her main area of research is synthesis of nanomaterials for different applications.



**Satyabrata Mohapatra** is working as Assistant Professor of Nanoscience and Technology at School of Basic and Applied Sciences, Guru Gobind Singh Indraprastha University, New Delhi, India. He received Ph.D. degree from Institute of Physics (IOP), Bhubaneswar, India. He has worked as Postdoctoral Research Associate at Inter University Accelerator Centre (IUAC), New Delhi, India. His current research involves synthesis and ion beam engineering of multifunctional hybrid nanostructures and plasmonic nanocomposites for the development of ultra-sensitive chemical and biosensors, gas sensors and highly efficient photocatalysts.

## Introduction

Noble metal nanoparticles find promising applications in fields ranging from nano to biotechnology due to their unique shape and size-dependent optical and electronic properties [1]. When excited by light noble metal nanoparticles exhibit wavelength selective photon absorption and huge enhancement in local electric fields, due to a phenomenon known as surface plasmon resonance (SPR), which forms the basis of their diverse applications.

Among the noble metal nanoparticles, silver nanoparticles exhibit the strongest SPR absorption and find widespread applications in sensing [2-4], catalysis [5], photonics [6], medicine [7], antimicrobials [8-12], and surface enhanced Raman spectroscopy [13,14]. Silver nanoparticles have been synthesized by various physical and chemical methods [15-24]. While the physical methods are costly, chemical methods employ toxic and hazardous chemicals which pose serious threat to the environment and the synthesized silver nanoparticles can have adverse effects in biomedical applications because of the toxic chemicals adsorbed on their surface. This has led to the development of environmentally benign nanoparticle synthesis protocols that do not use toxic chemicals. Biosynthesis using various microorganisms or plants is a promising route to eradication of this problem by preparing silver nanoparticles with improved biocompatibility [25, 26]. Among the biosynthetic routes, plant mediated synthesis of nanoparticles is particularly interesting, simple and advantageous since it avoids maintaining cell cultures, needed to handle microorganisms [27, 28].

Biosynthesis of silver nanoparticles using plant extracts, which usually contain a combination of biomolecules *viz.* amino acids, polysaccharides, enzymes, proteins, vitamins, and organic acids, is environmentally benign but complex. Plant extracts can act as reducing as well as capping agents in synthesis of silver nanoparticles by bioreduction of silver ions. Both intra- and extra-cellular synthesis of silver nanoparticles using living plants and plant extracts have been reported by various research groups. Gardea-Torresdey et al. [29] were the first to report synthesis of silver nanoparticles within living alfalfa plants which uptake silver ions from the solid media. They also showed that silver nanoparticles were formed by rapid bioreduction of silver ions when geranium leaf extract came in contact with silver nitrate solution [30]. Biosynthesis using leaf extract of neem (*Azadirachta indica*) revealed competing reduction of  $\text{Ag}^+$  and  $\text{Au}^{3+}$  ions [31-33]. Vilchis-Nestor et al. [34] reported simple biosynthesis of silver nanoparticles using green tea extract. Biosynthesis of silver nanoparticles using leaf extracts of *Emblica officinalis* [35], *Aloe vera* [36], *Chenopodium album* [37], *Murraya Koenigii* [38] and *Cinnamon camphora* [38], *Hibiscus rosa sinensis* [39], *Rosa rugosa* [40], *Cochlospermum gossypium* [41], *Citrus limon* [42], *Mangifera indica* [43], banana peel extract [44], seed extract of *Jatropha curcas* [46] and flower extract of *Saraca indica* [47] have also been reported. Though there has been various works on the biosynthesis of silver nanoparticles concentrating on the size and shape control, little progress has been made towards rapid biosynthesis of stable aqueous dispersions of silver nanoparticles using plant extracts.

In the present study, we have synthesized stable aqueous dispersions of silver nanoparticles with high concentration by a facile, rapid and green synthetic route by treating silver ions with aqueous *Citrus limon* extract, which was used as a reducing and capping agent. The effects of Ag concentration, extract concentration, in-situ and ex-situ pH variations upon NaOH addition on the structural, optical and plasmonic properties of the as-synthesized Ag nanoparticles have been investigated. We have demonstrated that NaOH addition leads to formation

of stable aqueous dispersions silver nanoparticles with high concentration and stronger plasmonic response.

## Experimental

### Materials

Fresh *Citrus limon* fruits,  $\text{AgNO}_3$  and NaOH were used as starting materials for green synthesis of Ag nanoparticles. Fresh *Citrus limon* fruits were purchased from Dwarka market, while  $\text{AgNO}_3$  was purchased from Merck, India. The chemicals used were of analytical grade and were used without further purification. Double distilled water was used as the solvent in all the experiments.

### Synthesis of dispersions of silver nanoparticles

Lemon juice extracted from fresh *Citrus limon* fruits was filtered through filter paper and then centrifuged to remove the unwanted materials. The supernatant was collected and diluted 10 times with double distilled water and then used as the reducing agent as well as for capping agent in the green synthesis of Ag nanoparticles. In a typical synthesis, glass vials with 10 mL of the aqueous *Citrus limon* extract were kept in a water bath maintained at 90°C. Different amounts (0.5, 1, 2 and 4 mL) of aqueous 10 mM  $\text{AgNO}_3$  solutions were added into these hot solutions to reach varying  $\text{AgNO}_3$  concentrations in different vials. These samples with different  $\text{AgNO}_3$  concentrations of 0.48, 0.91, 1.67 and 2.86 mM are hereafter referred to as A1, A2, A3 and A4, respectively. The color of the solutions changed from faint yellow to stronger reddish brown color depending on the starting  $\text{AgNO}_3$  concentration. After  $\text{AgNO}_3$  addition, the vials were removed from the hot bath after different durations of time. Another set of samples were synthesized by adding different amounts of aqueous 5 mM  $\text{AgNO}_3$  solutions into 10 mL diluted lemon extract solutions. These solutions were then heated at 90°C to synthesize Ag nanoparticle dispersions. The pH of these solutions before addition of  $\text{AgNO}_3$  as well as after the synthesis of Ag nanoparticle dispersions was varied from 3 to 11 by addition of different amounts of aqueous 0.1 M NaOH solution.

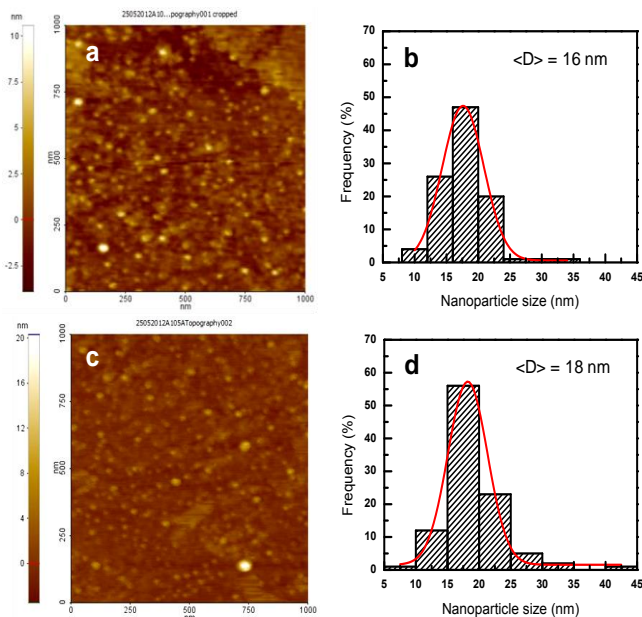
The effects of concentration of *Citrus limon* extract on the synthesis of Ag nanoparticle colloids were also studied by using dilutions (1:1, 1:5, 1:10) of the extract with double distilled water. For this study, 10 mL of aqueous 2 mM  $\text{AgNO}_3$  solution was taken in three vials and kept in the bath maintained at 90°C. Aqueous 2 mL solutions of different dilutions (1:1, 1:5, 1:10) of the *Citrus limon* extract were added into these vials and heated at 90°C for synthesis of Ag nanoparticles.

### Characterization

The optical and plasmonic properties of as-synthesized colloidal solutions were characterized by UV-visible absorption spectroscopy in the wavelength range 300 to 800 nm using HITACHI U3300 spectrophotometer. The structural properties of the synthesized Ag nanoparticles were studied by X-ray diffraction (XRD). The morphology of the synthesized nanoparticles coated onto Si substrates was studied using Park Systems XE-70 atomic force microscope.

## Results and discussion

Atomic force microscopy (AFM) was used to study the morphology and the size distribution of the as-synthesized silver nanoparticles, deposited onto Si substrates. **Fig. 1(a)** and **(c)** show the AFM images of the as-synthesized silver nanoparticles in the samples A3 and A4, respectively. The average sizes of nanoparticles in these two samples were estimated to be 16 and 18 nm, respectively from Gaussian fitting of the size distribution histograms shown in **Fig. 1(b)** and **(d)**. It can be clearly seen that increase in Ag concentration from 1.67 and 2.86 mM resulted in a slight increase in the size of synthesized Ag nanoparticles. **Fig. 2(a)** and **(b)** show the 3D AFM images of the samples A3 and A4, respectively.

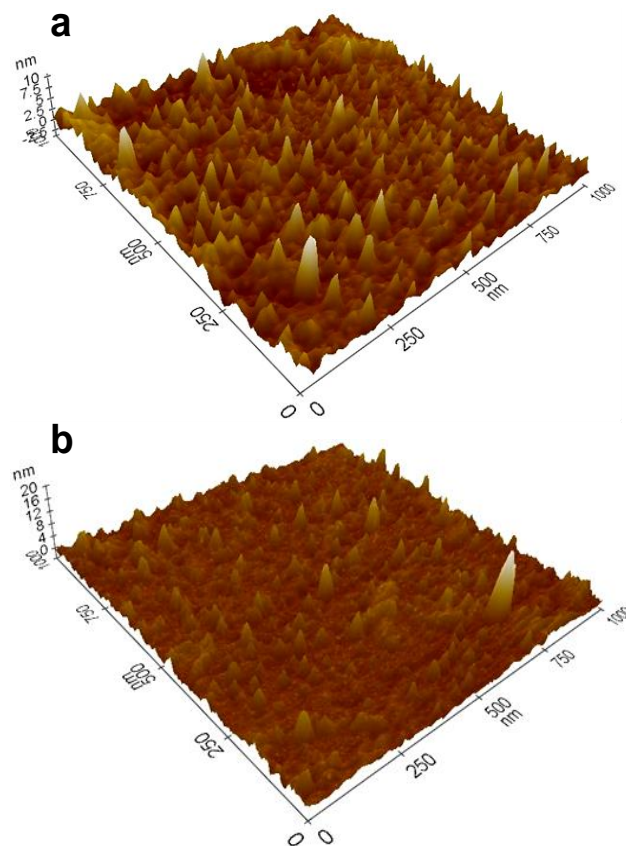


**Fig. 1.** AFM images of Ag nanoparticles in as-synthesized sample (a) A3 and (c) A4, (b) and (d) corresponding size distributions of Ag nanoparticles.

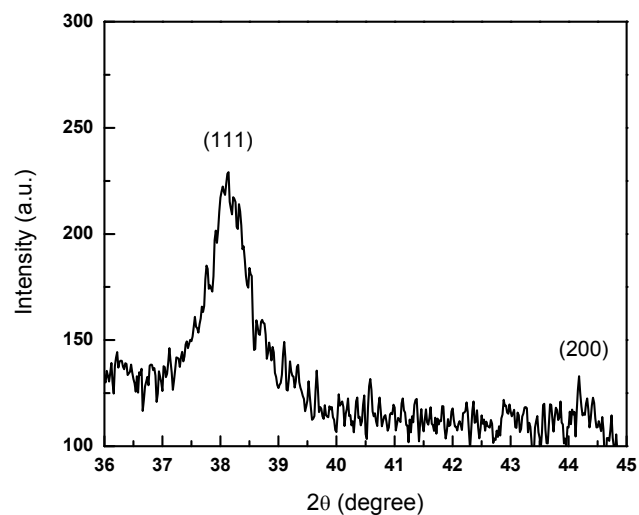
**Fig. 3** shows the XRD pattern from the synthesized sample A4. The presence of distinct diffraction peaks at  $38.14^\circ$  and  $44.28^\circ$  corresponding to the (111) and (200) reflections, respectively confirm the presence of Ag nanoparticles with FCC structure (JCPDS card no. 04-0783) in the sample.

**Fig. 4(a)** shows the optical absorption spectra of as-synthesized samples A1, A2, A3 and A4 prepared with varying  $\text{AgNO}_3$  concentrations of 0.48, 0.91, 1.67 and 2.86 mM, respectively. The spectrum for sample A1 does not show any clear peak in the visible region, while the spectrum for sample A2 shows a broad absorption band around 465 nm, which is due to SPR absorption of small Ag nanoparticles formed in the solution. Increasing the Ag concentration to 1.67 mM (sample A3) resulted in a significant enhancement in intensity, narrowing together with a marked blue shift of 47 nm (465 to 418 nm) in the SPR peak of Ag nanoparticles. Further increase in Ag concentration to 2.86 mM (sample A4) led to an increase in intensity of SPR peak, which significantly broadened and red shifted to about 450 nm. The photographs of the vials with the as-synthesized Ag nanoparticle dispersions are

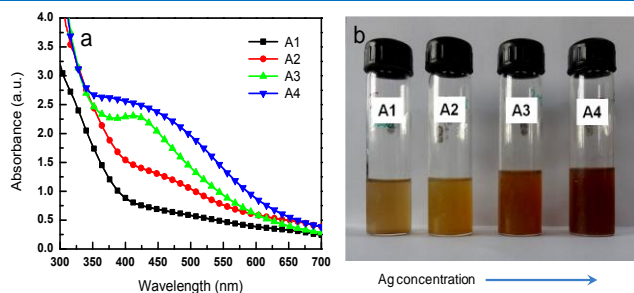
shown in **Fig. 4(b)**. The yellowish color confirms the presence of Ag nanoparticles in these samples. It can be clearly seen that the color of the dispersions changes from pale yellow to reddish brown color as Ag concentration is increased from 0.48 to 2.86 mM. The reddish brown appearance of the dispersions indicates the presence of Ag nanoparticles at high concentrations. It must be pointed out here that this set of samples were prepared using 1:10 diluted extract solution with highly acidic pH of 3.



**Fig. 2.** 3D AFM images of as-synthesized sample (a) A3 and (b) A4.

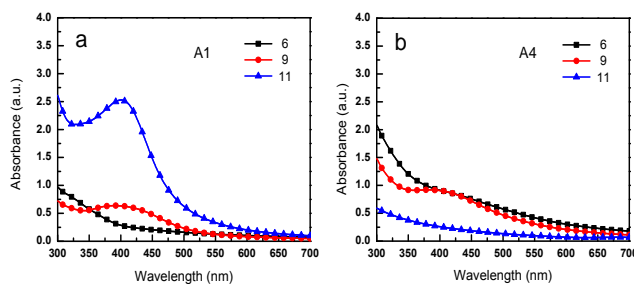


**Fig. 3.** Typical XRD pattern of biosynthesized Ag nanoparticles in sample A4.



**Fig. 4.** (a) Optical absorption spectra of samples A1, A2, A3 and A4, prepared with different  $\text{AgNO}_3$  concentrations using 1:10 diluted aqueous lemon extract at a pH of  $\sim 3$ , (b) Photographs of vials with the above Ag nanoparticle samples A1, A2, A3 and A4.

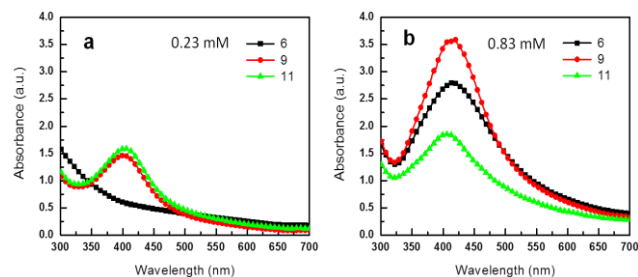
In order to study the effects of pH on the formation and growth of Ag nanoparticles using *Citrus limon* extract, an aqueous 0.1 M NaOH solution was added into the solution before addition of  $\text{AgNO}_3$  into the diluted extract. **Fig. 5(a)** shows the optical absorption spectra of sample A1 synthesized at different pH values (6, 9 and 11) attained with the addition of different amounts of 0.1 M NaOH solution, before the addition of 0.48 mM  $\text{AgNO}_3$  into the extract. No SPR peak could be seen for pH of 6, indicating the absence of Ag nanoparticles. It can be clearly seen that as the pH of the growth solution is increased to 9, SPR peak appears at 394 nm. Further increase in pH to 11 resulted in a significant enhancement in intensity, narrowing (FWHM decreases from 0.84 to 0.61 eV) and red shift (394 to 401 nm) of the SPR peak of Ag nanoparticles. This clearly indicates growth of Ag nanoparticles with higher number density in the dispersion. **Fig. 5(b)** shows the optical absorption spectra for sample A4 synthesized at different pH values of 6, 9 and 11. A very broad absorption band around 430 nm can be seen in the absorption spectrum of sample prepared at pH of 6. For the sample prepared at pH of 9, the SPR peak has been found to blue shift to 408 nm with an increase in the intensity. No SPR peak could be seen in the sample prepared at pH of 11. Surprisingly, the SPR peak observed at lower pH values completely disappears when the pH of the solution before  $\text{AgNO}_3$  addition is increased to 11. To understand the effects of pH variation by NaOH addition on the formation and growth of Ag nanoparticles and their plasmonic response better, two more samples prepared with different  $\text{AgNO}_3$  concentrations were also studied.



**Fig. 5.** Optical absorption spectra of samples (a) A1 and (b) A4, prepared with different  $\text{AgNO}_3$  concentrations using 1:10 diluted aqueous lemon extract with pH adjusted to 6, 9 and 11 before  $\text{AgNO}_3$  addition.

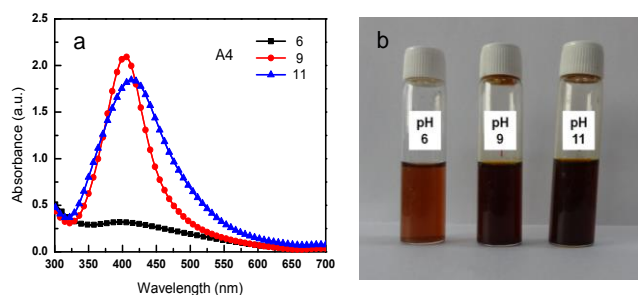
**Fig. 6(a)** and **(b)** show the optical absorption spectra of the samples prepared with  $\text{AgNO}_3$  concentrations of 0.23

mM and 0.83 mM, respectively using 1:10 diluted aqueous lemon extract with pH adjusted to 6, 9 and 11 by adding NaOH solution before  $\text{AgNO}_3$  addition. It can be clearly seen that at lower Ag concentration, increase in pH leads to significant enhancement in the plasmonic response, in the form of increased intensity and narrowing of the SPR peak. For the sample prepared with 0.83 mM  $\text{AgNO}_3$ , the SPR peak increased in intensity and narrowed as the pH was increased to 9 by adding NaOH before  $\text{AgNO}_3$  addition, while it decreased in intensity as the pH is increased to 11. The observed changes in optical and plasmonic properties of biosynthesized Ag nanoparticle dispersions with in-situ pH change with NaOH are very interesting and promising for diverse applications in nanobiotechnology.



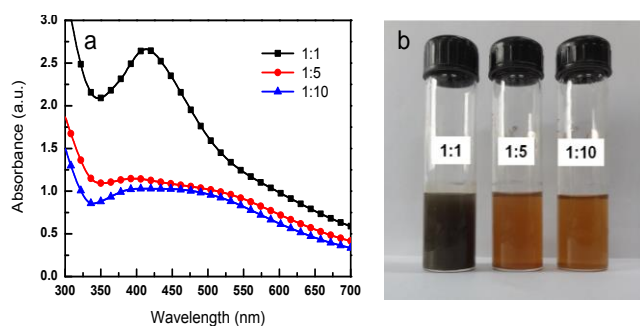
**Fig. 6.** Optical absorption spectra of samples prepared with  $\text{AgNO}_3$  concentrations of (a) 0.23 mM and (b) 0.83 mM using 1:10 diluted aqueous lemon extract with pH adjusted to 6, 9 and 11 before  $\text{AgNO}_3$  addition.

In order to study the effects of pH on the stability of the synthesized dispersions of Ag nanoparticles, 0.1 M NaOH was added into the as-synthesized sample A4 to adjust the pH to 6, 9 and 11. The optical absorption spectra of sample A4 with Ag nanoparticles, following ex-situ addition of NaOH to vary the pH from 6 to 11 are shown in **Fig. 7(a)**. The absorption spectrum of the sample at pH 6 shows a SPR peak at 401 nm. Increase in pH of the Ag nanoparticle dispersion to 9 resulted in a significant enhancement in the intensity, narrowing (FWHM decreases from 1.03 to 0.56 eV) of the SPR peak which is slightly red shifted to 405 nm. It can be clearly seen that further increase in pH of the sample to 11 led to a slight decrease in intensity along with appreciable broadening (FWHM increases from 0.56 to 0.82 eV) and red shift in the SPR peak to 415 nm. The photographs of the dispersions in vials are shown in **Fig. 7(b)**, which reveals distinct changes in the color from brown to dark reddish brown color at higher pH values.



**Fig. 7.** (a) Optical absorption spectra of Ag nanoparticles sample A4 with pH adjusted to 6, 9 and 11 with NaOH addition after synthesis of Ag nanoparticles and (b) Photographs of vials with Ag nanoparticles dispersions sample A4 with pH adjusted to 6, 9 and 11 with NaOH after synthesis of Ag nanoparticles.

The effects of *Citrus limon* extract concentration on formation and growth of Ag nanoparticles and their optical and plasmonic properties have been studied using different dilutions of the aqueous extract for the synthesis. **Fig. 8(a)** shows the optical absorption spectra of Ag nanoparticle dispersions synthesized using 2 mM  $\text{AgNO}_3$  and three different dilutions (1:1, 1:5 and 1:10) of the aqueous extract. The absorption spectrum of sample prepared with 1:1 diluted extract shows SPR peak at 415 nm with maximum intensity among the three samples. For the sample prepared with 1:5 diluted extract, a broad SPR band consisting of two distinct peaks at 397 and 525 nm are observed. The sample prepared with the most dilute (1:10) concentration of the extract, broad SPR consisting of two peaks at 397 and 501 nm are observed. The observed decrease in intensity and broadening leading to two distinct peaks clearly reveal aggregation of Ag nanoparticles due to reduced capping action of the diluted extract. The increased aggregation of Ag nanoparticles leads to red shift of the SPR peak due to stronger electromagnetic coupling within Ag nanoparticles. The photographs of these three Ag nanoparticle dispersions prepared at different extract concentrations are shown in **Fig. 8(b)**. The color of the dispersion changes from dark brown to yellowish brown color with decrease in the concentration of the extract. The yellowish brown color indicates the presence of large density of small Ag nanoparticles, aggregation of which leads to the emergence of additional SPR band which is red shifted to  $\sim 500$  nm. The reduced intensity of the SPR peak and emergence of an additional red shifted SPR peak clearly indicate that lower concentration of extract have inefficient capping action leading to the increased aggregation of Ag nanoparticles.



**Fig. 8.** (a) Optical absorption spectra of Ag nanoparticle dispersions synthesized using 2 mM  $\text{AgNO}_3$  and three different aqueous dilutions (1:1, 1:5 and 1:10) of the extract and (b) Photographs of the vials with the above three Ag nanoparticle dispersions.

The formation of Ag nanoparticles by bioreduction of silver ions with *Citrus limon* extract can be understood as follows. *Citrus limon* extract is a rich source of citric acid and ascorbic acid [48, 49] both of which act as reducing agents for  $\text{Ag}^+$  ions. In addition, *Citrus limon* extract also contains a number of phytonutrients including flavonones-hesperidin, eriocitrin and phenolic compounds such as umbelliferone and glycosides-quercetin [50]. The capping action of citric acid during Ag nanoparticle growth by chemical methods is well known and has been reported by various groups. The formation of stable dispersion of Ag nanoparticles by bioreduction of silver ions using *Citrus limon* extract mainly relies on the reducing action of citric

acid and ascorbic acid in addition to other constituents and the capping action of citric acid. With increase in  $\text{AgNO}_3$  concentration, the concentration of reduced Ag atoms in the solution reaches supersaturation leading to nucleation of Ag clusters, which act as nuclei and grow in size taking more Ag atoms resulting in the formation of Ag nanoparticles. It has been shown that addition of NaOH leads to enhancement in the reducing action of ascorbic acid and reduction of  $\text{Ag}^+$  ions in an alkaline medium favors the synthesis of Ag nanoparticles [51]. The addition of NaOH controls the pH of the reaction dispersion and alters the ionic environment by supplying  $-\text{OH}$  radicals which can interact with the capping agent, reducing agent and the metal ion species. In the absence of NaOH addition, the rate of formation of Ag nanoparticles is much slower. When NaOH is added before  $\text{AgNO}_3$  addition, the reduction of  $\text{Ag}^+$  ions by *Citrus limon* extract is completed within few tens of minutes, indicating the strong catalytic activity of NaOH in the bioreduction process. Such rapid synthesis is very important for diverse applications as it minimizes the cost significantly saving energy and produces highly biocompatible Ag nanoparticles. It must be pointed out here that the important factors controlling the rapid biosynthesis of stable aqueous dispersions of Ag nanoparticles using NaOH addition include (i) change in the reactivity of  $\text{Ag}^+$  ions with varying pH, which depends on the NaOH concentration, and (ii) the enhancement in the reducing capability of ascorbic acid and citric acid in the extract by NaOH and (iii) the change in the capping action of citric acid for Ag nanoparticles. In addition to the enhancement of reducing capability of ascorbic acid and citric acid, NaOH addition also results in the formation of  $\text{AgOH}$  nanoprecipitates, due to reaction of  $\text{Ag}^+$  ions with  $-\text{OH}$  radicals supplied by NaOH, which transform into  $\text{Ag}_2\text{O}$  nanoparticles at  $90^\circ\text{C}$ . Due to this NaOH addition results in a large density of small  $\text{Ag}_2\text{O}$  nanoparticles by heterogeneous nucleation in the reaction dispersion. The enhanced reducing action of citric acid and ascorbic acid in the presence of NaOH leading to an alkaline medium, results in the formation of high density of Ag nanoparticles, stabilized well by the efficient capping action of citric acid in the *Citrus limon* extract. Our optical absorption results also go in line with this. We have demonstrated a simple way to rapid biosynthesis of stable dispersions of high concentration of Ag nanoparticles.

## Conclusion

We report on an environmentally benign, inexpensive and facile method of preparing stable dispersions of high concentration silver nanoparticles in the size range of 10-30 nm by a green synthetic route involving bioreduction of silver ions with aqueous *Citrus limon* extract. Citric acid and ascorbic acid present in *Citrus limon* extract are believed to be responsible for the reduction of silver ions, leading to formation of silver nanoparticles. The synthesized aqueous dispersions of silver nanoparticles were found to be stable due to the efficient capping action of citric acid in the extract. UV-visible absorption studies revealed SPR peak of Ag nanoparticles which showed blue shift with increase in Ag concentration and pH. We have demonstrated a simple way to rapid biosynthesis of Ag nanoparticles by introducing NaOH as a reaction initiator to

accelerate the bioreduction of Ag ions leading to the formation of high density of Ag nanoparticles. The synthesized stable aqueous dispersions of Ag nanoparticles are ideal for diverse industrial and biomedical applications.

#### Acknowledgements

SM is grateful to Department of Science and Technology (DST), New Delhi for providing AFM and XRD facilities under Nano Mission program. SK is thankful to Guru Gobind Singh Indraprastha University, New Delhi for providing financial assistance through IPR Fellowship. JS gratefully acknowledges the support from UGC, New Delhi in the form of Maulana Azad National Fellowship.

#### Reference

- Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.  
DOI: [10.1021/jp026731y](https://doi.org/10.1021/jp026731y)
- Jiang, X. C.; Yu, A. B. *Langmuir* **2008**, *24*, 4300.  
DOI: [10.1021/la703225x](https://doi.org/10.1021/la703225x)
- Murray, B. J.; Walter, E. C.; Penner, R. M. *Nano Lett.* **2004**, *4*, 665.  
DOI: [10.1021/nl049841k](https://doi.org/10.1021/nl049841k)
- Dubas, S. T.; Pimpan, V. *Talanta* **2008**, *76*, 29.  
DOI: [10.1016/j.talanta.2008.01.062](https://doi.org/10.1016/j.talanta.2008.01.062)
- Rashid, Md. H.; Mandal, T. K. *J. Phys. Chem. C* **2007**, *111*, 16750.  
DOI: [10.1021/jp074963x](https://doi.org/10.1021/jp074963x)
- Liu, B.; Zhao, X.; Zhu, W.; Luo, W.; Cheng, X. *Adv. Funct. Mater.* **2008**, *18*, 3523.  
DOI: [10.1002/adfm.200800444](https://doi.org/10.1002/adfm.200800444)
- Shrivastava, S.; Bera, T.; Singh, S. K.; Singh, G.; Ramachandrarao, P.; Dash, D. *ACS Nano* **2009**, *3*, 1357.  
DOI: [10.1021/nn900277t](https://doi.org/10.1021/nn900277t)
- Ruparelia, J. P.; Chatterjee, A. K.; Duttagupta, S. P.; Mukherji, S. *Acta Biomater.* **2008**, *4*, 707.  
DOI: [10.1016/j.actbio.2007.11.006](https://doi.org/10.1016/j.actbio.2007.11.006)
- Smetana, A. B.; Klambunde, K. J.; Marchin, G. R.; Sorensen, C. M. *Langmuir* **2008**, *24*, 7457.  
DOI: [10.1021/la800091y](https://doi.org/10.1021/la800091y)
- Sharma, V. K.; Yngard, R. A.; Lin, Y. *Adv. Colloid Interface Sci.* **2009**, *145*, 83.  
DOI: [10.1016/j.cis.2008.09.002](https://doi.org/10.1016/j.cis.2008.09.002)
- Panacek, A.; Kvittek, L.; Prucek, R.; Kolar, M.; Vecerova, R.; Pizurova, N.; Sharma, V. K.; Nevecna, T.; Zboril, R. *J. Phys. Chem. B* **2006**, *110*, 16248.  
DOI: [10.1021/jp063826h](https://doi.org/10.1021/jp063826h)
- Kumar, A.; Vemula, P. K.; Ajayan, P. M.; John, G. *Nat. Mater.* **2008**, *7*, 236.  
DOI: [10.1038/nmat2099](https://doi.org/10.1038/nmat2099)
- Nie, S. and Emory, S. R. *Science* **1997**, *275*, 1102.  
DOI: [10.1126/science.275.5303.1102](https://doi.org/10.1126/science.275.5303.1102)
- Fan, M. and Brolo, A. G. *Phys. Chem. Chem. Phys.*, **2009**, *11*, 7381.  
DOI: [10.1039/B904744A](https://doi.org/10.1039/B904744A)
- Pal, T.; Sau, T. K.; Jana, N. R. *Langmuir* **1997**, *13*, 1481.  
DOI: [10.1021/la960834o](https://doi.org/10.1021/la960834o)
- Rodriguez-Sanchez, M. L.; Blanco, M. C.; Lopez-Quintela, M. A. *J. Phys. Chem. B* **2000**, *104*, 9683.  
DOI: [10.1021/jp001761r](https://doi.org/10.1021/jp001761r)
- Munro, C.H.; Smith, W. E.; Garner, M.; Clarkson, J.; White, P. C. *Langmuir* **1995**, *11*, 3712.  
DOI: [10.1021/la00010a021](https://doi.org/10.1021/la00010a021)
- Zhu, J.; Liu, S.; Palchik, O.; Kolytyn, Y.; Gedanken, A. *Langmuir* **2000**, *16*, 6396.  
DOI: [10.1021/la991507u](https://doi.org/10.1021/la991507u)
- Pastoriza-Santos, I.; Liz-Marzan, L. M. *Langmuir* **2002**, *18*, 2888.  
DOI: [10.1021/la015578g](https://doi.org/10.1021/la015578g)
- Mishra, Y. K.; Mohapatra, S.; Kabiraj, D.; Mohanta, B.; Lalla, N.P.; Pivin, J. C.; Avasthi, D. K. *Scripta Mater.* **2007**, *56*, 629.  
DOI: [10.1016/j.scriptamat.2006.12.008](https://doi.org/10.1016/j.scriptamat.2006.12.008)
- Mohapatra, S.; Mishra, Y. K.; Ghatak, J.; Kabiraj, D.; Avasthi, D. K. *J. Nanosci. Nanotechnol.* **2008**, *8*, 4285.  
DOI: [10.1166/jnn.2008.AN30](https://doi.org/10.1166/jnn.2008.AN30)
- Mohapatra, S. *J. Alloys Comp.* **2014**, *598*, 11.  
DOI: [10.1016/j.jallcom.2014.02.021](https://doi.org/10.1016/j.jallcom.2014.02.021)
- Schurmann, U.; Hartung, W. A.; Takele, H.; Zaporozhchenko, V.; Faupel, F. *Nanotechnology* **2005**, *16*, 1078.  
DOI: [10.1088/0957-4484/16/8/014](https://doi.org/10.1088/0957-4484/16/8/014)
- Lee, K. J.; Jun, B. H.; Choi, J.; Lee, Y.; Joung, J.; Oh, Y. S. *Nanotechnology* **2007**, *18*, 335601.  
DOI: [10.1088/0957-4484/18/33/335601](https://doi.org/10.1088/0957-4484/18/33/335601)
- Sinha, S.; Pan, L.; Chanda, P.; Sen, S. K. *J. Appl. Biosci.* **2009**, *19*, 1113.
- Nune, S. K.; Chanda, N.; Shukla, R.; Katti, K.; Kulkarni, R. R.; Thilakavathy, S.; Mekapothula, S.; Kannan, R.; Katti, K. V. *J. Mater. Chem.* **2009**, *19*, 2912–2920.  
DOI: [10.1039/b822015h](https://doi.org/10.1039/b822015h)
- Kumar, V.; Yadav, S. K. *J. Chem. Technol. Biotechnol.* **2008**, *84*, 151.  
DOI: [10.1002/jctb.2023](https://doi.org/10.1002/jctb.2023)
- Jha, A.K.; Prasad, K.; Prasad, K.; Kulkarni, A.R. *Colloids Surf. B* **2009**, *73*, 219.  
DOI: [10.1016/j.colsurfb.2009.05.018](https://doi.org/10.1016/j.colsurfb.2009.05.018)
- Gardea-Torresdey, J. L.; Parsons, J. G.; Gomez, E.; Peralta-Videa, J.; Troiani, H. E.; Santiago, P.; Jose-Yacamán, M. *Nano Lett.* **2002**, *2*, 397.  
DOI: [10.1021/nl015673+](https://doi.org/10.1021/nl015673+)
- Gardea-Torresdey, J. L.; Gomez, E.; Peralta-Videa, J. R.; Parsons, J. G.; Troiani, H.; Jose-Yacamán, M. *Langmuir* **2003**, *19*, 1357.  
DOI: [10.1021/la020835i](https://doi.org/10.1021/la020835i)
- Shiv Shankar, S.; Ahmad, A.; Sastry, M. *Biotechnol Prog* **2003**, *19*, 1627.  
DOI: [10.1021/bp034070w](https://doi.org/10.1021/bp034070w)
- Shiv Shankar, S.; Rai, A.; Ahmad, A.; Sastry, M. *J. Colloid Inter. Sci.* **2004**, *275*, 496.  
DOI: [10.1016/j.jcis.2004.03.003](https://doi.org/10.1016/j.jcis.2004.03.003)
- Prathna, T. C.; Chandrasekaran, N.; Raichur, A. M.; Mukherjee, A. *Colloids Surf. A* **2011**, *377*, 212.  
DOI: [10.1016/j.colsurfa.2010.12.047](https://doi.org/10.1016/j.colsurfa.2010.12.047)
- Vilchis-Nestor, A. R.; Sanchez-Mendieta, V.; Camacho-Lopez, M. A.; Gomez-Espinosa, R. M.; Camacho-Lopez, M. A.; Arenas-Altortor, J. A. *Mater. Lett.* **2008**, *62*, 3103.  
DOI: [10.1016/j.matlet.2008.01.138](https://doi.org/10.1016/j.matlet.2008.01.138)
- Ankamwar, B.; Damle, C.; Absar, A.; Mural, S. *J. Nanosci. Nanotechnol.* **2005**, *10*, 1665.  
DOI: [10.1166/jnn.2005.184](https://doi.org/10.1166/jnn.2005.184)
- Chandran, S. P.; Chaudhary, M.; Pasricha, R.; Ahmad, A.; Sastry, M. *Biotechnol. Prog.* **2006**, *22*, 577.  
DOI: [10.1021/bp0501423](https://doi.org/10.1021/bp0501423)
- Dwivedi, A. D.; Gopal, K. *Colloids Surf. A* **2010**, *369*, 27.  
DOI: [10.1016/j.colsurfa.2010.07.020](https://doi.org/10.1016/j.colsurfa.2010.07.020)
- Philip, D.; Unni, C.; Aromal, S. A.; Vidhu, V. K. *Spectrochimica Acta Part A* **2011**, *78*, 899.  
DOI: [10.1016/j.saa.2010.12.060](https://doi.org/10.1016/j.saa.2010.12.060)
- Huang, J.; Li, Q.; Sun, D.; Lu, Y.; Su, Y.; Yang, X.; Wang, H.; Wang, Y.; Shao, W.; He, N.; Hong, J.; Chen, C. *Nanotechnology* **2007**, *18*, 105104.  
DOI: [10.1088/0957-4484/18/10/105104](https://doi.org/10.1088/0957-4484/18/10/105104)
- Philip, D. *Physica E* **2010**, *42*, 1417.  
DOI: [10.1016/j.physe.2009.11.081](https://doi.org/10.1016/j.physe.2009.11.081)
- Dubey, S. P.; Lahtinen, M. and Sillanpää, M. *Colloids. Surf. A* **2010**, *364*, 34.  
DOI: [10.1016/j.colsurfa.2010.04.023](https://doi.org/10.1016/j.colsurfa.2010.04.023)
- Kora, A. J., Sashidhar, R. B. and Arunachalam, J. *Carbohydr. Polym.* **2010**, *82*, 670.  
DOI: [10.1016/j.carbpol.2010.05.034](https://doi.org/10.1016/j.carbpol.2010.05.034)
- Prathna, T. C.; Chandrasekaran, N.; Raichur, M. A. and Mukherjee, A. *Colloids. Surf. B* **2011**, *82*, 152.  
DOI: [10.1016/j.colsurfb.2010.08.036](https://doi.org/10.1016/j.colsurfb.2010.08.036)
- Philip, D. *Spectrochim Acta A: Mol. Biomol. Spectrosc.* **2011**, *78*, 327.  
DOI: [10.1016/j.saa.2010.10.015](https://doi.org/10.1016/j.saa.2010.10.015)
- Bankar, A.; Joshi, B.; Ravi, K. A. and Zinjarde, S. *Colloids Surf. A* **2010**, *368*, 58.  
DOI: [10.1016/j.colsurfa.2010.07.024](https://doi.org/10.1016/j.colsurfa.2010.07.024)
- Bar, H.; Bhui, D. K.; Sahoo, G. P.; Sarkar, P.; Pyne, S.; Misra, A. *Colloids. Surf. A* **2009**, *348*, 212.  
DOI: [10.1016/j.colsurfa.2009.07.021](https://doi.org/10.1016/j.colsurfa.2009.07.021)
- Vidhu, V. K.; Philip, D. *Spectrochimica Acta Part A* **2014**, *117*, 102.  
DOI: [10.1016/j.saa.2013.08.015](https://doi.org/10.1016/j.saa.2013.08.015)
- Vinson, J. A.; Su, X.; Zubik, L.; Bose, P. *J. Agric. Food Chem.* **2001**, *49*, 5315.  
DOI: [10.1021/jf0009293](https://doi.org/10.1021/jf0009293)

49. Garcia, O. B.; Castillo, J.; Marin, J. R.; Ortuno, A.; Del Rio, J. A. *J. Agric. Food Chem.* **1997**, *45*, 4505.  
DOI: [10.1021/jf970373s](https://doi.org/10.1021/jf970373s)
50. Vandercook, C. E.; Stephenson, R. G. *J. Food Agric. Chem.* **1966**, *14*, 450.  
DOI: [10.1021/jf60147a003](https://doi.org/10.1021/jf60147a003)
51. Chen, B.; Jiao, X.; Chen, D. *Cryst. Growth Des.* **2010**, *10*, 3378.  
DOI: [10.1021/cg901497p](https://doi.org/10.1021/cg901497p)

## ***Advanced Materials Letters***

### **Publish your article in this journal**

[ADVANCED MATERIALS Letters](#) is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including [DOAJ](#) and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

