Synthesis and characterization of monodispersed silver nanoparticles

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Abstract
Synthesis of silver nanoparticles (NPs) has become a fascinating and important field of applied chemical research. In this paper silver NPs were prepared using silver nitrate (AgNO3), gelatin, and cetyl trimethyl ammonium bromide (CTAB). The prepared silver NPs were exposed under the laser ablation. In our photochemical procedure, gelatin acts as a biopolymer and CTAB acts as a reducing agent. The appearance of surface plasmon band around 410 nm indicates the formation of silver NPs. The nature of the prepared silver NPs in the face-centered cubic (fcc) structure are confirmed by the peaks in the x-ray diffraction (XRD) pattern corresponding to (111), (200), (220) and (311) planes. Monodispersed, stable, spherical silver NPs with diameter about 10 nm were obtained and confirmed by high-resolution transmission electron microscope (HRTEM).

Keywords: silver nanoparticles, surface plasmon, optical properties, HRTEM

Classification number: 4.02

1. Introduction
The development of uniform nanometer sized particles has been intensively pursued because of their technological and fundamental scientific importance [1–6]. These nanomaterials often exhibit very interesting electrical, optical, magnetic and chemical properties, which cannot be achieved by their bulk counterparts [7–11]. Synthesis, chemical and physical properties of metal nanoparticles are currently of considerable interest because of their potential application in material science and commercial industries. Owing to the small size of the building blocks and high surface-to-volume ratio, these materials are expected to demonstrate unique properties. Besides various types of nanomaterials such as copper, zinc, titanium [12] magnesium, gold [13], alginate [14] and silver which have emerged, silver nanoparticles (NPs) have proved to be more effective as they have good antimicrobial efficacy against bacteria, viruses and other eukaryotic micro-organisms [15].

Among many methods that were utilized for NPs fabrication, laser ablation in liquid as a nonchemical approach for the production of colloidal NPs is worthy of consideration. Some interesting specifications of this technique are simplicity and influence of the surrounding solvent [16–18]. A number of important physical and chemical effects of solvent are cooling, confinement and oxidation or reduction [18–21]. There are also some reports about the influence of surrounding solution on stability and particle size [22, 23]. The big challenge in the preparation of NPs is their agglomeration. To prevent this problem, various types of stabilizers have been used, such as long-chain fatty acids (stearic, palmitic and lauric acids) [24], polyvinyl pyrrolidone [25], soluble starch [26] and gelatin [27]. Gelatin is a biopolymer widely used in the pharmaceutical industry and for medical device applications. As a result of the growing interest in regenerative medicine, in the recent past gelatin has begun to be studied also as a candidate material for obtaining scaffolds with similar qualities of natural media for a wide range of tissues [28–32]. Current investigation supports that using silver ion or metallic silver as well as silver NPs can be exploited in medicine for burn treatment, dental materials, coating stainless steel materials, textile fabrics, water treatment, sunscreen lotions, etc, as they possess low toxicity to human cells, high thermal stability and low volatility [33]. Engineered nanoparticles are used in biomedical applications such as antibacterial implants.
or catheters, modification of textiles and refinement of polymers [34]. Our team has also reported a possible way to synthesize silver NPs using D. carota extract [35]. Silver NPs are also used in biosensors for glucose monitoring in diabetes patients and other medical health related targets. Electrosprun gelatin fiber mats containing silver NPs [36] and electrosprun gelatin nanofibers functionalized with silver NPs [37] have also been reported. In the present study, silver NPs were prepared using gelatin as a biopolymer and cetyl trimethyl ammonium bromide (CTAB) as reducing agent.

2. Experimental

2.1. Materials

Silver nitrate (AgNO₃), gelatin and CTAB were analytical grade reagents and used as received.

2.2. Preparation of silver NPs

The silver NPs were prepared using gelatin (0.001%) with a mixture with AgNO₃ (10⁻² M) and CTAB (10⁻² M). Initially, 2 ml of gelatin and AgNO₃ solution were added and the solution was kept under laser ablation for 1 h. Then 1 ml of 10⁻² M of CTAB was added. All the solutions were prepared using double distilled water. The solution was continuously stirred with the magnetic stirrer during laser irradiation.

2.3. Characterization

Shimadzu UV–1700 UV–visible spectrophotometer was used to carry out the optical measurements. The x-ray diffraction (XRD) patterns were recorded on an x-ray diffractometer using Cu-Kα radiation (λ = 0.1542 nm) operated at 50 kV and 100 mA. The experiments were performed in the diffraction angle range of 2θ = 20–80°. The size, composition and atomic structure of the NPs were analyzed by high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) using a 200 KeV JEOL 2010F microscope with a NORAN Vantage DI+EDS system. The spherical (Cs) and chromatic aberration (Cc) coefficients of the objective lens were 0.5 and 1.1 mm respectively. The point-to-point resolution was 0.194 nm at Scherzer focus (42 nm). The samples were made by depositing the silver NPs on a carbon coated Cu grid, and size measurements were performed manually on HRTEM images.

3. Results and discussion

Figure 1 shows the optical absorption spectra of silver NPs in the region 320–620 nm. The absorption spectra show one prominent symmetric peak around 410 nm, which is due to the characteristic surface plasmon resonance of spherical silver NPs. The prepared solution is golden yellow in color which indicates the formation of silver NPs. This absorption band results from interactions of free electrons confined to small metallic spherical objects with incident electromagnetic radiation. Electronic modes in silver NPs are particularly sensitive to their shape and size, leading to pronounced effects in the visible part of the spectrum. One interesting feature is the increase of the bandwidth of the resonance with the decrease of the size of the particles due to electron scattering enhancement at the surface. The shift of the resonance and the variation of its bandwidth are thus interesting parameters to characterize the metal nanoparticles. The observed plasmon band around 410 nm shows that the silver NPs are spherical in shape [38]. The observed band at 410 nm is due to the out-of-plane dipole plasmon resonance [39]. The full-width at half-maximum (FWHM) is reported to be quite useful in understanding the particle size and their distribution within the medium. By adopting the concept of Brown et al [40], in the present work the FWHM of the colloidal silver is 124 nm. It is understood that a FWHM of 124 nm is generally indicative of a narrow size distribution. Therefore, the present approach can be considered a suitable methodology for obtaining uniform silver NPs with a narrow size distribution.

Figure 2 shows the XRD pattern of the prepared silver NPs. In the XRD pattern (figure 2), four diffraction
peaks were observed at $2\theta = 37.85^\circ$, $44.0^\circ$, $64.2^\circ$ and $77.2^\circ$, which correspond to (111), (200), (220) and (311) Bragg’s reflections of the face-centered cubic (fcc) structure of metallic silver, respectively. All diffraction peaks are in good agreement with the standard value (JCPDS card No. 04-0783). This XRD line width can be used to estimate the size of the particle by using the Debye–Scherrer formula $d = \frac{0.94 \lambda}{\beta \cos \theta}$, where $d$ is the particle size, $\lambda$ is the wavelength of x-ray radiation ($1.5406 \, \text{Å}$), $\beta$ is the FWHM of the peak (in radians) and $2\theta$ is the Bragg angle. The calculated average particle size is found to be around 18 nm.

TEM is a high spatial resolution structural and chemical characterization tool and provides exact information about particle size and shape [41, 42]. A modern HRTEM has the capability to directly image atoms in specimens at resolutions close to 1 Å, smaller than inter-atomic distance. This type of analysis is extremely important for characterizing materials at a length scale from atoms to hundreds of nanometers. Figure 3 shows HRTEM image of silver NPs. The silver NPs all have a spherical shape with diameter about 10 nm. The observed spherical shape of the prepared silver NPs are highly in agreement with the fact given by Mock et al [38] confirming that surface plasmon band around 410 nm shows that the silver NPs are spherical in shape. The silver NPs were observed to be mono dispersed and stable.

4. Conclusion

In this paper mono dispersed silver NPs were synthesized by a chemical reduction method processed under laser irradiation. The nanoparticles were characterized by UV–Vis, XRD and HRTEM. The nature of the silver NPs is evident from HRTEM images and peaks in XRD pattern. The prepared silver NPs are around 10 nm which is suitable for future use as the base of conductive ink. It could also be used in sensing and imaging field. The silver NPs are prepared by a cost effective, simple and fast method. Future work will include the size related synthesis and applications of silver NPs.

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References

[1] Alivisatos A P 1996 Science 271 933
[2] Andres R P, Bein T, Dorogi M, Feng S, Henderson J I, Kubiak C P, Mahoney W, Osifchin R G and Reifenberger R 1996 Science 272 1323
[3] Weller H 1993 Angew. Chem., Int. Ed. Engl. 32 41
[4] Schmid G (ed) 1994 Clusters and Colloids (New York: VCH)
[5] Fendler J H 1998 Nanoparticles and Nanostructured Films (Weinheim: Wiley)
[6] Klabunde K J (ed) 2001 Nanoscale Materials in Chemistry (New York: Wiley Interscience)
[7] Majetich S A and Jin Y 1999 Science 284 470
[8] Murray C B, Kagan C R and Bawendi M G 1995 Science 270 1335
[9] Zarur A J and Ying J Y 2000 Nature 403 65
[10] Stephan L and Mostafa A E S 1999 J. Phys. Chem. B 103 8410
[11] Jose H, Hodak A H and Gregory V H 2000 J. Phys. Chem. B 104 9954
[12] Retchkiman-Schabes P S, Canizal G, Becerra-Herrera R, Zorrilla C, Liu H B and Ascencio J A 2006 Opt. Mater. 29 95
[13] Hongwei G, Ho P L, Tong E, Wang L and Xu B 2003 Nano Lett. 3 1261
[14] Ahmad Z, Pandey R, Sharma S and Khuller G K 2005 Indian J. Chest Dis. Allied Sci. 48 171
[15] Gong P, Li H, He X, Wang K, Hu J and Tan W 2007 Nanotechnology 18 604
[16] Kreibig U and Vollmer M 1995 Optical Properties of Metal Clusters (Berlin: Springer)
[17] Darroudi M, Ahmad M B, Zamiri R, Abdullah A H, Ibrahim N A, Shaneli K and Husin M S 2011 J. Alloys Compdoun. 509 1301
[18] Tsuji T, Kakita T and Tsuji M 2003 Appl. Surf. Sci. 206 314
[19] Kabashin A V, Meunier M, Kingston C and Luong J H T 2003 J. Phys. Chem. B 107 4527
[20] Tsuji T, Hamagami T, Kawamura T, Yamaki J and Tsuji M 2005 Appl. Surf. Sci. 243 214
[21] Liang C H, Sasaki T, Shimizu Y and Koshizaki N 2004 Chem. Phys. Lett. 389 58
[22] Liang C H, Shimizu Y, Sasaki T and Koshizaki N 2003 J. Phys. Chem. B 107 9220
[23] Mafune F, Kohno J, Takeda Y, Kondow T and Sawabe H 2001 J. Phys. Chem. B 105 5114
[24] Rao C R K and Trivedi D C 2005 Synth. Met. 155 324
[25] Tsuji T, Thang D H, Okazaki Y, Tsuboi M N Y and Tsuji M 2008 Appl. Surf. Sci. 254 5224
[26] Vigneshwaran N, Nachane R P, Balasubramanyam R H and Varadarajan P V 2006 Carbohydr. Res. 341 2012
[27] Zamiri R, Azmi B Z, Darroudi M, Sadrolhosseini A R, Husin M S, Wahab Z A and Mahdi M A 2011 Appl. Phys. A 102 189
[28] Li M, Mondrinos M J, Gandhi M R, Ko F K, Weiss A S and Lelkes P I 2005 Biomaterials 26 5999
[29] Liao S, Bojun L, Ziwei M, Wei H, Chan C and Ramakrishna S 2006 Biomed. Mater. 1 R45
[30] Langer R and Tirrell D A 2004 Nature 428 487
[31] Dankers P Y W, Harmse M C, Brouwer L A, van Luyn M J and Meijer E W 2005 Nature Mater. 4 568
[32] Huang Z M, Zhang Y Z, Kotaki M and Ramakrishna S 2003 Compos. Sci. Technol. 63 2223
[33] Duran N, Marcarro P D, De Souza G I H, Alves O L and Esposito E 2007 J. Biomed. Nanotechnol. 3 203
[34] Barcikowski S, Menéndez-Manjón A, Chichkov B N, Brika M and Račiukaitis G 2007 Appl. Phys. Lett. 91 083113
[35] Umadevi M, Shalini S and Bindhu M R 2012 Adv. Nat. Sci. 3 025008
[36] Rujitanaroj P-O, Pimpha N and Supaphol P 2008 Polymer 49 4723
[37] Tofoleanu F et al 2008 J. Optoelectron. Adv. Mater. 10 3512
[38] Mock J J, Barbic M, Smith D R, Schultz D A and Schultz S 2002 J. Chem. Phys. 116 6755
[39] Jin R, Cao Y, Mirkin C A, Kelly K L, Schatz G C and Zheng J G 2001 Science 294 1901
[40] Brown K R, Walter D G and Natan M 2000 J. Chem. Mater. 12 306
[41] Link S and El-Sayed M A 2000 Int. Rev. Phys. Chem. 19 409
[42] Wang Z L 2000 J. Phys. Chem. B 104 1153