Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 95 (2012) 305–309

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Novel synthesis of silver nanoparticles using 2,3,5,6-tetrakis-(morpholinomethyl) hydroquinone as reducing agent

P. Manivel [a], A. Balamurugan [a], N. Ponpandian [a], D. Mangalaraj [a], C. Viswanathan [a,b,*]

[a] Department of Nanoscience and Technology, Bharathiar University, Coimbatore 641046, Tamilnadu, India
[b] DRDO-BU-Center for Life Science, Physics Division, Bharathiar University, Coimbatore 641046, Tamilnadu, India

ARTICLE INFO

Article history:
Received 22 January 2012
Received in revised form 19 March 2012
Accepted 25 March 2012
Available online 6 April 2012

Keywords:
TMMH
Nanoparticles
Reducing agent
FTIR
Organic
Crystalline size

ABSTRACT

2,3,5,6-Tetrakis-(morpholinomethyl) hydroquinone (TMMH) was used as a reducing agent to synthesize spherical shaped silver nanoparticles in water–ethanol medium without using any stabilizing and capping agents. The reducing agent TMMH is prepared by Mannich-type reaction method and ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy techniques were used to characterize the compound (TMMH). The nature of bonding, structural and optical properties of the final product were analyzed using different techniques such as UV–Vis spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). The interaction between silver and reducing agent was confirmed by using FTIR analysis. The final product obtained showed higher crystallinity with cubic structure and an average crystalline size of about 20 nm. The results revealed that it is possible to synthesize crystalline Ag nanoparticles using organic compound as reducing agent.

Introduction

Nanoparticles are used, due to their potential applications in various fields like optical device, chemical sensor, bimolecular sensor and DNA detection [1]. Among various metals, silver nanoparticles are an interesting one because of their size and shape dependent optical properties which render them very useful for technical applications [2]. In particular, there is a remarkable interest to produce silver nanoparticles dispersion at large scale [3–4]. Several methods have been reported for the synthesis of silver nanoparticles, including chemical reduction in aqueous solution with or without stabilizing agents [5]. Thermal decomposition in organic solvents [6], chemical and photo reduction in reverse micelles [7] and microwave assistance [8], are some of the factors for the formation of silver nanoparticles. Most of the researchers previously described the stable silver dispersion only at relatively low concentrations of metal. Hence, they are not suitable for large-scale production [9]. The simplest, cost effective and the most commonly used bulk-solution synthetic method for metal nanoparticles is the chemical reduction of metal salts [10]. In fact, production of nanoscale metal silver particles with different morphologies and sizes using chemical reduction of silver salts has been reported [11,12].

The effective method to generate silver nanoparticles in narrow size distribution of aqueous medium is achieved by the reduction method using citrate of sodium [13]. Other reducing agents that have been used are ascorbic acid, hydrazine hydrate and sodium dodecyl sulfate. In fact, formation of nanosized silver particles with different morphologies and sizes using chemical reduction of silver salts has been reported [12]. A mixture of hydrazine hydrate and citrate of sodium as a reducing agent in the isolation of silver nanoparticles has been reported by Guzman et al. [14]. Tripathy and Yu [15] reported the synthesis of ω-mercaptoundecanoic acid generated silver nanoparticles. The nanoparticles were also obtained by chemical reduction of $AgNO_3$ in ethanol, using triethylenetetramine as surfactant [16]. In this method control of the size of the nanoparticles has been achieved by regulating the ratio of metal chloride to the organic reagent. Recently gold nanoparticles were obtained by 2,3,5,6-tetrakis-(morpholinomethyl) hydroquinone as reducing agent [17]. The above approach is well enough to justify our effort to report a new and effective reducing agent for the preparation of silver nanoparticles.

In the present work we have made an attempt to synthesize the silver nanoparticles using TMMH as reducing agent. The as-synthesized compound (TMMH) after purification was used to synthesize final silver nanoparticles. The secondary hydroxyl groups and nitrogen of TMMH compound have been used for the reduction of $AgNO_3$. This approach is a simple, cost-effective, stable for long time, reproducible and previously unexploited method. We found that the size of nanoparticles can be modulated by varying the

---

* Corresponding author at: Department of Nanoscience and Technology, Bharathiar University, Coimbatore 641046, Tamilnadu, India. Tel.: +91 422 2428422.
E-mail address: viswanathan@buc.edu.in (C. Viswanathan).

1386-1425/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2012.03.081

amount of TMMH compound in the reaction medium. Even spherical aggregation of Ag nanoparticles could also be obtained with low and high concentrations of TMMH. To our knowledge there are no reports on the use of TMMH as a reducing agent in the synthesis of silver nanoparticles using chemical reduction. Hence a systematic study of synthesis and characterization is undertaken.

Experimental procedure

Ultra-pure water was used throughout this study and its resistivity was >18 MΩ cm. Silver nitrate ($AgNO_3$), hydroquinone, paraformaldehyde, morpholine, 1,4-dioxane and potassium hydroxide were of analytical grade and were not further purified before use. Thin layer chromatography (TLC) analysis was carried out using silica gel plates.

Morpholine (18.9 g, 0.2179 mol) and paraformaldehyde (8.18 g, 0.272 mol) were dissolved in 1,4-dioxane (60 mL) and stirred vigorously. The solution was refluxed at 100 °C for 2 h. Then hydroquinone (3 g, 0.0272 mol) was added drop wise and the reflux process was continued for another 24 h at 100 °C. The reaction was continued until the hydroquinone was bonded to the imines and confirmed through TLC. Finally, the solution was cooled to room temperature and filtered, concentrated on a rotary evaporator to dryness and kept overnight under vacuum. The as-prepared TMMH mixture was purified using column chromatography and the obtained product was eluted using $CHCl_3$:MeOH (95:5) until the formation of light-yellow powder. The structure of the isolated TMMH compound was compared with the previously reported spectral values. The complete reaction mechanism for the formation of TMMH is shown in Fig. 1.

A series of volume (2.5–10 ml) of a 10^{-3} M ethanol solution of TMMH was added into 5 ml of 2×10^{-3} M aqueous $AgNO_3$ solution under vigorous stirring at room temperature. After 1 min the solution was gradually changed from colorless to pale yellow color. Then potassium hydroxide was added into the solution to adjust the pH (pH 8), which makes the solution change from pale yellow to dark brown colored solution indicating the formation of Ag nanoparticles.

^{1}H and ^{13}C NMR spectra were recorded by JEOL 300 MHz spectrometer to conform the TMMH structure. FTIR spectra were obtained on a Nicolet-6700 spectrometer, with samples prepared as KBr pellets. The absorption spectra were recorded by double-beam Jasco V-530 UV–Vis spectrometer. X-ray diffraction (XRD) measurements of the TMMH capped colloidal silver nanoparticles drop-coated onto glass substrates were done on a PANalytical X' Pert Pro MPD instrument operating at a voltage 40 kV and a current of 30 mA with Cu Kα radiation (Ni filter). The morphology of Ag nanoparticles was analyzed from ICON Quanta Make II Environmental SEM.

Results and discussion

Spectral analysis of pure compound (TMMH)

Fig. S1 shows ^{1}H NMR spectra of TMMH (see Supplementary material). A multiplet 16 protons were obtained at δ 2.52 due to morpholine in $N—\underline{CH_2}—CH_2$. A multiplet at δ 3.67 was obtained due to 16 protons of morpholine in $O—\underline{CH_2}—CH_2$ and 18 protons in $Ar—\underline{CH_2}—N$. A broad singlet at δ 10.09 was due to aromatic OH groups. This ^{1}H NMR spectra of the TMMH were quite comparable with previous reports [17].

Fig. S2 shows ^{13}C NMR spectra of TMMH (see Supplementary material). A peak at δ 149.6 (2C) is due to C_1 and $C_4—OH$ and a peak at δ 121.4 (4C) is due to C_2, C_3, C_5 and C_6. Three more peaks at δ 66.9 (8C), 54.6 (4C) and 52.8 (8C) are due to the presence of morpholine $O—\underline{CH_2}—CH_2$, $Ar—\underline{CH_2}$ attached C_2, C_3, C_5 and C_6 and morpholine $N—\underline{CH_2}—CH_2$, respectively.

Fig. S3 shows FT-IR spectra of TMMH (see Supplementary material). A stretching vibration at 3430 cm^{-1} is due to the presence of O—H groups, and two strong vibrational frequencies at 1115 and 1007 cm^{-1} are due to C—C and C—O groups, respectively. The stretching C—H bonds are characteristic and they give rise to strong bands in the region 2852 cm^{-1}.

TMMH capped silver nanoparticles

UV–Vis absorption spectra have been proven to be quite sensitive for the formation of silver colloids because the silver nanoparticles can exhibit an intense absorption peak due to the surface plasmon (it describes the collective excitation of conduction

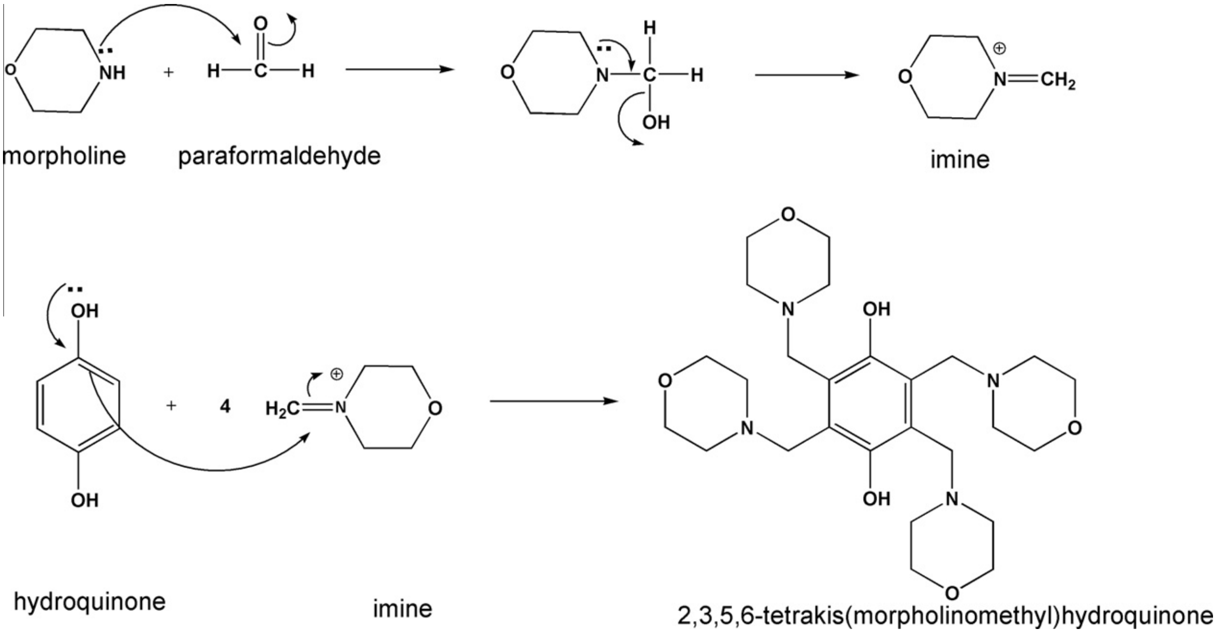

Fig. 1. Schematic diagram of the reaction mechanism of TMMH.

electrons in a metal) excitation [13]. Formation and stability of silver nanoparticles in aqueous colloidal solution are confirmed by UV–Vis spectral analysis. Fig. 2 shows the UV–Vis spectra of TMMH capped silver nanoparticles formation at constant volume of $AgNO_3$ with different volume of TMMH [(a) 2.5 mL, (b) 5 mL, (c) 7.5 mL and (d) 10 mL] in water ethanol medium. It is worthwhile mentioning that $AgNO_3$ can be completely reduced to form silver nanoparticles, which is confirmed by the observation that there is no further change in UV–Vis spectrum after TMMH is introduced into silver solution. Our result showed that there are two strong absorption bands appeared upon varying the volume of TMMH in the reaction medium. In the presence of TMMH, it exhibited well resolved absorption bands at 420 nm (curves b and d of Fig. 2). Also the UV absorption intensity increased with increase in the volume of TMMH in the solution phase.

The XRD technique was used to determine the crystal structure of silver nanoparticles. Fig. 3 shows the XRD pattern of TMMH capped silver nanoparticles. In order to study the crystallinity of silver nanoparticles, the colloidal solution was drop coated onto a glass substrate to obtain a film and dried at ambient temperature. The entire reflection of well defined peaks, which were obtained from XRD, confirms the formation of silver nanoparticles to face-centered cubic structure (Fig. 3(a) 1:1 volume ratio and (b) 2:1 volume ratio). Face center cubic structure was revealed with 2θ values of 38, 44, 64, 77 and 81 corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystalline planes, respectively (JCPDS PDF No. 89-3722). Thus XRD pattern clearly demonstrated that the nanoparticles formed by chemical reduction of Ag+ ions, were crystalline in nature. The reflections were observed at lower angles compared to the standard which might be due to a slight increase in lattice parameters of nano-phased silver. Also, the broadening of the diffraction peaks was observed due to the effect of nano-sized particles. The background observed was high, which could be from glass substrate used for data collection and also because of the presence of organic moieties in TMMH and ethanol that were used for nanoparticle synthesis. As indicated in Fig. 3, the highly intense diffraction peak was located at $2\theta = 37.96°$. So, we can conclude that (1 1 1) lattice plane is the preferred orientation for these silver nanoparticles, attributable to its lower surface free energy compared to other planes [18]. In addition, high atom density facets such as (1 1 1) are used for their high antiviral activity [19].

We obtained the average crystal size by Williamson–Hall (W–H) plot. Before estimation the instrument was corrected to control the background effect. In order to measure the instrumental contribution to line broadening, the diffraction pattern was recorded for the sample with standard silicon (Si). The instrumental correction of line broadening, (β_{hkl}) [20] corresponding to each diffraction peak of silver nanoparticles was estimated using the equation

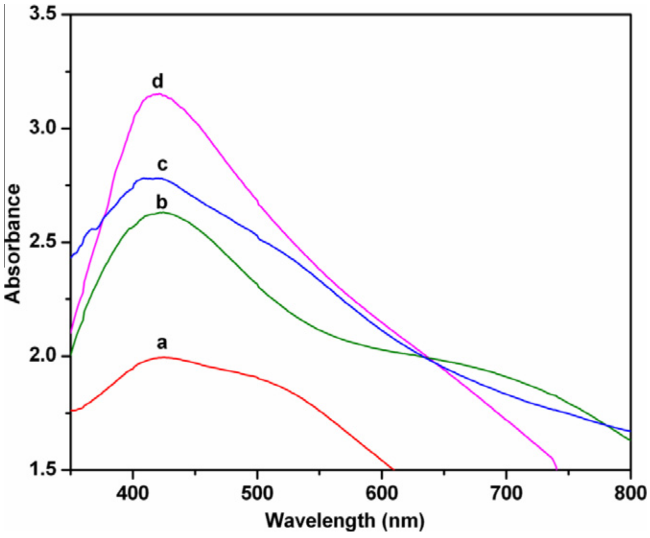

Fig. 2. UV–Vis spectra of silver nanoparticles synthesized using 5 mL $AgNO_3$ (2×10^{-3} M) with different volume of TMMH (a) 2.5 mL, (b) 5 mL, (c) 7.5 mL and (d) 10 mL.

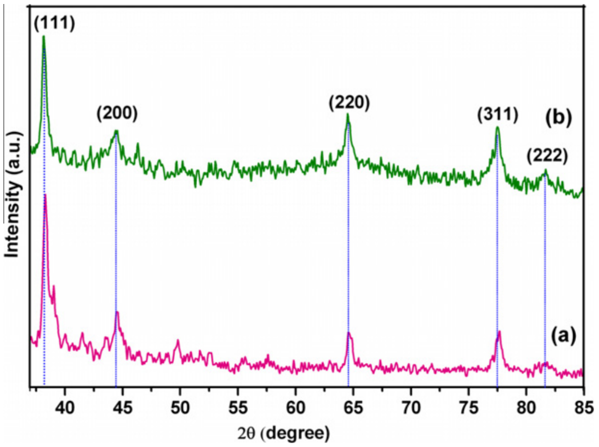

Fig. 3. XRD pattern of TMMH capped silver nanoparticles (TMMH:$AgNO_3$): (a) 1:1 volume ratio (b) 2:1 volume ratio.

$$\beta_{hkl} = [(\beta_{hkl})^2\text{measured} - (\beta)^2\text{measured}]^{1/2} \quad (1)$$

Williamson and Hall proposed a method of deconvoluting size and strain broadening by looking at the peak width as a function of diffracting angle 2θ and obtained a mathematical expression [21] as

$$\beta_{hkl} = \left(\frac{K\lambda}{D_v \cos\theta}\right) + (4\varepsilon \tan\theta) \quad (2)$$

or by rearranging

$$\beta_{hkl} \cos\theta = \left(\frac{K\lambda}{D_v}\right) + (4\varepsilon \sin\theta) \quad (3)$$

where β_{hkl} is instrumental corrected integral breadth of the reflection (in radians) located at 2θ, k is the shape factor (0.9 for spherical shape), D_v is the volume weighted crystallite size, and θ is the angle of reflection (in degrees). A plot is drawn for 4 sinθ along the X-axis and β_{hkl} cosθ along the Y-axis for prepared Ag nanoparticles and is shown in Fig. 4. For the entire W–H model, the plot is drawn only for the preferred orientation peaks of Ag with the face-centered cubic phase. The lattice planes corresponding to those preferred peaks are (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2). The crystallite size is intercept of the linear fit made to the plot. The as-estimated value of the crystallite size is 19 nm for (TMMH:$AgNO_3$) 1:1 volume ratio (Fig. 4(a)) and 16 nm for 2:1 volume ratio (Fig. 4(b)) prepared sample.

The morphology and size of the prepared silver nanoparticle were investigated using scanning electron microscopy. Fig. 5(a and b) shows surface morphology and particle size distribution of silver nanoparticles synthesized from 1:1 volume ratio of TMMH with $AgNO_3$. All the nanoparticles are nearly in spherical shape and the average diameter was 42.4 ± 5 nm (150 nanoparticles were measured for averaging). Fig. 5(c and d) shows representative silver nanoparticles synthesized using 2:1 volume ratio of TMMH with $AgNO_3$. Also, it has been confirmed that all the silver nanoparticles are in spherical shape. The average diameter was 26 ± 4.2 nm (160 nanoparticles were measured for averaging). The size of the silver nanoparticles was found to be decreased with an increase in TMMH reducing agent. The self-assembled nanoparticles can

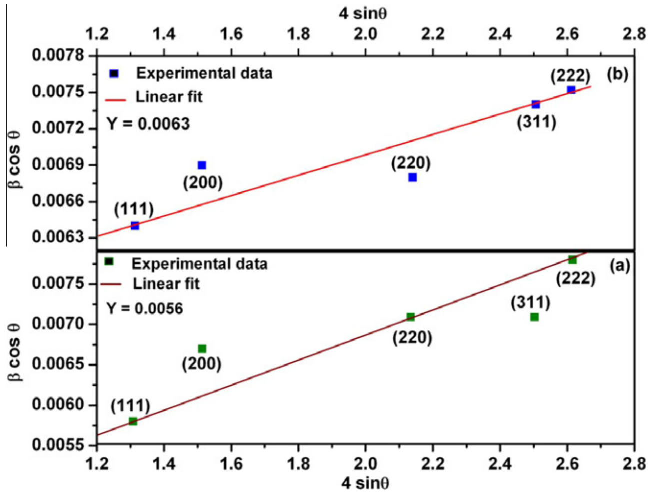

Fig. 4. W–H plot of silver nanoparticles (TMMH:AgNO$_3$): (a) 1:1volume ratio, (b) 2:1 volume ratio.

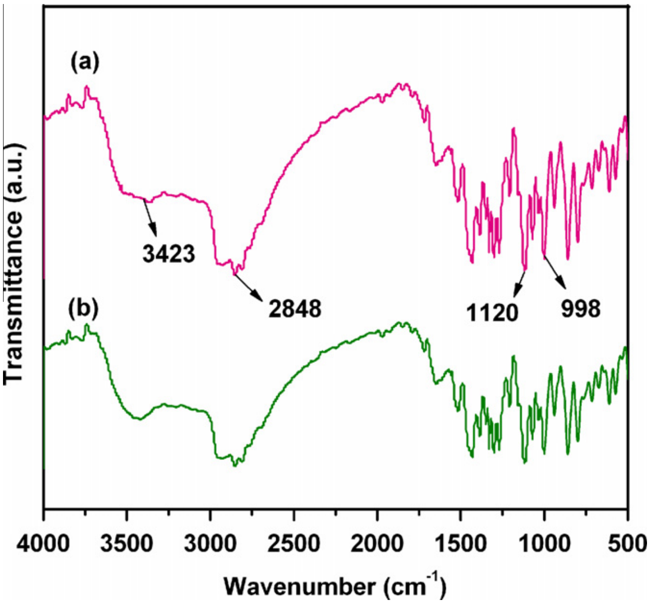

Fig. 6. FT-IR spectra of silver nanoparticles (a) 1:1 volume ratio TMMH with Ag and (b) 2:1 volume ratio TMMH with Ag.

be regulated smoothly and the growth can be controlled by the critical TMMH/AgNO$_3$ volume ratio.

The interaction of Ag nanoparticles with TMMH compound was confirmed by FT-IR spectra (Fig. 6). The strong vibration band (pure TMMH) was corresponding to the stretching of C—C bond assigned at 1115 cm^{-1}, C—O bond assigned at 1007 cm^{-1}, C—H stretching assigned at 2852 cm^{-1}, respectively. While the intense broad peak observed at 3430 cm^{-1} was corresponding to stretching vibration of —OH bond. After the reduction with AgNO$_3$, the shift in the peak at 3430 toward lower frequency which is attributed to the binding of —OH group with nanoparticles is shown in Fig. 6(a and b). Also, the —OH peak suppresses in the presence of nanoparticles, which

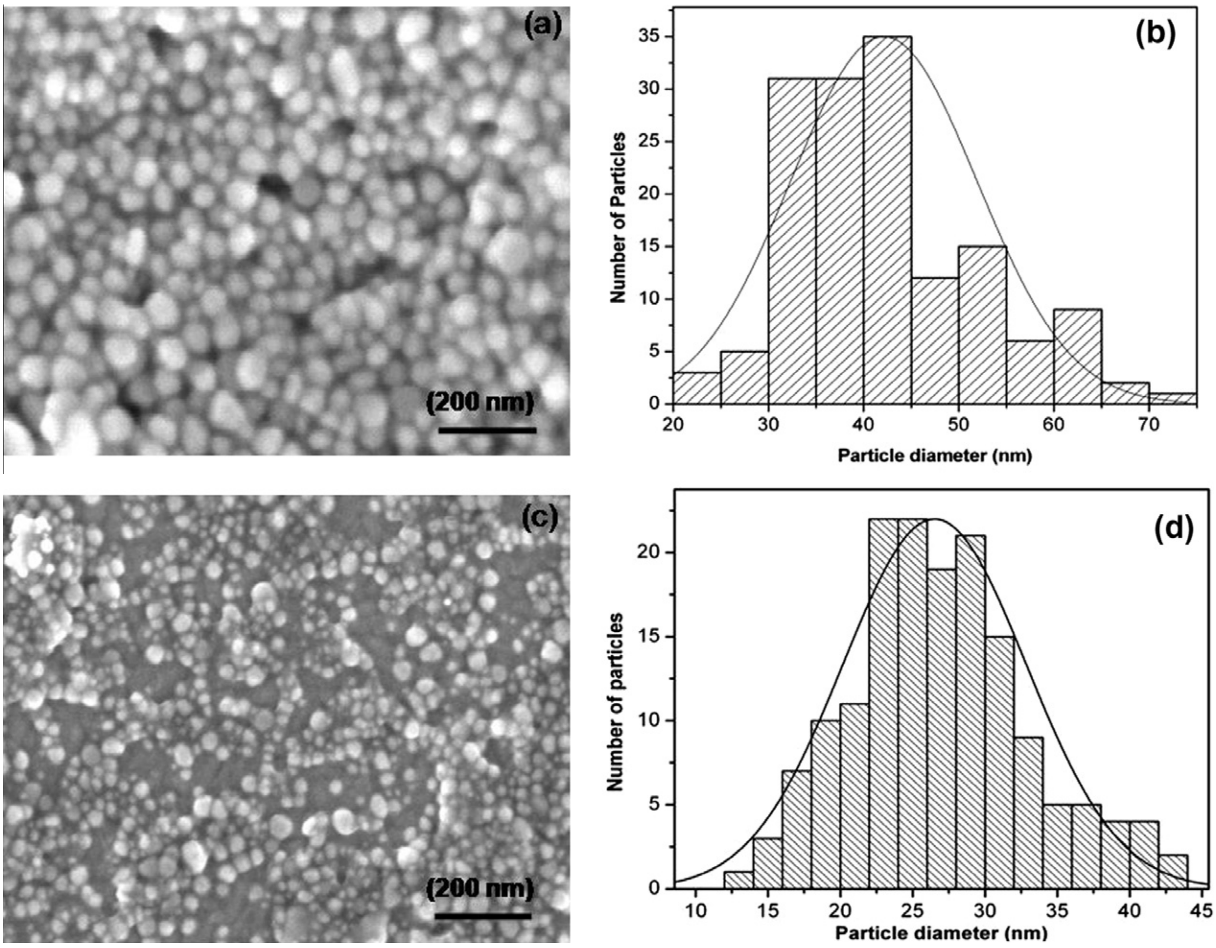

Fig. 5. SEM image of Ag nanoparticles; (a) 1:1 volume ratio and (b) corresponding size distribution histogram, (c) 2:1 volume ratio and (d) corresponding size distribution histogram.

indicates that Ag^+ ions are reduced with the hydroxyl groups of TMMH. Similarly, the stretching vibrations of C—H, C—O and C—C bonds are slightly shifted with low intense. In conventional liquid phase preparation of TMMH capped silver nanoparticle, the interaction between the two components appeared clearly either as changes in the wave number or changes in the intensity of some absorption peaks of TMMH [22].

Conclusion

We have successfully prepared 2,3,5,6-tetrakis-(morpholinomethyl) hydroquinone and used for size reduction of silver nanoparticles. This compound behaves as a capping agent for silver nanoparticle synthesis. Size of the silver nanoparticles was well controlled by varying the volume ratio of TMMH compound. These nanoparticles are found to be stable in water for more than three months that can be attributed to surface binding of TMMH compound with the reduced materials. It was clearly seen that the TMMH has played an important role in the stabilization of silver nanoparticles through the electrostatic interaction between hydroxyl groups with silver ion. This route of silver nanoparticles may have useful potential applications such as anti bacterial, antiviral activities.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.03.081.

References

[1] D.L. Feldheim, C.A. Foss, Metal Nanoparticles: Synthesis, Characterization, and Applications, first ed., CRC Press Publisher, 2002.
[2] V.M. Rotello, Nanoparticles: Building Blocks for Nanotechnology, Academic/Plenum Publishers, New York, 2004.
[3] D.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Langmuir 9 (1993) 162–169.
[4] L.M. Liz Marzan, I. Lado Tourino, Langmuir 12 (1993) 3585–3589.
[5] I. Sondi, D.V. Goia, E. Matijevi, J. Colloid Interface Sci. 260 (2003) 75–81.
[6] K. Esumi, T. Tano, K. Torigoe, K. Meguro, Chem. Mater. 2 (1990) 564–567.
[7] H.W. Lu, S.H. Liu, X.L. Wang, X.F. Qian, J. Yin, Z.K. Zhu, Mater. Chem. Phys. 81 (2003) 104–107.
[8] H. Katsuki, S. Komarneni, J. Mater. Res. 18 (2003) 747–750.
[9] M.V. Roldan, L.B. Scaffardi, O.D. Sanctis, N. Pellegri, Mater. Chem. Phys. 112 (2008) 984–990.
[10] V.R. Chaudhari, S.K. Haram, S.K. Kulshreshtha, Colloids Surf. A 301 (2007) 475–480.
[11] Z. Chen, L. Gao, J. Mater. Res. Bull. 42 (2007) 1657–1661.
[12] A. Kumar, H. Joshi, R. Pasricha, A.B. Mandale, M. Sastry, J. Colloid Interface Sci. 264 (2003) 396–401.
[13] A. Sileikaite, I. Prosycevas, J. Puiso, A. Juraitis, A. Guobiene, Mater. Sci. 12 (2006) 287–291.
[14] M.G. Guzman, J. Dille, S. Godet, PWASET 33 (2008) 2070–3740.
[15] S.K. Tripathy, Y.T. Yu, Spectrochim. Acta A 72 (2009) 841–844.
[16] L. Ramajo, R. Parra, M. Reboredo, M. Castro, J. Chem. Sci. 121 (2009) 83–87.
[17] P. Roy, K. Dhara, M. Manassero, P. Banerjee, Polyhedron 27 (2008) 3085–3090.
[18] P.S.K. Murthy, Y.M. Mohan, K. Varaprasad, B. Sreedhar, K.M. Raju, J. Colloid Interface Sci. 318 (2008) 217–224.
[19] J.R. Morones, J.L. Elechiguerra, A. Camacho, K. Holt, J.B. Kouri, J.T. Ramirez, M.J. Yacaman, Nanotechnology 16 (2005) 2346–2353.
[20] K. Venkateswarlu, A. ChandraBose, N. Rameshbabu, Physica B 405 (2010) 4256–4261.
[21] R. Yogamalar, R. Srinivasan, A. Vinu, K. Ariga, A. Chandra Bose, Solid State Commun. 149 (2009) 1919–1923.
[22] K.H. Lee, S.C. Rah, S.G. Kim, J. Sol–Gel Sci. Technol. 45 (2008) 187–193.