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Biphasic synthesis of fatty acids stabilized silver nanoparticles: Role of experimental conditions on particle size

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Abstract

Synthesis of silver nanoparticles stabilized by stearic, palmitic and lauric acids is reported. Three reducing agents, which are moderate strong to mild, formaldehyde, triethanolamine and dimethylformamide, are used. The synthesized nanoparticles are dispersible in non-polar solvents such as benzene and toluene. The IR spectra showed the existence of adsorbed fatty acids. The toluene solution of these nanoparticles exhibited a surface plasmon resonance in the range 420–432 nm. It is shown that the silver nanoparticles have an enhanced stability with increasing chain length of the fatty acid. The size of the nanoparticles is greatly influenced by the experimental conditions such as temperature and concentration. The nanoparticles are characterized by UV–vis, FTIR, XRD, AFM and TEM techniques.

Keywords: Silver; Nanoparticle; Reduction; Stabilization; Plasmon resonance; Fatty acid

1. Introduction

Fine metal particles have applications in the area of catalysis, opto-electronics due to their size-dependent optical, electrical and electronic properties [1–4]. A quantum confinement sets in when the particle size is less than 5 nm [1]. Silver nanoparticles are a class of materials with interesting properties such as absorptions in the UV–vis region due to the surface plasmon resonance (SPR), catalysis [5] and biosensing [6]. Spherical nanoparticles with a different thin metal coating (i.e., core–shell) are especially interesting in view of their unusual optical properties. Due to coupling of surface plasmons corresponding to the two interfaces, the shift in *Mie* resonances can be tailored to any desired wavelength in the visible region by choosing core size, layer thickness and coating material [7]. Such composite nanoparticles are important substrates for organic molecules in surface-enhanced Raman scattering (SERS) studies. Silver is a potential antibacterial agent [8] and hence used as sterilizers and for removal of bacteria from drinking water [9,10]. Silver ion kills microorganisms instantly by blocking the respiratory enzyme system while having no negative effect on human cells. The antibacterial activity of silver ions and their biological impact have been demonstrated by many works [11]. Based on its antibacterial properties, many applications using pure silver nanoparticles or its composites can be thought, such as antibacterial textile [12]. Fiber can be infused with minute silver particles, which are claimed to be 99.9% effective in preventing infections including pneumobacilli and fungi-causing athlete's foot. More recently, physicians have used silver-coated dressing (Acticoat$^{\text{TM}}$) to treat major burn injuries [13,14]. Silver-based inorganic antibacterial agents are available in the market, which are known as "antibacterial ceramics" [15]. These are available in powder/pellet (e.g., from BIOSERA, NANUX Inc.) form to be used as liquids to clean home appliances and also as main material for artificial bones or teeth.

Long-chained molecules such as stearic acid, octadecyl amine are used as stabilizers, which adsorb on the surface (passivation) of the as formed nanoparticle and prevent aggregation [16–19]. The passivated nanoparticles are stable under normal conditions as solutions, films, and dry powders. The powders can be dispersed in non-polar solvents. Various reducing agents such as H_2, $NaBH_4$, N_2H_4, NH_2OH, $(CH_3)_2NH{\cdot}BH_3$, ethanol, ethylene glycols, Tollen's reagent, ascorbic acid and aliphatic amines are used to effect the reduction for the synthesis of the noble metal nanoparticles [20–31].

In order to control the size of the nanoparticles, always wet chemical methods are preferred [32–35] in which homogeneous solutions containing metal in low concentrations and large

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amount of stabilizer are used to avoid rapid aggregation of the formed metal core. On the other hand, recent literature showed [11,19,35] that high concentrations of metal could be used if the ligand of the precursor acts as the stabilizer. Based on this concept, in the present paper, we report the synthesis of silver nanoparticles from silver–fatty acid salts. The fatty acids from the precursor stabilize the newly born Ag(0) clusters. Reducing agents, which are strong to mild namely formaldehyde, dimethylformamide and triethanolamine are used. In addition to its reducing property, triethanolamine can act as good chelater to captcher silver ions which can influence the growth of the nucleation and hence particle size. Present article describes the synthesis of silver nanoparticles by these reducing agents from aqueous–organic biphasic mixtures. Characterization of the resulting nanoparticles by UV–vis, XRD, AFM, TEM and the role of experimental conditions on the particle size is presented and discussed.

2. Experimental

All the chemicals used were of analytical grade. Stearic acid (STA), palmitic acid (PAL) and lauric acid (LAU) were obtained from S.d. Fine Chemicals and were converted to their sodium salts by reaction with sodium hydroxide. Salts Ag–STA, –PAL and –LAU were freshly prepared from the respective sodium salts and silver nitrate just before the synthesis of nanoparticles. All the experiments were conducted in a well-equipped hood. XRD experiments were carried out on JEOL JDX-8030 instrument. UV–vis spectra were recorded on CARRY 50 SCAN UV–vis-Spectrophotometer. Atomic force microscopy (AFM) analyses were carried out on 'Molecular Imaging' instrument. TEM experiments were performed on JEOL JEM-200FXII instrument operating at an accelerating voltage of 200 kV. Drop of toluene solution of the samples were placed on the TEM carbon grids. The films on the TEM grids were allowed to dry for 2 min following which the extra solution was removed using blotting paper. Thermogravimetric analyses were performed under air on model no. STA 1500 of PL Thermal Sciences. Cyclic voltammograms (CV) were recorded on IM6 BAS system using Pt working electrode (0.5 cm^2), Ag/AgCl reference electrode and Pt wire auxiliary electrode. The nanoparticles were deposited on the working electrode by dropping concentrated toluene solution and drying at room temperature and subsequently used for the C.V investigation.

2.1. Preparation of silver salt of fatty acids

Sodium salts of fatty acids were prepared according to a literature procedure [19]. Silver stearate, silver palmate and silver laurate were prepared in a similar synthetic procedure. In a typical reaction, pulverized sodium stearate (2 g, 6.5 MM) was taken in 100 ml of distilled water and stirred for half-an-hour to get a homogeneous mixture. To this, was added 50 ml water containing silver nitrate (1.10 g, 6.6 mM) dropwise and stirring was continued for another 1 h by which time white solids of silver stearate precipitated. The product (2.5 g) was filtered and washed with copious amounts of water to remove excess silver nitrate and dried at room temperature in the dark.

2.2. Preparation of nanoparticles using triethanolamine (TEA)

Finely ground silver laurate (0.307 g, 1.0 mM) was poured into 10 ml of triethanolamine (67 mM) and stirred to a homogeneous suspension. A toluene layer (100 ml) was carefully placed on this suspension and slowly heated up to 45 °C while gentle stirring is maintained. Heating is continued for 10 more minutes by which time the white silver laurate powder slowly turned into brown residues, which readily transferred into toluene layer. The brown toluene layer containing silver nanoparticles is quickly decanted through Whatmann filter paper no. 42 to remove any small unreacted lumps of silver laurate. The triethanolamine layer is again extracted with 50 ml of toluene. The combined organic phase is removed at room temperature and the brown free-flowing product is collected and desiccated. Yield is 0.120 g.

2.3. Preparation of nanoparticles using formaldehyde (FA)

Finely ground silver stearate (0.5 g, 1.27 mM) was poured into 10 ml of (37% w/v) of formaldehyde and slowly heated upto 70–80 °C while stirring within 30 mts. Heating is continued for 15 more minutes by which time the white silver stearate powder slowly turned into brown tiny lumps. At this juncture, 100 ml of toluene was added to the mixture while gentle stirring is maintained for another 15 min. The boiling brown toluene layer containing silver nanoparticles is quickly decanted through Whatmann filter paper no. 42 to remove any small unreacted lumps of silver stearate. The aqueous layer containing formaldehyde is again extracted with 50 ml of toluene. The toluene solvent is removed at room temperature and the brown free-flowing product is collected and desiccated. Yield is 0.200 g. These solids are re-dispersible in non-polar solvents like toluene, benzene and hexane.

2.4. Preparation of nanoparticles using dimethylformamide (DMF)

Finely ground silver palmate (0.363 g, 1.0 mM) was poured into 5 ml of dimethylformamide (68.5 mM) and slowly heated up to 40–45 °C while gentle stirring was maintained. When white silver salt changed to brown solids, toluene (100 ml) was added to this suspension and heating was continued for 15–20 more minutes. The brown toluene–DMF solution was quickly filtered through Whatmann 42 filter paper to get clear nanoparticle solution.

3. Results and discussion

3.1. Synthesis

The fatty acids, under the present study namely, stearic ($C_{18}H_{36}O_2$), palmitic ($C_{16}H_{32}O_2$) and lauric acids ($C_{12}H_{24}O_2$), which have different chain lengths, are used to protect the formed silver nanoparticles. Three types of reducing agents, namely, triethanolamine, formaldehyde and dimethylformamide are used to prepare silver nanoparticles in water–toluene biphasic mixture. When these reducing agents are used, silver nanoparticles are readily formed from silver stearate at temperatures 40–80 °C. The readiness of formation of nanoparticles is progressively decreased from stearate to laurate. It means that the formation of these particles is dependent on chain length of the protecting fatty acid. Very often gray-black elemental silver is instantly formed as soon as the silver palmate or laurate is added into formaldehyde solution. To avoid this, temperatures lower than 70 °C, preferably 40–45 °C, should be maintained during the synthesis of these nanoparticles. More over layering of toluene on the reaction mixture is essential at the beginning of the synthesis, so that the formed and stabilized nanoparticle is immediately phase transferred into toluene.

Highly homogeneous and light brown toluene layers were obtained when triethanolamine was used as reducing agent from the salts Ag–STA, –PAL and –LAU. In this case free-flowing powder of nanoparticles was not readily obtained due to mixing of minute amounts of triethanolamine into toluene layers and the product tended to absorb moisture. However, careful washings with acetone gave pure dry samples. The stability of the Ag–toluene solutions obtained by TEA and FA are highest up to several months.

Table 1
Surface plasmon and FT-IR data of the silver nanoparticles

System	IR bands (cm^{-1})[a]	Reducing agent		
		Triethanolamine λ_{max} (nm)[b]	Formaldehyde λ_{max} (nm)[b]	Dimethylformamide λ_{max} (nm)[b]
Ag–STA	3414, 2918, 2849, 1638	420	424	420
Ag–PAL	3416, 2921, 2850, 1637	423	434	427
Ag–LAU	3416, 2921, 2849, 1639	432	421	422

[a] As KBr pellet.
[b] In toluene.

When DMF is used as reducing agent, it mixes into toluene layers and is difficult to remove from the solution at room temperature. Hence the nanoparticles are stored as such. These nanoparticle solutions are stable up to only few hours. However, free-flowing solid nanoparticles can also be obtained in low yield (<40%), using DMF when the procedure is slightly modified. The required amounts (1 mM) of starting materials are taken in DMF and are slowly heated up to a maximum temperature of 45 °C for 30 min. The brown solid lumps obtained were filtered, washed with acetone and extracted with toluene. Removal of solvent yielded free-flowing nanoparticles.

3.2. The mechanism of reduction

The reduction of silver ion by formaldehyde is a simple chemical reaction (Eq. (1)), which is akin to silver mirror test shown by aldehydes:

$$2Ag^{+}(RCOO^{-}) + HCHO + H_2O \rightarrow 2(Ag^{0} - RCOOH) + HCOOH \quad (1)$$

Several routes are proposed for the oxidation of DMF, which is usually accompanied by evolution of H_2 or CO_2 [36,37]. However, during the synthesis of nanoparticles we did not observe any gas evolution suggesting that the reduction mechanism involved is

$$2Ag^{+}(RCOO^{-}) + HCONMe_2 + H_2O \rightarrow 2(Ag^{0} - RCOOH) + Me_2NCOOH \quad (2)$$

The reaction proceeds at a temperature range of 60–80 °C and care must be taken to quench the reaction as soon as all the white silver stearate turned into dark brown material which is quickly phase transferred into toluene layers by gentle stirring. When DMF is used as reducing agent, nanoparticles are readily formed for stearic and palmitic acids while mild heating is are required when lauric acid is used as stabilizer.

When triethanolamine used as reducing agent a different mechanism seems to operate. As triethanolamine is a strong chelater, it is expected to form a complex/adduct [species "A," Eq. (3)] with silver ion at lower temperature. This is followed by reduction of Ag^{+} by coordinated triethanolamine as the temperature increases to ≈70 °C as shown below:

$$Ag(OOCR) + [N(CH_2CH_2OH)_3] \rightarrow [AgN(CH_2CH_2OH)_3]^{+}[^{-}OOCR][\text{complex 'A'}] \quad (3)$$

Similar complexation by triethylamine, which later on acted as a reducing agent [16], is reported in literature. As the Ag^{+} ion is bonded to the reducing agent itself, the reduction of latter is facile and is responsible in obtaining lower size particles. It is believed that, as soon as the silver nanoparticle is formed, triethanolamine ligand withdraws the coordination and releases the nanoparticle, which in turn is stabilized by the fatty acid.

3.3. Characterization

FT-IR spectra of the samples exhibited bands due to adsorbed fatty acids [38]. In general the spectra exhibited bands due to ν_{OH} of the acid around 3414 cm^{-1}, symmetric and asymmetric stretching of the long chain $-CH_2-$ groups around 2900 cm^{-1}, and corboxylate group stretchings around 1633 cm^{-1}. The IR spectra of the samples obtained by each of the reducing agents are identical and super imposable. The IR data of the samples are given in Table 1. A representative FT-IR spectrum (Fig. 1) is shown for Ag–STA system reduced by formaldehyde. From Fig. 1, it is seen that intense bands are observed in the range 2850–2950 cm^{-1} arising due to symmetric and asymmetric stretching of $-CH_2-$ groups and terminal CH_3- groups. Band at 1460 cm^{-1} is due to CH_2- deformation or due to C–O–H in plane bending. The asymmetric COO^{-} stretch is seen at around

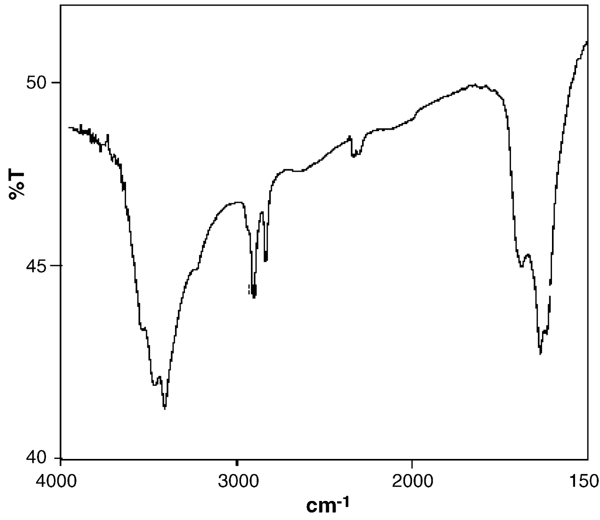

Fig. 1. Segment of FT-IR spectrum of silver nanoparticles recorded as KBr pellet.

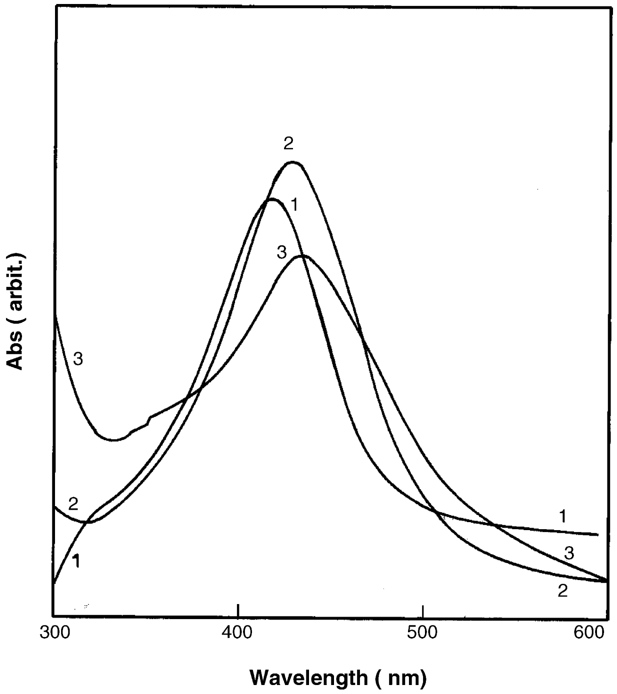

Fig. 2. UV–vis spectra of the nanoparticles: (1) Ag–STA/TEA; (2) Ag–LAU/FA; (3) Ag–PAL/DMF in toluene.

1630 cm^{-1}. The ν_{CO} band is seen with medium intensity at around 1700 cm^{-1}. A band attributable to CH_2 rocking mode is observed at around 720 cm^{-1}. Overall the results are comparable to those fatty acid stabilized silver nanoparticles obtained in different methods reported in literature [39].

Originally described by Ritchie [40], surface plasmon resonance is an important optical property of nanoparticles and is described as coherent fluctuations in electron density occurring at a “free electron” metal/dielectric interface. “Free electron” metals are those metals, which have lone electron in valence shell such as Au, Ag, Al and Cu. The surface plasmon absorptions are responsible for “red” and “yellow” colours of the gold and silver colloids, respectively. In general bare silver nanoparticles exhibit surface plasmon resonance in the region 380–400 nm [17]. This shifts to higher wavelength when the size of the nanoparticle increases due to capping agents [34]. In the present systems, we observed bands in the range 420–432 nm suggesting slightly larger size nanoparticles (Table 1). Fig. 2 shows UV–vis spectra of the Ag–fatty acid systems reduced by triethanolamine, formaldehyde and dimethylformamide.

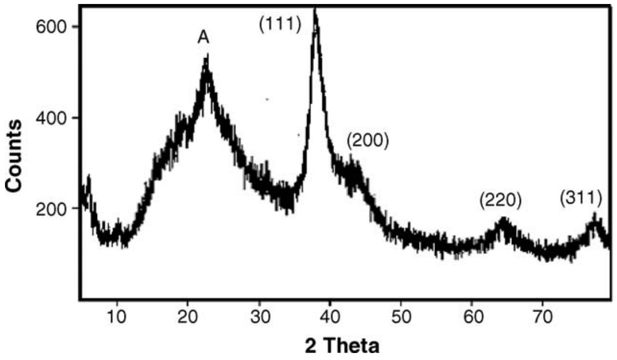

Fig. 3. X-ray diffraction of Ag–STA system obtained from reduction by TEA.

The formation of nanosized silver particles is confirmed by X-ray diffraction analysis. XRD analysis on the sample Ag–STA/TEA showed a broad pattern (Fig. 3). The peak positions can be assigned to that of an fcc silver. The peaks are substantially broadened indicating that the material is composed of very small particles. The peaks observed at $2\theta = 38.54$, 43.90, 64.72, 77.39 are assigned to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections, respectively. (Peak labeled ‘A’ is originating from substrate material used.) The size of the particles calculated from full width at half maxima (FWHM) of (1 1 1) peak using Scherer formula is about 23.5 nm. The size of the particles obtained from dimethylformamide is around 40 nm.

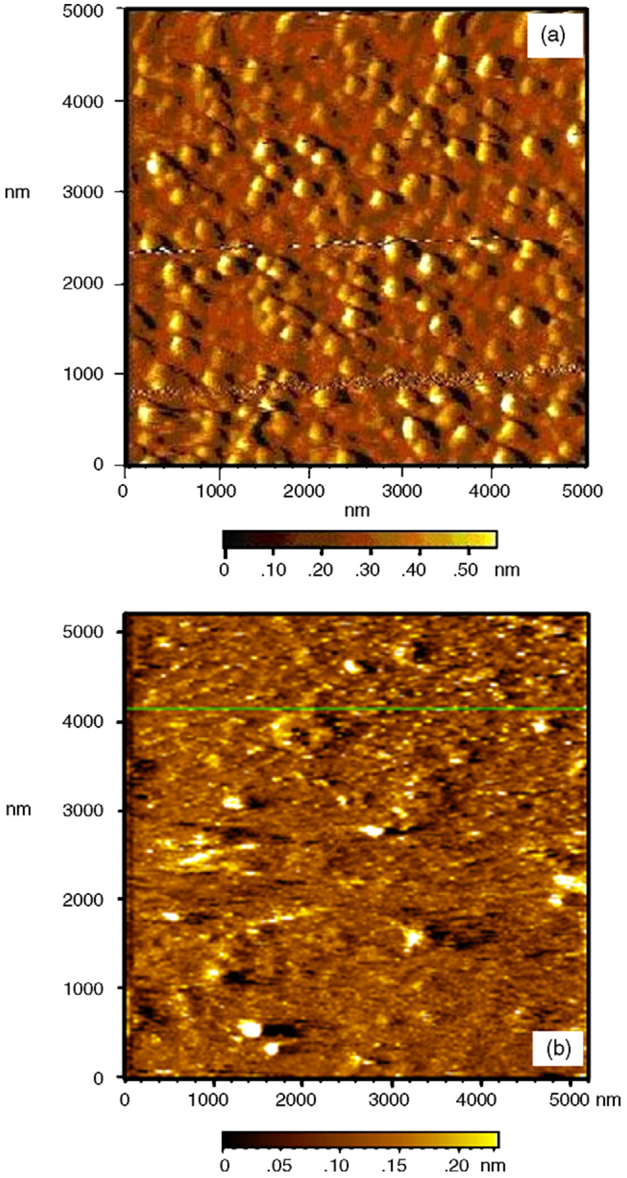

Fig. 4. AFMs of thin film of (a) Ag–STA; (b) Ag–LAU nanoparticles formed by formaldehyde obtained by drop cast method on glass slides.

3.4. Size dependence on the experimental conditions

The size of the particles is greatly influenced by experimental conditions. At higher temperatures and higher concentration of metal ions, the cluster growth is faster hence larger size particles are obtained. For the preparation of lower size particles, starting material concentration must be kept low. It is also essential that toluene layer should be present from the initial stages of the experiment and the heating must be slow, preferably in the range 45–50 °C. Lager size nanoparticles are formed when toluene is added in latter stages or when the reaction temperature is high, in the range 70–80 °C. For example, the particle size of the sample Ag–STA/FA (obtained by "delayed" addition of toluene at 70–80 °C) as described in 2.3.0 as analyzed by atomic force microscopy is higher, i.e. 180 nm. Fig. 4a shows mapping of a 5 × 5 um area on the surface of thin film of these nanoparticles, obtained by drop casting on a glass slide. Essentially it consists of evenly distributed spherical silver particles. The size of the particle is in the range 175–200 nm. On the other hand, when the concentration of the starting material, silver laurate, is low (e.g., 0.102, 0.33 mM, in presence of toluene layer at around 45 °C) the particles size obtained is in the range 1–2 nm (Fig. 4b). However, we could not observe such lower size particle formation with DMF. Thus over all, triethanolamine and formaldehyde are effective in achieving lower particle sizes. TEM (Fig. 5) analysis on the particles formed by formaldehyde showed that they are almost monodisperse (low polydisperse) with particles size ranging 1.4–2.1 nm. A maximum of 50% particles fall in this range (Fig. 5b). The corresponding selected area electron diffraction (SAED) is shown in Fig. 5c.

Redox properties of the nanoparticles are investigated by cyclic voltammetry. Fig. 6 shows cyclic voltammogram of Ag–STA/TEA nanoparticle system recorded in 0.1 M $KClO_4$ acetonitrile/water (100:10; 50 ml) solution. The figure shows broad cathodic peak centered at 15 mV at a scan rate of 4 mV s^{-1}. This observation is similar to the silver nanoparticles stabilized by dodecanethiol, reported in the literature [31]. There are no

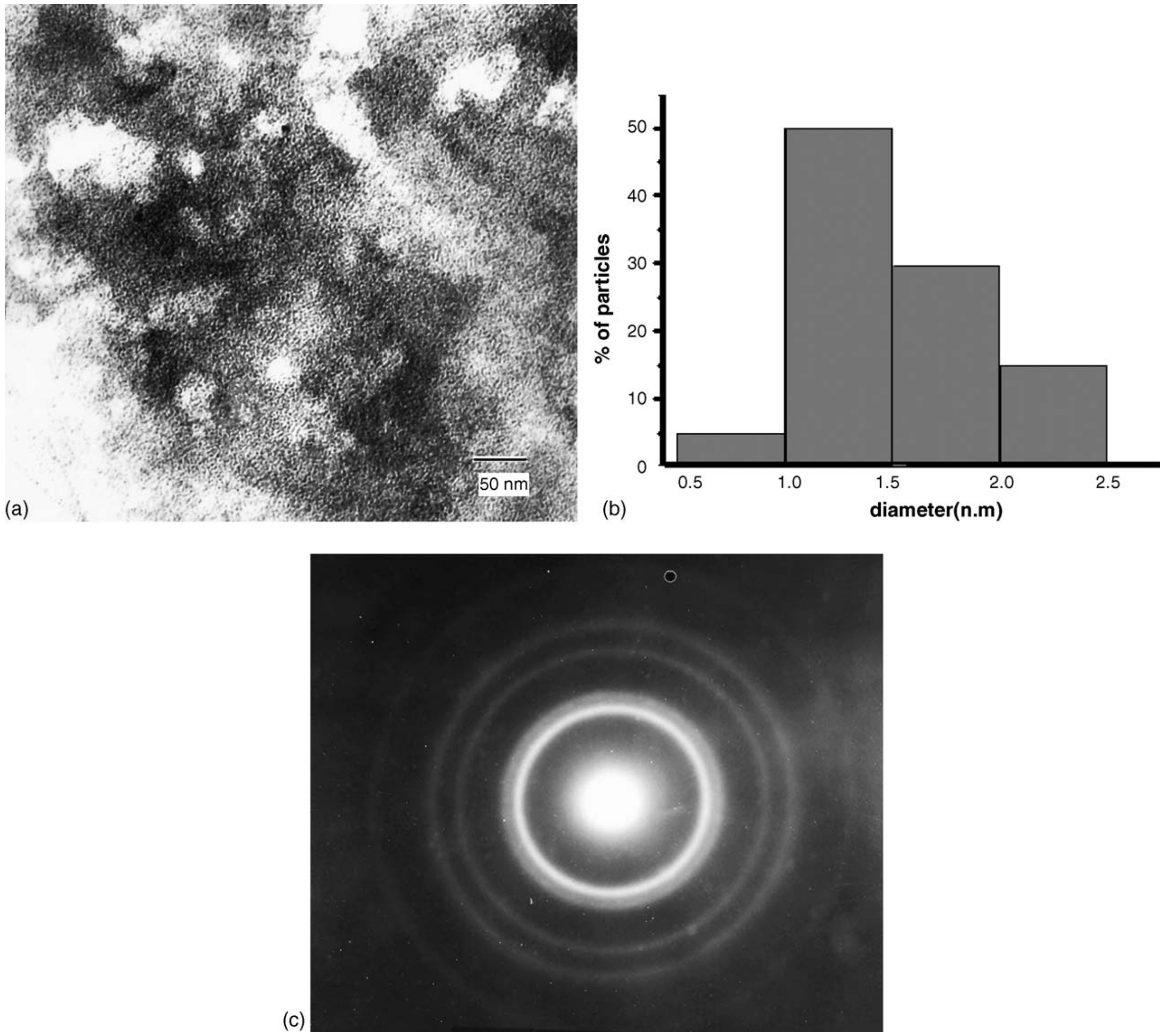

Fig. 5. (a) TEM micrograph of Ag–STA/FA nanoparticles system; (b) particle size distribution; (c) the corresponding selected area electron diffraction (SAED) of the above nanoparticle system.

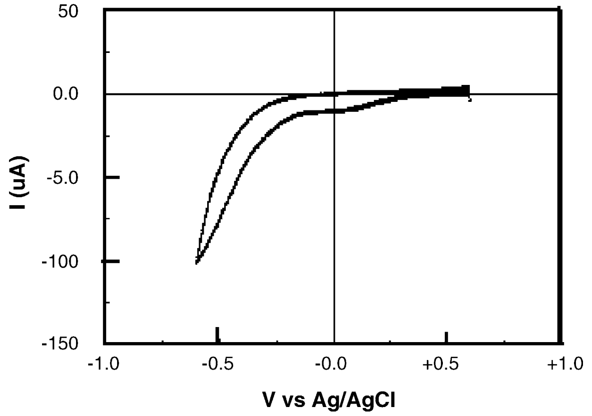

Fig. 6. Cyclic voltammetry exhibited by Ag–STA nanoparticles at platinum electrode. The scan rate is 4 mv s^{-1} in acetonitrile–water mixture (1:1).

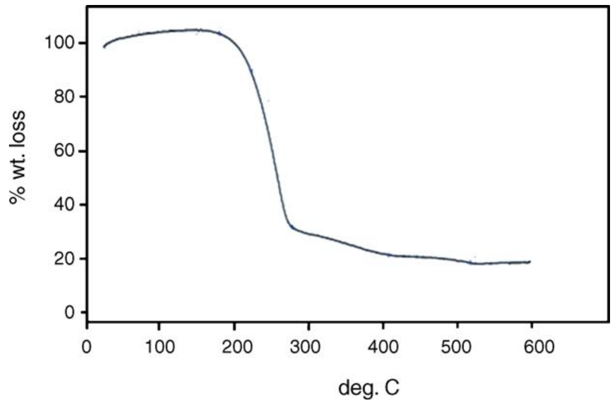

Fig. 7. TGA profile exhibited by Ag–STA nanoparticles.

observable anodic peaks suggesting that the nanoparticles are stable against oxidation.

The silver nanoparticles are capped with fatty acid molecules that provided sufficient hydrophobicity to the nanoparticles to accomplish their phase transfer to toluene layer. The toluene dispersions of the nanoparticles are stable up to few months at room temperature. To understand the stability of these systems at higher temperatures, thermogravimetric analyses were performed on purified samples. The TGA profile for Ag–STA/FA system is shown in Fig. 7. All other systems behaved in a similar fashion. From the figure it is understood that the nanoparticle are stable up to a temperature of 200 °C. Above this temperature, a 70% weight loss is recorded when the temperature of the sample reaches 275 °C. The loss is due to decomposition/desorption of the fatty acid molecules from the surface of the silver nanoparticle. There is a further loss of about 10% in the temperature range 275–400 °C. The curve also suggests 70% of capping agent and 30% silver stoichiometry for the nanoparticles.

4. Conclusions

Stable Ag nanoparticles are formed using triethanolamine, formaldehyde and dimethylformamide as reducing agents with particle size ranging from 25 to 40 nm. FA and TEA are better reducing agents than DMF. The size of the particles is largely dependent on the temperature and concentration of the precursor, silver salt. Lower size particles (1–2 nm) can be obtained with TEA and FA under "dilute" experimental conditions at lower temperatures. The presence of toluene layer, at the beginning of the experiment and lower temperatures are essential conditions for obtaining lower size particles.

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