Synthesis of Silver Nanoparticles in Aqueous Solution: Ionic Liquid Used as a Shape Transformer

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Abstract: Silver nanoparticles were synthesized using block copolymer (Pluronic® P123) spherical micelles as a template. In aqueous Ag^+ ions may be electrostatically complexed with the anionic surfactant or ionic liquids. The silver ions were reduced *in situ* by introducing sodium borohydride as a reducing agent. We found that the size of the silver nanoparticles was exclusively depends on the size of block copolymer micelles. Addition of ionic liquid (IL) (1-decyl-3-methyl imidazolium dodecyl sulphate ($C_{10}MimDs$)) induced sphere – ribbon transition of Silver nanoparticles. The size of the nano ribbon can be tuned by controlling concentration of ionic liquid as well as reducing agents. The silver nanoparticles were observed to be extremely stable in solution suggesting that the modified IL molecules stabilized them. The nanoparticles were characterized by UV-Vis absorbance, dynamic light scattering (DLS) as well as Transmission electron microscope (TEM).

Keywords: Silver Nanoparticles, Ionic Liquids, Block Copolymer

1. Introduction

Poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) block copolymers are well known as dispersion stabilizers, pharmaceutical ingredients, biomedical materials, and templates for the synthesis of mesoporous materials and nanoparticles [1, 2]. Variation of the PEO-PPO-PEO block copolymer molecular characteristics, concentration and temperature allows for unique tenability of block copolymer self-assembly in the presence of selective solvents such as water [3]. There are several reports in which these amphiphilic block copolymers are used as reducing as well as size controlling agents [4]. In Recent year, noble metal nanoparticles have been extensively studied and various approaches have been employed for the preparation of silver nanoparticles [5-13]. They have been the subjects of focused researches due to their unique electronic, optical, mechanical, magnetic and chemical properties that are significantly different from those of bulk materials. These special and unique properties could be attributed to their small sizes and large specific area. For

these reasons, metallic silver nanoparticles have uses in many applications in different field Such as Catalysis, electronics and photonics etc. [14]. Non-metal particles especially Silver have drawn the attention of scientist because of their extensive application in the development of new technologies in the area of electronics material sciences and medicine in the nano-scale. The silver nanoparticles have many applications i.e. they might be used as spectrally selective coatings for solar energy absorption, intercalation materials, for electrical batteries, for catalyst in chemical reactions, for bio-labelling and as antimicrobials [15].

Many approaches were developed to synthesized silver nanoparticles having different sizes and shapes including microwave processing [16], thermal decomposition [17] photochemical methods [18] etc. In most of these methods non-ionic surfactants were used as a capping or stabilizing agents. Due to large number of applications, shape transformations have also been the focus of recent studies. In view of this, here we report facile one port method for sphere to ribbon transition in silver nanoparticles using ionic liquid. The silver nanoparticles were synthesized by reduction of

silver ions in the presence of the non-ionic surfactants P123 and ionic liquids. Different techniques like UV-Visible Spectroscopy, Dynamic light scattering (DLS) and Transmission electron microscopy (TEM) were employed to characterize the silver nanoparticles.

2. Materials and Methods

2.1. Materials

Silver nitrate ($AgNO_3$, 99.9%), Sodium borohydried ($NaBH_4$, 99%) and Pluronic® block copolymer P123 (MW = 5750 g.mol^{-1}) were purchased from Sigma-Aldrich and All these materials were of analytical grade and used as a received and IL, 1-decyl-3-methyl imidazolium dodecyl sulphate ($C_{10}MimDs$) was synthesized in laboratory. Millipore water was used for the preparation of solutions.

2.2. Reaction Scheme for Synthesis of IL

Synthesis of 1-decyl-3-methyl imidazolium dodecyl sulphate ($C_{10}MimDs$): In order to get desired IL, first 1-methyl imidazole was used as a starting material and reacted with 1-decyl chloride. Sodium dodecyl sulphate was then added to replace the chloride ions with dodecyl sulphate anions forming the desired IL (*Fig. 1*) [19].
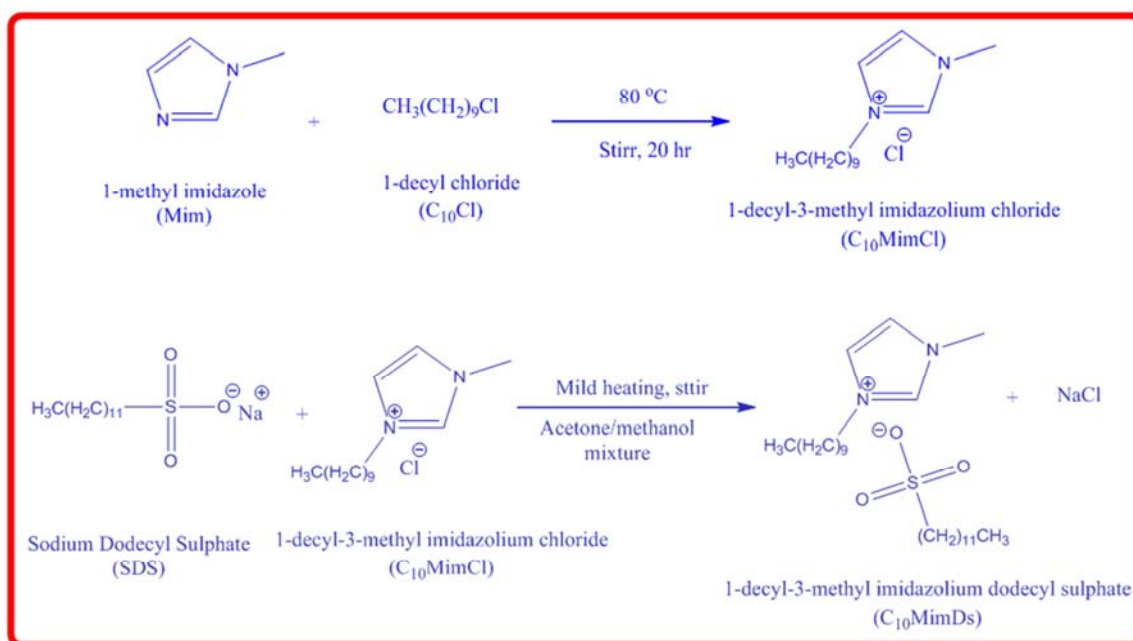

Fig. 1. *Reaction scheme for synthesis and modification of TSIL.*

2.3. Preparation of Silver Nanoparticles

The P123 stabilized silver nanoparticles were synthesized as follows; (i) 0.02ml AgNO$_3$(0.01M) and 5ml of 5% P123 Solution were thoroughly mixed in a bottle, (ii) 0.02ml of fresh NaBH$_4$(0.01M) solutions was then slowly added to mixed solution prepared in step 1. The mixed solutions immediately turns into yellow upon the addition of NaBH$_4$ indicating the rapid formation of silver nanoparticles. The same procedure was repeated in presence of modified IL which was added during the preparation of solution 1. The resultant silver nanoparticles were characterization by UV-Visible, DLS and TEM.

2.4. Instrumentation for Characterization

The synthesized silver nanoparticles were characterized spectrophotocally using UV-visible spectrophotometer Shimadzu, Japan. Light scattering measurements were carried out at 90° on a photon correlation spectrophotometer (PCS) Zetasizer 3000 HAS equipped with a digital autocorrelator from Malvern Instrument, UK. The Transmission electron microscopy (TEM) measurements were performed on a Philips, Holland Model Techai-20 instrument operated at an accelerating voltage of 200 KV. Sample for TEM Study were prepared by placing drops of the silver nanoparticles solution on carbon coated TEM grids. The film on TEM grids were allowed to dry in air for 5 min following removal of extra solvent using a blotting paper [20, 21].

3. Results and Discussion

Silver nanoparticles were synthesized according to the method described in the previous section, the colloidal solution turned pale yellow indicates that the silver nanoparticles were formed. UV-Visible spectra have been proved to be quite sensitive to the form silver nanoparticles exhibit a characteristic peak around 400nm due to the surface plasmon excitation. Fig. 3 illustrates the absorption spectra of Ag nanoparticles prepared in presence and absence of IL using P123 micelles. It is observed that the strong absorbance band at around ~ 410 nm is clearly indicating the presence of

spherical or roughly spherical Ag NPs using P123 micelles. This size of Ag NPs is comparable with the size of P123 micelle in water, which indicates that the size of Ag NPs depends on micellar size. The photograph of synthesized silver nanoparticles at various conditions is given in Fig. 2. The particle size histograms of silver particles show that the particles range in size from 17–25 nm with mean diameter 20 nm from DLS. TEM imaging confirmed this size of Ag NPs.
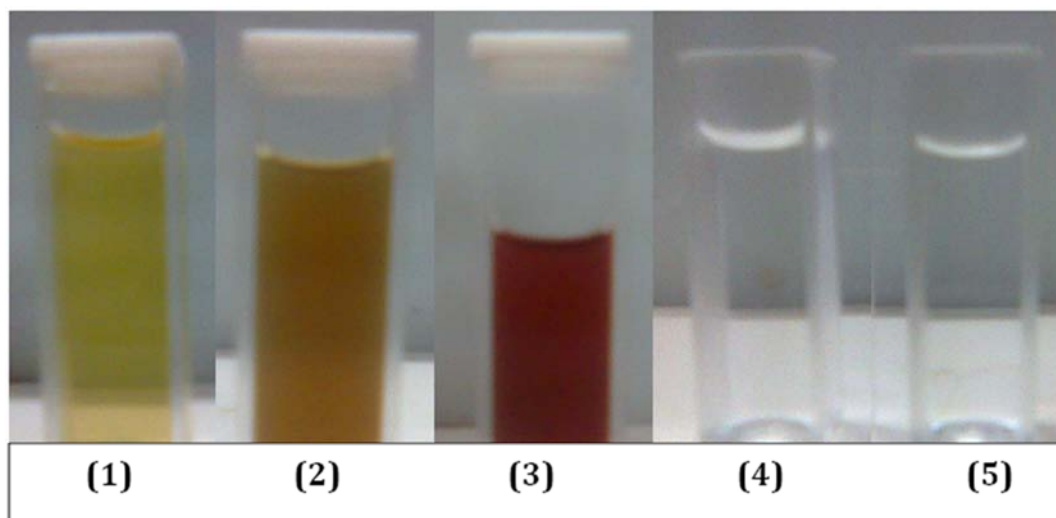

Fig. 2. *Photo graph of Ag NPs in various condition (1) 5 % P123 in IL (0.02 ml AgNO₃ + 0.02 ml NaBH₄), (2) 5 % P123 in IL (0.1 ml AgNO₃ + 0.1 ml NaBH₄), (3) 5 % P123 in IL (0.4 ml AgNO₃ + 0.4 ml NaBH₄), (4) 5 % P123 in (0.02 ml AgNO₃), (5) 5 % P123 in (0.02 ml NaBH₄).*

3.1. UV-Visible Spectroscopy

UV-Visible spectra have been proved to be quite sensitive to the form silver nanoparticles exhibit a characteristic peak around 400 nm due to the surface Plasmon excitation. Fig. 4 illustrates the absorption spectra of Ag nanoparticles prepared at different time of reaction with and without IL. It is observed that the strong absorbance band at around 400 nm is clearly indicating the presence of spherical or roughly spherical Ag NPs, and TEM image confirmed this.
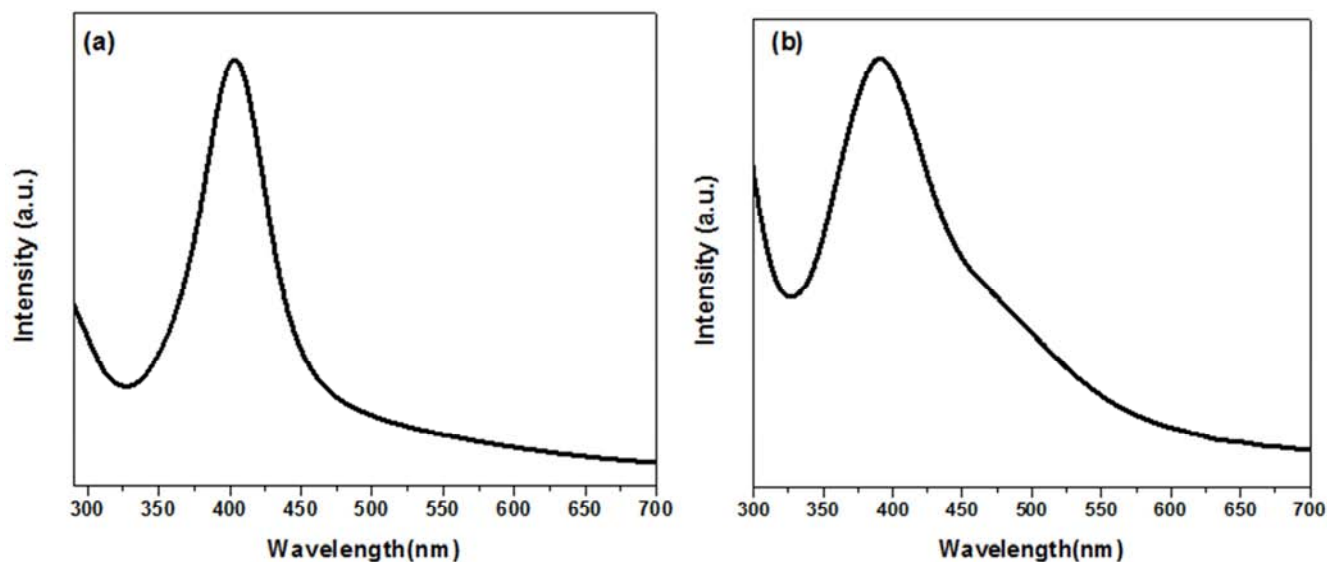

Fig. 3. *UV-Visible Spectra of Ag NPs (a) without IL (b) with IL, in 5 % P123 solution.*

From Fig. 2 it can be seen that the absorbance of the SPR band increases with time but with little change in the absorption value, which indicates that the presence of the IL facilitates the growth of the particles, and the equilibriums is reached within a short time. The absorbance value at equilibrium is ~1.2 (Fig. 4(b)) which is quite high (almost 2 fold) compared to AgNPs prepared without the IL (Fig. 4(a)).

Apart from this, the following observations are made upon comparison of the UV-Vis spectra (Fig. 4) of AgNPs prepared in the absence and presence of an IL: *(a)* the absorption values of the SPR bands are decreases as function of time, *(b)* an additional band appears between 480-540 nm. The presence of the additional band indicates that the system contains particles with a different size.
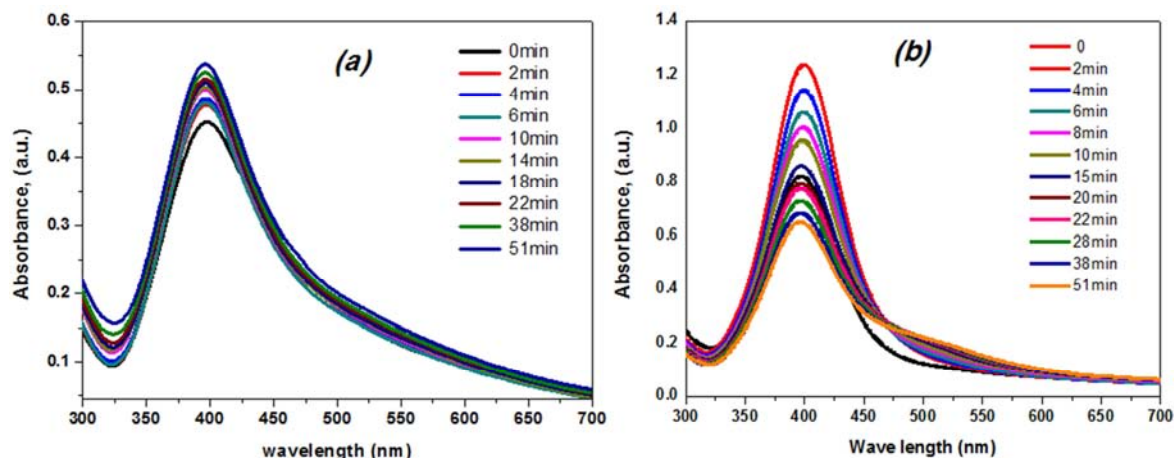
Fig. 4. *UV-Visible Spectra of silver nanoparticles recorded as a function of reaction time; (a) without IL, (b) with IL.*

The mechanism behind this is that addition of Ag^+ salt charges the micelles of P123 through ionic complexes with PEO part of amphiphilic block copolymers and upon addition of sodium borohydride these silver ions were reduced and get the shape of P123 micelles. So, if we can tune the size of P123 micelle than we were able to change the shape of silver nanoparticles. In view of this, we have selected the IL (C_{10}MimDs) which is basically increasing the size and shape of the P123 micelles (from sphere to elongated rods). Upon addition of IL, the size of Ag NPs increases enormously i.e. sphere to ribbons. Fig. 3 (b) indicates the shifting of Plasmon excitation peak to the lower wavelength; this indicates the anisotropic elongated Ag NPs. The same was confirmed with the particle size histogram and also with TEM. From TEM, it was found that Ag NPs are ribbon like and its size is around 115 nm and we also found the agglomeration of ribbons of Ag NPs. The small shoulder observed in UV-vis. spectra near

500 nm confirms the presence of different size of Ag NPs. It might be possible that some of the particles will be smaller in size and same was found in the particle size distribution bar diagram. The size and shape of the Ag NPs can be tuned by changing the concentration of modified IL.

3.2. Dynamic Light Scattering (DLS)

Dynamic Light Scattering (DLS) is a technique in physics which can be used to determine the size distribution profile of small particles in suspension or polymers in solution. Light scattering technique was used to determine the size distribution profile of nanoparticles in suspension [22]. The mean average size of silver nanoparticles comes out to 20 ± 3 nm in Spherical Shape and 112 ± 5 nm in ribbon shape as shown in Fig. 5 [(a) and (b)].
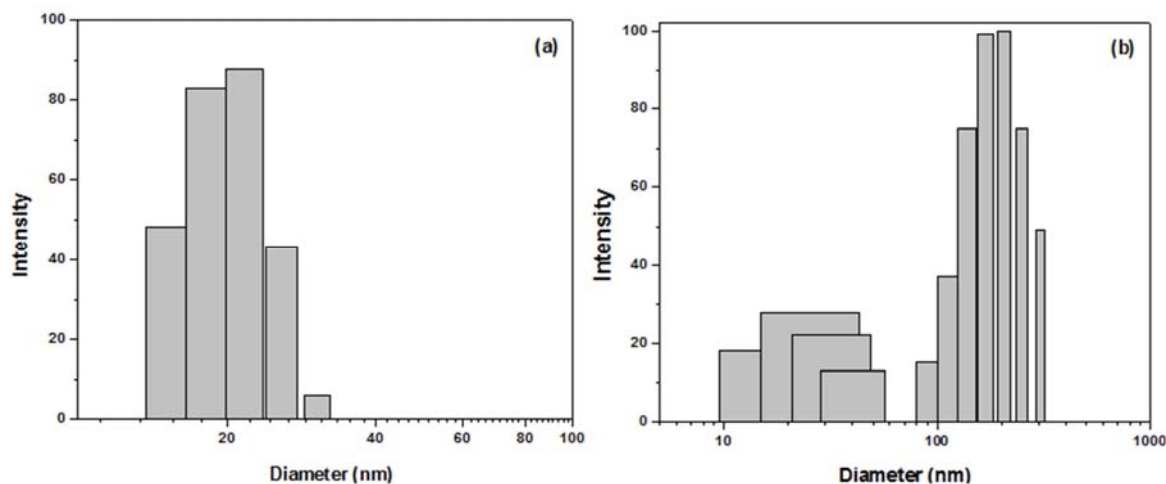

Fig. 5. *Particle size distribution profiles of Ag NPs (a) in 5% P123 (b) in 5% P123 & in presence of modified ionic liquid.*

3.3. Transmission Electron Microscopy Measurements (TEM)

TEM image Fig. 6(a) of the IL stabilized Ag NPs reveal that the obtained Ag NPs are Spherical or roughly Spherical

in shape and reasonably uniform in size. The Ag NPs in Fig. 6(a) and 6(b) are range in size 17.07nm to 49.35nm and 32.75nm to 60.28nm with mean diameter 37.55nm and 50 nm respectively. Even in dried state, no aggregation of Ag NPs was observed, suggesting that the Ag NPs stable and

uniformly distributed in the aqueous solution [23]. For the same sample in presence of IL, we observed ribbon like morphology along with quite aggregation. The Ag NPs in Fig. 6(b) are range in size 42.21 nm to 81.33 nm and 45.57 nm to 78.74 nm with mean diameter 68.18 nm and 63.41 nm respectively.
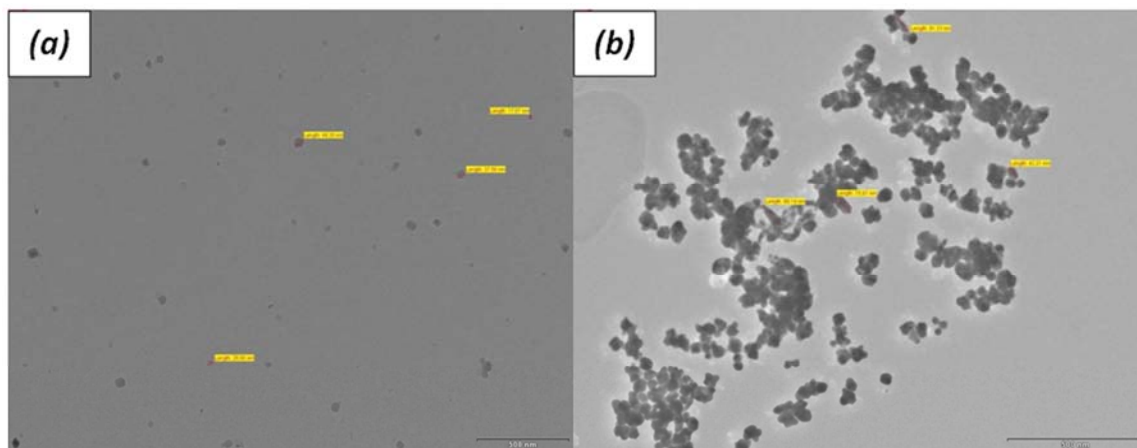

Fig. 6. *TEM micrograph of the Ag NPs; (a) without IL (Spherical shape) and (b) with IL (C_{10}MimDs) stabilized (non-spherical shape).*

4. Conclusions

The formation of silver nanoparticles in liquid forms stabilized by modified ionic liquid has been described. The process of silver ions entrapment in the form and their in situ reduction results in the formation of silver nanostructures of variable morphology in the form. So formed particles were characterized directly in solution using UV-Vis spectroscopy, TEM, DLS. Morphologies of the particles range from spherical to ribbon shape as shown in TEM micrograph. Average diameter of the particle ranges from 17.07nm to 49.35nm in Spherical morphology and 42.21nm to 81.33nm in ribbon morphology as suggested by DLS measurements. The variation in morphology in the silver nano crystals is believed to occur due to the differences in structure of the foam.

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