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SONOCHEMICAL SYNTHESIS OF SILVER NANOPARTICLES IN THE IONIC LIQUID 1-ETHYL-3-METHYLIMIDAZOLIUM TRIFLUOROMETHYLSULFONATE

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ABSTRACT

The present paper deals with the ultrasonic-assisted synthesis of silver nanoparticles via a displacement reaction of silver trifluoromethylsulfonate with copper turnings in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfnate. The results revealed the formation of spherical silver nanoparticles. The obtained nanoparticles were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD) and ultraviolet-visible spectroscopy (UV-vis). The EDX analysis of Ag nanoparticles showed the presence of high purity silver and no signals for other impurities were recorded. The average particle size determined by TEM and XRD was found to be 25 nm. The UV-vis spectroscopy exhibited the presence of the surface plasmon absorption of Ag nanoparticles.

Keywords: Silver, nanoparticles, ionic liquid, sonochemical synthesis.

INTRODUCTION

Nanosized metallic particles exhibit size and shape dependent physicochemical properties, including optical, electronic and catalytic properties that make them highly interesting for diverse applications such as, e.g, catalysts, sensors, optics, biocides and data storage (Sudrik *et al.*, 2006; Choi *et al*., 2007; Yoosaf *et al.*, 2007; Sun *et al.*, 2000; Vilchis-Nestor *et al.*, 2008).

Among metallic nanoparticles, silver shows attractive properties such as, high electrical and thermal conductivity, surface-enhanced Raman scattering, chemical stability, catalytic activity and biocidal impacts (Sharma *et al.*, 2009; Krutyakov *et al.*, 2008; Monterio *et al.*, 2009; Ahamed *et al.*, 2010). Colloidal silver exhibits antimicrobial properties and is known to be non-toxic and environmentally friendly biocide (Dorjnamjin *et al.*, 2008).

Ionic liquids provide an excellent medium for the formation and stabilization of metal nanoparticles, enabling the preparation of nanoparticles without any stabilizing additives or capping molecules (Migowski and Dupont, 2007; Parvulescu and Hardacre, 2007; Ott *et al.*, 2007). Thus, employing ionic liquids is of advantageous in contrast with the nanoparticle preparation in aqueous or conventional organic solvents, which unavoidably require the addition of stabilizing agents, such as thiols, amines, or polymers to prevent the coalescence of particles. Ionic liquids are able to offer exceptional properties as media for the synthesis of nanomaterials. They are regarded as multifunctional solvents as they can act as templates, stabilizers and crystal growth modifiers. Furthermore, they offer, depending on the type of ionic liquids, environmentally benign conditions for synthesis of nanomaterials as the use of organic solvents and synthetic stabilizing agents is harmful to the environment.

Stable noble-metal nanoparticles were chemically synthesized by simple chemical reduction of metal complexes or metal salts in ionic liquids without any additives. Iridium nanoparticles with average sizes of 2.0 nm were synthesized from $[IrCl(cod)]_2$ (cod=1,5-cyclooctadiene) in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIm]PF_6$) in hydrogen atmosphere at 75^{o}C (Dupont *et al.*, 2002). Gold nanoparticles were prepared via reduction of $HAuCl_4$ by CO in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIm]BF_4$ (Guo *et al.*, 2005). Also, gold nanoparticles with different sizes and shapes were also fabricated by the reduction of Au(III) by soft reducing agents: ascorbate and/or citrate in ionic liquids (Ryu *et al.*, 2008; Zhang and Cui, 2009; Dinda *et al.*, 2008). Isolated silver nanoparticles were made via a plasma electrochemical approach in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethylsulfnate ([BMIm]TfO) by applying plasma as mechanically contact-free electrodes (Meiss *et al.*, 2007; Zein El

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Abedin *et al.*, 2007). In the present study an ultrasonic-assisted route for the synthesis of stabilized silver nanoparticles via reduction of silver trifluoromethylsulfonate (Ag(TfO)) by copper turnings in the ionic liquid [EMIm]TfO is reported. To our knowledge this approach has not yet reported for the synthesis of silver nanoparticles in ionic liquids. The fabrication of silver particles coated with poly(vinyl pyrolidone) through the reduction of silver nitrate by copper turnings in aqueous solutions was reported (Khanna *et al.*, 2004). In the present study, the employed ionic liquid dually functions as both a solvent and a particle stabilizer. In addition, the application of ultrasonic irradiation would influence the growth of the particles and prevent their aggregation. The irradiation of liquids with ultrasonic waves causes alternating high and low pressures resulting in the formation of ultrasonic cavitations that induce a variety of physical and chemical effects, which could provide a unique environment for chemical reactions under extreme conditions (Suslick *et al*. 1991; Jiang *et al.* 2004). The obtained silver powder was characterized by SEM-EDX, XRD and UV-visible spectroscopy.

MATERIALS AND METHODS

Materials

The ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]TfO) with a purity 99% (Io.Li.Tec., Germany) was employed. The ionic liquid was used as received without further purification or drying. The water content of the ionic liquid was determined by Karl-Fisher-titration to be 238 ppm. Silver trifluoromethylsulfonate (Alfa, 99%) was used as a source of silver, and 0.2 mol/L solutions were prepared for the fabrication of silver particles. Copper turnings (Alfa Aesar 99.9 %, typical sizes 1-12 mm) were used for the reduction of silver ions. Absolute ethanol was used for washing the synthesized silver nanopowder. All glassware utilized in the synthesis process was thoroughly cleaned prior to use by boiling in deionized water containing hydrogen peroxide and then boiling twice in water.

Characterization and Techniques

The ultrasonic-assisted synthesis of silver nanoparticles was performed using an ordinary ultrasonic cleaner (S 120 H Elmasonic) with an operating frequency of 37 kHz. Various techniques were employed for the characterization of the synthesized silver powder. A high resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini) was utilized to investigate the surface morphology of the obtained silver particles, and energy dispersive X-ray analysis was used to determine the chemical composition. The crystallinity and the particle sizes were investigated by x-ray diffraction using a PANalytical diffractometer with CuK_{α} radiation. The particle sizes were also investigated using a JEOL JEM-2100 transmission electron microscope (TEM). Ultraviolet-visible (UV-vis.) spectroscopy was performed using a Cary Series UV-VIS-NIR spectrophotometer (Agilent Technologies) with quartz cuvettes of 1 cm optical path length.

RESULTS AND DISCUSSION

Silver nanoparticles were prepared via a simple displacement reaction of Ag(TfO) with copper in the ionic liquid [EMIm]TfO under ultrasonic irradiation. As known, copper can replace silver from solutions due to its higher activity compared with silver. An ionic liquid solution containing 0.2 mol/L Ag(TfO) was prepared and then an appropriate amount of copper turnings was added. After addition of copper to the ionic liquid solution, the reaction pot was directly immersed in an ultrasonic bath and kept under sonication for one hour. The colour of the solution changed from yellow to dark grey over the reaction time as a result of the formation of silver particles. The following equation describes the displacement reaction of Ag(TfO) with copper:

$$Cu + Ag(TfO) \rightarrow Ag + Cu(TfO) \quad (1)$$

The synthesized silver particles were reclaimed from the solution by centrifugation and subsequently were thoroughly washed with ethanol for several times to remove the ionic liquid residues. The obtained powder was then dried in vacuum at room temperature for about 2 hours.

The morphology and composition of the synthesized silver powder were investigated by SEM-EDX. Figure 1 show high resolution SEM micrographs (Fig. 1a and b) and an EDX spectrum (Fig. 1c) of the obtained powder. As seen, the powder contains very fine particles with sizes in the nanometer regime. A few agglomerates comprising nanoparticles are also shown. The EDX profile reveals the synthesis of high purity silver nanoparticles as no signals of other impurities were recorded. Also, there are no hints on the presence of ionic liquid residues. The sizes of Ag nanoparticles range from 25 to 100 nm, as shown in figure 1b. Some of the nanoparticales exhibit a large size as a result of aggregation of small particles.

In order to have a precise estimation of the particle size, the synthesized silver powder was examined by transmission electron microscopy. The TEM micrograph of the silver particles is shown in figure 2. It is clearly seen that roughly spherical Ag nanoparticles with sizes between 15-30 nm were observed.

Figure 3 shows the x-ray diffraction patterns of the obtained silver powder. As seen five diffraction peaks were recorded at $2\theta = 38.18^{o}$, 44.32^{o}, 64.54^{o}, 77.45^{o} and 81.63^{o} which are corresponding to the (111), (200), (220),

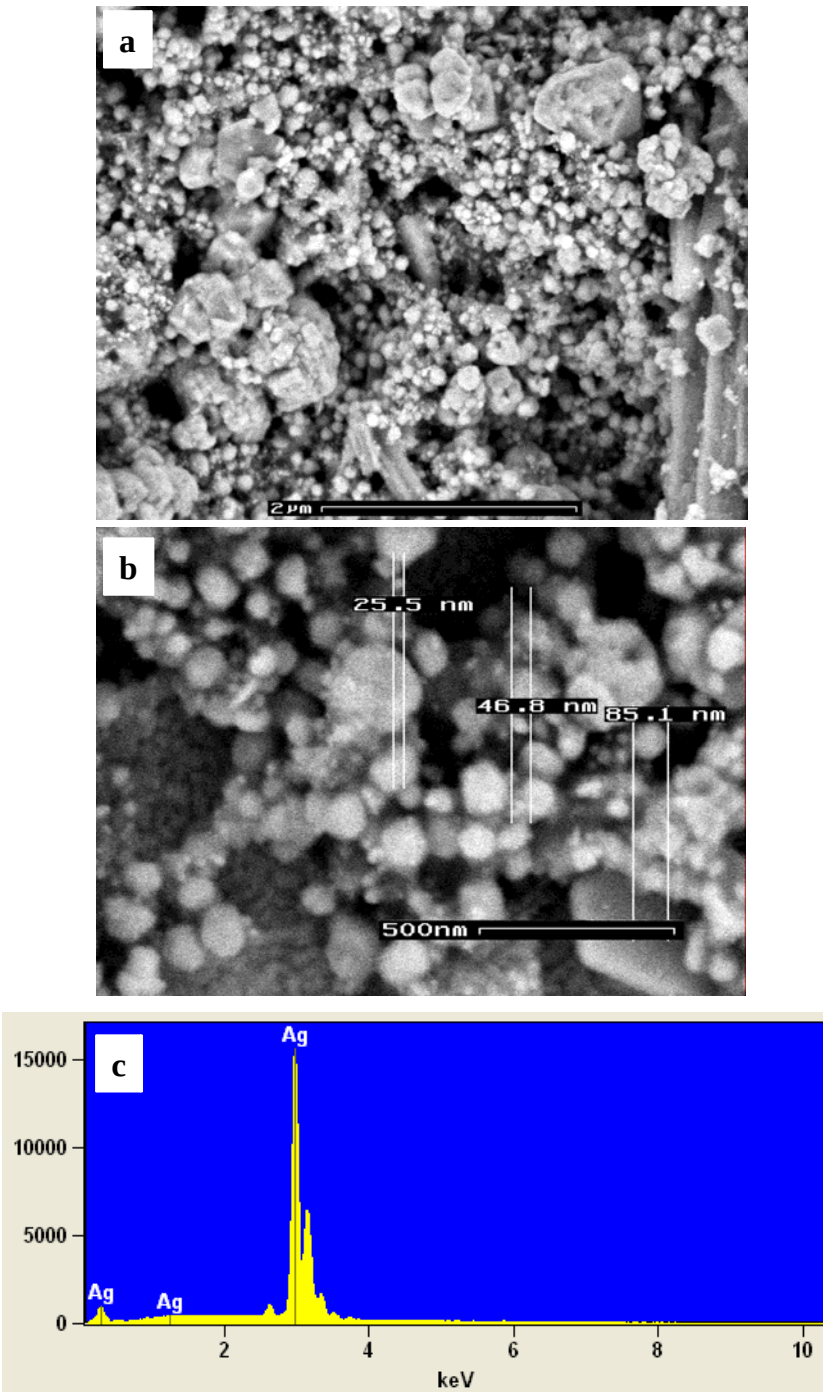

Fig. 1 a) and b) SEM micrographs of the synthesized Ag nanoparticles with different magnifications. c) EDX profile of Ag nanoparticles.

(311) and (222) diffractions of face centred cubic silver (JCPDS File No. 04-0783). The observed diffraction peaks are relatively broad signifying the formation of nancrystalline particles. The average particle size was determined according to Scherrer's equation (Scherrer, 1918):

$$d = 0.9\lambda / \beta_{1/2} \cos \theta \quad (2)$$

where, d is the particle diameter, λ the x-ray wavelength (1.5418 A^o for CuKα), $\beta_{1/2}$ the full-width half maximum (FWHM) and θ is the diffraction angle. The inset of figure 3 shows the broadening of the intense (111) diffraction peak of silver used for estimation of the particle size. The average particle diameter was found to be 25 nm which is consistent with the TEM results. Unlike the TEM and XRD results, the SEM results showed particle diameters ranging from 25-100 nm. This might be attributed to the formation of some aggregates as a result of drying during the sample preparation.

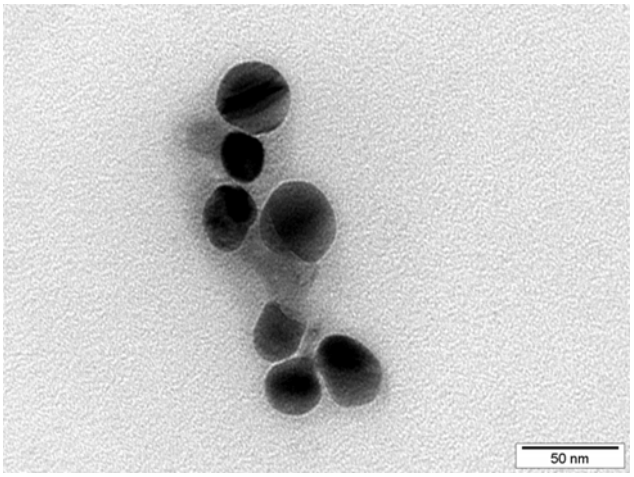

Fig. 2. TEM micrograph of the synthesized Ag nanoparticles.

In the light of these results, it can be stated that the ultrasonic-assisted synthesis of silver powder in the ionic liquid [EMIm]TfO leads to the formation of nanocrystalline, spherical Ag particles. The employed ionic liquid is capable to be adsorbed on the formed silver particles avoiding their further growth which, in turn, leads to the formation of nanocrystalline particles. Furthermore, the adsorption of ionic liquid species (cations and/or anions) might hinder the agglomeration of silver particles and the subsequent formation of large particles. The adsorption of ionic liquids on metal surfaces was previously reported. It was found that about 5-7 ionic liquid layers can be formed onto the surface, and the strength of adsorption is dependent on the type of ionic liquid (Atkin *et. al.*, 2009). The application of ultrasonic irradiation also influences the growth of the particles and diminishes their aggregation.

The synthesized Ag nanoparticles were also investigated by UV-vis. spectroscopy and the recorded spectrum is displayed in figure 4. The UV spectrum exhibits two weak absorption bands at 338 and 452 nm which are correlated to the presence of Ag^+ and the surface plasmon resonance of Ag nanoparticles, respectively. The presence of surface plasmon absorption band is characteristic to Ag nanoparticles. However, the observed weak absorption and the absence of the usual bell-shaped band of the plasmon resonance might be attributable to either the formation of strongly bonded ionic liquid layers on the surface of Ag particles, that can influence the surface

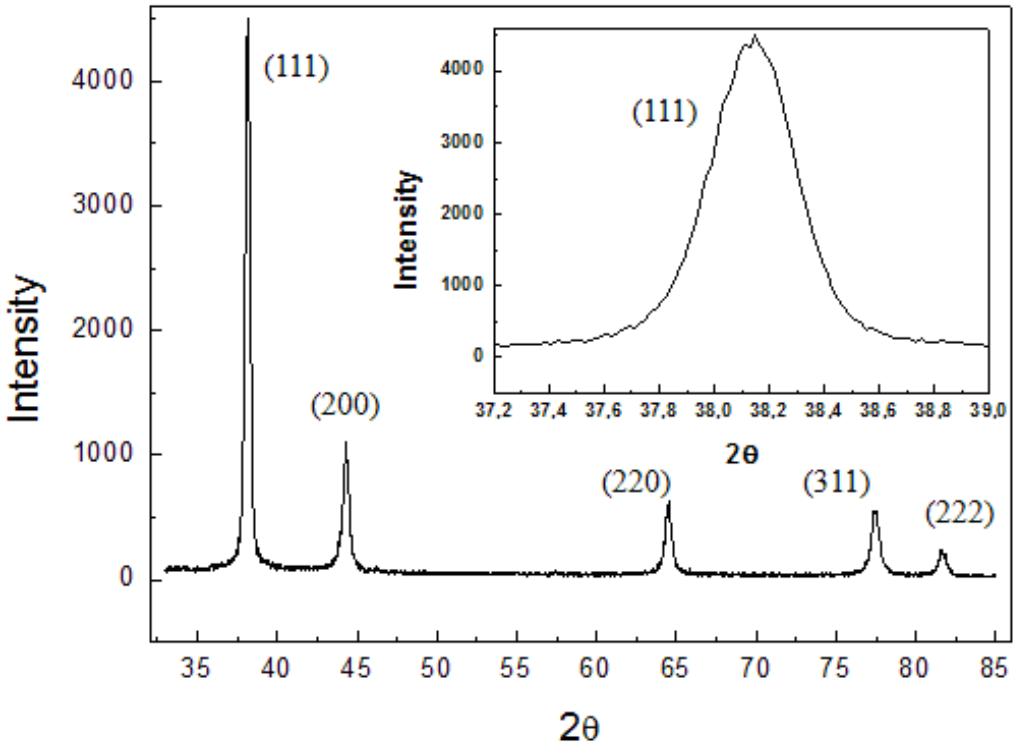

Fig. 3. XRD patterns of the synthesized Ag powder. Inset: The broadening of the intense (111) diffraction peak.

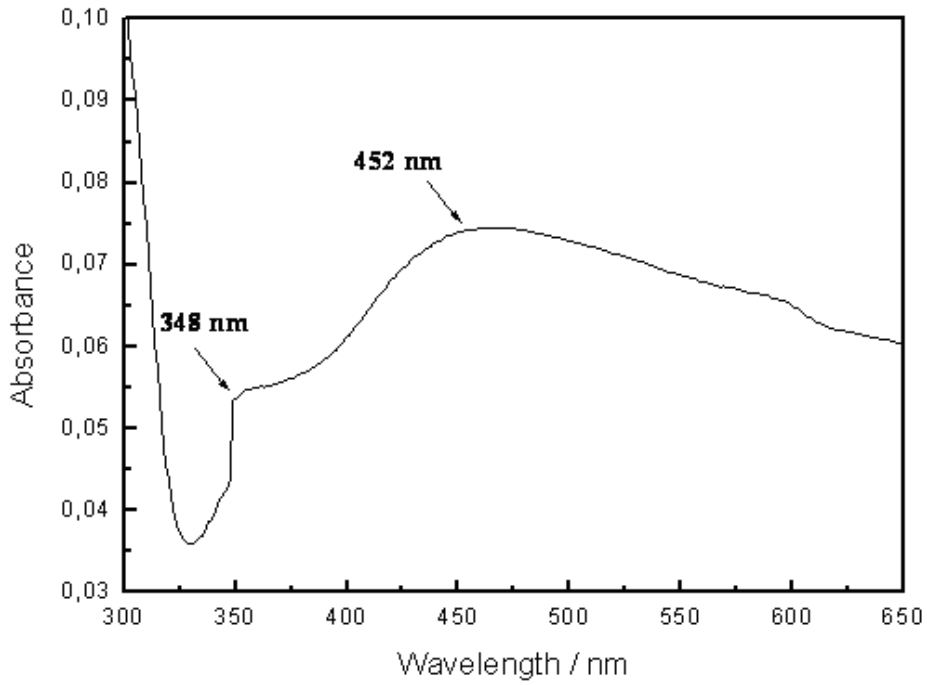

Fig. 4. UV-visible spectrum of the synthesized silver nanoparticles.

plasmon resonance, or to the agglomeration of particles. The position and shape of surface plasmon absorption band depend on the particle size and shape as well as the dielectric constant of the surrounding medium (Guzman *et al.*, 2008). A similar UV spectrum of coated Ag nanoparticles was previously reported by Khanna *et al.* (2004).

CONCLUSION

Spherical silver nanoparticles were synthesized in the ionic liquid [EMIm]TfO by a simple displacement reaction of Ag(TfO) with copper in the presence of ultrasonic irradiation. The employed ionic liquid has the ability to be adsorbed on the formed silver particles avoiding their further growth and leading to the formation of nanocrystalline particles. Furthermore, the application of ultrasonic irradiation lessens the particles aggregation. The average particle size was found to be 25 nm. The XRD and EDX results showed the crystallinity and the purity of the synthesized silver nanoparticles, respectively. Furthermore, the UV-vis. spectroscopy exhibited the characteristic surface plasmon resonance of Ag nanoparticles.

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