

Solvent-Free Synthesis of Silver-Nanoparticles and their Use as Additive in Poly (Dicyclopentadiene)

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Summary: A solvent-free environmentally benign synthesis of oleylamine capped silver nanoparticles is presented. Upon heating 10 equivalents of oleylamine and silver nitrate at 165°C for 30 min followed by a precipitation step using ethanol as the precipitant particles characterized by an Z-average diameter of 63 nm were obtained. Dried particles can be easily redispersed in nonpolar solvents or monomers, which pave the way for using them as an antimicrobial additive in polymeric materials. In particular, newly prepared Ag-particles were dispersed in dicyclopentadiene and the mixture was cured using ring opening metathesis polymerization yielding an antimicrobially equipped duroplastic material.

Introduction

Until lately, silver nanoparticles have gained remarkable importance for their use in optical sensors, printed electronics, photonics, antimicrobial coatings and materials and many other advanced applications [1]. In particular, the antimicrobial effect of these materials makes them versatile substrates to be used in health and environment [2]. Recently, oleylamine has been appeared to be a powerful capping and reducing agent in the synthesis of nanoparticles due to its ease of availability from renewable resources, low cost and most of all strong tendency to reduce silver from its salts [3]. Upon variation of the reaction media, i.e. using different reducing agents, heating systems and solvents nanoparticles with different size, shape and orientation have been obtained [4]. The latter properties, in turn, define the applicability of the Ag-particles. For example, ultra-refined nanoparticles synthesized via illumination by UV-light can be used as fluorescent materials [5]. The requirements for Ag-nanoparticles in antimicrobially equipped polymeric materials are less strict, e.g. 1 w% of Ag-nanoparticles of 50-100 nm in size were used to equip Nylon 6,6 with antimicrobial activity [6]. Another exemplary application was presented by Samsung where silver nano-washing machines releases silver ion-nanoparticles useful for disinfectant cleaning of clothes in place of hot water or bleaching [7]. Herein we wish to disclose an environmentally benign synthesis of silver-nanoparticles along with their characterization and will demonstrate for the first time antimicrobially equipped poly(dicyclopentadiene) (DCPD) made by ring opening metathesis polymerization (ROMP) [8]. Dicyclopentadiene is a by-product of steam cracking

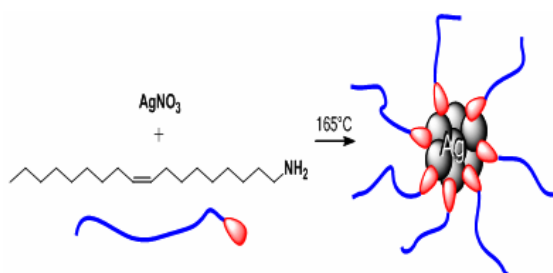
of naphtha and gas oils which is very cheap and readily available. polyDCPD is a thermoset material which is very rigid and tough exhibiting high impact resistance, high chemical corrosion resistance and a high heat deflection temperature and finds applications as a substitute for epoxy-resins [9].

Results and Discussion

As it was the aim to disclose a more environment friendly route for the synthesis of Ag-nanoparticles with oleylamine, first attempts to find homogeneous reaction conditions at room temperature were made. However, no ideal solvent, i.e. a solvent which can dissolve both reactants at the same time at room temperature, could be identified. Accordingly a mixture of water and ethanol (v/v = 50/50) was tried. This solvent combination guaranteed the dissolving of oleylamine and silver nitrate and is fulfilling the desired green aspects. Unfortunately, although the solubility issue was resolved still no defined nanoparticles could be obtained under all tested reaction conditions (variation of reaction time and temperature). In a next step, the reaction was tried in the presence of different reducing agents, which were selected on the basis of their green nature. Accordingly, glucose, tartaric acid and citric acid, good reducing agents for the synthesis of nanoparticles according to the literature [10], were used and 78°C at various reaction times were used as the conditions (*cf.* Table-1). However, properly defined nanoparticles with appropriate size and shape could not be obtained in this way. In a next step, based on a report of obtaining AgAu-nanoparticles from a octadecene

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solution of oleylamine and proper metal precursors [11], we omitted the octadecen and heated AgNO_3 in excess of oleylamine at 150°C . No further additive or solvent was used in this reaction. Until 80°C the reaction mixture is heterogeneous but approximately at this temperature a homogenous yellow solution formed, which changed upon further heating to dark brown. Finally, upon heating for 30 min at 150°C a black precipitate formed together with traces of shiny silver metallic components at the glass wall. For the isolation, the reaction mixture was poured into ethanol and the precipitate was collected on a glass frit and was repeatedly washed with ethanol. In that way 96% yield of a black shiny powder could be obtained. Upon optimization of the AgNO_3 oleylamine ratio it was found that at least 10 equivalents of oleylamine in respect to Ag^+ are necessary to form the particles in a reproducible way. Using less oleylamine led to a lower yield of nanoparticles and using more oleylamine or using longer reaction times did not improve the yield.



Scheme-1: Synthesis of Ag-nanoparticles stabilized by oleylamine.

Table-1: Synthesis of Ag-nanoparticles in presence of different reducing agents.

Entry	Silver salt + Doping agent	Reducing agent	Solvent	Temp [°C]	Nanoparticle* Formation
1	AgNO_3 + Oleylamine	Citric acid	$\text{EtOH} + \text{H}_2\text{O}$	80	-
2	AgNO_3 + Oleylamine	Tartaric acid	$\text{EtOH} + \text{H}_2\text{O}$	80	-
3	AgNO_3 + Oleylamine	Glucose	$\text{EtOH} + \text{H}_2\text{O}$	80	-
4	AgNO_3 + Oleylamine	Oleylamine	$\text{EtOH} + \text{H}_2\text{O}$	80	-
5	AgNO_3 + Oleylamine	Oleylamine	-	150	+

* Nanoparticle formation was evaluated by investigating a suspension in ethanol by DLS measurements

The black powder was characterized by thermo gravimetric means by heating the sample ($10^\circ\text{C}/\text{min}$) in an inert atmosphere of nitrogen until 500°C . At approximately 100°C the mass loss commenced and proceeded slowly until about 400°C resulting in an overall mass loss of 10 %. Accordingly, an empirical formula of $(\text{C}_{18}\text{H}_{37}\text{N})\text{Ag}_{22}$ can be postulated. Elemental analysis of the sample confirmed this assumption. The black shiny powder

could be readily dispersed in a variety of unpolar solvents such as *n*-pentane, toluene, chloroform or dichloromethane. For further characterization, the Ag-nanoparticles were redispersed in chloroform to obtain a 1w% solution and the sample was investigated by dynamic light scattering (DLS) revealing a Z-average size of 63 nm with a polydispersity of 0.3.

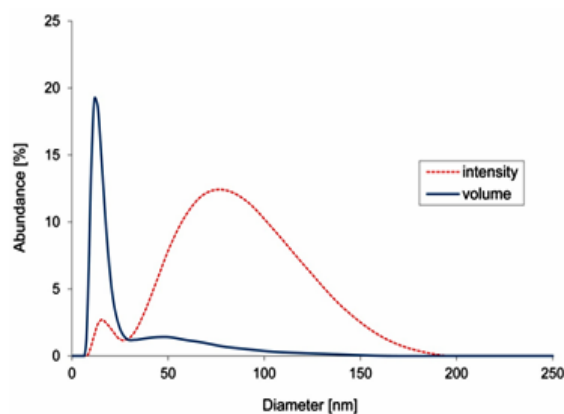


Fig. 1a: Volume and intensity size distribution of Ag-nanoparticles (1w% in CHCl_3).

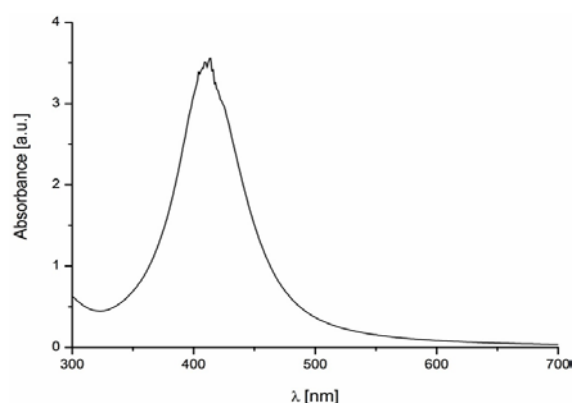


Fig. 1b: Absorption spectrum of Ag-nanoparticles (1w% in CHCl_3).

Having a closer look to the scattering curves (*cf.* Fig. 1a) the bimodality of the sample became obvious. The volume size distribution showed a maximum at 19 nm, while the intensity size distribution gave the maximum at 78 nm. UV-VIS spectroscopy was used to record the absorbance spectrum of this sample, which showed the characteristic peak of spherical Ag-nanoparticles at 415 nm (*cf.* Fig. 1b) [12].

To demonstrate the applicability of the nanoparticles, dispersions in DCPD were prepared

and subsequently cured upon addition of 20 ppm Umicore **M2** initiator (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene) (tricyclohexylphosphine) ruthenium) in a mould upon heating at 60°C for 2 h [9]. The maximal loading of Ag-nanoparticles under these conditions was about 1w%. Above this amount more initiator and/or longer curing time is necessary to preserve the mechanical properties of poly(DCPD) [13]. Fortunately 1w% of Ag-nanoparticles is the amount commonly used to equip polymeric material with antimicrobial properties. In principle, the Ag-nanoparticles can be either physically entrapped in the poly(DCPD) network or covalently incorporated via cross metathesis of the oleylamines double bonds. In a previous work, it has been shown that oleylamine is not undergoing cross metathesis reactions without introducing a protecting group. Additionally, much higher loadings of the catalysts were required in the transformation of the protected amine [14]. Therefore covalent incorporation seems to be less likely.

As a last point antimicrobial tests of 4x4 cm poly(DCPD) plates containing 1w% Ag-nanoparticles were done according to a modified Japanese Industrial Standard (JIZ) Z2801:2000 protocol [15]. The film-based methodology is applied for the antimicrobial assessment of duroplasts, thermoplastic materials, and lacquers and reduction of the colony forming unit higher than two log levels is defined as a microbiocidal action. *Escherichia coli* (DSM 10290), was used as test organism. After 24 h of contact only dead bacteria cells could be observed. Accordingly, the principal proof of the antimicrobial properties of Ag-nanoparticle equipped poly(DCPD) is provided.

Experimental

All chemicals and solvents used were purchased from commercial sources. Catalyst **M2** was obtained from UMICORE AG and other solvents and auxiliaries were used as received. All reactions were carried out under nitrogen in pre-dried glassware using Schlenk technique. Other materials were obtained from commercial sources (Aldrich, Fluka or Alfa Aesar) and were used without further purification. UV-visible absorption spectra were performed on a Varian Cary 50 Conc UV-Visible Spectrophotometer using a cell made of quartz glass (Hellma, d: 10 mm, spectral range: 200-2500 nm). Particle sizes were determined with a Malvern Instruments ZetaSizer NanoZS provided with a 633 nm laser. If not otherwise mentioned, the polymers were measured against a polystyrene latex standard at

20 °C, sample concentration was 5 mg ml⁻¹ and the equilibration time was 24 h. TGA measurements were performed with a Netzsch Simultaneous Thermal Analyzer STA 449C (crucibles: aluminium from Netzsch). A helium flow of 50 ml/min was used in combination with a protective flow of 8 mL/min. Elemental analyses were carried out on a Elementar Vario EL III machine.

Typical Procedure for the Synthesis of Nanoparticles

In a flame dried Schlenk tube silver nitrate (169.7 mg, 1 mmol) and oleylamine (2.67 g, 10 mmol) were added under inert atmosphere of argon and the temperature was raised to 165 °C. After constantly stirring at this temperature for 30 min the reaction mixture was cooled down to room temperature and nanoparticles were obtained upon precipitation of the reaction mixture into ethanol. Upon washing the nanoparticles three times with ethanol and drying in vacuum 180 mg of black solid nanoparticles were obtained. Yield: 96 %. According to thermogravimetric analysis 10w% of oleylamine are present in the sample. Anal. calcd for C₁₈H₃₇Ag₂₂N: C, 8.19, H 1.41, N 0.53; found: C 7.99, H 1.78, N. 0.33.

Procedure for the Preparation of Nanoparticle Containing pDCPD Plates

DCPD was heated to 30 °C in a water bath to melt it. 5 mg of the nanoparticles were put into a glass vial and dissolved in 10 g of DCPD to give a homogenous brownish mixture. 4.7 mg **M2** (0.005 mmol) were dissolved in 2 ml freshly degassed dichloromethane. 300 µL of the solution were put into a vial, 5 ml of the DCPD mixture were added with a syringe, thus perfectly mixing the batch. The prepared mould was filled with the mixture and left 10 min at room temperature. Then, it was put into a preheated oven at 60°C for 2 h. The mould was opened and the transparent, greyish poly(DCPD) plate was removed.

Antimicrobial Tests

Antimicrobial tests were performed at the Technologie Transfer Zentrum Bremerhaven, Germany. The polymer test samples were 4 x 4 cm in size. The procedure chosen was a modified JIS Z 2801:2000 protocol. The bacteria strain tested was *E. coli* DSM 10290. 50 µl of the inoculated working culture were diluted in a 1:10 ratio, until a final concentration of approximately 4.0 x 10⁵ cells ml⁻¹ was reached. Glass slides were coated three times with 75 µL of the diluted bacteria suspension, capped

with sterile cover glasses, and incubated for 24 h at 35°C. Samples were transferred in a casein peptone-soya meal peptone nutrient solution and eluted. Dilutions were dripped on a culture medium and again incubated for 44 h. Then CFUs were counted.

Conclusions

To sum up, a new environment friendly solvent free method for the synthesis of silver nanoparticles is reported. The Ag-nanoparticles are dispersible in unpolar media which paves the way for using them as antimicrobial additive in polymers, as it was exemplarily shown for poly(dicyclopentadiene). In this case up to at least 1 w% of the Ag-nanoparticles can be dissolved in DCPD and upon curing the mixture in the presence of an olefin metathesis initiator in a mould duroplastic, antimicrobially equipped work pieces can be obtained. In general, a straight forward way for the synthesis of Ag-nanoparticle filled polymeric materials was disclosed and might lead to a manifold of practical applications [16].

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