



Aspherical silver nanoparticles by thermal decomposition of a single-source-precursor



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ABSTRACT

The synthesis and characterization of silver(I) 2-phenyl-3,6,9-trioxadecanoate (**3**) is described. Thermal decomposition of **3** at 100–165 °C in a long-chained amine resulted in the formation of monodisperse silver nanoparticles with sizes of about 7–10 nm. By variation of the reaction conditions aspherical silver nanoparticles with hexagonal contours could be obtained, which is a novelty for silver nanoparticles prepared by thermal decomposition.

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1. Introduction

During the last decades numerous preparation methods of metallic nanoparticles were developed which give access to various particle forms such as spheres, plates, rods and others [1,2]. For example, plate-like silver nanoparticles have been synthesized by boiling silver salts in reducing solvents (e. g., AgNO₃ with poly (*N*-vinylpyrrolidone) in *N,N*-dimethylformamide [3]) or with other mild reducing agents [4], by light-mediated approaches [5], or by nanosphere lithography [6].

An alternative route to silver nanoparticles is the thermal decomposition of silver(I) compounds. Usually fatty acid carboxylates are used [7–19]. This approach is well established for the synthesis of spherical nanoparticles. However, to the best of our knowledge this method has never been used for the preparation of aspherical nanoparticles.

In recent years our group described the use of ethylene glycol-functionalized metal carboxylates as single source precursors for the generation of spherical and aspherical gold and copper nanoparticles [20–23]. Additionally, the preparation of silver nanoparticles on solid supports for catalytic applications was reported [24]. Herein, we describe the synthesis and properties of an ethylene glycol-functionalized silver(I) carboxylate as well as its application in the formation of aspherical and spherical silver nanoparticles by thermal decomposition in solution.

2. Experimental

2.1. Materials and methods

rac-2-Phenyl-3,6,9-trioxadecanoic acid was prepared by a nucleophilic substitution from *rac*-2-bromo-2-phenylacetic acid and 3,6-dioxahexanol, as reported before [25]. All other chemicals were obtained from commercial suppliers and were used without further purification. All reactions were carried out under inert conditions with solvents dried by standard techniques [26].

Elemental analysis (EA) was performed using a Thermo FLA-SHEA 112 Series instrument. Infrared (IR) spectra were recorded with a Nicolet iS 10 from Thermo Scientific. ¹H NMR spectra were recorded with a Bruker Avance III 500 spectrometer operating at 500.30 MHz in the Fourier transform mode; ¹³C{¹H} NMR spectra were recorded at 125.80 MHz. Chemical shifts are given relative to the internal standard tetramethylsilane. Mass spectra were recorded using a micrOTOF QII Bruker Daltonics workstation. TG and DSC experiments were performed using a Mettler Toledo TGA/DSC1 1600 system with an MX1 balance. UV–Vis spectra were recorded using a Thermo Genesis 6 spectrometer. DLS was measured with a Zetasizer Nano-S90 from Malvern Instruments. The obtained data were fitted mathematically with a Gauss curve. TEM imaging was performed with a PHILIPS CM 20 FEG instrument operated at 200 kV.

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Table 1

Reaction conditions for the preparation of silver nanoparticles by thermal decomposition of silver(I) 2-phenyl-3,6,9-trioxadecanoate (**3**) in "hexadecylamine (*d*: diameter, σ : standard deviation).

Sample	<i>c</i> [mM]	<i>T</i> [°C]	<i>t</i> [min]	<i>d</i> ^a [nm]	σ ^a [nm]
1	1	165	10	9.7	1.0
2	10	165	10	7.5	0.9
3	1	125	4–60	7.8	1.0
4	1	100	24–60	^b	^b
5	10	165	60	7.3	1.2

^a Obtained by TEM measurements (*vide infra*).

^b Bimodal distribution.

2.2. Synthesis

Silver(I) 2-phenyl-3,6,9-trioxadecanoate (3**):** A mixture of 4.15 mL triethylamine and 7.62 g (30 mmol) *rac*-2-phenyl-3,6,9-trioxadecanoic acid (**1**) was slowly added to a solution of 5.10 g (30 mmol) silver(I) nitrate (**2**) in a mixture of 3.5 mL acetonitrile and 50 mL of ethanol. The reaction mixture was stirred with an effective stirrer at ambient temperature for 30 min. After heating it to 75 °C, a mixture of acetonitrile and ethanol (*v:v*, ratio 2:8) was added until a clear solution was formed. After cooling to –25 °C the precipitating solid was filtered off, washed with ethanol and dried *in vacuo*. Colorless solid. Mp. 165 °C (decomp.). *Anal. Calc.* for C₁₃H₁₇O₅Ag (361.13): C, 43.23; H, 4.74. Found: C, 42.67; H, 4.65%. IR (KBr): $\tilde{\nu}$ = 3060 (w), 2917 (m), 1602 (s), 1453 (w), 1386 (s), 1307 (w), 1248 (w), 1197 (w), 1089 (s), 1028 (m), 899 (w), 849 (w), 740 (m), 701 (m), 668 (w) cm^{–1}. ¹H NMR (D₂O): δ = 3.40 (s, 3 H, CH₃), 3.61–3.65 (m, 3 H, CH₂), 3.69–3.71 (m, 2 H, CH₂), 3.74–3.76 (m, 2 H, CH₂), 3.78–3.82 (m, 1 H, CH₂), 4.85 (s, 1 H, CH), 7.44–7.53 (m, 5 H, CH) ppm. ¹³C{¹H} NMR (D₂O): δ = 58.1 (CH₃), 67.9 (CH₂), 69.4 (CH₂), 69.7 (CH₂), 71.0 (CH₂), 83.4 (OCH), 127.5 (CCH), 128.3 (CCH), 128.6 (CCH), 138.3 (CCH), 178.2 (CO₂) ppm. MS (ESI, dichloromethane): *m/z* 361.0259 (M+H⁺, ber. 361.0200, RI = 100%), 468.9144 (M+Ag⁺, ber. 468.9170, RI = 4.6%), 723.0306 (2 M+H⁺, ber. 723.0325, RI = 4.9%), 828.9271 (2 M+Ag⁺, ber. 828.9297, RI = 3.9%).

Silver nanoparticles: 10 mL of a solution of silver(I) 2-phenyl-3,6,9-trioxadecanoate (**3**) in "hexadecylamine (1–10 mM, Table 1) was heated to 75 °C, followed by heating to the reaction temperature (100–165 °C, Table 1) with a pre-heated oil bath. After a defined reaction time (10 min to 24 h, Table 1) the mixture was air-cooled. After adding of 10 mL of ethanol the particles were separated by centrifugation (2200g, 30 min) and cleaned by repeated dispersing in ethanol and centrifugal isolation.

3. Results and discussion

Silver(I) 2-phenyl-3,6,9-trioxadecanoate (racemic mixture, **3**) is accessible by the reaction of the corresponding carbonic acid (**1**) with silver(I) nitrate (**2**) in presence of triethylamine (Scheme 1) [24]. Complex **3** is a colorless solid which decomposes slowly under light but otherwise is stable even under aerial conditions. Its solubility is best in hot polar and coordinating solvents such as acetonitrile or *N,N*-dimethylformamide.

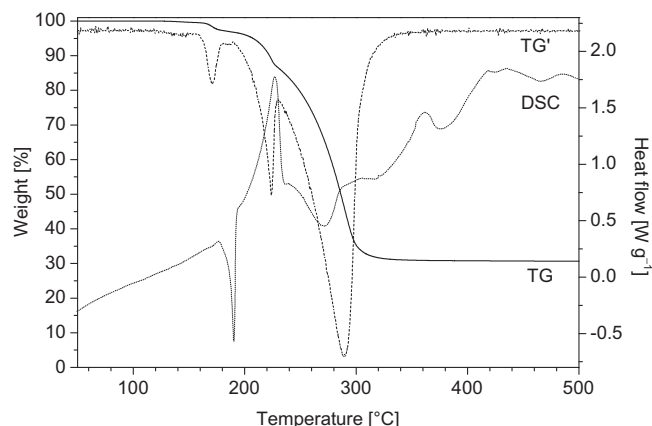


Fig. 1. TG (black line), TG' (dashed line) and DSC (dotted line) traces of silver(I) 2-phenyl-3,6,9-trioxadecanoate (**3**) (heating rate 10 K min^{–1}, N₂ flow 60 mL min^{–1}).

Complex **3** was characterized by elemental analysis, IR and NMR spectroscopy as well as ESI-TOF mass spectrometry. All investigations gave the expected results.

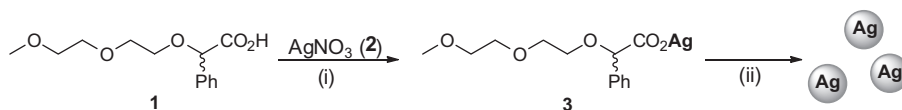
The IR spectrum of **3** shows carboxylato valence vibrations at $\tilde{\nu}_{\text{sym}}^{\text{CO}_2} = 1386$ and $\tilde{\nu}_{\text{asym}}^{\text{CO}_2} = 1601$ cm^{–1}. The difference $\Delta\tilde{\nu}_{\text{CO}_2} = 215$ cm^{–1} is only a little smaller than the value of the corresponding potassium salt (233 cm^{–1}) [27]. This implies either a bidentate chelating or a bidentate bridging coordination mode [28]. Similar results were found for the corresponding copper(II) carboxylate [27].

The ESI mass spectrum of **3** shows signals for di- and trinuclear molecular species. This indicates the tendency of silver(I) carboxylates to form higher aggregated or polymeric coordination complexes and fits to its poor solubility in non-coordinating solvents.

The thermal behaviour of the silver complex was investigated by thermogravimetry and differential scanning calorimetry (Fig. 1). It was found that the decomposition starts at a temperature of 165 °C which is about 50 °C lower than for the α -unsubstituted complex [24] and about 100 °C lower than for a typical fatty acid carboxylate [18]. This behaviour has been explained by the thermodynamic stability of the intermediate decomposition products [25]. The first derivative of the TG trace allows to distinguish three decomposition steps. The DSC reveals that the first and third step are connected to exothermic processes, whereas the second is endothermic. The mass decay of the first two steps fits well to a decarboxylation reaction ($\Delta m = -13.6\%$, calcd. -12.2%). By TG-MS analysis (see SI) the corresponding fragment (*m/z* 44, CO₂) could be detected, whereas the third step is accompanied by ions such as *m/z* 31, 45 or 58 which can be explained as fragments of the ethylene glycol chain (e.g. OCH₂⁺, C₂H₅O⁺, C₂H₂O₂⁺). The final decomposition residue has a weight of 30.5%, which is close to the silver content of the complex (29.8%). An XRPD measurement (see SI) shows all reflexions expected for metallic silver (ICDD 00-004-0738). No additional reflexions were found.

By further experiments it could be shown that a solution of complex **3** can be decomposed at even lower temperatures, e.g. in boiling water.

Complex **3** was used to prepare silver nanoparticles by thermal decomposition in solution. Hexadecylamine was applied as



Scheme 1. Synthesis of **3** and its thermal decomposition to silver nanoparticles: (i) NEt₃, EtOH/MeCN, 25 °C; (ii) C₁₆H₃₂NH₂, 1–10 mM, 100–165 °C, 10 min–24 h.

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