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Silver nanoparticles from the thermal decomposition of a two-dimensional nano-coordination polymer

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ABSTRACT

Nanostructures of the two-dimensional coordination polymer $[Ag(\mu_3-Hma)]_n$ (1) $[H_2ma = maleic acid]$ have been synthesized by the reaction of KHma and AgNO₃ by a sonochemical process and with oleic acid treatment at 453 K. The single-crystal X-ray data of compound 1 shows the formation of a hemi paddle-wheel structure. The coordination number of the Ag¹ ions in compound 1 is three and there is an argentophillic interaction. Silver nanostructures and silver nanoparticles were synthesized by calcination and thermal decomposition of the compound 1 nanostructures, respectively. These nanostructures and nanoparticles were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The thermal stability of compound 1 was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

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1. Introduction

Recently nanosized coordination polymers (NCPs) with finite repeating units have aroused a growing interest due to their special properties, distinctive from conventional bulk coordination polymers (CPs) [1]. For this reason, such nano-sized materials are interesting candidates for applications in many fields, including electronics, catalysis, separation, biology, medical imagery and others [2]. Recently, we and others have shown how such structures can be transformed into nano- and microparticle materials through controlled precipitation methods [3–7]. For example, attempts to reduce the crystal size of metal coordination polymers to the nanometer scale have appeared using the reverse micelles technique, the Langmuir–Blodgett method, template synthesis, film formation and the simple mixing of starting complexes in the presence of an organic stabilizer [8], but examples of the formation NCPs by the sonochemical process are scarce [5–7].

Among polymeric coinage d^{10} metal complexes, silver(I) coordination polymers have received much attention because silver(I) shows a tendency to form coordination polymers with unique metal–carbon [9–13] and metal–metal [14,15] interactions. Silver has been extensively used in a variety of applications such as catalysis, electronics, photonics, photography, biology and medicine-science due to its unique properties. For example, silver has the highest electrical conductivity, thermal conductivity and reflectivity of all metals [16]. Several methods can be applied to synthesize silver nanoparticles with well-defined shapes but the use of silver CPs or silver NCPs to prepare silver nano structures is scarce [17]. Among the coordination polymers, structures with a two-dimensional organization are of particular interest because of their potential for offering optimized optical or electrical functions [18]. Continuing our previous work on silver(I) CPs [19–22] and studies on the relation between the silver(I) coordination polymer dimension and the dimension of the resulting silver nano-structure [17,23], the synthesis of a two-dimensional Ag^I NCP of maleic acid by the sonochemical process and oleic acid as a surfactant is reported. Also silver nano-structures have been fabricated from this silver(I) NCP by the calcination method and by a thermal decomposition process.

2. Experimental

2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available and used as received. Double distilled water was used to prepare the aqueous solutions. A multiwave ultrasonic generator (Sonicator_3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/transducer and a titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W and an ultrasonic bath (Tecna 6; 50–60 Hz and 0.138 KW) were used for the ultrasonic irradiation. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Perkin–Elmer 597 and





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Nicolet 510P spectrophotometers. The thermal behavior was measured with a PL-STA 1500 apparatus between 35 and 600 °C in a static atmosphere of nitrogen. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo K α radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 . Structure solution and refinement was accomplished using SHELXL-97 program packages [24]. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using MERCURY software [25]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromatized Cu K α radiation. The samples were characterized with a scanning electron microscope with a gold coating.

2.2. Synthesis of $[Ag(\mu_3-Hma)]_n$ (1) and preparation of its single crystals

In 20 ml CH₃CN, 0.116 g (1 mmol) maleic acid were mixed and stirred with a solution of 0.057 g (1 mmol) KOH in 3 ml H₂O to form a clear solution. Addition of 0.170 g (1 mmol) AgNO₃ in 5 ml CH₃CN still maintained a clear solution. The resulting solution was stirred and then allowed to stand in darkness at room temperature to evaporate for several days to obtain suitable crystals. The crystals were washed with acetone and air dried. D.p. = 150 °C. Yield: 0.167 g (75% based on final product). IR (selected bands; in cm⁻¹): 553w, 649w, 705s, 871s, 992s, 1080w, 1192s, 1267w, 1350vs, 1391vs, 1491vs, 1578vs, 1618s, 1700s, 3045w, 3445w. *Anal.* Calc. for C₄H₃AgO₄: C, 21.53; H, 1.34. Found: C, 20.65; H, 1.40%.

2.3. Synthesis of $[Ag(\mu_3-Hma)]_n$ (1) nanostructures by the sonochemical process

To prepare nanostructures of $[Ag(\mu_3-Hma)]_n$ by the sonochemical method, a high-density ultrasonic probe was immersed directly into a solution of KHma (50 ml, 0.1 M) in MeOH, then into this solution a proper volume of AgNO₃ aqueous solution (10 ml, 0.5 M) was added in a dropwise manner. The solution was ultrasonically irradiated with a power of 27 W for 1 h. The obtained precipitates were filtered, subsequently washed with MeOH and then dried, (found C, 21.20; H, 1.29%). IR (selected bands; in cm⁻¹): 555w, 650w, 708s, 878s, 994s, 1085w, 1191s, 1267w, 1351vs, 1392vs, 1498vs, 1577vs, 1618s, 1701s, 3046, 3449w. Before the usage of the sonicator unit, we used an ultrasonic bath for the ultrasonic irradiation with different concentrations of metal and ligand solutions (0.025, 0.05, 0.1, 0.2, 0.4 and 0.8 M) and a power of 0.138 KW for 1 h, but we could not obtain a precipitate of compound **1** with the three initial concentrations of metal and ligand solutions, and the SEM images of three samples with higher concentrations were not acceptable. In order to obtain silver nanostructures, precipitates of compound **1** nanostructures, which were obtained from 0.1 to 0.5 M solutions of the initial reagents with the sonicator unit, were calcinated at 673 K in a furnace under a static atmosphere of air for 5 h.

2.4. Synthesis of $[Ag(\mu_3-Hma)]_n$ (1) nanoparticles by surfactant

To prepare compound **1** nanostructures by surfactant, precipitates of compound **1** nanostructures (223 mg, 1 mmol) were dispersed in 16 mL (50 mmol) oleic acid (OA). This solution was heated to 453 K for 1 h under an air atmosphere in an electric furnace. At the end of the reaction, a black precipitate was formed. A small amount of toluene and a large excess of EtOH were added to the reaction solution, and compound **1** precipitate was separated by centrifugation. The solid was washed with EtOH and dried, (Found C, 21.40; H, 1.36%). IR (selected bands; in cm⁻¹): 553w, 650w, 706s, 875s, 991s, 1085w, 1196s, 1268w, 1353vs, 1397vs, 1495vs, 1576vs, 1615s, 1704s, 3045w, 3447w.

2.5. Synthesis of silver nanoparticles by surfactant

To prepare silver nanoparticles by surfactant [26], precipitates of compound **1** nanostructures (446 mg, 2.0 mmol), obtained from the sonochemical process, were dispersed in oleic acid (OA), (16 mL, 50 mmol) to form an homogenous emulsion solution. This solution was degassed for 15 min and then heated to 523 K for 1 h under an air atmosphere in an electric furnace. At the end of the reaction, a black precipitate was formed. A small amount of toluene and a large excess of EtOH were added to the reaction solution, finally metallic silver was separated by centrifugation. The solid was washed with EtOH and dried, neither d.p. nor IR bands were observed.

3. Results and discussion

3.1. Structure description

The Scheme 1 shows the reaction between silver(I) nitrate and KHma by two different methods.

The reaction between maleic acid (H_2ma) and $AgNO_3$ provided a crystalline material of the general formula $[Ag(\mu_3-Hma)]_n$ (1). Determination of the structure of 1 by X-ray crystallography (Tables 1 and 2), showed the complex to be a novel two-dimensional polymer (Fig. 1). The silver atoms can be considered to be three-coordinate. As a result of the reaction conditions, partial deprotonation of the H₂ma ligand occurs. The carboxylate and carboxylic acid groups of the Hma⁻ ligand do not act as bridging groups.



Scheme 1. The produced materials from the reaction of the KHma ligand with silver(I) nitrate by two different methods and fabrication of silver nanostructures from compound 1 nano-coordination polymer.

Table 1

Crystal data and structure refinement for compound [Ag(u ₃ -H	lma)l	n (1	I).
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Empirical formula	$C_4H_3AgO_4$
Formula weight	222.93
T (K)	298(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	10.5896(16)
b (Å)	3.7140(6)
c (Å)	16.5617(18)
α (°)	90.00
β (°)	128.618(6)
γ (°)	90.00
$V(Å^3)$	508.93(13)
Z	4
D_{calc} (g cm ⁻³)	2.910
Absorption coefficient (mm ⁻¹)	3.881
$F(0\ 0\ 0)$	424
Crystal size (mm ³)	0.23 imes 0.21 imes 0.15
θ range for data collection (°)	2.46-25.10
Index ranges	$-8 \leqslant h \leqslant 12, -4 \leqslant k \leqslant 4,$
	$-19 \leqslant l \leqslant 14$
Reflections collected	2336
Independent reflections (R_{int})	916 (0.1180)
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.5537 and 0.4289
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	916/0/84
Goodness-of-fit (GOF) on F^2	1.136
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0455, wR_2 = 0.1100$
R Indices (all data)	$R_1 = 0.0466, wR_2 = 0.1112$
Largest difference in peak and hole	1.496 and -1.678
(e Å ⁻³)	

Table 2

Selected bond lengths (Å) and angles (°) for compound $[Ag(\mu_3-Hma)]_n$ (1).

Ag1-O4 ⁱ	2.226(3)	04 ⁱ -Ag1-O3 ⁱⁱ	158.15(9)
Ag1–O3 ⁱⁱ	2.276(2)	04 ⁱ -Ag1-01	106.85(9)
Ag1-01	2.418(2)	03 ⁱⁱ -Ag1-01	94.88(8)
Ag1–Ag1 ⁱⁱⁱ	2.9915(8)	O4 ⁱ -Ag1-Ag1 ⁱⁱⁱ	80.38(6)
O3–Ag1 ^{iv}	2.276(2)	O3 ⁱⁱ –Ag1–Ag1 ⁱⁱⁱ	79.33(5)
04–Ag1 ^v	2.226(3)	O1–Ag1–Ag1 ⁱⁱⁱ	163.10(7)

Symmetry transformations used to generate equivalent atoms; i: x + 1, -y - 1/2, z + 1/2, ii: -x + 2, y + 1/2, -z + 3/2, iii: -x + 3, -y, -z + 2, iv: -x + 2, y - 1/2, -z + 3/2, v: x - 1, -y - 1/2, z - 1/2.

The two carboxylate groups of two Hma⁻ ligands coordinate to two Ag⁺ ions and form a hemi paddlewheel structure (Figs. 1a and 2). The oxygen atom of the carboxylic acid C=O group occupies the axial position of another hemi paddlewheel structure. Another feature of this hemi paddlewheel structure is the formation of Ag-Ag bonds between two Ag atoms of this structure (Figs. 1a and 2). The Ag–Ag interactions in compound **1**, Ag1–Ag1 = 2.997 Å, are longer than the Ag-Ag distances in similar dinuclear complexes (i.e., 2.704(2), 2.669(1) and 2.726(1)Å) [27-31] and slightly shorter than those in the polymeric structure [32-35]. The relatively short Ag-Ag bonds found here may thus be considered to be only d^{10} ... d^{10} non-covalent interactions [27–35]. Thus compound **1** can be considered to contain silver atoms with three-fold coordination and an O₃Ag···AgO₃ coordination environment. The structure of compound **1** could be considered as a parallel one-dimensional corrugated tape polymers along the *a*-axis, which are connected to each other and form a two-dimensional network (Fig. 1b). Hydrogen bonding interactions are present between the -OH and -COO⁻ groups of the Hma⁻ ligand in compound **1** (Fig. 2).

Fig. 3a shows the simulated XRD pattern from single crystal Xray data of the above compound and Fig. 3b shows the XRD pattern of typical samples of $[Ag(\mu_3-Hma)]_n$ (1) prepared by the sonochem-



Fig. 1. A fragment of the two-dimensional network in **1**; (a) along crystallographic c axis, showing hemi paddlewheel structure, (b) along crystallographic a axis, showing parallel one-dimensional corrugated tape polymers which are connected to each other to form a two-dimensional network, H atoms have been omitted for clarity (Ag = violet, O = red, C = gray). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. A fragment of the two-dimensional network in **1**, along the crystallographic *b*-axis, showing hydrogen bonding interactions as dashed lines and the hemi paddlewheel structure, (Ag = purple, O = red, C = gray, H = white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ical process and treatment with oleic acid at 453 K. Acceptable matches, with slight differences in 2θ , were observed between the simulated patterns from single-crystal X-ray data (Fig. 3a) and the experimental powder X-ray diffraction patterns for a nano-



Fig. 3. XRD patterns; (a) simulated pattern based on single crystal data of compound **1**, (b) nanostructures of compound **1** prepared by the sonochemical process and treatment with oleic acid, (c) silver nanostructures and silver nanoparticles prepared by calcination and thermal decomposition of compound **1** nanostructures.

2-theta

structure crystalline sample as obtained from the synthesis by the sonochemical process and treatment with oleic acid at 453 K (Fig. 3b). The results of the XRD powder patterns indicate that the experimental data are in good agreement with the simulated XRD powder patterns based on single crystal data, hence this compound is obtained as a mono-phase. The morphology, structure and size of the five samples which were prepared by the sonochemical process and treatment with oleic acid were investigated by scanning electron microscopy (SEM). Fig. S1a-c shows the SEM images of compound 1, for three samples obtained by the sonochemical process in an ultrasonic bath. As could be observed from this figure, acceptable results were not obtained from this process and the power of ultrasonic bath was not appropriate to fabricate compound 1 nanostructures. On the other hand, with lower concentrations of ligand and metal solutions, no precipitate of compound 1 was formed. In order to obtain compound 1 nanostructures using the sonochemical process, we used a multiwave ultrasonic generator. Fig. 4(top) and Fig. S2 show the SEM images of compound 1 nanostructures with an average diameter of 350 nm. obtained by the sonochemical process with a multiwave ultrasonic generator. Treatment of compound 1 nanostructures with oleic acid as a surfactant at 453 K results in the formation of compound 1 nanostructure aggregates from nanoparticles of this compound, with a diameter of about 30-90 nm and average diameter of 50 nm, which can be observed in Fig. 4(bottom).

Thermal gravimetric (TG) and differential thermal analyses (DTA) of compound **1** single crystals show that the crystalline form



Fig. 4. SEM images of compound **1** nanostructures prepared by the sonochemical process (top) and treatment with oleic acid at 453 K (bottom).



Fig. 5. Thermal behavior of compound 1 single crystals.

is stable up to 156 °C (Fig. 5), at which temperature decomposition and pyrolysis of compound **1** starts in two steps with endothermic and exothermic effects at 217 and 307 °C, respectively. In these two steps, removal of Hma⁻ occurs between 156 and 362 °C with a mass loss of 48.7% (calc. 51.6%). Mass loss calculations show that the final decomposition product is metallic silver.

Fig. 3c shows the XRD pattern of the residue obtained from calcinations of compound **1** nanostructures at 673 K. The obtained patterns match with the standard patterns of cubic silver with lattice parameters (a = 4.0862 Å and z = 4) which are close to the reported values, (JCPDS card number 04-0783). SEM images (Fig. 6,



Fig. 6. SEM images of the spongy silver nanostructure prepared by calcination of compound 1 at 673 K (top and middle) and silver nanoparticles prepared by oleic acid at 523 K (bottom).

middle and top) of the residue obtained from calcinations of compound **1** nanostructures at 673 K show that nanoparticles of metallic silver with an average diameter of 50 nm were agglomerated to form this spongy nanostructure. Formation of this spongy nanostructure solid is the result of decomposition and pyrolysis of the Hma⁻ ligand, with removal of the resulting gases, such as CO₂. In order to obtain silver nanoparticles from nanostructures of compound **1** polymer and to prevent from agglomeration we used oleic acid, as a surfactant for the thermal decomposition of compound **1** occurs in the resulting micelles [26]. The XRD pattern of the residue (Fig. 3c) shows that the resulting residue was cubic silver with the lattice parameters mentioned above. The SEM image of the resulting residue shows the formation of silver nanoparticles with an average diameter of about 50 nm (Fig. 6, bottom). In our previous work, silver nanoparticles were also obtained from silver(I) nano-coordination polymers (NCPs) [17,23,36] and in this work, we obtained similar results from a 2D coordination polymer with argentophilic interactions.

4. Conclusions

Nanostructures of a 2D silver(I) coordination polymer with a hemi paddlewheel structure were synthesized by a sonochemical process and with oleic acid at 453 K. Treatment of the sonochemically synthesized nanostructures of compound **1** with oleic acid led to the formation of agglomerated nanostructures of **1** from nanoparticles. The silver nanostructures were fabricated by two methods; (i) calcination of compound **1** nanostructures, obtained from the sonochemical process, which led to silver nanostructure agglomerates from silver nanoparticles and (ii) thermal decomposition of compound **1** nanostructures in oleic acid at 523 K to fabricate silver nanoparticles with an average diameter of 50 nm.

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Appendix A. Supplementary data

Supplementary data CCDC 639612 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.09.011.

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