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Particle-free gold metal–organic decomposition ink for inkjet printing of gold structures

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ABSTRACT

The application of liquid $[AuO_2CCH_2(OCH_2CH_2)_2OCH_3(^nBu_3P)]$ (**1**) as a metal–organic decomposition ink containing 34.2 wt.% of gold is reported. Chemical and physical properties of **1** are discussed. The ink formulated of 20 wt.% of **1** in toluene (gold concentration 6.9 wt.%) exhibits rheological properties well-suited for piezo inkjet printing. Conversion into electrically conductive gold was accomplished by thermal treatment optimized to provide best possible conductivity, contour accuracy, and layer homogeneity.

The thermal decomposition of **1** was studied by thermogravimetry–mass spectrometry coupling experiments. It was found that at first decarboxylation takes place forming $[AuCH_2(OCH_2CH_2)_2OCH_3(P^nBu_3)]$, further heating cleaves the Au–P bond and releases P^nBu_3. This resulting compound decomposes via Au–C, C–C and C–O bond cleavage processes giving gold and appropriate organics ($C_xH_yO_z$ ($x \geq 3$)). The printed features exhibit conductivities of up to 1.9×10^7 S·m^{-1} on glass which corresponds to 43% of bulk gold conductivity.

1. Introduction

Due to its resource efficiency as an additive tool for structured deposition and its flexibility regarding printable substrates, inkjet printing has been explored as a fabrication method for a number of electronic applications including organic light-emitting diodes [1], thin film transistors [2,3], flexible displays [4], and radio-frequency identification tags [5]. Further applications include filter media [6] and spherical nanoparticle aggregates with potential use in photonics or the biomedical field [7]. Recent efforts have focused on the application of inkjet technology for the production of low-cost conductors for circuitry and microelectronic devices [8]. Silver has been proven to be a suitable material for the manufacture of conducting electrodes [9,10]. Gold is another prospective material; due to its high conductivity, low contact resistivity and oxidation resistance, it is frequently utilized as a contact material. Besides its role in micro- and nanoelectronics, gold is of considerable interest for clinical applications, due to its outstanding biocompatible properties. Non-toxicity and non-immunogenicity render it a promising material for cancer imaging and tumor-targeted drug delivery in cancer therapy [11].

The formulation of functional inks is one of the greatest challenges for the inkjet printing of electronic devices. The development of processable materials is increasing, but availability is still limited. Due to the complexity of the inkjet printing process, producing an ink that performs optimally during printing requires that it adheres to narrow tolerances. Ink formulations determine not only the jetting performance, but also the quality of the printed structures. Metal–Organic Decomposition (MOD) inks have proven to be a viable alternative to nanoparticle inks as the most frequently used functional material. As solutions of metal–organic complexes, their main advantage lies in their superior processability by methods such as inkjet printing. Limitations of MOD processing include the volume change effect which occurs during the required thermal post-treatment step and results in comparatively thin films.

Gold(III) and gold(I) organometallic and metal–organic compounds including $[Au(CH_3)_2R^1]$ (R^1 = acac (= $CH_3C(O)CHC(O)CH_3$), tfacac (= $CF_3C(O)CHC(O)CH_3$), hfacac (= $CF_3C(O)CHC(O)CF_3$)) [12,13], $[Au(CH_3)_2(CO_2R^2)]$ ($R^2 = CH_3$, $^tC_4H_9$) [14] and $[Au(CO_2R^3)(PR^4_3)]$ ($R^3 = CH_3$, $^tC_4H_9$, CF_3, ….; $R^4 = CH_3$, C_2H_5, C_6H_5, …) [15–17], respectively, serve as precursors for different metallization processes such as chemical vapor deposition as well as spin-coating and dip-coating technologies [18]. Gold(III) β-diketonates are usually very reactive and decompose readily at ambient temperatures [19]. In contrast, phosphane gold(I) carboxylates are stable, easy to handle and can be prepared by straightforward synthesis methodologies [20].

Following the inkjet printing step, annealing of the (pre-)functional ink layers is a key process step in inorganic layer manufacturing as it

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provides the as-printed structures with the desired physical and chemical properties [21]. The most common functional ink materials, i.e. inorganic particle or nanoparticle dispersions, need stabilizing components such as alkyl thiols [22] or polyaniline in order to improve processability [23]. The structures produced from particle-based inks have to be sintered in order to remove the solvent and to annihilate additives such as surfactants, dispersants, humectants, and adhesion enhancers present in the ink allowing the formation of a continuous percolating structure. By contrast, the solution-based MOD inks can be prepared without additional stabilizing additives. Sintering effectuates the removal of the solvent from the system, triggers the decomposition of the metal–organic compounds, initiates the evaporation of the organic moiety, and has the newly formed nanoparticle coalesce [24]. In previous studies we have shown that metal–organic gold carboxylates of type $[AuO_2CCH_2(OCH_2CH_2)_nOCH_3(R_3P)]$ ($R = C_6H_5$, $^nC_4H_9$; $n = 2-6$) are able to generate and stabilize gold nanoparticles of size 3.3 (±0.6) to 6.5 (±0.9) nm without addition of any reducing agent and further stabilizing components, respectively [25].

In this work, we demonstrate the application of $[(^nBu_3P)AuO_2CCH_2(OCH_2CH_2)_2OCH_3]$ as a particle-free MOD inkjet ink. The thermal behavior determined by thermogravimetry (TG) and thermogravimetry–mass spectrometry (TG–MS) coupling experiments is discussed as well. We further evaluate the optimum combination of sintering temperature and sintering duration necessary to obtain continuous gold structures with high conductivity, uniform layer thickness, and high edge definition. These qualities are considered particularly crucial for the fabrication of electronic devices from stacked layers.

2. Experimental details

Metal–organic $[AgO_2CCH_2(OCH_2CH_2)_2OCH_3]$ and $[AuCl(^nBu_3P)]$ were synthesized according to literature procedures [26,27]. The gold MOD ink was prepared by dispersing $[AuO_2CCH_2(OCH_2CH_2)_2OCH_3(^nBu_3P)]$ in toluene at a concentration of 20 wt.%. Prior to printing, the emulsion was filtered through a 0.45 μm filter.

TG experiments were carried out using a *Mettler Toledo* TGA/DSC1 1100 system with an UMX1 balance. TG–MS experiments were performed with a *Mettler Toledo* TGA/DSC1 1600 equipment with an MX1 balance. The gas outlet of the TG device is coupled with a *Pfeiffer Vacuum* MS ThermoStar GSD 301 T2 mass spectrometer ($(m/z)_{max} =$ 300 amu) by a heated (200 °C) transfer capillary. Measurements were carried out with a heating rate of $5\ K\cdot min^{-1}$ in the temperature range of 40 to 450 °C in an atmosphere of argon ($60\ mL\cdot min^{-1}$). The whole composition of the released gaseous components was determined by an overview scan from $m/z = 1$ to 300 amu. Gaseous fragments with $m/z = 12$ (C^+) to 103 ($C_4H_7O_3^+$) were detected. From this information a *2nd* TG–MS scan was performed in order to detect the temperature dependent intensities of the main fragments $m/z = 15$ (CH_3^+), $m/z = 29$ (CHO^+), $m/z = 30$ (CH_2O^+), $m/z = 31$ (CH_3O^+), $m/z = 44$ (CO_2^+) and $m/z = 88$ ($C_4H_9P^+$). The ^1H NMR (NMR = Nuclear Magnetic Resonance) spectrum was recorded with a *Bruker* Avance III 500 spectrometer operating at 500.30 MHz in the Fourier transform mode. The $^{13}C\{^1H\}$ NMR data were recorded at 125.80 MHz and the $^{31}P\{^1H\}$ NMR spectrum at 202.53 MHz. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane for ^1H and $^{13}C\{^1H\}$ NMR spectra, and external 85% H_3PO_4 for the $^{31}P\{^1H\}$ NMR spectrum. Microanalysis was performed with a *Thermo Fisher Scientific* FLASHEA 1112 Series instrument. The infrared spectrum was recorded with a FT-Nicolet IR 200 spectrometer. An *Anton Paar* Physica MCR 301 rheometer was used to determine the dynamic viscosity at a shear rate of $1000\ s^{-1}$. The surface tension of the ink was determined by the pendant drop method using an OCA-20 contact angle measurement system from *DataPhysics Instruments*. An Autodrop micro-dosing system (AD-E, MD-P-802-D-11-08, *Microdrop Technologies GmbH*, Norderstedt, Germany) equipped with a dispenser head MD-K-130 with a nozzle diameter of 50 μm was used for the printing experiments. The customized waveform consisted of one individual pulse with a maximum voltage of 85 V applied for 20 μs. Printing was carried out neither heating the dispenser head nor the substrate. Pretreatment of the substrates comprised initial cleaning with toluene and subsequent ultrasonication in acetone and isopropanol for 15 min. After the substrate materials were dried with compressed air, they were placed on a heating plate at 280 °C for 5 min and then cooled to ambient temperature. Thermal conversion of the printed ink into conductive gold was accomplished using a VMS-C7 heating plate from *VWR International*. Morphological characteristics of the printed structures were examined using a DekTak 8 M profilometer from *Veeco Instruments* with an apex of 12.5 μm and a stylus force of 3 mg. The sheet resistances of the sintered gold patterns were measured at ambient conditions using a *Süss Microtec* PM5 probe unit in conjunction with a 2400 source measurement unit (*Keithley Instruments*) applying the van-der-Pauw method (four-point measurement with ohmic contacts). A *FEI* NOVA Nano SEM 200 equipment was used to record Scanning Electron Microscopy (SEM) images and performing Energy Dispersive X-ray (EDX) analyzes at an excitation voltage of 18 kV. In the EDX experiments, the count rate was kept in the order of 1 to10 kcps. The usual range of the dead time for this type of analysis is 30 to 60%.

*2.1. Synthesis of $[AuO_2CCH_2(OCH_2CH_2)_2OCH_3(^nBu_3P)]$ (**1**)*

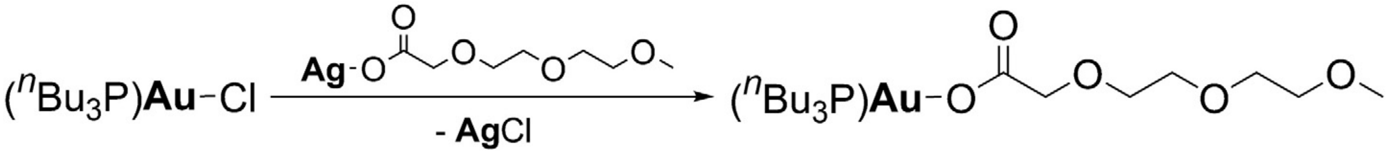
$[AuCl(^nBu_3P)]$ (0.32 g, 0.64 mmol) dissolved in toluene (10 mL) was treated with $[AgO_2CCH_2(OCH_2CH_2)_2OCH_3]$. The slurry was stirred for 12 h at 25 °C in absence of light followed by filtration through a pad of Celite. All volatile materials were evaporated in oil pump vacuum to afford 0.38 g (94%) of **1** as yellow viscous oil (Scheme 1).

2.1.1. Elemental analysis

Calculated for $C_{19}H_{40}AuO_5P$ (576.46) C 39.59%, H 6.99%, Found: C 39.22%, H 7.06%. ^1H-NMR ($CDCl_3$) 0.94 (t, $^3J_{HH} = 0.94$ Hz, 9 H), 1.45 (m, 6 H,), 1.55 (m, 6 H), 1.77 (m, 6 H), 3.37 (s, 3 H), 3.45 (m, 2 H), 3.65 (m, 2 H), 3.70 (m, 2 H), 4.09 (s, 2 H). $^{13}C\{^1H\}$-NMR ($CDCl_3$) 13.50, 23.90 (d, $^3J_{CP} = 14.92$ Hz), 25.30 (d, $^2J_{CP} = 37.83$ Hz), 27.20, 58.91, 70.20, 70.36, 70.58, 71.86, 175.04. ^{31}P-NMR ($CDCl_3$) 16.06. FT-IR (NaCl, cm^{-1}): 2955, 2927, 2870, 1608, 1461, 1413, 1322, 1096, 910, 721. HRMS m/z: calculated for $C_{24}H_{54}P_2Au$: 601.3361; found 601.3356 $[(^nBu_3P)_2Au^+]$.

3. Results and discussion

Metal–organic $[AuO_2CCH_2(OCH_2CH_2)_2OCH_3(^nBu_3P)]$ (**1**) was synthesized by treatment of $[AuCl(^nBu_3P)]$ with the silver(I) carboxylate $[AgO_2CCH_2(OCH_2CH_2)_2OCH_3]$ under absence of light using toluene as solvent at 25 °C. After appropriate workup, metal–organic **1** was



Scheme 1. Synthesis protocol for the preparation of **1**.