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Inkjet printing of sol–gel derived tungsten oxide inks

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ABSTRACT

Tungsten (VI) oxide – WO_3 is a widely studied functional inorganic semiconductor material with exceptional chromogenic properties. It is used in energy efficient systems such as smart windows, sensors, displays, storage units, photocatalysts and solar cells. Layers of WO_3 are generally produced using expensive vacuum deposition techniques. In this paper, the inkjet printing of sol–gel derived tungsten inks on glass and transparent conductive oxide is reported. Peroxo sol–gel synthesis was used to prepare peroxopolytungstic acid sols which were then modified using different solvents to obtain a suitable jetting ink. Described are the rheological and structural properties of WO_3 inks, the dynamics of WO_3 droplets and the morphology and quality of WO_3 printouts. The functionality of these transparent WO_3 layers is successfully demonstrated in an electrochromic device.
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1. Introduction

Tungsten (VI) oxide–WO_3 is arguably the most efficient inorganic electrochromic material with excellent electrochromic properties both in the visible and infrared part of the spectrum. It allows high coloration efficiencies ($21-167\ cm^2/C$) and is relatively inexpensive with typical electrochromic systems costing between 10 and 1000 $\$/m^2$ [1–4]. It can be used as either a buffer layer or as a p-/n-type semiconductor, in sensors, displays, storage units, photocatalysts and solar cells [5]. More recently attention has focussed on integrating inorganic metal oxide layers (e.g. WO_3, V_2O_5, and MoO_3) into organic optoelectronic systems such as organic photovoltaics (OPV) and organic light emitting diodes (OLED) as a means of improving efficiency, stability and system longevity [6,7].

Tungsten (VI) oxide has a defect perovskite structure based on corner sharing WO_6 octahedra. Crystallization occurs in a variety of modifications including monoclinic, tetragonal and cubic phase depending on how the WO_6 octahedra are interconnect. This in turn depends on synthesis, deposition and process parameters: such as annealing temperature and surface treatment (O_2 or H_2 plasma) of the WO_3 layers [3–8]. Its structure is also affected by ion intercalation where the electrochemical insertion of Li ions leads to the ordering of the crystalline structure from monoclinic through tetragonal and finally to the cubic phase [9]. The structure of the WO_3 layer influences semiconductor properties, coloration efficiency, stability and coloring–bleaching kinetics [3–8].

The layers of WO_3 are typically created by RF vacuum sputtering, chemical vapor deposition (CVD), electrodeposition or from either dip-coating or spin-coating coating suspensions or solutions made by sol–gel processing [1]. Unfortunately, these methods do not meet the requirements of today's electronic production systems, which demand cheaper and variable mass production methods. For example coating techniques are limited in their control of deposition, multi-layered structures and patterning. The increasing demands of consumable electronics search for low-cost deposition techniques, therefore digital printing techniques are gaining importance. Amongst them inkjet printing is one of the most promising methods. It allows precise and contact-less transfer, the use of diverse materials, sampling and multi-layer construction at low price [10]. This will require the development of new functional inks that will avoid inhomogeneous film formation, formation of cracks, irregular and deformed printed lines and defects like coffee ring and fishbone effects [11,12]. To obtain homogeneous layers optimum properties of the ink (viscosity, surface tension and evaporation rate) and printing settings (voltage, the shape of pulse, substrate and ink temperature, size and speed of ink drops) must be adopted [13]. The properties of printable functional ink can be controlled by combining solvents to control viscosity, surface tension and evaporation rate, as recently reported by Chouki and Schoeftner [14]. An ideal ink for a Drop on Demand – DOD inkjet system should have a viscosity of $0.002-0.03$ Pa s and a surface tension of 30 mN/m [15]. Additionally, ink viscosity needs to allow the smooth delivery of the ink between the printer head and the cartridge. The other important property is the surface tension of the ink which plays an important role on the interaction between the printer nozzle and ink, as well

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as on the spreading of the drops over the substrate surface. Ideally the surface tension must be such that the printing ink is held in the nozzle without dripping while allowing a droplet to spread over the substrate to form a continuous film [16].

The rheological and structural properties of WO_3 inks vary according to temperature, pH, water content and the concentration of H_2O_2 [17]. The sols referred to inks are Newtonian fluids, which mean that their viscosity is independent of flow rate, whereas the gels show non-Newtonian behavior and become dilatants, whose viscosity increases with the rate of shear strain [18]. Importantly, the homogeneity of printouts depends on the mechanism of drop formation and this varies with a fluid's and surface properties. Various dynamic phenomena are also observed during drop formation such as splashing, spreading, receding, bouncing and crown formation. Rioboo et al. [19] have analyzed the phases of drop spreading: kinematic phase, spreading phase, relaxation phase and wetting phase. Drop dynamics and film formation can be predicted with various computational simulations and studied using the Weber number ($We=\delta v^2 d/\sigma$), Ohnesorge number (Oh=η/sqrt(δσd)=1/Z) or Z number ($Z=\delta\sigma d/\eta$) and Reynolds number ($Re=\delta v^2 d/\eta$), where δ is the density, v is the drop velocity, d is the diameter of nozzle, σ is the surface tension and η is the viscosity of the printable liquid. Drop dynamics and the impact of droplets on the substrate surface are of great interest in deposition techniques such as spraying or inkjet printing. These models were developed for Newtonian fluids and despite that most commercially available inks are non-Newtonian and contain various additives these models can still be used to assess the printability of the inks [20–23].

Printing of functional sol–gel materials is a new and under-explored area of research. There exist a few reports describing inkjet printing of for example SiO_2, ZnO, TiO_2, and V_2O_5 inorganic layers by applying sol–gel made inks. These were used as transparent electrically conductive (TCO) and dielectric substrates, components for photoactive layers, layers for chromogenic systems and sensors [9]. To our knowledge no publication exists with regards to printing of WO_3 sols. The only relevant publication [24] describes the inkjet printing of suspensions based on TiO_2 and WO_3 nano-powders using different solvents and additives. Inkjet printing of sol–gel functional materials is complex and besides the necessary fine tuning of their rheological properties, there is a need to control gelation of inks and how materials interact.

In this paper, the focus is on inkjet printing of inorganic sol–gel derived tungsten inks. The aim was to obtain homogenous transparent WO_3 printouts applicable for use in electrochromic devices. The tungsten inks were synthesized following the peroxo sol–gel route [25] but modified for inkjet printing on glass and transparent conductive oxide (TCO) substrates. Different WO_3 inks were synthesized based on different solvent compositions having different rheological and physicochemical properties. Their effects on inkjet printing on glass and TCO–glass substrates are discussed.

2. Experimental

2.1. Preparation of a WO_3 ink

Step one involved the synthesis of a WO_3 sol. First, peroxotungsten acid (PTA) was synthesized by reacting 5 g of tungsten monocrystalline powder (99.9%, Aldrich) with 20 ml of hydrogen peroxide (30%, Belinka). The reaction is strongly exothermic. Sols where then prepared by adding solvent to the PTA solution at 120 °C. Two WO_3 sols used in this study as inks where prepared with two different solvents: 2-propanol (puriss, Sigma-Aldrich) and a mixture of 2-propanol and 2-propoxy ethanol (puriss, Sigma-Aldrich). The inks are referred to as WO_3-1 for a WO_3 sol based on 2-propanol and as WO_3-2 for a WO_3 sol based on a mixture of 2-propanol and 2-propoxy ethanol.

The addition of alcohol resulted in the formation of the W-ether (esterification) that polymerizes to peroxopolytungstic acid (P-PTA) [25]. The ink appeared slightly orange and contained 27.7 mmol of tungsten per 30 ml of sol. To improve the ink stability and inkjet jetting properties the primary inks were further diluted to 60 ml with solvent. The diluted inks are marked as d-WO_3-1 and d-WO_3-2.

2.2. Deposition of WO_3 layers

A layer of WO_3 was printed on glass and glass coated with a fluorine doped SnO_2–K-glass (sheet resistance 13 Ω/□) substrates. Substrates were initially cleaned with 2 vol% mucasol (Sigma Aldrich) aqueous solution, distilled water and 2-propanol or 2-propanol/2-propoxy ethanol. Inkjet printing was performed using a piezoelectric Dimatix Materials Printer Series 2800 (Fujifilm Dimatix Inc.) equipped with a silicon print head cartridges having 16 nozzles, each with a nominal drop volume of 10 pL. We varied different printing settings, such as substrate, ink temperature, jetting voltage, printing frequency, drop spacing and cartridge angle.

2.3. Characterization

The viscosity of the WO_3 inks was measured at 20 °C using Vibro Viscometer model SV-1A. Contact angles, surface tension and surface energy measurements of the substrates were made using a Krüss DSA 100 goniometer using the static sessile drop method. The contact angle was evaluated by the circle fitting method, based on the outline of a droplet as shown in Fig. 1. The surface tension was then calculated from the measured contact angles of distilled water, diiodomethane and formamide using the Owens–Wendt model. Surface tension of the WO_3 inks was determined using the stalagmometric method.

The chemical structure of the WO_3 inks was determined using a Perkin Elmer FT-IR System Spectrum GX in the geometry of the attenuated total internal reflection – ATR ($500-4000\ cm^{-1}$). Quality and morphology were monitored with a digital optical camera (Digi 2.0 Micro Scale) and a scanning electron microscope (JSM 6060-LV, JEOL). Image analysis (ImageJ tools) was used to show the shape and size of droplets printed at voltages from 10 to 40 V using different formulations of WO_3 inks. The thickness of the WO_3 layers was measured with a surface profilometer (Taylor-Hobson Ltd.). Estimated thickness of WO_3 layers was between 0.2 and 1.0 μm and dependent on the concentration of WO_3 inks, printer settings and the annealing process. The quality of adhesion

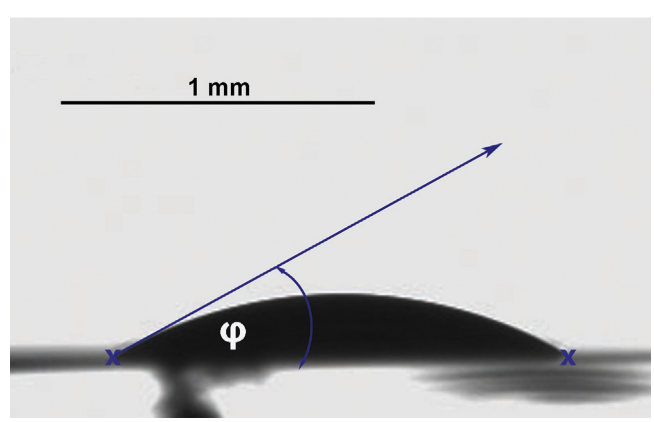

Fig. 1. Contact angle of distilled water on glass substrate.

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