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Paper-supported nanostructured ultrathin gold film electrodes – Characterization and functionalization

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ABSTRACT

Ultrathin gold films (UTGFs) were fabricated on a nanostructured latex-coated paper substrate by physical vapour deposition (PVD) with the aim to provide low-cost and flexible conductive electrodes in paper-based electronics. Morphological, electric and optical properties of UTGFs were dependent on the deposited film thickness. In addition, UTGFs were functionalized with insulating and hydrophobic 1-octadecanethiol self-assembled monolayer and inkjet-printed conductive and hydrophilic poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT–PSS) layer and their electrochemical properties were examined. Results showed that sufficient mechanical stability and adhesion of UTGFs deposited on latex-coated paper was achieved without the need on any additional adhesive layers, enabling a more robust fabrication process of the electrodes. UTGF electrodes tolerated extensive bending without adverse effects and conductivity comparable to the bulk gold was obtained already with the film thickness of 6 nm. Although not been fabricated with the high-throughput method like printing, a very low material consumption (~12 μg/cm^2) together with a high conductivity (resistivity < 3×10^{-6} Ω cm) makes the UTGFs electrodes potential candidates low-cost components in flexible electronics. In addition, the excellent stability of the UTGF electrodes in electrochemical experiments enables their application in the development of paper-based electrochemical platforms, e.g. for biosensing purposes.

1. Introduction

Paper electronics has over the last decade emerged as a new and exciting research topic that holds great scientific and technological interest worldwide. Great efforts are currently being put in the development of paper-based electronic devices and electrochemical platforms [1–14]. The aim is not to replace conventional electronics, but to create a completely new generation of applications, especially in large area electronics, with low-cost, disposable, flexible and robust design. The motivation to use paper as substrate for electronics does not arise only from its low-cost, recyclable and flexible characteristics but also from the fact that physicochemical properties like nano- and microscale topography, surface chemistry and optical transparency can be modified quite conveniently by various coating materials and post-processing methods [2,8,15–17].

Several different paper grades, including porous cellulose-based chromatography type papers, pigment-coated papers and plastic-laminated photo papers have been used as supporting matrices, deposition substrates or active components in paper electronics [7,8,10–12,16,18–20]. In addition, various deposition methods have been considered for the fabrication of the electric components, including sputtering, evaporation, catalytic growth and printing [6,7,9–11,18–20,25].

Printing has intuitively been the main choice for fabrication of paper-based electronic devices and gadgets. In particular, inkjet printing has emerged as one of the most promising high-resolution and cost-effective techniques to fabricate conductive metal thin films due to its low material consumption and highly customized processing [1,8,21]. Among printable conducting materials, gold has been considered as an important material especially in bio-electronics, because of its chemical inertness. Gold also has excellent resistance to oxidation and acids and it is biocompatible [22–24]. For example, gold films with thicknesses as low as 200–300 nm and sufficient conductivity (~1/7th of conductivity of bulk gold) have been produced and utilized in electrochemical applications [14,25–28]. The material costs for such inkjet-printed

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electrodes in lab-scale were estimated to be around 0.04 €/cm^2. Still, from the applicability and cost issue point of view, there could be a need for further reduce film thickness down to the ultrathin film range.

Ultrathin metal films, defined as being under 10 nm thick, play an important role in several fields of materials science and nanotechnology, finding applications in electronic, magnetic and electro-optical devices [29]. Especially, ultrathin gold films (UTGFs) are often used in microfabricated devices due to their high electrical conductivity, optical reflectively and chemical inertness [30–35]. The existing techniques for fabrication of UTGFs are essentially based on a physical vapour deposition (PVD) process in high or ultrahigh vacuum conditions, the most common ones being sputtering, thermal evaporation and laser ablation [36]. Both crystalline and polymeric materials can be used as substrates [37–41]. One particular research area is metallized polymers and their use as electrical contacts on active polymeric layers in organic electronic devices, such as transistors, diodes and solar cells [42–44]. In addition, UTGF electrodes could find applications in analytical and bioanalytical fields. Ultrathin metal films have been reported to result in an enhanced sensitivity in electrochemical immunosensors [45].

One of the main challenges regarding the applicability of UTGFs in microfabrication technology is their comparable weak adhesion to inert and commonly used substrate materials such as glass and silica even when using adhesion promoting processes such as the use of a thin (5–10 nm) oxidative metal underlayer [46,47]. Furthermore, these adhesive metal oxides tend to diffuse to the surface and significantly affect the morphological, optical and electrical properties of the gold films [48,49]. Alternative strategies such as precoating the substrate with a self-assembled layer of, e.g. mercapto- or amine silane have been reported for enhancing the adhesion [50,51]. On the other hand, an excellent adhesion of UTGFs on polymeric substrates has been achieved without the need of an adhesive layer [39,41,52].

This study demonstrates that mechanically stable UTGFs can be fabricated on paper substrate. A nanostructured latex-coated paper was used as a substrate for the vacuum deposited UTGFs with varying thicknesses. The UTGF electrodes were successfully functionalized with hydrophobic alkyl thiol self-assembled monolayers (SAM) and inkjet-printed conductive polymer layer and their electrochemical properties were compared to bare electrodes. Topographical, chemical, electrical and electrochemical characterization of the UTGFs was conducted using atomic force microscopy, contact angle goniometry, X-ray photoelectron spectroscopy, hot-probe technique, cyclic voltammetry and electrochemical impedance spectroscopy. In addition, the mechanical stability and optical properties of the UTGFs were qualitatively examined.

2. Materials and methods

2.1. Paper substrate

A multi-layer curtain coated paper was used as a substrate for the nanostructured two-component latex coating (see details in Appendix Fig A.1). The used paper substrate was developed for printed electronics and has excellent barrier properties against water and solvent penetration and contains components normally used in paper making [53]. The two-component latex blend was applied on the multi-layer coated paper by rod-coating. Details of the fabrication and application of nanostructured latex-coated papers have been described elsewhere [54–56]. In brief, a blend of two latex components with different glass transition temperatures (T_g) was used. The low-T_g (soft) component was an emulsion polymerized carboxylated styrene butadiene acrylonitrile copolymer with T_g = 8–10 °C and an average particle size of 140 nm (DL920, DOW Chemicals). The high-T_g (hard) component was modified polystyrene with T_g > 90 °C and an average particle size of 140 nm (DPP3710, DOW Chemicals). The hard latex particles provide blocking resistance, mechanical strength and integrity to the film, while the soft latex particles act as a film-forming component. The two-component latex blend was prepared by mixing the low-T_g and high-T_g components so that the final weight ratio in the blend was 3:2. The nanostructured surface texture was created by irradiating the latex-coated paper with a short-wavelength infrared (IR) heater for 60 s (IRT systems, Hedson Technologies AB, Sweden). The schematic presentation of the two-phase nanostructure and the relevant surface properties are given in Appendix Fig. A.2.

2.2. Preparation and functionalization of the UTGF electrodes

PVD with electrically resistive heating was used to fabricate gold films. A shadow mask was used for electrode patterning. The evaporation was done under high vacuum (10^{-6} mbar) during two separate runs utilizing a heated aluminium-coated tungsten basket. The evaporation rate was set to 12 nm/min. A deposition monitor (XTM/2, Inficon) was used for gravimetric determination of the amount of evaporated gold on the latex surface. Gold film with nominal thickness of 10 nm (UTGF-10 nm), 20 nm (UTGF-20 nm) and 40 nm (UTGF-40 nm) were fabricated.

The functionalization of UTGFs with alkyl thiol SAMs were conducted using 1-octadecanethiol (ODT, Fluka Chemika). Before the thiolation, the evaporated UTGF electrodes were cleaned with plasma (air) flow (PDC-326, Harrick) for 2 min, rinsed with absolute ethanol and dried with nitrogen gas. The paper-supported UTGFs were sealed between two silicon rings in a custom built liquid flow cell (FIAlab Instruments, Inc., USA) and exposed to a solution of ODT (250 μL, 5 mM) for 16 h at room temperature in the dark under a cap. After SAM formation, the electrodes were removed from the solution, rinsed immediately with absolute ethanol, and dried with nitrogen gas.

Two consecutive print layers of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT–PSS) ink (Orgacon™ IJ-1005, Afga) were inkjet–printed on the working electrode using a drop spacing of 30 μm and firing voltage of 23 V. To ensure optimal jetting conditions and good film quality, the ink cartridge temperature was set to 28 °C and the printing plate temperature was set to 48 °C. After printing, the PEDOT–PSS film was dried at RT at least 12 h prior to further analyses.

2.3. Contact angle measurements and surface energy determination

A CAM 200 contact angle goniometer (KSV Instruments Ltd., Finland) was used for the determination of the static contact angle of the samples. Purified water (MilliQ), diiodomethane (DIM, Sigma) and ethylene glycol (EG, Sigma–Aldrich) were used as probe liquids with drop volume of 1 μL. Contact angles were measured in air in ambient conditions (RH = 25 ± 5%, T = 20 ± 3 °C) and obtained using the software supplied with the instrument, which utilizes a Laplace fit to the projected drop curvature. For surface energy calculations, the Owens–Wendt method [57,58] was applied using the probe liquid surface tension component values suggested by Della Volpe and Siboni [59].

2.4. Atomic force microscopy

An NTEGRA Prima (NT-MDT, Russia) atomic force microscope (AFM) was used to analyze the topography of the samples in intermittent-contact mode. The images (1024 × 1024 pixels) were captured in ambient conditions (RH = 20 ± 2%, T = 26 ± 1 °C) using silicon cantilevers with a nominal tip radius of 10 nm (Model: