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Hierarchically structured self-supported latex films for flexible and semi-transparent electronics

Anni Määttänen [a,*], Petri Ihalainen [a], Björn Törngren [a], Emil Rosqvist [a], Markus Pesonen [b], Jouko Peltonen [a]

[a] Laboratory of Physical Chemistry, Faculty of Science and Engineering, Center for Functional Materials, Åbo Akademi University, Porthaninkatu 3, 20500, Turku, Finland
[b] Physics, Faculty of Science and Engineering, Center for Functional Materials, Åbo Akademi University, Porthaninkatu 3, 20500, Turku, Finland

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Different length scale alterations in topography, surface texture, and symmetry are known to evoke diverse cell behavior, including adhesion, orientation, motility, cytoskeletal condensation, and modulation of intracellular signaling pathways. In this work, self-supported latex films with well-defined isotropic/anisotropic surface features and hierarchical morphologies were fabricated by a peel-off process from different template surfaces. In addition, the latex films were used as substrates for evaporated ultrathin gold films with nominal thicknesses of 10 and 20 nm. Optical properties and topography of the samples were characterized using UV–vis spectroscopy and Atomic Force Microscopy (AFM) measurements, respectively. The latex films showed high-level transmittance of visible light, enabling the fabrication of semi-transparent gold electrodes. Electrochemical impedance spectroscopy (EIS) measurements were carried out for a number of days to investigate the long-term stability of the electrodes. The effect of 1-octadecanethiol (ODT) and $HS(CH_2)_{11}OH$ (MuOH) thiolation and protein (human serum albumin, HSA) adsorption on the impedance and capacitance was studied. In addition, cyclic voltammetry (CV) measurements were carried out to determine active medicinal components, i.e., caffeic acid with interesting biological activities and poorly water-soluble anti-inflammatory drug, piroxicam. The results show that the fabrication procedure presented in this study enables the formation of platforms with hierarchical morphologies for multimodal (optical and electrical) real-time monitoring of length-scale-dependent biomaterial-surface interactions.

1. Introduction

The control and monitoring of protein-material and cell-protein-material interactions are important subjects with implications for the biosensor field [1,2] and the medical field dealing with surgical implant-associated bacterial infections [3,4], compatibility issues [5,6], tissue engineering [7,8], organ transplant rejection [9] and wound healing [10]. In the quickly evolving field of bioelectronics, electronics and biological interfaces are coupled to improve biochemical sensing, tissue characterization, organ monitoring, therapeutics, and diagnostics [11]. Electrical methods are able to detect low concentrations of biological analytes and these methods require no labeling. On the other hand also electrical [12,13] and optical [14] measurements can be carried out simultaneously provided that transparent or semitransparent conductive electrodes and substrates are used [11,15,16].

Traditionally, in vitro cell culture studies have been carried out using flat and clear plastic 2D surfaces [17]. It is, however, well known that on flat and hard substrates, cells behave in a different manner compared to the environments in living tissues [18–22]. For example, stem cells may differentiate into neurons, osteoblasts or myocytes depending on the stiffness of the substrate [23]. To enhance the well-being of cells and to induce a more in vivo like behavior, the influence of surface topography and in vivo mimicking of 3D features have been studied [17,18,24–26]. Textured surfaces have been fabricated by several methods, often by photolithography and etching [25]. In addition, nanoimprinting [27] and different laser modification techniques have been also used for this purpose [28,29]. Biodegradable thin films of poly-L-lactic acid

* Corresponding author.
E-mail addresses: anni.maattanen@abo.fi (A. Määttänen), petri.ihalainen@abo.fi (P. Ihalainen), bjorn.torngren@abo.fi (B. Törngren), emil.rosqvist@abo.fi (E. Rosqvist), markus.pesonen@abo.fi (M. Pesonen), jouko.peltonen@abo.fi (J. Peltonen).

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[30] and chitosan [31] have been fabricated using soft lithographic techniques by applying the polymer solutions on the template surfaces and by peeling them off after solvent evaporation. Recently, De Rosa et al. described a solvent treatment method for creating pores on flat polystyrene surfaces thereby gaining improved cell function mainly by enabling cells to form 3D aggregates [17]. Strain responsive wrinkling technique was used by Choi et al. to create structured PDMS substrates [32]. Zhang et al. used focused ion beam milling to create regularly patterned gold films with a wide palette of colors without employing any form of chemical modification [33]. Morariu et al. described an electric field-induced sub-100 nm scale structure formation process using polymer bilayers [34].

In this work, we expand our previous work with paper supported latex films [35–37] and show the fabrication of hierarchically structured self-supported latex films with high-level transmittance of visible light. In addition, the use of the self-supported films as potential substrates for transparent electronics is demonstrated. The films were prepared by a peel-off process from different surfaces. Atomic Force Microscopy (AFM) calibration grids with accurately determined dimensions, glass slides and a more mass-scale compatible roll-to-roll fabricated curtain coated paper substrate were used as templates. The peeled latex films include a characteristic primary structure of a two-component latex coating material [35–37] and an additional secondary structural feature determined by the surface morphology of the used template substrate. Evaporated gold electrodes were fabricated on the self-supported latex films to enable electrical functions.

2. Materials and methods

2.1. Template substrates

Four different AFM calibration grids (models: TGG1, TGZ2, TGT1 and TGX1, NT-MDT, Russia), microscope glass slides (Menzel-Gläser, Thermo scientific, Germany), Polydimethylsiloxane (PDMS) [36] (Wacker, Germany) and a multilayer curtain coated paper [38] were used as model template substrates from which the latex coatings were peeled off.

2.2. Coating material

The two component coating latex blend with a weight ratio of 1:1 was prepared by mixing aqueous dispersions of polystyrene particles (HPY83; average particle size = 140 nm, T_g = 105 °C, wt.% = 48.0, DOW) and styrene butadiene acrylonitrile copolymer (DL920; average particle size = 140 nm, T_g = 8–10 °C, wt.% = 49.5–50.5, DOW).

2.3. Latex film fabrication

Different film fabrication methods were used, for example rod coating was applied on the paper and glass substrates and drop-casting was used on the calibration grids. After the films appeared dry they were sintered using an IR-lamp (IRT systems, Hedson Technologies AB, Sweden) for 45–60 s in order to fuse the particles together. The samples were immersed in water and washed in an ultrasound bath (FinnSonic m08) for 10 s and then the latex films were peeled off from the template substrates. The fidelity of the replication technique greatly depends on the properties of the template materials. For example peeling off of a thin latex film from a more porous precipitated calcium carbonate (PCC) coated paper substrate was not feasible. On the other hand, polydimethylsiloxane (PDMS) polymers with low surface energy and low adhesive force, durability and flexibility can be considered as great materials for template fabrication [39]. Thickness of the latex film also has an influence, i.e., thicker latex films are generally easier to peel off from the templates, but their drying time is longer and transparency lower. In addition, the shape, size, and depth of features of a template also somewhat influence the fidelity of the peeling process. For example the latex film was easier to peel off from the TGZ2 grid compared to TGX1 grid with chessboard-like array of square pillars with sharp undercut edges [40]. With a low coating amount the IR-treatment reached throughout the whole coating thickness creating the characteristic nanopatterned structure within the higher hierarchical pattern. In case of thicker coating amounts, an additional IR-treatment could be performed after the peeling process to obtain a typical heat-treated surface structure also on the bottom side.

2.4. Fabrication and functionalization of ultrathin gold film electrodes

The ultrathin gold films (UTGF) with nominal thicknesses of 10 and 20 nm were fabricated on the self-supported latex films using physical vapor deposition (PVD) with resistive heating. The film was attached on the shadow mask that was used for patterning. The gap between the evaporated gold electrodes was ~190 μm and the width of the electrodes 5 mm. The dimensions of the contacts were 1 mm × 12 mm. The evaporation was done under high vacuum 2.5 × 10^{-6} mbar during two separate runs using a heated aluminium-coated tungsten basket. The evaporation rate was set to 1 Å/s. A deposition monitor (XTM/2, Inficon) was used for gravimetric determination of the amount of evaporated gold on the film surface. The topographical characterization and electrochemical application of the UTGF electrodes on paper-supported latex coatings have been previously described elsewhere [41]. Briefly, a nominal thickness of 10 nm yielded UTGF electrodes with semiconducting (n-type) characteristics and polycrystalline grain structure with grain thickness of about 2 nm. Respectively, a nominal thickness of 20 nm yielded conductive UTGF electrodes (resistivity: 2.6 × 10^{-6} Ωcm) with grain thickness of about 6 nm. Similar characteristics were observed also for the UTGF electrodes on the self-supported latex film.

Functionalization of the UTGF electrodes with a self-assembled monolayers (SAMs) were carried out with a hydrophobic 1-octadecanethiol (ODT, Fluka Chemika) in ethanol and with a hydrophilic $HS(CH_2)_{11}OH$ (MuOH, Sigma-Aldrich) in water. Before thiolation, the evaporated UTGF electrodes were cleaned with plasma (air) flow (PDC-326, Harrick) for 2 min and rinsed or immersed in absolute ethanol. The plasma treated self-supported latex films with UTGFs were placed on a microscope glass support and sealed with a silicone ring in a custom-built liquid flow cell (FIAlab Instruments, Inc., USA) (Appendix, A1) and exposed to the thiol solution (ODT: 500 μL, 5 mM/MuOH: 500 μL, 446 μM) for 24 h at room temperature under a cap. After the SAM formation, the ODT-functionalized electrodes were rinsed with absolute ethanol and 0.1 M KCl and the MuOH-functionalized electrodes with water and 0.1 M KCl solution. The HSA protein adsorption studies were conducted using 0.1 M KCl as the supporting electrolyte.

2.5. Characterization

Transmission UV–vis spectroscopy measurements were carried out through a black board mask with a 5 mm x 5 mm hole using a Perkin-Elmer Lambda 900 with an integrating sphere setup.

Electrical impedance spectroscopy (EIS) measurements were performed using a portable electrochemical interface and impedance analyzer (CompactStat, Ivium Technologies, The Netherlands). The experiments were carried out with a two-electrode setup for keeping the electrode construction planar and simple. An aluminum foil was placed on top of the ultrathin gold