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Sacrificial Layer and Supporting Layer Techniques for the Fabrication of Ultra-Thin Free-Standing PEDOT:PSS Nanosheets

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ABSTRACT

Aim of this work was to realize free-standing conductive nanofilms having very large surface area with typical nano-scale thickness (40-120 nm) by modifying existing approaches for nanostructured thin films assembly. We tested and optimized two different fabrication methods for the obtainment of free-standing conductive ultra-thin nanosheets based on the conductive polymer poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS). Supporting Layer and Sacrificial Layer techniques permitted the obtainment of single layer nanofilms that can be released in water and of LbL multilayer nanosheets (PEDOT:PSS/Polyelectrolytes) that can be released in acetone, respectively. Here we describe the details of both the proposed fabrication methods and compare the properties of the realized nanosheets in terms of thickness, contact angle and conductivity. Interestingly, the realized free-standing nanosheets, despite their low thickness, are very robust and compliant while maintaining their structure and functionality. Possible applications are foreseen in the field of sensing and actuation, as well as in the biomedical field, e.g. as smart conductive substrates for cell culturing and stimulation.

INTRODUCTION

Ultra-thin polymeric films have been extensively studied also in the form of free-standing nanosheets, characterized by a very large surface area (up to tens of cm^2) and by a thickness in the order of tens of nanometers [1]. Features such as biocompatibility, flexibility and the possibility to be functionalized make them attractive in the biomedical field [2]. Multilayered thin films are commonly fabricated by layer-by-layer (LbL) assembly technique [3]. While the use of LbL technique for obtaining polyelectrolyte multilayer structures [4] is particularly common, literature reports only one attempt to obtain free-standing conductive ultra thin films [5]. However, the proposed procedure is quite complex, involving many expensive, time consuming and delicate steps towards the obtainment of composite graphene/conductive polymer composite nanofilms. Only very recently a very innovative and easy method for the fabrication of conductive polymer free-standing nanofilms has been proposed by our group [6]. This technique allows to obtain conductive nanofilms that can be manipulated, folded and unfolded in water many times without suffering from cracks or from loss of conductive properties.

In this paper we describe two different fabrication methods for the obtainment of free-standing conductive ultra-thin nanosheets based on the conductive polymer poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS). [7-9]. We compare the morphological, electrical and surface properties of conductive nanofilms obtained by the two

fabrication processes based on properly modified Sacrificial and Supporting Layer techniques. The first one permits the fabrication of multilayer nanosheets including an electrostatic LbL assembly of polyelectrolytes (PAH/PSS) with a conductive layer of PEDOT:PSS. The second one allows to obtain single layer PEDOT:PSS nanofilms. Thanks to the good PEDOT:PSS biocompatibility [8,9] the developed nanofilms could be used in biomedical applications, e.g. in tissue engineering for the development of systems for cells stimulation and growth.

EXPERIMENTAL DETAILS

Multilayer nanofilm preparation (Sacrificial Layer Technique)

Cellulose acetate (CA) (weight average molecular weight M_w = 30000 Da, Aldrich) was used as sacrificial layer and was deposited by spin coating its solution in acetone (c = 30 mg/ml) at 3000 rpm for 15 s on clean silicon surface. Poly(styrene sulfonate) (c = 5 mg/ml in DI water, PSS M_w = 70 kDa, Sigma Aldrich) and poly(allylamine hydrochloride) (c = 5 mg/ml in DI water, PAH M_w = 60 kDa, Abcr) were used as anionic and cationic polymers. The spin assisted LbL (SA-LbL) deposition onto sacrificial layer followed these steps: the polyelectrolyte solutions were spin coated at 3000 rpm for 15 s; after the deposition of each polyelectrolyte layer, the substrates were rinsed twice with DI water and then dried by spinning for 15 s at 4500 rpm. The polycation/polyanion deposition steps were repeated to obtain an intermediate double layer of polyelectrolytes. PEDOT:PSS aqueous dispersion (Clevios™ PH 1000, H.C. Starck GmbH, Leverkusen, Germany) was used after filtration and spin-coated over the LbL assembled film at different speed from 1000 to 5000 rpm for 60 s. Then, samples underwent a thermal treatment (1 h; T = 170 °C). The multilayer free-standing nanofilms were finally released by dissolving the sacrificial layer, through immersion of samples in acetone. The floating nanofilms could be transferred in water.

Single layer nanofilm preparation (Supporting Layer Technique)

Single Layer free-standing PEDOT:PSS nanofilms were prepared by spin coated assisted deposition following the procedure already described by our group [6]. Briefly, a film of poly(dimethylsiloxane) (PDMS) with thickness t ≈ 800 nm on Si was used as substrate. The wettability of the PDMS surface was temporarily improved by an air plasma treatment (Harrick PDC-002 Plasma Cleaner, Harrick Plasma). PEDOT:PSS aqueous dispersion (Clevios™ PH 1000) was filtrated and spin-coated over the PDMS film at speed 1000 to 5000 rpm for 60 s. Thermal annealing (1 h; *T* = 170 °C) was provided. A poly(vinylalcohol) aqueous solution (c = 100 mg/ml in DI water; weight average molecular weight M_w = 30 kDa, Sigma-Aldrich) was then drop cast over the samples and dried overnight in order to form a supporting layer. Sample edges were cut with a razor blade and the bilayered film was carefully peeled off from the PDMS substrate with the aid of tweezers. The PEDOT:PSS free-standing nanofilm was finally released by dissolving the supporting PVA layer in DI water.

Thickness measurements

Nanofilms thickness was measured by stylus profilometer KLA Tencor P6. All measurements were performed in air, at room temperature, on films collected and dried on a

clean Si wafer after release. Nanofilms were scratched with a thin needle and the height profile was measured across the edge of the scratch permitting the estimation of the thickness *t* of the nanofilm.

Measurement of contact angle

Contact angles were measured using the Sessile Drop method [10]. Measurements were taken on a single side in the case of single layer nanofilms and on both sides for multilayer nanofilms. DI water droplets with 10 µl volume were used in the measurement, and optical images were taken by using a Hirox KH7700 digital microscope (Hirox Co Ltd., Tokyo, Japan).

Measurement of electrical properties

Sheet resistance of the nanofilms was evaluated by using a homemade four probes apparatus. Sheet resistance *Rs* of nanofilm samples was measured and the related conductivity σ has been calculated making use of formulae: $Rs = \pi/\ln 2\ (V/i)$; $\sigma = 1/\ Rs\ t$ where *t* was the nanofilm thickness as determined by profilometry.

DISCUSSION

Nanofilms obtained by the two different approaches (Figure 1) are structurally different: multilayer nanofilms are obtained through Sacrificial Layer technique and they could be more easily functionalized with nanoparticles or biomolecules thanks to the different functionalities on either surface; nanofilms prepared via Supporting Layer method are single layer PEDOT: PSS thin membranes, in which both sides are functionally equivalent.

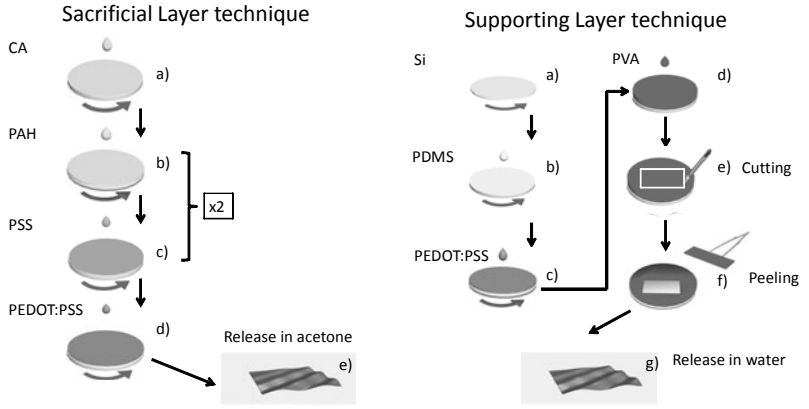

Figure 1. Schematic representation of the main steps of fabrication and release for obtaining conductive nanofilms by a Sacrificial Layer technique (left) and Supporting Layer technique (right).

In both cases, the resulting free-standing nanofilms could be easily manipulated with tweezers or pipettes, folded and unfolded multiple times without breaking. From the freely suspended state, the films could be transferred onto rigid substrates such as Si, steel, glass as well as onto compliant ones, e.g. elastomers, paper, or also plastic frames and metal meshes. All the prepared nanofilms were investigated with morphological, electrical and surface characterization.

The surface properties of free-standing conductive nanofilms obtained with the two different approaches are strikingly different as shown by contact angle characterization (Figure 2). Lower contact angles are obtained in the case of nanofilms prepared with the sacrificial layer technique (multilayer nanofilms), respect to supporting layer ones (single layer nanofilms), in the overall range of thickness. Larger differences between single layer and multilayer nanofilms are observed for thickest films in the series. Moreover, in the case of sacrificial layer technique, contact angle increases as thickness decreases, for both PEDOT and PAH/PSS side. The lower values of contact angles obtained in the case of multilayer nanofilms (sacrificial layer technique) is ascribable to the increase of surface hydrophilicity due to the inclusion of polyelectrolytes in the polymer matrix [11]. As a matter of fact, contact angle of the opposite sides of the multilayer nanofilm are similar, and this suggests that polymer chains interpenetration occurs (Figure 3).

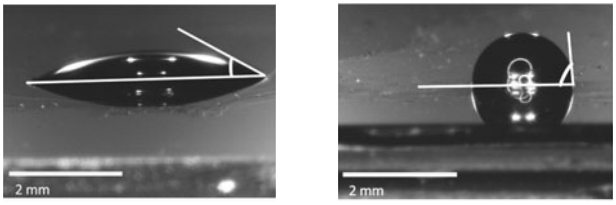

Figure 2. Comparison of contact angle measurement of: (left) multilayer nanofilm (PEDOT:PSS side) and (right) single layer nanofilm. Samples with PEDOT:PSS layer spin-coated at 2000 rpm.

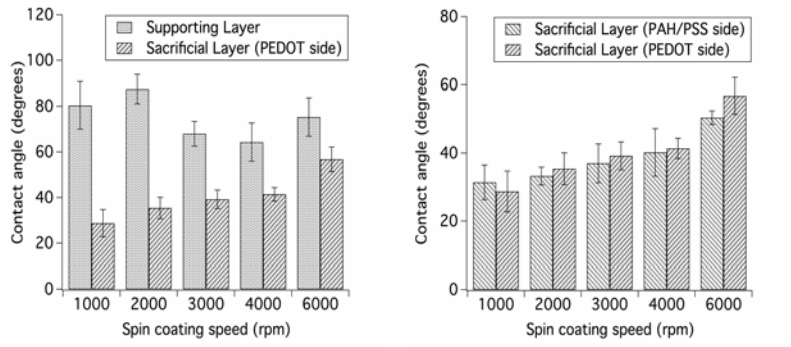

Figure 3. Comparison between contact angle of multilayer and single layer nanofilms (left); comparison of the opposite sides of the multilayer nanofilm (right).

The thickness of the nanofilms was measured by profilometer. The measure has been performed over a scratched area in perpendicular direction with respect to the scratch edge. Figure 4.a displays the estimated thickness as a function of spin-coating speed *s*, comparing the results obtained for the two types of nanofilms. As spin-coating speed is further increased over $s > 4000$ rpm, thickness is assessing to $t \approx 43$ nm as average value for nanofilms realized with supporting layer technique and $t \approx 49$ nm for those realized with sacrificial layer technique. Such behavior is probably due to the inclusion of the double layer of polyelectrolytes in nanofilms structure (s. Experimental). As already reported [6], the minimum achievable thickness is known to be related to the dimension of the PEDOT:PSS primary particles and so the thinnest films consist of a monolayer of loosely packed PEDOT:PSS primary particles.

Sheet resistance of free-standing nanofilms was measured after the release in acetone for the multilayer nanofilms and after the release in water for the single layer nanofilms. Results are shown in Figure 4.b. Nanofilms obtained with Sacrificial Layer technique show lower values of conductivity with respect to Supporting Layer ones, as an effect of the inclusion of polyelectrolytes in the polymer matrix. Measurements performed after transfer of nanofilms in water show improved conductivity due to the concurrent effects of changes in nanofilm morphology and of residual water in the structures, as already described for supporting layer nanofilms [6]. Here, we confirmed a similar behavior also in the case of multilayer nanofilms in which the transfer from acetone to water induced a moderate increase in conductivity, as shown in Figure 5. Moreover, we can anticipate that nanofilms conductivity could be improved by making use of polar solvents (e.g. dimethylsulfoxide) as we already tested in supported PEDOT:PSS thin films [12]. In the case of nanofilms obtained with supporting layer technique, the inclusion of 5% of DMSO in nanofilms could lead to a 200 times improvement of conductivity with no adverse effect on stability.

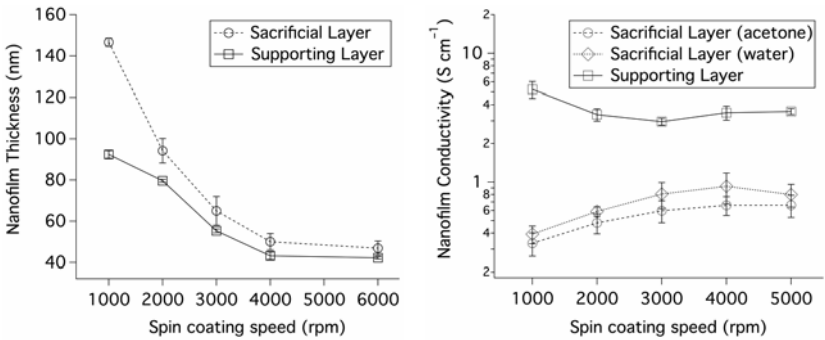

Figure 4. a) Conductive nanofilms thickness as a function of spin-coating speed: comparison between thickness of multilayer nanofilms (open circles) and thickness of single layer nanofilms (open squares). **b)** Comparison between conductivity of single layer nanofilms after release in water (open squares), multilayer nanofilms after release in acetone (open circles) and multilayer nanofilms after release in water (open rumbles).

CONCLUSIONS

Large area free-standing conductive ultra-thin films based on PEDOT:PSS have been realized. In this paper we compared two different fabrication methods to obtain free-standing conductive nanosheets based on Supporting Layer and Sacrificial Layer techniques. In the first case we obtained a single layer nanofilm formed only by PEDOT:PSS while in the second case we obtained a multilayer nanofilm where only one side is composed by PEDOT:PSS. The proposed fabrication processes provide a fast and reliable way to produce large area conductive nanofilms that can be released in water and collected onto several different substrates, while retaining their functional properties. Thickness and surface properties (contact angle) of the obtained nanofilms have been investigated and put in relation with their conductive properties clearly evidencing differences in structure and function for the two nanofilms types. In conclusion, both methods allow to obtain conductive nanofilms that, despite their low thickness, are very robust and compliant while maintaining their structure and functionality also after manipulation with pipettes and folding/unfolding in fluids. Furthermore different applications can be foreseen for the obtained nanofilms such as in tissue engineering and in the development of systems for cells stimulation and growth. With the aim to realize similar applications our group is recently optimizing several techniques allowing for micropatterning of nanofilms surface.

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