Electronic Supplementary Information (ESI) for Soft Matter

Supplementary Information

Ultra-thin conductive free-standing PEDOT/PSS nanofilms

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Free-standing Nanofilms Fabrication Process Details

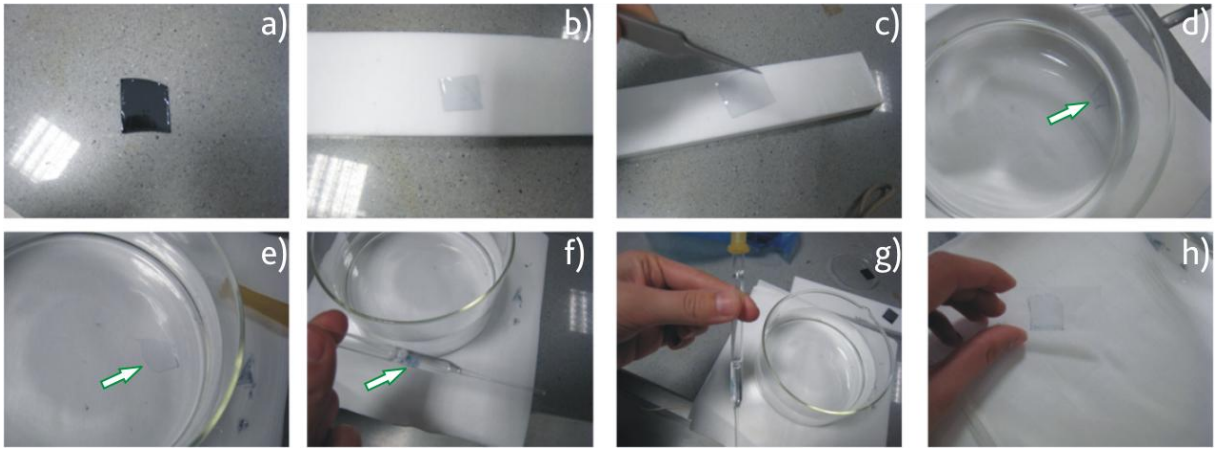

Figure S1. Pictures sequence showing the release in water, manipulation and recovery of a PEDOT/PSS free-standing nanofilm prepared with the proposed Supporting Layer technique. a) pristine bilayered film (PVA supporting layer + PEDOT/PSS nanofilm) onto a Si+PDMS substrate before the release; b,c) bilayered film peeled off from the substrate and manipulated with tweezers; d) release of the PEDOT/PSS nanofilm by dissolving the PVA supporting layer in DI water; e) free standing PEDOT/PSS nanofilm floating in DI water; f,g) aspiration and transfer of a free-standing nanofilm with the aid of a pipette; h) nanofilm collected onto a glass slide.

Comparison between different PEDOT/PSS formulations

The Clevios™ PH1000 PEDOT/PSS formulation employed in the present study still lacks in literature of a precise and comprehensive characterization due to its recent introduction. For this reason we used, in addition to the reported PH1000 grade, a different formulation of PEDOT/PSS, namely Clevios™ P AG formulation, to compare the results with those reported in literature for similar materials deposited and anchored to substrates or to free-standing thicker films. The two different formulations of PEDOT/PSS were expected to display different electrical properties. Both P AG and PH1000 materials contain a PEDOT/PSS ratio of 1:2.5 by weight, while slightly differing for the solid content and viscosity of the waterborne dispersion, i.e. viscosity at 20°C and 100 s^{-1} is v = 50-90 mPa s for P AG and v = 15-50 mPa s for PH1000 as reported by the supplier (H.C. Starck, Leverkusen, Germany).

In particular we concentrated the study on morphology and conductivity properties, thus focusing the comparison on silicon and PDMS supported films for the two formulations (respectively: PH1000@Si and PAG@Si on silicon substrate; PH1000@PDMS and PAG@PDMS on PDMS substrate).

As reported in the paper, thickness estimation has been performed by AFM measurement (see Figure S2). The nanofilms fabricated with the two grades of conducting polymer showed similar values of thickness when prepared at the same spin-coating speed (Figure S3). A notable deviation is only seen for the thickest films of the series, i.e. at spin-coating speed s = 1000 rpm thickness of P AG and PH1000 nanofilms is around 120 nm and 93 nm, respectively, probably due to the slightly different viscosity of the two products.

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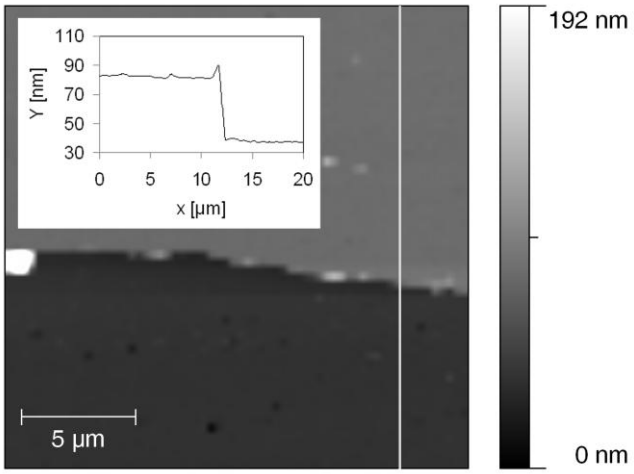

Figure S2. 20 µm x 20 µm AFM topographic image near the edge of a PEDOT/PSS nanofilm on Si (PH1000, spin coating speed 5000 rpm), used for thickness estimation. Inset shows the height profile along the highlighted line.

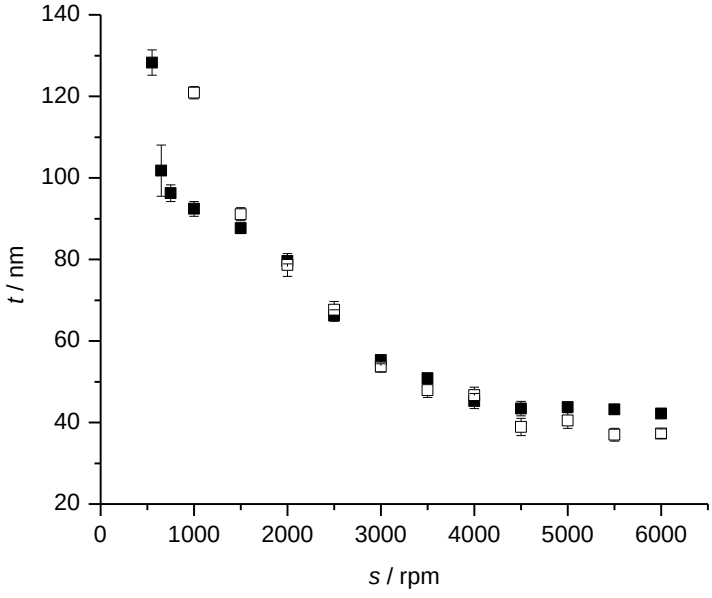

Figure S3. PEDOT/PSS nanosheet thickness *t* as a function of spin-coating speed *s*. Comparison between two different material formulations, PAG (open squares) and PH1000 (solid squares) as measured by AFM.

Concerning the morphology, some differences between the two formulations have been highlighted by analysis of AFM images of samples on silicon substrate (Figure S4). In particular for PAG@Si samples (Figure S4.b) the occurrence of some protrusions of agglomerates was pointed out, surrounded by an almost uniform and flat surface very similar to that observed for PH1000@Si nanofilms, (Figure S4.a). These "clusters", ascribable to aggregates of dried gel particles already observed in previous works,[17] were emerging from the surface for few tens of nanometers, thus increasing the average roughness of the samples, as calculated on the overall scanned surface, R_a = 2.34±0.67 nm,. The size of these clusters seems to be independent on the spin-coating speed; in the whole series of samples the average area of the clusters was measured as 0.045±0.009 μm^2.

Making use of software analysis, it was possible to identify the clusters in the AFM topographical images and mark them with a mask using a simple height threshold algorithm. The average roughness of the samples was then calculated excluding the masked area. Considering only the smooth areas of the surface, the average roughness was measured as R_a = 1.25±0.29 nm, independently on the spin-coating speed, a value that can be considered identical to PH1000 one (that was 1.02±0.20 nm).

In conclusion, regarding surface topography, PAG@Si samples differ from PH1000@Si samples only for the presence of clusters that make the former surface inhomogeneous; indeed, neglecting the contribution of localized clusters, the different materials showed a very similar topography and comparable values of surface roughness.

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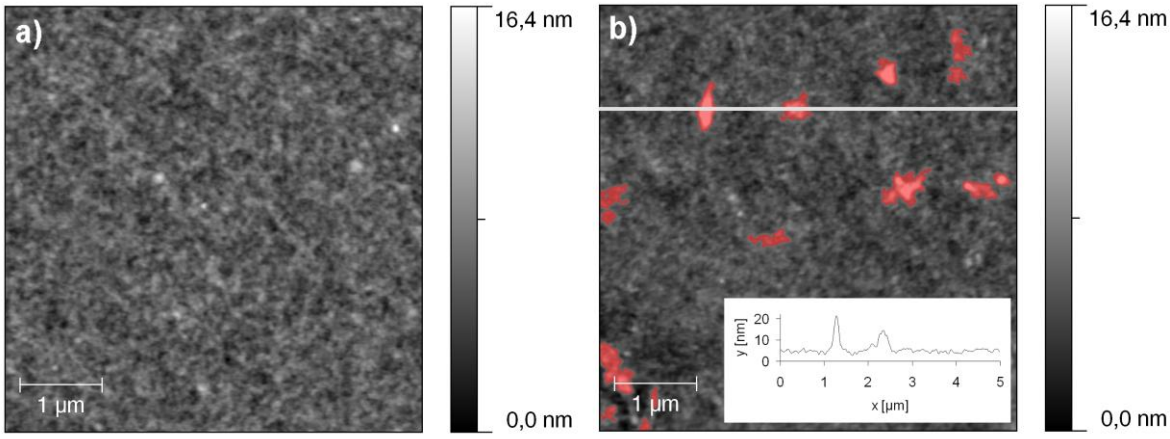

Figure S4. 5 µm x 5 µm AFM topographic images of PEDOT/PSS nanofilms on Si. a) PH1000 sample with thickness 78.6 nm (spin coated at 2000 rpm); b) PAG sample with thickness 79.6 nm (spin coated at 2000 rpm). The inset shows a line section while highlighted red areas (selected with a mask using a height threshold algorithm) identify aggregates emerging from the surface.

Concerning the conductivity of the two different PEDOT/PSS formulations, the expected difference has been verified on samples supported on PDMS before the release of the free standing nanofilms (PH1000@PDMS and PAG@PDMS samples). The typical conductivities for the thinnest films in the series varying from $\sigma \approx 0.70$ S cm^{-1} for P AG grade to $\sigma \approx 0.90$ S cm^{-1} of the PH1000 (Figure S5). The peculiar trend of conductivity versus thickness described in the paper for PH1000 and rationalized in terms of a percolation mechanism, has been shown to operate similarly for P AG formulation, with a minimum of conductivity found for thickness $t \approx 80$ nm. Viceversa, despite the increase of σ seen for $t >$ 80 nm, conductivity of thickest nanofilms in the studied range does not surpass the values found for low thickness; this could be maybe due to different dimensions of particles in the two formulations and to different arrangement of particles, as AFM measurements seem to suggest.

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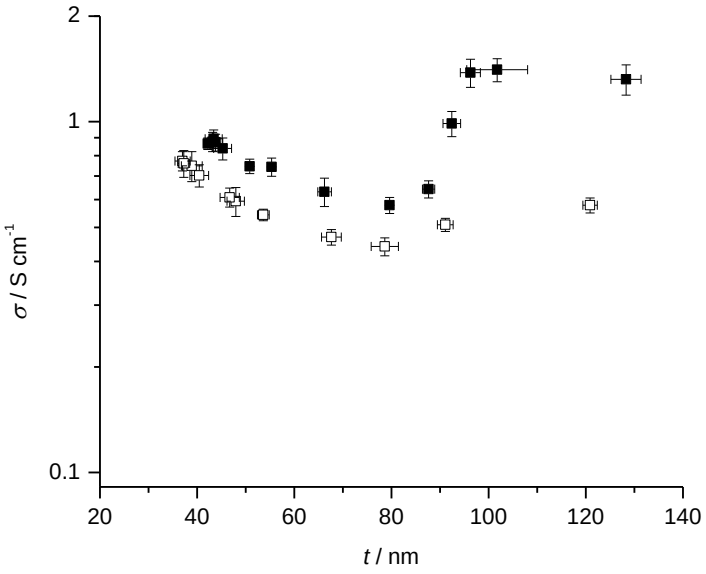

Figure S5. Comparison of the conductivity σ of two formulations of PEDOT/PSS nanofilms supported onto PDMS prior to release as a function of their thickness t: PAG@PDMS (open squares), PH1000@PDMS (solid squares).

Nanofilms surface topography and thickness change after release in water

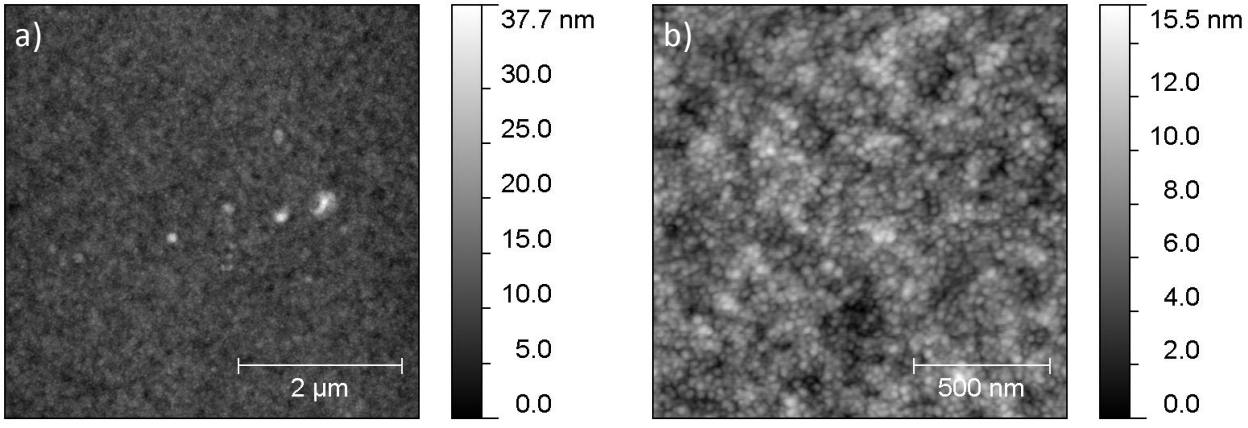

Figure S6. 5 µm x 5 µm (left) and 1.5 µm x 1.5 µm (right) AFM topographic images of PEDOT/PSS PH1000 nanofilm (prepared at spin coating speed 2000 rpm) collected on Si after its release in water. Surface topography made up of individual grains is evidenced.

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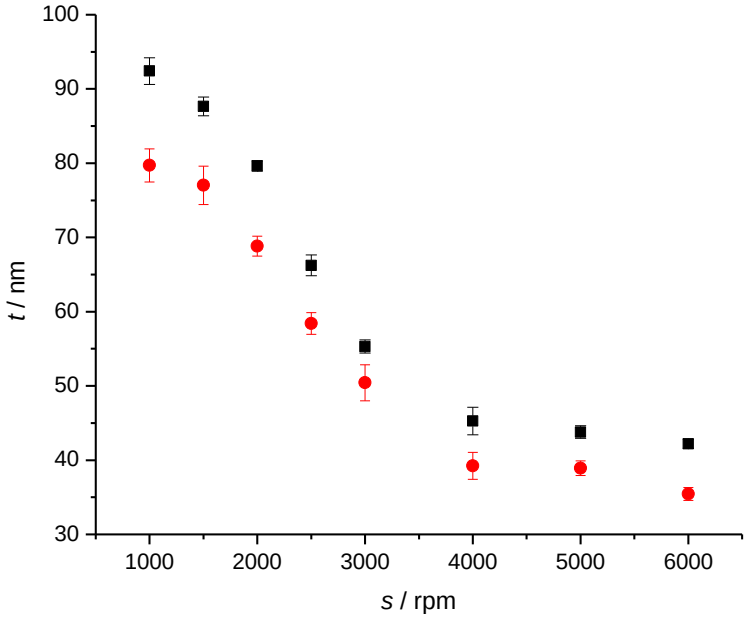

Figure S7. PEDOT/PSS PH1000 nanofilm thickness *t* as a function of spin-coating speed *s*. Comparison of thickness before (black squares) and after release in water (red circles) as measured by AFM.