

## Supporting Information

# Fabrication and nanoscale properties of PEDOT:PSS conducting polymer nanospheres

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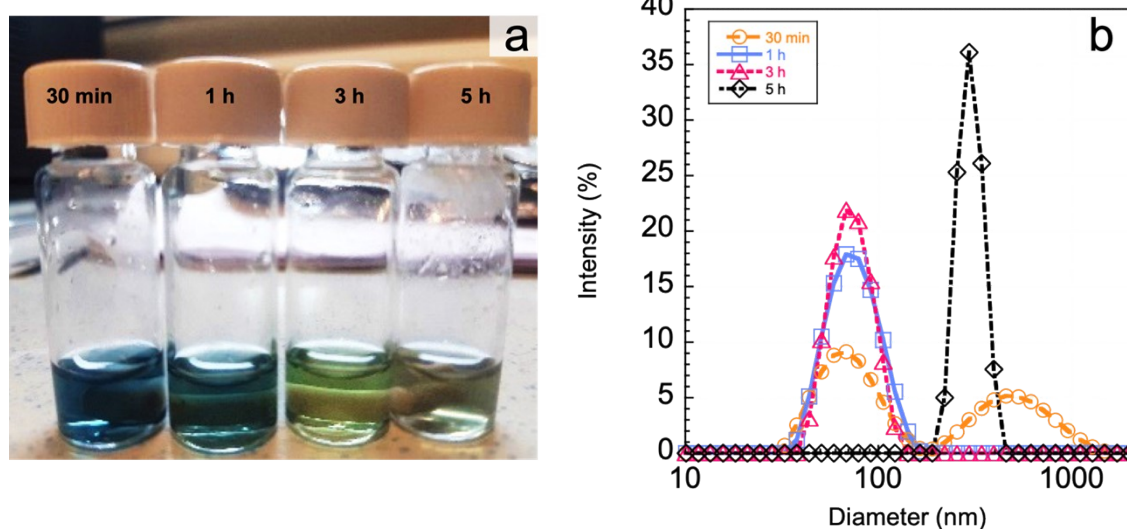
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### 1. PEDOT:PSS solubility in ethylene glycol



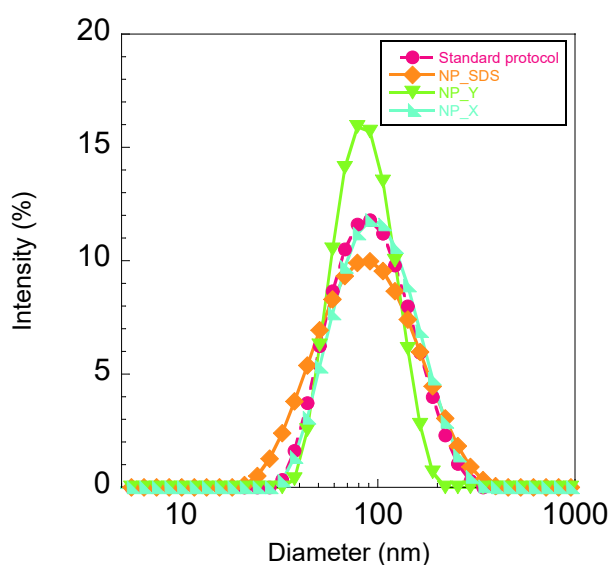
**Figure S1.** (a) Photographs of PEDOT:PSS solutions in EG, after 30 min, 1 hour, 3 hours, and 5 hours. (b) DLS measurements of the PEDOT:PSS solutions as a function of time.

The results presented in Figure S1 reveal that aggregation occurs for dissolution times longer than 3 hours under stirring at 130° C. In the same conditions, as alternatives to EG, we also tested the high boiling point solvents DMSO and DMF to dissolve PEDOT:PSS, but no good dispersion was observed.

## 2. Other reprecipitation protocols for PEDOT:PSS nanospheres fabrication

The preparation method presented in the Main Manuscript, was found to be the optimal case for obtaining monodisperse PEDOT:PSS nanospheres, as detailed in the following lines. Increasing the concentration of PEDOT:PSS in EG to, and above, 5 mg/mL resulted in an insoluble mixture. This fact hindered the possibility of preparing potentially bigger features, as previously reported for other polymers using this method [1]. In order to tune the size of the PEDOT:PSS nanospheres, we tested other preparation protocols as a variant of the selected method. In a first case, we followed the same process presented in the main manuscript, but reduced the volume of non-solvent ( $H_2O$ ) to 1 mL (we will refer to this sample as  $NP^y$ ). In a second approach, we changed the non-solvent to a solution of sodium dodecyl sulfate (SDS) (100 mg/mL) in water, with an unchanged solvent/non-solvent ratio (1 to 10 v/v) during the reprecipitation step (we will refer to this sample as  $NP^{SDS}$ ). Finally, in a third scenario, instead of the reprecipitation, we followed a dialysis nanoprecipitation process of the PEDOT:PSS/EG solution into water (we will refer to this sample as  $NP^x$ ). This last process was implemented following the same parameters reported for other polymeric systems [2,3].

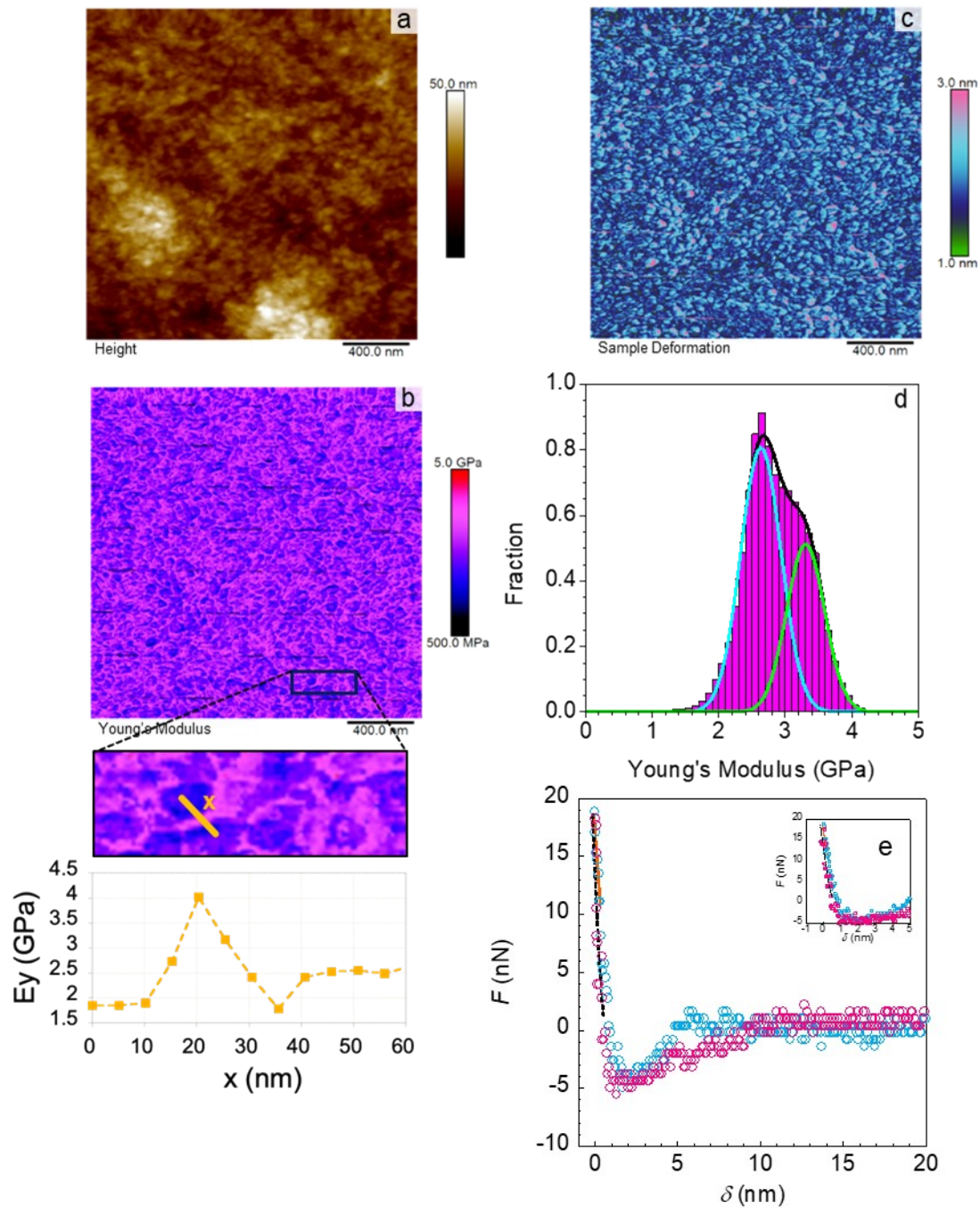
To evaluate the obtained nanospheres, Figure S2 shows DLS measurements. For all cases, these experiments were subjected to the same purification process as the one reported in the Main Manuscript. The obtained results showed no dramatic changes in the mean diameter of the obtained nanospheres, as observed from the maxima of the peaks. In particular, for a reduced volume of non-solvent,  $NP^y$  case, no increase of the diameter was observed (90 nm), while using SDS,  $NP^{SDS}$  case, it decreased slightly (80 nm). Changing the preparation method,  $NP^x$  case, we observed a diameter comparable to the sample prepared by the standard protocol (90 nm). Although all the peaks' relative widths did not show particularly strong differences, considering the four cases,  $NP^y$  presented a narrower size distribution while the  $NP^{SDS}$  one was the broadest.



**Figure S2.** DLS measurements of the PEDOT:PSS nanospheres for different preparation methods. Sample concentration  $\sim 0.1$  mg/mL.

### 3. Nanomechanical properties of PEDOT:PSS thin film

Figure S3 presents the nanomechanical results for PEDOT:PSS thin film deposited on ITO, using the commercial product. In the  $2 \times 2 \mu\text{m}^2$  topography image (Figure S3a) we observed that spin casting resulted in a continuous thin film with a characteristic thickness of  $\sim 430$  nm, as determined by AFM. This sample, showed the characteristic structure of PEDOT:PSS, comprised by stacking of small grains with a diameter of about 50 nm, leading to a surface roughness of 3.5 nm.

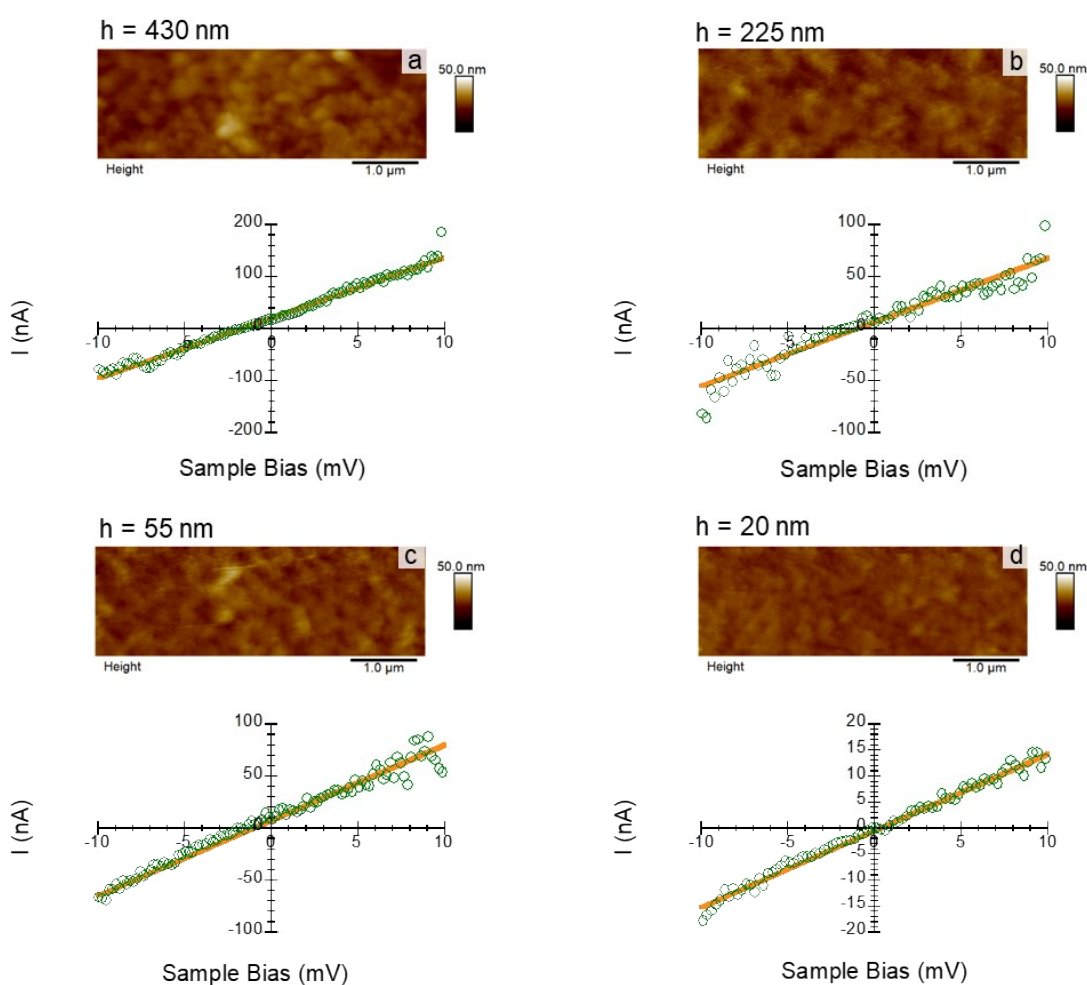


**Figure S3.** Nanomechanical results for pristine PEDOT:PSS. (a) Topography, (b) Young's modulus (with relative zoom-in and cross-section), and (c) deformation. (d) Distribution of Young's modulus. (e) Force spectroscopy measurement results.

The corresponding PF-QNM maps, Young's modulus and sample deformation, showed a slight mechanical contrast, as determined by the results of Figures S3(b,c). In both cases, we observed that the grains were characterized by lower Young's moduli and higher deformations, compared to the surrounding phase. As an example, Figure S3b shows a profile of the Young's modulus map, where the quantitative differences between different phases can be detailed. In order to quantify the mechanical response associated with this contrast, Figure 3d presents a histogram of Young's modulus values, calculated using the map presented in Figure 3b. The histogram showed a bimodal distribution, as fitted by a sum of two Gaussian functions (black line in Figure S3d). We can ascribe these functions to the representation of two distinct modulus populations (light blue and green curves in Figure S3d). The mean values ( $\mu$ ) for these populations were  $\mu_1 = 2.6$  GPa and  $\mu_2 = 3.3$  GPa, respectively, with comparable standard deviations of  $\sim 0.4$ . These populations can be related to local mechanical differences between the PEDOT:PSS rich grains and a PSS interconnecting layer. These findings were in line with previous reports, where it was shown that the PSS rich phase in PEDOT:PSS was characterized by higher modulus than the granules constituting the material [4]. Finally, Figure S3e shows a representative force spectroscopy measurement on this thin film. The obtained analysis are presented in the main manuscript.

#### 4. Nanoelectrical properties of commercial PEDOT:PSS thin films

Figure S4 presents the nanoelectrical results for PEDOT:PSS thin films of different thicknesses. For each case, we present the thin film topography and an I-V curve captured at the center of the topography image. The PEDOT:PSS thin films were prepared by spin coating (3000 rpm, 120 s) the commercial dispersion onto Indium Tin Oxide (ITO) substrates (Ossila, product #S111). The ITO substrates were cleaned by ultrasonication in acetone for 15 min, at room temperature, prior use. All the deposited samples were left in a vacuum chamber (pressure  $< 10^{-4}$  bar) for at least 24 h before measurements. PEDOT:PSS thin films of different thicknesses were obtained by diluting the commercial product using distilled water (from  $\sim 30$  mg/mL to  $\sim 5$  mg/mL).



**Figure S4.** Nanoelectrical analysis on PEDOT:PSS thin films at different thickness, for each case are presented the topography images with a representative IV curve acquired on a random spot of the surface (on the bottom of the corresponding sample image).

## References

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