Supporting information

Highly Resolved Nanostructured PEDOT on Large Area by Nanosphere Lithography and Electrodeposition

*Van Quynh Nguyen, Delphine Schaming, Pascal Martin and Jean-Christophe Lacroix**

Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France.

lacroix@univ-paris-diderot.fr

Theoretical pore depth according to the deposition charge

A triangular paving of the electrode can be drawn in order to simplify the development of the formula. Indeed, if we consider an electrode of surface *S* covered with nanospheres of radius *R*, we can divide this surface in *N* triangles defined by the centre of three nanospheres as represented Figure SI1a.

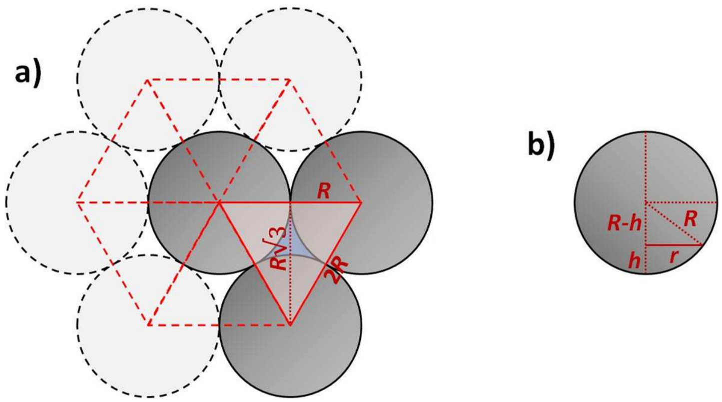

Figure S1 a) Top view of a nanosphere (radius *R*) monolayer, with the triangular paving. **b)** Side view of a nanosphere, with a section of radius *r* at a height *h*.

The area of one triangle is:

$$A_{\mathrm{t}} = \sqrt{3}R^2$$

Consequently, the surface of the electrode can be expressed as:

$$S = N\sqrt{3}R^2$$

At a height *h*, radius of a nanosphere equals to (Figure SI1b):

$$r = \sqrt{2Rh - h^2}$$

As a consequence, area occupied with portions of nanospheres inside one triangle at a height *h* is:

$$A_{\mathrm{occ}} = \frac{\pi}{2}(2Rh - h^2)$$

Then, section of a cavity between nanospheres at a height *h* is:

$$A_{\mathrm{cavity}} = \sqrt{3}R^2 - \pi Rh + \frac{\pi}{2}h^2$$

Integration of A_{cavity} between $h = 0$ and $h = e$, with *e* the pore depth, leads to the volume of a cavity between nanospheres:

$$V_{\mathrm{cavity}} = \int_{h=0}^{e} A_{\mathrm{cavity}} dh = \sqrt{3}R^2 e - \frac{\pi}{2}Re^2 + \frac{\pi}{6}e^3$$

Consequently, for an electrode of surface *S*, free volume between nanospheres at a height *e* is given by the formula:

$$V_{\mathrm{free}} = NV_{\mathrm{cavity}} = \frac{S}{\sqrt{3}R^2}\left(\sqrt{3}R^2 e - \frac{\pi}{2} R e^2 + \frac{\pi}{6} e^3\right)$$

The free volume between nanospheres on electrode can also be related to the deposited charge Q as:

$$V_{\mathrm{free}} = \frac{MQ}{2.2F\rho}$$

with F the Faraday constant, ρ the PEDOT density and M its molar mass ($M = M_{\mathrm{EDOT}} + M_{\mathrm{dodecylsulfate}}$).

It results the relation between the deposition charge Q and the pore depth e:

$$\frac{Q}{S} = \frac{2.2F\rho e}{M_{EDOT} + 0.2M_{dodecylsulfate}}\left(1 - \frac{\pi}{2\sqrt{3}}\frac{e}{R} + \frac{\pi}{6\sqrt{3}}\frac{e^2}{R^2}\right)$$

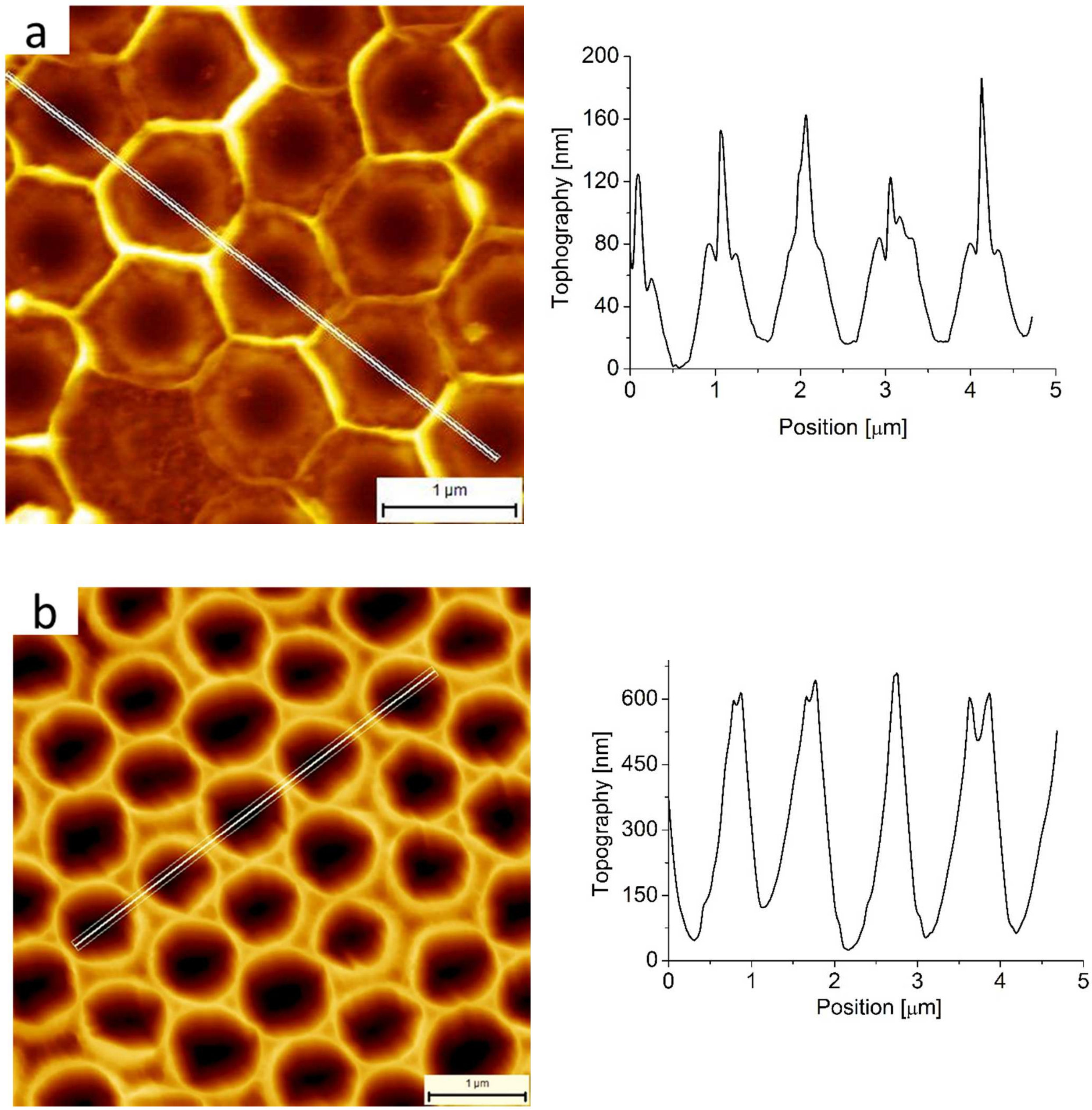

Figure S2: (a) AFM characterization and topographic profile of two PEDOT nanostructures generated using deposition charge of 16 and 40 mC cm^{-2} in 0.02 M EDOT, 0.1 M SDS and 0.1 M $LiClO_4$ aqueous solution. (b) Corresponding average pore deepness of 150 and 550 nm respectively.

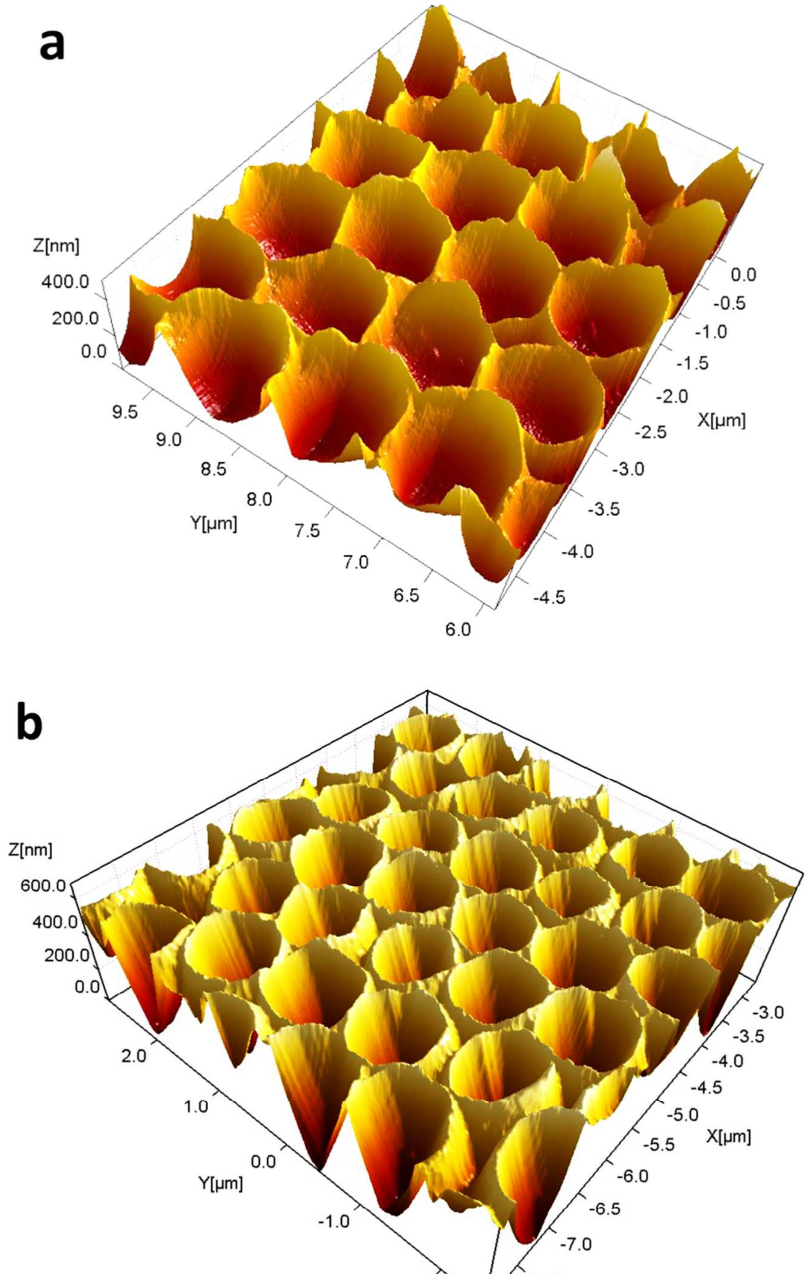

Figure S3: 3D images of a PEDOT nanostructure with (a) 380nm and (b) 550 nm pores depth generated in 0.02 M EDOT, 0.1 M SDS and 0.1 M $LiClO_4$ aqueous solution.

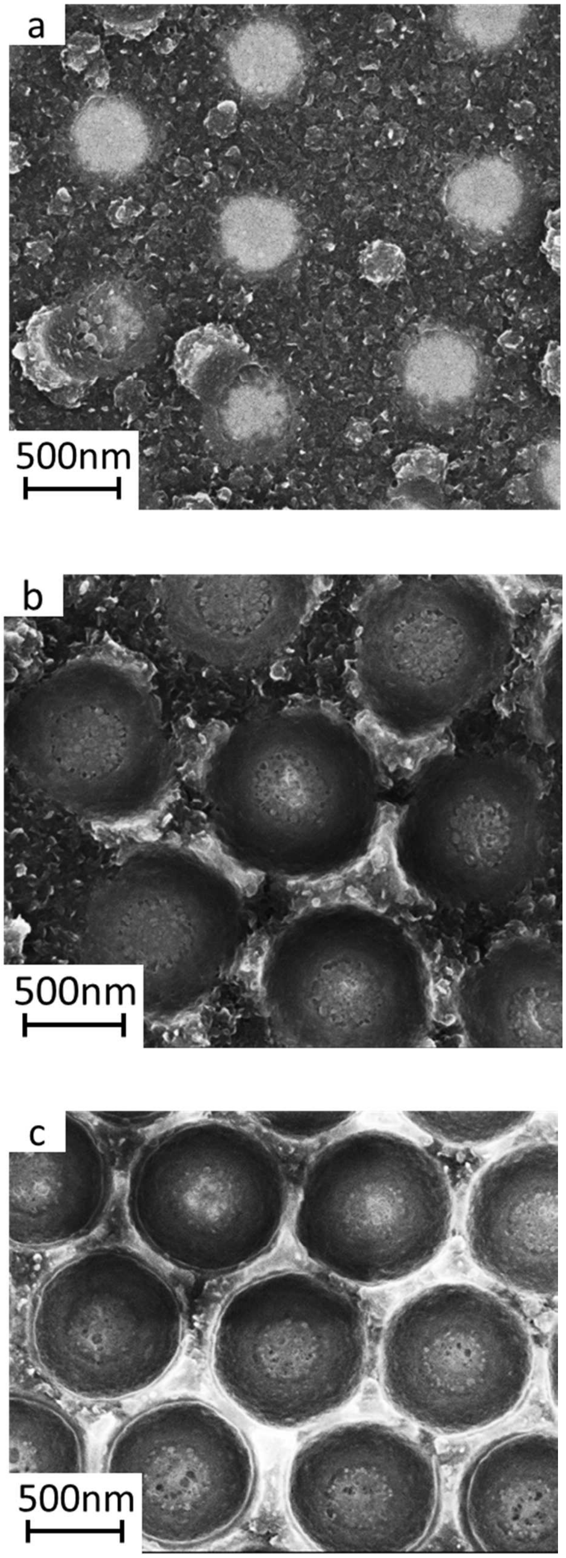

Figure S4: SEM image of a PEDOT nanostructure generated in LiClO4 0.1M, EDOT 0.02M, water solution without SDS. Charge density used during deposition is (a) 12 $mC.cm^{-2}$, (b) 22 $mC.cm^{-2}$ and (c) 40 $mC.cm^{-2}$ respectively

Sample number		1	2	3	4	5	6	Bulk PEDOT
Pore Depth (nm)		65	200	290	350	430	520	200
Contact angles (°)	Min	84.4	77.6	114.4	122	124.1	125.7	61.3
	Max	87.8	92.15	117.1	123.15	126.8	129.6	63.8
	Average	**86**	**85**	**116**	**123**	**125**	**128**	**62.5**

Table S1: Contact angle measured on nanostructured PEDOT films of various thicknesses and of bulk PEDOT all samples are prepared in 0.02 M EDOT, 0.1 M SDS and 0.1 M $LiClO_4$ aqueous solution