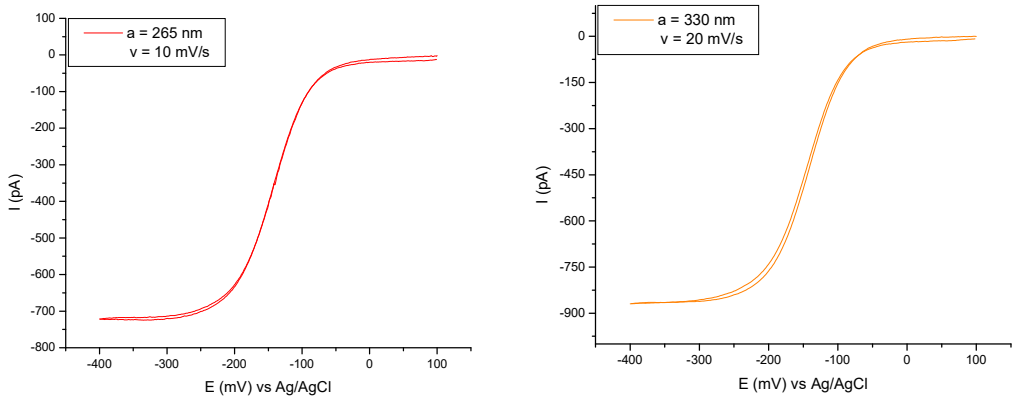

Fig. S1- Steady-state voltammograms recorded at the indicated scan rates at Pt nanoelectrodes of different radii (as indicated) in an aqueous solution containing 10 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl as supporting electrolyte.

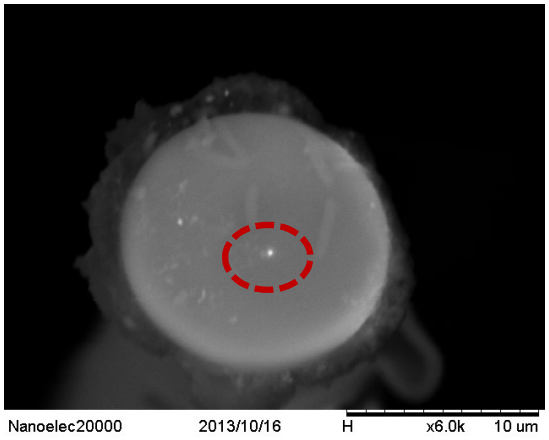

Fig. S2 - SEM image of a Pt nonoelectrode sealed in a quartz capillary.

Section S1

Assuming cylindrical geometry of the Pt wire sealed in quartz, the length (l) of the portion at which the H-UPD takes place can be obtained by the following relationships:

$$A_R = \pi a^2 + 2\pi a l \quad (1)$$

$$A_G = \pi a^2 \quad (2)$$

The roughness factor of the electrode is given by:

$$RF = \frac{A_R}{A_G} \quad (3)$$

The combination of equations (1) – (3) provides

$$RF = \frac{\pi a^2 + 2\pi a l}{\pi a^2} \quad (4)$$

and after simplification:

$$RF = 1 + 2l/a \quad (5)$$

From equation (5) one obtains:

$$l = a(RF - 1)/2 \quad (6)$$

where A_R and A_G are the real and the geometric surface areas of the active Pt involved in the measurements; *RF* is the roughness factor; *a* is the radius of the disk electrode.