**Supporting Information**

# Improving the photoelectrochemical response of $TiO_2$ nanotubes upon decoration with quantum-sized anatase nanowires

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## 1. Effect of the ultrasonic bath treatment

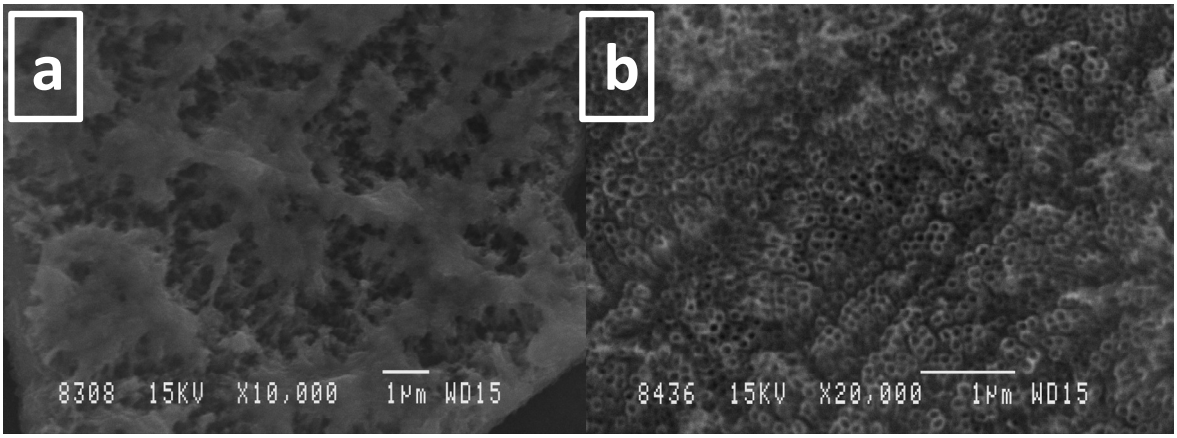


**Figure S1.** SEM images (top view) of $TiO_2$ NTs (anodization time 5 h) before (a) and after (b) ultrasonic cleaning in ethanol.

## 2. Dependence of the NT length on the anodization time and on the charge of the accumulation region

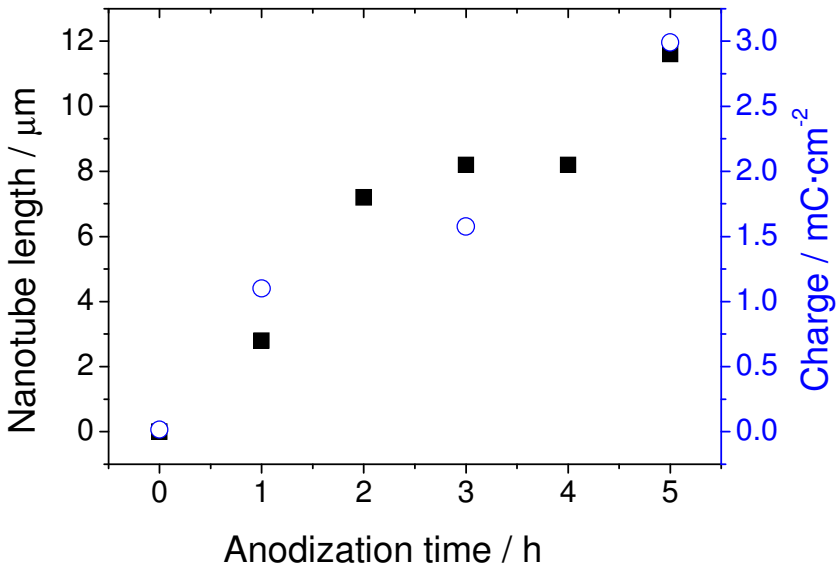


**Figure S2.** Dependence of the NT length and the charge of the accumulation region on the anodization time.

## 3. TEM images of $TiO_2$ NTs decorated with anatase NWs

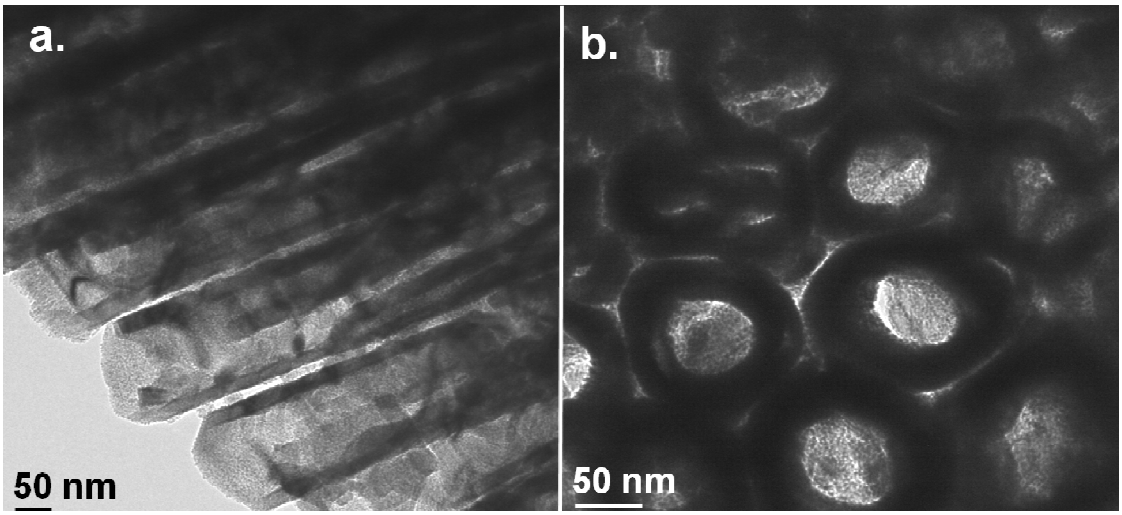


**Figure S3.** TEM image showing an array of $TiO_2$ NTs filled with anatase NWs: side (a.) and top view (b.).

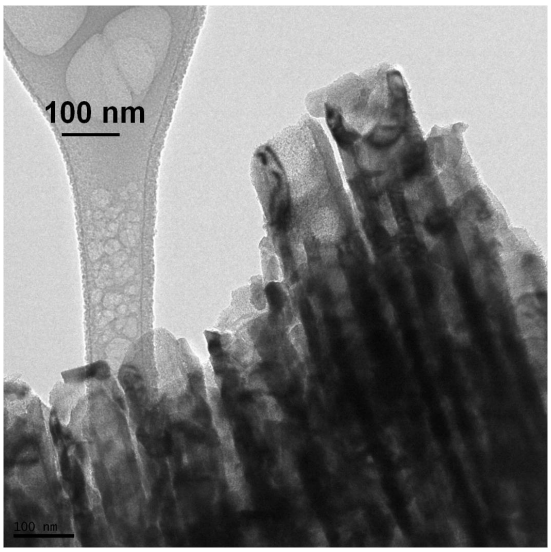


**Figure S4.** TEM image showing an array of $TiO_2$ NTs filled with anatase NWs

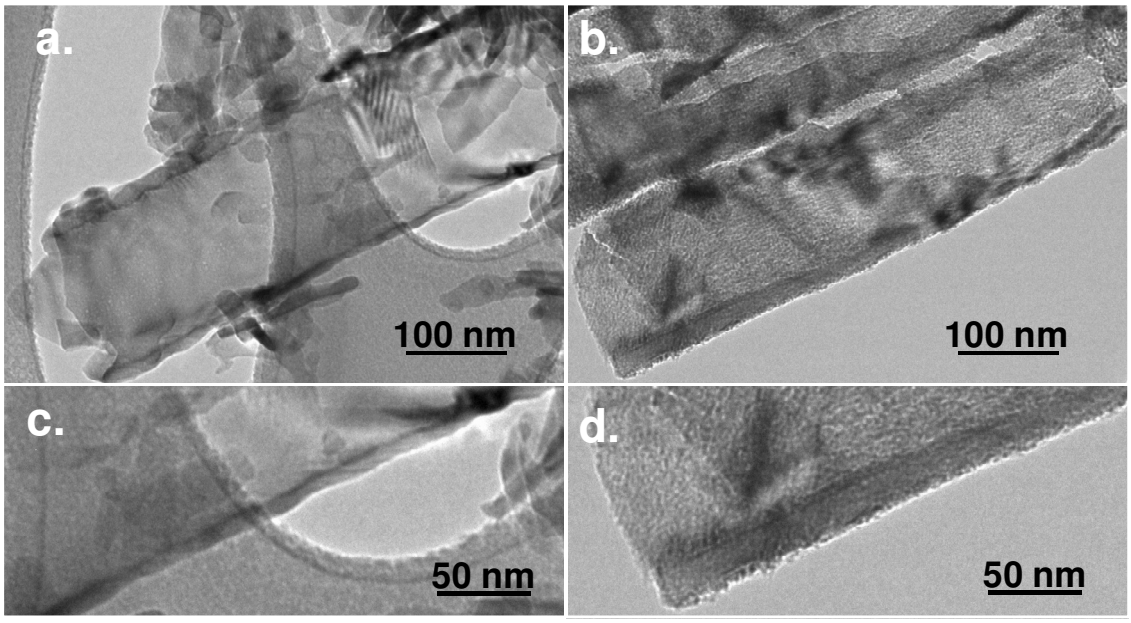


**Figure S5.** TEM image of a bare $TiO_2$ NT (a.,c.) with smooth walls and the corresponding image after decoration with anatase NWs (b.,d.). As observed an apparent increase in the wall thickness takes place, together with an enhancement of the surface rugosity.

## 4. Discussion about the electroactivity of the NWs inside the NTs

We can estimate the length of the NWs that would be necessary to explain the electrochemical results if exclusively the NWs anchored on the NT walls are electroactive. Assuming an hexagonal compact structure for the NW arrangement and considering the NW diameter (2 nm) and the multiplication factor of the interfacial area after 45 minutes (about 11), the NWs should be as long as 40 nm to induce such an enhancement of the interfacial area. As the inner diameter of the NTs is 100 nm, this is a good indication that the deposit inside the NTs is electroactive.

On the other hand, we have measured, the charge of the accumulation region for a NW thin film of 400 nm thickness deposited on FTO under the same conditions as in Figure 7. A charge as large as 1.99 $mC \cdot cm^{-2}$, i.e. 49.7 $C \cdot cm^{-3}$ is obtained. We have measured the charge of the accumulation region for the NTs ($Q_{NT}$) and the NTs modified with NWs ($Q_{NT+NW}$) within the same potential range (0.8 to -0.6 V). The charge ascribed to electron accumulation in the NWs ($Q_{NW}$) can be calculated as $Q_{NW} = Q_{NT+NW}-Q_{NT}$. Considering the charge per unit volume obtained for the thin film (49.7 $C \cdot cm^{-3}$) we estimate the volume occupied by the NWs within the NTs ($V_Q$). This volume can be compared with the volume inside the NTs calculated from the array morphology ($V_{Geo}$).We have assumed that the NT (inner and outer diameter of 100 and 130 nm, respectively) are arranged with an hexagonal compact structure. They have different lengths according with the anodization time.

| NT length / μm | $Q_{NT+NW}$ / mC·cm$^{-2}$ | $Q_{NT}$ / mA·cm$^{-2}$ | $Q_{NW}$ / mA·cm$^{-2}$ | $V_Q$ / cm$^3$·cm$^{-2}$ | $V_{Geo}$ / cm$^3$·cm$^{-2}$ |
|---|---|---|---|---|---|
| 3 | 3.63 | 0.153 | 3.48 | $7.01 \cdot 10^{-5}$ | $5.37 \cdot 10^{-5}$ |
| 6 | 6.64 | 0.537 | 6.11 | $1.23 \cdot 10^{-4}$ | $1.07 \cdot 10^{-4}$ |
| 11 | 9.90 | 1.10 | 8.80 | $1.77 \cdot 10^{-4}$ | $1.96 \cdot 10^{-4}$ |

Considering all the approximations that have been made, we can conclude that both volumes are in good agreement. Therefore, we believe that, not only the NWs that grow directly on the surface are electroactive, but also those that grow inside the pores forming bundles.

## 5. CVs in the dark and under illumination

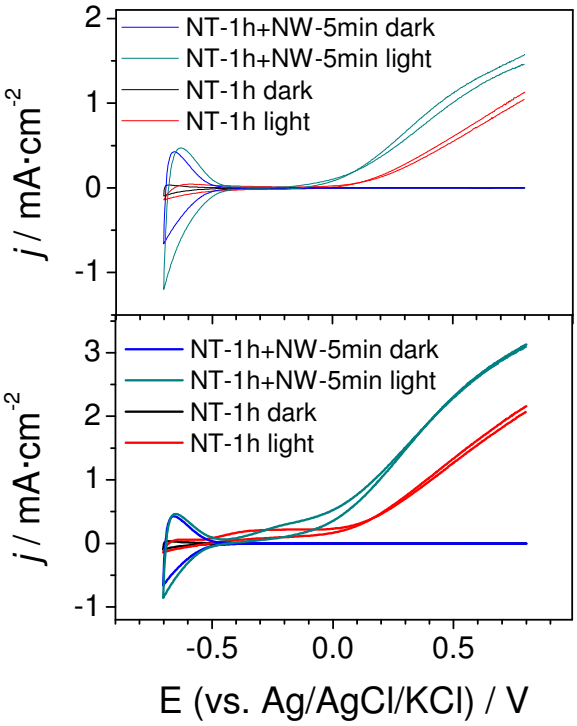


**Figure S6.** CVs for a $TiO_2$ NT array before and after decoration with anatase NWs (5 min CBD time) in the dark and under illumination in $N_2$-purged 0.1 M $HClO_4$ in the absence (a.) and in the presence (b.) of oxalic acid. Scan rate: 20 mV·s$^{-1}$. Illumination source: full output of a 300 W Xe arc lamp equipped with a water filter.

**6. Presence of electronic traps at an electrode composed of NT + rutile NWs grown for 300 minutes**

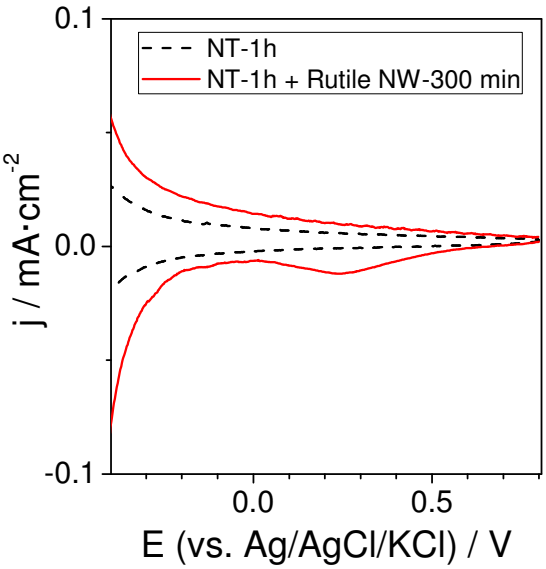


**Figure S7.** Cyclic voltammograms for NT electrode prior and after rutile NW deposition in nitrogen-purged 0.1 M $HClO_4$. Scan rate: 20 $mV \cdot s^{-1}$