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Electronic Supplementary Information for:

One step synthesis of niobium doped titanium dioxide nanotubes arrays by anodization to form (N,Nb) co-doped TiO_2 with an enhanced visible light photoelectrochemical activity.

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1. Supplementary SEM images:

On figure S1 is presented the SEM images for Nb doped TiO_2-NTs synthesized from an electrolyte containing only ammonium fluoroniobate salt and $5\%_{v/v}$ of H_2O. For this sample the niobium on metallic cation ratio at the surface is only 2 ± 0.1 % whereas it reaches 15 ± 0.1 % for a sample synthesized in an electrolyte containing 1 $\%_{v/v}$ of H_2O. This suggests a faster hydrolysis of the fluoroniobate complex when the water content increases.

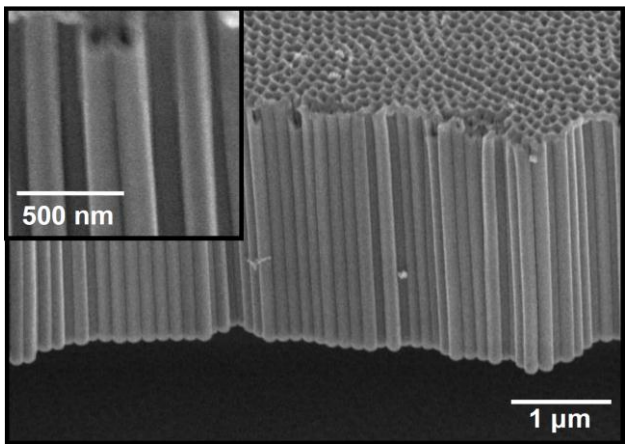

Figure S1. SEM images at 45° inclined view of 1 Nb/TiO_2-NTs synthesized with an electrolyte containing $5\%_{v/v}$ H_2O. The inset is a magnification of

2. EDX measurements:

EDX experiments were conducted in TEM for 1 Nb/TiO_2-NTs samples to compare the niobium concentration with the results obtained by XPS. EDX spectra and the corresponding TEM image are presented in figure S2. The EDX spectra analysis indicates that niobium represents 4 ± 0.2 % of the total cations in the nanotube. For comparison, XPS result indicates a Nb/(Nb+Ti) ratio of 15 ± 0.1 % for the same sample. This difference suggests the presence of a niobium rich layer at the surface of the nanotubes.

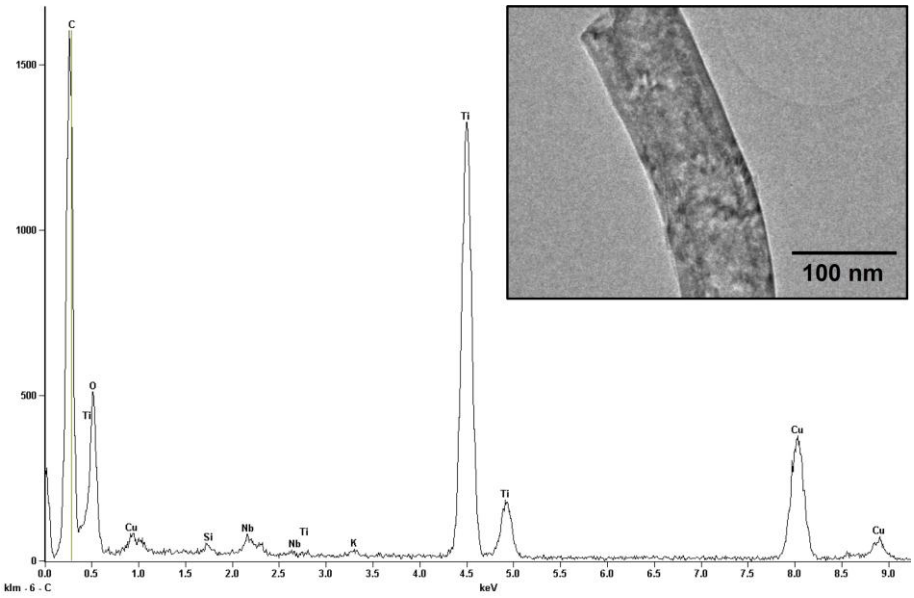

Figure S2. EDX spectrum for 1 Nb/TiO_2-NTs sample. The inset is the analyzed TEM image.

3. XPS

XPS spectra of TiO_2-NTs samples annealed in different conditions are presented in figure S3. For TiO_2-NTs annealed in diluted NH_3 flux, the contribution of β-N peak represent 20 % of the total nitrogen detected in surface, whereas for the sample annealed in pure NH_3 it represent 39 %. For the 1 Nb/TiO_2-NTs samples, the XPS spectra are presented on figure S4.b and the same effect is observable. The N 1s peak attributed to β-N peak represent 14 % of the total nitrogen for the sample annealed in diluted ammonia, instead of 68 % for the sample annealed in pure NH_3. The ratio between β-N peak and Niobium for 1.0 Nb/TiO_2-NTs annealed in pure and diluted ammonia is 0.46 and 0.08, respectively.

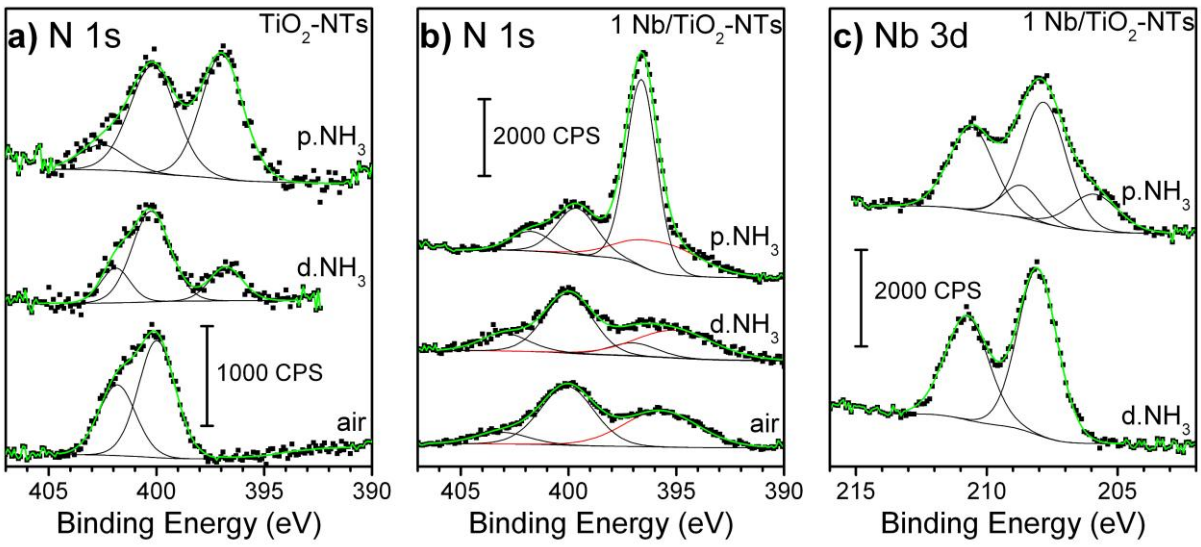

Figure S3. N 1s XPS spectra of a) TiO_2-NTs and b) 1 Nb/TiO_2-NTs annealed in different atmosphere. c) Nb 3d spectra of 1 Nb/TiO_2-NTs annealed in pure or diluted ammonia. Black squares are the experimental data, green line represent fit results and red lines are the satellite peaks of Nb 3p satellite.

It should be noted that for the 1 Nb/TiO_2-NTs sample annealed in pure ammonia flux, new contributions of Nb 3d appears at lower binding energy. These new peak located 205.8 and 208.6 eV are attributed niobium oxynitride (ref. 50 of the article). This new phase represent 24 % of the total niobium present in surface and is not observed for sample annealed in diluted ammonia.

Samples annealed under pure NH_3 flux, are almost inactive for photoelectrochemical measurements. This is probably due to a too high concentration of nitrogen atoms which would not only participate to a reduction of the bandgap, but also can act as recombination centers. For instance, a decrease of the photocatalytical activity of N-doped TiO_2 was already pointed out when the amount of β-N is too high in the structure (ref. 16 of the article text). Furthermore, in this annealing condition, the presence of niobium oxynitride or suboxide identified in surface by XPS spectra (Figure S3.c) can also explain the inactivity of these samples. Thus for the samples tested in photoelectrochemical experiments, the annealing is conducted in a flow of ammonia diluted in nitrogen (20 % NH_3/80 % N_2). Under these conditions no reduced niobium is observed and the quantity of atomic β-N is strongly reduced.

4. UV/visible spectroscopy

UV/visible spectra are recorded on a CARY UV-100 (Varian Inc.) in diffuse reflectance mode. The reflectance of a Titanium foil was used as a reference. The Kubelka-Munk function was calculated classically and the normalized results are presented on figure S4.

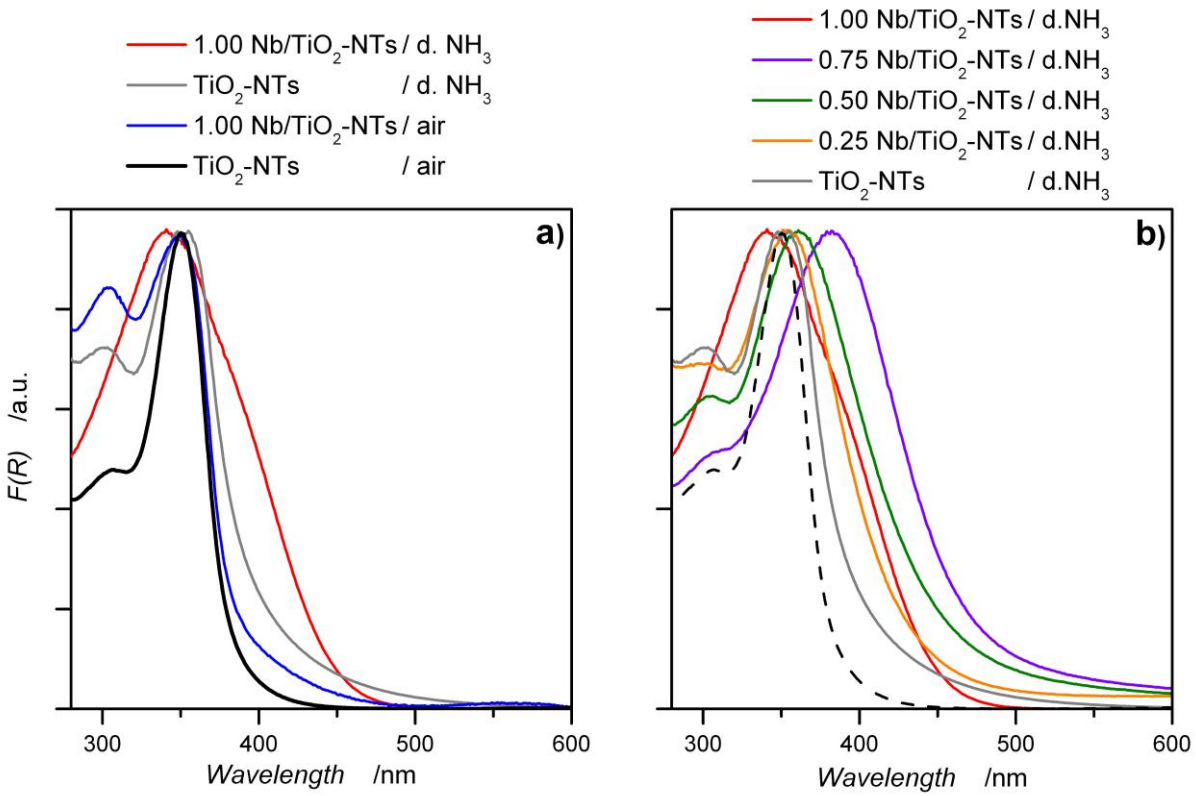

Figure S4. UV visible spectra for a) TiO_2-NTs, N-, Nb- and (N,Nb)-doped TiO_2-NTs. b) UV visible spectra for (N,Nb) co-doped TiO_2-NTs with different content of niobium annealed in NH_3. The dashed line corresponds to the TiO_2-NTs sample annealed in air.