## **Supporting information**

The "Avantage 4.67" software was used for XPS data acquisition and processing. Elemental atomic concentrations were calculated from the XPS peak areas and the corresponding Scofield sensitivity factors corrected with the analyzer transmission work function. The result of high resolution peak fitting of C1s and O2s signals of the two representative samples of the studied TiO<sub>2</sub>/Ti nanostructures, namely AT-24-80 and AT-72-100, are given here after.



Fig. SI-1 Peak fitting of C1s (up) and O2s (down) signals of the two representative samples of the studied  $TiO_2/Ti$  nanostructures, namely AT-24-80 (left side) and AT-72-100 (right side)

As explained previously in the experimental section, Methylene blue (MB) substrate was chosen as a pollutant model to evaluate the photocatalytic efficiency of the prepared TiO<sub>2</sub>/Ti photocatalysts under UV irradiation ( $\lambda$ = 365 nm).The variation of the relative MB concentration as a function of UV

exposition time is given hereafter for all the produced catalysts. It clearly shows a rapid MB degradation with AT-24-80 and AT-72-100 samples compared to AT-48-80, AT-72-80, AT-48-100 and AT-24-100 ones.



Fig. SI-2 Quantitative comparison of MB degradation using  $TiO_2/Ti$  nanostructures prepared at 80 (a) and 100 °C (b) for different heating times.

Finally, the microstructure of all the produced nanostructures was checked after PC and PEC tests. It appears to be stable and almost unchanged after prolonged wastewater and/or electrolyte contact time as illustrated in Fig. SI-3 and SI-4, respectively.



Fig. SI-3 FEG-SEM top view images recorded on  $TiO_2/Ti$  nanostructures after photocatalytic degradation cycles: a), b) and c) correspond to samples prepared at 80°C at 24, 48 and 72 h, respectively and d), e) and f) to those prepared at 100°C for the same treatment times, respectively.



Fig. SI-4 Survey and high-resolution XPS spectra of  $TiO_2/Ti$  nanostructures after photocatalytic degradation cycles: correspond to samples prepared for 24 h at 80°C (a) and 100 °C (b), respectively.