Electronic Supplementary Material (ESI) for RSC Advances.

Nitroaldol Condensation Catalyzed by Topologically-modulable Cooperative Acid-Base Chitosan-TiO_2 Hybrid Materials

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Supporting informations :

S1. Material's preparation procedures:

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1.1. Preparation of **CS-aero**

An aqueous solution of chitosan was obtained by dissolving 1g of chitosan in 100 mL of a solution of acetic acid (0.055 mol L^{-1}) corresponding to a stoechiometric amount of acid with respect to the amount of NH_2 functions. Total dissolution was obtained under stirring over one night at room temperature. This solution was dropped into a NaOH solution (4N) through a 0.8 mm gauge syringe needle providing gelified chitosan microspheres. The chitosan beads were stored in the alkaline solution for 2 h and then dehydrated by immersion successively in a series of ethanol–water baths containing more and more ethanol until 100% ethanol bath. The native microspheres were then dried under supercritical CO_2 conditions (74 bar, 31.5 °C) in a Polaron 3100 apparatus to lead to **CS-aero.** The chitosan aerogel beads present a porous network featuring high surface area and large pore diameter as determined by nitrogen sorption measurements.

1.2 Preparation of **CS-lyo**

The same aqueous solution of chitosan prepared above was dropped into a liquid nitrogene through a 0.8 mm gauge syringe needle providing spontaneous freezing of chitosan microspheres. The chitosan beads were liophilized and stabilized by successive immersion in a series of ethanol/NaOH (0.1M) baths containing more and more of NaOH (100/0, 50/50 and 0/100). The native microspheres were then immersed in ethanol and dried under supercritical CO2 conditions (74 bar, 31.5 °C).

1.3 Preparation of **CS-F**

Electrospun Nanofibers Scaffolds. The electrospinning solution was prepared by mixing 3 g of chitosan solution (at 10.5% in 6.5% acetic acid) and 1 g of PEG solution (at 4% in distilled water). We then poured 2 mL in a 5 mL plastic syringe fitted with blunt-tipped stainless steel needles (gauge 18 and 21). The solution feed was driven using a syringe pump (Razel

Scientific Instruments). A 30 kV electrospinning voltage was applied between the needle and the collector (aluminum foil) by the use of a Spellman SL10 power supply. The positive electrode of a high voltage power supply was connected to a metal capillary by copper wires. The distance between the tip of the needle and the surface of the aluminum foil used as a collector was 15 cm, and the flow rate of the solution was 0.75 mL/h. All electrospinning procedures were performed at room temperature. The scaffolds were then stabilized by immersion into 1MNaOH before extensive washing in distilled water. At this step, biophysical analyses revealed that nanofibers were formed from chitosan only, PEG having been solubilized and removed during the successive washing steps;

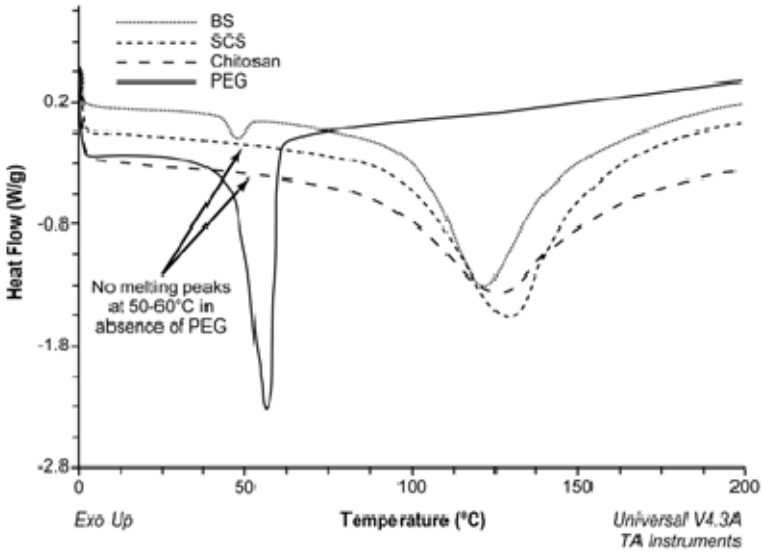
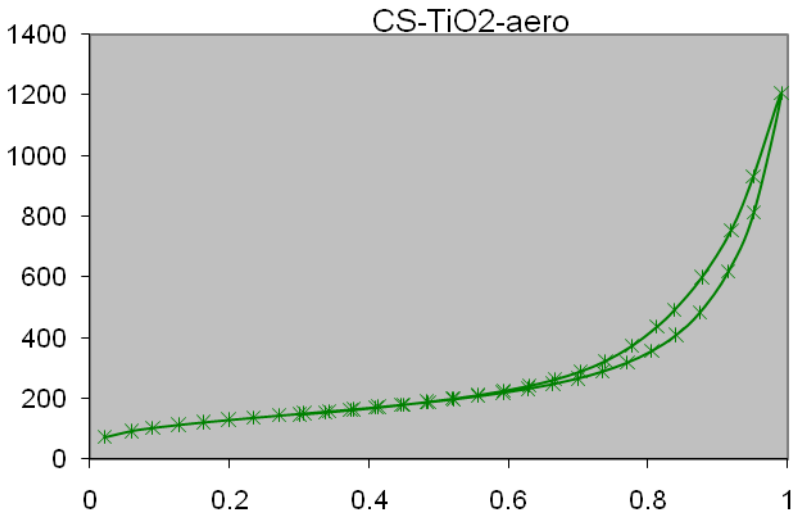


Figure S1. Thermal behaviour of pure PEG, pure chitosan and electrospun scaffold, before (BS) and after stabilization (SCS).

1.4 General procedure for the preparation of **CS-TiO_2**

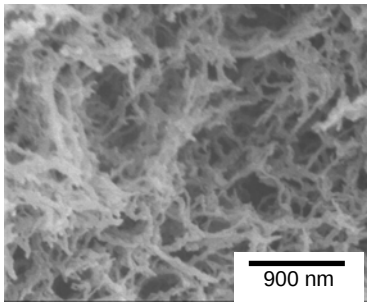
The titania solution was prepared with titanium alcoxyde source ($Ti(acac)_2(OiPr)_2$ and isopropanol (Ti:iPrOH) 1:10). The beads of chitosan swelled in ethanol (250 mg) were suspended in the titania solution (4 mmol) at room temperature for 48 h. The microspheres were washed first with isopropanol twice and then with ethanol. The hybrid microspheres were dried by supercritical CO_2 leading aerogel microsphere materials. The obtained materials present a porous network featuring high surface area and large pore diameter as determined by nitrogen sorption measurements.

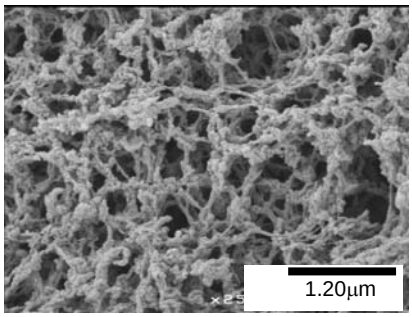
S2. Nitrogen physisorption isotherms



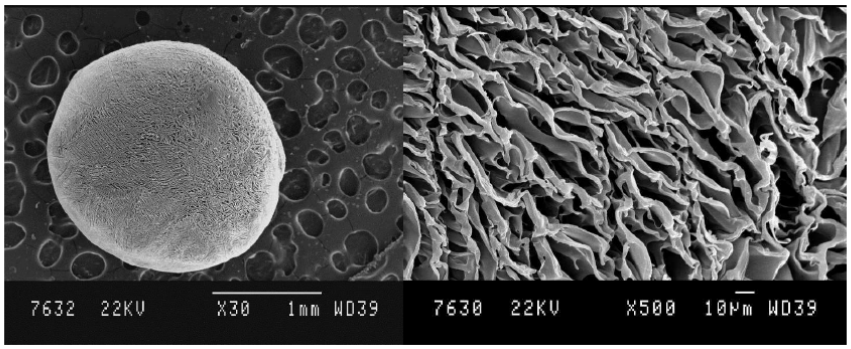
S3. SEM analysis

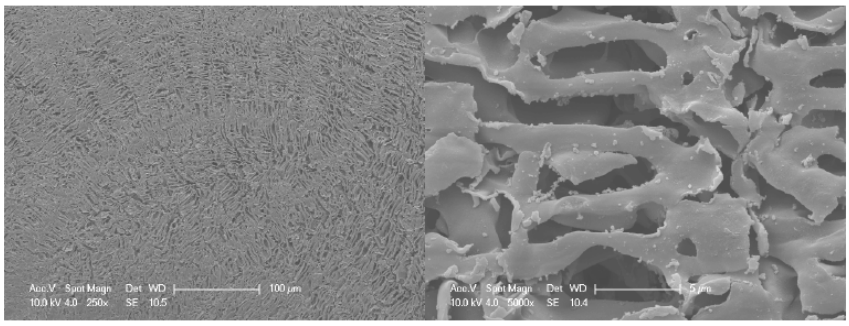
SEM of **CS aero** (up) and **CS-TiO_2-aero** (bottom).



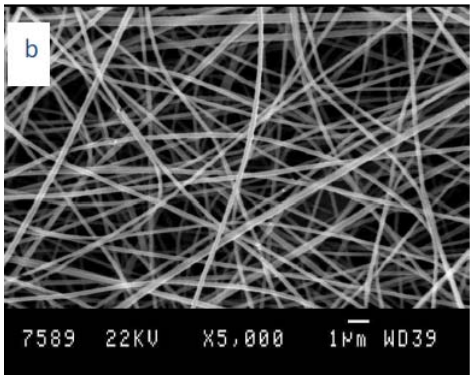


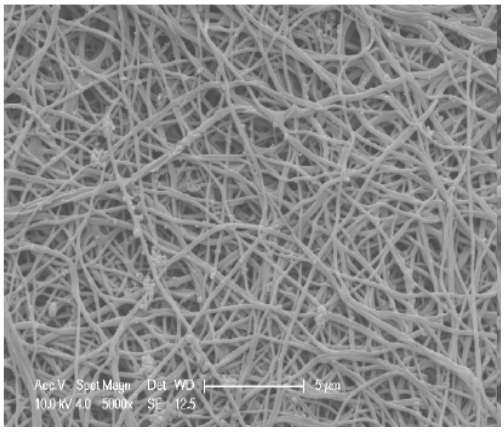
SEM of **CS-lyo** (up) and **CS-TiO_2-lyo** (bottom).



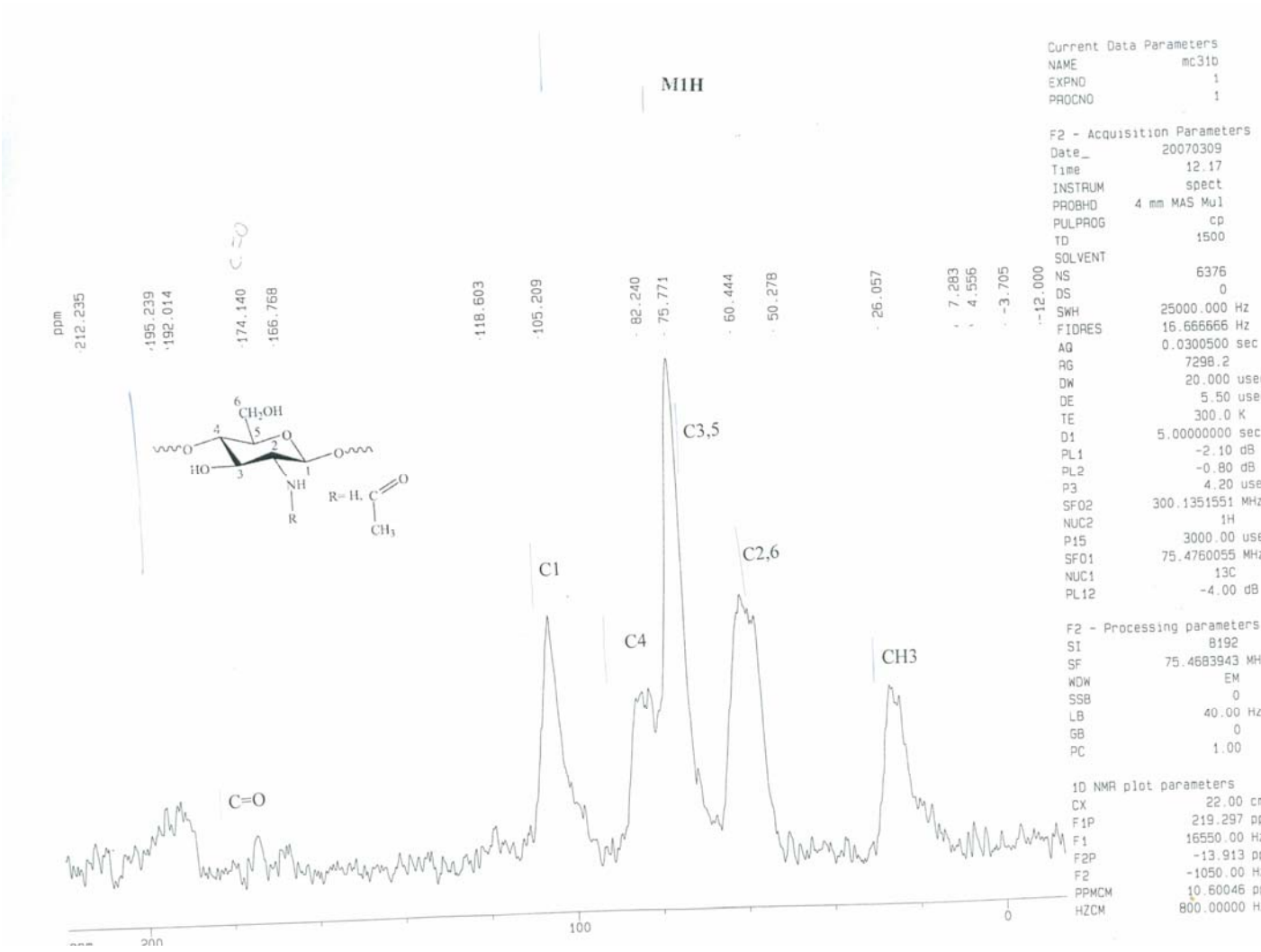


SEM of **CS-F** (up) and **CS-TiO_2-F** (bottom).



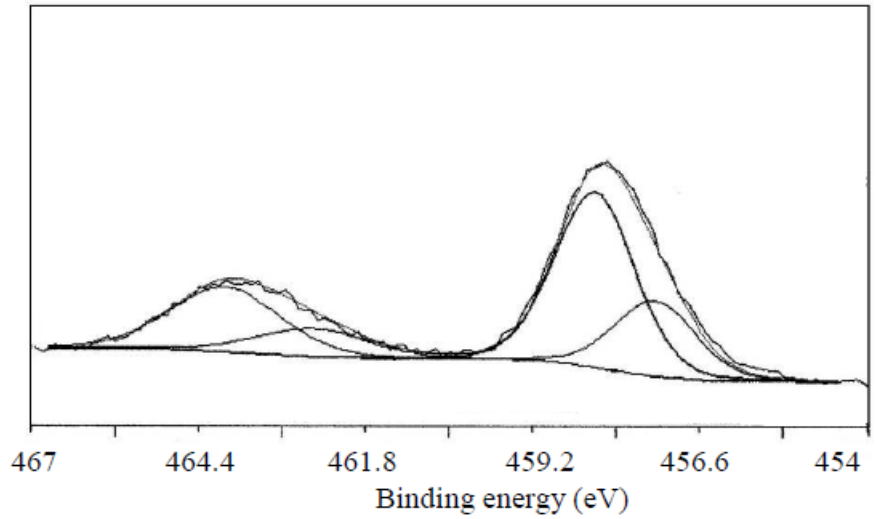


S4. CP MAS ^{13}C NMR of CS-TiO_2-Aero

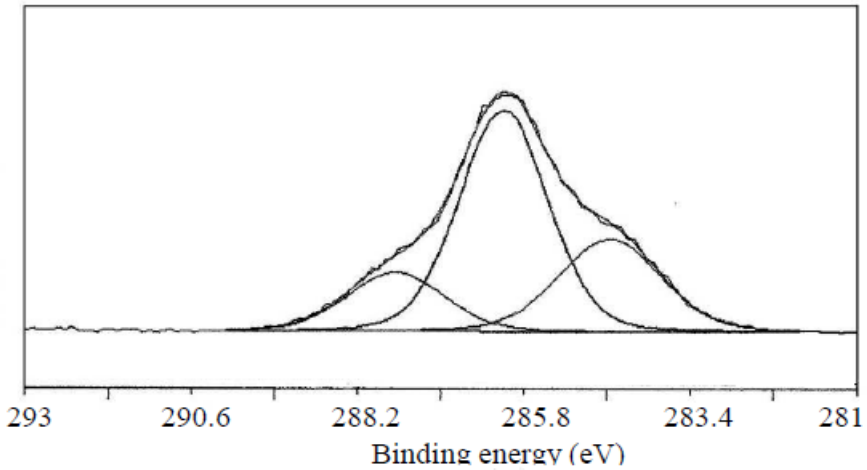


S5. XPS analysis of CS-TiO_2

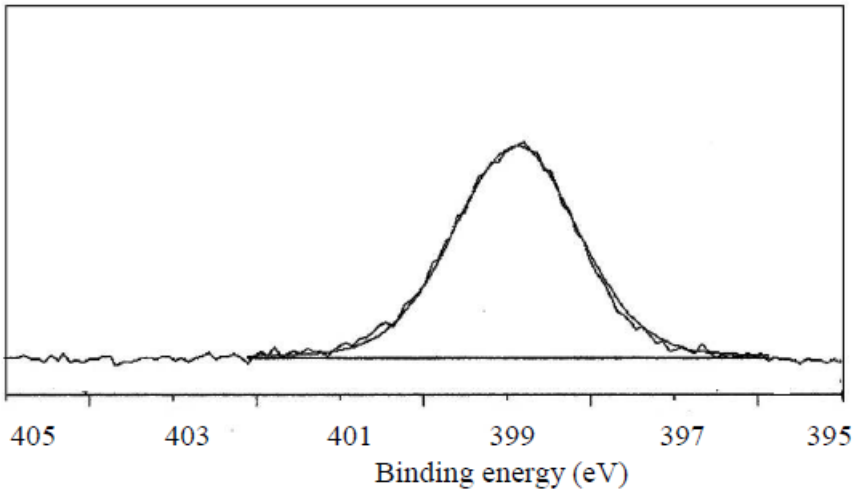
XPS analysis constitutes an efficient tool to better elucidate the nature of chemical species presents both in the surface and in the whole of the materials. Grinding the samples and their analysis allow us to provide additional information about the distribution of titanium species across the microspheres. First, it was found that the percent of inorganic titanium clusters was slightly more important (by ~ 7%) in the surface than in the bulk. The presence of absorption peaks at 458.3 eV for **CS-TiO_2-Aero** confirms the presence of titanium oligomeric clusters inside of the beads matrices. Characteristic adsorption of CH_3 and CH_2 (at 286.6) and of NH_2 (399 eV) are also shown. Spectra recorded for **CS-TiO_2-Aero** are given as example.



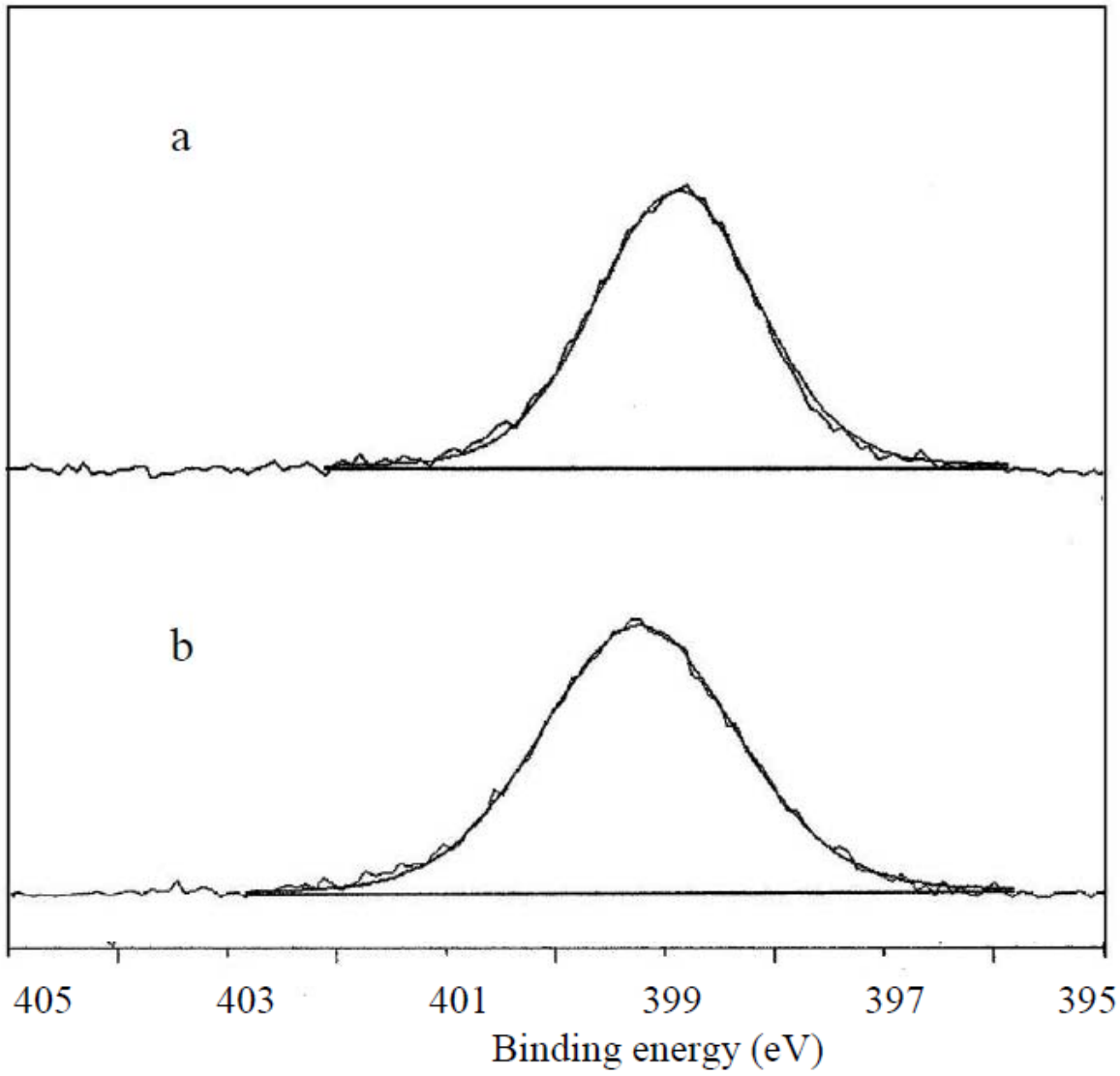
XPS spectra of titanium Ti 2p for **CS-TiO_2-Aero**



XPS spectra of carbon C1s of **CS-TiO_2-Aero**

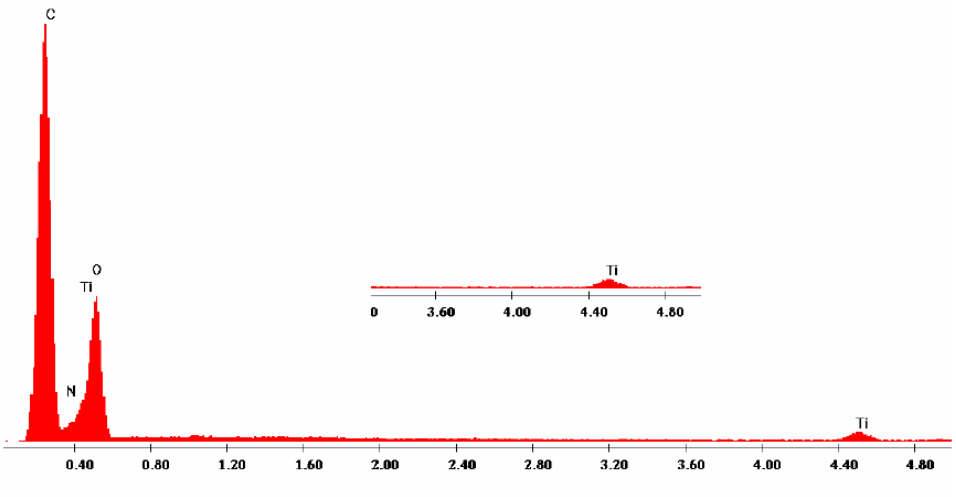


XPS spectra of nitrogen N1s (NH_2) of **CS-TiO_2-Aero**

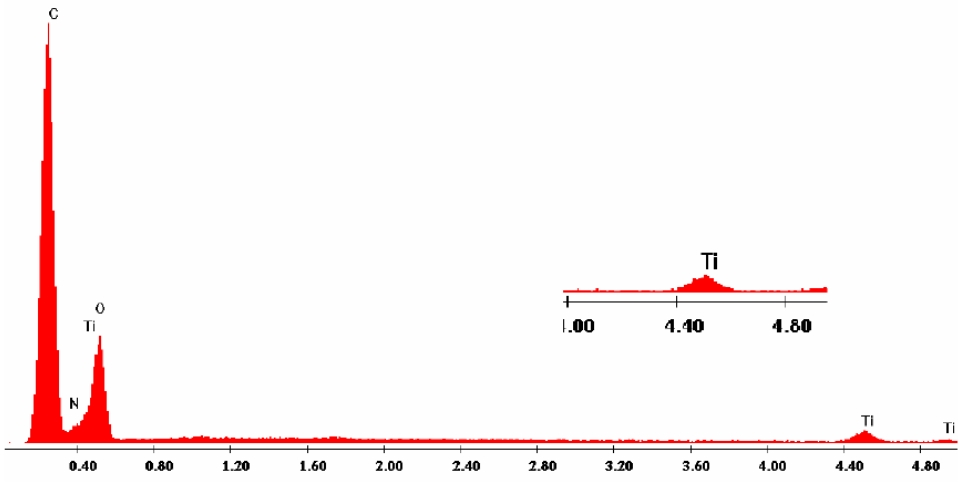


Comparison of the XPS signal of N in : a) CS and b) CS-TiO_2-Aero

S6. EDX analysis



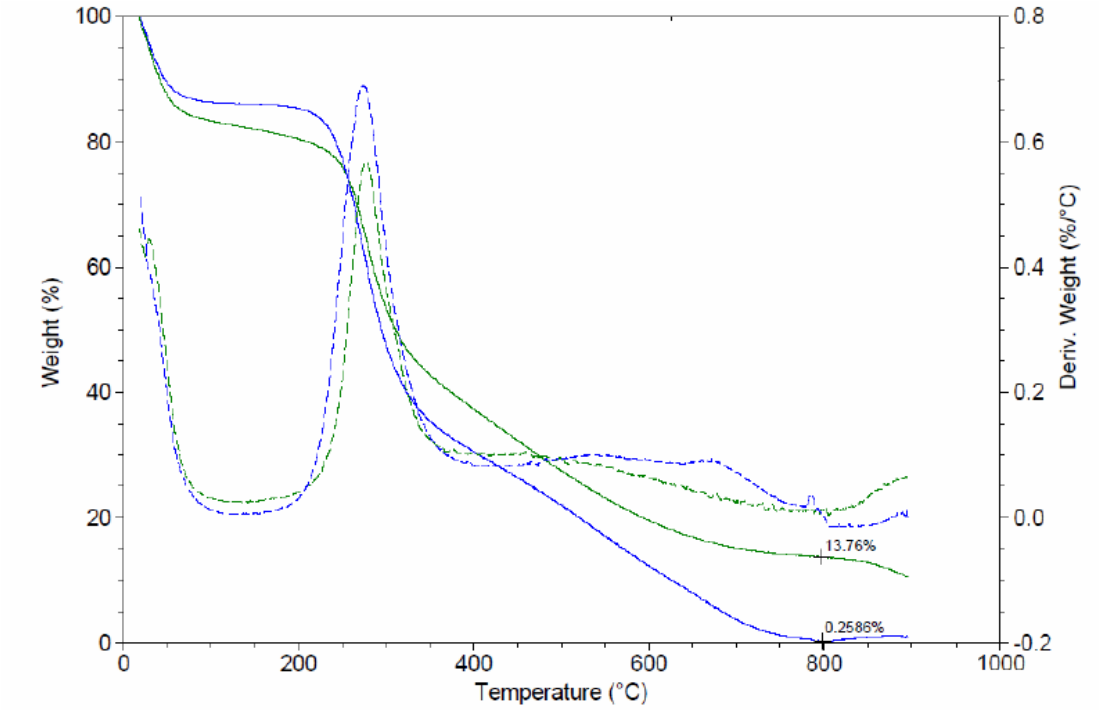
EDX analysis of **CS-TiO_2-lyo**



EDX analysis of **CS-TiO_2-F**

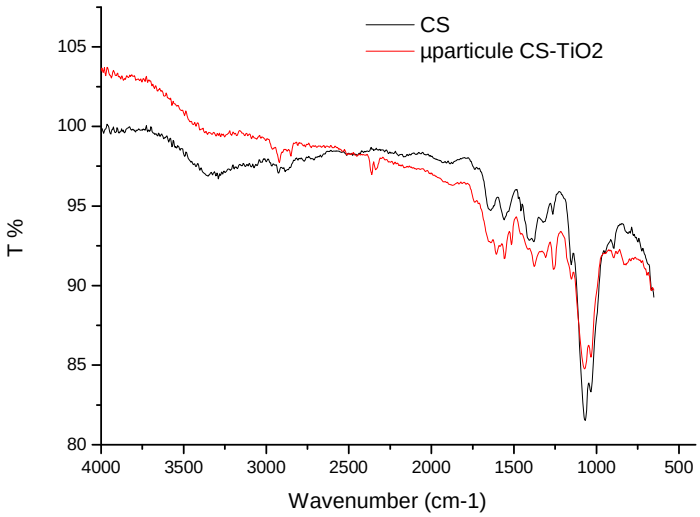
S7. Typical example of thermogravimetric analysis

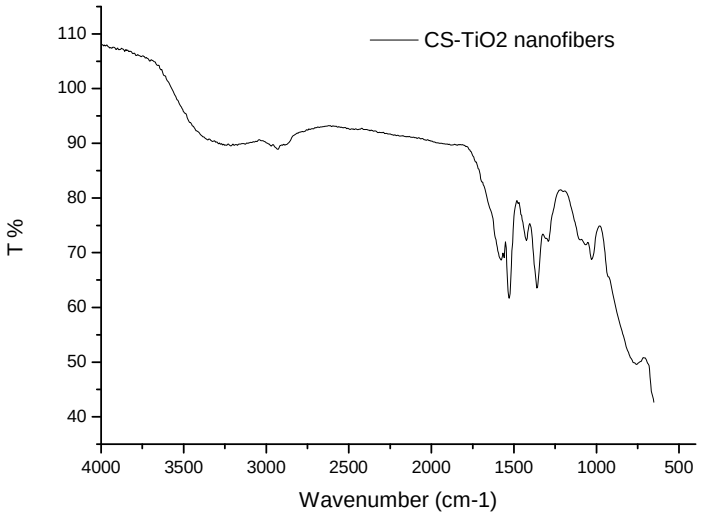
TGA of **CS-lyo** and **CS-TiO_2-lyo**



S8. DRIFT analysis

DRIFT of **CS-lyo** and **CS-TiO_2-lyo**




CS-TiO2 nanofibers
T %
110
100
90
80
70
60
50
40
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

S9. Recycling experiments.