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Triply green polyaniline: UV irradiation-induced synthesis of highly porous PANI/TiO_2 composite and its application in dye removal

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Electronic Supporting Information

S1. Materials and methods

The used reagents were analytical grade and were purchased from Sigma-Aldrich, unless stated otherwise. Milli-Q water was used for the preparation of solution and suspensions.

Sample preparation

The aniline's dimer (*N*-(4-aminophenyl aniline)) was adopted as starting compound and 1 g of dimer was dissolved in an HCl solution prepared by mixing 290 mL of MilliQ water and 2.25 mL of HCl 37%. Then, 174 mg of commercial nanostructured TiO_2 (Evonik P25) was added. The suspension was irradiated under UV light (Jelosil HG500 lamp; effective irradiation power: 30 mW cm^{-2}) for 135 min while stirring vigorously. During irradiation, the suspension colour turned from grey to light purple. After irradiation, the suspension was stirred for 4 h in the dark and then 0.55 mL of 30% H_2O_2 aqueous solution was added giving rise to the formation of a dark green precipitate. After 18 h, the precipitate was collected by filtration and washed several times with water and acetone. This sample was named PANI_TiO_2.

In order to clarify the reaction mechanism, two samples were prepared adopting the same synthetic procedure but without the addition of TiO_2 (PANI_noTiO_2) and without UV irradiation (PANI_ TiO_2noUV). A test in the same synthetic conditions was carried out with the use of a much longer irradiation time (390 min) as an alternative to the subsequent addition of H_2O_2. However, in this case, the reaction did not proceed beyond the oligomerization step, as testified by the absence of the typical green colour of the PANI emeraldine polymer.

For the sake of comparability, two reference samples were also prepared according to synthetic approaches reported in the literature.

The first reference sample was prepared according to a conventional synthetic approach [1][2]. In brief, 1.0 g of aniline was dissolved in 250 mL of MilliQ water and 9 mL of HCl 37% and cooled in an ice bath. 100 mL of a 0.16 mM $K_2S_2O_8$ aqueous solution was added dropwise to the aniline solution under stirring. After 8 h, a dark green precipitate was recovered by filtration and washed several times with water and acetone. This sample was labelled as PANI1.

A second reference sample was prepared by a green synthesis previously reported by some of us [3][4]. In this case, 1 g of *N*-(4-aminophenyl aniline) was dissolved in a solution of 250 mL of MilliQ water and 2.27 mL of HCl 37%. Then, 2.35 mL of 30% H_2O_2 aqueous solution was added drop-wise at room temperature and while stirring, followed by the addition of 0.15 mL of a 5 mg mL^{-1} $FeCl_3$ aqueous solution. After 24 h, a dark green powder was collected by filtration and washed extensively with water and acetone. This sample will be referred to as PANI2.

The reaction yields were calculated according to the formula:

$$Reaction\ Yield\ \% = \frac{m_{sample}}{m_{dimer} + \frac{m_{dimer} \cdot MW_{HCl}}{MW_{dimer}} + m_{TiO_2}} \cdot 100$$

Materials characterization

The PANI samples were characterized with X-ray Powder Diffraction (XRPD) analyses using a Philips PW 3710 Bragg-Brentano goniometer with a scintillation counter and 1° divergence slit, 0.2 mm receiving slit and 0.04° Soller slit systems. It was employed a graphite-monochromated Cu Kα radiation at 40 kV × 40 mA nominal X-ray power. The 2θ range used to record the diffractograms was 10-80°.

The UV-vis absorption spectra of PANI samples were collected by a Shimadzu UV-2600 UV-vis spectrophotometer in the 200-1000 nm range in DMF solution both with and without HCl.

Fourier Transform Infrared (FTIR) analysis were performed on a PerkinElmer Spectrum 100 FT-IR (ATR) spectrometer. The spectra were acquired in the 400-4000 cm^{-1} range.

The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method with a Coulter SA3100 instrument. The pore size distribution of selected samples was determined via the Barrett, Joyner, Halenda (BJH) method from the desorption isotherms.

A Malvern Zetasizer Nano instrument was used to measure the ζ-potential on 0.5 mg mL^{-1} sample suspensions in 10^{-2} M KNO_3 aqueous solutions.

Scanning electron microscopy (SEM) images were acquired on a Zeiss LEO 1430 instrument.

The molecular weight distributions of the dimethylformamide (DMF) soluble fractions of PANI_TiO_2 were determined by size exclusion chromatography (SEC) using a Shimadzu LC10ADVP HPLC equipped with a refractive index (RI) as the detector. A Phenomenex Phenogel 5 u 55 A (300 x 4.6 mm) was used as the column. Measurements were carried out at room temperature, using ultra-pure DMF as the eluent, at a flow rate of 0.3 mL/min and the injection volume was 20 µL. Calibration was carried out using polystyrene standards. Sample for SEC analysis was prepared dissolving approximately 10 mg of the material in 5 mL of DMF under sonication for 20 minutes at room temperature. Only the soluble fraction was analysed, after filtration.

Liquid chromatography-mass spectrometry (LC-MS) analyses were carried out on a LCQ Fleet ion trap mass spectrometer equipped with a UPLC UltiMate™ 3000 system containing UV detector. A Zorbax RX-C18 (2.1x150 mm-5 µm) was used as column. The column oven was maintained at 30 °C. Chromatographic separations were carried out using a gradient elution at a flow rate of 0.25mL min^{-1}. The mobile phases were made of 0.1% formic acid in water (solvent A) and 0.1% formic acid in acetonitrile (solvent B). Run time was 25 min with gradient elution: 0.0–2 min (5% B), 2–20 min (100% B), 20-25 min (5% B). The injection volume was 5 µL and the detection wavelength was 285 nm. The mass spectrometer was operated with electrospray ionization in the positive ion mode. Full-scan mass spectra were recorded in the mass/charge (m/z) range of 50–1000.

Dye absorption and release tests

The absorption capability of the prepared polyaniline samples was investigated using methyl orange (MO). A suspension of 50 mg of polyaniline in 20 mL of a 50 ppm MO solution was stirred for 20 min at room temperature and spontaneous pH, then the sample was retrieved by centrifugation. The residual MO concentration in the solution was determined by UV-vis spectroscopy (Shimadzu UV-2600 UV-vis spectrophotometer) at its maximum absorption wavelength (504 nm).

The release of the absorbed dye from the PANI sample was obtained by stirring the collected powder in 20 mL of water, then the pH was adjusted with a 1 M NaOH aqueous solution to a final pH of 10; the suspension was stirred for 24 h. The powder was separated by centrifugation and the MO released in the solution was measured by UV-vis spectroscopy.

Recycle tests were made to evaluate the reusability of the PANI_TiO_2. At the end of an absorption-release test, the recovered PANI powder was resuspended in fresh 20 mL of 50 ppm MO solution and the pH was adjusted to 3 with an HCl 37% solution.

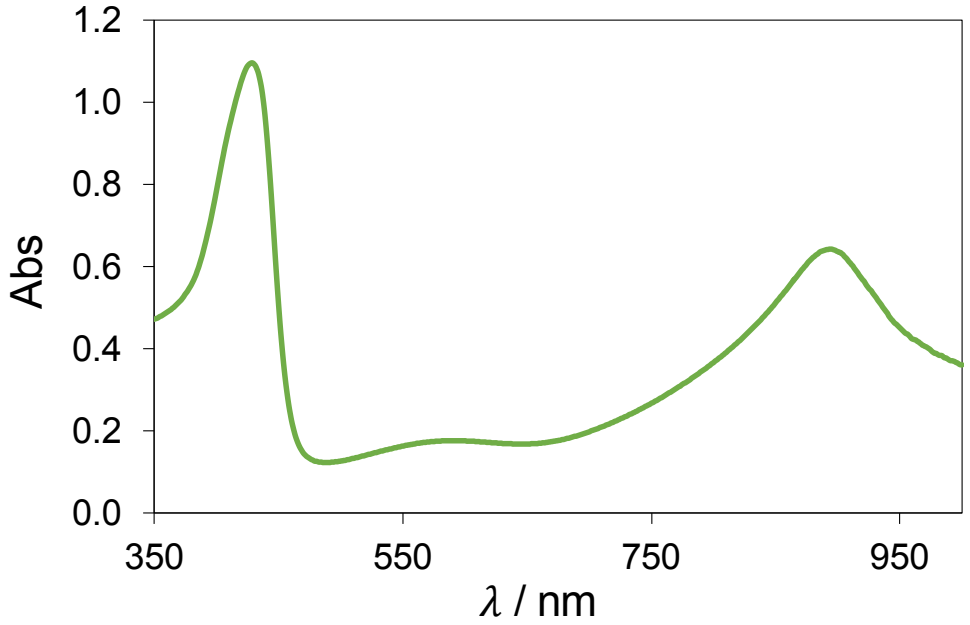


Figure S1 – UV-vis absorption spectra of PANI_TiO_2 in DMF and acidified by HCl.

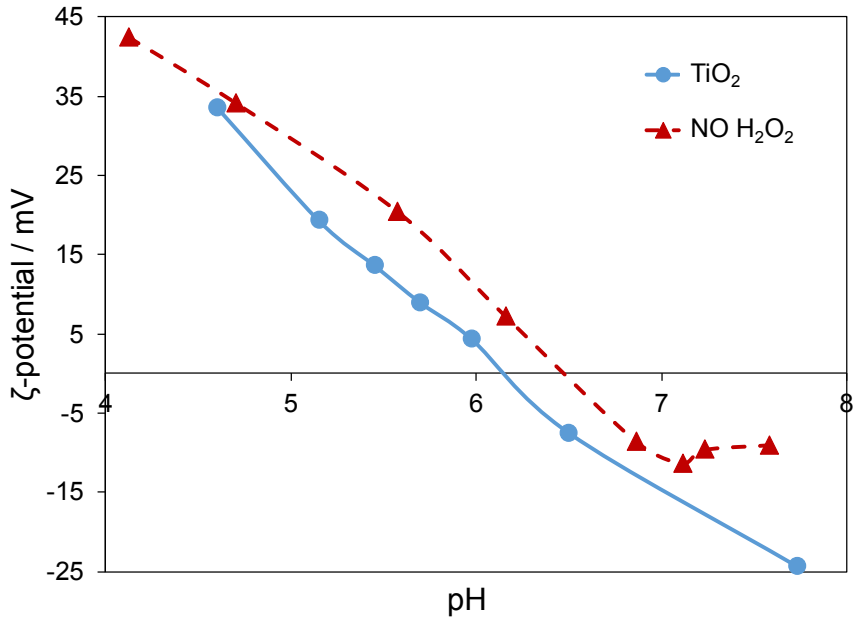


Figure S2 – Isoelectric point determinations for pristine TiO_2 and for a reaction product sampled after the end of the UV irradiation, before the H_2O_2 addition.

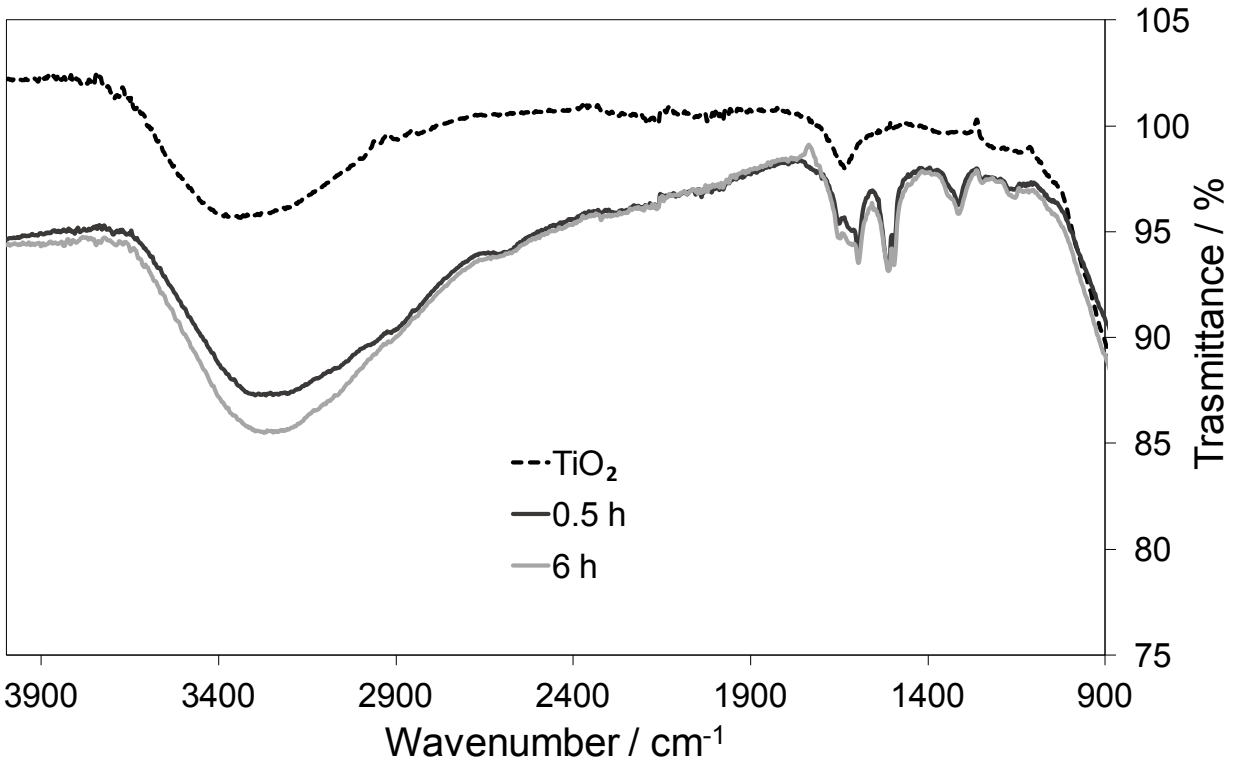
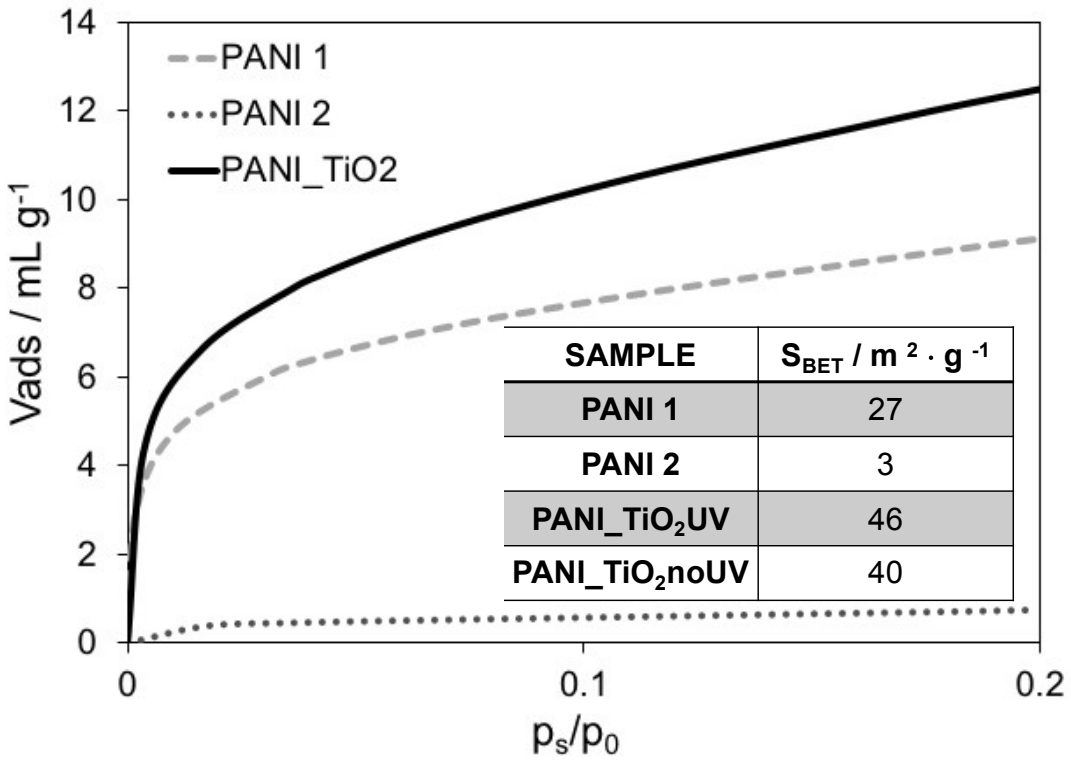


Figure S3 – FTIR spectra of bare TiO_2 and a reaction product sampled before the H_2O_2 addition during synthesis without UV irradiation.



SAMPLE	S_{BET} / $m^2 \cdot g^{-1}$
PANI 1	27
PANI 2	3
PANI_TiO_2UV	46
PANI_TiO_2noUV	40

Figure S4 – Samples' N_2 adsorption isotherms. Inset: specific surface area values (S_{BET}).

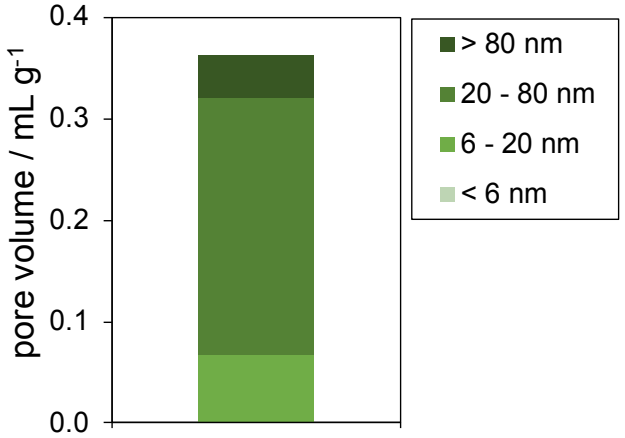


Figure S5 – Pore size distribution of PANI_TiO_2.

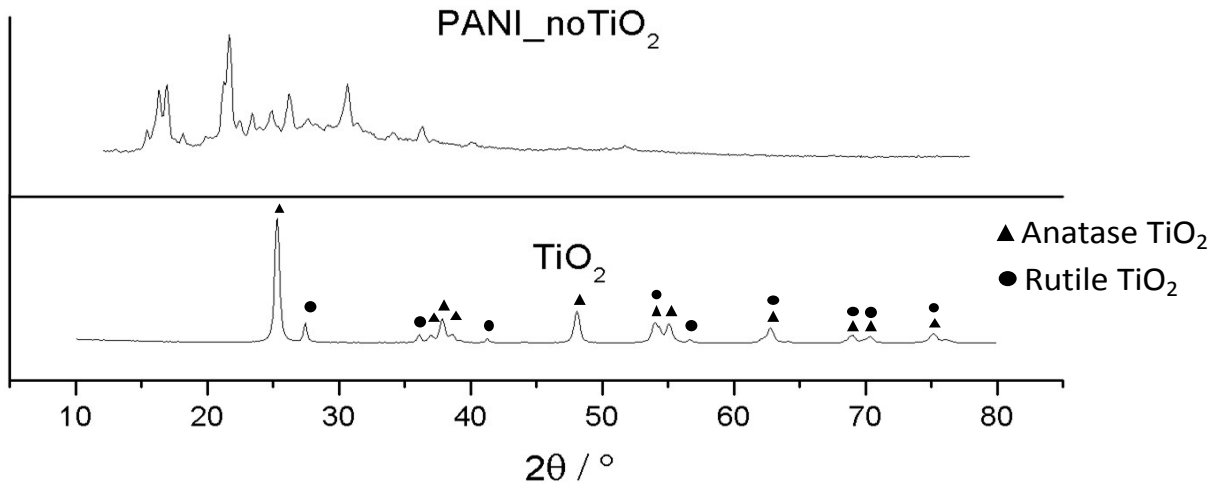


Figure S6 – XRPD patterns of pistine TiO_2 and PANI_noTiO_2.

References

[1] J.C. Chang, A.G. MacDiarmi, *Synthetic Metals* 1986, **13**, 193–205.

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[3] Z. Chen, C. Della Pina, E. Falletta, M. Rossi, *Journal of Catalysis* 2009, **367**, 93-96.

[4] E. Falletta, P. Costa, C. Della Pina, S. Lanceros-Mendez, *Sensors and Actuators A: Physical*, 2014, **220** (2014) 13-21.