# Modulation of the photocatalytic activity and crystallinity of F-TiO<sub>2</sub> nanoparticles by using green natural carboxylic acids

Miguel Díaz-Sánchez,<sup>a</sup> Paula Delgado-Álvarez,<sup>a</sup> I. Jénnifer Gómez,<sup>b</sup> Diana Díaz-García,<sup>a</sup> Sanjiv Prashar,<sup>a</sup> Santiago Gómez-Ruiz<sup>a,\*</sup>

<sup>a</sup>COMET-NANO Group, Departamento de Biología y Geología, Física y Química Inorgánica, E.S.C.E.T., Universidad Rey Juan Carlos, Calle Tulipán s/n, E-28933 Móstoles, Madrid, Spain.

<sup>b</sup>Department of Condensed Matter Physics, Faculty of Science, Masaryk University, 61137 Brno, Czech Republic

Corresponding author: santiago.gomez@urjc.es

## SUPPLEMENTARY MATERIAL

This supplementary material contains:

- 1) Materials and characterization techniques.
- 2) Synthesis of nano-sized nanostructured aggregates of TiO<sub>2</sub>.
- **3)** Comparative photodegradation study of the TiO<sub>2</sub> materials.
- Detailed evaluation of the photocatalytic activity of the most active material F-TiO<sub>2</sub>-AA-550.
- 5) Evaluation of kinetic parameters of  $F-TiO_2-AA-550$ .
- 6) Evaluation of photocatalytic mechanism of  $F-TiO_2-AA-550$
- 7) Photocatalytic degradation of different real pollutants in water.
- 8) Synthesis of Pd nanoparticles supported on TiO<sub>2</sub>.
- 9) Applications of hybrid doped TiO<sub>2</sub>-Pd nanoparticles in Suzuki-Miyaura reactions.
- 10) F-TiO<sub>2</sub> synthesis product using ascorbic acid as medium at pH 2 (Figure S1).
- 11) F-TiO<sub>2</sub> synthesis product using ascorbic acid pre and post calcination 550 °C (Figure S2).
- 12) Thermogravimetric studies of F-TiO2-AA and F-TiO2-AA-550 material (Figure S3).
- 13) SEM images of F-TiO<sub>2</sub>-AA before and after calcination process (Figure S4).
- 14) SEM-EDS images of F-TiO<sub>2</sub>-AA materials series (Figure S5)
- 15) Ti species analysis of F-TiO<sub>2</sub>-AA calcinated materials by XPS (Figure S6).
- 16) Brookite phase detail in X-ray diffraction patterns of TiO<sub>2</sub>-NA-500 and F-TiO<sub>2</sub>-NA-500 samples (Figure S7).
- 17) X-ray diffraction patterns for F-TiO<sub>2</sub>-NA and F-TiO<sub>2</sub>-AA samples calcined at 450 °C, 500 °C and 550 °C (Figure S8).
- 18) Particle size distribution for materials synthesized with different acids (Figure S9).
- 19) TEM images and particle size distribution for calcinated studied materials (Figure S10).
- **20)** Diffuse reflectance spectra of the synthesized  $F-TiO_2$  materials (Figure S11).
- 21) Images obtained by High-resolution TEM of F-TiO<sub>2</sub>-AA-550 (Figures S12)
- 22) Comparative kinetic study of the photocatalytic degradation of F-TiO<sub>2</sub>-AA-550 and Degussa P25 titanium dioxide under UV-light (36 W) (Figure S13).

- 23) Study of the kinetic of the photocatalytic degradation of MB (0.25 mM) with F-TiO<sub>2</sub>-AA-550 under UV-light (36 W) (Figure S14).
- 24) Study of kinetics comportment of F-TiO<sub>2</sub>-AA-550 under UV-light (300 W) (Figure S15).
- 25) Study of the kinetic of the photocatalytic degradation of MB (0.04 mM) under visible light (300 W) with F-TiO<sub>2</sub>-AA-550 (Figure S16).
- 26) Study of the possible kinetic mechanism of the photocatalytic degradation of MB (0.04 mM) with F-TiO<sub>2</sub>-AA-550 (Figure S17).
- 27) High-resolution TEM images of F-TiO<sub>2</sub>-AA-550-Pd (Figure S18).
- 28) Spectrum of High-resolution TEM-EDS of F-TiO<sub>2</sub>-AA-450-Pd (Figure S19).
- 29) SEM-EDS images of F-TiO<sub>2</sub>-AA-450-Pd (Figure S20).
- **30)** Composition of different **F-TiO<sub>2</sub>-AA** materials determined by XPS (**Table S1**).
- 31) Evaluation of kinetic parameters of (Table S2).
- **32)** Suzuki-Miyaura coupling reaction results using titanium dioxide-based materials as catalysts (**Table S3**).
- 33) ICP Analysis of the palladium content in the catalyst F-TiO<sub>2</sub>-AA-450-Pd (Table S4).
- 34) Recyclability for F-TiO<sub>2</sub>-AA calcinated series material at 4h (Table S5).

### 1) Materials and characterization techniques

For this study the following reagents were used as received without further purification: Titanium(IV) oxide nanopowder, 21 nm primary particle size (TEM),  $\geq$ 99.5% trace metals basis Aeroxide® P25 (Aldrich); titanium(IV) isopropoxide 98% (Acros Organics); sodium fluoride  $\geq$  99% (Fluka Chemika); 2-propanol (Fluka Analitical); HNO<sub>3</sub> 65% (Scharlau); citric acid anhydrous extra pure (Scharlau); ascorbic acid reagent grade (Scharlau); benzoic acid synthesis grade (Scharlau); salicylic acid > 99,5% (Labkem); DMF (VWR Chemical); phenylboronic acid  $\geq$  98% (Fluorochem), iodobencene  $\geq$  98% (Aldrich), potassium carbonate  $\geq$  99% (Aldrich), phenyl sulfide  $\geq$  99% (Fluorochem), Benzyl alcohol > 99,5% (Chem-Lab); hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>) 30 % (Honeywell), methylene blue (Scharlau), phenol (Sigma-Aldrich), 4-chlorophenol (Acros Organics) ciprofloxacin (Fluorochem) and naproxene (Fluorochem).

FT-IR analysis was determined with a PerkinElmer Spectrum Two FT-IR spectrometer. Thermogravimmetry (TG) analyses were obtained with a Shimadzu mod. DSC-50Q operating between 30 and 800 °C (ramp 20 °C/min) at an intensity of 50 A in nitrogen. X-Ray diffraction (XRD) measurements were carried out on a Philips diffractometer PW3040/00 X'Pert MPD/MRD at 45 KV and 40 mA with Cu-K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) and using a high-angle measuring between 2 $\theta$  (10°-90°). Adsorption-desorption isotherms of nitrogen were measured with a Micromeritics ASAP 2020. DRUV-Vis spectra were recorded on a Varian Cary 500 spectrophotometer in diffuse reflectance mode. Transmission electron microscopy (TEM) images were taken with a JEOL JEM1010 at 100 kV. High resolution TEM images were recorded with a JEOL JEM 2100HT at 200 kV. Scanning electron microscopy (SEM) with energy-dispersive X- ray spectroscopy (EDS) detector was used for acquiring both morphological and elemental mapping images with Verios 460L instrument (FEI, USA) with an electron beam accelerating voltage of 5 kV and 10 kV and instrument Thermo Fisher PRISMA-E with an electron beam accelerating voltage of 10 kV. The XPS was performed with the Axis Supra spectrometer (Kratos Analytical Ltd, UK) where the quantitative composition was determined from detailed spectra taken at the pass energy of 80 eV, in addition, lower pass energy of 20 eV was used to attain well-resolved spectra for fitting. The deconvolution of XPS spectra to individual components was done in the Casa XPS 2.3.17 software. For the fitting, the Shirley-type background subtraction was used, and all curves were defined as 30% Lorentzian, 70% Gaussian. Besides, constrains of the full width at a half maximum (FWHM) and the peak positions were applied. Binding energy calibration was based on adventitious carbon at 284.8 eV. For quantification of the palladium content the materials were digested and analyzed directly by inductively coupled plasma atomic emission spectroscopy with a Varian Vista AX Pro ( $\lambda$ Pd = 340.458 nm) instrument.

### 2) Synthesis of nano-sized nanostructured aggregates of TiO<sub>2</sub>

Nanostructured aggregates of TiO<sub>2</sub> were prepared by the sol-gel method reported by our group through a hydrothermal variant. The process was based on the hydrolysis and condensation of a titanium alkoxide, Ti(OiPr)<sub>4</sub> (TTIP), in a solution of ultrapure water at pH 2 by using different acids, namely, nitric acid (NA), ascorbic acid (AA), citric acid (CA), benzoic acid (BA) and salicylic acid (SA) also incorporating fluorine as a doping agent in a one-pot reaction. This method consisted in the simultaneous dropwise addition of 8 mL of TTIP, dissolved in dry 2propanol (v:v 2:5), together with a solution of 0.24 g of NaF (5% wt. in fluorine) in 25 mL of ultrapure water to a medium of 400 mL of each of the acids acid (NA, AA, CA, BA or SA) at pH 2. To carry out the hydrothermal treatment, the above mixture was transferred to a teflon autoclave of 600 ml which was hermetically sealed and deposited in a muffle for 12 h at 200°C. Subsequently, the autoclave reactor was cooled to room temperature and the resulting suspension was separated by centrifugation and washed copiously with deionized water and pure ethanol. The product was dried in an oven at 80°C overnight and grained in a mortar to obtain a regular powder to facilitate the homogenization for subsequent calcination step. A fraction of each material was calcined in air in a Carbolite AAF 1100 furnace at 500 °C (12 h) with a temperature ramp of 0.8 °C/min. In the case of materials with the most promising photocatalytic activity, F-TiO2-NA and F-TiO2-AA series calcination at 450 °C and 550 °C was also carried out for comparison purposes.

To elucidate the effect of fluorine on the photocatalytic activity of the material, the same synthetic process was carried out without fluorine doping to obtain the reference material **TiO<sub>2</sub>-NA-500**.

### 3) Comparative photodegradation study of the TiO<sub>2</sub> materials

Regular photodegradation experiments were carry out using 15 mg of the synthesized  $TiO_2$  materials and  $TiO_2$  Degussa P25 dispersed in 50 mL of a 0.04 mM solution of methylene blue (MB). The suspensions were stirred for 1 h in the dark to reach the adsorption-desorption equilibrium and to ensure that the photocatalyst surface was saturated with dye before irradiation started. Two comparative studies were conducted to determine the activity of the different photocatalysts obtained:

- The kinetic constants were calculated by measuring the absorbance of the dye solution under UV light every 10 minutes.
- 2) The MB degraded was analysed under the same reaction conditions for 1 h, measuring the absorbance at 30 min and 1 h. The % of MB degradation was calculated following equation:

% of degradation (X) = 
$$\frac{C_i - C_f}{C_i} x 100$$
 (eq. 1)

where (X) is the % of degradation and  $C_i$  and  $C_f$  are the initial and final dye concentrations, respectively. The result is given in Table 2.

The first study of  $TiO_2$  materials was carried out to determine the efficiency of the presence of fluorine through the comparison of photocatalysts  $TiO_2$ -NA-500 and F-TiO\_2-NA-500, both synthesized under the same process and calcined at the same temperature. Once it was concluded that the doped material exhibits higher photoactivity, a second study was carried out by modifying the acidic medium (HNO<sub>3</sub>) with different organic acids. In order to minimize the influencing factors, the photodegradation comparative experiments were carried out with the materials calcined at the same temperature (500 °C).

The comparation was verified that the photocatalysts **F-TiO<sub>2</sub>-NA-500** and **F-TiO<sub>2</sub>-AA-500** had the highest photoactivity, a final study was carried out with **F-TiO<sub>2</sub>-NA** and **F-TiO<sub>2</sub>-AA** series whit different calcination treatments (450 and 550 °C, giving the materials **F-TiO<sub>2</sub>-NA-450**, **F-TiO<sub>2</sub>-NA-450**, **F-TiO<sub>2</sub>-AA-550**).

All photodegradation experiments were carried out applied an UV irradiation of 370 nm and 36 W (4 × 9 W), with a reactor dimension of 10 × 22 × 24 cm (irradiation intensity of  $1.02 \cdot 10^3$  mW·cm<sup>-2</sup>).

## Detailed evaluation of the photocatalytic activity of the most active material F-TiO<sub>2</sub>-AA-550

The material with highest photocatalytic activity tested, **F-TiO<sub>2</sub>-AA-550** was studied in the degradation of concentrated solutions of organic pollutants in water using mixtures of 0.25 mM (80 ppm) of MB. All photodegradation experiments were carried out applied an UV irradiation of

370 nm and 36 W (4 × 9 W), with a reactor dimension of 10 × 22 × 24 cm (irradiation intensity of  $1.02 \cdot 10^3$  mW·cm<sup>-2</sup>).

The analysis of **F-TiO<sub>2</sub>-AA-550** was completed with the study of the radiation source influence on the photocatalytic activity. For this purpose, 10 mg or 5 mg of photocatalyst was dispersed in 20 mL of a 0.04 mM solution of MB and stirred for 1 h in the dark to reach the adsorption-desorption equilibrium. The suspensions were irradiated using a Newport Xenon UV-Light Source, 300 W Ozone Free (with an irradiation intensity of  $1.57 \cdot 10^4$  mW·cm<sup>-2</sup>), and the absorbance of the mixture measured at different times to determine the apparent kinetic constant and the degradation capacity (eq. 1). The experiment showed that the optimum catalyst quantity was 5 mg, subsequently, a recyclability study was conducted using this amount. The analysis was completed with a photodegradation study under visible light using the same irradiation system, applying a coloured-glass filter 420 nm long wave pass cut-on, to eliminate all the radiation energy below this value working using only white light. In all cases, the absorbance measurements were carried out at the maximum of MB (664 nm) using a spectrophotometer (Jenway 7315). Each experiment was performed in double triplicate.

### 5) Evaluation of kinetic parameters of F-TiO<sub>2</sub>-AA-550

For a more detailed analysis of the behaviour of **F-TiO<sub>2</sub>-AA-550** as a photocatalyst, a complete study using MB as a model pollutant was carried out. Firstly, the reaction order was investigated using the Langmuir-Hinshelwood (L-H) model [30–32]. A photocatalytic reaction proceeds through this mechanism when a linear reciprocal relationship between the reaction rate and the concentration of substrate in a solution is observed. The L-H model is described as follows:

$$\frac{1}{k} = \frac{[C]_o}{k_L} + \frac{1}{k_{LH} k_L} \quad \text{(eq. 2)}$$

Where *k* is the pseudo-first-order rate constant (s<sup>-1</sup>), [C]<sub>o</sub> is the initial concentration of MB (mM),  $k_{LH}$  presents the L-H adsorption constant of MB over **F-TiO<sub>2</sub>-AA-550** surface (mM<sup>-1</sup>), and  $k_L$  is the intrinsic reaction rate constant (mM/s). For this purpose, a series of experiments were carried out using different initial concentrations of a solution of MB (50 mL) between 0.05 and 0.02 mM using 15 mg of material.

#### 6) Evaluation of photocatalytic mechanism of F-TiO<sub>2</sub>-AA-550

To understand the potential mechanism of photodegradation of the material with the most promising activity, namely, **F-TiO<sub>2</sub>-AA-550**, different analyses about the presence of radicals generated during the process were carry out. First, the study was focused on the effect of NaCl during the photocatalytic process degradation of MB by adding 20 mg of this salt in 50 mL solution of dye (0.04 mM). [33–35] A second study was focused on the addition of 50 mL of a coumarin-

3-carboxylic acid solution (20 ppm) for the determination of activity hydroxyl radicals during the advanced oxidation process [36]. In a second study, **F-TiO<sub>2</sub>-AA-550** was applied in an alternative oxidation process. In this experiment, the aqueous medium is replaced by an organic solvent, in which the photocatalytic action will not depend on the radicals formed by the presence of H<sub>2</sub>O. The reaction (Scheme 1) was carried out under an inert atmosphere and using 5 mL N,N-dimethylformamide (DMF) freshly degassed by N<sub>2</sub> bubbling and 0.150 mL of H<sub>2</sub>O<sub>2</sub> (4.4 mmol). Before the start of the reaction, a mixture of catalyst and the solid reagents were introduced in a Schlenk tube and treated to three vacuum-nitrogen cycles to eliminate the atmospheric oxygen.



Scheme 1. Oxidation reactions applied in the photocatalytic study.

The photocatalytic studies were performed under UV irradiation of 370 nm and 36 W (using the same conditions described in the section 2.4.1.) and using 15 mg of **F-TiO<sub>2</sub>-AA-550**. The process was monitored by using a Jenway<sup>TM</sup> Model 7315 Single Beam UV/Visible Spectrophotometer in the first two cases and a gas chromatographer (GC, Perkin-Elmer Clarus 580 with FID detector and H<sub>2</sub> generator FID-Station Plus 150) in the case of the reaction carried out in DMF, in order to quantify reagents and products for the catalytic study of oxidation.

#### 7) Photocatalytic degradation of different real pollutants in water

To determine the real applicability of **F-TiO<sub>2</sub>-AA-550**, it was used for the photodegradation of common industrial pollutants such as phenol (ph-OH) and 4-chlorophenol (4-CP), and some emerging contaminants, such as the drugs ciprofloxacin (CPX) and naproxen (NPX). The long-term exposure of the organisms to these pollutants, even at low concentrations, can cause irreversible damage in humans and the environment. In all studies, 10 mg of **F-TiO<sub>2</sub>-AA-550** was dispersed in solutions (20 mg/L) of the pollutant in ultrapure water. Initially, the suspensions were stirred for 1 h in the dark to reach adsorption-desorption equilibrium. The degradation was carried out under UV-light (Newport Xenon UV-Light Source, 300 W Ozone Free) to determine the kinetic constant with concentration measurements every 15 min for phenol, every 5 min for 4-clorophenol and every 2 min for ciprofloxacin and naproxen. To determine the total degradation time, the contaminants were exposed under the same UV radiation conditions to achieve contaminant degradation above 99%. The quantification of the pollutants was carried out using UV spectroscopy with absorbance measurements at 273 nm (PhOH), 272 nm (CPX), 231 nm (NPX) and 225 nm (4-CP) using a spectrophotometer (Jenway 7315).

Subsequently, a second photocatalytic degradation study under the same lamp was carried to elucidate the efficiency of the photocatalyst using lower energy radiation such as visible

white light through the application of a coloured-glass filter 420 nm long wave pass cut-on, to eliminate all the radiation below that wavelength, with absorbance measurements performed every 30 min in all cases.

Each experiment was performed in triple duplicate. Equation 1 was used for the calculation of the % of degradation for each pollutant.

#### 8) Synthesis of Pd nanoparticles supported on TiO<sub>2</sub>

Fluorine-doped TiO<sub>2</sub> materials synthesized with different acidic media were used as supports for Pd nanoparticles in order to determine their potential ability for catalytic applications. To avoid morphological influence caused by different calcination temperatures, all materials calcined at 500 °C, were used in the comparative study. In addition, the catalytic tests were completed used the non-doped reference system TiO2-NA-500 and the F-TiO2-AA complete series calcined at different temperatures (F-TiO2-AA-450, F-TiO2-AA-500 and F-TiO2-AA-550), to determine the potential influence of the adsorption of carbon species in the surface of the material. Doping with 1% wt Pd was incorporated in all materials by reduction of an organometallic Pd(II) salt, [Pd(cod)Cl<sub>2</sub>], using a simple synthetic method described by our research group [29, 37]. The synthesis of the supported Pd-systems was carried out as follows: a solid mixture of 6.77 mg of  $[Pd(cod)Cl_2]$  and 250 mg of the TiO<sub>2</sub> material were introduced in a Schlenk tube and several vacuum/N<sub>2</sub> cycles were applied for 30 minutes. Subsequently, 10 mL of dimethylformamide freshly degassed by N<sub>2</sub> bubbling was added under inert atmosphere. The mixture was then heated at 110 °C and stirred for 3 h. The resulting grey product was centrifuged, and the isolated solid washed with DMF, ultrapure water and ethanol. The material was finally dried overnight in a stove at 80 °C.

## 9) Applications of hybrid doped TiO<sub>2</sub>-Pd nanoparticles in Suzuki-Miyaura reactions

Suzuki-Miyaura reactions of C-C coupling (Scheme 2) were carried out using a solid mixture of 25 mg of each catalytic material, 0.110 g of phenylboronic acid PhB(OH)<sub>2</sub> (0.9 mmol) and 0.124 g of K<sub>2</sub>CO<sub>3</sub> (0.9 mmol), which were introduced in a Schlenk tube. After that, three vacuum-nitrogen cycles were carried out to eliminate the adsorbed moisture and create an oxygen-free atmosphere. Subsequently, a solution of 0.084 mL (0.75 mmol) of iodobenzene (Ph-I) dissolved in 5 mL N,N-dimethylformamide (DMF), (freshly degassed by 5 min N<sub>2</sub> bubbling) was added. The reaction was stirred and heated to 110 °C, and the products was monitored at 2, 4, 8 h. The mixture was filtered, and analysed by gas chromatography (GC, Perkin-Elmer Clarus 580 with FID detector and H<sub>2</sub> generator FID-Station Plus 150) in order to quantify reagents and products. The quantification by GC-methods allowed the calculation of TON and TOF for each catalytic reaction. Finally, a recyclability study of the materials was carried out for those systems

which showed the highest activity. The catalyst obtained by centrifugation of the catalytic mixture in reactions of 4 h was used in recyclability studies under the same conditions.



Scheme 2. C-C coupling reaction of phenylboronic acid and iodobenzene.

# 10) F-TiO<sub>2</sub> synthesis product using ascorbic acid as medium at pH 2 (Figure S1)



Figure S1. F-TiO<sub>2</sub> synthesis product using ascorbic acid medium before washing and drying.

# 11) F-TiO<sub>2</sub> synthesis product using ascorbic acid pre and post calcination 550 °C (Figure S2)



Figure S2. (a) Dry F-TiO<sub>2</sub>-AA before calcination and (b) F-TiO<sub>2</sub>-AA-550 after calcination treatment 550 °C.

12) Thermogravimetric study of F-TiO<sub>2</sub>-AA material (Figure S3)



Figure S3. Thermogravimetric studie of F-TiO<sub>2</sub>-AA and F-TiO<sub>2</sub>-AA-500 material.

13) SEM images of F-TiO<sub>2</sub>-AA before and after calcination process (Figure S4)



Figure S4. SEM images of (a) F-TiO<sub>2</sub>-AA nanoparticles with rough surface caused by the presence of organic adsorbate and (b) F-TiO<sub>2</sub>-AA-500 free of surface organic load.



## 14) SEM-EDS images of F-TiO<sub>2</sub>-AA materials series (Figure S5)

Figure S5. SEM-EDS images of F-TiO<sub>2</sub>-AA, F-TiO<sub>2</sub>-AA-450 and F-TiO<sub>2</sub>-AA-500.



## 15) Ti species analysis of F-TiO<sub>2</sub>-AA calcinated materials by XPS (Figure S6)

Figure S6. High-resolution XPS spectra of F-TiO<sub>2</sub>-AA-450 and F-TiO<sub>2</sub>-AA-550 from the Ti region (Ti 2p).

## 16) Brookite phase detail in X-ray diffraction patterns of TiO<sub>2</sub>-NA-500 and F-TiO<sub>2</sub>-NA samples (Figure S7)



Figure S7. X-ray diffraction patterns of TiO<sub>2</sub>-NA-500 and F-TiO<sub>2</sub>-NA-500 samples.





Figure S8. X-ray diffraction patterns of F-TiO<sub>2</sub>-NA and F-TiO<sub>2</sub>-AA samples calcined at 450 °C, 500 °C and 550 °C.

18) Particle size distribution for materials synthesized with different acids (Figure S9)



Figure S9. Particle size distribution for materials synthesized with different acids.

19) TEM images and particle size distribution for calcinated studied materials (Figure S10)



Figure S10. TEM images and particle size distribution for calcinated F-TiO<sub>2</sub>-NA and F-TiO<sub>2</sub>-AA series.

### 20) Diffuse reflectance spectra of the synthesized F-TiO<sub>2</sub> materials (Figure S11)



Figure S11. Diffuse reflectance spectra of the synthesized  $F-TiO_2$  materials.

## 21) Images obtained by High-resolution TEM of F-TiO<sub>2</sub>-AA-550 (Figures S12)



Figure S12. High-resolution TEM images of F-TiO<sub>2</sub>-AA-550.

22) Comparative kinetic study of the photocatalytic degradation of F-TiO<sub>2</sub>-AA-550 and Degussa P25 titanium dioxide under UV-light (36 W) (Figure S13)



Figure S13. Kinetic study of the photocatalytic degradation of MB between the material F-TiO<sub>2</sub>-AA-550 and Degussa P25

# 23) Study of the kinetic of the photocatalytic degradation of MB (0.25 mM) with $F-TiO_2$ -AA-550 under UV-light (36 W) (Figure S14)



Figure S14. Study of the kinetic of the photocatalytic degradation of MB (0.25 mM) under UV-light (36W) with  $F-TiO_2-AA-550$ .

# 24) Study of kinetics comportment of F-TiO<sub>2</sub>-AA-550 under UV-light (300 W) (Figure S15)



**Figure S15.** (a) Solution of MB (0.04 mM) after 15 min with **F-TiO<sub>2</sub>-AA-550** (5 mg and 10 mg) and (b) Study of the kinetics and recyclability of the photocatalytic degradation of MB under UV-light (300 W).

# 25) Study of the kinetic of the photocatalytic degradation of MB (0.04 mM) under visible light (300 W) with F-TiO<sub>2</sub>-AA-550 (Figure S16)



Figure S16. Kinetic photodegradation of MB in visible light (300 W) with 5 mg or 10 mg of F-TiO<sub>2</sub>-AA-550
26) Study of the possible kinetic mechanism of the photocatalytic degradation of MB (0.04 mM) with F-TiO<sub>2</sub>-AA-550 (Figure S17)



**Figure S17. (a)** Study of the kinetic photodegradation of MB under UV-light (36W) with **F-TiO<sub>2</sub>-AA-550** using 20 mg of NaCl and **(b)** study of the influence of radicals <sup>-</sup>OH in the transformation of coumarin-3-carboxylic acid.

27) High-resolution TEM images of F-TiO<sub>2</sub>-AA-450-Pd (Figure S18)



Figure S18. High-resolution TEM images to determinate the present of Pd in F-TiO<sub>2</sub>-AA-450-Pd sample.

### 28) Spectrum of High-resolution TEM-EDS F-TiO<sub>2</sub>-AA-450-Pd (Figure S19)



Figure S19. Spectrum of High-resolution TEM-EDS F-TiO<sub>2</sub>-AA-450-Pd. The presence of Cu is due to the composition of the sample holder

### 29) SEM-EDS images of F-TiO<sub>2</sub>-AA-450-Pd (Figure S19)



Figure S20. SEM-EDS images of F-TiO2-AA-450-Pd and mapping of Pd (orange).

# 30) Composition of different F-TiO<sub>2</sub>-AA materials determined by XPS (Table S1)

Table S1. Atomic composition and binding energies of different F-TiO<sub>2</sub>-AA materials determined by XPS.

Material	Core level	Binding Energy (eV)	Atomic (%)
	C 1s	284.80	79.95
	Ti 2p	458.99	0.32
F-1102-AA	O 1s	532.99	19.74
	F 1s	-	-
	C 1s	284.80	21.72
E-TIO 0 0-450	Ti 2p	458.53	25.79
F-1102-AA-450	O 1s	529.73	52.46
	F 1s	684.03	0.03
	C 1s	284.80	17.94
E-TIO A A-500	Ti 2p	458.52	27.12
1-110 <sub>2</sub> -AA-300	O 1s	529.82	54.31
	F 1s	683.62	0.63
	C 1s	284.80	17.82
F-TiO00-550	Ti 2p	458.51	25.95
1-1102-AA-JJU	O 1s	529.71	54.49
	F 1s	683.91	1.74

31) Recyclability study for F-TiO<sub>2</sub>-AA-500-Pd material at 4h (Table S2)

<b>F-TiO₂-AA-550</b> UV-light (36W)	k (s⁻¹)	Adsorption (%)	Degradation 30' (%)	Degradation 1h (%)
Without NaCl	9.7·10 <sup>-4</sup>	17	89	98
20 mg NaCl	4.7·10 <sup>-4</sup>	11	53	82
[MB] <sub>o</sub> (0.25 mM)	8.1·10 <sup>-5</sup>	14	28	46

Table S2. Evaluation of kinetic parameters of  $F-TiO_2-AA-550$  under UV-light (36W)

# 32) Suzuki-Miyaura coupling reaction results using titanium dioxide-based materials as catalysts (Table S3)

Table S3.	Suzuki-Miyaura	coupling	reaction results	s using titanium	dioxide-based	materials as catal	ysts.
	3						-

Reaction time	8h						
Materials	Conv. (%)	Yield (%)	TON <sup>a</sup>	TOF (h <sup>-1</sup> )			
F-TiO <sub>2</sub> -NA-500-Pd	89	28	90	11			
F-TiO <sub>2</sub> -AA-450-Pd	98	45	145	18			
F-TiO <sub>2</sub> -AA-500-Pd	94	38	123	15			
F-TiO <sub>2</sub> -AA-550-Pd	87	30	96	12			
F-TiO <sub>2</sub> -CA-500-Pd	71	27	85	11			
F-TiO <sub>2</sub> -SA-500-Pd	51	23	73	9			
F-TiO <sub>2</sub> -BA-500-Pd	76	25	79	10			

<sup>a</sup>Referred to 1% theoretical Pd.

# 33) ICP Analysis of the palladium content in the catalyst F-TiO<sub>2</sub>-AA-450-Pd (Table S4)

F-TiO₂-AA-450-Pd	Pd (% in mass)	Pd (ppm)		
Catalyst (solid)	0.83	8.27 ± 0.04		

Table S4. ICP Analysis of the Pd content in the catalyst  $F-TiO_2-AA-450-Pd$ .

### Experimental procedure for ICP analysis

For quantification of the palladium content, the functionalized materials were digested. Each material (25 mg) was suspended in 8 mL of a mixture of HCl and HNO<sub>3</sub> (1:3 v/v) The solution was kept under vigorous stirring for 72 h. The resulting solution was centrifuged (6000 rpm, 10 min), filtered through a nylon filter (0.2  $\mu$ m), and analyzed directly by inductively coupled plasma atomic emission spectroscopy in triplicate with a Varian Vista AX Pro ( $\lambda_{Pd}$  = 340.458 nm) instrument. The palladium content was determined upon comparison with a palladium standard solution.

## 34) Recyclability for F-TiO<sub>2</sub>-AA calcinated series material at 4h (Table S5)

 Table S5.
 Study of the catalytic activity and recyclability of the synthesized titanium dioxide materials in

 Suzuki-Miyaura C-C coupling of phenylboronic acid PhB(OH)<sub>2</sub> with iodobenzene (Ph-I) in 5 consecutive reaction cycles.

Reaction time 4h	Fresh		R <sub>1</sub>		R <sub>2</sub>		R <sub>3</sub>		R <sub>4</sub>	
Materials	Conv. (%)	Yield (%)	Conv. (%)	Yield (%)	Conv. (%)	Yield (%)	Conv. (%)	Yield (%)	Conv. (%)	Yield (%)
F-TiO <sub>2</sub> -AA-450-Pd	92	41	84	36	79	27	69	21	63	17
F-TiO₂-AA-500-Pd	88	32	69	28	63	22	56	17	50	14
F-TiO₂-AA-550-Pd	71	27	61	23	54	17	49	14	43	10