# Electronic Supplementary Information

## *Evidence of Upconversion Luminescence Contribution to the Improved Photoactivity of Erbium doped $TiO_2$ System*

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## Experimental details.

### *Synthesis of Photocatalysts.*

$TiO_2$ sample was obtained by means of a hydrothermal method elsewhere described. In brief, a $TiO_2$ colloidal solution was obtained by adding certain amount of $Ti^{4+}$-isopropanol solution (38,4 ml of *TTiP* + 38,2 ml of isopropanol) to 400 ml of distilled water at pH=2 achieved by means of acetic acid. After *TTiP* addition a white precipitate is obtained that upon stirring at room temperature for one week evolve to a milky homogeneous solution. A certain amount of triethylamine (*TEA*) was then added drop wise to the Ti-solution aliquot till the pH value was 9. Afterwards, the obtained white precipitate suspension was then placed in a Teflon recipient inside of stainless steel autoclave reactor. The hydrothermal treatment was performed at 140ºC, 20 hours. The as obtained precipitate was then filtered, repeatedly washed and dried overnight at 120ºC. Then $TiO_2$ powder was submitted to a further calcination treatment at 300ºC for 2 hours.

Erbium doped $TiO_2$ were obtained based on the above described methods for the preparation of single pristine photocatalysts. Thus, to the $TiO_2$ solution the appropriate amount of $Er(NO_3)_3$ was added in order to accomplish the desired $Er^{3+}$-$TiO_2$ relationship (0,5, 1, 2, 3 and 4 at.%). Then, similar procedure is followed to achieve to the final composite photocatalyst.

### *Materials characterization.*

BET surface area and porosity measurements were carried out by $N_2$ adsorption at 77 K using a Micromeritics 2010 instrument.

X-ray diffraction (XRD) patterns were obtained using a Siemens D-501 diffractometer with Ni filter and graphite monochromator. The X-ray source was Cu Kα radiation (0,15406 nm). Rietveld analyses were performed by using XPert HighScore Plus software over selected samples. The diffraction patterns were recorded from 2θ 10º to 120º with step of 0,017º and 400 s per step.

Micro-Raman measurements were performed using a LabRAM Jobin Yvon spectrometer equipped with a microscope. Laser radiation (λ = 532 nm or 780 nm) was used as excitation source at 5 mW. All measurements were recorded under the same conditions (2 s of integration time and 30 accumulations) using a 100x magnification objective and a 125 mm pinhole.

The morphology of the samples and the dispersion and size of surface metal deposits were studied by transmission electron microscopy (TEM) using a Philips CM 200 instrument. The microscope was equipped with a top-entry holder and ion pumping system, operating at 200 kV and employing a nominal structural resolution of 0.21 nm. Samples were prepared by dispersing the powders in ethanol using ultrasound and dropping onto a carbon grid.

UV–vis spectra (Shimadzu, AV2101) were recorded in the diffuse reflectance mode (R) and transformed to a magnitude proportional to the extinction coefficient (K) through the Kubelka–Munk function, $F(R\infty)$. Samples were mixed with $BaSO_4$ that does not absorb in the UV–vis radiation range (white standard). Scans range was 240–800 nm.

XPS data were recorded on 4x4 $mm^2$ pellets, 0,5 mm thick, prepared by slightly pressing the powered materials which were outgassed in the prechamber of the instrument at room temperature up to a pressure $< 2 \cdot 10^{-8}$ to remove chemisorbed water from their surfaces. The SPECS spectrometer main chamber, working at a pressure $< 6 \cdot 10^{-9}$ torr, was equipped with a PHOIBOS 100 multichannel hemispherical electron analyser with a dual X-ray source working with Al Kα (hν=1486,6 eV) at 120 W, 20 mA using C 1s as energy reference (284,6 eV). Surface chemical compositions were estimated from XP-spectra, by calculating the integral of each peak after subtraction of the "S-shaped" Shirley-type background using the appropriate experimental sensitivity factors using UNIFIT 2012 software.[†]

*Photocatalytic Experimental Details.*

Phenol oxidation reactions were performed using a batch reactor (250 ml) using an arc lamp source (Oriel Instruments) equipped with an Hg-Xe lamp of 200 W. The intensity of the incident UVA and visible light on the solution was measured with an HD2302 photometer (Delta OHM) using LP 471 UVA and LP 471 RAD sensors (spectral responses 315-400 nm and 400-1050 nm respectively). The intensity of the lamp under different irradiation conditions is summarised in **Table 1**. In the oxidation tests, an oxygen flow was employed what produces a homogenous suspension of the catalyst in the solution. Before each experiment, the catalysts (1 g/l) were settled in suspension with the reagent mixture for 15 min. The evolution of the initial phenol concentration (ca. 30 ppm) was followed through the evolution of the characteristic 270 nm band using a centrifuged aliquot ca. 2 ml of the suspension (microcentrifuge Minispin, Eppendorf). In order to distinguish the different contributions of the different ranges of the lamp spectrum, *UV-vis-NIR*, *visible-NIR* and *visible* photocatalytic experiments were performed by using a *UV* and *IR* cut-off filters (λ<420 nm and λ>800 nm respectively). Additionally, for *vis-*

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[†] Hesse, R.; UNIFIT FOR WINDOWS: Spectrum Processing, Analysis and Presentation Software for Photoelectron Spectra, Version 2012, Leipzig http://www.unifit-software.de.

*NIR* experiments, the degradation of methylene blue (ca. 10 ppm of *MB* and 1 g/l catalysts loading) was followed through the evolution of the characteristic 664 nm. Reaction rates were calculated assuming a zero order kinetic.

# Tables.

**Table 1.** Lamp irradiance (W/m$^2$) under different conditions.

| **Luxometer sensor** | ***UV-vis-IR*** | ***UV-vis*** | ***vis-IR*** | ***vis*** |
|---|---|---|---|---|
| **LP471 UVA** (315-400 nm) | 124 | 74 | 0.3 | 0.3 |
| **LP471 RAD** (400-1050 nm) | 542 | 209 | 482 | 163 |

**Table 2.** Surface, structural and photocatalytic characterization for $Er^{3+}$ doped $TiO_2$ catalysts.

| **Samples** | **Crystallite size (nm)** | **BET ($m^2/g$)** | **Average pore size (nm)** | **Band gap (eV)** | **$Er^{3+}$ content (%)** | |
|---|---|---|---|---|---|---|
| | | | | | **EDX** | ***XPS*** |
| $TiO_2$ | 15,8 | 102 | 8,7 | 3,16 | --- | --- |
| Er-$TiO_2$ 0,5% | 14,6 | 110 | 9,5 | 3,16 | --- | 0,4 |
| Er-$TiO_2$ 1% | 14,0 | 110 | 10,9 | 3,18 | 1,2 | 0,9 |
| Er-$TiO_2$ 2% | 14,1 | 110 | 11,1 | 3,18 | 1,9 | 1,8 |
| Er-$TiO_2$ 3% | 12,8 | 112 | 12,2 | 3,18 | 2,7 | 2,8 |
| Er-$TiO_2$ 4% | 12,1 | 116 | 12,5 | 3,20 | 4,0 | 3,7 |

**Table 3.** Photocatalytic reaction rates for phenol and methylene blue degradation by $Er^{3+}$ doped $TiO_2$ catalysts under different irradiation conditions.

| **Samples** | ***k*** ($\cdot 10^{-10}$ mol/l$\cdot$s$^{-1}$) | | | ***k* *** ($\cdot 10^{-11}$ mol/l$\cdot$s$^{-1}$) |
|---|---|---|---|---|
| | ***UV-vis-IR*** | ***UV-vis*** | ***vis-IR*** | ***vis-IR*** |
| $TiO_2$ | 3,78 | 1,47 | 0,065 | 1,80 |
| Er-$TiO_2$ 0,5% | 3,97 | 1,64 | ------- | 2,78 |
| Er-$TiO_2$ 1% | 4,75 | 2,36 | 0,173 | 4,71 |
| Er-$TiO_2$ 2% | 6,13 | 2,57 | 0,404 | 8,60 |
| Er-$TiO_2$ 3% | 5,94 | 2,49 | 0,302 | 6,32 |
| Er-$TiO_2$ 4% | 4,89 | 2,20 | 0,260 | 4,78 |

* *Degradation of methylene blue.*

**Figure S1.** Raman spectra for $Er^{3+}$-$TiO_2$ catalysts obtained at pH=9 after hydrothermal treatment at 140ºC, 20h.

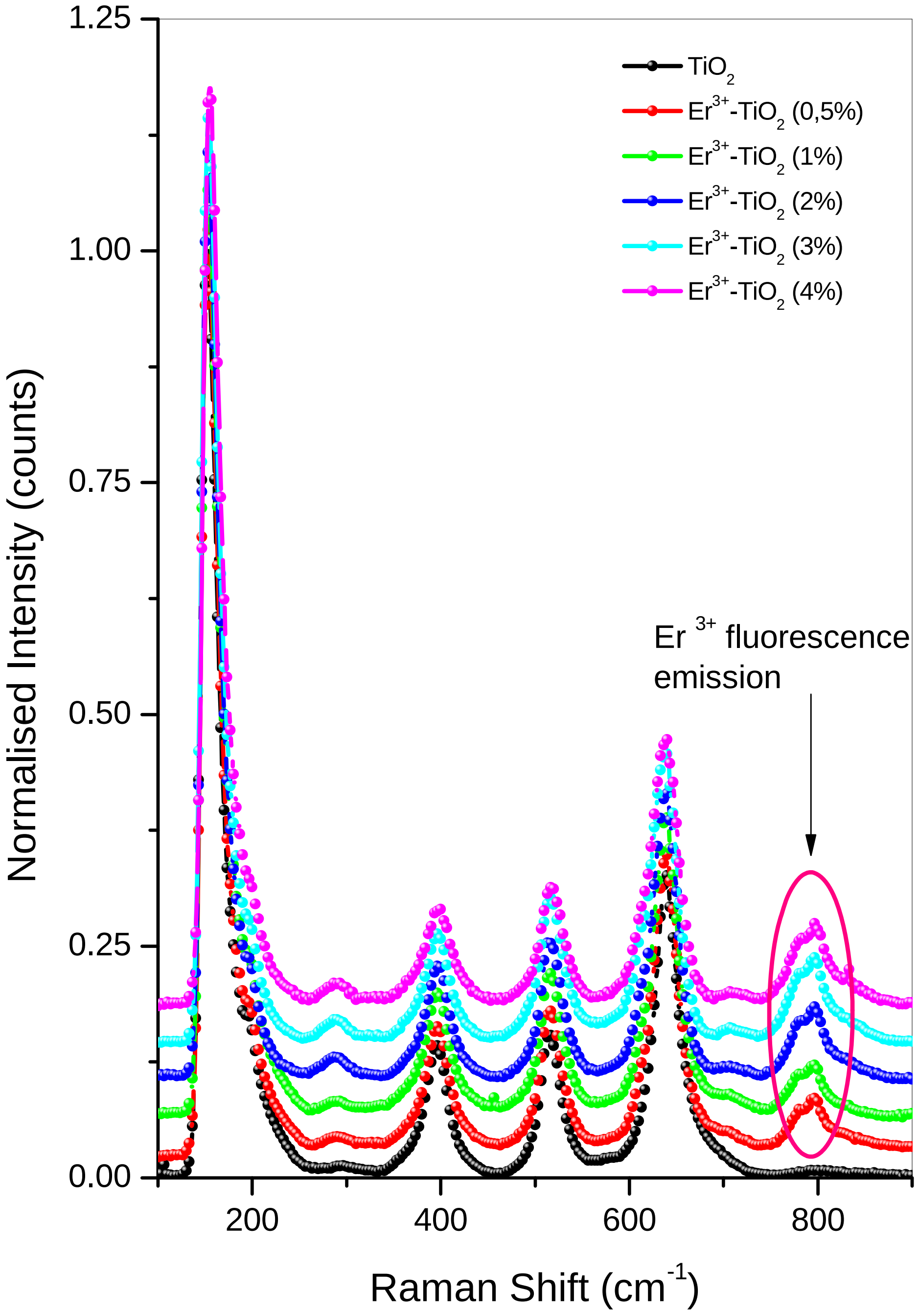

**Figure S2.** TEM images of a) $TiO_2$, b) $Er^{3+}$-$TiO_2$ 2 at% and c) $Er^{3+}$-$TiO_2$ 4 at% catalysts obtained at pH=9 after hydrothermal treatment at 140ºC, 20h.