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## Short Communication

Low-frequency ultrasound induces oxygen vacancies formation and visible light absorption in TiO<sub>2</sub> P-25 nanoparticlesPaula A. Osorio-Vargas<sup>a</sup>, Cesar Pulgarin<sup>a</sup>, Andrzej Sienkiewicz<sup>b</sup>, Luis R. Pizzio<sup>c</sup>, Mirta N. Blanco<sup>c</sup>, Ricardo A. Torres-Palma<sup>d</sup>, Christian Pétrier<sup>e</sup>, Julián A. Rengifo-Herrera<sup>c,\*</sup><sup>a</sup> SB-ISIC-GGEC, Station 6, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland<sup>b</sup> SB-IPMC-LPMC, Station 3, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland<sup>c</sup> Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J.J. Ronco", CINDECA, Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT, La Plata, CONICET, Calle 47 No. 257, 1900 La Plata, Buenos Aires, Argentina<sup>d</sup> Instituto de Química, Facultad de Ciencias Naturales y Exactas, Universidad de Antioquia, A.A. 1226, Medellín, Colombia<sup>e</sup> Laboratoire de Rhéologie et Procédés, Université Joseph Fourier, BP 53, 38041 Grenoble, France

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## ABSTRACT

Low-frequency ultrasound (LFUS) irradiation induces morphological, optical and surface changes in the commercial nano-TiO<sub>2</sub>-based photocatalyst, Evonik–Degussa P-25. Low-temperature electron spin resonance (ESR) measurements performed on this material provided the first experimental evidence for the formation of oxygen vacancies ( $V_o$ ), which were also found responsible for the visible-light absorption. The  $V_o$  surface defects might result from high-speed inter-particle collisions and shock waves generated by LFUS sonication impacting the TiO<sub>2</sub> particles. This is in contrast to a number of well-established technologies, where the formation of oxygen vacancies on the TiO<sub>2</sub> surface often requires harsh technological conditions and complicated procedures, such as annealing at high temperatures, radio-frequency-induced plasma or ion sputtering.

Thus, this study reports for the first time the preparation of visible-light responsive TiO<sub>2</sub>-based photocatalysts by using a simple LFUS-based approach to induce oxygen vacancies at the nano-TiO<sub>2</sub> surface. These findings might open new avenues for synthesis of novel nano-TiO<sub>2</sub>-based photocatalysts capable of destroying water or airborne pollutants and microorganisms under visible light illumination.

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## 1. Introduction

Heterogeneous photocatalysis with using TiO<sub>2</sub> seems to be a promising technology to eliminate water-borne pollutants and pathogen microorganisms [1–3]. The main drawback of TiO<sub>2</sub> as a photocatalyst is related to the band energy gap of 3.0 eV and 3.2 eV, for rutile and anatase, respectively. This limits practical applications of TiO<sub>2</sub> to the ultraviolet light portion, accounting only for ~4–7% of the total solar light energy and being much smaller than the visible light portion (~45% of the total solar energy).

Recently, multiple efforts have been undertaken to extend the TiO<sub>2</sub> absorption towards the visible wavelengths. Doping of TiO<sub>2</sub> nano-particles with metallic or non-metallic elements have been extensively studied on the literature [4,5]. However, there is increasing evidence that these materials might not achieve

suitable photocatalytic properties since they yield valence band holes and/or reactive oxygen species with too low oxidation potentials [6,7].

Another possible strategy to prepare visible light-response TiO<sub>2</sub> is creating oxygen vacancies [8] ( $V_o$ ) through very expensive and complicated procedures such as annealing at high temperatures under reductive atmospheres, RF plasma treatment and magnetron sputtering [9–11]. Therefore, finding novel routes to prepare visible light-responsive TiO<sub>2</sub> is today an important scientific and technological challenge.

Low- or high-frequency ultrasound irradiation has been often used to prepare via sol-gel synthesis, well crystallized and dispersed meso-structured TiO<sub>2</sub> materials, to deposit metal particles on TiO<sub>2</sub> surfaces or simply to destroy water-borne organic pollutants [12–15].

Here, we report for the first time, the preparation of visible light absorbing Degussa–Evonik P-25 TiO<sub>2</sub> nano-particles by a very simple method consisting of using low-frequency ultrasound (LFUS) irradiation, without the necessity of adding any organic or inorganic precursor.

\* Corresponding author. Tel./fax: +54 221 4211353x125.

E-mail address: [julianregifo@quimica.unlp.edu.ar](mailto:julianregifo@quimica.unlp.edu.ar) (J.A. Rengifo-Herrera).

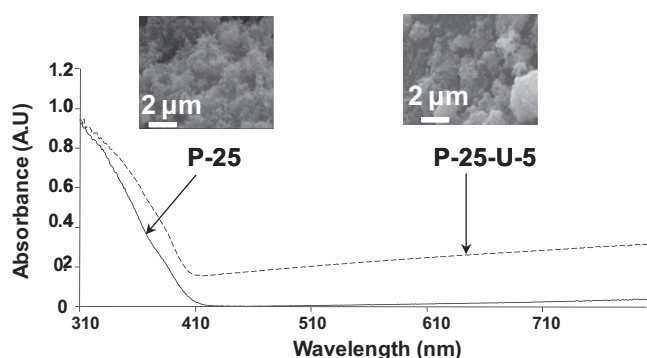


Fig. 1. DRS spectra and SEM images (inserts) of sonicated and non-sonicated P-25 powders.

## 2. Experimental section

### 2.1. Preparation of visible-light responsive $\text{TiO}_2$ by low-frequency ultrasound (LFUS) irradiation

Slurries of Degussa–Evonik P-25 powder (composed of anatase rutile in a ratio 70:30, respectively and having the specific surface area of  $50 \text{ g m}^{-2}$ ) containing  $5 \text{ g L}^{-1}$  were dispersed in 15 mL of ultra-pure water (Milli Q-Water). Then, these slurries were added to the ultrasonic bath consisting of a direct-immersion ultrasonic horn operating at 20 kHz with an acoustic intensity of  $1.2 \text{ W mL}^{-1}$ , immersed in a double-walled Pyrex-glass reactor, with circulating water to provide temperature stabilization.  $\text{TiO}_2$  slurries were exposed to LFUS irradiation during 6 h. Finally, powders were filtered using Millipore membranes ( $0.22 \mu\text{m}$ ) and dried at  $60^\circ\text{C}$  during 24 h.

### 2.2. Morphological, optical and surface characterization

#### 2.2.1. Scanning electron microscopy (SEM)

Electron micrographs of the samples were obtained by scanning electron microscopy (SEM), using Philips Model 505 equipment.

#### 2.2.2. Diffuse reflectance spectroscopy (DRS)

The diffuse reflectance spectra (DRS) of the materials were recorded in the 250–800 nm wavelength range by using an

UV–Visible Lambda 35, PerkinElmer spectrophotometer, to which a diffuse reflectance chamber Labsphere RSA-PE-20, with an integrating sphere of 50 mm in diameter and internal Spectralon coating, was attached.

#### 2.2.3. X-ray photoelectron spectroscopy (XPS)

XPS analyses were carried out on a XPS Analyzer Kratos model Axis Ultra with a monochromatic  $\text{AlK}\alpha$  and charge neutralizer.

The deconvolution software program was provided by the manufacturer of the XPS instrument (Kratos).

All the binding energies were referenced to the  $\text{C1s}$  peak at 285 eV of adventitious carbon. Powder samples were prepared by deposition of catalyst on carbon type stuck to sample holder.

#### 2.2.4. Low-temperature electron spin resonance (ESR)

Low-temperature continuous wave (cw) ESR measurements were carried out with a Bruker ESR spectrometer E500 EleXsys Series (Bruker Biospin GmbH) equipped with a Gunn diode-based microwave bridge (model SuperX), a Bruker ER 4122 SHQE cavity and an Oxford Instruments Helium-gas continuous flow cryostat (ESR900). The 100 kHz modulation amplitude was kept at 2 G (0.2 mT) to avoid modulation broadening. The deoxygenated samples were prepared by directing a stream of helium gas directly into the ESR capillary for ca. 30 min prior to performing ESR measurements.

## 3. Results and discussion

SEM micrographs (inserts to Fig. 1) show that P-25 powders underwent morphological changes evidenced by an important particle aggregation after the ultrasonic treatment. Besides, surprisingly, Fig. 1 reveals also changes in photo-optical properties, which were detected by DRS measurements. P-25-U-5 powder up showed grayish color, which remained stable even after 4 months of aging under exposure to air. Moreover, a marked absorption of visible light in the range 400–700 nm was detected.

Survey XPS spectrum (Fig. 2) revealed that sample P-25-U-5 contains Ti, O, C and Na, this later coming from the Pyrex glass reactor. High resolution XPS spectra (Fig. 3) showed Ti 2p signals at 458 eV and 464 eV and O 1s at 530 eV typical of  $\text{TiO}_2$  [8]. No new XPS signals were found but however XPS Ti 2p and O 1s peaks reveal broadening and decreasing of their intensities after the

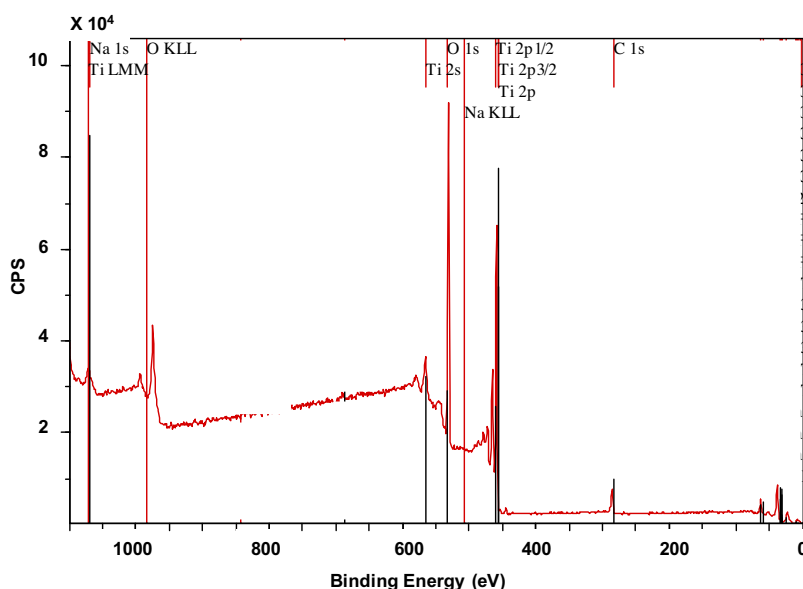


Fig. 2. XPS survey spectrum of P-25-U-5 sample.

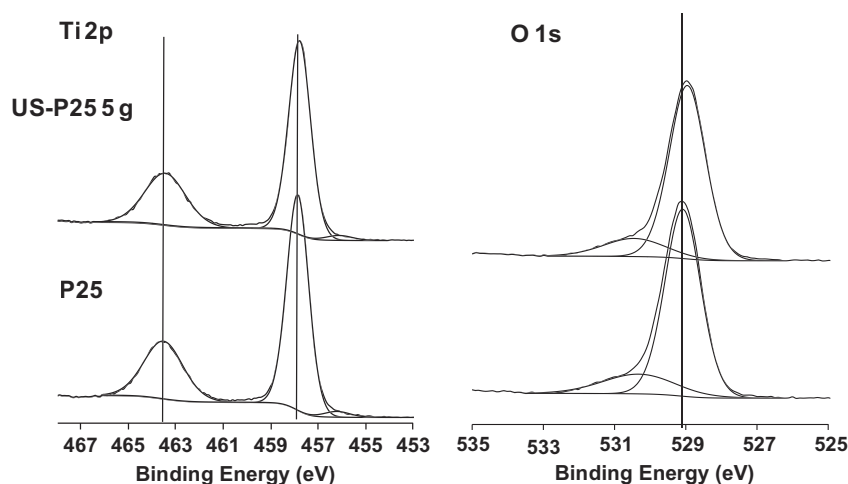


Fig. 3. O 1s and Ti 2p XPS high-resolution spectra of ultrasound treated and no treated P-25 powders.

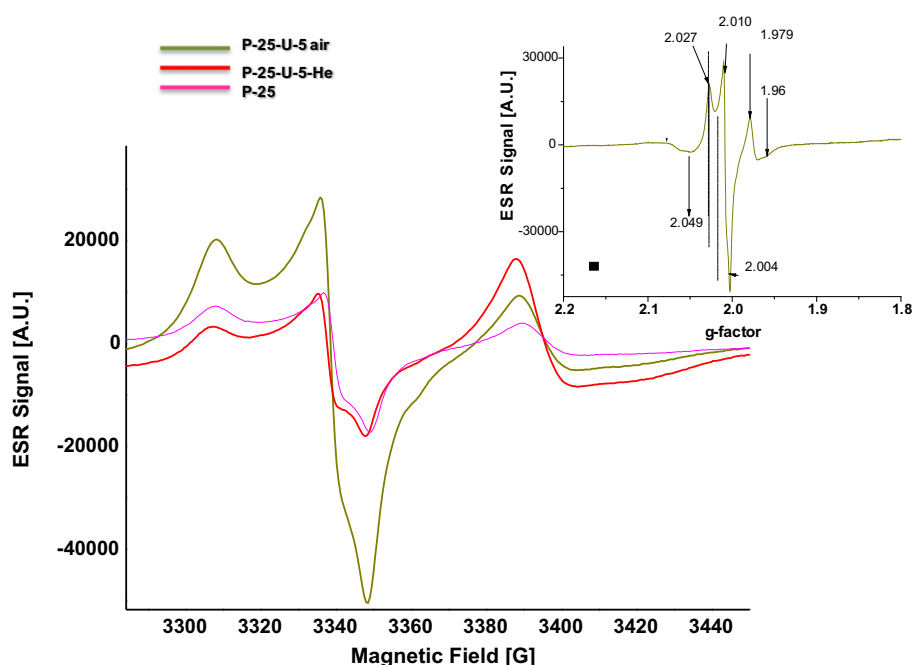


Fig. 4. Low-temperature ESR spectrum of sonicated (P25-U-5) and non-sonicated P25 powders in the presence of air or helium.

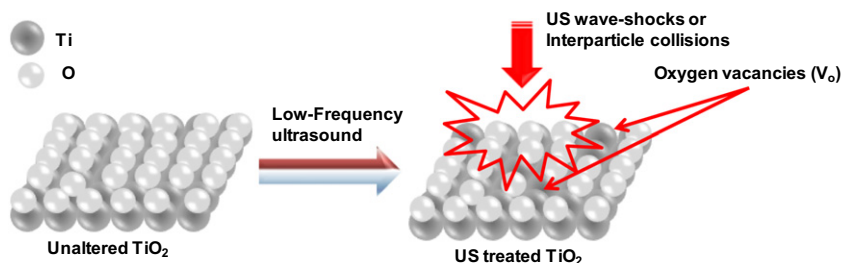


Fig. 5. Scheme suggesting the formation of oxygen vacancies induced by low-frequency ultrasound.

ultrasonic treatment, indicating possible surface changes [9]. Low-temperature ESR spectra of P-25 and P-25-U-5 powders (Fig. 4) acquired at 10 K and in presence of  $O_2$  from the air, showed pronounced resonant features at magnetic fields of 3300–3350 G

and around 3390 G. For P-25-U-5 powders, both ESR signals were sensible to exposure to oxygen from the air or helium. In particular, the ESR features in the field range of 3300–3350 G strongly increased in presence of oxygen and subsequently decreased in

presence of helium. In contrast, the ESR signal at 3390 G showed an opposite behavior. For P-25-U-5 material, as shown in insert to Fig. 3, signals with characteristic  $g$ -factors values of 2.027, 2.010 and 2.004, were identified in the field range of 3300–3350 G. The ESR feature at 3390 G had the characteristic  $g$ -factor values of 1.96 and 1.979.

Signals with  $g$ -factors values  $>2$  (ESR features in the field range 3320–3340 G) were previously observed both in rutile and anatase  $\text{TiO}_2$  [16,17] and can be ascribed to superoxide radicals ( $\text{O}_2^-$ ) adsorbed and stabilized on  $\text{Ti}^{4+}$  centers or oxygen vacancies ( $V_o$ ). On the other hand, signals with  $g$ -factors of 1.96 and 1.979 match well with  $\text{Ti}^{3+}$  centers [18,19].

We suggest that LFUS, which is well known for being capable of producing physical effects in solid–liquid interfaces [20,21], might also be responsible for morphological, optical and surface changes in nano- $\text{TiO}_2$  such as particle aggregation, visible light absorption and  $V_o$  formation on  $\text{TiO}_2$  nano-particles. This is mainly due to the fact that ultrasound can generate high speed inter-particle collisions (responsible for particle aggregation) and shock waves which can impact on semiconductor surface and produce surface damage responsible of  $V_o$  formation [22] (Fig. 5). Some of these  $V_o$  might be stabilized by molecular oxygen adsorption yielding superoxide radicals trapped on  $\text{TiO}_2$ . Oxygen vacancies induce the creation of localized states into  $\text{TiO}_2$  band gap at 0.75 eV and 1.18 eV below its conduction band, allowing its visible light absorption [23].

#### 4. Conclusions

Preparation of visible light absorbing Degussa–Evonik P-25  $\text{TiO}_2$  nano-particles was achieved by a very simple method consisting of using low-frequency ultrasound irradiation (LFUS), without the necessity of adding any organic or inorganic precursor. Morphological changes of P-25 nano-particles were evidenced by SEM micrographs. Moreover, low temperature ESR measures showed the presence of oxygen vacancies ( $V_o$ ) on the ultrasonic-treated powders. The  $V_o$  species could be responsible of visible light absorption.

It is suggested that low-frequency ultrasound could induce morphological, optical and surface changes, such as particle aggregation, visible light absorption and  $V_o$  formation on P-25  $\text{TiO}_2$  nano-particles, mainly due to the generation of high speed inter-particle collisions (responsible for particle aggregation) and shock waves which impact on semiconductor surface and produce surface damage responsible of  $V_o$  formation.

In spite of these encouraging results, further efforts are necessary (1) to better control the process of oxygen vacancies ( $V_o$ ) formation by low-frequency ultrasonic irradiation, and (2) to study the stability these modified powders and to evaluate their photocatalytic activity under visible light irradiation.

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