Short Communication

Low-frequency ultrasound induces oxygen vacancies formation and visible light absorption in TiO₂ P-25 nanoparticles

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A B S T R A C T

Low-frequency ultrasound (LFUS) irradiation induces morphological, optical and surface changes in the commercial nano-TiO₂-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 (Vₒ), which were also found responsible for the visible-light absorption. The Vₒ surface defects might result from high-speed inter-particle collisions and shock waves generated by LFUS sonication impacting the TiO₂ particles. This is in contrast to a number of well-established technologies, where the formation of oxygen vacancies on the TiO₂ 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 TiO₂-based photocatalysts by using a simple LFUS-based approach to induce oxygen vacancies at the nano-TiO₂ surface. These findings might open new avenues for synthesis of novel nano-TiO₂-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 TiO₂ seems to be a promising technology to eliminate water-borne pollutants and pathogen microorganisms [1–3]. The main drawback of TiO₂ 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 TiO₂ 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 TiO₂ absorption towards the visible wavelengths. Doping of TiO₂ 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 TiO₂ is creating oxygen vacancies [8] (Vₒ) 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 TiO₂ 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 TiO₂ materials, to deposit metal particles on TiO₂ 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 TiO₂ 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.
2. Experimental section

2.1. Preparation of visible-light responsive TiO₂ 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 g m⁻²) containing 5 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 W mL⁻¹, immersed in a double-walled Pyrex-glass reactor, with circulating water to provide temperature stabilization. TiO₂ slurries were exposed to LFUS irradiation during 6 h. Finally, powders were filtered using Millipore membranes (0.22 µm) and dried at 60°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 AlKα 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 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 TiO₂ [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
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 O₂ 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

![Graph 1](image1.png)

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

![Graph 2](image2.png)

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

![Diagram](image3.png)

**Fig. 5.** Scheme suggesting the formation of oxygen vacancies induced by low-frequency ultrasound.
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 TiO₂ [16,17] and can be ascribed to superoxide radicals (O₂⁻) adsorbed and stabilized on Ti⁴⁺ centers or oxygen vacancies (V_o). On the other hand, signals with g-factors of 1.96 and 1.979 match well with Ti⁴⁺ 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-TiO₂ such as particle aggregation, visible light absorption and V_o formation on TiO₂ 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 TiO₂. Oxygen vacancies induce the creation of localized states into TiO₂ 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 TiO₂ 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 ultrasonically-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 TiO₂ 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 of these modified powders and to evaluate their photocatalytic activity under visible light irradiation.

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