Hierarchical nano ZnO-micro TiO₂ composites: high UV protection yield lowering photodegradation in sunscreens

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Abstract

TiO₂ is a commonly used semiconductor photocatalyst but, as a paradox, it is also widely used as UV filter in sunscreens. Moreover, its capacity to form free radicals under UV irradiation generates reactive free radicals that provoke sunscreens degradation. In this work a hierarchical composite made of ZnO nanoparticles anchored onto TiO₂ microparticles is developed in a safe-by-design way by using the sol-gel method. The aim of this composite is to gain the advantages of inorganic nanoparticles avoiding their potential drawbacks. The hierarchical composite presents higher UV absorption than the pure TiO₂ or ZnO counterparts. The functional stability study on standard sunscreen reveals a 50% high Solar Protection Factor (SPF) values over time for the hierarchical composite lowering the photodegradation of the formulation. Under authors' knowledge, it is the first time that the combination of these oxides increases the UV attenuation as inhibits the negative effects of free radicals. The high UV absorption without degradation opens a new orientation for the effective use of UV-absorbers without the photocatalyst adverse effects. The results in sunscreens generate a proposed mechanism of functionality that explains the observed differences on the efficiency of photocatalytic activity of these materials for other application fields.

Keywords: TiO₂, ZnO, composite, high UV yield, free radicals

1. Introduction

Photocatalytic semiconductor nanoparticles are being studied for a wide range of applications including water treatment, dye-sensitized solar cells, photoelectronic devices and self-cleaning surfaces [1,2]. TiO₂ nanoparticles, the most commonly used engineered nanomaterial, are found in numerous industrial products and applications [3]. ZnO is also widely studied for its photocatalytic ability and it is used in several commercial applications [4]. It is established that ZnO-TiO₂ coupling achieves a more efficient separation of photogenerated electron-hole pairs [5]. This, in turn, leads to an improvement on the photocatalytic activity, resulting from a synergic effect. For instance, it is mentioned that probably ZnO grafted on titanium nanotubes acts as surface-interface shallow traps that favor the suppression of electron-hole pairs [6]. In addition, it is demonstrated that ZnO/TiO₂ heterostructure shows enhanced separation efficiency of photoexcited charge carriers when they are compared by themselves. [7]

Because of the growing of the volume of TiO₂ and ZnO nano-particles, there is a concern over their massive release into the environment and possible health problems. The reason are that as semiconductor materials, they produce free radicals and reactive oxygen species (ROS) when are irradiated, which are implicated in a number of potential environmental problems [8]; when they are present into human body in form of nanoparticles could provoke health issues, such as DNA damage [9].

Both oxides act as inorganic UV blockers, so they are used into sunscreens in order to protect the skin, but the effective degradation of organic substances by the photocatalyst effect is contrary to applications in which the matrix must be preserved as paints, paper, plastics or cosmetics. In these cases, a proposed solution consists of doping trap centers into TiO₂ and ZnO, resulting in the elimination of free radicals generation and ROS [4]. Also, the aggregation of metal oxide nanoparticles has been found to decrease the photocatalytic properties in the generation of the mentioned species [5,10].

Nowadays, sunscreens are formulated by using TiO₂ nanoparticles and ZnO nanoparticles because they are more efficient inorganic UV filters than microparticles [11]. The UV attenuation results from both reflection and scattering of UV radiation and visible light. The high yield of UV light absorption of TiO₂ and ZnO is attributed to the high efficiency of generation, mobility, and separation of photoinduced electrons and holes [12,13]. The use of nanoparticles instead of microparticles is regarding to both the UV attenuation and sunscreen properties. In fact, micro-sized TiO₂ and ZnO have been increasingly replaced by TiO₂ and ZnO nanoparticles in order to solve the cosmetic drawback of whiteness. In this case, nanoparticles have higher specific surface and reactivity which could potentially have toxic health effects associated with human exposure [14]. In this sense, dispersed nanoparticles into sunscreens increase the SPF value, but it means a possible leading to their incorporation into the stratum corneum, the outer layer of the skin [15]. A possible solution is to use nano-free UV filter throughout controlled agglomeration of nano and micro UV filters.

In this scenario, the aim of this work is to design and to evaluate the functional response of hierarchical compo-site made of ZnO nanoparticles anchored onto TiO₂ microparticles via sol-gel, acting as UV absorber material for sunscreens. The synergic effect of both materials, which are disposed as a nano-micro composite, is studied in order to determine their effectiveness as UV absorbers and the formation of free radicals for the stability of sunscreens.

In addition, the architecture of hierarchically micro–nano particles reduces notably the nanoparticles content and the possibility of penetration into skin as nanoparticles, and thus minimized their potential toxicity effects. Moreover, a drastic reduction of photodegradation is reported and a mechanism explaining this effect is proposed.

2. Materials and methods

2.1. Composite design

Rutile TiO₂ (Than et Mulhouse) with specific surface of 2.5m²/g and a particle size of D(v,0.5) 1.60μm were selected as starting microparticles. The ZnO nanoparticles were produced by a sol-gel route. The reagents used to prepare the sol-gel are: zinc acetate 99% (AcZn, Sigma Aldrich) as ZnO precursor, ethanol absolute 99.9% (EtOH, MERCK, Germany) as solvent and ethylamine (EA, MERCK) to produce the hydrolysis. The reagent molar ratio of the prepared sol-gel is 1AcZn:25EtOH:1.45EA. Two different ZnO sol-gels were prepared: one of them as it is; the other one, covering the TiO₂ microparticles. In this case, the amount of formed ZnO was estimated as a layer of 10nm in thickness over TiO₂ surface, taking into account the specific surface. A total of 10.89g of sol-gel composition was prepared in order to obtain a ZnO:TiO₂ weight ratio of 95:5. In the sol-gel process the AcZn is hydrolyzed in presence of water. The hydrolyzed molecules polymerized forming a network of ZnO. After sol preparation, 10,00g of TiO₂ microparticles were added and the mixture was continuously stirred until the hydrolysis reaction is finishing [16]. The mixture was dried ~~overnight~~ for 15 hours at 60°C. The obtained powder was grinded and thermally treated up to 600°C, 1 hour with heating and cooling rate of 10°C/min. For sake of clarity, we will refer thereafter as ZnO and TiO₂-ZnO composite to the thermal treated samples.

For both, the initial TiO₂ and the formed TiO₂-ZnO composite, the BET Specific surface was measured with an ASAP 2020 (Micromeritics).

In order to study the thermal characterization of the samples, Differential Thermal Analysis and Thermogravimetry (DTA-Tg) of the powder precursor of TiO₂-ZnO composite obtained by the sol-gel process was performed using a Netzsch STA 409/C equipment (Selb/Bavaria, Germany), up to 900°C with a heating rate of 10°/min in air atmosphere. In addition, UV-Vis diffuse reflectance spectra of the samples were recorded using a Perkin Elmer Lambda 650 UV-Vis spectrophotometer. The Kubelka-Munk function was used to transform the results from diffuse reflectance to absorbance. The spectra were measured every 2 nm each second. The band gaps were calculated from Tauc plot, taken into account the absorbance which was

converted by Kubelka–Munk function. To study the morphology both the microparticles and the obtained composite were observed by using a Field Emission Scanning Electronic Microscope (FESEM Hitachi S-4700, Hitachi).

The chemical analysis of the composite was realized by melting the sample with the help of $\text{Li}_2\text{B}_4\text{O}_7$. The ZnO content was determined by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis by using an Iris Advantage Spectrometer from Termo Jarrel Ash.

Optical properties of the initial TiO_2 microparticles, ZnO nanoparticles from sol-gel and TiO_2 -ZnO composite was investigated by measuring the emission spectra. The photoluminescence spectra were recorded with a spectrofluorometer (Fluorolog[®]-3, HORIBA Jobin Yvon) at room temperature (RT). The emission spectrum was measured by using a Xenon arc lamp as excitation source. The applied energy for excitation of TiO_2 in samples was $\lambda=290\text{nm}$, and for the excitation of ZnO $\lambda=360\text{nm}$.

2.2. Composite application

To study the performance of the developed UV filter, a sunscreen cream was prepared following the manufacturing method of the European Cosmetics Association, COLIPA.[17] The sunscreen formula is showed in **Table I**. The processing of the sunscreen consists of melting the ingredients of the fatty phase at 80 °C and adding it to the aqueous phase (previously heated at 80 °C) under stirring. The inorganic UV filter (5 wt.%) was added to the aqueous phase. The mix was cooled down to room temperature under stirring.

The Solar ~~Power~~ Protection Factor, SPF, of the sunscreen was measured by an in vitro test.

Three Poly(methyl methacrylate), PMMA, plates of 50 mm × 50 mm were prepared for each product to be tested and nine measurements were performed on each plate. 1.3 mg/cm² of sunscreen were spread with a coated finger.

Transmission measurements between 290 and 400 nm were carried out by using a spectrophotometer UV Transmittance Analyzer (UV1000S, Labsphere). The SPF values were obtained according to the following formula (**Equation 1**) [18,19]:

$$\text{Equation} \quad \text{SPF} = \frac{\sum_{290}^{400} E_{\lambda} S_{\lambda} \Delta_{\lambda}}{\sum_{290}^{400} E_{\lambda} S_{\lambda} T_{\lambda} \Delta_{\lambda}} \quad (1)$$

where E_{λ} is CIE erythema spectral effectiveness, S_{λ} is solar spectral irradiance and T_{λ} is spectral transmittance of the sample. Sunscreens photostability was studied after irradiating the samples by using a Solar Oriel Simulator 94011A lamp of 100W. The variation of color after exposing the samples to the simulated solar light was measured in CIELab coordinates field by using a Konica Minolta Spectrophotometer-colorimeter CM-2500d.

3. Results and discussion

3.1 Results

The thermal evolution of TiO₂-ZnO composite by DTA/Tg is shown in Fig. 1. There are three main processes that produce mass losses in the composite and are correlated with different exothermic peaks. The mayor exothermic peaks occur at 167°C and 364°C that correspond with the elimination of the solvent trapped in the dried gel and of the organic parts of the sol-gel precursors, respectively. Small exothermic peaks, signaled as (*), denote the thermal decomposition of different organic species. The DTA base line increases continuously as an indication of the increase in heat capacity of the composite due to its densification. This effect occurs without significant mass losses. The total mass loss of the sample is about 12%wt.

From the above results, the selected thermal treatment for TiO₂-ZnO composite and ZnO sol-gel were 600°C in order to complete the formation of ZnO [20,21].

The crystalline behavior of initial TiO₂ microparticles treated at 600°C, the formation of crystalline ZnO from sol-gel composition after 600°C thermal treatment and the presence of

ZnO in the thermally treated composite sample were determined by XRD (Fig. S1, supplementary material). For sake of clarity, only the XRD study of the thermally treated composite sample is shown in Fig. 2. The main crystalline phase observed is TiO₂ in the form of Rutile, whereas ZnO is a minor phase.

The main diffraction peak of Rutile ($2\theta \approx 27.4^\circ$) corresponding to [110] plane was carefully studied. The diffraction peaks in TiO₂ microparticles thermally treated at 600°C (Fig. 2b) and in composite (Fig. 2c) present a Lorentzian peak adjustment. Crystallinity of TiO₂ microparticles as Rutile is not affected by the thermal treatment. In the case of the composite, a shoulder appears on the XRD [110] peak at lower 2θ angle; hence the distance between diffraction crystallographic planes increases. Also, after the adjustment, the FWHM of the main Lorentzian decreases because of the apparition of the shoulder. From the area ratio of the adjusted diffraction peaks under $R^2=0.999$, the amount of structurally modified TiO₂ corresponds to a ~20%. As it was demonstrated by TiO₂ microparticles, these modifications in the structure are not attributed to the thermal treatment. This means that the shoulder represents variations in the crystal structure because of the presence of ZnO. Initially, it can be thought that the difference in ionic radius (0.61 Å for Ti⁴⁺ and 0.74 Å for Zn²⁺) provokes the displacement of the XRD peaks at lower 2θ when Zn²⁺ incorporates onto TiO₂ crystalline network, as Scherrer Equation represents. But the phases diagram of ZnO and TiO₂ does not consider the solid solution at low temperatures, only the formation of Zinc titanate.

Additionally, this phase is not observed by XRD. Otherwise, the variation in TiO₂ structure could be attributed to the formation of an interface between both materials, which supposes the formation of a defect-rich region.

The morphology of TiO₂ microparticles corresponds with agglomerates that resemble a “flower like” structure (Fig. 3a). BET specific surface is 2.52 m²/g (Table S1, supplementary information). The primary TiO₂ particles possess an acicular shape morphology having well faceted faces. These primary particles are irregular in size distribution with an average of

length ca.150nm x 350nm. The TiO₂-ZnO after the sol-gel process (previous the heating process) shows TiO₂ microparticles surrounded by sol-gel in which spaces between primary TiO₂ particles are filled, and the top of the TiO₂ primary particles are still visible, Fig. 2b. After the thermal treatment the composite presents a BET surface of 2.70m²/g (higher than for the initial TiO₂ microparticles) and shows aggregates of nanoparticles that correspond to ZnO nanoparticles onto TiO₂ microparticles, Fig. 2c. ZnO particles size is ca. 50nm (similar to ZnO formed from sol-gel; Fig. S2, supplementary material) and they cover partially and irregularly the surface of TiO₂ microparticles. In fact, they are forming aggregates of different number of nanoparticles and these nanoparticles are well differentiated between them. Regarding the amount of ZnO formed in the composite, ICP-OES analysis shows that ZnO/TiO₂ ratio was 4.1/95.9 (wt.%).

It is also observed in Fig. 3c that primary TiO₂ particles grow up ca. 250nm and the particle faces smoothes, so they are not so elongated. This morphology evolution of TiO₂ with the thermal treatment indicates occurrence of mass transport in the TiO₂ microparticles which is related to the high reactivity of the ZnO.

Fig. 4 shows the absorbance curves of the mentioned samples and its band gap calculation from Tauc Plot, $(\alpha h\nu)^{1/n}$ versus $(h\nu)$. For TiO₂ Rutile the band gap was calculated as an indirect allowed configuration, where n=2, whereas for ZnO it was calculated as a direct allowed transition, where n=1/2 [22,23]. In the case of the composite, an indirect allowed transition was chosen because of the high amount of TiO₂ in the sample and because it was only partially covered by aggregates of ZnO nanoparticles. For TiO₂, the bands at the UV range correspond to the electronic transition from the valence band (formed by the O-2p states) to the transition band (formed by Ti-3d states) [24]. In the case of ZnO, the bands which are localized at the UV range are due to the transition from the last occupied level (valence band formed by O-2p states) to the first free level in the conduction band, corresponding to Zn-4s levels [25]. The absorbance decreases for the formed composite in

comparison to the initial microparticles. This fact is attributed to the hierarchical disposition of the ZnO nanoparticles aggregates along the surface of TiO₂ microparticles, which provokes a higher scattering of the light.

TiO₂ microparticles present an absorption maximum at 365nm and a band gap of 3.15eV; whereas, ZnO nanoparticles from sol-gel show a maximum of absorption at 370nm and the band gap is 3.05eV. The composite presents an absorption maximum at 368nm and 3.08eV as band gap. The redshift of the band gap (in comparison with TiO₂ microparticles) correlates with the presence of ZnO nanoparticles onto TiO₂ microparticles. The displacement of the bands is related to the intrinsic properties of each material and to their particle size. In fact, the values for the maximum of absorbance (354nm) and for band gap (3.20eV) of ZnO microparticles in bibliography [15,26] are far from the values of the present composite. So both effects, the crystallization of ZnO and its nanometric particle size, promote the displacement of the absorption band of TiO₂ microparticles in composite [27].

Fig. 5 resumes the photoluminescence (PL) emission of TiO₂ microparticles, ZnO nanoparticles from sol-gel and TiO₂-ZnO composite. Three bands appeared for TiO₂ photoluminescence emission spectra in both, the TiO₂ microparticles (Fig. 5a) and the composite (Fig. 5b), with overlapping broad bands between 350-550 nm (3.54-2.25eV) and a strong band at ~580nm (2.14eV). The overlapping bands are attributed to the electron-hole recombination across the conduction band and the valence band (band-gap) and to shallow surface traps emissions due to oxygen vacancies (Vo) trap states [28,29]. The band at ~580nm comes from intra gap surface states originated from Ti⁴⁺ ions which stay adjacent to oxygen vacancies [30]. Oxygen vacancies are considered as the most common defects that act as radiative centers in luminescence processes [31].

Some authors [32] indicate that the intensity of PL signal in ZnO-TiO₂ composites decreases respecting pure TiO₂ because doping TiO₂ with ZnO is helpful to inhibit the recombination of electron-holes and hence the photocatalytic activity is improved. Nevertheless, it is worth to

1 mention that in our composite the intensity of the overlapping bands corresponding to band
2 gap at 350-550nm (electron-hole recombination across the conduction band and valence band)
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4 keeps the intensity, so this time no inhibition of electrons-holes recombination is observed.
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6 Whereas the band, which corresponds to the intra-gap surface states at 580nm, decreases in
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8 the composite respecting initial TiO₂ microparticles. Then, the defects of TiO₂ in composite
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10 vary from TiO₂ microparticles and this fact corroborates the differences observed by XDR.
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12 Regarding the PL emission spectra of ZnO, three peaks with different intensities are observed.
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14 The emission peak in the UV region at 385nm (3.22eV) is originated from excitonic
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16 recombination which corresponds to the emission band at near the edge of ZnO [33]. In the
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18 case of ZnO, it is usual that the photon energy at the UV emission range is greater than the
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20 measured band-gap. Hence, this emission may be attributed to the interbonding transition of
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22 the photogenerated electrons [34]. It means that the emission is caused by the radiative
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24 recombination of a photogenerated hole with an electron. The band at 430nm (2.88eV)
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26 corresponds to the oxygen vacancies (V_o) in the samples, whereas the emission band at 475-
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28 650 nm (2.61-1.91eV) is associated to interstitial oxygens (O_i) [35]. In the case of PL study of
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30 ZnO in composite, the intensity of the bands is less than one magnitude order in comparison
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32 with PL spectrum of ZnO nanoparticles. The main reason is the difference of ZnO amount in
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34 composite versus the whole sample of ZnO nanoparticles. In add, the relationship of the bands
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36 at 385/430nm (in composite) differs from the relationship of the same bands in whole sample
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38 of ZnO nanoparticles, which indicates a decrease of the excitonic recombination at ZnO
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40 nanoparticles in composite. Hence, when the PL emission spectra of ZnO or TiO₂ alone are
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42 compared with the ones forming the composite, a relevant variation in intensity is observed in
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44 addition of the variations in the wavelength position of the PL bands. The decrease of the
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46 intensity accounts for a redistribution of the excitation energy in addition of changes in the
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48 electronic structure. These facts and the structural changes, which were determined in TiO₂
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50 microparticles by XRD, corroborate the formation of defect barriers at the interfaces of the
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composite between TiO₂ and ZnO particles, due to the bending of the energy bands. The band gap values for TiO₂ and ZnO are nearly similar (3.15 and 3.05eV, respectively) and the position of the conduction band of ZnO layer is higher than that of TiO₂ as Rutile [36]. When TiO₂ is in contact with ZnO, the Fermi levels move to equilibrate their energy and a Type II band alignment occurs. At the contact regions of both semiconductors a potential barrier (type Schottky defects barrier) is established.

A sunscreen with 5%wt of the initial TiO₂ microparticles was prepared and it was compared with a sunscreen with 5%wt of the composite. In order to evaluate the behavior of the composite as UV filter, the Solar Protection Factors (SPF) of the formulated sunscreens by COLIPA method were evaluated in Fig. 6a and 6b. The followed methodology is showed in Fig. S3, supplementary material. The maximum values of SPF are nearly coincident. So in the case of the composite, the presence of ZnO in nanometric particle size does not provoke a significant variation of λ at the maximum SPF value. Nevertheless, the aggregates of ZnO nanoparticles onto TiO₂ microparticles improve the SPF value as a direct consequence of the high scattering enhancement. In fact, the SPF value in Fig. 6 is 3.77 for the sunscreen which was prepared from 5wt% of TiO₂ microparticles whereas the value increases to 4.45 (increment of ~18%) for the sample which was prepared by adding 5wt% of the TiO₂-ZnO composite.

SPF values along exposition time to the UV radiation show the photostability of the sunscreen. The photostability is higher for the sunscreen which made of TiO₂-ZnO composite than in the case of the sunscreen which was prepared from TiO₂ microparticles. In the case of the composite, the SPF value hardly varies after 3 hours of sun exposition of the sample (SPF = 4.22, which means a decrease of ~5%) whereas in the case of TiO₂ microparticles (treated under similar conditions) the SPF value decreased up to 2.35. It means that the effectiveness of protection of TiO₂ microparticles as UV filter decreases ~38% after 3 hours under sun light. The ratio corresponding to the areas under the SPF curves before and after 3 hours of sun

exposition was calculated in Fig. 6c. Sunscreen made of TiO_2 -ZnO composite presents a SPF value nearly constant with the sun exposition whereas sunscreen made of TiO_2 microparticles decreases the SPF value in the percentage previously indicated.

Hence, it is demonstrated that anchored ZnO nanoparticles keep the UV protection of the TiO_2 microparticles into the sunscreen. In this case, ZnO helps to increase the SPF value and improves the behavior of the sunscreen regarding the photostability.

The photostability in TiO_2 UV filters are typically attained by inorganic coating as Al_2O_3 or SiO_2 , in order to decrease the effect of free radicals [37] or to enhance their photocatalytic activity.[38] The mechanism for UV absorption by TiO_2 covers the effects of reflection, scattering and absorption of the light. The absorption mechanism is related to the formation of electron-hole pairs, and these pairs are responsible for free radical formation and ROS. In fact, the combination of TiO_2 and ZnO usually promotes high UV absorption with an increase of free radicals formation. It is known that the presence of free radicals increases the degradation of organic ingredients of the sunscreens, which provokes that sunscreens change their color to yellow tones [39]. It is worth to mention the lack of normative to determine the photocatalytic degradation of sunscreens [40,41]. In this work, the photodegradation of TiO_2 -ZnO composite is evaluated by means of both the SPF stability and the CIELab field color of sunscreens when they are irradiated with simulated solar light, Fig. 7.

Fig. 7a shows the initial sunscreens made of TiO_2 microparticles and of TiO_2 -ZnO composite, which were spread out the PMMA support for the photodegradation study. The variation of color from initial sunscreens to sunscreens which were previously exposed under solar radiation is clearly visible. Sunscreen with TiO_2 microparticles shows yellow color after exposing to solar light, which is related to the degradation of organic compounds in the sunscreen; whereas, the white color of the sunscreen made of composite is typically of fresh sunscreens. The SPF of sunscreen with TiO_2 microparticles decreases and the one for sunscreen with TiO_2 -ZnO composite keeps nearly constant after sun exposition. So, higher

amount of free radicals took place in sunscreen with TiO₂ microparticles. This observation is close to the SPF value after sun exposition and confirms the advantages that the ZnO-TiO₂ composite obtained in this work: composite improves the SPF value and partially prevents the production of free radicals and ROS. The change in color of sunscreens is quantified in Fig. 7b. The sunscreen made of composite keeps the color coordinates nearly constant after being UV irradiated and the color coordinates are similar to the sample made of TiO₂ microparticles before irradiation. Nevertheless, an evident change of ~4 points in CIELab coordinate +b* towards yellow color is observed when sunscreen sample, which was made of TiO₂ microparticles, is exposed to simulated sun light.

3.2 Discussion

Fig. 8 resumes the electronic mechanisms during the photodegradation process in order to explain the reduction of free radicals formation as the UV absorption takes place. Two different mechanisms denote the free radicals formation and evolution according to the ZnO presence or not. In the case of TiO₂, left side in Fig. 8a, it is described [3,42] the formation of a hole (h⁺) in the valence band because of the promotion of an electron (e⁻) to the conduction band when TiO₂ is irradiated. The valence band hole represents a highly localized electron vacancy in the semiconductor particle. In most cases h⁺ and e⁻ rapidly recombine, but in other cases both of them can reach the crystal surface of the particle in a redox reaction. At the surface, the electronic transference occurs with adsorbed compounds, giving raise to free radicals or to reactive oxygen species (ROS).

Therefore, under aqueous conditions, the key reactions from irradiated TiO₂ include (among others): reduction of O₂ by a conduction band electron, giving rise to activated oxygen species as superoxide radical anion (·O₂⁻); and oxidation of hydroxide by a valence band hole, forming a hydroxyl radical (·OH) [5,43]. In the case of fatty phase, the electron interacts with organic compounds forming carbon center radicals. Hence, TiO₂ particles in sunscreens act as

oxidizing organic material. However, in ZnO-TiO₂ composite the suppression of free radicals formation is observed from the application as sunscreen. In a first time, an increase of the light dispersion and scattering occurs because of the increase of roughness due to ZnO deposition as nanoparticles onto TiO₂ microparticles, as it is represented in Fig. 8a (right side, TiO₂ with ZnO nanoparticles). Hence, the possibility of free radicals formation lowers thanks to the reduction of light absorption of the composite. In addition, some authors point that the ZnO/TiO₂ interface induces a better separation of charge carriers (e⁻ and h⁺), because of a Schottky barrier formation that prevents the fast charge carriers recombination (quenching) [44]. Nevertheless, the application of here processed composite depletes the photoinduced redox reactions.

The proposed mechanism considers the widely reported Schottky barrier formation, the confinement of ZnO nanoparticles as aggregates at the surface of TiO₂ microparticles and defects at TiO₂ surface (Fig. 8b). Hence, on the one hand, the interfaces between the two semiconducting oxides mean a potential barrier that provokes the charges separation. In this sense, due to the energy disposition of ZnO and TiO₂ bands, an injection of electrons from ZnO to TiO₂ takes place [32]. On the other hand, the disposition of ZnO nanoparticles as aggregates means an active area for photoabsorption that indicates a high number of electrons-holes. Finally, in the case of ZnO, the existence of charges separation increases the possibility of their recombination with the photogenerated charges; whereas for TiO₂ microparticles, the same mechanism takes place in addition of the existence of a high number of defects (previously observed by XRD and PL studies) which indicates areas of recombination for charges too.

Therefore in the composite the electrons (e⁻) and holes (h⁺) recombine at ZnO and TiO₂ surface and they are not transmitted to the sunscreen medium. The recombination explains the lower number of carriers that reach the edge of the crystal, which is responsible of lowering the associated free radicals [44].

1 The increase of SPF value takes place in the new ZnO-TiO₂ composite. It was observed by
2 spectroscopy techniques (UV-Visible and Photoluminescence) that the light absorption of
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4 composite decreases. It is due to the light scattering thanks to the presence of ZnO
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6 nanoparticles anchored onto TiO₂ microparticles surface which increases the specific surface
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8 of the final composite. In addition, both semiconducting compounds, TiO₂ and ZnO, present
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10 the ability of absorbing UV-light. The contribution of both mechanisms, scattering and
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12 absorption, provokes the SPF increase. In other hand, the structural changes in TiO₂ (oxygen
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14 defects formation) and also the oxygen defects at the new formed ZnO nanoparticles explain
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16 the formation of a potential barrier at the interface of the materials. This interface acts as an
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18 area for separation of charges and at ZnO and TiO₂ surface the recombination of the carriers,
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20 electrons (e⁻) and holes (h⁺), takes place. This fact is translated into the avoidance of
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22 sunscreen degradation by the lowering of the free radicals formation.
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27 The presence of ZnO nanoparticles correctly anchored onto TiO₂ microparticles avoids a
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29 possible leading of the nanoparticles incorporation into the stratum cornea, the outer layer of
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31 the skin. This disposition allows a high UV absorption composite without degradation by free
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33 radicals. The composite opens a new orientation for the effective use of UV-absorbers without
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35 the photocatalysis adverse effects.
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46 **4. Conclusions**

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48 In this work, new hierarchical composite combining TiO₂ microparticles and aggregates of
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50 ZnO nanoparticles has been achieved by using the sol-gel method. A synergy between them
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52 increased their photoactivity and inhibited the free radicals formation. These effects were
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54 demonstrated by incorporating the new TiO₂-ZnO micro-nano composite as UV filter in a
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56 sunscreen application where a higher SPF value and a lower photodegradation respect to TiO₂
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58 microparticles were obtained.
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1 A mechanism explaining the mentioned effect is described. Basically, the hierarchical
2 disposition increases the specific surface of the inorganic solar filter so higher scattering of
3 the light occurs and stimulates the apparition of active interfaces between TiO_2 and ZnO
4 which generates a potential barrier that promotes the photoinduced electrons-holes separation.
5 The formation of charges by photoactivity and the possibility of charges recombination
6 increases thanks to the presence of charges from the potential barrier.
7 The hierarchical disposition of ZnO nanoparticles onto TiO_2 microparticles allows decreasing
8 the possible penetration of nanoparticles into the human skin. The authors believe that the
9 formation of recombination interface would open a way to design safe products for skin
10 human applications.
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29 Acknowledgements

30 The authors express their thanks to the MINECO project MAT2013-48009-C4-1-P for their
31 financial support. C.M. Alvarez-Docio for a FPI grant, which are co-financed with FEDER
32 funds.
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Figures legends

Fig. 1. DTA/Tg curves of TiO₂-ZnO composite by Zn²⁺ sol-gel.

Fig. 2. XRD study. a) Thermally treated TiO₂-ZnO composite and the magnification of the signal by using logarithmic scale. b) Detail of [110] X-Ray Diffraction peak of thermally treated TiO₂ microparticles (Rutile). c) Detail of [110] Rutile X-Ray Diffraction peak of thermally treated composite.

Fig. 3. FESEM micrographs of: a) starting TiO₂ microparticles. b) TiO₂-ZnO composite as obtained from dried sol-gel c) TiO₂-ZnO composite after thermal treatment.

Fig. 4. UV–Vis absorption spectra of (a) ZnO nano and microparticles. Composite and TiO₂ microparticles. (b) Tauc Plot representation for TiO₂-ZnO Composite and TiO₂ microparticles.

Fig. 5. Photoluminescence emission study of thermally treated at 600°C 1 hour: a) TiO₂ microparticles; b) ZnO nanoparticles; c and d) Composite.

Fig. 6. SPF response for sunscreens with a) TiO₂ microparticles b)TiO₂-ZnO composite. c) Sunscreens degradation from SPF photostability study.

Fig. 7. a) Sunscreens on PMMA supports before and after irradiation by simulated solar light. b) CIELab coordinates representation of the sunscreens with TiO₂ microparticles and with composite before and after the irradiation by simulated solar light.

Fig. 8. Schema of mechanism of TiO₂ and TiO₂/ZnO micro-nano composite when it is irradiated on sunscreen; a) left side: mechanism of formation of free radicals from TiO₂

particles; right side: increase of light scattering because of the hierarchical ZnO-TiO₂ composite and recombination of electron-holes after a potential barrier formation. b) Detail of charges recombination mechanism from charge separation due to the potential barrier and photo-induced charges in ZnO and TiO₂.

Tables legends

Table 1. Sunscreen formulation from COLIPA.

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