



Unusual photodegradation reactions of *Asteraceae* and *Poaceae* grass pollen enzymatic extracts on P25 photocatalyst

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Abstract

In previous studies, it was demonstrated that photocatalysis by TiO₂ nanoparticles can be effective for decomposition of pollen grains and pollen allergen extracts (PAEs) for *Cupressus arizonica* and *Platanus hybrida* species. In this work, the chemical and photochemical processes of five types of PAEs belonging to family *Asteraceae*, tribe *Astereae*, and family *Poaceae*, tribes *Poeae* and *Triticeae*, were studied. It was confirmed that the PAEs suffered almost complete decomposition, which likely led to gaseous final products. For the species of *Poeae* tribe, i.e., *Poa pratensis*, *Festuca pratensis*, and *Avena sativa*, an unusual surface chemical modification of the photocatalyst consisting in the appearance of new bands on fine core level spectra of Ti 2p, C 1s, and O 1s was observed. These changes were associated with possible doping of TiO₂ with C and N by pollen extracts. This was accompanied by a red shift of absorption spectra. The results suggest that some components of *Poeae* pollen can be grafted on TiO₂ surface and they can activate the photocatalyst in the visible range. These findings can open a new pathway to eco-friendly chemical engineering of photocatalysts using organic biological compounds.

Keywords Pollen · Enzymatic extract · TiO₂ · Photocatalyst · Chemical modification

Introduction

Since the 1990s, photocatalysis has been proved as a facile, cost-effective, and environmentally friendly technology (Fujishima et al. 2000, Hingorani et al. 2020, Yang and Wang 2018 for air disinfection from waterborne and airborne microbial pathogens, including viruses, bacteria, fungi, algae, and protozoa, with minimized harmful byproducts (Jimenez-Relinque et al. 2020a, Kim and Jang 2018, Laxma Reddy et al. 2017, Nevshupa et al. 2020, Regmi et al. 2018, Vohra et al. 2006, Zhang et al. 2019). So far, several immobilized photocatalysts have been commercialized (Fernandez et al.

1995; Jimenez-Relinque et al. 2020b). The disinfection mechanism was associated with advanced oxidation processes occurring in the presence of a semiconductor photocatalyst upon receiving the photon energy higher than the band gap energy. Generation of various reactive species such as reactive oxygen species, reactive nitrogen species, oxygen, and hydroxyl radicals induces the destruction of microbes through oxidative stress, decreasing the cellular metabolism, etc. (Regmi et al. 2018). In previous studies (Jimenez-Relinque et al. 2016; Sapiña et al. 2013; Sapiña et al. 2017), we found that photocatalysis is also effective for a drastic decrease of allergenic activity of pollen for the species *Platanus hybrida* (*Platanus acerifolia*) (*Pla.*) and *Cupressus arizonica* (*Cup.*) belonging to *Angiospermae* and *Gymnospermae* groups, respectively. Even one of the most chemically stable natural biopolymers, which composes the pollen outer stratum—sporopollenin—was found to be prone to rapid photocatalytic degradation (Sapiña et al. 2017). On the other hand, when subjected to special chemical treatment, pollen itself can become an advanced organic photocatalyst due to porous structures and hierarchical morphologies of a carbon skeleton (Wang et al. 2019). For instance, the chemically treated rapeseed pollen (*Brassicales* order) exhibited an outstanding photocatalytic

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performance and excellent quantum efficiency without any co-catalysts and sacrificial agents. All this demonstrates a very complex chemical and photochemical behavior of pollen, which is not yet fully understood. Among various families of the *Angiospermae* group, grass species have a major impact on human health since grass pollen causes severe pollinosis throughout the European continent (D'Amato and Liccardi 1994; Depciuch et al. 2016; Jung et al. 2019). The plants of the *Poaceae* family and other herbaceous plants such as mugwort (*Artemisia*) have been in the focus of this study since they have significant pollen-producing capability during a high spring–summer pollen season and are responsible for a summer–autumn pollen season in the Mediterranean area. In contrast to our previous work (Jimenez-Relinque et al. 2016; Sapiña et al. 2013; Sapiña et al. 2017), which were focused specifically on the degradation of pollen grains and allergens, in this paper, new findings related to unusual surface chemical modifications on the P25 (TiO₂) photocatalyst by the extracts of *Poeae* species are reported.

Materials and methods

Pollen allergenic extracts and experimental configurations

Pollen allergenic extracts containing pollen enzymes were obtained from Greerlab in the form of lyophilized cakes sealed in glass vials under a protective atmosphere. Immediately before the experiments, 2.5 ml of extra pure (18 MΩ cm) water was added to a vial to obtain a liquid extract. Five species belonging to two *Angiospermae* families: *Asteraceae* and *Poaceae*, and three tribes: *Astereae*, *Poeae*, and *Triticeae*, were studied (Fig. 1).

The commonly used reference Aeroxide® TiO₂-P25 from Evonik was used as a photocatalyst (PhC) in the form of suspension of 6 g of P25 powder in 100 ml of extra pure water. For the sake of simplicity, the photocatalyst was unsupported in this exploratory study. Four tests were carried out in accordance with the methodology previously described (Jimenez-Relinque et al. 2016). The design of the experiment was developed in such a way that the effect of photocatalysis, UV irradiation, and non-photocatalytic chemical reactivity between the PAEs and the PhC can be figured out

independently. To prepare the test samples (test layouts I and II), a drop of PAE extract of 30 µL was extended over the surface of the support (gilded glass support for XPS analysis and aluminum support for SEM characterization) and dried. In tests III and IV, first, 30 µl of the suspension of P25 was placed on the support, and after drying, the extract of PAE was placed on the top of the photocatalyst (PhC) layer and dried.

In cases II and IV, sample irradiation was performed during 24 h using LEDs with sharp emission in the UV region at 365 nm and power 5 W.

The test layouts and labeling adopted are given in Table 1.

Methods

The surface chemical composition of the samples as well as the bonding of the principal chemical elements were studied using energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). In comparison with other conventional spectroscopy techniques such as FTIR, which have been broadly used for the analysis of organic chemical degradation of pollen components under various environmental circumstances and experimental conditions (Cravanzola et al. 2017; Depciuch et al. 2016; Sapiña et al. 2017), XPS can provide information on the elemental chemical environment in both organic phases (Martínez et al. 2011) and the proper photocatalyst (Mohamed and Rohani 2018).

The scanning electron microscopy (SEM) and the EDX spatially resolved elemental analysis were performed after each of the four tests (Table 1) using a Hitachi S-4800 electron microscope, with an electron acceleration 0.5–30 kV. The microanalysis was carried out with a Si detector, 167 XFlash Detector 5030, Bruker.

For XPS analysis, an ultrahigh vacuum system with a base pressure of 1×10^{-8} Pa was used. A source of X-ray radiation was Mg Kα (1253.6 eV). The plane of the sample surface was at 60° to the entrance of the hemispherical analyzer. The broad spectra were recorded with pass energy 40 eV and energy step 0.25 eV. The high-resolution spectra were measured for the main elements (C 1s, O 1s, N 1s, Ti 2p, and Au 4f) with energy pass 15 eV. The binding energy (BE) scale was calibrated with respect to the Au 4f at 84 eV. The contribution of Mg Kα line was subtracted and the background was removed using Shirley's routine before the calculation of elemental

Fig. 1 Classification of the species which were studied in this work (from family *Asteraceae*, tribe *Astereae*, and family *Poaceae*, tribes *Poeae* and *Triticeae*) and in previous works (*Cupressus* and *Platanus*) (Jimenez-Relinque et al. 2016)

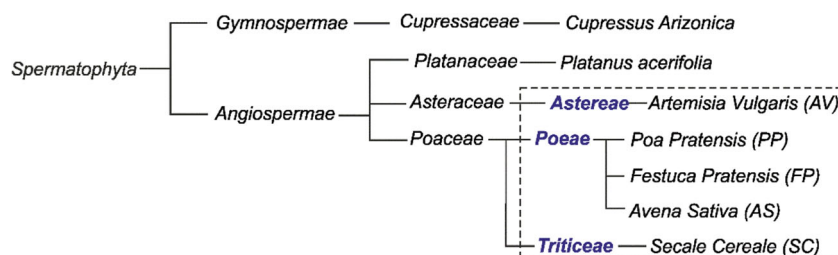


Table 1 Test layout and labeling adopted

Test code	Layout	Meaning
I	PAE	Pollen allergenic extract on an inert substrate
II	PAE+UV	UV-irradiated pollen allergenic extract on an inert substrate
III	PAE+PhC	Non-irradiated pollen allergenic extract on an active substrate ¹
IV	PAE+PhC+UV	UV-irradiated pollen allergenic extract on an active substrate ¹

¹ Active substrate refers to a photocatalytic layer on the inert substrate

composition. The relative elemental concentrations were determined from the areas of the corresponding peaks obtained by deconvolution of the measured spectra using reference sensitivity factors (Briggs and Seah 1990) and following the procedure and constraints, which were explained in detail previously (Jimenez-Relinque et al. 2016). An XPS analysis of PAEs of various species on irradiated and unirradiated PhC substrates was carried out in order to determine the chemical bonding of the main elements. Special attention was paid to the analysis of Ti spectra which probed a possible interaction between the PAEs and the substrate.

The apparent band gap was calculated from the absorbance coefficients determined by diffuse reflectance spectroscopy (DRS) conducted on a Shimadzu UV-2600 UV-vis spectrophotometer.

Results and discussion

SEM-EDX

Figures 2 and 3 show the SEM images (gray scale) combined with the elemental maps for C (red) or Ti (blue). Carbon is associated with the organic components, which disappear due to photocatalytic degradation leaving no solid residues behind. Decomposition of PAE solid phases into low molecular weight volatile compounds agrees with the mechanisms of amino acid photodegradation with two main steps leading to NH_3 and CO_2 final products (Hidaka et al. 1997). Consequently, bare photocatalyst emerges that is evident from the increase of Ti intensity. In tests I (benchmark) and II, no significant variation in C distribution over the surface was found (Fig. 2). This indicates that UV radiation without photocatalytic material did not cause volatilization of solid organic components. This is in line with our previous study of *Cupressus* and *Platanus* pollen (Jimenez-Relinque et al. 2016). When the PAEs were placed on the PhC surface without exposure to UV light (test III), the carbon concentration for the *Poeae* tribe (AS, FP, and PP) decreased, but for the other two species (SC and AV), it remained nearly unchanged. In test IV (UV irradiated PAE on top of the PhC), carbon concentration decreased substantially for all species. For *Poeae* tribe species, the decrease of C in test IV was more

significant, than in test III. It is noteworthy that the map of C distribution is nearly the negative image of the map of Ti distribution that means that the PAE decomposition occurred mainly on the PhC surface.

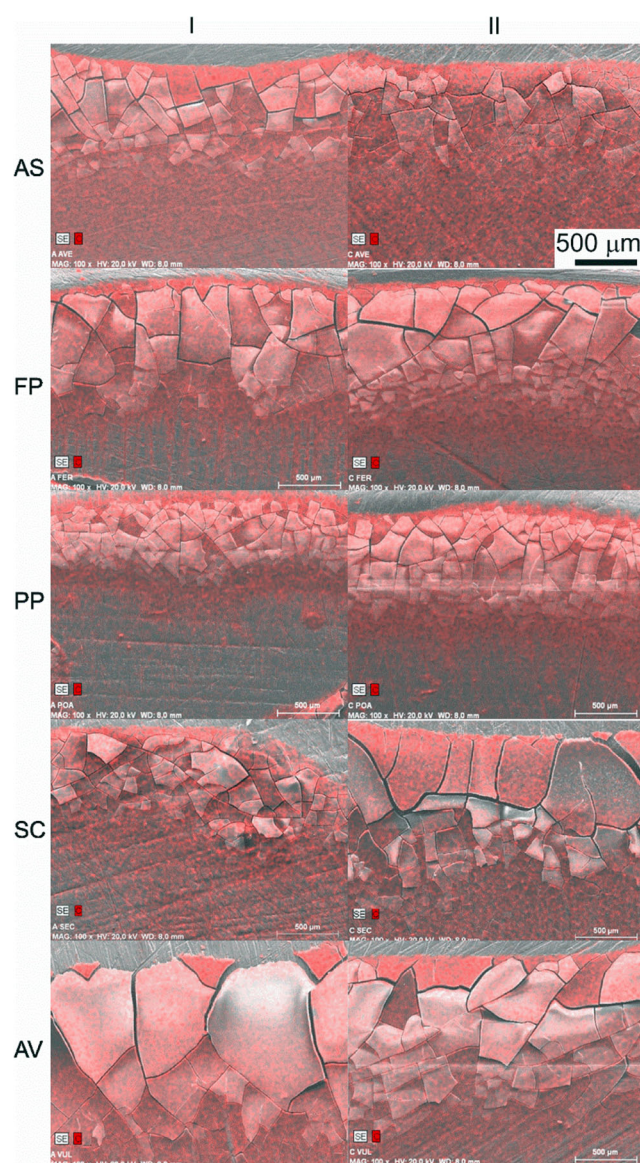


Fig. 2 Images of SEM (in gray) and carbon mapping (in red) measured by EDS for PAEs of different species in test layouts I and II

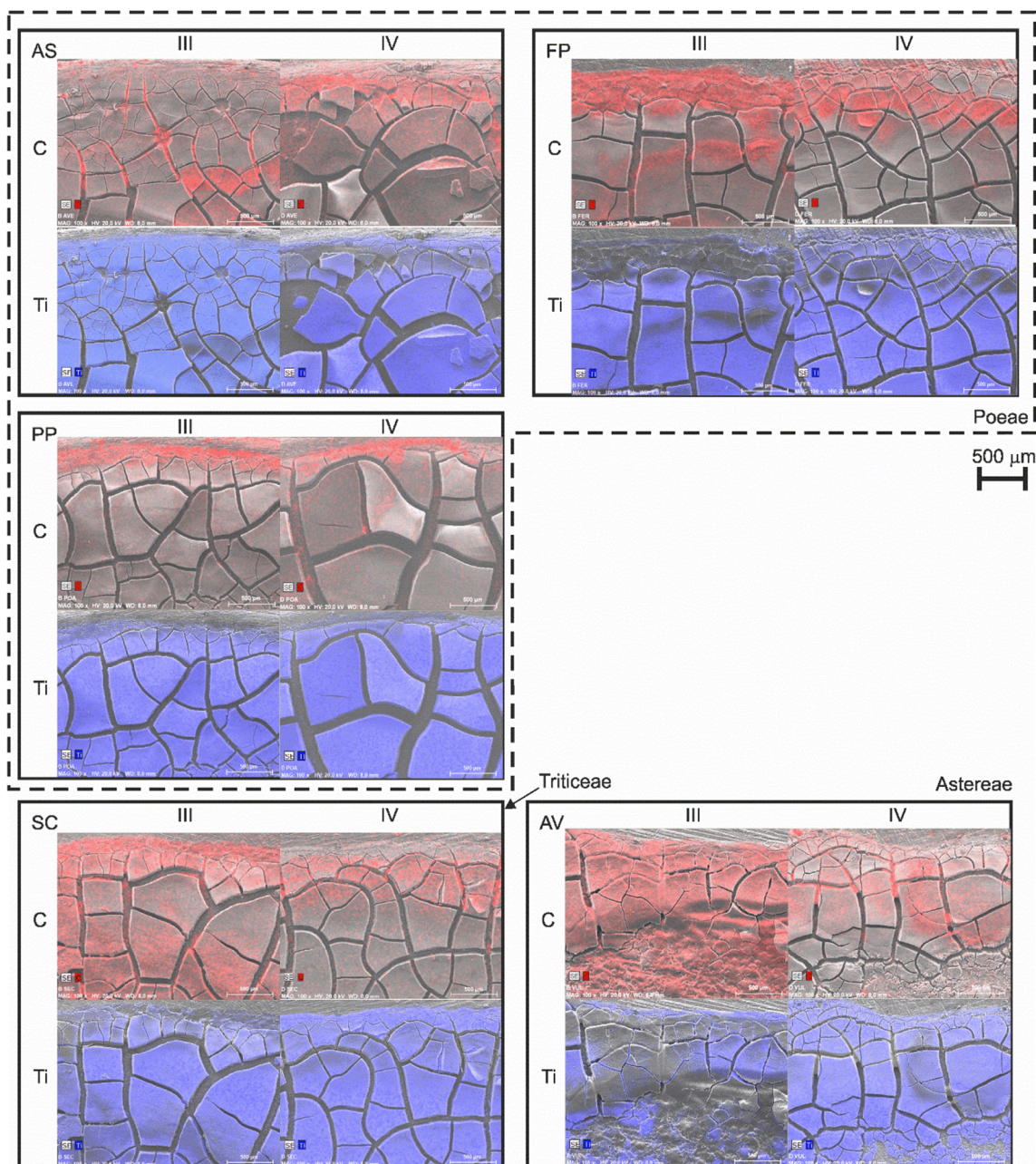


Fig. 3 Images of SEM (in gray), C map (in red), and Ti map (in blue) measured by EDX for the PAEs of various species in tests III and IV. Mosaic polygon structures were formed due to shrinkage of a photocatalytic suspension during drying

XPS results

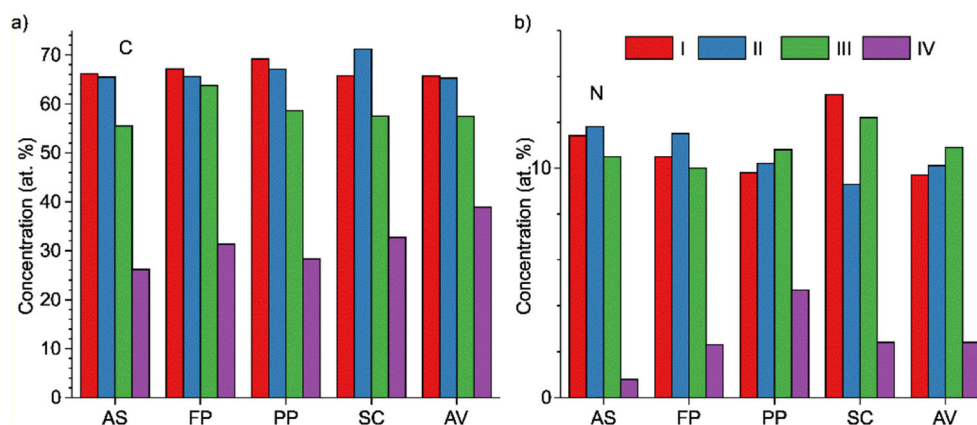
Total elemental concentration

Figure 4 shows C and N surface atomic concentrations, which are related with the organic components of the PAEs. In line with our previous studies, the most important decrease in C and N was observed in test IV, when the PAE was subjected to photocatalysis. In test III, a certain decrease in C concentration was also found in agreement with the EDX results.

Ti 2p

Before getting deep into the analysis of fine XPS spectra for various pollen samples, the spectrum of the bare PhC sample was carefully measured. This spectrum was used as a benchmark to trace possible modification of the photocatalyst surface due to reactions with PAEs. Figure 5 shows Ti 2p fine spectrum with two bands at 459.4 and 465.1 eV corresponding to Ti 2p_{3/2} and 2p_{1/2}, respectively. The band position and separation (5.7 eV) correspond to Ti⁴⁺ oxidation state (Mayer et al. 1995; Moulder et al. 1995) (Table 2).

Fig. 4 Total concentration of **a** C and **b** N on the surfaces of PAE of various species as function of the test layout



When PAEs were applied on the top of the PhC (without UV irradiation), the fine Ti 2p spectra did not change for all PAEs, except for PP, which showed broadening of Ti 2p_{3/2} component, whose full width at the half of the maximum (FWHM) rose from 1.3 eV to about 2.0 eV. According to Mayer et al. (1995), this can be associated with the reduction of surface Ti⁴⁺ species to intermediate oxidation states.

Further UV irradiation of PAEs applied onto PhC led to significant changes in Ti 2p spectra for all three *Poeae* species but left unchanged the spectra for SC and AV. The changes were both with respect to the corresponding initial spectra (test

III) and the benchmark. Concerning the latter, the Ti 2p peak became wider and skewer. The spectra could not be fitted using only the bands of 4+ (Ti1) and 3+ (Ti3) oxidation states (McCafferty and Wightman 1999). Thus, two other components at 458.3 (Ti2) associated with Ti 2p_{3/2} and 464 eV (Ti4) associated with Ti 2p_{1/2} were added. For the sake of simplicity, the spectrum deconvolution is shown only for FP. Wang et. al reported that oxygen vacancies in titania lead to shifting the Ti 2p_{3/2} band to lower energy (458.1 eV) (Wang et al. 2009), while Avasarala and Haldar assigned the band between 456.9 and 457.2 eV to nonstoichiometric titanium oxynitrides (Avasarala and Haldar 2010).

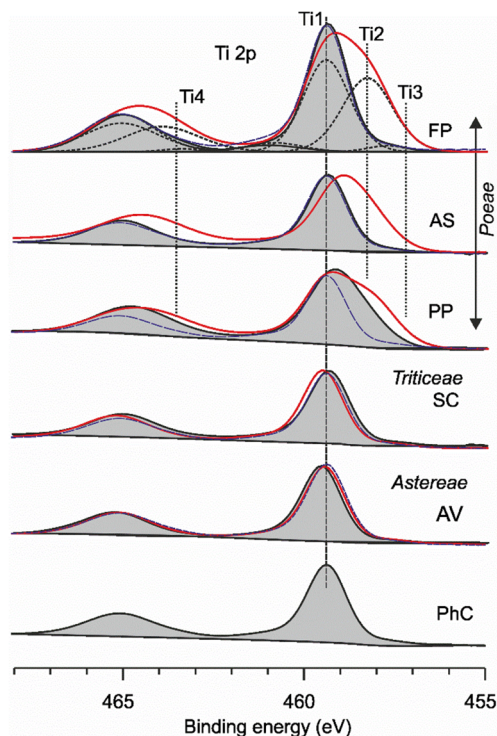


Fig. 5 Fine core level spectra of Ti 2p for the PAE-loaded photocatalyst without UV irradiation (black solid lines and shadowed) and after UV irradiation (red line). The spectrum of bare PhC is shown for reference by a dashed blue line

O 1s

Fine core level O 1s spectra are shown in Fig. 6. The band at 530.6 eV (O1) in the benchmark spectrum was associated with O²⁻ of titania. The tail at higher binding energies could be due to adsorbed hydroxyl, water, and carbonaceous groups.

For all unirradiated PAEs placed on the PhC (test III), there was an asymmetric broad band in the range 530–535 eV due to the organic components of PAE. The center of this band was 2 to 2.3 eV higher than for O1. Once irradiated, the samples exhibited different behaviors. For non-*Poeae* PAEs (SC and AV), the “organic” band completely vanished, and the resulting spectrum became nearly identical to the spectrum of bare PhC. This supports our previous findings on complete photocatalytic degradation of PAEs leading to volatile and gaseous products. However, for all three *Poeae* species, the “organic” band did not fully fade off. Furthermore, a new low-energy band O5 at 529.3 eV emerged. This band can be associated with oxygen vacancies in titania. Previously, Wang et al. reported that O 1s band shifts to 529.5 eV after the treatment of TiO₂ nanobelts with NH₃ at 600 °C (Wang et al. 2009). In this study, a similar effect was achieved without heating, just by chemical and photochemical processes under normal temperature and pressure.

Table 2 XPS bands and corresponding possible chemical bonds

Element	Component	Energy (eV)	Bonds
Ti2p _{3/2}	Ti1	459.3 (Ti ⁴⁺)	O–Ti–O
	Ti2	458.3	N–Ti–O, C–Ti–O
O1s	O1	530.4	O–Ti–O
	O2	531.8	C–OH, O=C–O, O=C–N, C–O–C–O–C
	O3	533	O=C–OH, O=C–O–C
	O4	534	O singly bound of cyclic O–(C=O)–O carbonate esters (C=O)–O–(C=O), carboxylic acid anhydride
	O5	529.3	O vacancies in TiO ₂
C1s	C1	284.5	C–C, C–H, C–S
	C2	285.7	C–N–C=O, C=C–N, C–COO
	C3	287.3	N=C–N, O=C–NH–C, C–OH, C–O–C, C–O–C=O
	C4	289	C–O–C=O, O=C–OH, O=C–N
	C5	282.8	Ti carbide (?)
N1s	N1	399.0	Amine C–N–H, C–N–C; imine C=N–C
	N2	400.5	Imide (C=O)–N–(C=O)
	N3	403.0	Nitrite NO ₂ [–]

N 1s

In the benchmark spectrum, a weak single N 1s band at about 400.6 eV could be due to airborne contamination (Fig. 7a).

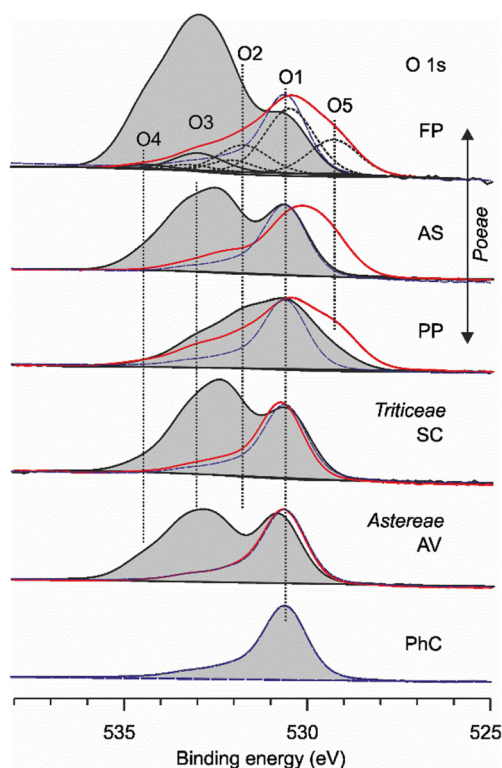


Fig. 6 Fine core level spectra of O 1s for the PAE-loaded photocatalyst before UV irradiation (black solid lines and shadowed) and after UV irradiation (red line). The spectrum of bare PhC is shown for reference by a dashed blue line

When PAE was applied on the top of PhC, a strong band at 401 eV and FWHM 1.8 eV (N2) assigned to NH or NH₂ amino groups (Rouxhet and Genet 2011) emerged. Additionally, PP PAE showed a downshift on 0.7 eV and broadening (FWHM 2.6 eV) of the band N1. After UV irradiation, all three *Poa* species behaved differently from non-*Poa* species again—a new strong band at 399.0 eV (N1) and a weak band at 403 eV appeared. The assignment of N1 band to a specific bond is not clear yet. In literature, binding energies 396.9 eV and 398.1 eV were usually associated with the N–Ti bond of TiN and TiCN (Cheng and Zheng 2007). Two or three bands in the range 398 to 402 eV were found for N-doped TiO₂, which was obtained by calcination at 450–700 °C of TiO₂ previously dipped in organic solutions (El-Sheikh et al. 2014). However, when a hydrothermal process was employed for doping nanoparticulate TiO₂ using small amine molecules at a lower temperature, only one band at 399.5 eV was found (Bao et al. 2013). In the case of SC, the N 1s spectrum did not present any significant changes except for the variation in the total intensity of the band.

C 1s

In the benchmark spectrum, an asymmetric carbon band with its maximum at 285.7 eV (Fig. 7b) was ascribed to airborne contamination of PhC. It was deconvoluted using three bands: C2, C3, and C4 (Table 2). When PAEs were placed on the PhC, the intensity of C3 and C4 increased, but it did not make them shift. In the case of *Poa pratensis*, a broadening of the spectrum with respect to the benchmark could be due to the band C1 at 284.5 eV, which is usually ascribed to *sp*³ C, graphite, and C–C, C–H bonds (Díaz et al. 1996).

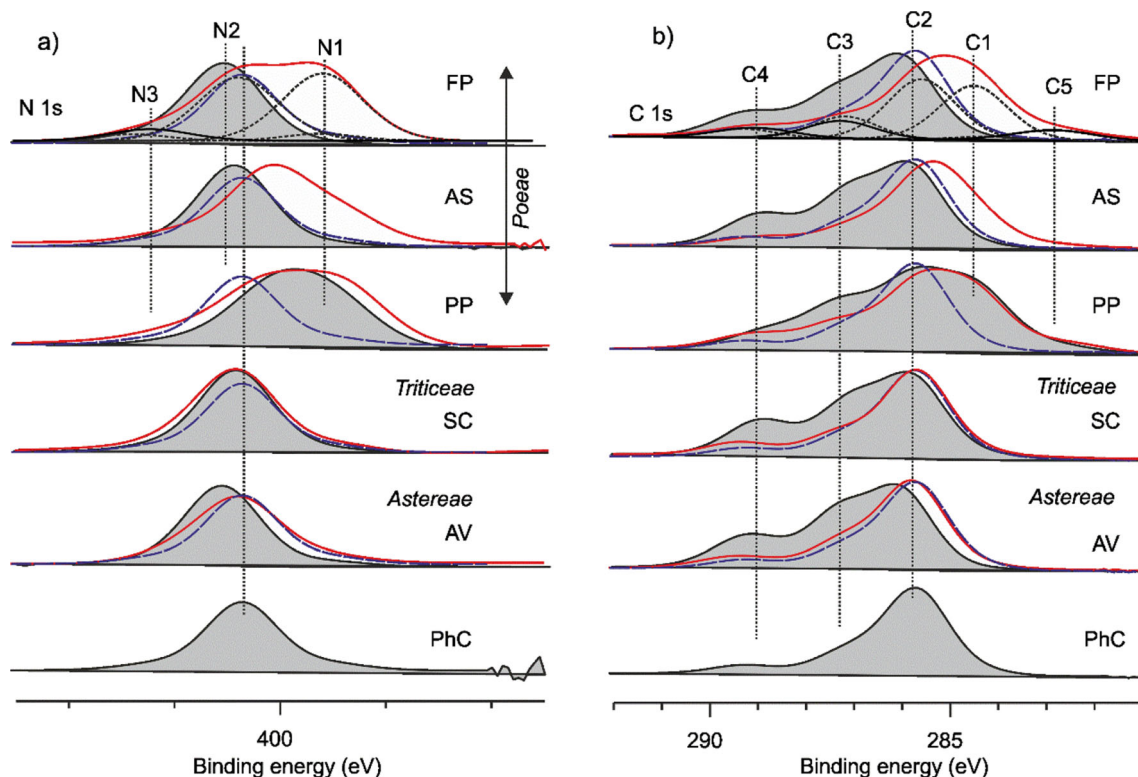


Fig. 7 Fine core level spectra of N 1s (a) and C 1s (b) for the PAE-loaded photocatalyst before UV irradiation (black solid lines and shadowed) and after UV irradiation (red line). The spectrum of bare PhC is shown for reference by a dashed blue line

After exposure to UV light, the spectra suffered significant changes. For FP, the C1/C2 ratio increased to nearly a unity that suggests possible strong chemical interaction between the components of the PAE and PhC and/or formation of amorphous carbon. For all *Poeae* species, a new component at 282.8 eV (C5) appeared which was not found for SC and AV. Neither organic carbon compounds nor allotropic carbon (nanotubes, fullerenes, graphene, graphite, etc.) has any bonds with the binding energy lower than C1. Although titanium carbides and oxycarbides may have a band around 282 eV (Zhang and Koka 1998), the absence of Ti band at 455 eV does not support assigning C5 to TiC.

Band gap

The diffuse reflectance spectroscopic (DRS) values for case IV for the different PAEs as well as for bare P25 are shown in Fig. 8. The Kubelka–Munk optical absorption coefficients were determined from the Tauc equation. This method is useful for the characterization of bulk and thin film semiconductor materials including oxide photocatalysts (Cheng and Zheng 2007; Murphy 2007). In comparison to bare P25, all species showed a red shift of the absorption edges. The apparent band gaps were calculated according to linear extrapolation to the x -axis of the absorption coefficients $(F(R)h\nu)^{0.5}$ vs. $h\nu$. All the graphs for PAE samples coincided almost perfectly and yielded an average band gap 2.93 ± 0.79 eV, while for bare

P25, it was 3.25 ± 0.087 eV. These data are very close to the results reported for C- and S-doped TiO_2 , which showed a shift from about 3.25 to 3 or even 2.8 eV (Kim and Jang 2018; Mohamed et al. 2017). In addition to the main band gap, there was a secondary one with a much smaller effect. For P25 loaded with the PAEs, the secondary band gap also suffered a significant red shift to around 1.8 eV for all species. The secondary band gap has been usually observed for doped TiO_2 and ascribed to the effect of the electronic levels of the foreign dopants (Bai et al. 2018; Gharaei et al. 2018; Mohamed and Rohani 2018).

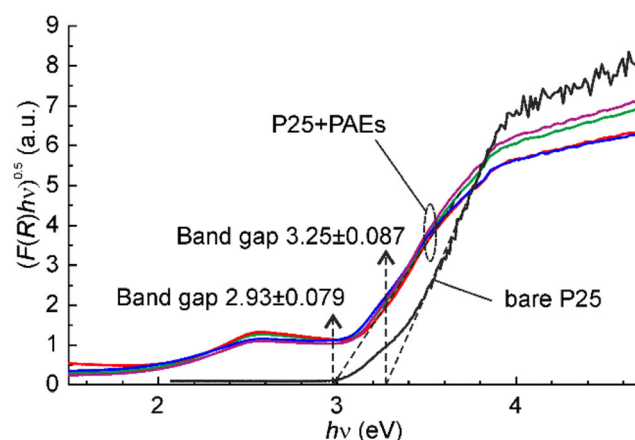


Fig. 8 Band gap for various PAE-loaded photocatalytic samples and the band gap for bare P25

Discussion

The XPS analysis confirmed that solid organic components of the five pollen allergenic extracts degraded to volatile and gaseous products due to photocatalytic oxidation. This comes from a significant decrease in C and N concentrations on PAEs placed on top of the PhC after UV irradiation. This is not surprising since the mechanistic insight into photocatalytic degradation of amino acids in their cationic or zwitterionic forms revealed that the main steps lead to formation of NH_3 or CO_2 as final products, while only one of four secondary steps can yield nitrates (Hidaka et al. 1997; Kim and Choi 2002; Tran et al. 2006). The degradation is related to photocatalytic processes and not to UV irradiation, since for PAEs placed on inert substrates no significant variation in C and N was found.

The PAEs of the *Poeae* tribe of the *Poaceae* family exhibited a singular behavior on photocatalytically active substrates both under and without UV irradiation. The features of XPS fine core level spectra suggest that PAEs chemically interact with the photocatalyst. New bands at lower energies were observed for Ti, O, N, and C after UV irradiation. In the case of PP, these bands appeared even without UV irradiation. The new bands did not belong to the organic components of PAE nor to the bare PhC. The energy shift of Ti 2p and O 1s suggests creation of oxygen vacancies in titania. It can also point at a possible N and/or C incorporation onto interstitial position of PhC or grafting of a carbonaceous layer onto the PhC surface. Previously, covalent bonding between titania and various organic molecules such as arginine, lauryl sulfate, and salicylic acid was reported (Makarova et al. 2000). In case of adsorbed arginine, it conducted electrons from the valence band of TiO_2 to the target contaminant molecules, but the arginine was not affected by photocatalytic reactions. Other studies (Kavil et al. 2017; Lo Presti et al. 2014; Smith et al. 2015; Wang et al. 2014; Zou et al. 2012) explored the use of polyaniline, glycine, aliphatic amines, peptides, etc. for modification of TiO_2 and enhancing quantum yield for photodegradation of various organic substances.

The hypothesis of possible doping of P25 by non-metal elements and/or its self-doping by Ti^{+3} by PAEs is further supported by the observed red shift in the absorption spectra. It should be noticed that due to obvious methodological limitations the band gap in the test layout III, i.e., without UV irradiation, could not be measured by UV–vis diffuse reflectance method. The findings drawn from XPS analysis that showed chemical modification of P25 by *Poeae* species and the absence of such modification for other studied species suggests that *Poeae* species caused a more pronounced decrease of the apparent band gap than other species. However, no differences between the Tauc plots for *Poeae* and non-*Poeae* PAEs were observed. This apparent contradiction can be explained considering the differences of

characteristic analysis depth of XPS and diffuse reflectance methods. The former yields information on chemical bonding in a very thin surface layer with thickness typically below 10 nm (Ray and Shard 2011). In turn, in the reflectance measurement, the light penetration depth for TiO_2 is of the order of several tens of nanometers (Mo and Ching 1995; Stevanovic et al. 2012). Therefore, the apparent band gap determined by diffuse reflectance method provides an average value over the entire surface layer and is virtually insensitive to the topmost adsorbed/modified layer.

Although the exact composition of the pollen allergenic extracts is not known, it is likely that the three extracts belonging to *Poeae* tribe have common, unknown yet components which were grafted onto the surface of TiO_2 that narrowed the band gap in the same way as many technologies do via self-doping by Ti^{3+} (Li et al. 2015b), doping by non-metal elements (Bengtsson et al. 2009; Cravanzola et al. 2017; Li et al. 2015a), etc. in order to activate the photocatalyst in the visible range. This may have important implications for future eco-friendly technologies of photocatalyst engineering through modification of native photocatalyst by a simple surface treatment.

Conclusions

In addition to the two species studied in the previous study, this work proved that photocatalysis is effective for degradation of pollen allergenic enzymes of five species belonging to *Poaceae* and *Asteraceae* families of plants. Photocatalysis caused almost complete decomposition of organic substances to low molecular weight volatile products that agree to the mechanisms of amino acid photodegradation. For the species of the *Poeae* tribe, i.e., *Poa pratensis*, *Festuca pratensis*, and *Avena sativa*, an unusual surface chemical modification of P25 photocatalyst was observed. New bands on fine core level spectra of Ti 2p, C 1s, and O 1s appeared and they were attributed to the formation of oxygen vacancies and possible reactions between TiO_2 and organic components. The observed chemical modifications were similar to those which are usually pursued through chemical engineering of photocatalyst, e.g., self-doping by Ti^{+3} , doping with non-metal elements, etc., seeking for reduction of band gap and sensitization of photocatalyst in the visible spectral range. However, the determination of the apparent band gap using a diffusive reflectance method did not reveal any significant differences between the species. This was attributed to the fact that the diffusive reflectance method is virtually insensitive to the topmost adsorbed layer, where the chemical modification must occur. The observed chemical modifications occurred without any heating or other technological processing of the photocatalyst, just under normal temperature and pressure, and in the presence of UV radiation. These findings can be

useful for eco-friendly chemical engineering of photocatalysts using organic biological compounds. Further interdisciplinary studies focused on surface chemistry, identification of active components of *Poeae* pollen, mechanistic aspects of TiO₂ chemical modification, and photocatalytic properties of modified materials are necessary.

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Author contribution MS: writing the original draft and investigation; EJ: writing, review, and editing; RN: investigation and writing, review, and editing; ER: investigation and writing, review, and editing; MC: conceptualization, methodology, writing, review, and editing.

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Declarations

Ethics approval Not applicable

Consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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