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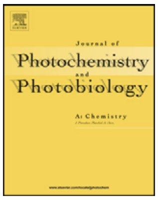

Singlet oxygen generation in the presence of titanium dioxide materials used as sunscreens in suntan lotions

Marta Buchalska, Gabriela Kras, Marcin Oszajca, Wiesław Łasocha, Wojciech Macyk*

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

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ABSTRACT

The goal of this study was to test photoreactivity of commercially available suntan lotions and their components (mainly TiO_2). Isolated water insoluble components containing titanium dioxide appeared almost non-active in the tests of 4-chlorophenol degradation, however a fast UV-light induced degradation of azur B and oxidation of α-terpinene to ascaridol in the presence of these materials was observed. The photoreactivity of suntan lotions and their components was compared to the photoactivity of phenalenone (an efficient $^1O_2$ photosensitizer). The results have proven a relatively low efficiency of hydroxyl radicals formation, however significant rates of reactions involving singlet oxygen were observed in the presence of either the components of the cosmetics or the suntan lotions used as received. Moreover, an efficient photocurrent generation by photoelectrodes made of isolated TiO_2 materials reflects their photoredox properties. Although singlet oxygen scavengers used as additives in suntan lotions might decrease the risk related to generation of this reactive oxygen species, producers of cosmetics containing titanium dioxide should consider testing TiO_2 photoactivity in reference to $^1O_2$ generation.

1. Introduction

Topical sunscreens can be divided into two main categories: organic and inorganic. The category of inorganic sunscreens is represented by titanium dioxide and zinc oxide. These compounds in the nano- or microcrystalline forms constitute an opaque barrier reflecting and scattering, but mainly absorbing ultraviolet light (both UV-A and UV-B). Titanium dioxide has been registered (US Federal Register, 43FR38206, 25 August 1978) to be a safe physical sunscreen [1]. TiO_2 is photostable and inert towards organic components of suntans [2] and shows no skin irritating properties [3]. Micronisation and encapsulation of titanium dioxide improve quality of inorganic sunscreens since such materials show lowered scattering of visible light and shift of the onset of absorbed light to shorter wavelengths (quantum-size effect) [4].

Titanium dioxide occurs in three crystalline forms: anatase, rutile and brookite. Absorption properties of anatase and rutile are perfectly fitted to their applications as sunscreens [5–7] since their absorption onsets around 400 nm fall to the frontier between visible and UV-light. Anatase shows usually a better photocatalytic activity as compared to rutile and is used as an active component of the self-cleaning and self-sterilizing surfaces [8,9]. Rutile, used as a white paint pigment, whitener in a toothpaste and UV absorber in sunscreens [10] in general shows a lower photoactivity although the mixtures of anatase and rutile appear to be particularly efficient photocatalysts. Photocatalytic processes at TiO_2 are based on an electron–hole pair photogeneration followed by the interfacial electron transfer (IFET) or energy transfer processes resulting in reactive oxygen species (ROS) formation [8,9,11]. Hydroxyl radicals $OH^\bullet$, superoxide $O_2^{\bullet-}$, hydrogen peroxide H_2O_2 are main representatives of ROS formed as a result of IFET. Another reactive oxidant, singlet oxygen $^1O_2$, can be a product of the energy transfer to adsorbed oxygen molecule [12–14] or a superoxide-hole recombination [15]. ROS may be responsible for oxidation of organic components of suntan lotions [16] as well as for ageing and destruction of skin. Previous studies on TiO_2 isolated from commercial suntan lotions have proven, that titanium dioxide used as a sunscreen may be photoactive—photocatalyzed phenol oxidation and DNA damage were observed [1,17]. Therefore sunscreens based on titanium dioxide or zinc oxide should contain additional antioxidants, *e.g.* glutathione, α-tocopherol (vitamin E), ascorbic acid or β-carotene (an excellent $^1O_2$ quencher [18]). A particularly good protection against unwanted ROS can be achieved by a smart titanium dioxide modification which might inhibit its photocatalytic activity. An example of such system was recently described by Lee et al. who applied a hydrophobic multicomponent polymer coating for nanocrystalline TiO_2, containing natural antioxidants from grape seeds [19]. The resulting composite material showed good

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[*] Corresponding author. Tel.: +48 126632005; fax: +48 126335392.
E-mail address: macyk@chemia.uj.edu.pl (W. Macyk).

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screening properties against UV protecting DNA from a photodamage.

Penetration of inorganic materials into the skin is still discussed. There are reports confirming ZnO [20], TiO_2 [21,22] and micronized TiO_2 [23] penetration, but on the other hand various *in vivo* and *in vitro* studies disproved the penetration of titanium dioxide into the skin [3]. Aggregation of nano- and microparticles into larger structures should prevent from the unwanted penetration.

In this paper we present tests of photocatalytic activity of insoluble components containing TiO_2 isolated from three different commercial suntan lotions. Their photoreactivity was compared to the photoreactivity of the whole composition of the lotions and photoreactivity of phenalenone commonly used as an efficient singlet oxygen photosensitizer. Our goal was to check a possibility of ROS generation as a result of electron and/or energy transfer mechanism. In particular, our efforts were directed to answer the following question: can TiO_2 – as a component of suntan lotions – be responsible for singlet oxygen generation?

2. Materials and methods

2.1. Materials

TiO_2 samples were isolated from three suntan lotions available in drugstores (samples S1, S2 and S3). In order to isolate higher amounts of titanium dioxide the suntan lotions of high SPF were selected (30–50). Most of the organic content of the lotions was washed out with chloroform or methanol. Remaining white residues after washing were dried at room temperature and ground in the agate mortar.

2.2. Methods

Diffuse reflectance spectra of the isolated TiO_2 samples were recorded at *Perkin Elmer* Lambda 12 spectrophotometer equipped with the integrating sphere (5 cm dia.). Samples were ground with $BaSO_4$ (used also as a reference) in the agate mortar (weight ratio *ca.* 1:50, sample:$BaSO_4$). Recorded reflectance spectra were converted by Kubelka–Munk function $F(R) = (1-R)^2/2R$, where R is a reflectance. Crystal structures of investigated materials were confirmed by XRD phase analysis using an *X'PERT PRO MPD* diffractometer, *X'PERT Highscore* software and *PDF-4+* database.

Photocatalytic activity was tested by monitoring the progress of 4-chlorophenol (4-CP) or azur B (AB) photodegradation. The suspensions of titanium dioxide samples (20 ml, 1 g dm^{-3}) in aqueous solutions of 4-CP (0.25 mmol dm^{-3}) or AB (0.25 mmol dm^{-3}) were sonicated for 15 min. pH of the suspensions varied between 6.0 and 6.8. The samples were irradiated with high pressure mercury lamp HBO-200 through the 10 cm water filter and 320 or 495 nm cut-off filters. During irradiation suspensions were stirred magnetically in an opened cuvette facilitating a good contact with air. Samples collected during irradiation were filtered through the Millipore filter and subjected to the analysis. The degradation progress was evaluated monitoring the absorbance changes recorded at 225 and 650 nm for 4-CP and AB, respectively. Absorption spectra were collected at *Hewlett Packard* HP8453 spectrophotometer. Photocatalytic activities of the isolated titanium dioxide samples were compared to those of *Degussa* P25 TiO_2 (composed of 70% anatase and 30% rutile) and *Kerr-McGee* Tronox TR (exclusively rutile phase). In addition, analogous experiments with phenalenone (0.1 mmol dm^{-3}, water/methanol 1:1 mixture used as a solvent, $\lambda > 320$ nm) instead of TiO_2 material were performed under otherwise identical conditions.

Photoactivity of studied samples was also tested in the process of α-terpinene oxidation (1 mmol dm^{-3} methanolic solution). Irradiation was performed under conditions applied in 4-CP and AB degradation tests through the 320 nm cut-off filter. After filtration, collected samples were subjected to HPLC analysis (*Perkin Elmer* Series 200 with UV–vis detector, C18 column, methanol as the eluent, detection–absorbance at 220 nm).

A three-electrode set-up was used for photoelectrochemical measurements. The electrolyte solution, 0.1 mol dm^{-3} KNO_3, was air-equilibrated. The working electrodes, prepared by casting an appropriate material sample onto the ITO (indium–tin oxide) foil, were irradiated from the backside (through the ITO-foil) in order to minimize the influence of the material layer thickness on the photocurrent values. Platinum and Ag/AgCl were used as counter and reference electrodes, respectively. Irradiation of the working electrode was realized with 150 W XBO lamp (*Osram*) equipped with a water cooled housing, LPS 200 power supply (*Photon Technology International*) and an automatically controlled monochromator with a shutter. The electrochemical measurements (CV + chopped light, photocurrent action spectra) were controlled by a BAS 50W (*Bioanalytical Systems*) electrochemical analyzer. Cyclic voltammograms were recorded at 10 mV s^{-1} scan rate. Photocurrent action spectra were recorded under potentiostatic conditions at 700 mV vs. Ag/AgCl and were not corrected for changes in light intensity.

Table 1
Carbon content, XRD analysis and band-gap energies (E_g) of studied materials.

Sample	C content, % (±0.1)	XRD analysis	E_g, eV (±0.05)
S1	6.4	TiO_2 (rutile) + ZnO (wurtzite)	3.10
S2	15.9	TiO_2 (rutile)	2.94
S3	37.5	TiO_2 (rutile)	3.02
P25	–	TiO_2 (anatase + rutile)	3.12
TR	–	TiO_2 (rutile)	3.03

3. Results

3.1. Materials

White solid materials were isolated from suntan lotions by washing out the organic components of lotions. S1 and S3 samples appeared fine-crystalline powders while S2 was coarse and slightly glitter. All materials were insoluble in water. The elemental analysis has shown relatively high contents of organic compounds remaining in the samples (Table 1).

XRD measurements confirmed presence of rutile-TiO_2 in every sample (Fig. 1). The S1 sample contains also certain amounts of ZnO (wurtzite type of structure). Zinc oxide is also listed by the producer as an ingredient of the corresponding suntan lotion. Peaks present at 38.39° and 44.60° 2θ in the dataset for sample S1 (highlighted with stars) result from X-ray scattering on the sample holder. The S2 sample contains small amount (approximately 4 vol.%) of anatase as determined by analysis of small peaks (highlighted with arrows in Fig. 1) present in the diffractogram. Unidentified peaks in diffractograms may be attributed to the organic content present in every sample. Using Scherrer's equation the size of rutile-TiO_2 crystallites was estimated to be within the range of 30–50 nm for S1 and S3 samples. In the case of S2 sample the line broadening may suggest an anisotropic shape of the crystallites (most probably platelets like).

The electronic absorption spectra shown as Kubelka–Munk functions are presented in Fig. 2. Table 1 summarizes band-gap energies of all tested samples estimated from the plots of $(F(R)h\nu)^{0.5}$ vs. $h\nu$ (plots are not shown) [24]. The low band-gap energies of S2 and S3 samples confirm the rutile structure of these materials. The larger band-gap energy measured for S1 may result from the ZnO content in this material.

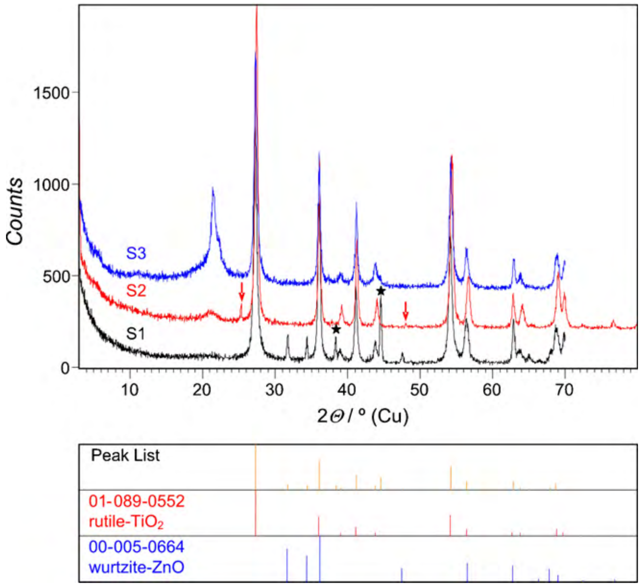

Fig. 1. XRD analysis of isolated S1–S3 samples and reference patterns for rutile-TiO_2 and wurtzite-ZnO.

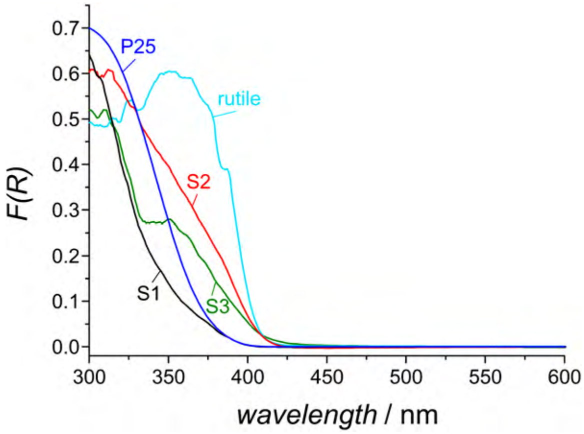

Fig. 2. Electronic spectra (Kubelka–Munk function) of materials isolated from suntan lotions.

3.2. Photocatalytic degradation of 4-CP and AB

Selection of organic compounds for photocatalytic tests was based on their reactivity with various reactive oxygen species that may be generated upon titanium dioxide irradiation. 4-chlorophenol can be oxidized by hydroxyl radicals or holes photogenerated in the valence band of TiO_2 [25,26]. Azur B (Fig. 3), a dye belonging to the same group of thiazine dyes as methylene blue [27], is also degraded by these oxidants, however it might be also oxidized with singlet oxygen. This can be demonstrated in the test with any photosensitizer capable of singlet oxygen generation. Fig. 4 shows the results of AB and 4-CP degradation tests in the presence of phenalenone, a sensitizer that generates $^1O_2$ with the quantum yield of *ca.* 0.9 [28]. Moreover, photogeneration of hydroxyl radicals in the presence of irradiated phenalenone is negligible. While 4-CP degradation was not observed under applied conditions, oxidation of AB proceeds very efficiently. This experiment demonstrates the selectivity of $^1O_2$ reactivity towards 4-CP and AB.

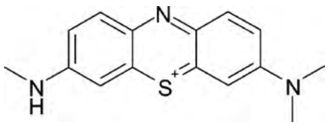

Fig. 3. Azur B.

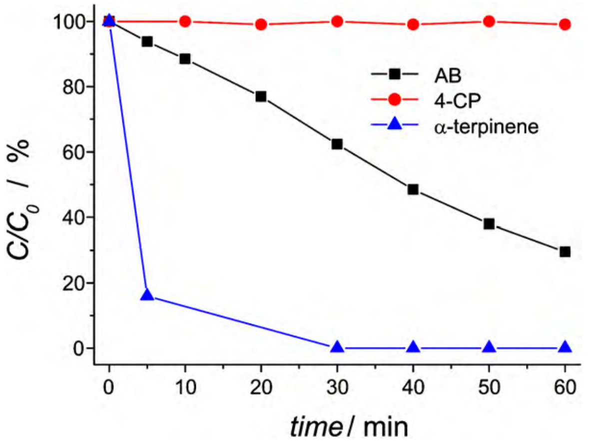

Fig. 4. Photodegradation of AB (squares), 4-CP (circles) and α-terpinene (triangles) in the presence of phenalenone (λ > 320 nm).

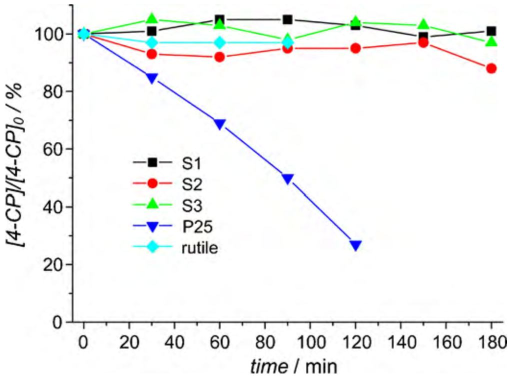

Fig. 5. Photodegradation of 4-chlorophenol in the presence of materials (λ > 320 nm).

In the timescale of experiment (up to 3 h) in the absence of either titanium dioxide samples or phenalenone, both 4-CP and AB were photostable under applied irradiation conditions. 4-chlorophenol appeared to be relatively stable also in the presence of irradiated S1–S3 and TR materials (Fig. 5). Only P25 induced a fast degradation

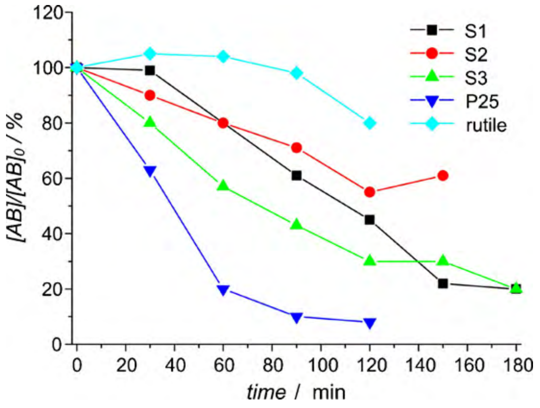

Fig. 6. Photodegradation of azur B in the presence of isolated materials and reference samples (λ > 320 nm).

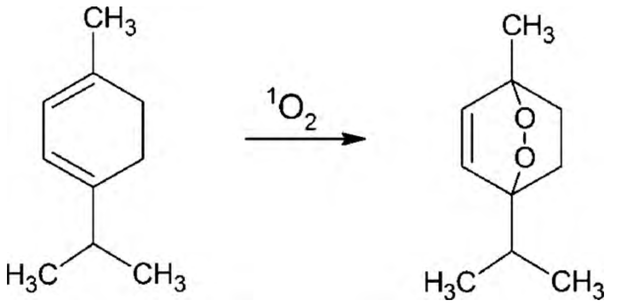

Fig. 7. Formation of ascaridol—oxidation of α-terpinene with singlet oxygen.

of 4-CP. In contrast to 4-CP, photodegradation of AB was significant in the presence of most of the tested TiO_2 samples (Fig. 6). All samples S1–S3 appeared to be more active than rutile-TiO_2, TR. The observed highest rate of AB photodegradation in the presence of P25 is associated with the highest efficiency of various ROS generation by this material.

3.3. *Photocatalytic oxidation of α-terpinene*

Oxidation of α-terpinene with singlet oxygen results in formation of ascaridol (endoperoxide, Fig. 7), according to the Diels–Alder mechanism [29,30]. Oxidation of α-terpinene in the presence of phenalenone is very fast and efficient (Fig. 8). The oxidation of α-terpinene was monitored both as a disappearence of the substrate and formation of ascaridol. Similarly this process proceeds efficiently in the presence of P25 and rutile form of titanium dioxide (Fig. 8), but also S1–S3 samples induced analogous changes (Fig. 9). Photoactivity of S1, the sample containing both TiO_2 and ZnO, was the highest. The lowest yields of ascaridol formation were observed in the case of S3, the sample of the highest content of organic residue.

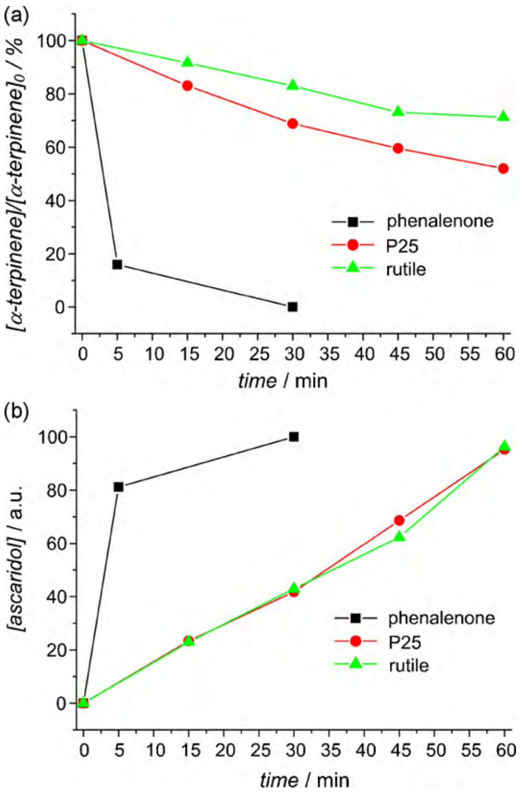

Fig. 8. Oxidation of α-terpinene (a) and formation of ascaridol (b) in the presence of reference samples ($\lambda > 320$ nm).

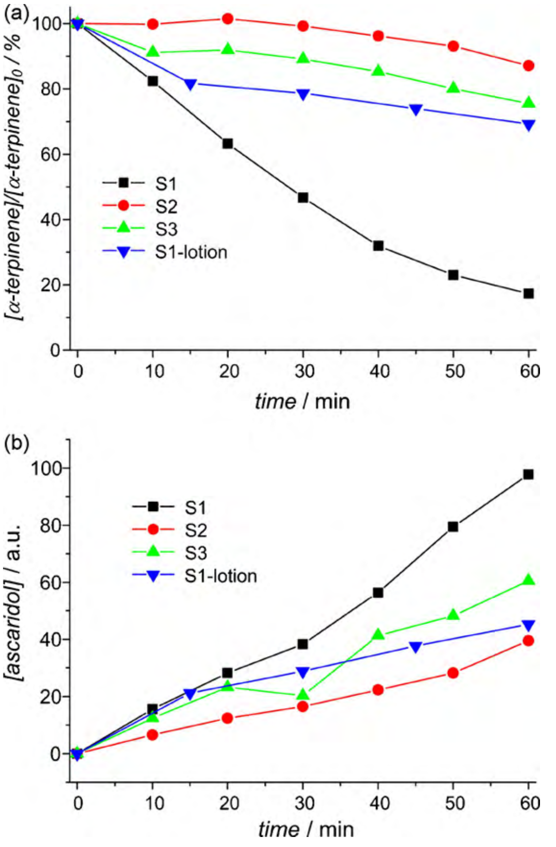

Fig. 9. Oxidation of α-terpinene (a) and formation of ascaridol (b) in the presence of tested samples ($\lambda > 320$ nm).

Tests made for one of the suntan lotions (used for the S1 sample extraction) have shown also a considerable photoactivity of this cosmetic. Although smaller than those observed for extracted S1 material, the yields of ascaridol formation were not negligible.

3.4. *Photoelectrochemical measurements*

Photoinduced interfacial electron transfer is responsible for formation of reactive oxygen species as well as for a photocurrent generation. Photoelectrochemical measurements were performed with electrodes covered with S1, S3 and P25 materials. Photoelectrodes covered with the S2 sample appeared to be unstable and therefore they could not be applied in these measurements.

Similarly to P25, the S1 and S3 samples generated anodic photocurrents in a broad range of potentials (0–1000 mV; Fig. 10a). Although smaller than those measured for P25, the photocurrents were well developed proving a relatively efficient interfacial electron transfer process. A similar conclusion comes from the photocurrent action spectra (not corrected for changes in light intensity) presented in Fig. 10b. Although the highest photocurrents were observed for all materials upon UV irradiation, the S3 sample showed also a detectable photoactivity extending up to *ca.* 480 nm. Visible light-induced photocurrents were not observed either for S1 or P25 samples. The difference must be related to organics present in S3 that sensitize titanium dioxide. This type of photosensitization was observed for TiO_2 modified with surface Ti^{IV} complexes [31].

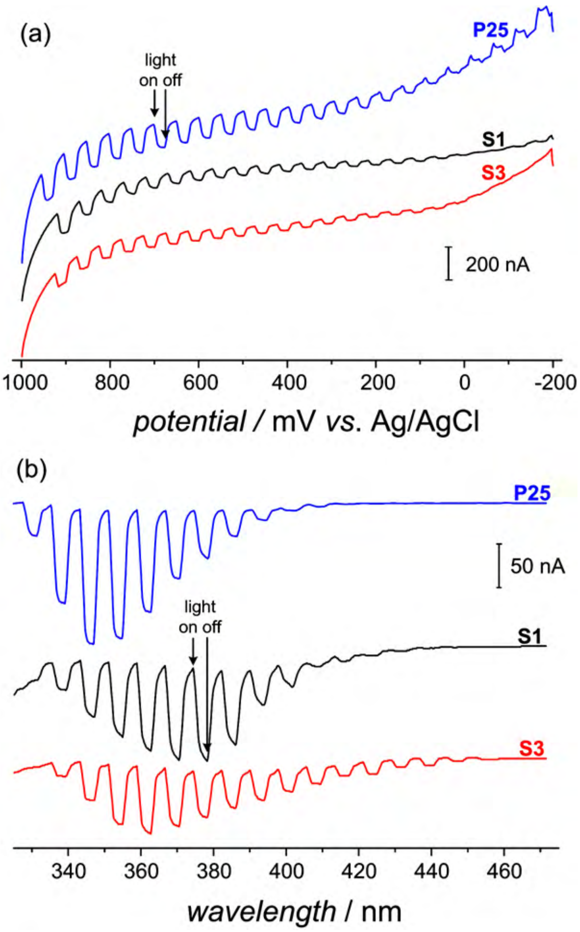

Fig. 10. (a) CV + chopped light ($\lambda = 350$ nm) recorded for electrodes made of tested materials. (b) Photocurrents generated at photoelectrodes upon irradiation with monochromatic light (constant potential, 700 mV vs. Ag/AgCl).

4. Discussion

Isolated materials generate photocurrents, therefore the interfacial electron transfer processes at TiO_2 proceed relatively efficiently leading to formation of organic radicals and reactive oxygen species. On the other hand 4-CP photodegradation in the presence of S1–S3 samples is negligible. These observations point at low efficiencies of hydroxyl radicals and superoxide anions generation by S1–S3 most probably due to effective quenching of generated $OH^\bullet$ and $O_2^{\bullet-}$ by organic content of the samples. Therefore due to low concentrations of available $OH^\bullet$ and $O_2^{\bullet-}$ under tested conditions observed degradation of AB can result either from its photooxidation associated with an electron injection from the excited state of AB to the conduction band of titanium dioxide (so called *indirect* photocatalysis [32]) or from its oxidation with singlet oxygen, as observed in the presence of phenalenone. In order to exclude a possibility of the indirect photocatalysis the suspensions were irradiated through the cut-off filter 495 nm. Under these conditions AB can be excited within its absorption band extending from *ca*. 550 to 700 nm, but not titanium dioxide. Only a negligible discoloration of the AB solution was observed within 3 h of irradiation (data not shown) disproving a possibility of the electron injection from the excited state of AB to the conduction band of TiO_2. Therefore photodegradation of azur B should result mainly from its oxidation with photogenerated singlet oxygen. The other redox processes, involving direct substrate oxidation with valence band holes or reaction with ROS other than $^1O_2$ present at low concentrations, may additionally take part in photodegradation of AB. The yields of these reactions and their relative efficiencies depend on the tested sample—most likely in the case of S2 and S3 samples they are more efficient than in the case of S1 (compare Figs. 6 and 9a).

A further evidence for the crucial role of singlet oxygen in the process of AB degradation comes from the results of AB bleaching in the presence of TiO_2 samples in water/ethanol suspensions. Alcohols are good $OH^\bullet$ scavengers, but on the other hand they also increase the lifetime of singlet oxygen. In the presence of ethanol AB discoloration was very efficient supporting a major role of singlet oxygen in AB bleaching in our tests (data not shown).

Formation of ascaridol also supports the hypothesis of singlet oxygen photogeneration in the presence of S1–S3 samples and their parent lotions. However, an alternative mechanism of ascaridol formation involving electron transfer processes and oxygen radicals [30,33,34] cannot be completely ruled out. In this process the photosensitizer in its excited state forms an adduct with diene and induces dislocation of its π-electrons. In the next step superoxide reacts with α-terpinene forming ascaridol and other oxidation products [34]. Nevertheless in our studied systems this mechanism seems unlikely since in the presence of oxygen radicals 4-CP would also undergo an efficient oxidation.

Our previous studies have shown, that surface modification of titanium dioxide may enhance singlet oxygen formation [12]. In the case of complex mixtures of organic and inorganic components of suntan lotions and other cosmetics, the TiO_2 surface is certainly bound with various organic species since it shows a high affinity to carboxylic acids, catechol and salicylic acid derivatives, phosphates and many others [31]. Although all suntan lotions used in our studies contain substances used as antioxidants (*e.g.* α-tocopherol) the photoactivity of titanium dioxide (in one case in combination with zinc oxide) is not completely suppressed.

5. Conclusions

The results of 4-CP photodegradation in the presence of TiO_2 isolated from suntan lotions prove a low efficiency of hydroxyl radicals and superoxide anions photogeneration by these materials. Nevertheless, as demonstrated in photoelectrochemical measurements, the photoinduced electron transfer takes place in the case of all tested samples. This process might be responsible for other side redox reactions. Independently on low yields of $O_2^{\bullet-}$ and $OH^\bullet$ photogeneration, singlet oxygen can be produced quite efficiently. While $O_2^{\bullet-}$ and $OH^\bullet$ are formed in the processes of photoinduced electron transfer, formation of $^1O_2$ might proceed either *via* electron [15] or energy transfer mechanisms [35]. Previously we demonstrated, that surface or structural modifications of titanium dioxide resulting in decreased efficiencies of interfacial electron transfer may enhance yields of energy transfer processes leading to formation of harmful singlet oxygen [12]. Application of rutile-TiO_2 in suntan lotions, *i.e.* the form of titanium dioxide generally regarded as significantly less photoactive than anatase-TiO_2, does not prevent from photogeneration of all reactive oxygen species, especially in combination with photoactive zinc oxide. Although singlet oxygen scavengers used as additives in suntan lotions might decrease the risk related to this reactive oxygen species, producers of cosmetics containing titanium dioxide should consider testing TiO_2 photoactivity in reference to $^1O_2$ generation.

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References

[1] R. Dunford, A. Salinaro, L. Cai, N. Serpone, S. Horikoshi, H. Hidaka, J. Knowland, Chemical oxidation and DNA damage catalysed by inorganic sunscreen ingreadients, FEBS Lett. 418 (1997) 87–91.

[2] M.A. Mitchnick, D. Fairhurst, S.R. Pinnell, Microfine zinc oxide (Z-cote) as a photostable UVA/UVB sunblock agent, J. Am. Acad. Dermatol. 40 (1999) 85–90.

[3] J.F. Nash, Human safety and efficacy of ultraviolet filters and sunscreen products, Dermatol. Clin. 24 (2006) 35–51.

[4] R. Roelandts, Shedding light on sunscreens, Clin. Exp. Dermatol. 23 (1998) 147–157.

[5] L.E. West, Sun protection, Dermatol. Trends 2 (2004) 81–95.

[6] R. Bestak, R.S.C. Barnetson, M.R. Nearn, G.M. Halliday, Sunscreen protection of contact hypersensitivity responses from chronic solar-stimulated ultraviolet irradiation correlates with the absorption spectrum of sunscreen, J. Invest. Dermatol. 105 (1995) 345–351.

[7] R.G. van der Molen, H.M.H. Hurks, C. Out-Luiting, F. Spies, J.M. van't Noordende, H.K. Koerten, A.M. Mommaas, Efficacy of micronized titanium dioxide-containing compounds in protection against UVB-induced immunosuppression in humans in vivo, J. Photochem. Photobiol. B: Biol. 44 (1998) 143–150.

[8] K. Szaciłowski, W. Macyk, A. Drzewiecka-Matuszek, M. Brindell, G. Stochel, Bioinorganic photochemistry: frontiers and mechanisms, Chem. Rev. 105 (2005) 2647–2694.

[9] G. Stochel, M. Brindell, W. Macyk, Z. Stasicka, K. Szaciłowski, Bioinorganic Photochemistry, Wiley, Chichester, 2009.

[10] R. Zallen, M.P. More, The optical absorption edge of brookite TiO_2, Solid State Commun. 137 (2006) 154–159.

[11] W. Macyk, A. Franke, G. Stochel, Metal compounds and small molecules activation—case studies, Coord. Chem. Rev. 249 (2005) 2437–2457.

[12] A. Jańczyk, E. Krakowska, G. Stochel, W. Macyk, Singlet oxygen photogeneration at surface modified titanium dioxide, J. Am. Chem. Soc. 128 (2006) 15574–15575.

[13] A. Jańczyk, A. Wolnicka-Głubisz, A. Urbanska, G. Stochel, W. Macyk, Photocytotoxicity of platinum(IV)-chloride surface modified TiO_2 irradiated with visible light against murine macrophages, J. Photochem. Photobiol. B: Biol. 92 (2008) 54–58.

[14] A. Jańczyk, A. Wolnicka-Głubisz, K. Urbańska, H. Kisch, G. Stochel, W. Macyk, Photodynamic activity of platinum(IV)-chloride surface modified TiO_2 irradiated with visible light, Free Radic. Biol. Med. 44 (2008) 1120–1130.

[15] T. Daimon, T. Hirakawa, M. Kitazawa, J. Suetake, Y. Nosaka, Formation of singlet molecular oxygen associated with the formation of superoxide radicals in aqueous suspensions of TiO_2 photocatalysts, Appl. Catal. A: Gen. 340 (2008) 169–175.

[16] A. Ricci, M.N. Chretien, L. Maretti, J.C. Scaiano, TiO_2-promoted mineralization of organic sunscreens in water suspension and sodium dodecyl sulfate micelles, Photochem. Photobiol. Sci. 2 (2003) 487–492.

[17] N. Serpone, A. Salinaro, S. Horikoshi, H. Hidaka, Beneficial effects of photo-inactive titanium dioxide specimens on plasmid DNA, human cells and yeast cells exposed to UVA/UVB simulated sunlight, J. Photochem. Photobiol. A: Chem. 179 (2006) 200–213.

[18] D.D. Buechter, Free radicals and oxygen toxicity, Pharm. Res. 5 (1988) 253–260.

[19] W.A. Lee, N. Pernodet, B. Li, C.H. Lin, E. Hatchwell, M.H. Rafailovich, Multicomponent polymer coating to block photocatalytic activity of TiO_2 nanoparticles, Chem. Commun. (2007) 4815–4817.

[20] M.S. Agren, Percutaneous absorption of zinc from zinc oxide applied topically to intact skin in man, Dermatologica 180 (1990) 36–39.

[21] A. Dupre, P. Touron, J. Daste, J. Lassere, J.L. Bonafe, R. Viraben, Titanium pigmentation: an electron probe microanalysis study, Arch. Dermatol. 121 (1985) 656–658.

[22] C.A. Moran, F.G. Mullick, K.G. Ishak, F.B. Johnson, W.B. Hummer, Identification of titanium in human tissues: probable role in pathologic processes, Hum. Pathol. 22 (1991) 450–454.

[23] M.-H. Tan, C.A. Commens, L. Burnett, P.J. Snitch, A pilot study on the percutaneous absorption of microfine titanium dioxide from sunscreens, Australas. J. Dermatol. 37 (1996) 185–187.

[24] J.I. Pankove, Optical Processes in Semiconductors, Prentience-Hall Inc., New Jersey, 1971.

[25] N. Venkatachalam, M. Palanichamy, V. Murugesan, Sol–gel preparation and characterization of alkaline earth metal doped nano TiO_2: efficient photocatalytic degradation of 4-chlorophenol, J. Mol. Catal. A: Chem. 273 (2007) 177–187.

[26] H.-H. Ou, S.-L. Lo, C.-H. Wu, Exploring the interparticle electron transfer process in the photocatalytic oxidation of 4-chlorophenol, J. Hazard. Mater. B 137 (2006), 1362-1361.

[27] H. Gnaser, M.R. Savina, W.F. Calaway, C.E. Tripa, I.V. Veryovkin, M.J. Pellin, Photocatalytic degradation of methylene blue on nanocrystalline TiO_2: surface mass spectrometry of reaction intermediates, Int. J. Mass Spectrom. 245 (2005) 61–67.

[28] E. Oliveros, S.H. Bossmann, S. Nonell, C. Martí, G. Heit, G. Tröscher, A. Neuner, C. Martínez, A.M. Braun, Photochemistry of the singlet oxygen $[O_2(^1\Delta_g)]$ sensitizer perinaphthenone (phenalenone) in *N,N′*-dimethylacetamide and 1,4-dioxane, New J. Chem. 9 (1999) 85–93.

[29] D.R. Kearns, Physical and chemical properties of singlet molecular oxygen, Chem. Rev. 71 (1971) 395–427.

[30] J.M. Aubry, Search for singlet oxygen in the decomposition of hydrogen peroxide by mineral compounds in aqueous solutions, J. Am. Chem. Soc. 107 (1985) 5844–5849.

[31] W. Macyk, K. Szaciłowski, G. Stochel, M. Buchalska, J. Kuncewicz, P. Łabuz, Titanium(IV) complexes as direct TiO_2 photosensitizers, Coord. Chem. Rev. (2010), doi:10.1016/j.ccr.2009.12.037.

[32] A. Mills, S.-K. Lee, A web-based overview of semiconductor photochemistry-based current commercial applications, J. Photochem. Photobiol. A: Chem. 152 (2002) 233–247.

[33] C. Karapire, H. Kolancilar, Ü. Oyman, S. Icli, Fluorescence emission and photooxidation studies with 5,6- and 6,7-benzocoumarins and a 5,6-benzochromone under direct and concentrated sun light, J. Photochem. Photobiol. A: Chem. 153 (2002) 173–184.

[34] C. Karapire, M. Kus, G. Turkmen, C.C. Trevithick-Sutton, C.S. Foote, S. Icli, Photooxidation studies with perylenediimides in solution, PVC and sol–gel thin films under concentrated sun light, Solar Energy 78 (2005) 5–17.

[35] R. Konaka, E. Kasahara, W.C. Dunlap, Y. Yamamoto, K.C. Chien, M. Inoue, Irradiation of titanium dioxide generates both singlet oxygen and superoxide anion, Free Radic. Biol. Med. 27 (1999) 294–300.