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Self-Cleaning Properties, Mechanical Stability, and Adhesion Strength of Transparent Photocatalytic TiO_2-ZnO Coatings on Polycarbonate

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Abstract

Transparent layers containing TiO_2 have been intensively studied based upon their interesting application potential including photocatalytically active and self-cleaning surfaces. In the present work, transparent TiO_2-ZnO thin films on a SiO_2 interlayer have been successfully deposited on the surface of polycarbonate to provide polymeric sheets with a self-cleaning, superhydrophilic, and photocatalytically active surface layer. To ensure a good adhesion of the SiO_2 interlayer, the polycarbonate sheets have been firstly modified by irradiation with UV(C) light. The prepared films were characterized by UV/Vis spectrophotometry, SEM, XRD, Raman spectroscopy, ellipsometry, and water contact angle measurements. All prepared films are transparent with thicknesses in the range between 120 and 250 nm and possess superhydrophilic properties. Moreover, they exhibit good adhesion qualities as defined quantitatively by cross-cut tests. On the other hand, their mechanical strengths, checked by felt-abrasion tests, differ by changing the molar TiO_2-ZnO ratio. The photocatalytic activity, expressed as photonic efficiency, of the coated surfaces was estimated from the kinetics of the photocatalytic degradation of methylene blue and methyl stearate. The combination between superhydrophilic properties and photocatalytic activity was determined by studying the change of water contact angle during the storage of the prepared films in the dark under ambient atmosphere and under an atmosphere containing either acetone or isopropanol followed by UV(A) irradiation. In addition, self-cleaning properties were examined by determining the changes of contact angle during the irradiation time after applying oleic acid to the surface. The results show that increasing the molar ratio of ZnO in TiO_2 coatings up to 5% yields maximum photonic efficiency values of 0.023% as assessed by the photocatalytic degradation of methylene blue. Moreover, the superhydrophilic coating with a molar TiO_2-ZnO ratio of 1: 0.05 exhibits the best self-cleaning properties combined with a good mechanical stability and a very good stability against UV irradiation.

Keywords: self-cleaning; adhesion, mechanical stability, photocatalysis, superhydrophilicity, and wettability.

Introduction

For many years the automotive industry has been replacing heavy and badly deformable materials by lighter materials that are easily shapeable to comply with modern design requirements. Following this trend glass has been replaced by polycarbonate in applications such as cover glasses of front and rear lamps and of instrument panel guards.

The applications of polycarbonate are by no means limited to the automotive industry but rather range from plastic vessels and machine parts to optical grade materials employed for compact discs and optical fibers. Moreover, polycarbonate is commonly utilized in the eyeglass industry.[1]

To enhance the properties of these products the task of this work was to provide polycarbonate sheets with a self-cleaning superhydrophilic and photocatalytically active surface layer. Demands such as high transparency, low reflectivity, and high mechanical stability have to be taken into consideration as boundary conditions during the development of such a coating.

Much attention has been focused on the development of materials that can demonstrate photocatalytic behaviour and reversible wettability properties under proper illumination condition for applications in diverse technological fields. For these purposes titanium dioxide (TiO_2) represents one of the most studied and widely used material due to its low cost, its good stability, and its ease of preparation.[2,3] On the other hand, ZnO is also an important semiconductor and has been investigated widely for its catalytic, optical, and photochemical properties.[4] Mixed oxide composite materials can often be more efficient photocatalysts than pure substances.[5,6] This is due to the generation of new active sites as a result of interactions between the oxides, to an increased surface area, and to improved mechanical strength and thermal stability.[7] It is well known that the coupling of two semiconductors,[8] in particular, of TiO_2 and ZnO,[9] is useful to achieve a more efficient separation of photogenerated electron–hole pairs. This, in turn, leads to an improvement in the photocatalytic activity.

Thin films have been prepared by a variety of techniques, such as reactive evaporation,[10] sputtering,[11] chemical vapour deposition,[12] pulsed laser deposition,[13] spray pyrolysis,[14] and sol–gel processing.[15-17] Among these techniques, the sol–gel process is particularly attractive because of the following reasons: ease of composition control, low processing temperature, large area coating, low equipment cost, good homogeneity of the coating, and good optical properties of the films. Particularly, sol–gel processes are efficient in producing thin, transparent, multi-component oxide layers on various substrates.[18]

Recently, thin transparent layers containing TiO_2 have been intensively studied based upon their interesting application potential including photocatalytically active, self-cleaning surfaces. Table S1 presents an overview of the literature [15, 16, 19-28] dealing with the preparation of photocatalytic layers on different polymeric surfaces by the sol-gel technique.

From a technical point of view a good self-cleaning coating should exhibit a high photocatalytic activity, an excellent wettability by water, a strong adhesion to the surface of the substrate and sufficient stability against exfoliation and abrasion, as well as optical properties appropriate for the intended application. The references given above have shown that photocatalytic coatings can indeed be provided on polycarbonate sheets with sufficient self-cleaning properties. However, an improvement of the adhesion strength, the mechanical stability, the wettability, and the photocatalytic activity of such coatings on polycarbonate surfaces is still needed. Hence, the main aim of the present work is to improve the polycarbonate surface by the formation of stable photocatalytic and superhydrophilic TiO_2-ZnO thin films employing a dip coating sol-gel method and to examine the respective adhesion strength, mechanical stability, and self-cleaning properties.

Experimental part

Film preparation

Modification of the polycarbonate surface

Polycarbonate sheets (PC, Makrolon AL 2647) (5 cm × 18 cm) were washed with water, distilled water, and isopropanol (Roth, ≥99.5 %) and then dried at 80°C. The surface modification of the polycarbonate was then performed via a photo Fries reaction by irradiation with UV(C) light (Philips PL-L 36 W) for 2 h.[29]

Preparation of the SiO_2 intermediate layer

SiO_2 were prepared from tetraethyl orthosilicate (TEOS). 29.2 ml TEOS (Roth ≥ 98%,) were dissolved in 5.8 ml ethanol (Roth 99.8%,) and mixed with 7.2 ml deionized water followed by 30 min stirring of the mixture . Subsequently, 0.03 ml hydrochloric acid (Fluka 37%,) were added into the solution to catalyze the hydrolysis followed by further stirring of the solution for 60 min. Finally, 10 ml of the resulting solution were diluted to 200 ml with absolute ethanol and then stirred at ambient temperature for 24 h. The resulting SiO_2 sol was deposited on the polycarbonate surfaces by a dip-coating process. The PC slides were withdrawn into open air with a pulling rate of 1 mm/s. The dip-coated films on the polycarbonate substrates were dried at 80°C for 24 h. It worth mentioning that all the samples studied in this work are prepared on PC substrates having a SiO_2 interlayer.

Preparation of the TiO_2 –ZnO layer

Titanium tetraisopropoxide (TIPT) (Aldrich, 97 wt %) and zinc acetate ($Zn(ac)_2$) (Fluka, 99.99wt%) were used as metal sources for the synthesis of TiO_2, ZnO, and TiO_2-ZnO porous films. The non-ionic amphiphilic triblock copolymer $(PEO)_{20}(PPO)_{70}(PEO)_{20}$ (Pluronic P123, Aldrich) was employed as a templating agent. TIPT/P123/HCl/C_2H_5OH molar ratios in the reacting solution were 1 : 0.01 : 0.5 : 41. First, Pluronic and ethanol were stirred at room temperature (RT) for 30 minutes. Then HCl and titanium tetraisopropoxide were added to prepare a TiO_2 sol. Varying amounts of $Zn(ac)_2$ were added to the sol (molar ratios of TIPT/$Zn(ac)_2$ 1 : 0, 1 : 0.025, 1 : 0.05, 1 : 0.1, 1 : 0.2, 0 : 0.1). The resulting suspension was stirred until the $Zn(ac)_2$ was totally dissolved. The resulting mixture was diluted with ethanol and stirred at RT for 24 h. Subsequently, the films on the SiO_2 coated polycarbonate were prepared by dip-coating. The dip-coated films on the polycarbonate substrates were aged for 24 h at 80°C and subsequently 2h at 120C° followed by irradiation with UV(A) light ($10Wm^{-2}$ 20 W UV tube, Eurolite).

Characterization of films and contact angle measurements

X-ray diffraction (XRD) patterns of the TiO_2-ZnO coatings were collected on a Huber G670 diffractometer with Mo Kα radiation ($\lambda = 0.07107$ nm). Field emission-scanning electron microscope (FE-SEM) measurements were carried out on a JEOL JSM-6700F field emission instrument using a secondary electron detector (SE) at an accelerating voltage of 2 kV. Raman spectroscopy measurements were carried out with SENTERRA Dispersive Raman Microscope (Bruker optics). The thickness of the prepared films was determined by means of ellipsometry (EL X– 02C, Dre, Germany). The optical properties of the prepared films were determined by recording the absorption spectra in the range 400-800 nm using a UV/VIS spectrophotometer Varian Cary 100 Bio. FT-IR spectra of the powders scratched from the prepared films were recorded with a BRUKER FRA 106 spectrometer using the standard KBr pellet method. The mechanical strength of the thin films was investigated by felt - abrasion tests (felt 2.5 cm × 3.5 cm, 70 g cm^{-2}, 74 min^{-1}). The hydrophilic properties of the films were determined by measuring the contact angle (CA) of water using a CAM 100 optical contact angle meter (KSV Instruments, Germany).

Evaluation of the photocatalytic activity of the films

The photocatalytic tests were performed with an aqueous solution of methylene blue (MB; Aldrich) and in the solid phase using methyl stearate (MS; Aldrich). First, each sample was rinsed with ethanol then with purified water, followed by drying for 24 h. After cleaning, the samples was irradiated with UV light (10 W m^{-2}, Radium UVASOL) for 24 h to decompose the remaining organic contamination by photocatalytic reaction. The rate of the photocatalytic decomposition of MB was determined according to the procedure described in the ISO standard method.[30] A cylindrically shaped glass reactor was used. 100 ml of an aqueous solution containing 0.02 mmol l^{-1} MB was poured into the test reactor and the dye was adsorbed in the dark for 12 h. After the adsorption of the dye was completed, the solution was replaced by the test solution (0.01 mmol l^{-1} MB) and the sample was irradiated with UV(A) light (10 W m^{-2}). The decomposition of the dye under UV light irradiation was determined by measuring the absorption spectra using a UV/Vis spectrophotometer Varian Cary 100Bio. For the solid phase tests, a thin film of methyl stearate was coated onto a surface area of the titania film being 5 cm × 7.5 cm in size by evenly spreading 0.5 ml of a 5 mM solution of methyl stearate in n-hexane. After illumination for 24 h (10 W m^{-2} UV(A)), the remaining methyl stearate film was washed from the surface employing 5 ml n-hexane. The concentration of methyl stearate was measured by gas chromatography GC–2010 (Shimadzu, Japan; column Rtx-5, carrier gas Helium, initial temperature 20 °C, final temperature 310 °C, heating rate 60 °C/min). The photonic efficiency PE is defined as the ratio of the degradation rate and the incident photon flux J_0 in mol photons. It is thus related to the illuminated area A and the volume V of the employed test solution.

Evaluation of the self-cleaning performance and the photoinduced hydrophilicity of the prepared films

The combined effect of photooxidation and photo-induced change in wettability was determined according to the procedure described in the ISO 27448 standard method.[31] 0.5% (by volume) solution of oleic acid (Merck, extra pure) in n-heptane (Sigma-Aldrich, anhydrous 99%) was used to dip the polycarbonate test pieces (3.5cm × 2.5cm) at a speed 60 cm min^{-1}. The test pieces were dried at 70° C for 15 min. Then they were irradiated at (10 ± 1) Wm^{-2}. The contact angle (CA) of water was measured during the irradiation time at five places on each test pieces. The experiment was carried out at a temperature of 21°C ± 1°C and a humidity of 44 % ± 3%.

The photo-induced hydrophilicity of the prepared films was evaluated by water contact angle measurements. First of all the prepared films were irradiated by UV(A) light. Then they were stored in the dark under ambient conditions or in the presence of either acetone or isopropanol until their contact angles increased. The water contact angles were measured during the storage time. Following the increase of the contact angle of the prepared films during their storage in the dark, the films were irradiated by UV(A) until a superhydrophilic surface was once again attained. Their contact angles were also measured during the irradiation time.

Quantitative estimate of the adhesion of the prepared films after UV irradiation

The prepared films were irradiated for three months using a UV(A) lamp (10 Wm^{-2}). A cross–cut test was subsequently applied according to a standard method ISO 2409 [32] to obtain a qualitative impression of the adhesion of the deposited layers on polycarbonate surface after this exposure to UV irradiation. The cross cut was applied manually. The coated polycarbonate sheets were crisscrossed to form small squares (0.5 cm × 0.5 cm) to facilitate the possible breakdown of the films, i.e., to investigate any exfoliation behaviour. An adhesive tape was stuck on the network surface and hauled almost with a constant force. A certain percentage of the squared surface crumbled from the edge of the squares. These crumbling are a measure of the adhesion quality. A microscope (Olympus IXSO) was used with zoom lenses of 40 × magnifications. According to ISO 2409, the quality of adhesion is ranked by different numbers ranging from 0 (excellent) to 5 (very poor) (cf. Table 1).

Results and Discussion

Light modification of polycarbonate and deposition of the intermediate layer

In order to prevent the polycarbonate sheet from being destroyed upon illumination by the effect of the photocatalytically active layer, the polymeric support and the photocatalytically active coatings have to be separated by a photocatalytically inactive, non-conducting layer.[33] For this purpose, a SiO_2 layer was successfully deposited by a dip-coating process onto the polycarbonate surface. The thickness of this layer was determined by ellipsometry to be (33 ± 9 nm) as shown in Table 2. This silica film plays two main roles. Firstly, it protects the polymer's surface from the action of the photocatalytically active films; secondly, it enhances the connection between the inorganic films, i.e., TiO_2, ZnO, and TiO_2-ZnO layers, and the organic polymer.

To ensure a good adhesion of the SiO_2 interlayer, the polycarbonate sheets have been firstly modified, before the deposition of any layer, by irradiation with UV(C) light. Polycarbonate (PC) will undergo a Photo-Fries reaction upon exposure to UV(C) illumination forming hydroxylated and/or carboxylated surfaces. The increase in the number of hydroxyl and carboxyl chain ends are the results of chain scission at the carbonyl groups in PC structure caused by the Photo-Fries rearrangement of the PC monomer yielding phenylsalicylates and dihydroxybenzophenones.[22,34]

Deposition of the photocatalytically active layers

TiO_2, ZnO, as well as TiO_2-ZnO thin films on a SiO_2 interlayer have been successfully deposited on the surface of polycarbonate sheets by dip-coating providing them with self-cleaning superhydrophilic and photocatalytically active surface layers. The change of the water contact angle of the freshly prepared coatings during UV(A) irradiation is shown in Figure 1. As can be seen from this Figure, the water contact angle of a TiO_2-ZnO (1:0.05) coated surface decreases from 85º to <5º during 18 h of UV(A) irradiation (light intensity = 10 $W.m^{-2}$) while TiO_2 and ZnO coated surfaces need 16 h and 20 h, respectively, of UV(A) irradiation to reach the water contact angle <5º. This decrease of the water contact angle is explained by the photocatalytic degradation of the triblock copolymer Pluronic P123 that has been used as a template for the pores during the preparation of the coating. After the photocatalytic degradation of Pluronic all TiO_2-ZnO coatings prepared in this study were found to be superhydrophilic, *i.e.*, with their respective water contact angle being < 5° (Table 2). The degradation of organic compounds originally present at their surfaces resulted in superhydrophilicity. However, it should be mentioned here that superhydrophilicity is not solely induced by the removal of organic contamination via photocatalysis, but is also associated with water adsorption most probably due to the appearance of hydroxyl groups on surface defects.[21] As a surface becomes more and more oxidized, or has more ionisable groups introduced to it, hydrogen bonding to the adjacent water becomes more facile resulting in a water droplet spreading along the hydrophilic surface, and thus a lower contact angle.[35]

Characterization of the films

The SEM images of TiO_2, ZnO, and TiO_2-ZnO (1:0.05) coatings are shown in Figure S1. Different morphologies of the three films are observed from these images. While the formed TiO_2 is very small granular, the formed ZnO is rod-like nanostructures with pointed tips.[36,37]

The XRD pattern of the TiO_2, the ZnO, and the TiO_2-ZnO (1:0.05) coatings, respectively, which are shown in Figure 2, indicate the formation of anatase TiO_2 with a good crystallinity and of zincite ZnO with a high crystallinity, when they are prepared separately.[38] The characteristic diffraction peaks for TiO_2 were observed at 2Θ = 25.0°, 37.3°, 47.7°,54.5°, and 62.4° correspond to (101), (004), (200), and (211) planes of anatase, while the diffraction peaks for ZnO were observed at 2Θ = 31.7°, 34.4°, 36.2°,47.5°, 56.5°, 62.8°, and 67.9° correspond to (100), (002), (101), (102), (110), (103), and (112) indexed to hexagonal wurtzite structure ZnO . New peak at 2Θ = 39.5° was observed in the TiO_2-ZnO sample which may be attributed to TiO_2 (004). However, in the case of the in situ preparation of TiO_2-ZnO mixtures, the particle formation and the crystallinity of both TiO_2 and ZnO are affected negatively. The broad peaks observed in the XRD profile of both TiO_2 and TiO_2-ZnO samples indicate small crystallite diameters of the thus formed oxide nanoparticles.[39]

Raman scattering has been used here as another effective technique to investigate the crystallinity. Figure 3 shows Raman spectra of the TiO_2, the ZnO, and the TiO_2-ZnO (1:0.05) coatings, respectively. In the case of TiO_2, Raman peaks are apparent at 155, 399, 517, and 641 cm^{-1}. The Raman spectrum of ZnO shows a sharp peak at 437 cm^{-1} confirming the formation of zincite ZnO.[40] It can be clearly seen from the Raman spectrum of TiO_2-ZnO (1:0.05) that the Ti-O structures are dominating as expected since the titanium precursor has been employed here in a twentyfold excess over the zinc precursor.[41] Moreover, the appearance of the Raman peak at 437 cm^{-1} indicates that the formed nanostructures are composed of the anatase TiO_2 mixed with ZnO.[40]

Table 2 shows also the values of the thickness of the intermediate layer (SiO_2) and of the prepared TiO_2-ZnO thin films on polycarbonate, which were measured at different points on the surface of the coated plates by ellipsometry. The thickness of the SiO_2 intermediate layer was found to be 33 ± 9 nm. The thicknesses of the prepared TiO_2-ZnO films were in the range between 120 and 250 nm. No clear relationship between the thickness of the films and the added amount of ZnO was observed.

The optical properties of the prepared films were determined by recording the absorption spectra in the range 400-800 nm. Transmission values of uncoated and coated polycarbonate plates at $\lambda = 500$ nm are summarized in Table 2 indicating that all coatings prepared here are highly transparent in the visible range.[42] It has previously been reported that the transmittance of TiO_2 films at 500 nm only decreases by 2% when they are prepared at temperatures below 200 °C [43] while it decreases by approx. 8% when the films are annealed at around 500 °C. Moreover, Raoufi et al. have prepared transparent ZnO films employing the Sol-Gel method.[44]

The coatings prepared here also exhibit a high optical quality. At wavelengths > 420 nm all samples show a high optical transmittance nearly achieving the values determined for the uncoated substrate. This high transparency of the prepared films can be attributed to their mesoporous structure that is obtained by the addition of Pluronic P123, a non-ionic template, during their preparation. The corresponding regularly arranged pores found in inorganic mesoporous materials provide a higher and more uniform penetration of the incident light. [45]

Photocatalytic activity of the films

The photonic efficiencies PE of the photocatalytic degradation of methylene blue (MB) and of methyl stearate (MS) as a measure for the photocatalytic activity of the prepared TiO_2-

ZnO thin films on polycarbonate were calculated from the kinetics of the respective degradation reactions. For comparison, the photonic efficiencies of the photocatalytic MB and MS degradation on the self-cleaning glass Pilkington Activ™ were determined as well. The respective values are given as bars in Figure 4. Insertion of ZnO into the TiO_2 coating resulted in an increased photocatalytic activity of the prepared coatings when the degradation of methylene blue was used as the test reaction but in a decrease of the photocatalytic activity of the prepared coatings in the case of methyl stearate being the probe molecule. All films prepared in this work exhibit photocatalytic activities, however, in all cases these photonic efficiencies were found to be lower than that of Pilkington Activ™. The value of the photonic efficiency for the degradation of MB for Pilkington Activ™ (ξ_{MB} = 0.026%) measured in this work is in good agreement with a value published recently (ξ_{MB} = 0.024%).[46] Pure TiO_2 and ZnO coatings show only little photocatalytic activity in the MB degradation test. As can be seen from Figure 4 all TiO_2-ZnO coatings exhibit higher photonic efficiencies for the photocatalytic MB degradation than pure TiO_2 or ZnO coatings, respectively. The TiO_2-ZnO coating with a molar ratio of 1: 0.05 shows the highest photonic efficiency (ξ_{MB} = 0.023%), which is only about 10% lower than the photonic efficiency determined with Pilkington Activ™. The photonic efficiencies for the photocatalytic MS degradation on the surface of the TiO_2-ZnO thin films were usually in the same range as these determined for Pilkington Activ™ (ξ_{MS} = 0.009%).

The modification of the electronic properties of the coupled materials with respect to the single ones is invoked to explain the increased activity of TiO_2-ZnO as compared with both pure materials. Thus, the electron transfer from the conduction band of ZnO to the conduction band of TiO_2 under illumination and, conversely, the hole transfer from the valence band of TiO_2 to the valence band of ZnO should result in a decrease of the rate of electron-hole recombination, i.e., to an increase of the lifetime of the charge carriers (see Figure S2). This modification increases the availability of the electron-hole pairs on the surface of the photocatalysts and consequently improves the occurrence of redox processes.[47] It has also been reported that the surface recombination occurs more easily in ZnO.[48] That gives an explanation for decreasing of photonic efficiencies at high molar ratio of ZnO. Moreover, the above-described porosity can also enhance the photocatalytic activity of the prepared films via the so-called antenna effect.[49] In this case, the three-dimensional mesoporous TiO_2 network acts as an antenna system transferring the initially generated electrons from the location of light absorption to the point on which the organic pollutant is adsorbed.

Mechanical stability and adhesion strength of the films

The mechanical stability of the thin films was examined by a felt-abrasion test followed by the measurement of the water contact angle and by the determination of the photonic efficiencies of the photocatalytic degradation of MB and MS. The respective experimental data are included in Table 2 and in Figure 4. As it is obvious from Table 2, the water contact angles of the samples usually increase by rubbing the surface with the felt but in all cases the superhydrophilic state with water contact angles <5° was reconstituted within 24 h by UV(A) irradiation. The photonic efficiency of the photocatalytic degradation of MB was considerably affected by the felt-abrasion test (Figure 4). The decrease of the photonic efficiency was most pronounced for the pure ZnO coating (87%), while for pure TiO_2 and ZnO rich TiO_2 thin films the photonic efficiencies decreased by 40% and more. On the contrary, the decrease of the photonic efficiencies of the TiO_2-ZnO thin films with a TiO_2-ZnO ratio $\leq 1 : 0.05$ was less than 25%.

Figure 5 shows images of the layers of SiO_2, TiO_2, ZnO, and TiO_2-ZnO mixtures with different molar ratios (0.025, 0.05, 0.075, 0.1, and 0.2) after the cross-cut tests. The adhesion of the prepared films after three months UV irradiation was estimated quantitatively employing ISO 2409 method. According to this ISO, the quality of the SiO_2 interlayer is ranked as 2 (good) (see Table 2). All TiO_2-ZnO films except TiO_2-ZnO with molar ratio 1:0.2 also exhibit a good adhesion quality. TiO_2, ZnO, and TiO_2-ZnO films with molar ratios of 0.025, 0.05, 0.075, and 0.1 are ranked as 0 (excellent) while the TiO_2-ZnO film with a molar ratio of 1:0.2 is ranked as 4 (poor). The SiO_2 interlayer apparently plays an important role in improving the adhesion between the films and the polycarbonate substrate forming covalent bonds between the polycarbonate substrate on the one side and TiO_2, ZnO, or TiO_2-ZnO on the other side. The corresponding binding strength apparently decreases as the molar ratio of ZnO increases.

Self-cleaning performance and photoinduced hydrophilicity of the prepared films

Directly after the preparation of the superhydrophilic films, the photoinduced properties of the films prepared at different conditions were studied and compared with the photoinduced properties of Pilkington Activ ^{TM}. The prepared films and Pilkington glass were stored in the dark under atmospheric conditions. Figure 6 shows the change of the contact angle of TiO_2, ZnO and TiO_2-ZnO(1:0.05) thin films on polycarbonate during their storage in the dark and subsequent during the UV(A) irradiation. The addition of ZnO to TiO_2 helps to improve the hydrophilicity of the prepared films. The contact angle of TiO_2 and ZnO increased after 7 days of storage under ambient conditions in the dark while Pilkington Activ^{TM} maintained a contact angle <5° for 9 days of storage in the dark. The contact angle of the prepared TiO_2-

ZnO film with a molar ratio 1:0.05 increased only after 13 days of dark storage. In all cases investigated here the contact angle decreased to a value <5° within 24h of UV(A) irradiation with an intensity of 10 W m^{-2}.

This increase of the comtact angle is assumed to be due to the adsorption of hydrocarbons existing in the ambient atmosphere onto the thin films. Following their irradiation by UV light with intensity of 10W m^{-2}, the adsorbed hydrocarbons are decomposed and the films become superhydrophilic again.

Exposure of the superhydrophilic films to an atmosphere containing a high concentration of an organic solvent (acetone or isopropanol) resulted in an increase of the contact angle from values <5° to values of >30° within two hours of exposure (Figure 7 and Figure 8).

When the prepared films and Pilkington Activ^{TM} were stored in the dark in an atmosphere containing isopropanol, the TiO_2 and ZnO films maintained their superhydrophilicity for 1h while the TiO_2-ZnO film with a molar ratio 1:0.05 and Pilkington Avtiv ^{TM} preserve their superhydrophilicity for 2h. After the increase of their water contact angles, all films were irradiated with UV light. As a consequence, the contact angles of the prepared films decreased to values < 5° after 4h whereas the contact angle of Pilkington Activ^{TM} became <5° after 10h (Figure 7).

The effect of the addition of ZnO to TiO_2 on the photoinduced properties was less pronounced in the case of acetone being the gas phase pollutant. Figure 8 presents the time dependence of the change in water contact angle for TiO_2-ZnO films during the storage in the dark under an atmosphere of acetone and during subsequent UV(A) irradiation with10 W m^{-2}. The contact angle of the TiO_2-ZnO (1:0.05) film increased after 1h of storage in the dark in an acetone containing atmosphere. After UV irradiation for 5h, its contact angle decreases again from 65° to <5°. The compared Pilkington film has stable superhydrophilic properties for 0.75h. After this time its contact angle increased. Then its surface was irradiated by UV(A) light. Consequently, its contact angle drops from 64° to <5° within 5h of UV irradiation.

The rate of the conversion of a surface from a hydrophilic to a hydrophobic state depends on the adsorption of the hydrocarbons onto these surfaces which depends on their polarity as well as on the polarity of the adsorbent pollutant. The recovery of their hydrophilicity depends on their photocatalytic activity and their water adsorption ability. Acetone and isopropanol were used here as organic pollutants. The polarity index of acetone and isopropanol are 5.1 and 3.9, respectively. This means that acetone should be adsorbed more strongly on polar surfaces than isopropanol. Indeed, it can be observed by the comparison between Figure 7 and

Figure 8 that acetone needs longer time than isopropanol to decompose on the surfaces and become superhydrophilic again (The calculated rates of conversions to superhydrophilic state for TiO_2-ZnO 1:0.05 and Pilkington Activ^{TM} are -9°/1h and -5°/1h respectively under isopropanolic atmosphere and -13°/1h and -12°/1h respectively under acetonic atmosphere). This can be attributed to the stability of adsorbed acetone on the surfaces. Thus, it has recently been proposed that weakly bound water is displaced simultaneously upon the adsorption of organic molecules such as acetone on hydroxylated anatase surfaces.[50,51]

The self-cleaning performance was tested according to ISO 27448. After the application of oleic acid to the surfaces of the prepared films, these surfaces were converted to the hydrophobic state (with different water contact angle values depending on the nature of these surfaces) due to the hydrophobic properties of the adsorbed oleic acid. Oleic acid was subsequently decomposed by the photocatalytic oxidation resulting in a decrease of the water contact angle. Figure S3 shows the change of the water contact angle under UV irradiation after dip coating of oleic acid on the prepared films. The contact angle of the TiO_2 film decreases exhibiting a quite good photoinduced hydrophilicity conversion rate to be < 5° after 120h of the UV irradiation. The contact angle of the ZnO film decreased gradually to be <5° after 180 h of the irradiation using UV light with an intensity of 10 $W.m^{-2}$. Hence, the photoinduced hydrophilicity conversion rate of the ZnO film was found to be much lower than that of the TiO_2 film. The addition of ZnO to the TiO_2 film at different molar ratio leads to an improvement of the photoinduced superhydrophilicity conversion rate. The TiO_2-ZnO film with a molar ratio 1: 0.05 coated by oleic acid becomes superhydrophilic after 100h of the UV irradiation due to the photocatalytic degradation of oleic acid. Furthermore, the addition of ZnO to theTiO_2 films at different molar ratio leads to the appearance a kind of threshold on the self-cleaning curve.

The main products of the photocatalytic degradation of oleic acid are nonanal and 9-oxononanoic acid.[52] After that, nonanal will be oxidized yielding azelaic acid and/or octanoic acid. On the other hand, oxononanoic acid will be degraded photocatalytically yielding nonanoic acid. It is well known that 9-oxononanoic acid is much more hydrophilic than nonanal.[52] The formation of 9-oxononanoic acid as the main product of the photocatalytic degradation of oleic acid leads to a faster decrease of the contact angle as compared with the formation of nonanal. On the other hand, the products of the photocatalytic degradation of nonanal are more hydrophilic than the products of the photocatalytic degradation of 9-oxononanoic acid.

All prepared films (TiO_2, ZnO, and TiO_2-ZnO with different molar ratios) were found to be transparent exhibiting high adhesion strengths and therefore sufficient mechanical stability.

Conclusion

Polycarbonate was successfully coated with transparent, superhydrophilic and photocatalytically active TiO_2-ZnO thin films via a sol–gel dip-coating method using zinc acetate and titanium tetraisopropoxide as precursors for the metal oxides, Pluronic P123 as an organic template, and ethanol as the solvent. The presence of HCl as a catalyst for the pre–hydrolysis of TIPT affects the thermal decomposition of zinc acetate used as a zinc oxide source. In comparison to a pure TiO_2 coating the photocatalytic activity was increased by the incorporation of ZnO in the layer. The superhydrophilic coating with a molar TiO_2-ZnO ratio of 1: 0.05 exhibits the highest photonic efficiency combined with a good mechanical stability and a very good stability against UV irradiation.

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ASSOCIATED CONTENT

Supporting Information

Table S1 presents an overview of the literature dealing with the preparation of photocatalytic layers on different polymeric surfaces by the sol-gel technique. The SEM images of TiO_2, ZnO, and TiO_2-ZnO (1:0.05) coatings are shown in Figure S1. Different morphologies of the three films are observed from these images. Figure S2 shows the electron transfer from the conduction band of ZnO to the conduction band of TiO_2 under illumination and, conversely, the hole transfer from the valence band of TiO_2 to the valence band of ZnO. Figure S3 shows the change of the water contact angle under UV irradiation after dip coating of oleic acid on the prepared films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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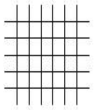
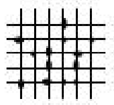
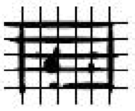
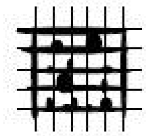
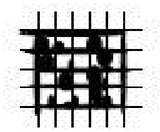
Table 1: Illustration of the quality of adhesion according to ISO 2409 standard.

Table 2: Mean contact angle and thickness of TiO_2-ZnO thin films on polycarbonate.

Crumbling	**Example**	**Explanation**
No		0 = Excellent
< 5%		1 = very good
5%-15%		2 = good
15%-35%		3 = moderate
35%-65%		4 = poor
> 65%	-	5 = very poor

Thin Film	**Thickness/ nm**	**Transparancy at 500nm/%**	**CA/ 1°**	**CA/ 1° after stability test (20 times)**	**CA/ 1°after stability test and UV(A) irradiation for 24 h**
none	-	97.92	85 ± 1	-	-
SiO_2	33 ± 9	97.91	57 ± 5	-	-
TiO_2	132 ± 10	97.52	<5	<5	<5
ZnO	210 ± 23	97.33	<5	56 ± 2	<5
TiO_2-ZnO (1:0.025)	248 ± 4	97.89	<5	<5	<5
TiO_2-ZnO (1:0.05)	169 ± 15	95.89	<5	<5	<5
TiO_2-ZnO (1:0.1)	202 ± 4	97.16	<5	35±1	<5
TiO_2-ZnO (1:0.2)	213 ± 10	98.15	<5	36 ± 1	<5

Figure 1: Change of the water contact angle of TiO_2, TiO_2*-ZnO(1:0.05) and ZnO films on polycarbonate during irradiation with UV(A).*

Figure 2: X – Ray diffractions of TiO_2*, ZnO and* TiO_2*-ZnO (1:0.05).*

Figure 3: Raman spectra of TiO_2*, ZnO and* TiO_2*-ZnO (1:0.05).*

Figure 4: Photonic efficiencies ξ *of the photocatalytic degradation of methylene blue (MB) and of methyl stearate MS on* TiO_2*-ZnO thin films on polycarbonate under UV (A) (*$10W.m^{-2}$*). The solid line presents the photocatalytic degradation of methylene blue (MB) after the stability test. The solid line expressed the percentage of decreasing in photonic efficiencies of the prepared films [▒ PE% for MB, ■PE% for MS].*

Figure 5: Photographs of the films after applying the cross cut test.

Figure 6: Change of contact angle on the thin films on polycarbonate after their storage in the dark and their irradiation by UV light.

Figure 7: Change of contact angle on TiO_2*-ZnO thin films on polycarbonate after their storage in the dark in presence of the isopropanol.*

Figure 8: Change of contact angle on TiO_2*-ZnO thin films on polycarbonate after their storage in the dark in presence of the acetone.*

Figure 1

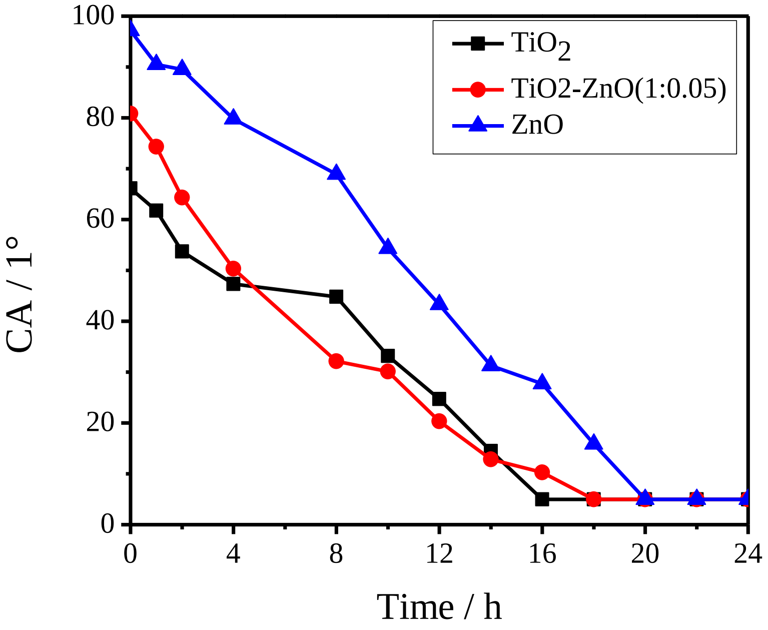


Figure 2

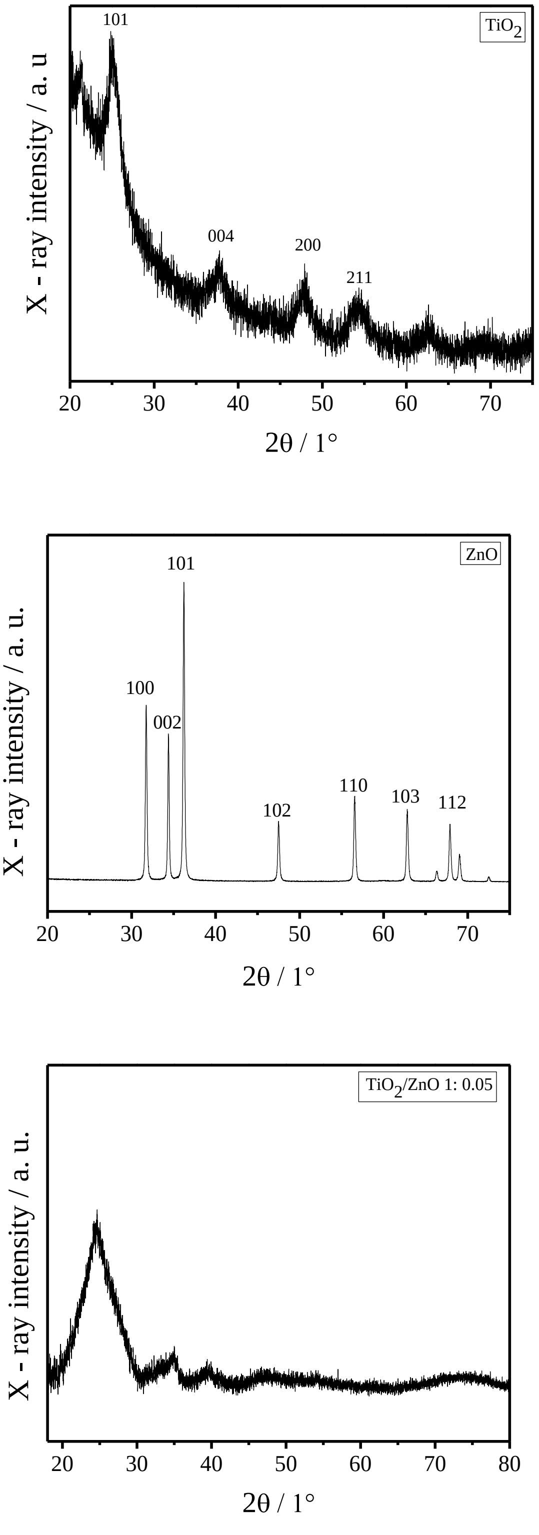

TiO2
101
004
200
211
X - ray intensity / a. u
20
30
40
50
60
70
2θ / 1°
ZnO
101
100
002
102
110
103
112
X - ray intensity / a. u.
20
30
40
50
60
70
2θ / 1°
TiO2/ZnO 1: 0.05
X - ray intensity / a. u.
20
30
40
50
60
70
80
2θ / 1°

Figure 3

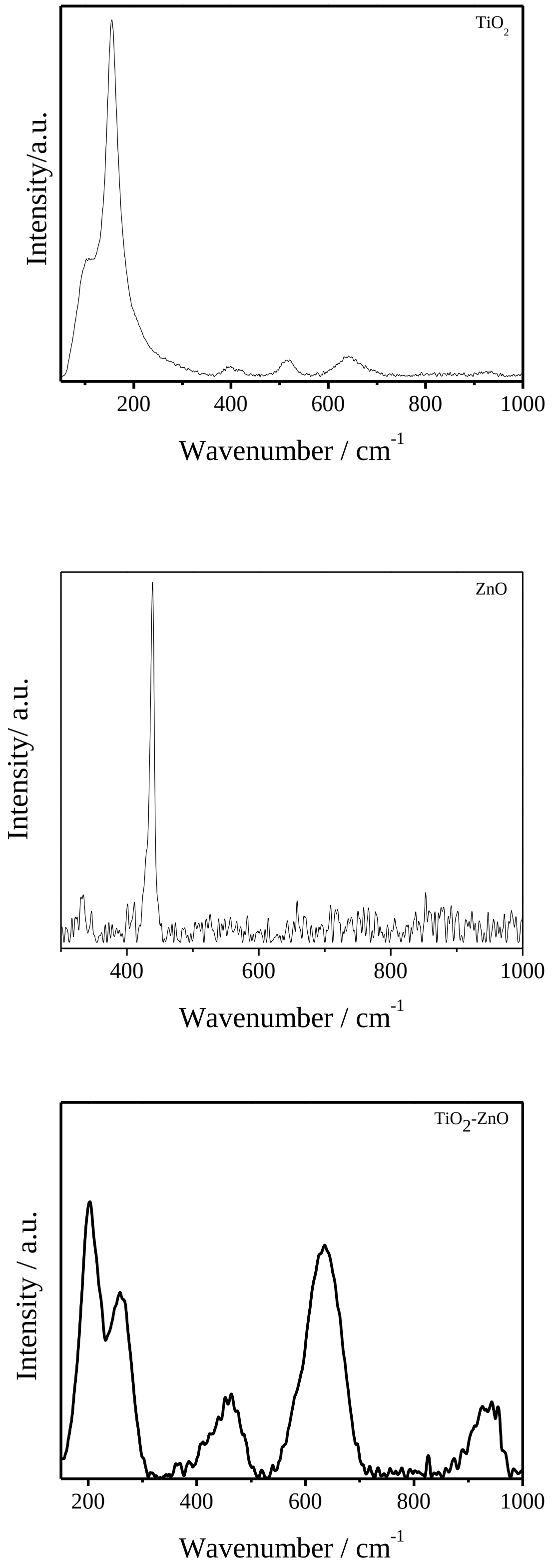

TiO2
Intensity/a.u.
200
400
600
800
1000
Wavenumber / cm-1
ZnO
Intensity/ a.u.
400
600
800
1000
Wavenumber / cm-1
TiO2-ZnO
Intensity / a.u.
200
400
600
800
1000
Wavenumber / cm-1

Figure 4

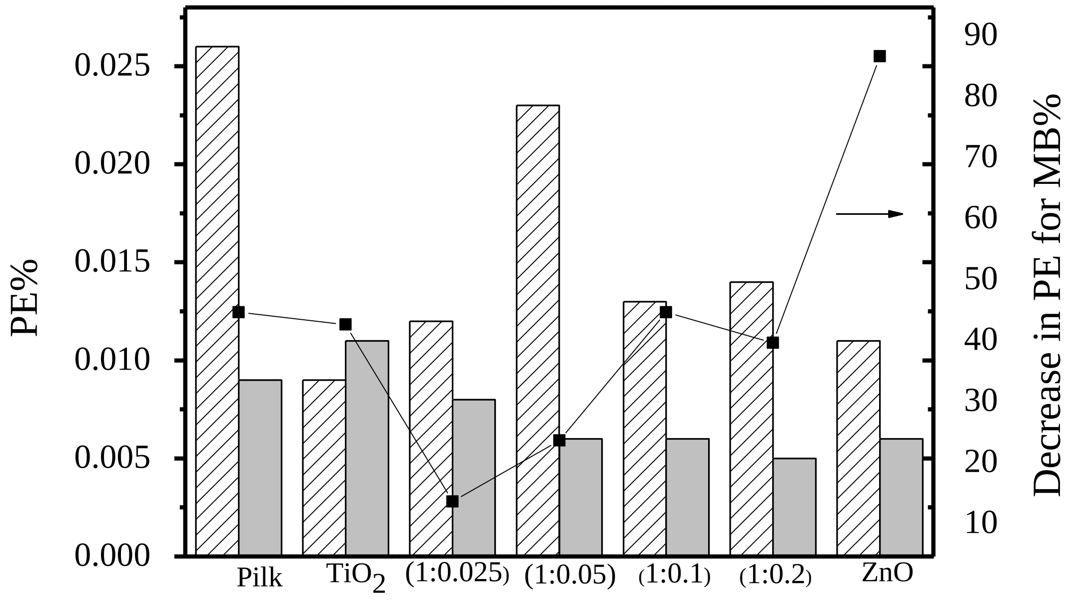

PE%
0.000
0.005
0.010
0.015
0.020
0.025
Decrease in PE for MB%
10
20
30
40
50
60
70
80
90
Pilk
TiO2
(1:0.025)
(1:0.05)
(1:0.1)
(1:0.2)
ZnO

Figure 5

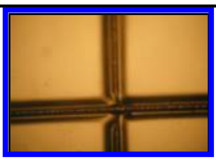
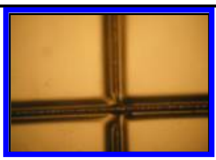
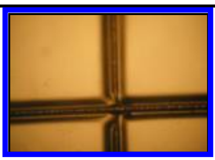
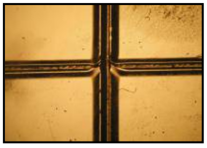
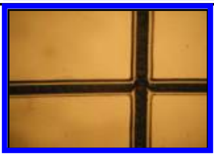
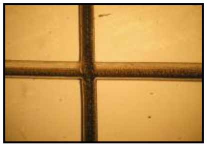
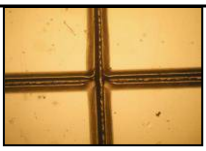
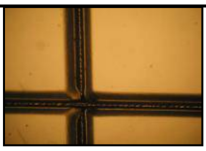
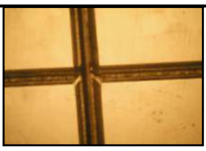
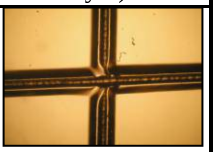
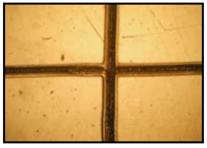
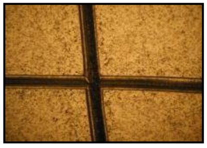
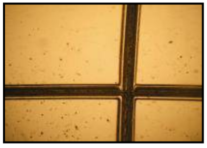
Film	TiO_2	TiO_2-ZnO =1:0.025	TiO_2-ZnO =1:0.05	TiO_2-ZnO =1:0.075
Befor irradiation				
After irradiation				
Film	TiO_2-ZnO =1:0.1	TiO_2-ZnO =1:0.2	ZnO	SiO_2 (intermediate layer)
Before irradiation				
After irradiation				

Figure 6

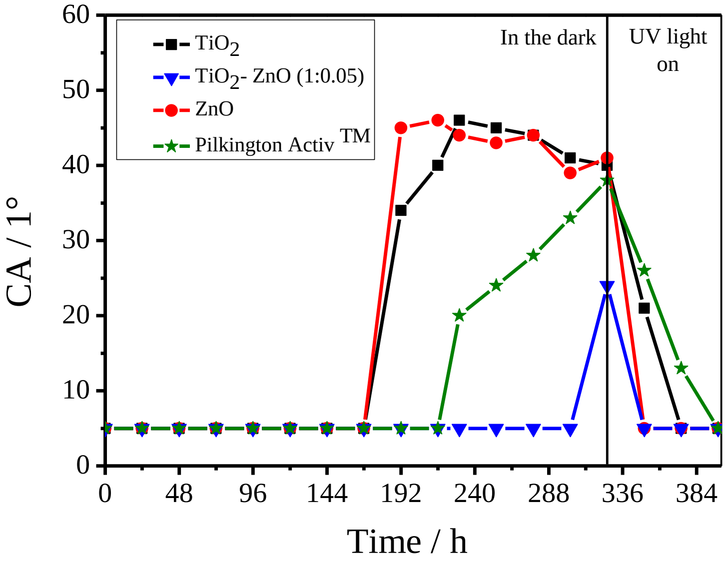


Figure 7

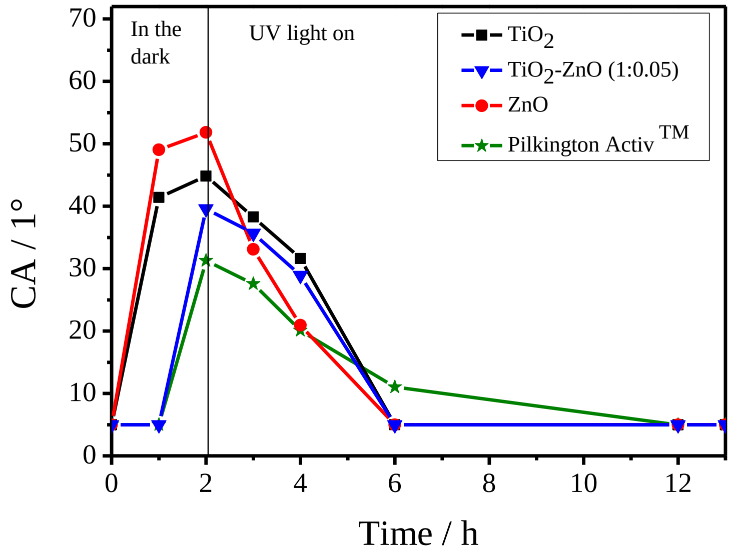
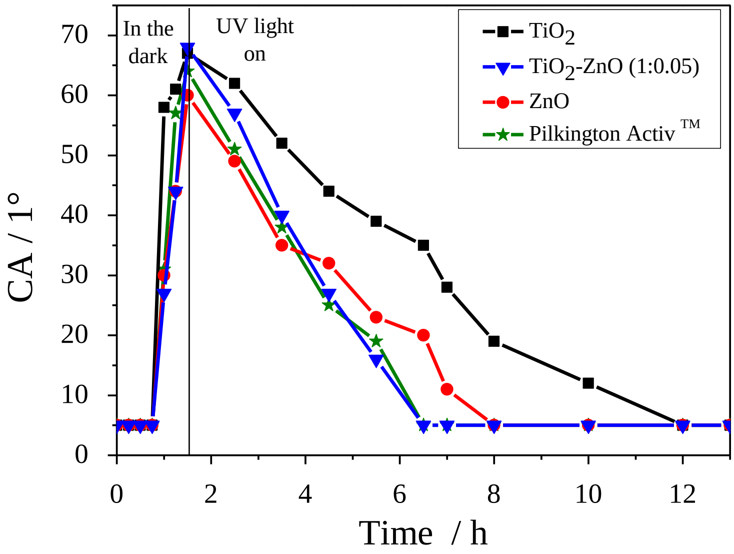


Figure 8



TOC