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Photoactive sol–gel hybrid coatings from modified fluorocarbon polymers and amorphous titania

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ABSTRACT

A series of organic–inorganic hybrid coatings was prepared through sol–gel chemistry by combining silanized chlorotrifluoroethylene-vinylether (FEVE) binders with tetraalkoxy silicon and titania sols under acidic conditions. The best compositions to obtain highly transparent and homogeneous coatings after thermal curing were determined. All the hybrid coatings easily pass the MEK test and show high scratch hardness. The atomic force microscopy (AFM) shows the formation of very smooth surfaces (R_{rms} routinely <1 nm) without clear phase separation phenomena. The typical size of the "objects" which may be individuated is in the range of 40–80 nm. Wettability through contact angle measurements shows the formation of moderately hydrophobic surfaces with a low contact angle hysteresis (∼20°) which is a further indication of very smooth, homogeneous and chemically stable surfaces. After irradiation with UV-B light only hybrid coatings containing titania phases show a significant switch to a superhydrophilic behavior with a contact angle against H_2O down to 6°, which is only partially recovered after storage of the material in the dark. Titania based hybrid coatings also showed a fast and efficient UV-induced discoloration of the resazurin ink. The formulation of the coatings with photostabilizers belonging to the class of radical scavengers and UV absorbers does not change the photoinduced surface properties while eliminating the yellowing of the coating after UV exposure. It is concluded that titania-fluoropolymer hybrid coating show photoactivity and UV-induced superhydrophylicity mostly through ionic mechanisms, which could be beneficial to develop high durability and self-cleaning protective coatings.

1. Introduction

The study of titanium dioxide as photocatalyst is a key topic in modern material science. Since Fujishima and Honda [1] have established that under UV exposition a TiO_2 electrode can decompose water to hydrogen and oxygen, the photoinduced properties of titania have been the object of a huge interest. For example photocatalytic properties of suspended titania powders have been studied for environmental uses such as water treatments and purifications [2], whereas thin films can find application as antibacterial and photoactive surfaces for deodorizing and purifying atmospheres [3,4]. The interest for TiO_2 thin films has broadened after finding that titania surfaces can exhibit photoinduced superhydrophilicity (contact angle values close to zero upon UV exposure) which has been exploited for antifogging applications. Among the most interesting applications there are the development of self-cleaning surfaces which rely on both photoinduced properties of titanium dioxide: photocatalysis (PCA) and photosuperhydrophilicity (PSH) working in a synergetic way to promote and maintain such functionality.

The self cleaning mechanism is the result of the mutual effect of the two photoinduced properties of TiO_2. Actually the PCA allows for organic compounds to be decomposed in aqueous environment under UV light irradiation, whereas PSH allows for water to spread completely across the surface [5]. In this way when the TiO_2 surface is irradiated with UV light, dirt and organic contaminants are decomposed and/or can be easily swept away by water through a simple rinsing operation or by the autonomous action of rain.

Both photoinduced properties proceed under light irradiation [6] with photon energy equal or greater than titania band gap (for anatase $h\nu > 3.2$ eV), which yields free photoelectrons e^- and holes h^+ (1) that successively can react in different ways.

$$TiO_2 + h\nu \rightarrow TiO_2 \quad (e^-_{cb} + h^+_{vb}) \tag{1}$$

The well established mechanism used to describe PCA is shown in (2) and (3) with formation of highly reactive free radicals:

$$e^- + O_2 \rightarrow \ast O_2^- \tag{2}$$

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$$h^+ + H_2O \rightarrow *OH + H^+ \quad (3)$$

On the other hand in PSH electrons and holes are produced but they react in a different way with formation of ionic species:

$$Ti^{4+} + e^- \rightarrow Ti^{3+} \quad (4)$$

$$O^{2-} + 2h^+ \rightarrow 1/2O_2 \quad (5)$$

In this process O_2 atoms are ejected and O_2 vacancies are created. Water molecules tend to occupy these O_2 vacancies producing absorbed OH groups which make surface extremely hydrophilic.

It is believed that each property reinforces and enhances the other one [7]. It is known that the classical photocatalytic reaction proceeds through a oxidative decomposition mechanism where strongly oxidant $^{\bullet}$OH radicals are the essential reactants [8].

The common mechanism of charge carriers photogeneration competes with recombination (6) which is the degradation of the photoelectric energy into heat, and strongly affects the photoefficiency of photoactive TiO_2 surfaces

$$e^- + h^+ \rightarrow N + E \quad (6)$$

where N is the neutral center and E the energy released under the form of light or heat [8].

This phenomenon is influenced by many parameters (particle size in powdered photocatalysts, porosity and thickness in thin films), and it has been shown that the defects are the main responsible for the recombination. It is commonly accepted that amorphous oxides contains high concentration of defects and impurities which act as recombination centers and promote the loss of the photoefficiency due to recombination [9]. This is why, so far, most of the researches concerns titania in its crystalline phase (especially in anatase form) although also amorphous TiO_2 is reported to show some photoactivity [9–11].

Crystallinity however influences more PCA than PSH, since the latter depends less critically on the film morphology; only a thin active surface layer is involved in the process and this reduces the recombination probability during migration of charge carriers toward surface.

With photoactive TiO_2 surfaces the contact angle against water approaches zero with UV irradiation. However, a hydrophobic recovery is restored comparatively quickly in the dark. The maintenance of hydrophilicity in the dark as well as PCA seem to be improved by TiO_2/SiO_2 mixed films [5]. Actually it has reported [12–14] that addition of SiO_2 in TiO_2 coatings can enhance the acidity of the composite oxide.

One of the most interesting development of modern sol–gel chemistry is the possibility to synthesize a wide array of organic/inorganic hybrid materials, which often show a synergistic combination of the properties of each moiety [15,16]. Many examples concern hybrids with silica sols and higher atomic number metal oxides (Al, Zr etc.) [17].

On the other hand, the practical exploitation of photoactive titania in combination with conventional organic binders for paints is made unfeasible by the fast photodegradation of the matrix; actually standard “white” titania pigments are normally surface treated to eliminate their photoactivity.

In the light of the above, one exception could be represented by fluorocarbon polymers, since due to the high strength of C—F bonds these materials possess outstanding outdoor durability like in the case of classical polyvinylidene fluoride or perfluoropolyether paints for coil coating or heavy duty [18–21]. Fluorocarbon polymers might be therefore compatible even with highly photoactive oxide phases being intrinsically resistant toward photooxidation. Moreover, the combination of oleophobicity typical of fluoropolymers with titania photoactivity could lead to the development of self-cleaning and highly durable protective coatings.

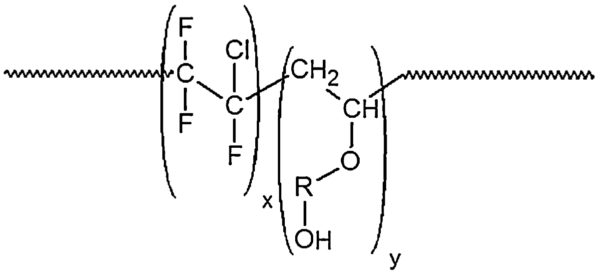

Fig. 1. FEVE resin chemical structure.

In this study, a hydroxyl-functional fluoropolymer binder belonging to the series of chlorotrifluoroethylene-vinylether copolymers [22] was selected and a series of polymeric organic/inorganic SiO_2-TiO_2 hybrid coatings were synthesized by sol–gel chemistry and characterized. In particular, the surface wettability and photoinduced properties were studied as a function of the TiO_2 amount.

2. Experimental

2.1. Materials

All the products were commercial grade, and used without any further purification. The inorganic precursors were tetraethylorthosilicate (TEOS) and titanium isopropoxide (TIPT) provided by Sigma–Aldrich. Water and hydrochloric acid (HCl 37%) were used for preparing the acidic solution and ethanol (EtOH) was the dilution solvent. UV stabilizers (TINUVIN® 400, 384 and 292, from Ciba) were used in some cases. The γ-propyl-isocyanate silane (from Fluka) was used for the fluorocarbon polymer functionalization. The fluorocarbon resin Lumiflon LF-910 LM (from Asahi Glass, Japan) is a chlorotrifluoroethylene-vinylether copolymer (FEVE in the following), and it was used as base fluoropolymer for the following functionalization steps. The main features are summarized in Table 1 and Fig. 1. The chemicals used for testing photocatalytic activity, namely hydroxyethylcellulose (HEC), glycerol (gly) and resazurin (Rz) were purchased by Sigma–Aldrich and used as received.

2.2. FEVE functionalization

The reaction of FEVE with γ-propyl-isocyanate triethoxysilane was performed under nitrogen at 75 °C maintaining magnetic stirring for 4 h. The reaction was monitored by FTIR for evaluating the disappearance of the NCO adsorption band (NCO stretching, 2260 cm^{-1}). The final product was diluted with EtOH up to a solid of 50%. One third of the existing OH groups were endcapped with the isocyanate silane as the best compromise between silanized resin shelf-life, and compatibility with inorganic sols. The functionalized resin will be labeled as FEVE-sil (see Table 2).

Table 1
FEVE resin characteristics.

Binder type	Hydroxy equivalent weight (g/eq)	Solid content	OH value (mg KOH/g polymer)	Density (g/cm^3)	Solvent
FEVE	367	66 (%)	100	1.16	Xylene 18%–ethylbenzene 16%