DESIGN AND PREPARATION OF NANOSTRUCTURED TIO$_2$ MATERIALS BY USING SUPERCRITICAL CO$_2$ SILANIZATION, AND POST-FUNCTIONALIZATION

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ABSTRACT

The present work presents the latest advances for the modification of TiO$_2$ surfaces by their functionalization with complex organic molecules through a scCO$_2$ strategy. Two strategies were followed: the first strategy involved the deposition under anhydrous conditions onto the TiO$_2$ surface of laboratory prepared silane containing nitro-phenyl and nitro-formyl groups, leading to the products designed as Ti-NP and Ti-FP. The second strategy involved the silanization of the commercial silane 3-(trimethoxysilyl)propyl methacrylate (MPTMS) on the TiO$_2$ surface, followed by the post functionalization with (1,2)-diaminocylohexane (Dac), using also scCO$_2$ as solvent. As a result, grafted TiO$_2$ nanoparticles designated as Ti-MP-Dac were obtained. Modified TiO$_2$ nanopowders were characterised by thermogravimetric analysis, ATR-IR spectroscopy, and UV–vis diffuse reflectance.

INTRODUCTION

Along the recent past, numerous authors have developed original tailor make molecular species, and designed new functional hybrid materials with improved properties, by functionalizing inorganic matrices via surface immobilization of functional groups. In particular, the functionalization of TiO$_2$ with organic species have been broadly employed and studied in numerous fields thus, the chemisorptions of organic self-assembled monolayers can be utilized in many ways. For example, organically modified TiO$_2$ can be used in electronic devices, where sulfonated-terminated molecules where used to form metal–oxide–metal nanowires by a "bottom-up" approach [1]. The ability to attach organic materials may have a large potential in hybrid microelectronic systems containing titanium dioxide together with organic components. This is the case of TiO$_2$ modified with a poly(triarylamine (PTAA)), that served to form the source and the drain of the transistor [2]. The functionalization of TiO$_2$ with perfluorododecyltrichlorosilane was used as conducting polymers en route to the formation of polymer-based transistors [3].The use of organically modified titanium dioxide in photovoltaics, is also well recognized. The attachment of different anchoring groups, including phosphonic acids, silanes, and carboxylic acids, has been investigated. Specifically, the grafting of TiO$_2$ with silane-bearing aniline compound (C$_6$H$_5$NHC$_3$H$_6$Si(OMe)$_3$) was used to form solvent-free and quasi-solid solar cells based on acid-doped polyaniline, although the efficiency quite small [4]. However, the use of aminopropylsilane resulted in an enhanced in the efficiency [5]. In order to replace the expensive dyes for cheaper analogues, 3-(trimethoxysilyl)propyl methacrylate attached were also used [6].
Regarding the use of TiO$_2$ as heterogeneous photocatalyst, large efforts are being made to develop catalysts that act selectively towards multiple contaminants, in a procedure

that it would handle preferentially those contaminants that are either highly toxic and/or nonbiodegradable. This is the case of chemisorbed self assembly monolayers (SAMs) of thiolated-β-cyclodextrin (TBCD) on TiO_2 [7], where different contaminants in water were degraded by using this system.

In this work we report on the preparation of nanostructure hybrid materials composed of nanometric TiO_2 as inorganic support, and organic functional moieties containing different covalent or non covalent binding sites to be used as potential supramolecular cages, by using an organic solvent free silanization strategy. The approach followed was based in a technique designed, developed and optimised in our research group. Since the $scCO_2$ silanization of TiO_2 has proven to provide a route capable of preparing highly ordered and densely packed monolayers of a wide variety of silane precursors [8-11], our step forward was to modify TiO_2 nanoparticles with advanced silanes possessing multiple functionalities.
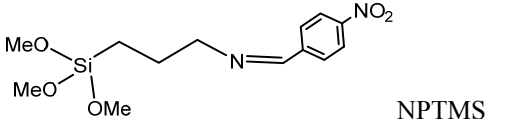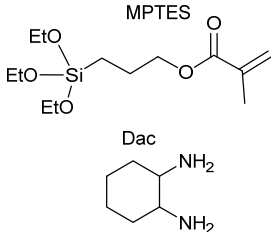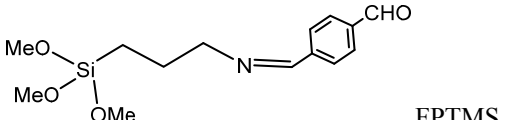
The first strategy involved the preparation of two new silanes with different functionalities, followed by the supercritical deposition under anhydrous conditions onto the TiO_2 surface. The second strategy involved the $scCO_2$ anhydrous deposition of a commercial silane on the TiO_2 surface, followed by the post functionalization with the required organic building block.

The technological significance of organically modified materials is highly documented, where the diversity of functional groups attached to an aromatic ring offers an opportunity to tailor the surface properties. Here we introduced the covalent attachment of organic molecules, since it can influence the surface electron affinity, chemical reactivity, wetting, radiation absorption, adhesion or biocompatibility [12,13]. Therefore, TiO_2 modified hybrid materials could be applied and extended from photovoltaic applications [14] to biosensor technology [15].

MATERIALS AND METHODS

Materials

TiO_2 nanometric particles (~ 20 nm in diameter) were supplied by Degussa (TiO_2 P25). CO_2 (Carburos Metálicos S.A.) was used as a solvent in the silanization process. , 4-nitrophenyl-(3-(trimethoxysilyl)-propyl)methanimine (NPTMS) and 4-(((3-(trimethoxysilyl)propyl)imino)methyl)-benzaldehyde (FPTMS) (table 1 a) were prepared as described in the literature [16]. MPTES and Dac (table 1.b) were purchased from Aldrich.

(a) **Structure of Prepared organosilanes [16].**	(b) **Structure of commercial MPTES and Dac**
NPTMS	MPTES
FPTMS	Dac

Table 1.- structure of prepared silanes (a) and commercial building blocks(b)

Methods

The silanization of the TiO_2 nanoparticles was carried out using the supercritical CO_2 engineered device previously reported by our research group [11]. The autoclave running in the batch mode was charged with ~ 0.5 g of TiO_2 enclosed in a 5 ml glass vial and covered with 0.45 μm pore filter paper. Liquid silane (0.5 mL) was added at the bottom of the reactor. The system was stirred at 300 rpm during the complete running time. At the end of each experiment, the system was slowly depressurized and allowed to cool to room temperature. The powder obtained was either washed with a current of $scCO_2$ or rinsed with ethanol or methanol, sonicated and centrifuged to remove the excess of deposited silane, and further dried under vacuum. In the post functionalization, the anchoring of the organic building block to the grafted silane was carried out in a similar way to that described for silanization. In this case, the already silanized particles were introduced in a 5 ml glass vial, and the organic building blocks were placed at the bottom of the reactor. Processing conditions of both silanization and post functionalization are listed in Table 2.

	Sample	P/[MPa]	T/ºC	t/h
Silanization	Ti-MP	15	75	3h
	Ti-NP	15	75	3h
	Ti-FP	15	75	3h
Post-functionalization	Ti-MP-Dac	10	85	3h

Table 2: Supercritical processing silanization and post-functionalization conditions

Characterization techniques

The quantification of the silanised and modified structures was carried out in a Thermogravimetric Analyzer (TGA, Perkin Elmer 7) apparatus under an Ar atmosphere and at 10 ºCmin^{-1} of temperature gradient. Modified powders were studied by ATR-FT (Attenuated total reflectance) spectroscopy using a Perkin Elmer Spectrum One spectrometer in the spectral range of 650 to 4000 cm^{-1}. The diffuse reflectance spectra of the processed solid samples were taken on a Carry 5000 UV-Vis-NIR spectrophotometer.

RESULTS AND DISCUSSION

Supercritical silanization and post functionalization process.

The silanization carried out on the TiO_2 nanoparticles surface was completed following the reported procedure [9-11]. In this work, the silanization of TiO_2 was carried out with both, the synthesised silanes and the commercial silanes, following the $scCO_2$ approach and, in both cases; the process is expected to proceed in the same way as in the described literature. The supercritical silanization has been described to proceed in four steps [17]. It starts with the hydrolysis of the alkoxy OR' groups of the silane molecule

to form silanols (RnSi(OH)$_4$-n), which can then interact with the OH groups on the surface of the inorganic particles (titanols in the case of TiO$_2$) by hydrogen bonding (Ti-OH...HO-Si), or with other silane molecules (Si-OH...HO-Si). Then, dehydration of the formed hydrogen bonds produce siloxane bonds between the silane and the surface (Ti-O-Si) and condensation of neighbouring silane molecules (Si-O-Si).
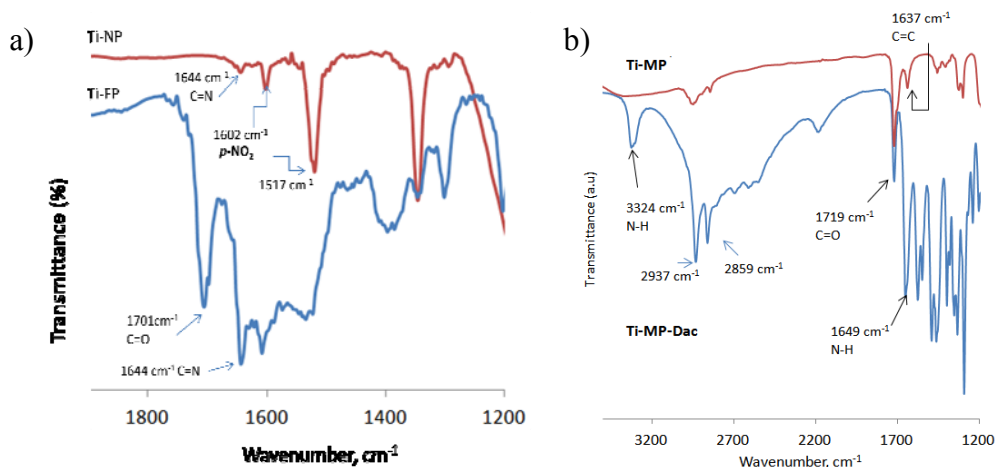
Fig. 1: ATR-F T spectra of laboratory prepared silanes grafted on TiO$_2$: a) Ti-NP and Ti-FP, and b) Ti-MP and Ti-MP-Dac, indicating the most representative infrared absorption bands.

Since the supercritical silanization proceeds in an anhydrous medium, the hydrolysis and condensation into polysiloxanes is minimised, and the formation of ordered self assembly monolayers is ensured. The post-functionalization process was also carried out following the scCO$_2$ approach, where the TiO$_2$ nanoparticles already silanized with the commercial silane (Ti-MP) were modified by a Michael-Aza reaction to yield Ti-MP-Dac.

ATR-FT and Diffuse reflectance UV–vis spectroscopies

The ATR-FT spectra of the NPTMS grafted on TiO$_2$ (Ti-NP) is shown in Fig. 1a. For the grafted Ti-NP it can be observed the C=N stretching band at 1644 cm^{-1}, as well as the bands at 1602 and 1517 cm^{-1} corresponding to the -NO$_2$ group attached to a benzene ring. The ATR-FT spectra of the Ti-FP are also shown in Fig. 1a. The signal corresponding to the C=N stretching band was found at 1644 cm^{-1} for the grafted silane, whereas in the free silane it was observed at 1643 cm^{-1}, as described in the literature [16], With regard to the carbonyl group, the stretching band was observed at 1705 cm^{-1} as expected. The data obtained in all the cases indicated a successful anchoring of the silane. Regarding the silanization with the commercial silanes, the binding of the MPTMS silane molecules onto TiO$_2$ (Ti-MP) surface was studied also by ATR-FT spectroscopy. Fig. 1b shows the spectra of the silanized TiO$_2$ together with the post-functionalized sample (Ti-MP-Dac). The most significant absorption bands for Ti-MP appeared at 1719 cm^{-1}, assigned to the stretching vibration of the C=O group, together with a band at 1637 cm^{-1}, assigned to the stretching vibration of the C=C band. The grafting of the silane on the TiO$_2$ did not produce any shift in the signal of the carbonyl group with reference to the ATR-FT spectrum of the free MPTMS. The absence of shift in the carbonyl absorption band was assumed to denote that the disposition of the silane towards the surface of the TiO$_2$ was perpendicular to the surface [8,16]. The spectrum of the modified Ti-MP-Dac also displayed a signal at 1719 cm^{-1} that was attributed to the

carbonyl group. However, the band that corresponds to the C=C double bond was not present in the spectrum of the Ti-MP-Dac, instead, an absorption band at 1649 cm^{-1} appeared, which was attributed to the presence of an amine bending absorption band. In addition, the spectrum showed a signal at 3324 cm^{-1}, corresponding to the primary amine, and the signals of the alkyl group at 2937 and 2859 cm^{-1}.

In contrast to the characteristic white colour of the TiO$_2$ raw material, some of the obtained silanized powders were coloured (orange and yellow for Ti-FP and T-NP respectively), thus diffuse reflectance UV–vis spectroscopy was carried out. For the studied grafted molecules, the organic part of each organic moiety contained different chromophore groups. The maxima of the absorption bands were observed at 591 nm for the Ti-FP and at 574 nm for Ti-NP. The sample Ti-NP showed the maximum absorption band at 594 nm, and it was obtained as a yellow powder, which is the characteristic colour of substances containing –NO$_2$ groups [18].
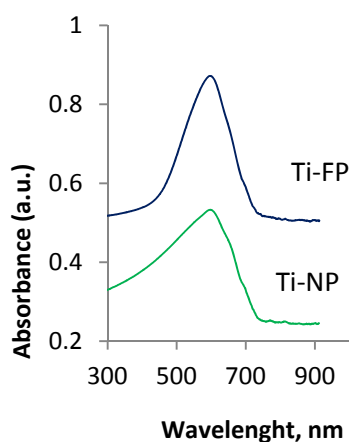

Fig. 2: UV-Vis spectra of grafted coloured silanes Ti-FP and Ti-NP

Thermal study (TGA) and grafting density.

The thermogravimetric analysis carried out for all of the studied samples, showed three characteristic weight loss regions: up to 200 ºC it was observed the desorption of water and non-hydrolyzed unbounded silane. Next, at ~200-350 ºC occurred the desorption of hydrolyzed silane not covalently reacted with OH on the surface, and finally form ~350 to 600 ºC took place the decomposition of the chemically bonded silane. In particular, the thermal analysis from 100 to 600 ºC of the grafted TiO$_2$ with the synthesised silanes is shown in Fig. 3 (a). The Ti-NP thermogram showed, at temperatures higher than 100 ºC, two main weight loss steps, as on the previous cases, the first one took place at 200-400 ºC, and it was attributed to the evaporation of the hydrolysable silane, not covalently bonded to the TiO$_2$ surface. The second one, occurring in the range 400-600 ºC, was attributed to the decomposition of the covalent bonded silane. The weight loss decay observed for Ti-FP (Fig. 3a) differed from the previous cases, since it cannot be observed the pronounced weight loss corresponding to the physically adsorbed silane. In this case, the weight loss decayed from 350 ºC upwards and was mainly attributed to decomposition of the covalent bonded silane, which is significantly lesser amount than the deposited silane in Ti-NP. This decrease was attributed to the possible formation of silane dimers from condensation of two silane molecules prior to deposition on the TiO$_2$ surface.

In the TGA profile of the post-functionalised sample (Fig. 3b), the weight loss observed for Ti-MP-Dac for the physisorbed silanes (temperature range 200-450 ºC) was of 4.89 wt% whereas the chemisorbed was of 2.88 wt% (total of adsorbed silane 7.77 wt%).
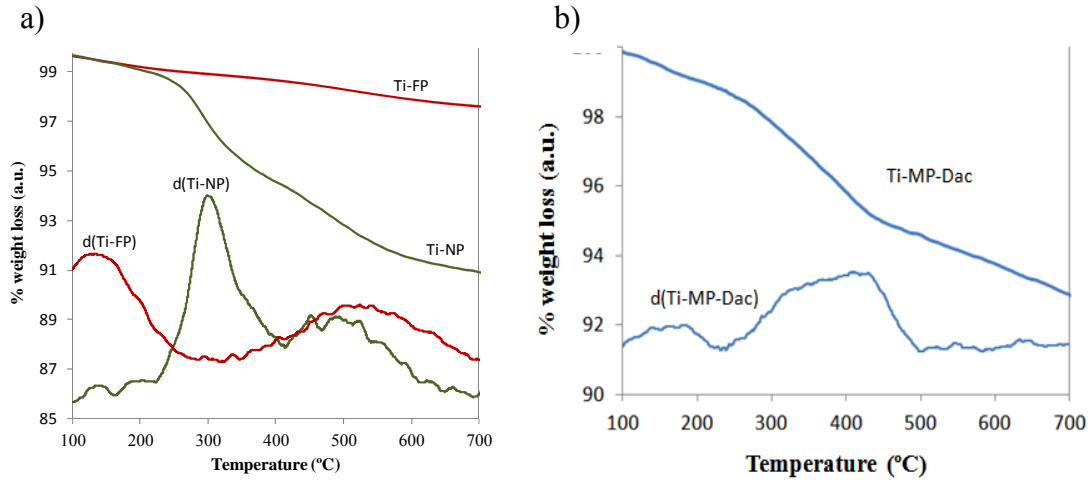
Fig 3.- TGA curves and derivative profiles of grafted TiO_2 with the prepared silanes Ti- FP and d(Ti-FP), and Ti- NP and d(Ti- NP). b) TGA curves and derivative profiles of functionalised Ti-MP-DAc and d(Ti-MP-Dac)

The weight loss data from the TGA for the grafted silanes on TiO_2 was used to estimate the concentration per nm^2 of silane molecules on the surface of treated particles [11]. The grafting density, defined as the number of silane molecules per square nanometer [N_s nm^{-2}], was calculated using the equation 1.

$$\frac{d_s \cdot 6 \cdot 10^{23}}{M_w' \cdot a_{s(TiO_2)}} = \text{Grafting density} \left[\text{molecules} \cdot nm^{-2} \right] \text{ [Eq. 1]}$$

The grafting density was calculated in a way that the weight loss was not dependent on the size of the grafted silane, since the difference in molecular weigh between the different silanes is large enough to influence the grafting density [11]]. Molecular weight calculations (M_w' [$g_{(silane)}mol^{-1}$]) were performed for the physically trapped silanols (molecular weight calculated as $RSi(OH)_3$) eliminated in the temperature interval approximated of 200-350 ºC, and for the chemisorbed siloxanes (molecular weight calculate as R) eliminated at temperatures higher than 350 ºC. Both the physically and chemically adsorbed silane was expressed in a single figure. Next, the obtained molar density was expressed as the number of silane molecules per gram of TiO_2. Finally, data was transformed to number of silane molecules per nm^2 dividing by the specific surface area measured for raw TiO_2 ($a_{s(TiO2)}$ [nm^2g^{-1}])=$5.4x10^{19}$ [19-22]. Table 3 shows the deposited silane data and the grafted density of selected samples. The total amount of grafted molecules on the TiO_2 surface in the shown experiments, showed values from 0.87 to 3.36 molecules per nm^2. Previous works estimated grafting densities of 3-4.5 as the maximum surface density for molecules per nm^2 for silanes with large hydrolysable groups, such as trialkoxysilanes [23]. For the laboratory prepared silanes, the data obtained for Ti-FP was significantly lower than for Ti-NP, with values laying in the range of commercial alkyl chains [11]. The fact that Ti-FP has

a value of 0.87 molecules per nm^2 was attributed to the scarcity of silane FPTMS monomers available for reaction [16].

The functionalization of the reactive sites of the grafted commercial silanes (Ti-MP-Dac) gave place to value of g_d of 2.44 molecules per nm^2. The increase in the value from 1.69 (in the case of Ti-MP [16]) to 2.44 molecules per nm^2 was attributed to the alkene reduction, and addition of the Dac that could led to an increase of the flexibility of the silane and the ability to accommodate a high number of flexible cyclohexane rings.

SAMPLE	Deposited silane$_s$ [$g_s g_m^{-1}$]	Grafting density $G_d[N_s nm^{-2}]$
Ti-NP	0.085	3.36
Ti- FP	0.021	0.87
Ti-MP-Dac	0.049	2.44

Table 3: Grafting efficiency of obtained from TGA analysis.

CONCLUSION

The grafting of organic molecules with various functional groups was carried out on nanosized TiO_2 particles using supercritical CO_2 as processing media. In the approach followed, where silanes were either synthesised prior the deposition on the TiO_2, we succeeded to prepare Ti-NP and Ti-FP. In the second approach, silanization of a commercial trialkoxysilane was carried out followed by the post functionalization with nitrogen containing organic molecules to yield Ti-MP-Dac. The analysis carried out in the obtained samples indicated the presence of the targeted molecules on the TiO_2 nanopowders.

ACKNOWLEDGEMENTS

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