

Synthesis of *para*-Amino Benzoic Acid–TiO₂ Hybrid Nanostructures of Controlled Functionality by an Aqueous One-Step Process

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In situ amino acid surface-modified TiO₂ nanoparticle syntheses were performed by a simple one-pot hydrolysis of heteroleptic titanium alkoxide [Ti(OiPr)₃(O₂CC₆H₄NH₂)]_m in water with NⁿBu₄Br. This process allowed precise control of the surface grafting rate by varying the amount of precursors and provided highly functionalized nanomaterials. Their compositions and microstructures were determined by C, H and N elemental analyses, TGA-MS, ¹³C CP-MAS NMR, XRD, TEM, BET, Raleigh diffusion, FTIR, Raman, XPS and UV/Vis experiments. The results indicated that (i) the aggre-

gation rate increased with an increase in the loading of the organic substrate and (ii) the amino acid is chemisorbed as a carboxylate group onto the TiO₂ nanoparticles, which leads to a strong interaction between the amino acid and the TiO₂ nanoparticle and good stability of these hybrids. Applications of low-aggregated nanomaterials were demonstrated as efficient protection additive against UVA + UVB radiations.

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Introduction

Hybrid oxide (TiO₂) nanostructured materials, which combine the properties of inorganic and organic constituents, have a large range of uses in the fields of composite materials, separation, catalysis, electrical and optical devices or in the biomedical area.^[1] The control of the aforementioned properties of the resulting nanomaterials depends strongly on the control of parameters such as size, shape, crystallinity, phase composition of the oxide nanoparticles, type of bonding and interface between the organic and the inorganic phases, the nature and the amount of the organic component and finally the degree of dispersion of the nanoobjects. Whereas elaborations of nanostructured TiO₂ hybrid particles of controlled size, morphology and phase are well documented in the literature, a synthesis method that allows good control over the compositions and surface chemistries still remains a challenge.^[2]

The attachment of organic moieties onto transition-metal oxide nanoparticles has been accomplished by either (i) post-functionalization processing with the use of functionalized polymers (e.g., polyaniline, polythiophene, etc.)^[3]

and organic compounds (e.g., carboxylic acids,^[4] phosphonic acids^[5] or amino-based^[6]) or by (ii) modification of molecular precursors such as alkoxides by polymers (e.g., polyimide, polyether sulfone, etc.)^[2f,2h,2i,7] and by β -diketonates^[8] and carboxylic,^[9] phosphonic^[10] and sulfonic acids.^[11] The conventional post-functionalization method implied the immersion of the nanoparticles or the films into an organic or aqueous solution containing the organic moieties. However, difficulties in getting well-dispersed nanoobjects and/or in filling efficiently the pores of nanosized aggregates are encountered, which can limit the control of the surface coverage. In addition, the pH of the aqueous solution hardly affected the adsorption, whereas heat treatment (e.g., of TiO₂ > 500 °C) noticeably lowered the adsorption.^[12] In contrast, the synthesis of organic–inorganic hybrids from modified precursors by sol–gel processing usually led to amorphous as-prepared materials and required acidic conditions to favour the ligand exchange for reorganization to generate the crystallization of the inorganic part. Sanchez et al. reported a one-step sol–gel method to obtain surface-protected nanocrystalline zirconium, titanium and tin dioxide particles in the presence of acetylacetone and *para*-toluenesulfonic acid.^[8] A nonaqueous, in situ surface functionalization process, which requires the addition of TiCl₄ to a mixture of benzyl alcohol and dopamine or 4-*tert*-butylcatechol, was also described by Niederberger et al. to tailor the surface and the solubility properties of the hybrid titania nanoparticles.^[13] However, under acidic conditions variation of the amount of surface-adsorbed species was possible only by changing the structure of the precursor (increasing the complexant/metal ratio)

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and the size of the nanoparticles (thus increasing the surface-to-volume ratio).

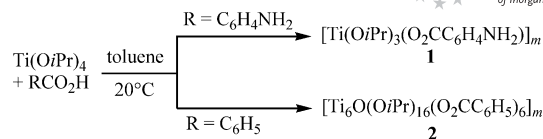
Recently, we reported the aqueous synthesis of nanocrystalline particles of titania at low temperature (100 °C) by a sol–gel process using titanium alkoxide and bromide ammonium salts.^[14] We then grafted iron phthalocyanine complexes onto the in situ generated titanium dioxide nanoparticles to prepare catalysts for an oxidation reaction.^[11a] Such experimental conditions allowed high loading of the catalytic complex on the surface of the particles, along with excellent activity in the oxidation of various substituted phenols that compared well with the parent homogeneous system. These results led us to investigate “ecosynthesis” and controlled functionality processing of nanohybrid titania materials starting from modified alkoxides.^[15]

Our interests lay in commercial sunscreen products that are creams containing opaque inorganic oxides, especially crystalline zinc oxide and/or titanium dioxide nanoparticles, and organic reagents in order to adjust the sun protection factor (SPF).^[16] Among the more widely used organic selective agents are amino acids such as *p*-amino benzoic acid (PABA), which absorbs UV-B radiation (290–320 nm) while letting UV-A radiation (320–400 nm) pass through to produce a tan. However, the less energetic UV-A zone is not quite innocuous, as it adds to the ability of UV-B rays to inflict damage, and repeated exposure to UV radiation over a longer period produces skin cancer, especially among fair-haired, light-skinned people. Hence, for the new generation of sunscreens, research is mainly focussing on developing a broad spectrum of active ingredients that provide consistent protection across all wavelengths, particularly in the UV-A range. Herein, we report the aqueous in situ synthesis and the characterization of inorganic–organic hybrid nanomaterials formed from crystalline TiO₂ nanoparticles and *para*-aminobenzoic acid. The effects of the amount of PABA anchored onto the TiO₂ nanoparticles were also addressed in terms of the interaction and optical properties of the nanoparticles.

Results and Discussion

Chemical Design and Nanoparticle Syntheses

The equimolar reaction between Ti(OiPr)₄ and *para*-aminobenzoic acid or benzoic acid in toluene at room temperature afforded [Ti(OiPr)₃(O₂CC₆H₄NH₂)₃]_m (**1**) and [Ti₆O(OiPr)₁₆(O₂CC₆H₅)₆]_m (**2**), respectively (Scheme 1). The difference in the formulation of **1** and **2** (presence of oxido ligands) is attributed to the immediate precipitation of **1** from the medium; thus, the hydrolysis reaction is avoided as a result of an esterification reaction between the acid and the alcohol generated by the substitution reaction. Previous similar species such as [Ti(OEt)₃(O₂CCH₂NH₂)₂]₂,^[17] [Ti₆(μ₃-O)₆(OCH₂C(CH₃)₃)₆(O₂CR)₆] (R = H,^[18] C₆H₅^[19]) and [Ti₆(μ₃-O)₆(OEt)₆(O₂CC₆H₄OC₆H₅)₆]^[20] were structurally identified.



Scheme 1. Syntheses of crystalline **1** and **2**.

Hydrolysis of **1** was performed without any organic solvent; the neat powder was added to deionized boiling water (100 mL) containing the *n*Bu₄Br salt (0.1 equiv.). The suspension was heated under reflux for 2 h and then centrifuged. The as-prepared precipitate was washed with deionized water and ethanol and then dried at 70 °C for ca. 12 h to yield a yellow powder (denoted *n*TiO₂/PABA-I to -VI).

Characterization of Hybrid Nanoparticles

The compositions and structures of the hybrid nanoparticles were characterized by nitrogen elemental analysis, thermogravimetric analysis (TGA), ¹³C CP-MAS NMR spectroscopy, dynamic light scattering, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), BET, Raman and UV/Vis spectroscopy. The organic loading of each hybrid material was determined by ICP experiments on nitrogen atoms and by thermogravimetric analysis.

Interestingly, as shown in Figure 1, the organic content could be easily controlled by hydrolyzing various amount of **1** (from 1 to about 6 g) and was demonstrated to be highly reproducible (average standard deviation of nitrogen percentage = ±0.01 %). The use of higher quantities of precursor (i.e., 6.77 g) resulted in ammonium contamination in the final *n*TiO₂/PABA-VI material, as confirmed by solid-state NMR spectroscopic data, and indicated a threshold for the amount of organic grafting. Other parameters such as the number of equivalents of NR₄Br (from 0.1 to 1 equiv.), the time of reflux (exceeding 2 h) and the volume of washing solutions (H₂O and ethanol, from 25 to 75 mL) did not show any significant effect on the final organic content. It is noteworthy that the same procedure applied to the glycine [Ti(OEt)₃(O₂CCH₂NH₂)₂]₂ complex afforded nanocrystalline TiO₂ with a trace amount of amino acid.

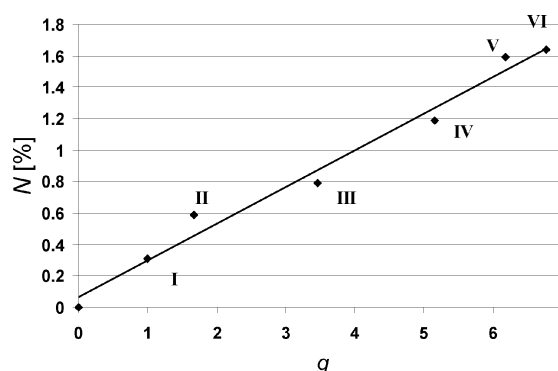


Figure 1. Nitrogen percentage versus weight of modified precursor.

This result showed that the aromatic moiety was necessary to strongly attach the carboxylic group onto the surface during this process.

Thermogravimetric analyses, carried out in air up to 900 °C, exhibited weight loss within the temperature range of 20–500 °C. Samples *n*TiO₂/PABA-I to -V showed only two weight losses (Figure 2). TGA coupled to mass spectrometry (TGA-MS) experiments confirmed that the first step (20–175 °C) corresponds to the loss of residual solvent (H₂O, ethanol) and the further steps (175–500 °C) result from the release and combustion of the organic groups (–OH, –O₂CC₆H₄NH₂). Weight losses between 175 and 500 °C of our *n*TiO₂/PABA-I to -V samples ranged from about 7 to 21% of organics (TG average weight losses: 6.9, 10.3, 11.7, 14.8, 20.8%), and each sample exhibited highly reproducible data as a very interesting feature (TG average standard deviation = ±0.3%).

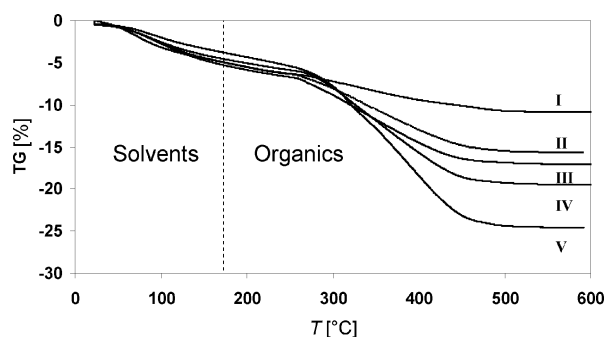


Figure 2. Thermogravimetric analyses of *n*TiO₂/PABA samples.

Correlations between nitrogen ICP data and TGA weight losses match only nanomaterials having a mean raw formula of TiO_x(OH)_y(O₂CC₆H₄NH₂)(solvent)_w (solvent = H₂O and/or ethanol), which indicates that hydroxy groups (–OH) are present on the surface (see Supporting Information). Under our experimental conditions, the ratio between surface bound O₂CC₆H₄NH₂ and free HO₂CC₆H₄NH₂ varied strongly (from 0.018 to 0.135 for *n*TiO₂/PABA-I and -V, respectively), which indicated that the reactions were not governed by a classical adsorption mechanism so that the carboxylate groups remained apparently bonded to the titanium atom during the process. The solid-state ¹³C CP-MAS NMR spectra of *n*TiO₂/PABA-I and -V exhibited a complex pattern with different chemical shifts for the COO carbon atom (174 ppm) and the aromatic carbon atoms [151 (C–NH₂), 131, 118 and 113 ppm] (see Supporting Information).

To compare with existing or standard methods, we carried out post-functionalization reactions between *para*-amino benzoic acid and different nanoparticulate titania samples as-prepared from Ti(O*i*Pr)₄ (243 m² g^{−1}) and commercial P25-Degussa (50 m² g^{−1}) and Hombikat UV 100 ones (250 m² g^{−1}). For instance, under the same conditions as those used in our process to obtain *n*TiO₂/PABA-II with 10.3 ± 0.2% loss of organics [in a typical experiment: 1.7 g of Ti(O*i*Pr)₃(PABA) and 100 mL of water were used to af-

ford 0.4 g of nanohybrids], we treated TiO₂ (0.4 g) with PABA (0.68 g, 1 equiv.) in water (100 mL) at 100 °C for 2 h. The TGA results, according to the weight losses between 175 and 500 °C, showed lower organic contents and large data discrepancies between three crops of the same sample of the as-prepared (6.8 ± 1.3%) or of the Hombikat UV 100 (7.3 ± 1.1%) titania samples, whereas P25-degussa TiO₂ was slightly functionalized (around 1%). The same procedure was applied to the as-prepared TiO₂ samples in order to synthesize *n*TiO₂/PABA-V; a weight loss of 8.4 ± 1.6% was obtained, which is in contrast to 20.8 ± 0.4% obtained with our process. This comparative study showed that in a classical adsorption experiment the nature of the surface, the degree of dispersion and/or the specific surface area can drastically influence the ability to modify the surface of the nanoparticles in a large range and with high precision. In contrast, our *in situ* process removed such drawbacks, and it appeared to be an efficient functionalization-controlled method for the synthesis of hybrid TiO₂ nanoparticles that could be used to adjust the organic/inorganic balance and thus the combined properties of the hybrid.

The XRD patterns of each *n*TiO₂/PABA sample were similar and contained only anatase as the crystalline phase (see Supporting Information). The average particle size, as estimated from line-broadening according to the Scherrer equation, was about 5 nm for all samples. The morphology of the particles was examined by transmission electron microscopy (TEM) and dense, homogeneous, spheroidal nanocrystallites of about 5–6 nm aggregated into submicron-sized secondary particles were revealed (Figure 3A). HRTEM images revealed the fringes from the continuous lattice structure of a typical crystallite, which illustrates the high crystallinity of TiO₂ even at 100 °C (Figure 3B). In addition, no amorphous layer was observed on the surface of the nanoparticles and all diffraction peaks could be assigned (Figure 3B,C). The results showed that the size, morphology, nature of the phase and crystallinity of the TiO₂ crystallite were the same for all the hybrid nanomaterials, and hence, the variation of the organic content was not due to the variation of the surface-to-volume ratio. One effect of the higher amount of organic surface species was the higher aggregation state of the nanocrystalline TiO₂ particles.

Figure 4 presents characteristic nitrogen adsorption–desorption isotherms for desorbed samples *n*TiO₂/PABA-I to -V (100 °C/6 h). The specific surface areas of the samples decreased in the order *n*TiO₂/PABA-I, -II, -III, -IV, -V (261, 247, 232, 208, 149 m² g^{−1}, respectively) as a consequence of the continuous shortening of the interparticulate distances (TiO₂ obtained by the same procedure: 243 m² g^{−1}). The total pore volume was 0.34, 0.28, 0.28, 0.23 and 0.22 cm³ g^{−1} for samples *n*TiO₂/PABA-I, -II, -III, -IV and -V, respectively (determined by the BJH method). The isotherm, a type IV with a capillary hysteresis loop of type-H2 (according to IUPAC terminology), attested that *n*TiO₂/PABA-I was a well-characterized mesoporous system with interconnected particles and that it was different from TiO₂ (less rigid texture). This self-assembly process gave an average

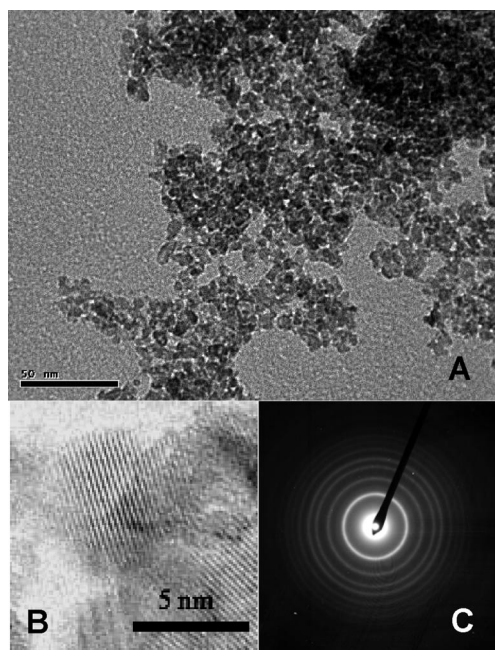


Figure 3. (A) TEM, (B) HRTEM and (C) SAED images of *n*TiO₂/PABA-I.

pore diameter with a large distribution of about 4–7 nm. Samples with a higher organic content (from *n*TiO₂/PABA-II to -V) possessed an unusual type-H4 loop hysteresis at p/p_0 between 0.4 and 0.5. Such hysteresis loops have already been observed in samples having aggregates of plate-like particles, which leads to a slit-shape structure,^[21] and in mesoporous aluminosilicate MCM-41 with void defects.^[22] These N₂-sorption isotherm patterns reflect an extensively interconnected porous network and a so-called “pore-blocking effect”. This is due to the opening of many intergranular pores at the same pressure, and this happens only for pore sizes lower than 4 nm. As a common feature, the aggregation state increased with an increase in the surface organic amount, which could be attributed to the increase in the bond interactions between the *para*-aminobenzoic groups of close particles (confirmed by TEM experiments). In addition, particle size measurements, carried out by dynamic light scattering, displayed average aggregates sizes of 160, 240 and 2200 nm for *n*TiO₂/PABA-I, -II and -V etha-

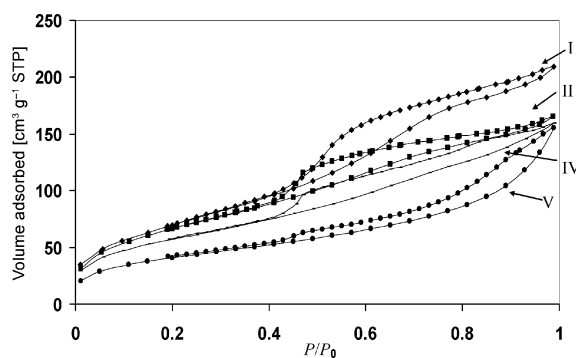


Figure 4. Nitrogen adsorption–desorption isotherms of *n*TiO₂/PABA samples (sample III was omitted for clarity).

nol suspensions, respectively, and we will mainly focus our further discussion on these three representative nanohybrid samples.

Characterization of the Chemical Interactions in TiO₂ Hybrid Nanoparticles

To shed light on the chemical interactions between PABA and the TiO₂ nanoparticles, FTIR, Raman and X-ray photoelectron spectroscopy (XPS) were carried out. Interestingly, all of the hybrid nanoparticles were found to be stable (no total leaching of the organic part, as confirmed by FTIR experiments) between ca. pH 2 (HNO₃) and 10 (NaOH) for at least 12 months. FTIR analysis of each of the as-prepared *n*TiO₂/PABA precipitates showed absorption peaks for the $\nu(\text{OH})$, $\nu(\text{CO}_2)$ and $\nu(\text{TiO})$ vibrations (see Supporting Information). The broad feature between 3700 and 2500 cm^{−1} was due to the O–H stretching vibrations of the hydroxy groups and adsorbed water and ethanol molecules, whereas the band at 1620 cm^{−1} was ascribed to the bending vibrations of the adsorbed molecules. It is worth noting that the C=O stretching band at 1665 cm^{−1} for the pure *para*-aminobenzoic acid is absent in the spectra. New sharp bands at 1606, 1534 and at 1486, 1406 cm^{−1} were attributed to asymmetric $\nu_{\text{as}}(\text{CO}_2^-)$ and symmetric $\nu_{\text{s}}(\text{CO}_2^-)$ stretches, respectively, as a result of the lower hydrolytic susceptibility of the carboxylate ligands relative to that of the alkoxides. This reveals that *para*-aminobenzoic acid is chemisorbed as a carboxylate onto the surface of TiO₂, and the value $\Delta\nu = [\nu_{\text{as}}(\text{CO}_2^-) - \nu_{\text{s}}(\text{CO}_2^-)]$ of around 120–130 cm^{−1} suggests a bidentate bridging/chelating coordination. This value agrees well with that found by Finnie et al., who concluded that benzoic acid attached to TiO₂ films through bridging or bidentate coordination.^[23] The low wavenumber region exhibited a strong vibration between 880 and 500 cm^{−1}, which can be assigned to $\nu(\text{Ti-O-Ti})$ of the titanium oxide framework. Raman experiments on various *n*TiO₂/PABA samples displayed characteristic anatase bands at 169, 400, 520 and 644 cm^{−1} besides several bands of weak intensity corresponding to the PABA moiety (see Supporting Information). The shift in the intense Raman band at greater wavenumbers (169 cm^{−1}) relative to that of TiO₂ powder at 143 cm^{−1} was due to the as-prepared nanosized TiO₂.^[24] Raman spectroscopy was less informative than FTIR and, in particular, new bands corresponding to the Ti–O–C(PABA) linkage could not be observed under our experimental conditions.

The XPS spectrum of the C1s core level of the free *para*-amino benzoic acid displayed four peaks at 284.6, 285.8, 288.6 and 290.7 eV, which are ascribed to the carbon atoms in the C=C, C–NH₂ and COOH bonds and to a shake-up line, respectively (Figure 5a). Interestingly, this latter peak due to $\pi \rightarrow \pi^*$ transition of the aromatic ring disappeared in the spectra of all nanohybrid *n*TiO₂/PABA samples, which confirms the absence of free acid on the TiO₂ surface, even for highly functionalized type V nanoparticles (Figure 5b). We observed the same phenomenon in the XPS spectrum

of the C1s core level of the sodium *para*-aminobenzoate salt. Such data are very scarce in the literature, and this is, to the best of our knowledge, the first example in which C1s shake-up lines are used to investigate the manner in which the carboxylate molecules interact with the TiO₂ surface. In addition, the O1s XPS spectrum obtained from the *n*TiO₂/PABA samples showed one single peak at 531.3 eV (besides the TiO₂ peak at 529.9 eV) instead of two non-equivalent peaks at 531.8 and 532.2 eV for the free *para*-aminobenzoic acid (Figure 5a). These results also confirm that the carboxylate group is bound symmetrically through its two oxygen atoms onto the TiO₂ surface.

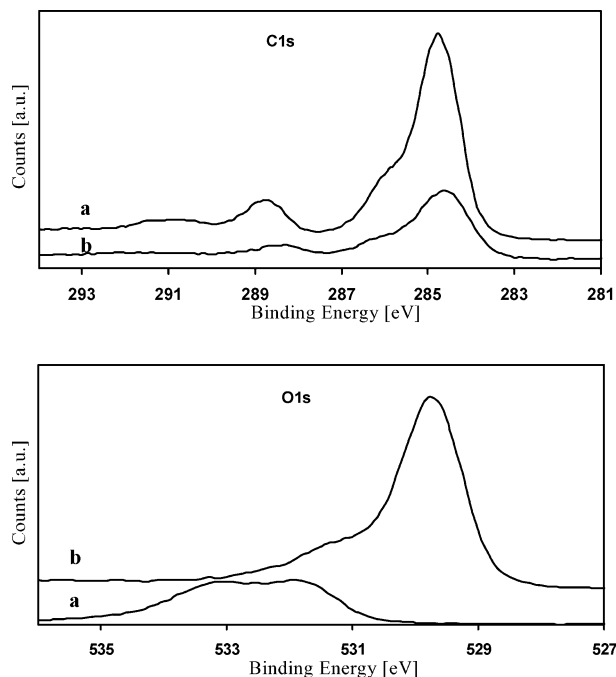


Figure 5. XPS C1s and O1s core level spectra of (a) *p*-amino benzoic acid and (b) *n*TiO₂/PABA-V.

UV/Vis absorbance spectra of TiO₂ (Degussa P25), *para*-amino benzoic acid and *n*TiO₂/PABA-I are given in Figure 6. The same spectra were observed for their ethanol suspensions. Measurements on the sample show that the bandgap absorption onset of the *n*TiO₂/PABA nanocrystals is redshifted from 380 to 650 nm relative to TiO₂ with an efficient and interesting protection in the UV-A domain (Figure 6). The large change in the PABA absorption spectrum in the presence of TiO₂ colloids implied strong binding of the PABA onto the TiO₂ surface.^[25] Such a material, which is based on dye-sensitized nanostructured semiconductors (i.e., ZnO, SnO₂ and TiO₂), was intensively investigated as a promising photoelectrochemical solar cell for low-cost solar energy conversion.^[4a,26]

The spectra of *n*TiO₂/PABA samples can be deconvoluted into two separate peaks. The lower wavelength peak (220–245 nm) can usually be assigned to the tetrahedral coordination of titanium in the framework, whereas the higher wavelength peak (>300 nm) is typical of five- and six-coordinate Ti atoms.^[27] Gianotti et al. showed that the

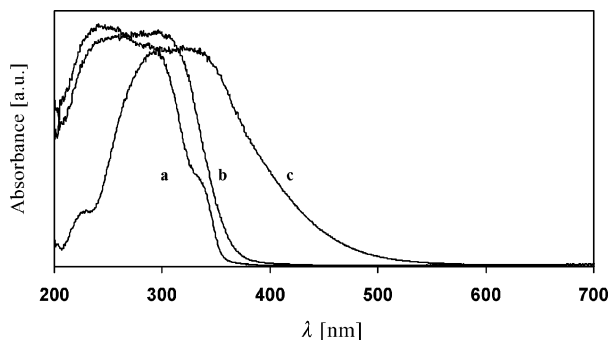


Figure 6. UV/Vis absorbance spectra of (a) *p*-amino benzoic acid, (b) TiO₂ (Degussa P25) and (c) *n*TiO₂/PABA-I.

diffuse reflectance spectra of Ti-MCM-41 materials was broadened and shifted to higher wavelengths as a result of the inserted NH₃ molecules and the coordination change of the Ti^{IV} sites from tetrahedral to octahedral.^[27a] In our samples containing a higher amount of amino acid, the ratio between the six- and four-fold titanium sites increased, which again confirmed the strong surface chemisorption of PABA molecules (Figure 7).

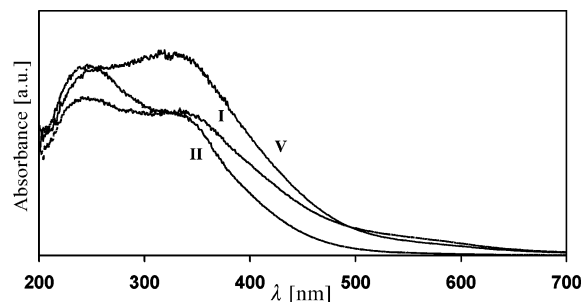


Figure 7. UV/Vis absorbance spectra of the *n*TiO₂/PABA samples.

Applications of TiO₂ Hybrid Nanoparticles: Solar Protection

Preliminary results of solar protection evaluation were obtained with 300-μm thick films by using the same mass of hybrid nanoparticles. The *n*TiO₂/PABA-I sample displayed uniform and grain-free films with low intensity of transmitted light. Such a nanomaterial appeared efficient to block out all the UV radiation at sea level, and it also seemed promising for cosmetic applications (lowest amount of organic UV filter).^[28] The aggregation effect, that is, for the PABA/TiO₂-V sample, led to inhomogeneous films and to an increase in the intensity of transmitted light in the UV-A radiation zone (Figure 8). These results demonstrated that precise control of the organic loading was an important parameter for adjusting the performance of nanohybrid titania for UVA solar protection applications. The use of such materials in the formulation of cosmetics is in progress to display their efficacy as UVA and UVB sunscreen actives.^[29]

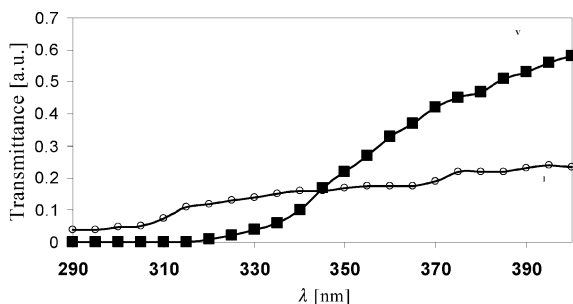


Figure 8. UV transmission through nanohybrid films.

Conclusions

We demonstrated the efficiency of a one-pot relevant synthetic route to elaborate hybrid nanostructure amino acid-crystalline TiO₂ nanoparticles of controlled functionality, starting from molecular heteroleptic alkoxides of titanium. This method offers the convenience and economical advantages of being environmentally friendly (organic-free solvent). The surface complexation rate could be adjusted by simply varying the amount of precursors (up to about 21% of organics) and was not governed by values observed at plateau in classical adsorption isotherms. Chemical and spectroscopic data were consistent with strong chemisorption of the amino acid molecules onto the TiO₂ nanoparticles surface through bidentate chelate or bridging coordination. Interestingly, the disappearance of the C1s shake-up line due to the $\pi \rightarrow \pi^*$ transition of the aromatic ring in the XPS spectra of all nanohybrid *n*TiO₂/PABA samples confirmed the absence of free acid on the TiO₂ surface, even for highly functionalized nanoparticles. Observed trends in the physicochemical properties of such hybrid nanomaterials were the increase in the aggregation state by increasing the surface organic rate. N₂-sorption isotherm patterns of highly functionalized nanomaterials demonstrated an extensively interconnected porous network and a so-called “pore-blocking effect”. Low aggregated nanomaterials have shown promising properties as candidate for UVA + UVB sunscreen additives. As perspectives, these results provided a simple and successful pathway for the fabrication of TiO₂ nanohybrids with mono- or polyfunctionalities by choosing the appropriate organic group to tailor their chemical and/or physical properties.

Experimental Section

Ti(O*i*Pr)₄ was distilled under vacuum and manipulated under an atmosphere of dry argon by using Schlenk tube techniques. *para*-Aminobenzoic acid and ammonium salts (N*n*Bu₄Br) were used as purchased. FTIR spectra were recorded as nujol suspensions (for **1**) or as KBr pellets (for hydrolyzed powders) with a Perkin–Elmer Paragon 500 FTIR spectrometer. TGA/TDA data were collected with a Setaram 92 system in air with a thermal ramp of 5 °C min^{−1}.

Powder X-ray diffraction data were obtained with a Siemens D 5000 diffractometer by using Cu-*K*_α radiation at the scan rate of 0.02°2θ s^{−1} with step times of 1 and 16 s for routine or for expanded region spectra, respectively. XPS experiments were performed with a KRATOS spectrometer by using monochromated Al-*K*_α radiation as the excitation source. TEM images were collected with a JEOL JEM-2010 electron microscope. BET experiments were carried out with an ASAP 2010 system after the samples were desorbed at 100 °C for 6 h. Raman experiments were carried out with LabRam HR equipment (Jobin Yvon). ¹H liquid and ¹³C CP-MAS solid-state NMR spectra were recorded with Avance 300 and Avance DSX 400 Bruker spectrometers (5 and 10 KHz), respectively. Dynamic light scattering experiments were carried out with a Coulter N4 Plus (20 °C, ethanol, 90°). C, H and N analytical data were obtained from the Service Central d’Analyses du CNRS (Verneuil, France) by ICP.

1: To a solution of Ti(O*i*Pr)₄ (2.5 mL, 8.4 mmol) in toluene (25 mL) was added dropwise a solution of *p*-NH₂C₆H₄CO₂H (1.15 g, 8.4 mmol) in toluene (10 mL) at room temperature. A dark-yellow precipitate appeared after 10 min, which was filtered and washed with hexane. The yellow powder was dried under vacuum to quantitatively yield 2.97 g of [Ti(O*i*Pr)₃(O₂CC₆H₄NH₂)]_{*n*} (**1**). Compound **1** is poorly soluble in hydrocarbon and soluble in THF and 2-propanol. ¹H NMR (300 MHz, CDCl₃, 20 °C): δ = 7.83 (d, ³*J* = 8.7 Hz, 2 H, CH_{ar}), 6.55 (d, ³*J* = 8.7 Hz, 2 H, CH_{ar}), 4.82 (sept., ³*J* = 5.9 Hz, 1 H, CH), 4.46 (sept., ³*J* = 5.9 Hz, 2 H, CH), 4.06 (s, 2 H, NH₂), 1.19 (d, ³*J* = 5.9 Hz, 18 H, CH₃) ppm. FTIR (nujol): $\tilde{\nu}$ = 3493 (w), 3474 (m), 3394 (m), 3343 (m), 3221 [w, ν(N–H)], 1633 (m), 1621 (m), 1602 (m), 1583 (w), 1533 (w), 1495 (s), 1462 (s), 1443 (s), 1423 (s), 1409 (s), 1377 (s), 1360 [m, ν(C=O), ν(C=C)], 1327 (m), 1309 (m); 1178 (m), 1166 (m), 1133 (s), 1115 [s, ν(C–O), ν(C–N)], 1016 (m), 989 (m), 949 (w), 933 (m), 873 (w), 853 (m), 825 (m), 788 (m), 706 (w); 645 (m), 624 (m), 596 (m), 559 (m), 506 (m), 476 [w, ν(Ti–O)] cm^{−1}. C₁₆H₂₇O₅N₁Ti (360.67): calcd. C 53.20, H 7.48, N 3.88; found C 53.02, H 7.42, N 3.86.

2: C₆H₅CO₂H (1.03 g, 8.4 mmol) in toluene (10 mL) was added dropwise to a solution of Ti(O*i*Pr)₄ (2.5 mL, 8.4 mmol) in toluene (25 mL). After 12 h of stirring at room temperature, the medium was dried under vacuum. The resulting powder was recrystallized from a minimum amount of hexane at −25 °C to afford 1.7 g (62%) of [Ti₆O(O₂CC₆H₅)₆(O*i*Pr)₁₆]_{*n*} (**2**). Compound **2** is highly soluble in common solvents. ¹H NMR (300 MHz, CDCl₃, 20 °C): δ = 8.12 (m, 12 H, CH_{ar}), 7.45–7.36 (m, 18 H, CH_{ar}), 5.25–4.86 (m, 16 H, CH), 1.43 (d, ³*J* = 6.0 Hz, 24 H, CH₃), 1.20 (d, ³*J* = 6.0 Hz, 72 H, CH₃) ppm. FTIR (nujol): $\tilde{\nu}$ = 1595 (w), 1597 (m), 1556 (s), 1522 (m), 1492 (w), 1462 (m), 1448 (m), 1383 [s, ν(C=O), ν(C=C)], 1332 (w), 1323 (w); 1162 (m), 1130 (s), 1069 [w, ν(C–O), ν(C–N)], 1023 (m), 1010 (s), 990 (s), 960 (w), 853 (m), 837 (w), 718 (s), 700 (m), 674 (m); 625 (s), 601 (m), 554 (w), 480 [m, ν(Ti–O)] cm^{−1}. C₉₀H₁₄₂O₂₉Ti₆ (1972.02): calcd. C 54.73, H 7.20; found C 54.53, H 7.22.

Hydrolysis of 1: In a typical synthesis, to a solution of N(*n*Bu)₄-Br heated at reflux in water (100 mL) was added neat [Ti(O*i*Pr)₃(O₂CC₆H₄NH₂)]_{*n*} [**1**; Ti/N(*n*Bu)₄Br = 10] under vigorous stirring; an immediate yellow precipitate appeared. The suspension was heated at reflux for 2 h and then centrifuged to yield a yellow solid. The as-prepared precipitate (denoted *n*TiO₂/PABA) was washed with deionized water (2 × 25 mL) and ethanol (50 mL) and then dried at 70 °C for ca. 12 h. The aqueous solution was recovered and used again for further syntheses. FTIR (KBr): $\tilde{\nu}$ = 3393 [m, ν(OH)], 1620 [m, δ(OH)], 1606 (m), 1534 (w), 1486 (m), 1406 [s, ν_s(COO), ν_{as}(COO), ν(C=C)], 1294 (m), 1182 [m, ν(C–O), ν(C–N)], 880–500 [s, ν(Ti–O)] cm^{−1}.

Standard Solar Protection Evaluation: $n\text{TiO}_2/\text{PABA}$ (0.5 g) in ricin oil (2 g) was grinded by using a J. Engelsmann AG type 25/53 apparatus for 200 rotations. The paste was mixed with nitrocellulose (1.35 g), ethyl acetate (3.83 g) and butyl acetate (3.83 g) and then sonicated for 15 min in a Sono-clean tank (Labo-moderne). Films with 300- μm thickness were applied on a glass slide by an automatic film-coater system (PIAB, Lab Vac LVX20). The samples were dried in ambient air, and measurements of transmitted light intensity through hybrid powders films were performed between 290 and 400 nm by using a spectrophotometer Scientec OL 754 with a 75W arc Xenon source to have an incident light close to solar one.

Supporting Information (see footnote on the first page of this article): ^{13}C CP-MAS NMR spectrum of $n\text{TiO}_2/\text{PABA-V}$ at 5 and 10 KHz spinning rate; XRD patterns of the $n\text{TiO}_2/\text{PABA}$ samples; FTIR spectra of PABA, TiO_2 and $n\text{TiO}_2/\text{PABA-II}$; FTIR spectra of all $n\text{TiO}_2/\text{PABA}$ samples; Raman spectrum of $n\text{TiO}_2/\text{PABA-V}$ and mean raw formula of compounds $n\text{TiO}_2/\text{PABA-I}$ to -V.

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