Ultra-Violet pretreatment of Titanium dioxide and Tin-doped Indium oxide surfaces as a promoter for adsorption of organic molecules in dry deposition processes: Light patterning of organic nanowires

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In this article we present the pre-activation of TiO₂ and ITO by UV irradiation in ambient conditions as a tool to enhance the incorporation of organic molecules on these oxides by evaporation at low pressures. The deposition of π -stacked molecules on TiO₂ and ITO at controlled substrate temperature and in presence of Ar is thoroughly followed by SEM, UV-Vis, XRD, RBS and photoluminescence spectroscopy and the effect exploited for the patterning formation of small molecules organic nanowires (ONWs). X-ray Photoelectron Spectroscopy (XPS) in situ experiments and molecular dynamics simulations add critical information to fully elucidate the mechanism behind the increase in the number of adsorption centers for the organic molecules. Finally, the formation of hybrid organic/inorganic semiconductors is also explored as a result of the controlled vacuum sublimation of organic molecules on the open thin film microstructure of mesoporous TiO₂.

1. INTRODUCTION

The study of π -conjugated organic semiconductors has experienced a spectacular rise in the last decades.[1-4] In particular, the development of 1D organic nanomaterials, specially nanowires (ONWs), has led to important advances in fields such as electronics, optoelectronics or sensors.[5-6] A key issue of ONWs resides in the delocalization of their π -electrons, which is responsible for the stacking of the molecules and leads to the development of outstanding conductive, magnetic and optical properties.[5-6] An important challenge in this field is the implementation of fabrication techniques enabling the patterned growth of organic single crystal nanowires with precise control at the microscale.[7] The preferential alignment of the organic crystals is also a critical issue for their potential applications in areas such as nanosensors, organic field effect transistors (OFET), organic light emitting diodes (OLED), organic waveguides or solar cells.[8-13] Previous works relying on solution routes have studied the

formation and patterned deposition of organic crystals on pretreated surfaces, mostly by using self-assembled monolayers (SAMs) as templates.[7,14-16] For example, Bao et al.[15] have demonstrated the preferential assembly of pre-grown CuPc crystals onto the hydrophilic regions of a gold substrate with patches of the hydrophobic 1-hexadecanethiol (HDT) molecules. By contrast, patterning methodologies of ONWs or similar organic single crystal nanostructures using full vacuum approaches are rarer.[17] An example is the patterned formation by vacuum transport of different small molecular structures on substrates previously printed with octadecyltriethoxysilane (OTS).[18] In that work, it was concluded that the roughness of the OTS surface played a critical role in the preferential formation of the crystal. In a recent publication, we have also found that roughness effects enhance the formation by vacuum deposition of ONWs on metal and oxide thin films.[19] Following the thread of these previous investigations, herein we further explore the formation of ONWs on TiO₂ and ITO thin film surfaces that are activated by UV illumination, which changes their wetting properties. Using this principle, we show that the selective formation of preferential growth sites by mask illumination leads to the patterned formation of ONWs on the surface of these substrates. As far as we know, this is the first time that such approach is presented in the literature. In the course of this investigation we have also developed a vacuum fabrication procedure of organic/inorganic thin films by temperature controlled sublimation of small molecules onto porous TiO₂ thin films, a process that may open alternative routes for hybrid materials fabrication. Although in this work we focus on Pd-octaethylporphyrin (PdOEP) molecules, similar results are expected for other small molecules.

TiO₂ is a wide band gap semiconductor extensively used in dye-sensitized (DSSCs) or polymer/TiO₂ solar cells.[20-23] The combination of TiO₂ with p-type organic semiconductor molecules such as metalloporphyrins brings about important advantages for the operation of

photoelectronic devices, such as the design of specific p-n heterojunctions or the possibility that the light absorber and charge transport materials are chosen independently to improve the characteristic of the final device.[22] On the other hand, Indium Tin Oxide (ITO) is probably the most widely transparent electrode currently utilized in hybrid and organic solar cells. The surface of these two oxides undergo a hydrophobic/hydrophilic conversion under UV irradiation[24] which in TiO_2 is attributed to the photo-catalytic removal of carbon residues from its surface and/or to the enhancement of the hydroxylation state of its surface.[25-27] Photo-activated TiO_2 thin films keep memory of this hydrophilic state for hours and even days, depending on the characteristic of the sample. In porous TiO_2 thin films, this “memory” effect has been previously utilized to selectively incorporate Rhodamine 800 molecules in preference to Rhodamine 6G from water solutions of these two molecules.[28] Great improvements in the attachment and growth of human osteoblast cells on the surface or irradiated TiO_2 is another reported effect of this pre-irradiation.[29] In the present work we use this effect to promote the nucleation of organic nanostructures on the surface of TiO_2 and ITO. Besides that, we analyze the interplay between nucleation effects and thin film porosity to control the formation of ONWs on the surface of these oxides. The basic process favoring a given TiO_2 -organic molecule interaction is by no means a well understood effect. The present investigation reports some theoretical calculations aiming at accounting for the factors favoring the nucleation and growth of ONWs on pre-illuminated, and hence fully hydrophilic, TiO_2 surfaces.

The combination of experiments with theoretical analysis and simulation provides a well-founded description of the phenomena occurring during the interaction of small molecules with pre-illuminated TiO_2 surfaces. This article also opens the way to the patterned formation of

ONWs arrays on the surface of this and other photoactive oxides by the mere UV light illumination through micro-scale masks.

2. EXPERIMENTAL SECTION

TiO₂ and ITO thin film substrates: Microporous, mesoporous columnar TiO₂ and microporous ITO thin films have served as substrates and/or host materials for the growth of ONWs (see SEM and AFM images in Figures S1-S2 in the Supporting Information Section). Microporous TiO₂ (MICRO-TiO₂) thin films were deposited by plasma enhanced chemical vapor deposition (PECVD)[30-31] with a thickness of 350 nm in remote configuration by ECR-MW plasma (see SI for additional experimental details). In previous works we have demonstrated that these samples present a total porosity lower than 20 % of the total volume, with pores consisting exclusively of micropores (pores diameters < 2 nm) and a surface roughness of 0.7 nm.[30] Amorphous MESO-TiO₂ thin films, with an approximate thickness of 350 nm, were prepared by glancing angle vacuum deposition (GLAD) in an electron bombardment evaporator using TiO pellets as target materials. Their microstructure is characterized by separated nanocolumns presenting a tilt angle with respect to the substrate.[31] with a total pore volume higher than 50%, presenting both micro and mesopores and a surface roughness of 3.4 nm.[31] Once prepared, these two types of films were stored in a desiccator for one week before proceeding to the illumination and ONWs deposition experiments. Commercially available ITO thin films (Präzisions Glas&Optik (P.G.O)) were also used as substrates. These thin films are crystalline and quite compact, with a total porosity much lower than that of the MESO-TiO₂ columnar films. TiO₂ substrates as well as the purchased ITO films, will be designated in the text as as-grown samples.

Deposition of ONWs: Growth of the ONWs by physical vapor deposition (PVD) has been detailed in previously references.[19, 32-35] Palladium Octaethyl Porphyrin (PdOEP) was acquired from Sigma-Aldrich and used as received. Sublimation of the molecule under 2×10^{-2} mbar of Ar was carried out by using a Knudsen cell placed at 8 cm from the heated substrates. The temperature of the Knudsen cell during the evaporation was settled between 235 and 240 °C measured through a thermocouple installed in its base. The growth rate and equivalent total thickness (i.e., as referred to a flat and compact layer of this materials) of deposited PdOEP were monitored using a quartz crystal microbalance (QCM) and the growth rate adjusted to 0.3 Å/s. The temperature of the substrate during the PdOEP deposition was fixed at 150 °C.

Characterization Methods: The static water contact angles (WCA) values were obtained in a Data Physic Instrument set up by depositing water drops (pH = 7) of a volume of 3µl. The data presented is the mean value of 5 droplets and the error bar has been assigned as the major error between these values. The illumination of the TiO₂ and ITO substrates was carried out with a Xe lamp in ambient conditions. The photon intensity at the position of the samples was 2 W cm⁻² for the complete spectrum of the lamp (i.e., UV, visible and IR photons). The patterns presented in Figures 3 and 4 were obtained by irradiation through TEM grids of different specifications purchased from Plano GmbH. High-resolution SEM images of the samples deposited on a silicon wafer were obtained in a Hitachi S4800. UV-Vis transmission spectra of samples deposited on glass slides were recorded in a Cary 50 spectrophotometer in the range from 200 to 1100 nm. Fluorescence spectra were recorded in a Jobin Yvon Fluorolog-3 spectrofluorometer using the front face configuration and grids of 4 and 2 nm for the excitation and emission monochromators, respectively. In situ XPS experiments were performed in a VG ESCALAB 210 spectrometer with a pre-chamber where all PdOEP depositions were carried out. For the in-situ

experiments, the PdOEP/oxide films samples were kept in vacuum and then transferred to the analysis chamber for XPS analysis. Spectra were collected in the pass energy constant mode at a value of 50 eV. A Mg K α source was used for the excitation of the spectra. The Ti2p5/2 peak at 458.5 eV was used as reference for the binding energy (BE) calibration. In the experiments carried out with ITO, XPS spectra were calibrated with the In3d5/2 at the position of 444.40 eV. Equivalent thicknesses ranging between 2 nm to 60 nm were selected in order to follow the first stages and full development of the ONWs. Rutherford Backscattering (RBS) characterizations were performed at the 3 MV tandem accelerator of the National Center of Accelerators (Seville, Spain). P-RBS measurements were performed with alpha particles protons of 1.560 MeV and a passivated implanted planar silicon (PIPS) detector located at 165 $^{\circ}$ scattering angle. Samples were tilted 7 $^{\circ}$ in order to avoid channeling effects in the Si substrate. Fitting of the experimental data was then performed to extract the element concentration profile in the samples by means of the software SIMNRA 6.0.[36] Glancing Angle X-ray Diffraction (GAXRD) was carried out in a Panalytical X'PERT PRO diffractometer at glancing angle of 0.2 $^{\circ}$.

Molecular simulation: The Lennard-Jones parameters employed to model the intermolecular interactions were taken from the Universal Force Field1 (UFF) and those used to model the surface were those developed by Predota et al.[37-38] The Lorentz-Berthelot mixing rules were used to calculate mixed Lennard-Jones parameters. The slab approximation was used to model the anatase TiO $_2$ (101) surfaces, with slab thicknesses of ca. 19 Å and vacuum slabs of 60 Å. The supercell dimensions of both the bare and fully hydroxylated surfaces are 32.66 Å x 30.21 Å x 80 Å. A third surface was also constructed, half hydroxylated and half non-hydroxylated, with a supercell size of 65.32 Å x 30.21 Å x 80 Å, since it is the result of combining the other two supercells. In order to speed up the simulations the atoms of the surfaces were kept fixed. The

atomic charges to model the PdOEP molecule were obtained by performing first a geometry optimization of the molecule, at the B3LYP level of theory, employing the Gaussian09 code.[39] For C, N and H atoms a 6-311++G** basis set was used, while the double-zeta plus polarization DGDZVP basis set[40,41] is used for the Pd atom. This type of calculation will be called B3LYP/6-311++G**(DGDZVP). The minimum energy structure of the molecule is shown in Figure S3 and Table S1. The charges of the atoms were then calculated by performing a fitting of the Molecular Electro Static Potential (MESP), with the CHelpG method.[42] The ESP is calculated from the B3LYP/6-311++G**(DGDZVP) electron density. All molecular dynamics simulations were performed using the RASPA code, which was developed by D. Dubbeldam, S. Calero, D. E. Ellis and R.Q. Snurr, and has been employed in several studies of adsorption of molecules in porous materials.[43]

Figure 1. Time evolution of the water contact angle of UV illuminated TiO₂ and ITO thin films.

3. RESULTS AND DISCUSSION

3.1 Effect of the TiO₂ and ITO thin films illumination on the formation of Organic Nanowires.

Both MESO- and MICRO-TiO₂ thin films presented a hydrophobic behavior (contact angles higher than 90°) in their as-grown state and experienced a complete hydrophilic conversion upon UV irradiation for 35 minutes (Figure 1). In a similar way, the surface of the ITO substrate also transformed from hydrophobic (with an initial WCA ~110°) to hydrophilic (Figure 1).

From the point of view of the ONWs nucleation and growth, the homogenous and smooth surfaces of the MICRO-TiO₂ samples[30,31] make them equivalent to a flat and compact substrate, due to the low number of nucleation centers required for the formation of ONWs.[19] As a consequence, under standard PdOEP sublimation conditions, organic crystals rather than well-defined ONWs formed on as-prepared MICRO-TiO₂ substrates. This is illustrated in Figure 2 a) showing a characteristic in-plane growth of PdOEP crystals with domain sizes ranging between 50 and 100 nm. The UV light pre-irradiation under ambient conditions of this substrate modified drastically the morphology of these organic nanostructures and promoted the formation of supported PdOEP single crystal NWs with typical lengths of 1 to 2 μm and thickness below 100 nm (Figure 2b). The ONW density was in the order of 1.5 ONWs μm⁻¹. A similar change in the morphology of the organic nanostructures was also found when a commercial ITO substrate was pre-illuminated with UV light (Figure 2 c-e). Figure 2c) shows the boundary area between the growth on the as-grown ITO (left side of the panel) and the illuminated surface (right side of the panel). Figure 2 d-e) presents higher magnification images with the characteristic growth on these regions. Thus, Figure 2d) reveals that on the original ITO, PdOEP forms finger-like features parallel to the substrate surface, with sizes of the order of 10 μm. Meanwhile, Figure 2e) demonstrates the formation of ONWs on the pre-illuminated areas with morphological characteristics similar to those formed on the UV activated MICRO-TiO₂. These results obtained on compact or micro-porous substrates clearly prove that formation of ONWs only occurs after

UV illumination, while other types of nanostructures develop on the as-grown samples. A different behavior was obtained when performing the deposition on an open-porous thin film, i.e. on the nano-columnar MESO-TiO₂. Figure 2 d) and e) shows that while a considerable amount of ONWs (with lengths in the range between 1 and 3 μm , thickness between 20 and 120 nm and a density up to 20 ONWs μm^{-2}) form on the pre-illuminated MESO-TiO₂ thin films, no nanostructure grows on the surface on these films in their as-grown state.

Figure 2. SEM images of surfaces formed by vacuum deposition of PdOEP on Micro-TiO₂ (a-b), ITO (c-e) and MESO-TiO₂ (f-g) substrates. “As-grown” surfaces are shown on the left, while panels on the right show the preferential formation of ONWs on the UV pre-activated surfaces; d-e) present a closer view of the PdOEP nanostructures deposited on different zones of the ITO substrate as-grown (c-left side, d), and after its UV illumination through a shadow mask, (c-right side, e).

We will show below in Section 3.5 that contrary to the as-grown MICRO-TiO₂ and ITO substrates where PdOEP mostly remains on the surface, in the MESO-TiO₂ it also diffuses to the interior of the films through their characteristic open porosity. GAXRD patterns in Figure S4 corroborate the results obtained by SEM. The diffractogram corresponding to the deposition on MESO-TiO₂ as-grown shows no peaks as consequence of the amorphous character of both, the TiO₂ thin film and the PdOEP dispersed in this porous host (Section 3.5). On other hand, the high density of ONWs formed on the pre-illuminated MESO-TiO₂ depicts a well-defined XRD pattern with a narrow peak at $2\theta \sim 8^\circ$ corresponding to the (1-10) planes[45] meanwhile the growth on the MICRO-TiO₂ as-grown produces a broad peak with lower intensity in good agreement with smaller crystal sizes and lower crystallinity.

3.2 Light controlled patterning of the ONWs growth on TiO₂ and ITO.

The UV irradiation of the substrates through micrometric shadow masks provides a light patterning procedure for the selective formation of ONWs in certain areas of the substrates. Micrographs in Figure 3 and 4 were captured for PdOEP nanostructures grown on a MICRO-TiO₂ (Fig. 3 a-c), ITO (Fig. 3 d) and MESO-TiO₂ (Fig. 4) samples pre-irradiated through metal grids with different meshes. The bright squares in these figures correspond to the pre-irradiated areas where formation of ONWs occurs. Besides the practical implication of this methodology, another clear advantage of using light to control the preferential patterned growth of ONWs is its

associated low geometrical constrictions. In this work, well defined patterns are formed in the range of the 10 μm , although the extension of the method to lower area ranges is foreseen by using masks with smaller feature sizes, or even by UV laser interferences at nanometric scales.[46] As far as we know this is the first time the light controlled patterning growth of ONWs has been demonstrated.

Figure 3. Normal view SEM images at different magnifications of the PdOEP growth on MICRO-TiO₂ (a-c) and ITO (d) samples UV pre-illuminated through a shadow mask consisting of a mesh formed by squares of different lengths.

Figure 4. Normal view SEM images at different magnifications of the PdOEP growth on MESO-TiO₂ showing the patterning formation of ONWs.

3.3 XPS in situ experiments on as-grown and pre-illuminated surfaces.

In situ XPS experiments were carried out in order to look for a deeper understanding of the effect that UV irradiation has on the surface formation of ONWs. Figure 5 gathers the results of

one of those experiments, where PdOEP was simultaneously deposited on as-grown and on pre-irradiated MESO-TiO₂ substrates at 150 °C. A spectrum obtained for PdOEP molecules grown onto a compact monocrystalline TiO₂ (rutile, TiO₂(100)) substrate has been included as a reference. Figure 5 a) shows the Pd(3d) spectrum evolution for increasing amounts of deposited material for the three substrates. From this series of spectra, it is remarkable that, for equivalent thicknesses lower than 15 nm, no Pd(3d) signal was detected for either the pre-illuminated or the as-prepared MESO-TiO₂ substrates. These results, together with the SEM image in Figure 2 f), were the first clues indicating that a significant amount of PdOEP molecules diffuse and are adsorbed inside the pores of these substrates, as it will be discussed in Section 3.5. For higher equivalent thicknesses, a clear Pd(3d) peak shows up increasing as the amount of deposited PdOEP. The Pd(3d)/Ti(2p) and C(1s)/Ti(2p) peak area ratios presented in Figure 5 b) provide additional information about the accumulation of molecules on the substrate surface. Firstly, it is worth noting that the substrates themselves present a relatively high amount of carbon previous to the deposition of the PdOEP. This carbon comes from the organic contamination inherent to the handling in air of the substrates previous to their insertion in the XPS prechamber and from their deposition processes. The TiO₂ is a photoactive material widely applied as photocatalytic oxide for pollutant removing. Thus, the photoactivation of the MESO-TiO₂ surface with UV light reduces the inherent carbon content in the pretreated substrates. On the other hand, at all stages of the evaporation experiment, the Pd(3d)/Ti(2p) ratios were significantly higher on the pre-irradiated sample than on the as-grown one and the difference increases with the amount of evaporated PdOEP. A similar trend was found for the C(1s)/Ti(2p) ratio, which experiences a significant increase for the pre-irradiated sample, but remains almost constant for the as-grown one. These results can be interpreted by assuming that, at the very initial stages of deposition at

150 °C, the molecules present a low sticking coefficient with the substrate, therefore, they are quite mobile and can either diffuse into the large pores of the MESO-TiO₂ substrate or move along the surface, where they reach suitable nucleation points. Driven by capillary or similar forces, diffusion to the interior would predominate for the as-prepared samples, while nucleation onto the surface to then form ONWs should occur on the illuminated substrate, reducing the amount of material drawn into the pores. XPS data agrees with this interpretation: the very low increase of the Pd(3d)/Ti(2p) and C(1s)/Ti(2p) ratios in the as-prepared sample indicates that most of the deposited PdOEP molecules are not exposed at the surface; by contrast, the rapid increase of these ratios for the pre-illuminated substrates supports the nucleation and growth of ONWs onto the surface (note the difference in Pd(3d) peak intensity with respect to that in the TiO₂ single crystal reference, where molecules are less prompt to agglomerate and form a more homogenous layer). A similar study was carried out on a non-porous ITO substrate (see Figure S5) where the growth rate of the Pd(3d) peak for the first amounts of deposited material was slightly higher on the pre-illuminated than on the original ITO substrate (Figure S5 b) and d). This trend is reversed above 15 nm likely due to the formation of ONWs instead of in plane features.

Figure 5. a) Evolution of the Pd(3d) peak for increasing nominal thicknesses of PdOEP deposited on different substrates as labelled. The signal for the TiO₂ (100) single crystal substrate corresponds to the evaporation of 60 nm (nominal thickness) of PdOEP. b) C(1s)/Ti(2p), Pd(3d)/Ti(2p) and N(1s)/Ti(2p) atomic ratios extracted from the areas of the C(1s), Ti(2p), N(1s) and Pd(3d) photoelectron peaks as a function of the nominal thickness evaporated (top) and a zoom-in showing the first stages of deposition (bottom).

3.4 Molecular dynamics simulation of the ONW growth on pre-illuminated TiO₂.

The quite different behavior of the evaporated PdOEP molecules on the as-prepared or pre-illuminated TiO₂ and ITO surfaces must be related to the development of some specific interactions in this latter case. Trying to get additional information on the adsorption and nucleation of these molecules on these photoactive oxides, we have carried out molecular dynamics (MD) simulations. For this study we choose the anatase (101) TiO₂ surface as adsorbent, assuming three different surface states: as-grown (or bare), UV-pretreated, here implying that irradiation generates a highly hydroxylated surface state and as-grown/hydroxylated patterned surfaces where surface hydroxylation has been concentrated on certain zones of the surface. This latter situation tries to model the adsorption of PdOEP on anatase surfaces with hydrophobic/hydrophilic domains (cf. Figures 3-4). A basic assumption connecting these simulations and the experimental observations about the effect of light on the growth of ONWs (cf. Figures 2-4) is that the UV illumination under ambient conditions of TiO₂ and ITO produces an enhancement in their hydroxylation state that converts their surfaces into superhydrophilic (c.f., Figure 1).[24-27] Note that this effect can be compatible with the photocatalytic removal of spurious carbon evidenced by the XPS experiments, an effect claimed by some authors to justify the change in wetting properties of these oxides. A close view of the

hydroxylated surface is shown in Figure S6 and reference by S. Hamad et al.[48] Details about the charges and force fields employed in the simulations are shown in the Experimental Section. In Figure 6 we show snapshots of the simulations on the adsorption on the three surfaces. There is a clear difference between the adsorption on the as-grown and fully hydroxylated surfaces; the PdOEP molecules interact more strongly with the hydroxylated surfaces than with the as-grown ones. In fact, in the simulations of the as-grown surface all the molecules are adsorbed on just one of the two surfaces (Figure 6 a), suggesting that porphyrin-porphyrin interactions are stronger than porphyrin-surface interactions. On the contrary, as can be seen in Figure 6 b), there is a full coverage of the hydroxylated surfaces, where the dominant interactions should be porphyrin-surface and the molecules are adsorbed parallel to the surface. This difference in adsorption can be rationalized in terms of adsorption energies. To retrieve data on this parameter we performed longer simulations, with only one PdOEP molecule adsorbed on each surface. The adsorption energies, averaged over 20 ns of simulation, are -33.5 kcal/mol and -54.9 kcal/mol on the as-grown and hydroxylated surfaces, respectively. These values clearly explain that the full coverage found on the hydroxylated surfaces is due to the large value of adsorption energy. Besides this preferential interaction of the PdOEP molecules with the hydroxylated surfaces, the snapshots in Figure 6 a) and b), also show that in the latter case, once a first monolayer of organic molecules is formed on the surface, the additional molecules tend to deploy relatively well ordered 1D nanostructures. This contrasts with the agglomeration in the form of a thick not well structured layer formed just on one side of the anatase slab found for the as-grown surfaces (Figure 6 a). Clearly, these simulation results connect with the experimental finding of a preferential growth of NWs on the UV illuminated samples. Further evidence in this sense is provided by the simulation where only certain parts of the surface are hydroxylated and the rest

remain in the as-grown, non-hydroxylated, state. The results in Figure 6 c) show that the hydroxylated area is able to attract more strongly the adsorbed molecules where they adsorb in the form of a first monolayer. This first monolayer promotes the preferential agglomeration of additional molecules in the form of a 1D nanostructure. In the non-hydroxylated areas, we observe that, as it happens with the simulations on non-hydroxylated surfaces (Figure 6 a), molecules adsorb on just one side of the anatase slab where they do not form a well- structured first layer, thus suggesting that direct porphyrin-porphyrin interactions are predominant.

Figure 6. Snapshots of the molecular dynamics simulations, for the bare (a), fully hydroxylated (b), and patterned as-prepared/hydroxylated (c) anatase (101) surfaces. The white spots at the anatase surface denote the presence of hydroxyl groups (see Fig. S3).

It is pertinent at this point to mention again that the hydrophobic/hydrophilic conversion under UV irradiation of the TiO_2 is attributed in the literature to the photo-catalytic removal of carbon residues from its surface and/or to the enhancement of the hydroxylation state of its surface.[25-27] The XPS experiments shown in the previous section indicated that the amount of carbon in the pre-irradiated samples is lower than in the as-grown surfaces in concordance with a photo-catalytic processes. On the other hand, several authors have published the patterning formation of ONWs from organic templates[49]. Those results could be in disagreement with the enhanced

formation of organic nanowires that we report herein for an UV-pretreated surface and, therefore, “free” of organic compounds that might act as nucleation sites for the development of the ONWs. However, in our case it is not necessary the presence of such organic centers. In fact, in a previous article[32] we demonstrated the enhanced formation of ONWs on silver nanoparticles subjected to an oxygen plasma treatment. In that case, although the plasma pre-treatment removed the organic pollutants coming from handling in air of the silver nanoparticles the density of ONWs was higher than for the non-treated substrate.

Hence, taking into consideration these results exposed above and the simulations in Figure 6 we propose that the enhanced formation of nucleation sites in the pre-illuminated surfaces is likely related to the formation of hydroxyl groups.

3.5 Effect of the substrate temperature and open porosity in the formation of hybrid materials.

In the course of this investigation it was realized that the deposition of the PdOEP on the MESO-TiO₂ thin films could lead either to the growth of a high density of ONWs (for the pre-illuminated surfaces, Figure 2 g) and 4) or to the coloration of the film with no sight of organic structures (Figure 2 f). In fact, UV-Vis and fluorescence spectra (Figures S7 and S8) of these samples demonstrate that both contain a comparable amount of PdOEP. On the other hand, in situ XPS studies have shown that at the first stage of the deposition at mild temperatures, PdOEP molecules are rather mobile, being necessary to evaporate a minimum amount of PdOEP on the top of the MESO-TiO₂ in order to detect the first traces of the molecules. In the previous sections, the role played by the UV illumination of the TiO₂ substrates has been revealed, herein, another critical experimental parameter, the substrate temperature, will be analyzed within the context of the vacuum deposition of hybrid organic/inorganic thin films. For a sample prepared

at 150 °C, the RBS spectrum (Figure 7) depicts a flat Pd band, sustaining that this element is distributed through the whole porous structure of the oxide film (black line). By contrast, when performing the evaporation with the substrate at room temperature the situation was different and the Pd feature appears as a relatively narrow peak, suggesting that PdOEP preferentially absorbs on the surface and/or at the external regions of the film (Figure 7 grey line).

Figure 7. RBS spectra of the samples corresponding to the vacuum deposition of PdOEP on Meso-TiO₂ (as-deposited) samples at 150 °C (black) and room temperature (gray). See comparison between acquired and simulated spectra in Figures S9 and S10.

Table 1. Atomic equivalent thickness simulated from the RBS data for the PdOEP deposition on Meso-TiO₂ at 150 °C. For this calculation a three-layer system has been simulated and compared with experimental results as presented in Figure S9.

	Thickness (10 ¹⁵ at/cm ²)	[Ti] (at. %)	[O] (at. %)	[Pd] (at. %)	[C] (at. %)
Surface	430	23,5	50,9	0,2	25,4
↓					
Substrate	465	21,9	49,0	0,3	28,8
e	440	19,0	44,9	0,3	35,8
Total	1335				

Table 2. Atomic equivalent thickness simulated from the RBS data for the PdOEP deposition on MESO-TiO₂ at room temperature. For this calculation a two-layer system has been simulated and compared with experimental results as presented in Figure S10.

	Thickness (10 ¹⁵ at/cm ²)	[Ti] (at. %)	[O] (at. %)	[Pd] (at. %)	[C] (at. %)
Surface	215	-	-	2,6	97,4
↓					
Substrate	1035	26,5	55,4	-	18,1
Total	1250				

Data in Table 1 showing the concentrations of Ti, O, Pd, and C deduced from the ion beam analysis experiments, confirm that at 150 °C the PdOEP molecules are homogeneously distributed through the TiO₂ thin films. A slightly higher concentration of PdOEP molecules can even be detected in the interface with the substrate, which might be an indication of the high mobility of these molecules under the chosen experimental conditions. On the contrary, Table 2, which gathers the percentage of the atomic elements after the room temperature deposition, reveals the preferential deposition of PdOEP on the top of the TiO₂ film. Further evidence that substrate temperature critically controls the diffusion of the PdOEP molecules into the thin film porous structure is provided by the SEM cross section images in Figure 8, corresponding to the deposition of PdOEP on the MESO-TiO₂ (as-grown) samples at 150 °C (a) and at room temperature (b). In the first case the micrograph does not present any characteristic feature of organic nanostructures onto the surface, although it is compatible with the infiltration of the organic compound into the porous structure. Meanwhile, the image corresponding to the sample prepared at room temperature demonstrates the growth of an organic deposit on top of the columnar nanostructure of the substrate (note that this agglomeration of organic material at the surface of the MESO-TiO₂ thin film is not equivalent to the ONWs formation at 150 °C onto the

pre-illuminated sample, see also GAXRD results in Figure S4). Therefore, these RBS, and SEM results show that the deposition of PdOEP at room temperature produces the accumulation of organic aggregates on top of the columnar TiO_2 substrate (i.e., as a bilayer structure) and that heating at 150 °C is required to favor the mobilization and diffusion of the organic molecules within the porous structure of Meso- TiO_2 substrates and the formation of a homogenous hybrid organic/oxide thin film material. In this article on the Meso- TiO_2 as host material because the markedly open porosity character of these samples has allowed the incorporation of the PdOEP molecule for reproducible high nominal thicknesses. In the case of MICRO- TiO_2 , its characteristic porosity (see Fig. S1 a) with low connectivity between the pores hampers the distribution of molecules along the cross section of the host material resulting in the rapid formation of an organic layer at the surface even for deposition at 150 °C. However, it is worth to mention that increasing the deposition temperature might provide mobility enough to the organic molecules to homogeneously distribute also along the MICRO- TiO_2 thickness.

Figure 8. Cross section SEM micrographs characteristics of the deposition of PdOEP on Meso- TiO_2 nanocolumnar substrates at 150 °C (a) and room temperature (b).

On the other hand, it is important to address that most reported procedures intending the incorporation of organic molecules into porous structures consist of wet methods,[28, 49-51] where a solvent fills the open pores of the host material and drags with it the dissolved organic

molecules. The direct evaporation of organic molecules in PVD produces directional beams of molecules, which might hamper the diffusion of the molecules in the porous due to shadowing effects. Cooling the evaporated beam and breaking its directional character can be achieved by interaction with a residual inert gas filling the evaporation chamber.[52] In the present work keeping a relatively high Argon pressure during evaporation was indispensable to get either the supported ONWs or to fabricate the hybrid layers of PdOEP infiltrated in the pores of the MESO-TiO₂ thin films. At the used pressure of 10⁻² mbar, the mean free path of a molecule with the typical size of the PdOEP is in the order of 1 nm. This distance is much smaller than the evaporator-substrate separation (8 cm) in our experimental arrangement, implying that the evaporated molecules thermalize by their multiple collisions with Argon atoms and completely lose their directionality.

CONCLUSIONS

In the present work, we have shown that photo-active oxide materials can be activated with light to promote the growth of well-structured ONWs on their surface. A key feature of this activation process is that it remains for relatively long periods of time, a “memory effect” that has been used here for the selective patterning of the surface of these oxides to promote the preferential growth of these 1D crystalline organic nanostructures on given zones of the illuminated substrates. We have associated this “memory effect” with the development of a peculiar hydroxylation state of the illuminated areas. Although further studies are still necessary to provide further proofs of this hypothesis, the MD simulations reported in Section 3.4, and previous results in our laboratory concerning the selective incorporation of Rhodamine molecules[28,50] or the enhancement of the osteoblast growth on illuminated surfaces of TiO₂,[29] are in line with this hypothesis. Thus, this article opens a way for the light patterning

of semiconducting oxides. It has been also shown the formation of hybrid organic/inorganic thin films by vacuum deposition of porphyrin molecules at mild temperature on the top of an open-porous inorganic thin film. We foresee that this last result, readily compatible with other organic/inorganic combinations, will be of the outmost importance in the incorporation of this type of materials on photonic and optoelectronic devices, serving as alternative to the wet routes.

Supporting Information

PdOEP chemical structure. Additional SEM, AFM, GAXRD, XPS, UV-Vis and photoluminescence results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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