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# Photoinduced ethylene polymerization on TiO<sub>2</sub> nanoparticles

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**Abstract:** Herein we report on the ability of H<sub>2</sub>-photoreduced TiO<sub>2</sub> nanoparticles in catalyzing ethylene polymerization without the use of any alkylating agent. Even more, we demonstrate that the same reaction occurs directly on stoichiometric TiO<sub>2</sub> in the presence of ethylene under UV-light irradiation at room temperature, thus without any pre-reduction step. The synergic use of electron paramagnetic resonance and diffuse reflectance UV-Vis-NIR spectroscopy allowed us to identify and correlate different Ti<sup>3+</sup> EPR signals and UV-Vis-NIR bands; while transmission FT-IR spectroscopy (applied under *in situ* UV-light irradiation) was fundamental to prove ethylene polymerization and to observe ethylene oxidation by-products. The possibility to easily polymerize ethylene in a one-step procedure can be a promising approach to increase the compatibility of TiO<sub>2</sub> as inorganic additive for polyethylene blends.

In the last decades nanostructured materials based on TiO<sub>2</sub> have attracted increasing interest owing to the possible applications in environmental pollution remediation, photovoltaics and photocatalytic hydrogen generation.<sup>[1]</sup> With respect to other semiconductors, TiO<sub>2</sub> offers several advantages including low toxicity, chemical and thermal stability, low cost and high resistance to photo-corrosion. Compared to the applications based on the photocatalytic properties, the number of those taking advantage from the surface chemical properties of TiO<sub>2</sub> is rather limited, in agreement with the stability of this oxide. For instance, despite the fact that most of the heterogeneous catalysts for olefins polymerization are based on supported Ti compounds, TiO<sub>2</sub> is inert toward ethylene polymerization. In this context, however, some of us have recently succeeded in transforming TiO<sub>2</sub> into a catalyst for ethylene polymerization, generating surface reduced Ti sites able to convert ethylene to polyethylene without the need of any activator.<sup>[2]</sup> These sites were obtained treating TiO<sub>2</sub> at high temperature (773 K) in H<sub>2</sub>, resulting in reduced materials characterized by both surface and bulk shallow-trap defect sites in analogy with the so-called "black titania".<sup>[3]</sup> However the hard treatment in H<sub>2</sub> at high temperature is not only expensive in terms of energy and time, but it can also induce an unwanted anatase-rutile conversion and morphological modifications.

The challenge is now to join the potential of photo-activity of TiO<sub>2</sub> with its ability to convert ethylene to polyethylene, operating the whole reaction in mild conditions. Interestingly, reduced species at the surface of oxides can be formed at room

temperature in H<sub>2</sub> atmosphere under UV illumination,<sup>[4]</sup> but it has not yet been reported whether or not the reduced Ti species obtained in this way are able to polymerize ethylene. Even more appealing would be the photo-induction of ethylene polymerization on TiO<sub>2</sub> at room temperature without any pre-reduction step, a strategy that could ensure evident advantages on the economy of the whole process.

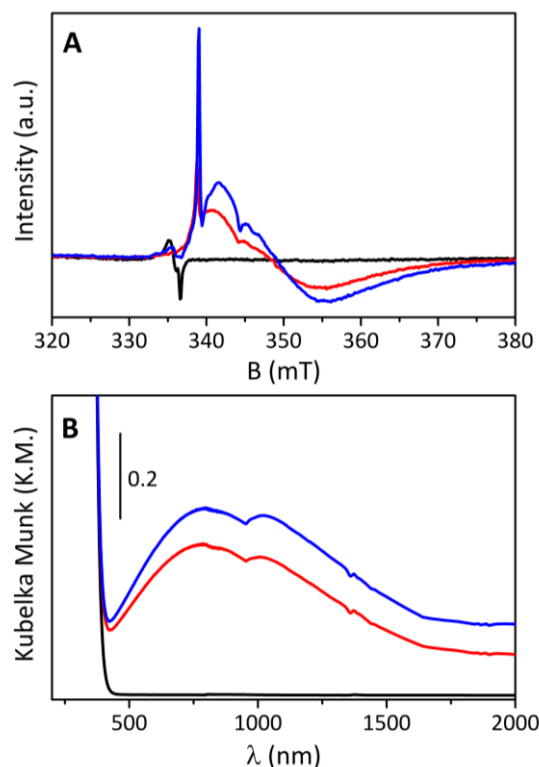
In this work we address both challenges by using electron paramagnetic resonance (EPR), Diffuse Reflectance (DR) UV-Vis-NIR and transmission FT-IR spectroscopies as fundamental tools to observe the effects of UV-light irradiation on TiO<sub>2</sub> in the presence of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. The investigated sample was a TiO<sub>2</sub> anatase obtained via sol-gel method, and the UV light irradiation was accomplished using a Newport 500 W Hg(Xe) arc lamp, equipped with a water filter to eliminate the infrared portion of the spectrum (more experimental details are given in Section S1 of the Supporting Information).

Our first goal was to monitor the evolution of the properties of TiO<sub>2</sub> when it is irradiated with UV-light at room temperature in H<sub>2</sub> atmosphere (hereafter H<sub>2</sub>-photoreduced sample). According to previous studies, this procedure leads to H<sub>2</sub> splitting and to the consequent formation of surface and sub-surface Ti<sup>3+</sup> centers.<sup>[4a]</sup> The EPR spectrum of the H<sub>2</sub>-photoreduced TiO<sub>2</sub> sample (Figure 1A, red) is dominated by a broad absorption feature ( $g_x=1.9452$ ,  $g_y=1.918$  and  $g_z=1.875$ ), assigned to Ti<sup>3+</sup> in a surface disordered environment<sup>[4b]</sup> and a second signal characterized by narrow lines and axial structure ( $g_{\perp}=1.992$ ,  $g_{\parallel}=1.962$ ), assigned to regular sub-surface or bulk lattice Ti<sup>3+</sup> centers.<sup>[5]</sup> The presence of these defective Ti<sup>3+</sup> sites is further confirmed by the DR UV-Vis-NIR spectrum (Figure 1B, red) characterized by a broad absorption in the 400-1700 nm region centered at 800 nm. The UV irradiation in H<sub>2</sub> atmosphere induces also the growth of a broad absorption in the MIR region having a maximum at ca. 2000 cm<sup>-1</sup> (Figure 2A and S2, red traces), which is absent in the spectrum of stoichiometric TiO<sub>2</sub> (black) and is ascribed to the presence of free conduction band electrons.<sup>[6]</sup> A more detailed discussion of the reduction process is reported in Section S2 of the Supporting Information.

As second step, we tested the reactivity of the H<sub>2</sub>-photoreduced sample towards ethylene at room temperature. Both EPR and DR UV-Vis-NIR spectra do not show significant changes at short contact times. A small increase in the overall spectral intensity is observed in both cases only after prolonged contact times (Figure 1, blue). Most probably, ethylene is slowly oxidized in a process involving surface O<sup>2-</sup> sites, generating further reduced Ti<sup>3+</sup> sites and oxidation products containing C=O groups (*vide infra*). Simultaneously, in the 2500-2000 nm NIR spectral region (Figure S3) three weak bands appear at 2305, 2355 and 2422 nm, ascribable to the combination of the  $\nu(\text{CH}_2)$  and  $\delta(\text{CH}_2)$  modes of polyethylene and thus testifying the occurrence of ethylene polymerization reaction.

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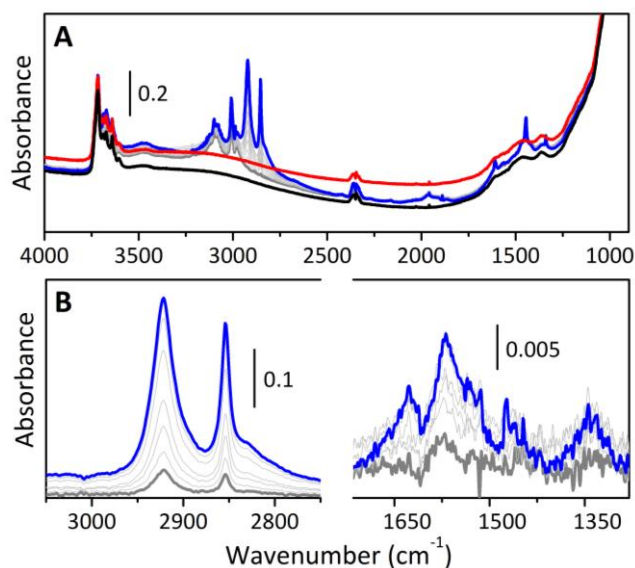
Supporting information for this article is given via a link at the end of the document.



**Figure 1.** EPR spectra (part A) and DR UV-Vis-NIR spectra (part B) of stoichiometric  $\text{TiO}_2$  activated at 773 K (black), the same sample after UV irradiation in the presence of 100 mbar of  $\text{H}_2$  (red) and after prolonged contact with 100 mbar of  $\text{C}_2\text{H}_4$  at room temperature (blue).

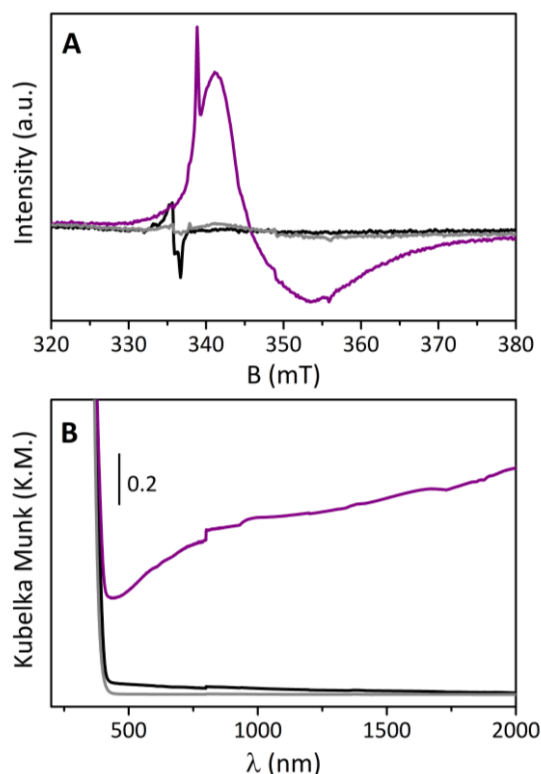
It is worth noticing that, as soon as ethylene gas is admitted into the reaction cell (Figure 2A, dark grey spectrum), the broad absorption centered at  $\sim 2000\text{ cm}^{-1}$  characteristic of the  $\text{H}_2$ -photoreduced sample (Figure 2A, red curve) is instantly and completely eroded, suggesting a fast recombination of the free conduction band electrons. In parallel, new IR absorption bands due to adsorbed ethylene (at  $3100$ ,  $3008$  and  $1608\text{ cm}^{-1}$ ) appear (for details see Section S3). For longer contact times, ethylene polymerization slowly takes place, as testified by the progressive growth of two IR absorption bands at  $2922$  and  $2853\text{ cm}^{-1}$  respectively assigned to the  $\nu_{\text{asymm}}(\text{CH}_2)$  and  $\nu_{\text{symm}}(\text{CH}_2)$  modes of polyethylene (Figure 2B, spectra from grey to blue). The position, evolution and intensity ratio of the  $\text{CH}_2$  bands, along with the absence of absorption bands due to  $\text{CH}_3$  moieties (expected at  $2965$  and  $2872\text{ cm}^{-1}$  for  $\nu(\text{CH}_3)$  and at  $1379\text{ cm}^{-1}$  for  $\delta(\text{CH}_3)$ )<sup>[7]</sup> are indicative of the formation of high-density polyethylene (HDPE) having a negligible amount of branches. Along with the spectroscopic features of polyethylene, extremely weak signals appear in the  $1650$ - $1350\text{ cm}^{-1}$  spectral region at  $1626$ ,  $1570$  and  $1343\text{ cm}^{-1}$ . These bands are attributed to products of ethylene oxidation, such as formaldehyde, acetaldehyde, formate, methylformate or acetate, which remain adsorbed on the surface of  $\text{TiO}_2$ .<sup>[8]</sup> The observation of these products testifies that ethylene is further reducing  $\text{TiO}_2$  in the present experimental conditions (low pressures). It is worth recalling here that the stoichiometric  $\text{TiO}_2$  sample does not polymerize ethylene at room temperature

(see Section S3), so confirming that the reduction is a necessary step to develop reactivity.



**Figure 2.** FT-IR spectra of stoichiometric  $\text{TiO}_2$  activated at 773 K (black), after UV irradiation in  $\text{H}_2$  (red) and contacted with 100 mbar of  $\text{C}_2\text{H}_4$  at room temperature up to 7 hours (grey to blue). Part A shows the whole  $4000$ - $1000\text{ cm}^{-1}$  spectral region. Magnifications of the  $3050$ - $2750$  and  $1715$ - $1300\text{ cm}^{-1}$  spectral regions are shown in part B, in which the initial spectrum in  $\text{C}_2\text{H}_4$  is subtracted from all curves.

The second challenge was to accomplish ethylene polymerization on stoichiometric  $\text{TiO}_2$ , exploiting the potential of ethylene itself to act as reducing agent under UV light irradiation. The feasibility of this route is demonstrated by both EPR and DR UV-Vis-NIR spectroscopies. The EPR spectrum (Figure 3A) of the stoichiometric anatase sample (black) is only slightly affected by the presence of ethylene (grey), while remarkable changes occur after 15 minutes of UV irradiation at room temperature (purple), resulting in the characteristic spectrum of  $\text{Ti}^{3+}$  species in anatase. Interestingly, in this case the ratio between the narrow line species and the broad absorption feature is inverted with respect to the  $\text{H}_2$ -photoreduced sample (Figure 1A). This observation indicates the formation of a larger fraction of surface  $\text{Ti}^{3+}$  species with respect to bulk ones. The DR UV-Vis-NIR spectra (Figure 3B, same color code) confirm the EPR results. Indeed, for  $\text{C}_2\text{H}_4$ -photoreduced  $\text{TiO}_2$  a broad and apparently featureless absorption band appears in the  $500$ - $2000\text{ nm}$  region, indicating the formation of  $\text{Ti}^{3+}$  species. This spectrum, however, is different from that of the  $\text{H}_2$ -photoreduced sample (Figure 1B), characterized by a more defined band centered at  $800\text{ nm}$ . Combining the EPR and UV-Vis-NIR data we propose that the band centered at  $800\text{ nm}$  in the UV-Vis-NIR spectrum can be associated to the narrow EPR lines and axial structure ( $g_{\perp}=1.992$ ,  $g_{\parallel}=1.962$ ) assigned to regular sub-surface or bulk lattice  $\text{Ti}^{3+}$  centers. On the contrary, the broad absorption extending in the NIR region beyond  $2000\text{ nm}$  can be linked to the EPR broad absorption feature ( $g_x=1.9452$ ,  $g_y=1.918$  and  $g_z=1.875$ ) and assigned to  $\text{Ti}^{3+}$  in a surface disordered environment.

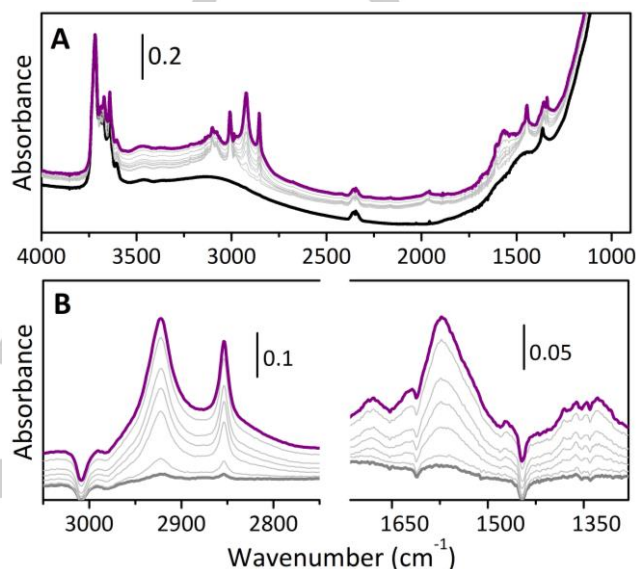


**Figure 3.** EPR spectra (part A) and DR UV-Vis-NIR spectra (part B) of the stoichiometric TiO<sub>2</sub> activated at 773 K (black) in contact with 100 mbar of ethylene (grey) and UV irradiation in ethylene (purple).

Summarizing, EPR and UV-Vis-NIR spectroscopies revealed that under UV irradiation ethylene reduces preferentially the TiO<sub>2</sub> surface with respect to atomic H•, which can diffuse in the solid,<sup>[9]</sup> generating subsurface and bulk Ti<sup>3+</sup> centers. However, they did not show if ethylene polymerization occurred. Indeed, the extension of the broad absorption to the NIR region hinders the observation of the  $\nu(\text{CH}_2)$  and  $\delta(\text{CH}_2)$  combination modes of polyethylene. To clarify this point we performed a time-resolved FT-IR experiment where a TiO<sub>2</sub> stoichiometric sample was continuously irradiated with the UV source in the presence of ethylene at room temperature. The experiment required the adoption of an *ad hoc* experimental set-up,<sup>[10]</sup> comprising an aspherical fiber bundle focusing assembly on the UV source and a large core liquid light guide which focused the radiation emitted by the lamp directly on the sample inside the FT-IR spectrophotometer (passing through the KBr windows of the IR cell). This set-up allowed us to observe the simultaneous occurrence of the TiO<sub>2</sub> reduction/ethylene oxidation and ethylene polymerization reactions (Figure 4).

The FT-IR spectrum of stoichiometric TiO<sub>2</sub> in contact with ethylene (dark grey curve in Figure 4) is dominated by the IR absorption bands of adsorbed ethylene (as discussed in section S3). At increasing irradiation time (from grey to purple) the whole spectra profile increases in absorbance, proving the occurrence of TiO<sub>2</sub> reduction. This broad absorption has a maximum at ca. 2000 cm<sup>-1</sup> and it is due to the excitation of electrons in the conduction band. Simultaneously, IR absorption bands grow at

2922 and 2853 cm<sup>-1</sup>, testifying the formation of polyethylene at the surface of the TiO<sub>2</sub> sample. New signals appear also in the 1700–1300 cm<sup>-1</sup> spectral region (main components at 1680, 1618 and 1572 with a shoulder at 1532 cm<sup>-1</sup>, along with a group of weaker bands in the 1380–1320 cm<sup>-1</sup> region), which are attributed to products of ethylene oxidation (i.e. formaldehyde, acetaldehyde, formate, methylformate or acetate).<sup>[8]</sup> These latter bands are considerably more intense with respect to those observed for the reaction of ethylene with H<sub>2</sub>-photoreduced TiO<sub>2</sub> (see Figure 2B). These data unequivocally demonstrate that concomitant TiO<sub>2</sub> reduction and ethylene polymerization occur under UV irradiation



of TiO<sub>2</sub> in the presence of ethylene.

**Figure 4.** FT-IR spectra of stoichiometric TiO<sub>2</sub> activated at 773 K (black), upon ethylene admission to the IR cell (grey) and after 1 hour of *in situ* UV irradiation (from grey to purple). Part A shows the whole 4000–1000 cm<sup>-1</sup> spectral region. Magnifications of the 3050–2750 and 1715–1300 cm<sup>-1</sup> spectral regions are shown in part B, in which the initial spectrum in C<sub>2</sub>H<sub>4</sub> before starting the UV irradiation is subtracted from all the spectra.

In conclusion, with respect to our previous work in which TiO<sub>2</sub> is reduced at high temperatures to promote ethylene polymerization,<sup>[2]</sup> we proposed here a much easier and quicker way to perform the same reaction. We demonstrated that ethylene polymerization occurs on TiO<sub>2</sub> nanoparticles reduced by UV-light in H<sub>2</sub> atmosphere at room temperature and without the use of any alkylating agents. We went much further this evidence, showing that ethylene polymerization takes place directly on TiO<sub>2</sub> under direct UV light irradiation, leading to a successful one-step production of a TiO<sub>2</sub>/polyethylene composite. Ethylene resulted more selective in the formation of Ti<sup>3+</sup> surface species with respect to H<sub>2</sub> under the same experimental conditions. We have also been able to identify and correlate the different Ti<sup>3+</sup> EPR signals with the UV-Vis-NIR bands. The spectroscopic results discussed in this work highlight the crucial role of Ti<sup>3+</sup> species in promoting ethylene polymerization, contributing to the debate present in the olefin oligomerization/polymerization literature.

Photoinduced ethylene polymerization on TiO<sub>2</sub> cannot compete with the existing highly efficient ethylene polymerization

processes, based on fragile catalyst supports which continuously fragment during ethylene polymerization, exposing new active sites. However, it might have a potential interest for producing TiO<sub>2</sub>/polyethylene composites to be used as additives in polyethylene blends, thus solving the problem of compatibility between the inorganic material and the polymer in a smart, simple and economic way.

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**Keywords:** Ti<sup>3+</sup>, H<sub>2</sub>-photoreduced TiO<sub>2</sub>, EPR spectroscopy, FT-IR spectroscopy, UV-Vis-NIR spectroscopy, HDPE.

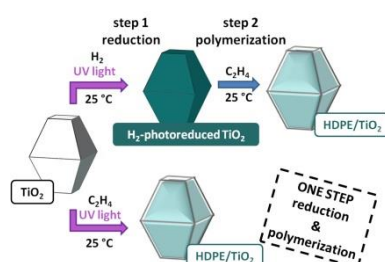
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## COMMUNICATION

**One-step is better:** UV light irradiation of  $\text{TiO}_2$  nanoparticles leads to the successful one-step production of a  $\text{TiO}_2$ /polyethylene composite without the use of any alkylating agent or pre-reduction step.



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