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THE CONTRIBUTION OF XPS TO THE UNDERSTANDING OF THE FUNCTIONAL PROPERTIES OF TITANIUM DIOXIDE

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The need to enhance specific functional properties of titanium dioxide, for instance to extend the photoresponsivity to visible light and to increase the photocatalytic efficiency, leads to different strategies for the modification of its electronic structure. The generation of point defects in the structure of TiO₂, producing sub stoichiometric oxides (TiO_{2-x}) and the conjugation with carbon or C-based materials are two convenient ways to modify the electronic features of TiO₂ [1]. In this work the X-ray photoelectron spectroscopy (XPS) was exploited for investigating TiO_{2-x} materials synthesized starting from hybrid chemical gels in which titanium is involved in a charge transfer complexation equilibrium with acetylacetonate and annealed in different environments, in order to identify the species responsible for their catalytic properties. XPS has proved to be a powerful technique for this scope. It provides evidence of the formation of the TiO₂ – acetylacetonate complex by C 1s photoelectron peak. Ti³⁺ and sub-oxides were clearly identified in the Ti 2p peaks of the samples calcined for 1h in a tubular furnace with the ends of the quartz tube open to air (static air conditions) (Figure 1). The extraordinary high concentration of Ti atoms with oxidation states lower than IV (about 26%) justify the unusual light absorption in the entire visible range [2]. When the hybrid TiO₂ – acetylacetonate samples were annealed at 400°C in laminar airflow, under nitrogen atmosphere or under a hydrogen/nitrogen mixture, no reduced Ti³⁺ was observed (Figure 1). Despite the absence of reduced Ti species, these materials showed significant yields of H₂, even without a metal co-catalyst both under UV irradiation and visible light. Also in this case, XPS provides an effective justification of the materials' properties. A detailed curve fitting of C 1s XP-peaks, following the approach developed to interpret complex carbon spectra of particulate matter [3], allowed us to observe the presence of a component due to elemental carbon at 284.2 eV (Figure 1), whose content increases from 7% for the air-annealed samples to 11-12% for the samples heated in H₂/N₂ mixture. No elemental carbon was detected in the samples annealed under static air conditions.

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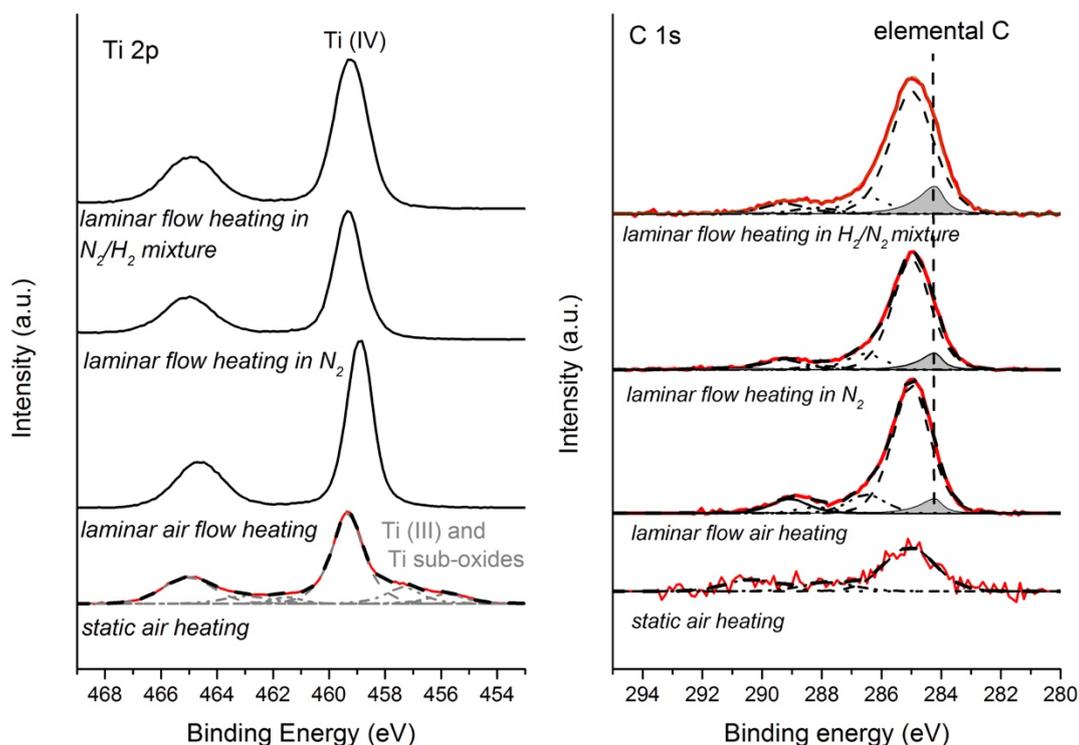


Figure 1. High-resolution XP- spectra of Ti 2p and C 1s acquired on samples heated at 400°C in various environments.

To clarify if the elemental carbon presence is due to C-doping of TiO₂, the XPS valence bands of the samples were also acquired and processed. The shape of the valence bands was typical for anatase for all the samples being the peak due to σ bonding O2p electrons more intense than the one due to π bonding. The binding energies of the valence band maxima, determined using the linear extraction method [4], were within the experimental error for all the samples, despite the different atmosphere of the thermal treatments. The absence of any extra electronic state above the valence band edge, which are supposed to be present in the case of C-doped TiO₂ [5] as well as the lack of any noticeable shift of XRD peaks lead us to exclude that carbon behaves as a dopant and supports the idea of the formation of graphitic carbon upon heating.

References

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