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# Electron transfer and H<sub>2</sub> evolution in hybrid systems based on [FeFe]-hydrogenase anchored on modified TiO<sub>2</sub>

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## ABSTRACT

The hybrid systems composed by [FeFe]-hydrogenase anchored to the surface of three distinct types of TiO<sub>2</sub> (anatase) have been investigated using Electron Paramagnetic Resonance (EPR) spectroscopy in dark and under illumination. The three supports were bare TiO<sub>2</sub>, nitrogen doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) and a sub-stoichiometric form of the same oxide (TiO<sub>2-x</sub>) exhibiting blue color. EPR spectroscopy has shown that the electrons photo-generated by irradiation of the supports are stabilised by the solid forming Ti<sup>3+</sup> paramagnetic ions while, in the case of the hybrid systems electrons are scavenged by the anchored protein becoming available for H<sup>+</sup> reduction. The ability of the three hybrid systems in hydrogen production under solar light illumination has been compared. The formation of H<sub>2</sub> is higher for the system containing N-TiO<sub>2</sub> (yellow) with respect to that based on the bare oxide (white) indicating that the visible light absorbed, due to the presence of N states, is actually exploited for hydrogen production. The system containing reduced blue TiO<sub>2</sub>, in spite of its deep coloration, is less active suggesting that a specific type of visible light absorption is needed to produce photoexcited electrons capable to interact with the anchored protein.

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## Introduction

Since the discovery, in 1972, of the photosplitting of water in hydrogen and oxygen [1] based on a photo-electrochemical cell with an anode made of titanium dioxide, this compound became a system of reference in the area of photochemical and photo-electrochemical applications. Titanium dioxide, or

titanium, is nowadays the most important photocatalyst employed in processes for pollutants abatement [2], as biocide [3,4], in odour control [5] and in self-cleaning of glasses or of external surfaces [6]. As to the mentioned applications for hydrogen production from water, the advent of more efficient (but often much more expensive) materials and of complex approaches both for the preparation of photoelectrodes and for the direct photocatalytic water splitting [7,8], eclipsed for

Abbreviations: EPR, electron paramagnetic resonance; TEOA, triethanolamine; N-TiO<sub>2</sub>, N-doped TiO<sub>2</sub>; rd-TiO<sub>2</sub>, reduced TiO<sub>2</sub>; XRD, X-ray diffraction; H<sub>ox</sub>, H<sub>ox</sub>-CO EPR detectable species of H-cluster of the protein.

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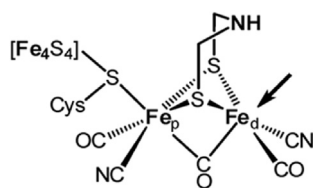
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quite a long time the role initially played by titania. This material, which has the great advantage to be cheap, abundant and non toxic, actually shows some serious drawbacks hampering its direct use in the process of water photo-splitting. The first one is the large value of the  $\text{TiO}_2$  band gap (around 3.2 eV for the anatase polymorph) that implicates the use of UV photons to perform the excitation of electrons from the valence band to the conduction band limiting therefore the use of sunlight (poor of UV components at the earth surface) in photochemical applications of this material. The second drawback is the electrochemical potential of the conduction band electrons which is only slightly more negative than the  $\text{H}^+/\text{H}_2$  potential thus limiting the reductive capability of photoexcited electrons. For this reason the most successful photocatalytic applications of titania are in the field of oxidation (e.g. pollutants remediation) so exploiting the excellent oxidative potential of the valence band holes [9].

The need of overcoming these two serious constraints is at the origin of a long activity aiming to modify the solid in order to improve its performances. Among the methods to adjust the photochemical properties of titania extending to the visible range its optical absorption, it is worth mentioning: i) the grafting of sensitizers at the surface of the solid [10] analogous to what done for Dye Sensitized Solar Cells (DSSC, photovoltaic applications); ii) the use of supported metal nanoparticles (mainly Au) to exploit light absorption due to plasmonic effect [11,12]; iii) the doping of the solid with various dopants. In the latter case the most intriguing case is that of doping with non-metals. In particular doping with nitrogen [13–16] or with combination of elements including nitrogen [17,18] has been the object of intense research activity and of warmly debated results. As a matter of fact, nitrogen doped titania is now currently used in photocatalytic applications employing visible light [19–21].

On the other hand, as far as the production of hydrogen by reduction is concerned, the use of co-catalysts is necessary to overcome the described potential limitation. In this case, beside the use of a typical noble metal hydrogenation catalyst like Pt nanoparticles, a particularly interesting approach is the use of a biocatalyst such as hydrogenase. In particular, the [FeFe]-hydrogenase enzyme is known to catalyse the reversible reduction of  $\text{H}^+$  ions to  $\text{H}_2$  and its action is due to an iron based catalytic center called H-cluster which is composed by two subclusters, an iron sulphur cubane [4Fe-4S] and a [2Fe] subcluster. The latter is based on an iron pair coordinated by two bridging sulphur atoms belonging to an organic ligand and by various non-protein ligands, namely three CO and two CN- groups (Fig. 1). Furthermore, this protein contains several



**Fig. 1** – Structure of the H-cluster active site of [FeFe]-hydrogenase; the arrow indicates the open metal coordination site.

[FeS] clusters, with suitable redox potentials allowing the electron transfer from an external electron donor to the H-cluster, where the electrons combine with protons to form dihydrogen molecules [22–25].

Quite recently hydrogenase- $\text{TiO}_2$  nanohybrid have been prepared and tested in photocatalytic process for hydrogen production based on solar light conversion [26–32].

The purpose of the present work is to investigate the hybrids prepared coupling hydrogenase with modified titanias. The latter are materials based on the anatase polymorph modified in order to make them capable of absorbing visible light. In particular we employed, comparing the results with those of a sample of bare anatase, two kind of materials: i) N-doped anatase, a yellow material, and ii) a substoichiometric reduced anatase which shows a deep blue color. In N-doped  $\text{TiO}_2$  the presence of nitrogen defects in the lattice of the oxide generates intra band gap energetic levels available to excite the electrons of the valence band to the conduction band under visible light. These states cause the yellow color of the powder [13–15,33].

The substoichiometric  $\text{TiO}_2$  is prepared via a particular synthetic route that lead to a partially reduced, blue-colored oxide ( $\text{TiO}_{2-x}$ ) which is stable in air and shows the presence of stable  $\text{Ti}^{3+}$  ions. The color in this case is due to the tail of a broad absorption centered in the infrared region and typical of reduced titanias [34–40].

Our aim is therefore to overcome the two limitations of titania described before, using doped solids, capable of harvesting some visible components of the solar spectrum and coupling them to an efficient enzyme for hydrogen reduction. Our attention is paid not only to the efficiency of the hydrogenase- $\text{TiO}_2$  materials in hydrogen production but also to the mechanism of interaction of the protein with the solid and to the effect of irradiation on the hybrid materials. All this has been monitored by Electron Paramagnetic Resonance (EPR). This technique has been widely used in recent years to investigate the active sites of hydrogenase some of which, in particular redox states, are paramagnetic [41–45]. EPR, however, has also been used to characterise the paramagnetic centers present in titanium dioxide. In particular the process of photo-induced charge separation creates an electron and a hole which can be stabilized by the solid or transferred from its surface to an adsorbed molecule always producing paramagnetic states [46–48]. The EPR technique is therefore much suited to follow the process occurring in the hydrogenase- $\text{TiO}_2$  system both in dark and under irradiation.

The EPR experiments of the present work have been performed in aqueous solutions containing thionine and triethanolamine (TEOA). TEOA molecule acts as a buffer and as sacrificial electron donor (or scavenger of the photogenerated holes) for  $\text{TiO}_2$  [28]. Thionine plays the role of stabilizing agent for the oxidized form of the H-cluster (named  $\text{H}_{\text{ox}}$  state) characterized by a diamagnetic  $[\text{4Fe4S}]^{2+}$  sub-cluster and a paramagnetic [Fe(I)-Fe(II)] sub-cluster [43].

In the present paper the results will be organized as follows: firstly the effect of the irradiation on the thionine-TEOA aqueous solution and on the suspension of the various bare supports in the same solution will be monitored by EPR in order to investigate the photoinduced processes in the absence of the enzyme. Then the same approach will be

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