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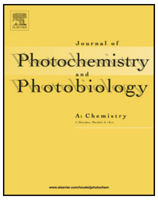

# Role of surface water molecules in stabilizing trapped hole centres in titanium dioxide (anatase) as monitored by electron paramagnetic resonance

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## ABSTRACT

A key factor affecting the photo-efficiency of $TiO_2$ is strictly related to the fate of charge carriers, electrons ($e^-$) and holes ($h^+$), generated upon band gap excitation. In the present paper we point our attention to the nature of the hole trapping sites in the anatase polymorph monitored coupling the conventional continuous wave EPR (CW-EPR) technique with pulse electron nuclear double resonance (ENDOR) experiments. The attention is focused on the role of surface adsorbed water (both in molecular and in dissociated form) in the stabilization of photogenerated hole centres.

CW-EPR results indicate that two distinct $O^{\bullet-}$ hole centres can be identified in Anatase ($O^{\bullet-}{}_{surf.}$ and $O^{\bullet-}{}_{subsurf.}$) and that the quantitative ratio (measured in terms of spectral intensity) of these two species is markedly conditioned by the presence of surface physisorbed water. For the first time a $h^+$-proton distance, evaluated via ENDOR measurement, is reported.

## 1. Introduction

Titanium dioxide ($TiO_2$) is by far one of the most widespread photocatalysts, of importance in several technological fields [1]. A key factor affecting the photo-efficiency of $TiO_2$ is strictly related to the fate of charge carriers, electrons ($e^-$) and holes ($h^+$), generated upon band gap excitation. While a large portion of the photogenerated charge pairs instantly recombine, a fraction can diffuse towards the surface. Surface trapped electrons and holes can then recombine or act as initiators for subsequent processes occurring at the surface [2]. In the absence of reactive molecules at the interface (i.e. for a system kept under vacuum) the charge carriers are stabilized respectively as $Ti^{3+}$ ($Ti^{4+} + e^- \rightarrow Ti^{3+}$) and $O^{\bullet-}$($O^{2-} + h^+ \rightarrow O^{\bullet-}$) that are two paramagnetic species and have been observed by Electron Paramagnetic Resonance spectroscopy (EPR). A key aspect for the photoactivity of titanium dioxide is the role of water adsorbed at the surface. Water adsorbed on $TiO_2$ can play a dual role, acting as promoter or as inhibitor of the photocatalytic process, depending on the experimental conditions [3,4]. The inhibition aspect is strictly related to the role of water as a site blocker [5,6], while the promoting effect is related to its role as a source of $OH^\bullet$ species [7]. The photo oxidation processes on $TiO_2$ in fact can occur as a consequence of direct hole ($h^+$) transfer or through $OH^\bullet$ radical species [8]. However, there is no general consensus on the mechanism leading to this last species. The $OH^\bullet$ in fact can be generated either via direct hole trapping by surface $OH^-$ groups ($h^+ + Ti(O\text{-}H)^- \rightarrow Ti(O\text{-}H)^\bullet$) or via hole transfer to water ($H_2O + h^+ \rightarrow OH^\bullet + H^+$). Alternatively it can be formed as a result of electron scavenging by dissolved oxygen with formation of hydrogen peroxide as intermediate ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 + h\nu \rightarrow 2\ OH^\bullet$) [9,10].

The capability to monitor the charge carrier localization within the oxide, and the role of adsorbed water on the carriers' fate, represents a key step to understand and selectively control the properties of titanium dioxide, with the final aim of reducing the undesired charge recombination in photocatalytic phenomena.

As far as the positive carriers are concerned, many experimental and computational studies have been performed to determine the nature and the localization of photogenerated trapped holes in titanium dioxide. Experimental evidence shows that oxidation sites are preferentially located at the (0 0 1) crystallographic face of anatase (the preferential face for rutile is the (1 1 1)) [11–13]. It is also generally accepted that holes can be trapped to form $O^{\bullet-}$centres, but there is no general consensus about the nature

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and location of the trapping site. Surface oxygen radical centres or alternatively sub-surface ones located in proximity of surface hydroxyl groups have been reported [2,7,14]. In the case of the rutile polymorph the stabilization of holes in sub-surface positions has been also recently suggested by theoretical studies [15,16].

Since charge carriers bear one unpaired electron, EPR spectroscopy represents a powerful technique to get information about the nature and localization within the solid of such species. In the literature a large bulk of EPR data related to trapped electrons (usually associated with $Ti^{3+}$ ions) is available, while a relatively lower number of papers is devoted to the characterization of trapped hole centres [17–27].

EPR spectroscopy allowed identifying two distinct signals ascribable to trapped hole centres [15]. In 1987 Howe and Grätzel [17] reported EPR evidence of trapped holes in $TiO_2$ generated upon irradiation of a hydrated anatase. Since the observed EPR signal of the hole centre (characterized by $g_1 = 2.016, g_2 = 2.012$ and $g_3 = 2.002$) was not affected by the presence of $O_2$, it was assigned to a sub-surface $O^{\bullet-}$centre and the following notation $Ti^{4+}O^{\bullet-}$ $Ti^{4+}OH^-$ was proposed [17]. In 1993 Micic et al. observed a hole centre with principal $g$ values $g_1 = 2.027, g_2 = 2.018$ and $g_3 = 2.003$. The corresponding paramagnetic centre was described as a surface trapped hole formed by the following mechanism: $h^+ + Ti^{4+}O^{2-}Ti^{4+}OH^- \rightarrow Ti^{4+}O^{2-}Ti^{4+}O^{\bullet-} + H^+$ [18].

Later in 1997, Y. Nakaoka and Y. Nosaka studied the dependence of the EPR features of trapped holes in $TiO_2$ samples calcined in air at different temperatures. In this case the authors were able to identify two distinct types of hole centres. The former ($g_1 = 2.018$, $g_2 = 2.014$ $g_3 = 2.004$) is similar to that reported by Howe [17] (see before), while the second one ($g_1 = 2.030, g_2 = 2.018$ and $g_3 = 2.004$) is close to those reported by Micic et al. [18] and ascribed by the authors to a surface hole centre [19]. Quite similar results were also reported by Lo et al. [20] and by Dimitrijevic et al. the dependence of the EPR signals of trapped charge carriers on the shape and size of the anatase crystals [21]. By combining pulse EPR measurements with the classic continuous wave EPR experiments (CW-EPR), the authors concluded that the **g** tensor of oxygen-centred radicals ($g_1 = 2.024, g_2 = 2.014, g_3 = 2.007$) was independent of the size and shape of the $TiO_2$ microcrystals, while the transverse relaxation time ($T_2$) of surface-trapped holes ($O^{\bullet-}_{surf.}$) was affected by the presence of surrounding protons [21].

The picture emerging from the above mentioned EPR results, in spite of some non-negligible contradiction, points to the existence of two families of trapped hole centres in anatase. These two families differ essentially in the value of the higher g component (classically indicated as $g_x$ at low magnetic field) which, as will be shown later, is the most sensitive to the surrounding crystal field. The $g_x$ of the first family lies in the range 2.016–2.018, while the $g_x$ of the second family lies at higher values, in the range 2.024–2.030. However, a general consensus on the location and on the structural features of these two kinds of centres is still missing.

Recently we have published a series of papers devoted to the rationalization of the EPR signals of trapped electrons ($Ti^{3+}$) in all the main polymorphs of $TiO_2$ [28–31]. In the present paper we turn our attention to the nature of the hole-trapping sites in anatase, coupling the conventional continuous wave (CW) EPR technique with pulse electron nuclear double resonance (ENDOR) experiments focusing, in particular, on the role of surface-adsorbed water (both in molecular and in dissociated form) in stabilizing the hole centre.

## 2. Materials and methods

### 2.1. Sample preparation

$TiO_2$ anatase was obtained via sol–gel synthesis, as described in a previous work [32]. Briefly, a titanium(IV) isopropoxide ($Ti(OC_3H_7)_4$) solution in 2-propanol (molar ratio 1:4) was reacted with water (molar ratio between alcohol and water 1:10) under constant stirring at room temperature. The obtained gel was aged overnight at room temperature (RT) to ensure the completion of the hydrolysis and was subsequently dried at 343 K. The dried material was eventually calcined at 773 K in air (heating rate 10 K/min) for 2 h. Basic structural, morphological and optical characterization of the as prepared material are reported as Supporting Information.

Two main types of $TiO_2$ specimens were employed in the spectroscopic investigation: an activated sample (ac-$TiO_2$) and an as-prepared one (ap-$TiO_2$). In the first case the sample was outgassed under high vacuum (residual pressure $<10^{-4}$ mbar) at 773 K for 0.5 h in order to remove adsorbed water, surface hydroxyl groups, and other surface impurities. Then oxidation with 20 mbar of $O_2$ was performed at the same temperature for 1 h to obtain a fully oxidized, stoichiometric oxide. The samples were then cooled to room temperature under $O_2$ atmosphere, and the gas phase was eventually removed at this temperature down to a residual pressure of $10^{-4}$ mbar. Samples prepared via this standard procedure will be indicated in the text as "activated" or ac-$TiO_2$.

The two kinds of $TiO_2$ systems considered in this work (activated and as-prepared $TiO_2$, respectively) differ in terms of the state of the surface. Previous careful studies on the hydration–dehydration of the anatase surface have clarified that the surface of the activated material, due to the high outgassing temperature, is free from both adsorbed water and hydroxyl groups. In contrast, the as-prepared material is partially hydroxylated (in particular the (001) surface) and also contains some adsorbed molecular water not eliminated by room temperature outgassing [33].

Samples prepared by simply outgassing the calcined material at RT will be referred to in the following as "as prepared" (ap-$TiO_2$).

### EPR characterization

For the spectroscopic characterization of all the samples a quartz tubular cell allowing *in situ* EPR measurements was employed. Trapped holes were generated upon *in situ* irradiation of the samples for 5 s at $T = 77$ K into the EPR cavity using a 1600W Xe Lamp (New Port Instruments) equipped with a IR water filter. Such irradiation time was chosen because it represents the optimal condition for monitoring the trapped holes. In fact, although at 77 K the EPR signals of the trapped holes, in both activated and as-prepared $TiO_2$ are stable for several hours, longer irradiation time causes a decrease of the EPR intensity likely due to the electron-hole recombination (see S.I.). X-band CW-EPR spectra were detected at 77 K on a Bruker EMX spectrometer (microwave frequency 9.46 GHz) equipped with a cylindrical cavity. A microwave power of 1 mW, a modulation amplitude of 0.2 mT and a modulation frequency of 100 KHz were used. Pulse EPR experiments at X-band (9.76 GHz) were performed on an ELEXYS 580 FT-EPR Bruker spectrometer equipped with a liquid-helium cryostat from Oxford Inc. The magnetic field was measured by means of a Bruker ER035 M NMR gauss meter.

X-band Electron-Spin-Echo- (ESE) detected EPR experiments were carried out with the pulse sequence: $\pi/2-\tau-\pi-\tau-$echo. Microwave pulse lengths $t_{\pi/2} = 16$ ns and $t_{\pi} = 32$ ns and a $\tau$ value of 200 ns were used. A 1 kHz repetition rate was used.

Mims ENDOR spectra were measured with the mw pulse sequence $\pi/2-\tau-\pi/2-T-\pi/2-\tau-echo$ with $t_{\pi/2} = 16$ ns. The time $\tau$ was 250 ns. During the time $T$ a radio frequency pulse was applied, the length of which has been optimized for $^1H$ by a nutation experiment. Optimal length was found to be 12 μs. The temperature adopted for the ENDOR experiments was 15 K. A shot