



2 **Electron and Energy Transfer Mechanisms: The Double**  
3 **Nature of TiO<sub>2</sub> Heterogeneous Photocatalysis**

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8 **Abstract**

9 Photocatalytic chemical transformations in the presence of irradiated TiO<sub>2</sub> are gen-  
10 erally considered in terms of interfacial electron transfer. However, more elusive  
11 energy-transfer-driven reactions have been also hypothesized to occur, mainly on the  
12 basis of the indirect evidence of detected reaction products whose existence could  
13 not be justified simply by electron transfer. Unlike in homogeneous and colloidal  
14 systems, where energy transfer mechanisms have been investigated deeply for sev-  
15 eral organic syntheses, understanding of similar processes in heterogeneous systems  
16 is at only a nascent level. However, this gap of knowledge can be filled by consid-  
17 ering the important achievements of synthetic heterogeneous photocatalysis, which  
18 bring the field closer to industrial exploitation. The present manuscript summarizes  
19 the main findings of previous literature reports and, also on the basis of some novel  
20 experimental evidences, tentatively proposes that the energy transfer in TiO<sub>2</sub> photo-  
21 catalysis could possess a Förster-like nature.

22 **Keywords** TiO<sub>2</sub> · Photocatalysis · Energy transfer · Electron transfer · Singlet  
23 oxygen

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## 24 1 Introduction

25 It is well known that photon absorption and the consequent charge separation,  
26 i.e., formation of electrons and holes within the conduction and valence band of  
27  $\text{TiO}_2$ , are the kick-off steps in heterogeneous photocatalytic processes [1]. There-  
28 after, in most cases, interfacial charge transfer between the semiconductor and  
29 adsorbed species triggers their chemical transformation. Even if the electron  
30 transfer event is widely recognized to prevail in the presence of bare semiconduc-  
31 tors such as  $\text{TiO}_2$ , some reports show evidence of energy-transfer-driven reactions  
32 based on the existence of products whose generation cannot be justified simply  
33 through electron transfer [2]. Moreover, it has been observed that the effects of  
34 parallel pathways due to energy transfer are more pronounced in the presence of  
35 surface-modified  $\text{TiO}_2$  [2, 3]. In our opinion, an organic interpretation of these  
36 results is desirable, and a rigorous analysis of the possible mechanisms of energy  
37 transfer, which are already well established in homogeneous and colloidal sys-  
38 tems, is virtually missing in heterogeneous photocatalysis reports. In fact, various  
39 organic reactions such as cyclizations, double bond isomerizations, and bond dis-  
40 sociations can be carried out catalytically through photosensitized energy transfer  
41 in the presence of excited metal complexes or organic molecules as the energy  
42 donors [4]. It is worth mentioning, for instance, that the production of rose oxide,  
43 one of the few photochemical processes applied industrially, can proceed through  
44 energy transfer mechanisms [5]. Unfortunately, in heterogeneous systems, basic  
45 knowledge has yet to be developed since, up to now, distinguishing between elec-  
46 tron- and energy-transfer-driven reactions is a very challenging task. In some  
47 reports, energy transfer processes have been invoked only tentatively to explain  
48 the specific behavior of rare photocatalytic reactions in the heterogeneous phase.  
49 Even more rarely, these products have been obtained selectively when competi-  
50 tive electron transfer could be somehow quenched [6].

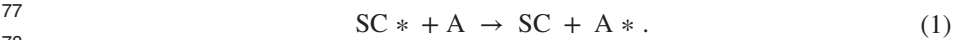
51 The presence of solid particles, in fact, generates light scattering phenomena  
52 that obstruct the application of spectroscopic and photo-physical techniques use-  
53 ful for describing the energy transfer process in a rigorous and direct way. On  
54 the other hand, surface adsorption and consecutive reactions frequently hide such  
55 intrinsic events and hinder correct interpretation of the results [7]. Moreover, it is  
56 not easy to ascribe the presence of the observed products unequivocally to one of  
57 the two possible mechanisms, and often both can give rise to the same species. In  
58 other cases, however, the product distribution obtained when electron transfer is  
59 the dominant mechanism differs from that obtained when mainly energy transfer-  
60 driven reactions occur. Therefore, the ability to switch from electron to energy  
61 transfer processes is an attractive perspective for heterogeneous photocatalytic  
62 syntheses of high-added value products, but also in emerging applications such as  
63 photodynamic therapy [8], molecular sensing and diagnostics [9], energy harvest-  
64 ing [10], and photonic logic gates [11].

65 In this report, we would like to frame the results of the literature in a more  
66 general perspective and stimulate new research on the double nature of the pho-  
67 toactivity of heterogeneous photocatalytic reactions. Preliminary considerations

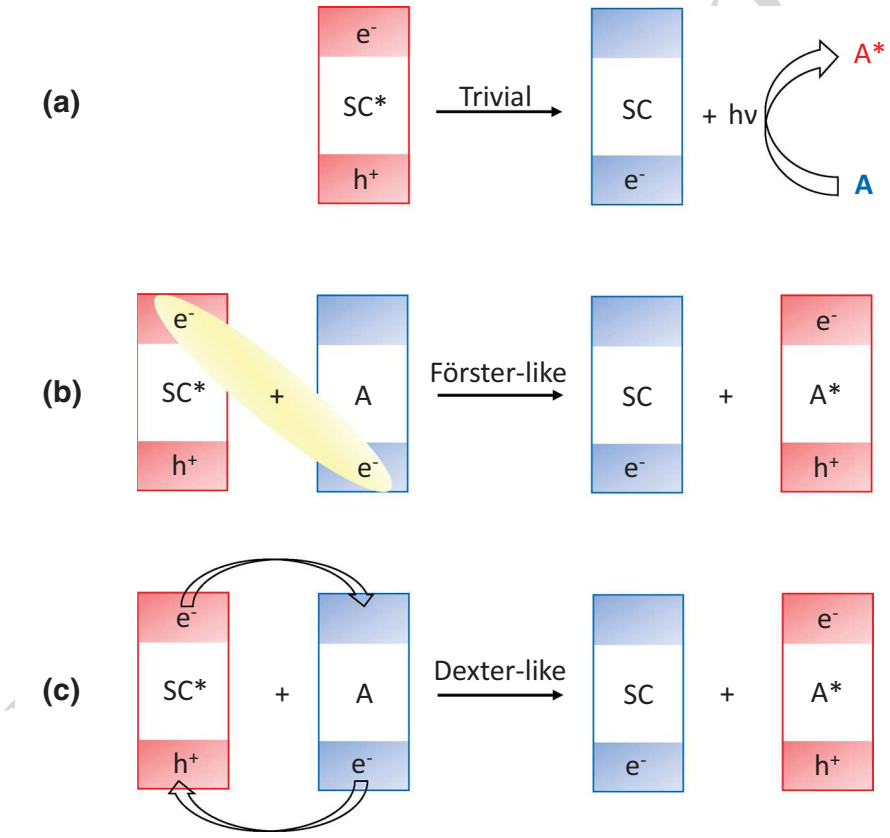
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68 on this topic have been reported in a previous paper [12]. In this work, novel EPR  
 69 results along with an updated and more detailed literature review, have allowed us  
 70 to shed light on issues that could not be approached before.

71 In heterogeneous photocatalysis, charge recombination is often seen as a par-  
 72 asitic phenomenon that dissipates the energy absorbed after irradiation through  
 73 radiative or non-radiative emission. However, this energy can, in principle, be  
 74 absorbed by species that possess suitable electronic features. By considering the  
 75 excited semiconductor (SC\*) as an energy donor and “A” as a generic energy  
 76 acceptor, the energy transfer process can be expressed by Eq. 1:



78  
 79 This process can proceed through three different mechanisms, which have  
 80 been accurately described in homogeneous systems [13], but can be provisionally



**Fig. 1 a–c** Energy transfer mechanisms inferred in heterogeneous photocatalysis: trivial (a), Förster-like (b), and Dexter-like (c). SC semiconductor, A energy acceptor, red excited states (with separated charges), blue ground states (with a representative electron in the HOMO orbitals), shaded yellow ellipse dipole–dipole interaction between the energy donor and acceptor

81 considered for heterogeneous systems as well (Fig. 1), even though, to the best of  
82 our knowledge, no direct evidence has been reported in this regard so far.

83 The trivial mechanism (Fig. 1a) is the only radiative mechanism, and relies on  
84 excitation of the energy acceptor ( $A \rightarrow A^*$ ) upon absorption of the photon emitted  
85 by the excited semiconductor. The Förster-like mechanism (Fig. 1b) occurs by oscil-  
86 lation of an electric field produced locally by the separated charges, which behaves  
87 as a virtual photon, exciting the acceptor through a dipole–dipole interaction [14].  
88 Therefore, it is worth stressing that the shaded yellow ellipse in Fig. 1b does not rep-  
89 resent a transfer of electrons but an interaction giving rise to energy transfer between  
90 donor and acceptor. On the other hand, the Dexter-like mechanism (Fig. 1c) is a  
91 double transfer of electrons in opposite directions that occurs simultaneously and,  
92 therefore, is an energy transfer path as it does not involve net charge transfer [15].

93 Both the trivial and Förster mechanisms require the superposition of the emis-  
94 sion spectrum of the semiconductor (energy donor) and the absorption spectrum of  
95  $A$  (energy acceptor). In the first case, this enables the absorption of photons, while  
96 resonance occurs in the second case. Furthermore, both these mechanisms ensue  
97 from long-range interactions and do not necessarily require contact between donor  
98 and acceptor. However, the occurrence of the Förster mechanism depends on the  
99 distance between the species involved and, consequently, its efficiency can change as  
100 a function of the distance between donor and acceptor.

101 On the other hand, the Dexter-like mechanism requires orbital overlapping of the  
102 donor and acceptor species, i.e., their collision, bonding, or close contact. In other  
103 words, Dexter-like energy transfer occurs only upon adsorption of the substrate  $A$  at  
104 the surface of the semiconductor. Notably, the initial electronic interaction between  
105 the semiconductor and the substrate is similar for both electron transfer and the Dex-  
106 ter mechanism. However, the situation diverges along the reaction coordinate, giving  
107 rise to net charge transfer only in the first case.

108 In the light of these basic concepts, we present some examples from the literature  
109 in an attempt to identify the energy transfer mechanisms that are more likely occur-  
110 ring in heterogeneous photocatalysis, and to suggest some future research directions  
111 to approach this intriguing topic.

## 112 2 Antenna Mechanism

113 Wang et al. [16] reported one of the first hypotheses of energy transfer in heteroge-  
114 neous photocatalysis by proposing the existence of an extended interaction between  
115  $\text{TiO}_2$  particles in contact with each other. This effect was named the “Antenna”  
116 mechanism by analogy with the natural photosynthetic process of Förster-like  
117 energy transfer from “antennae” light harvesting species to the reaction centers,  
118 which in turn fixate solar energy into chemical bonds.

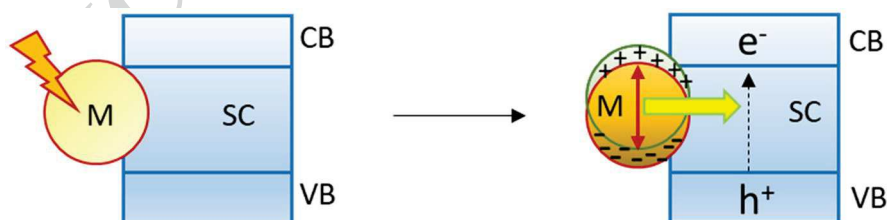
119 Some hypotheses on energy transfer in bulk solids have been reported. For  
120 instance, insulating  $\text{MgO}$  and  $\text{SrO}$  samples showed energy transfer from the five-  
121 and four- to the three-coordinated surface sites when they are excited at wavelengths  
122 corresponding to the abnormal absorption bands of surface sites in coordination  
123 lower than six [17]. Similarly, Förster like energy transfer has been demonstrated

124 from the excited state of the  $\text{Cu}^+$  species to the coexistent  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , or  $\text{Mn}^{2+}$  ions  
 125 when anchored within zeolite cavities [18]. Unlike these cases, the characteristics of  
 126 the energy transfer interaction occurring in  $\text{TiO}_2$  nanoparticles are still unclear.

### 127 3 Plasmon Induced Resonance Energy Transfer

128 Upon excitation of the metal nanoparticle, a dipole oscillating at the same frequency  
 129 of the electric field of the incident light is formed. This dipole is comprised of a  
 130 negative electron cloud and positive metal nuclei. This localized plasmon reso-  
 131 nance can interact with the electronic structure of the semiconductor in many ways.  
 132 Generally, a hot electron can be injected from the excited metal nanoparticle to the  
 133 conduction band of the semiconductor [19], but other effects such as local electro-  
 134 magnetic field enhancement [20], light scattering [21], and plasmonic heating effect  
 135 [22] have also been reported to contribute to enhancing the photoactivity of the  
 136 semiconductor. Recently, Li et al. [23] described for the first time the occurrence of  
 137 resonance energy transfer from excited metal nanoparticles to a solid semiconductor  
 138 (Fig. 2). Authors demonstrated that the plasmon-induced dipole can interact with  
 139 the band states of the semiconductor, inducing in the latter the formation of an elec-  
 140 tron–hole pair.

141 This mechanism is similar to the Förster resonance energy transfer (Fig. 1b).  
 142 Accordingly, its efficiency is related closely to the overlap integral of the localized  
 143 surface plasmon resonance absorption of the metal nanoparticle and the band gap  
 144 absorption of the semiconductor. However, it has peculiar features, which induced  
 145 the authors to use the specific name Plasmon induced resonance energy transfer  
 146 (PIRET) to identify it. In fact, in the Förster mechanism, energy is transferred non-  
 147 radiatively from a blue-shifted emitter to a red-shifted absorber by dipole–dipole  
 148 coupling. Conversely, reverse transfer, towards the short wavelength direction, is  
 149 allowed through plasmonics so that charge separation is eventually induced in the  
 150 semiconductor. Moreover, the PIRET mechanism occurs without Stoke's shift, pre-  
 151 sents non-local absorption effects and a strong dependence on the dephasing rate  
 152 of plasmon and dipole moment. More importantly, for the purpose of the present  
 153 perspective, the authors [23] experimentally observed the largest improvement in

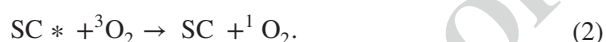


**Fig. 2** Plasmon induced resonance energy transfer (PIRET). Light excitation of the metal nanoparticle ( $M$ ) induces formation of an oscillating dipole (red up-down arrow). Energy transfer occurs through a resonance mechanism by dipole–dipole interaction (yellow arrow) from the excited metal nanoparticle to the semiconductor ( $SC$ ) in which an electron–hole pair is subsequently generated

154 plasmon-induced resonance energy transfer when a thin insulating silica layer (a few  
 155 nanometers) was interposed between the nanoparticles of gold and Cu<sub>2</sub>O as the sem-  
 156 iconductor. The silica layer prevented interfacial charge transfer, thus avoiding inter-  
 157 facial charge recombination losses and dephasing of the plasmon due to the injection  
 158 of hot electrons into the semiconductor conduction band.

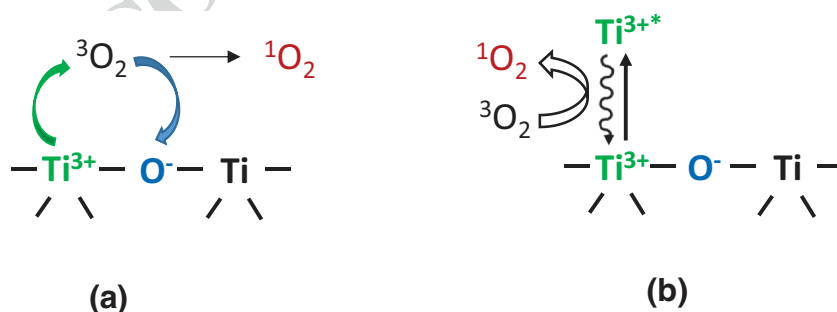
#### 159 4 Singlet Oxygen

160 Comparison experiments demonstrated the existence of singlet oxygen in TiO<sub>2</sub> sus-  
 161 pensions, but its quantification by reliable methods is not easy. The presence of this  
 162 species suggests, albeit indirectly, that energy transfer may occur in these heteroge-  
 163 neous systems. In fact, the transition from the triplet ground state to the singlet state  
 164 of molecular oxygen does not require a net charge transfer (Eq. 2):



166  
 167 Nosaka et al. [24] first reported the formation of singlet oxygen in irradiated sus-  
 168 pensions of TiO<sub>2</sub>. These authors hypothesized that electrons reduce molecular oxy-  
 169 gen to superoxide ion, which is in turn oxidized by photogenerated holes to singlet  
 170 oxygen. This mechanism relies on a double electron transfer in opposite directions  
 171 but it is not known whether the two steps occur consecutively (electron transfer) or  
 172 in a concerted way (energy transfer). We can speculate that, due to the short lifetime  
 173 of singlet oxygen and to the proximity (a few Angstroms) of the charge trapping  
 174 sites at the surface of TiO<sub>2</sub>, a concerted mechanism could be more plausible, and the  
 175 process may be seen as a Dexter-like energy transfer (Fig. 3a). Theoretical calcula-  
 176 tions might shed light, providing useful information to strengthen this hypothesis.  
 177 Similar concerted pathways have been also hypothesized for electron transfer reac-  
 178 tions such as hole-induced water oxidation [25], which proceeds through the cou-  
 179 pled electron-proton transfer on adjacent surface sites, and for the water-mediated  
 180 radical oxidation of nitrate ions [26].

181 Janczyk et al. [2] hypothesized that radiative band-to-band charge recombina-  
 182 tion in TiO<sub>2</sub> could be responsible for the formation of singlet oxygen through a

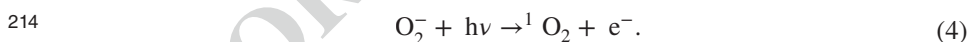
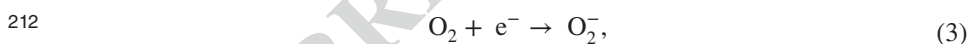


**Fig. 3** Singlet oxygen generation at the surface of TiO<sub>2</sub> through a Dexter-like mechanism (a) or long-range interaction (b). Ti<sup>3+</sup> and O<sup>-</sup> indicate localized electron and holes, respectively

183 long-range mechanism. However, Daimon and Nosaka [27] highlighted the mis-  
184 match between the energy emitted by TiO<sub>2</sub> through band-to-band recombination and  
185 that required to excite molecular oxygen. In fact, the energy level of the oxygen <sup>1</sup>Δ<sub>g</sub>  
186 state, the most stable of the two oxygen singlet states, also known as <sup>1</sup>O<sub>2</sub>, lies only  
187 95 kJ mol<sup>-1</sup> above the energy of the triplet state. On this basis, it was proposed  
188 that the energy emission responsible for oxygen excitation derives from intra-band  
189 rather than band-to-band recombination [3]. In fact, electrons localized in the con-  
190 duction band as Ti<sup>3+</sup> sites can be further excited to close energy states (Ti<sup>3+\*</sup>) local-  
191 ized within the conduction band. The energy emitted from these intra-band energy  
192 states (emission λ<sub>max</sub> ≈ 780 nm) is compatible with that required to excite molecular  
193 oxygen to its singlet state. Clearly the latter report opposes a trivial or Förster-like  
194 mechanism (Fig. 3b) to the Dexter-like mechanism proposed by Nosaka (Fig. 3a). In  
195 other words, a long-range interaction rather than a collision mechanism is assumed  
196 to be responsible for singlet oxygen formation.

197 Other mechanisms based on direct optical excitation of molecular oxygen  
198 adsorbed on the oxide surface have been proposed recently [28]. Authors used dif-  
199 ferent irradiation wavelengths to excite oxygen adsorbed at the surface of different  
200 oxides. The best results in terms of singlet oxygen generation were obtained in the  
201 presence of the wide band gap semiconductor yttrium oxide, which was more than  
202 an order of magnitude more efficient compared with other oxides, including TiO<sub>2</sub>.  
203 The authors explain this result by taking into account the lower hygroscopicity and  
204 the higher oxygen adsorption capability of yttrium oxide compared with that of  
205 other oxides.

206 Demyanenko et al. [29] proposed an alternative mechanism of photocatalytic gen-  
207 eration of singlet oxygen through photodetachment of an electron from the superox-  
208 ide radical anion. In other words, once generated through single electron reduction  
209 of oxygen (Eq. 3), the superoxide radical anion absorbs light, giving rise to singlet  
210 oxygen and releasing an electron (Eq. 4) which, in turn, can recombine or reduce  
211 another oxygen molecule.



216 Interpretation of these results, however, is still the subject of debate [29–31]. In  
217 particular, the near infrared emission at 1300 nm, which the authors assigned to sin-  
218 glet oxygen [29], has been attributed by Nosaka [30] to stray luminescence due to  
219 the large red shift with respect to the generally reported value of around 1270 nm.  
220 Moreover, there is no consensus on the absorption features of superoxide radicals at  
221 355 nm, on the pulsed energy dependence of the phosphorescence intensity and on  
222 their mechanistic consequences.

223 On the other hand, the hypothesis of long-range interaction is corroborated by  
224 the observation that singlet oxygen formation is favored when the surface of TiO<sub>2</sub> is  
225 opportunely modified, meaning when the direct donor–acceptor contact, i.e., their  
226 orbital overlapping, is hindered by the presence of surface grafting species. In fact,  
227 it has been reported that production of singlet oxygen occurs to a higher extent upon

substitution of the surface hydroxyl groups of  $\text{TiO}_2$  with metal complexes, organosilanes, fluoride, and other organic molecules [3]. Even if the quantification of singlet oxygen is challenging, its presence has also been confirmed indirectly both in degradative and synthetic photocatalysis. For instance, cyanuric acid can be degraded under UV irradiation in the presence of  $\text{TiO}_2$  modified with both fluorine groups and organosilanes, while the compound is stable in the presence of bare  $\text{TiO}_2$  [2]. In fact, hydroxyl radicals, superoxide anions and peroxides, deriving from electron-transfer-driven reactions, are not able to oxidize cyanuric acid, which instead undergoes degradation in the presence of singlet oxygen. On the basis of this observation, the authors concluded that singlet oxygen production on the surface of bare  $\text{TiO}_2$  was not sufficient to degrade the recalcitrant cyanuric acid, while in the presence of surface-modified  $\text{TiO}_2$ , the higher production of singlet oxygen allowed its degradation.

A similar indirect demonstration of increased singlet oxygen production in the presence of surface-modified  $\text{TiO}_2$  has been reported for the photocatalytic epoxidation of limonene to 1,2 limonene epoxide—a key precursor of valuable bio-derived polycarbonates [6, 32]. In this case, the surface modification of  $\text{TiO}_2$  provided a selectivity of ca. 90% towards limonene epoxide, while only ca. 30% could be obtained in the presence of the bare photocatalyst. In detail, while hydroxyl radicals produced in the presence of bare  $\text{TiO}_2$  favored limonene overoxidation, singlet oxygen generated mainly in the presence of modified  $\text{TiO}_2$  promoted the epoxidation of the substrate.

Similar results have been obtained in the presence of  $\text{TiO}_2$ , whose surface was partially covered by mesoporous silica nanoparticles [32].

More recently, organic–inorganic nanocomposites containing bare or surface-modified  $\text{TiO}_2$  embedded in a polymeric matrix have been synthesized as potential oxygen attractants for advanced applications [33]. The authors demonstrated that the higher oxygen scavenging ability of nanocomposites containing modified  $\text{TiO}_2$  relies on the favored formation of singlet oxygen with respect to the bare material.

All these experimental results suggest indirectly that, in the presence of surface-modified  $\text{TiO}_2$ , singlet oxygen formation could occur through long-range interactions, such as trivial or Förster-like paths, rather than Dexter-type mechanisms. Furthermore, the fact that superoxide, peroxides and hydroxyl radicals are produced to a greater extent than singlet oxygen in irradiated suspensions of bare  $\text{TiO}_2$ , indicates that the initial orbital overlapping evolves preferentially to electron transfer rather than Dexter-type energy transfer which, therefore, appears to play a negligible role.

## 5 Sensitized Photoisomerization Reactions

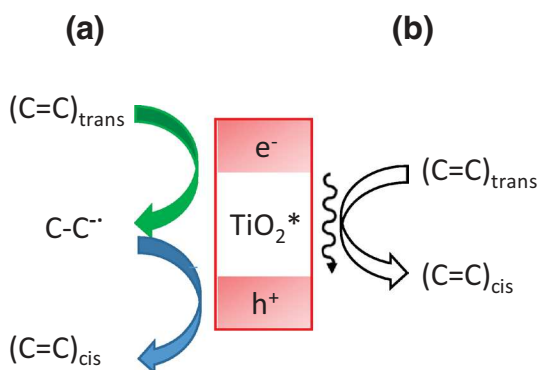
Photochemical cis/trans isomerization of compounds containing a double bond can proceed through direct or sensitized routes. In the former case, the unsaturated moiety absorbs light and, upon localization of the double bond, electrons on the participating atoms undergo free rotation giving rise to geometrical isomerization. In the latter case, a sensitizer (the light absorbing species) can induce isomerization through a radical chain mechanism induced by electron- or energy transfer.



270 All these paths are well documented in homogeneous systems, while rare reports  
 271 deal with sensitized isomerization in heterogeneous photocatalytic systems. The  
 272 heterogeneous photocatalytic isomerization of butene was reported by Anpo [34]  
 273 in the presence of degassed MgO under UV irradiation. The direct dependence of  
 274 the rate of photocatalytic isomerization on the intensity of photoluminescence indi-  
 275 cated that the energy transfer from the excited lower coordinated surface ions was  
 276 mainly responsible for the observed isomerization. The authors proposed the same  
 277 reaction in the presence of irradiated TiO<sub>2</sub> [35] and identified O<sup>-</sup> (localized holes)  
 278 or Ti<sup>3+</sup>-O<sup>-</sup> (electron-hole pairs) as the species responsible for the opening of the  
 279 double bond and the consequent isomerization. Oh et al. [36] proposed that the  
 280 photocatalytic isomerization of maleic and fumaric acids in the presence of TiO<sub>2</sub>  
 281 occurs on the surface of the photocatalyst through electron transfer followed by the  
 282 hole-induced oxidation of the resulting radical anion. The authors based this conclu-  
 283 sion on the fact that the presence of oxygen reduced the isomerization yield, and  
 284 explained this result in terms of competition between the substrates and oxygen for  
 285 photogenerated electrons. Although not explicitly claimed, their hypothesis is based  
 286 on a double transfer of electrons in two opposite directions and, unless the processes  
 287 are considered to occur simultaneously, the mechanism could resemble the Dexter-  
 288 like mechanism, similar to Nosaka's singlet oxygen generation (Fig. 4a).

289 More recently, the photocatalytic isomerization of caffeic acid in the presence of  
 290 TiO<sub>2</sub> has been reported [37]. In addition, in this case the presence of oxygen limited  
 291 the yield of isomerization, in agreement with Oh et al. [36], but due mainly to para-  
 292 sitic oxidation reactions that consumed the substrate. Under nitrogen atmosphere,  
 293 and in the presence of two-propanol as the hole trap, photocatalytic isomerization  
 294 was suppressed. This finding allows to exclude the reduction of caffeic acid as the  
 295 initial step of isomerization, because the presence of the hole trap would instead  
 296 have enhanced the availability of electrons. On the other hand, photocatalytic  
 297 isomerization could also proceed through initial oxidation of caffeic acid. However,  
 298 surface modification of TiO<sub>2</sub> with hexadecylsilane enhanced the isomerization yield  
 299 with respect to the bare material. This result suggests that also an initial oxidation  
 300 of the substrate is an unlikely event. In fact, the orbital overlapping, required for  
 301 the electron transfer (and for Dexter-like mechanism), is limited by the presence of

**Fig. 4** TiO<sub>2</sub>-induced geo-  
 metrical isomerization through  
 a Dexter-like mechanism (a)  
 or long-range interactions (b)



302 the grafted moieties. Accordingly, the orange color generated as a consequence of  
303 the charge transfer complex between caffeic acid and  $\text{TiO}_2$  was almost negligible in  
304 the presence of the surface-modified semiconductor, while it is very intense in the  
305 presence of bare  $\text{TiO}_2$ . This again suggests the reduced interfacial electron transfer  
306 in the presence of the silanized  $\text{TiO}_2$  and indicates the negligible role of Dexter-like  
307 mechanisms in the sensitized isomerization of caffeic acid. As in the case of singlet  
308 oxygen, a long-range interaction seems more plausible (Fig. 4b), even if distinguish-  
309 ing between Förster-like and trivial mechanism is not straightforward.

## 310 6 Some Additional Spectroscopic Evidences

311 The hypotheses on energy transfer mechanisms mentioned above are summarized in  
312 the following discussion.

313 In the presence of bare  $\text{TiO}_2$ , the initial donor–acceptor orbital overlapping  
314 evolves predominantly into electron transfer reactions, although the occurrence of  
315 Dexter mechanisms cannot be excluded. However, in the presence of silanized  $\text{TiO}_2$   
316 electron transfer and Dexter-like paths seem to be suppressed, while energy transfer  
317 reactions are favored through long-range interactions.

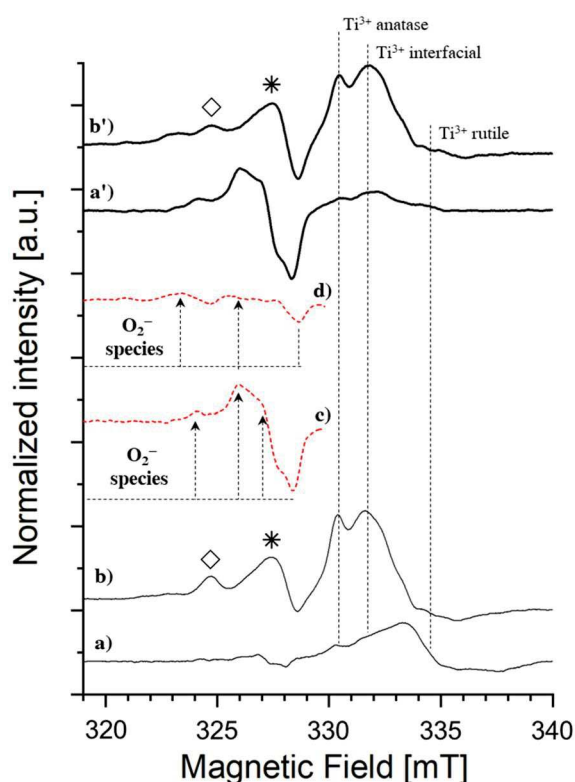
318 To corroborate these hypotheses, it is necessary to demonstrate that surface  
319 silanization hinders interfacial electron transfer. To this aim, electron spin reso-  
320 nance (ESR) spectroscopy was applied to  $\text{TiO}_2$  (Evonik Aeroxide P25), both bare  
321 and modified with hexadecylsilane ( $\text{TiO}_2@\text{Si}$ ). Notably, this surface modification  
322 has been reported to enhance both singlet oxygen generation and photocatalytic  
323 isomerization in the papers mentioned above. Details on the preparation and charac-  
324 terization of the samples are reported in the Supplementary Material. In particular,  
325 thermogravimetric analysis (Figure S1) revealed that only 2.8 silane molecules per  
326 square nanometer grafted the  $\text{TiO}_2$  surface, and thus the formation of a continuous  
327 bulky layer of  $\text{SiO}_2$  can be excluded.

328 By tracking the photogenerated paramagnetic centers using ESR spectroscopy,  
329 the interfacial electron transfer to oxygen giving rise to superoxide radical anion in  
330 functionalized ( $\text{TiO}_2@\text{Si}$ ) and naked  $\text{TiO}_2$  samples has been compared. Notably,  
331 even though quantitative analysis is not straightforward through ESR spectroscopy,  
332 simply detecting the presence of superoxide species is catalytically relevant. The  
333 possible formation of superoxide, therefore, would indicate the occurrence of an  
334 electron transfer.

335 In detail, ESR spectra were acquired after UV irradiation at 130 K, either in  
336 vacuo ( $p < 10^{-5}$  mbar) or in the presence of  $p(\text{O}_2) = 20$  mbar as an electron scavenger  
337 (Fig. 5).

338 UV irradiation in vacuo of bare  $\text{TiO}_2$  (Fig. 5, line a) leads to the appearance in  
339 the spectrum of broad and intense signals at magnetic fields higher than ca. 330  
340 mT related to different superimposed electron trap species ( $\text{Ti}^{3+}$  centers) and to weak  
341 signals of localized holes ( $\text{O}^-$  species) and superoxide anions ( $\text{O}_2^-$  species) at low  
342 magnetic fields (below ca. 328 mT) [38–41]. The presence of  $\text{O}_2^-$ , despite the fact  
343 that the UV irradiation is performed in vacuo, may be connected to the evolution of  
344 residual  $\text{OH}^-$  groups according to the mechanism proposed by Grätzel et al. [42].

**Fig. 5** Electron spin resonance (ESR) spectra at 130 K of TiO<sub>2</sub> and TiO<sub>2</sub>@Si samples after UV irradiation either in vacuo at  $p < 10^{-5}$  mbar (*a* and *b*, respectively), and under  $p(O_2) = 20$  mbar (*a'* and *b'*, respectively). Spectra *c* and *d* are obtained by subtracting *a* and *b* from *a'* and *b'*, respectively. Dashed lines are guides to describe the different paramagnetic species present at the anatase, rutile phases and at the interface. Signals labelled with open diamonds and asterisks can be tentatively related to Ti–O–Si≡ units at the oxide surface



345 The spectrum of the TiO<sub>2</sub>@Si sample after UV irradiation in vacuo again shows  
 346 the resonances of the Ti<sup>3+</sup> species (Fig. 5, line b) along with overlapped signals at  
 347 low magnetic field (labelled with  $\diamond$  and \*), which cannot be attributed solely to O<sup>-</sup>  
 348 centers. The origin and the chemical nature of this feature can be related tentatively  
 349 to the presence of Ti–O–Si≡ units at the oxide surface. However, the detailed  
 350 investigation and attribution of these paramagnetic defects in TiO<sub>2</sub>@Si is currently  
 351 underway.

352 It has to be noted that all the spectral features of TiO<sub>2</sub>@Si appear much more  
 353 intense than those of bare TiO<sub>2</sub>, suggesting that the surface functionalization helps  
 354 to prevent the recombination of photogenerated charge carriers, thus promoting their  
 355 trapping into lattice/surface defect centers.

356 After irradiation in  $p(O_2) = 20$  mbar, the intensity of the Ti<sup>3+</sup> centers in pure TiO<sub>2</sub>  
 357 becomes generally lower than that detected in vacuo and intense signals, ascribable  
 358 to different O<sub>2</sub><sup>-</sup> species, arise at low magnetic fields (Fig. 5, line a'). This implies an  
 359 improved reactivity of surface Ti<sup>3+</sup> traps in electron transfer reactions with oxygen  
 360 yielding superoxide species [43–46].

361 Conversely, the presence of oxygen only slightly affects the observed ESR sig-  
 362 nals of the irradiated TiO<sub>2</sub>@Si sample. In fact, UV irradiation in  $p(O_2) = 20$  mbar  
 363 of TiO<sub>2</sub>@Si sample (Fig. 5, line b') does not downgrade appreciably the inten-  
 364 sity of Ti<sup>3+</sup> centers, while the generation of a remarkably low amount of different

365  $O_2^-$  species is noticeable. This result is unveiled more clearly by spectra c and d,  
366 obtained by subtracting, in the low magnetic field range, the resonance features of  
367  $TiO_2$  and  $TiO_2@Si$  obtained after photoexcitation in  $O_2$  (lines a' and b', respec-  
368 tively), from those present in the spectra after irradiation in vacuo (lines a and b,  
369 respectively).

370 These outcomes foreshadow that, in  $TiO_2@Si$ , the surface functionalization,  
371 besides hindering recombination phenomena, effectively hampers interfacial elec-  
372 tron transfer. The suppression of superoxide radicals makes the photodetachment  
373 mechanism rather unrealistic in this case [31]. Moreover, Dexter-like mechanisms  
374 involving double electron transfer with oxygen seem unlikely in the surface func-  
375 tionalized sample, while the hypothesis of long-range interactions in the energy-  
376 transfer-driven formation of  $^1O_2$  is corroborated.

377 Finally, in order to distinguish between the two long-range interactions, i.e.,  
378 the preferential occurrence of radiative trivial or resonance Förster-like mecha-  
379 nisms, photoluminescence spectra of bare  $TiO_2$  and  $TiO_2@Si$  samples have been  
380 recorded. The surface modification does not result in significant changes of emis-  
381 sive behavior in the range between 400 and 800 nm (data not shown). Therefore,  
382 the prevailing energy transfer efficiency hypothesized in the presence of surface-  
383 functionalized samples in the photocatalytic reactions mentioned above is unlikely  
384 ascribable to trivial radiative mechanisms. For these reasons, energy transfer mech-  
385 anisms observed in the presence of surface-modified samples seem to possess a  
386 Förster-like nature.

## 387 7 Conclusions

388 The present manuscript proposes a novel perspective on a less well known energy  
389 transfer mechanism, which has often been invoked in previous reports based on  
390 indirect evidence. On the basis of literature results and of some novel evidence, the  
391 Förster-like nature of the energy transfer in irradiated  $TiO_2$  suspension is tentatively  
392 proposed. Notably, this perspective aims mainly at stimulating further research  
393 efforts, possibly supported by computational and/or photo-physical results, in order  
394 to provide tools to control the occurrence of electron and energy transfer paths in  
395 selective photocatalytic processes. In our view, this fundamental knowledge will  
396 prompt the development of novel selective organic syntheses as green alternatives  
397 to traditional synthetic routes. Results, discussed hereby mainly for irradiated  $TiO_2$   
398 suspensions should be generalized for other semiconducting systems in order to  
399 open new possibilities in emerging advanced applications.

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## 403 Declarations

404 **Conflict of Interest** The authors have no conflicts of interest or competing interests to declare.

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