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Energy Transfer in Heterogeneous Photocatalysis

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Abstract. Electron transfer reactions constitute one of the main pillars of chemistry and numerous examples can be found in nature and in technological applications. Energy transfer induced reactions are more elusive but equally important in phenomena related with natural photosynthesis and in general when light-matter interactions are relevant.

Heterogeneous photocatalysis is generally considered based on electron transfer reactions. In fact, absorption of photons of suitable energy induces formation of photogenerated charges (electron and holes) which in turn initiate redox reactions through interfacial electron transfer to (or from) surface species. However, rare examples of photocatalytic reactions induced by prevailing energy transfer have been recently reported in literature. Investigation in this field may be still defined at a nascent level, and the mechanistic aspects of energy transfer, widely investigated in photochemistry of homogeneous or colloidal systems should be clarified in heterogeneous photocatalysis.

In the manuscript the basic principles of energy transfer will be presented along with some known examples. These concepts will be inferred in the field of heterogeneous photocatalysis, by considering the excited solid semiconductor as the energy donor. Some rare examples of energy transfer induced heterogeneous photocatalytic reactions will be presented along with some tentative mechanistic hypotheses.

Keywords. Energy transfer; Heterogeneous photocatalysis; Green chemistry.

1. INTRODUCTION

Processes based on energy transfer are nowadays of great actuality. Even if the theoretical description of these phenomena has been clarified last century,[1,2] these basic processes find application in innovative technologies connecting chemistry, biology and physics in interdisciplinary approaches. For instance, techniques based on energy transfer processes have been used to monitor DNA hybridization and sequencing, protein conformation, enzyme activity, and cellular dynamics.[3-5] Other applications concern photonic logic gates[6,7] and energy harvesting.[8,9] The reason for this widespread interest in energy transfer based technologies lies on the extremely high sensitivity to conformational changes in the distance and orientation between energy donors and acceptors. The distance changes observable in this way range from 0.5 to 10 nm so, for this reason, energy transfer based techniques are also referred to as "molecular rulers".[10] Moreover, energy transfer mechanisms have been found to be fundamental for the capture and transmission of light in natural photosynthesis.[11] In fact, photosynthetic organisms use specialized complexes which are able to transfer the captured light energy through an efficiently distributed hierarchy of proteins. This energetic cascade efficiently proceeding in precise time and distance scales, eventually reaches the reaction centres where solar energy is fixed into chemical bonds.

The energy transfer process[12] can be summarized through Eq. 1:

$$D^* + A \rightarrow D + A^* \qquad (1)$$

in which the excited donor (D^*) is quenched to its ground state (D) and the released energy is absorbed by an acceptor (A) which in turn is promoted to its excited state (A^*).

The simplest energy transfer mechanism is radiative and is known with the name of "trivial". In this case, the emission spectrum of $^*D$ must overlap the absorption spectrum of A in order to make possible the absorption of the photon emitted by D^* by the acceptor A. This process depends on the extent of overlapping of the spectra, on the emission efficiency of D^* (i.e. its quantum yield of emission) and on the concentration of A in the path of photons emitted by D^*.

Energy transfer can also occur non-radiatively through Förster or Dexter mechanisms. Förster resonance energy transfer (FRET) occurs from a fluorescent donor to a lower energy acceptor via long-range dipole-dipole interactions. Therefore, FRET mechanism is favoured at a specific geometric orientation and it is highly sensitive to donor-acceptor distances.

The efficiency (E) of FRET can be described by Eq. 2:

$$E = \frac{R_0^6}{R_0^6 + R^6} \qquad (2)$$

where R is the distance between donor and acceptor, and R_0, typical for each donor-acceptor couple, is the distance at which the efficiency decreases of 50% (Forster distance). The FRET efficiency can be also expressed in terms of life time (τ) of the donor or of the fluorescence intensity (F) according to Eq. 3:

$$E = 1 - \frac{\tau_{DA}}{\tau_D} = 1 - \frac{F_{DA}}{F_D} \qquad (3)$$

where the subscripts D and DA refer to as the donor and the donor in the presence of the acceptor, respectively. According to Eq. 3, the decrease of the lifetime (or of the fluorescence intensity) of the donor in the presence of an acceptor indicates the existence of FRET.

Finally, the rate (k_t) of FRET is described by Eq. 4:

$$k_t = \frac{1}{\tau_D}\left(\frac{R_0^6}{R^6}\right) \qquad (4)$$

FRET mechanism requires a large overlapping between donor emission and acceptor absorption spectra. Energy transfer can also proceed through a "collision" mechanism which is often referred to as "Dexter" mechanism. In other words, the orbitals of the excited donor and of the acceptor in its ground state can overlap giving rise to a double electron transfer which does not modify the total charge of the system, but only its electronic configuration. In this case, the initial steps of the interaction are the same giving rise to electron transfer, but the system evolves differently along with the reaction coordinate and no net charge separation is obtained.

The rate (k) of Dexter energy transfer can be described by Eq. 5:

$$k = KJ\exp\left(-\frac{2R}{L}\right) \qquad (5)$$

where K is a constant related to the specific donor-acceptor couple, J is the normalized spectral overlap integral, R is the distance between donor and acceptor relative to their radii of van der Waals (L).

By comparing Eqs. 4 and 5 it is evident that the rate of energy transfer decreases with increasing R but with different dependence laws. In particular, unlike FRET, Dexter energy transfer becomes negligible when the distance between donor and acceptor increases of few Angstroms. This is quite obvious by considering that Dexter mechanism requires orbital (not only spectral) overlap.

Any fluorescent species such as organic dyes, fluorescent proteins, or nanoparticles can be potentially an energy donor.[13] In particular, semiconductor nanoparticles of few nanometres (quantum dots) have been deeply investigated due to their excellent photo-physical features, stability and versatility.[14-16] However, the donor behaviour of larger semiconductor nanoparticles in energy transfer processes is poorly understood as discussed throughout the text. Demonstrating and opportunely exploiting the presence of energy transfer mechanisms in heterogeneous systems is relevant, for instance, in the fields of photocatalysis and photoelectrocatalysis. These applications are generally based on electron transfer processes occurring on the surface of irradiated semiconductor nanoparticles suspended in a reacting medium or immobilized onto a support.[17,18] Both technologies can be performed in mild conditions of temperature and pressure, with water as the solvent, solar light as the driving force, and by using cheap, abundant and robust semiconductor nanoparticles. These technologies found traditional application in the field of environmental remediation for both water and gaseous effluents.[19] However, applications for the synthesis of high value added compounds are gaining increasing attention due to the appealing features of these processes in terms of conversions, selectivity and sustainability.[20] The product distribution of this traditionally "electron transfer driven" processes can be significantly different when energy transfer processes become the prevailing mechanisms. For these reasons, understanding these mechanisms in heterogeneous photocatalytic systems and developing the technological tools to control and switch them from electron to energy transfer driven processes is highly desired and could open the route to unexplored and exciting novel organic syntheses as green alternative to the traditional ones.

2. ELECTRON AND ENERGY TRANSFER IN HETEROGENEOUS PHOTOCATALYSIS

Charge recombination is generally seen as detrimental in photocatalytic reactions as the absorbed energy does not induce interfacial electron transfer but is radiatively or not radiatively emitted. This energy could be in principle transferred to other species in the reacting mixture similarly to colloidal or homogeneous systems. However, even if the formal similarity with energy transfer processes in homogeneous systems is plausible, in heterogeneous systems such as photocatalytic suspensions, it is often difficult to discriminate between electron and energy transfer, mainly due to the presence of solid particles. First of all, light scattering phenomena limit the use of spectroscopic techniques and the consequent achievement of the parameters required for a rigorous characterization of the energy transfer process. For these reasons, up to now energy transfer mechanisms have been highlighted indirectly by considering the product distribution of particular (and rare) reactions. The radiant field distribution in an irradiated slurry suspension is intrinsically not homogeneous and depends on features of the light absorbing species, reactor geometry and configuration, type of radiation and physico-chemical and optic characteristics of the photocatalyst.[21] Indeed, unlike reactants which can be mechanically mixed within the system, photons do not possess mass and their "concentration" decreases with the distance from the radiation source.[22] In these systems it is challenging to retrieve the local value of the rate of photon absorption (RPA) which in turn determines the intrinsic reaction rate.[23] In fact, only the average value of RPA is experimentally accessible while the local one, describing the intrinsic kinetics, i.e. the events occurring at a molecular level not depending on mass and energy transport phenomena, can be retrieved rigorously only by the laborious and time demanding solution of the radiation transfer equation (RTE) by means of numerical methods. Monte Carlo simulations[24] and discrete ordinate methods (DOM) are usually used.[25] This problem has been recently approached by demonstrating that the average values satisfactorily approximate the local ones at sufficiently low optical thickness of the suspension.[23] However, even if RPA could be approximatively retrieved, it is impossible to attribute it to the sole energy transfer events because the macroscopic chemical transformation observed in a photocatalytic reactor is the result of various processes differently interacting in a complex way. Only in few cases it has been possible to unequivocally attribute the formation of an intermediate product to energy transfer mechanisms. As a matter of fact, these cases are rare because the product distribution of electron and energy transfer reactions is often similar. Moreover, even if specific energy transfer derived products could be produced, they must be selectively obtained. This is not trivial, as the hydroxyl radicals photocatalytically produced oxidize almost any organic species with only few exception, and the selective formation of a specific compound is the result of the complex interaction between light, reactants, products, and the irradiated surface of the photocatalyst. Even if the specific compound is selectively obtained, consecutive reactions and adsorption phenomena could mask the identification of the prevailing mechanism. For these reasons, energy transfer mechanisms in heterogeneous photocatalysis have been often vaguely invoked but up to now never directly evidenced. The extent and the nature of the energy transfer processes, deeply clarified in the photochemistry of homogeneous systems, need to be investigated in heterogeneous photocatalysis.

In principle it is possible to hypothesize that the energy transfer mechanisms occurring in homogeneous systems also hold when an energy acceptor locally interact with the excited semiconductor acting as the energy donor. Only some mechanistic details for the formation of singlet oxygen in heterogeneous photocatalysis have been tentatively proposed while less is known when more complex systems are under investigation.[26]

Upon absorption of a photon of suitable energy, an electron (e^-_{CB}) and a hole (h^+_{VB}) are localized respectively in the conduction and valence band of a semiconductor (SC) according to Eq. 6:[27]

$$SC + h\nu \rightarrow SC^*(e^-_{CB}, h^+_{VB}) \tag{6}$$

The photogenerated charges migrate to the surface of the semiconductor where they undergo interfacial electron transfer (Eq. 7). In fact, they can reduce or oxidise electron donors (D) or acceptors (A) to the corresponding radical cation ($D^{+\cdot}$) and anion ($A^{\cdot-}$):

$$SC^*(e^-_{CB}, h^+_{VB}) + A + D \rightarrow SC + A^{\cdot-} + D^{+\cdot} \tag{7}$$

The interfacial electron transfer is thermodynamically feasible if the redox potentials of the couples $A/A^{\cdot-}$ and $D^{+\cdot}/D$ lie within those of the photogenerated charges. However, kinetic limitations or the absence of suitable A and D species in the reacting medium can favour quenching of SC* and, possibly, consequent energy transfer to a generic species B (Eq. 8):

$$SC^*(e^-_{CB}, h^+_{VB}) + B \rightarrow SC + B^* \tag{8}$$

It is worth to note that the difference between the redox potentials of the SC bands and those of D and A species is the driving force of electron transfer while the downhill character of the process in terms of energy (E(SC*) > E(B*)) mainly determines the rate of energy transfer. Moreover, while the electron transfer process creates a large charge re-distribution by generating charged species ($A^{\cdot-}$ and $D^{+\cdot}$), energy transfer generates a neutral excited state (B*). As a consequence, for instance the polarity of the solvent affects more the electron than the energy transfer processes. The quenching of the excited semiconductor can occur radiatively by emission of a photon. In this case the energy transfer to the species B occurs by absorption of the emitted photon similarly to the trivial mechanism expressed in homogeneous systems. This process is summarized in Eqs. 9-10 and in Figure 1:

$$SC^*(e^-_{CB}, h^+_{VB}) \rightarrow SC + h\nu \tag{9}$$

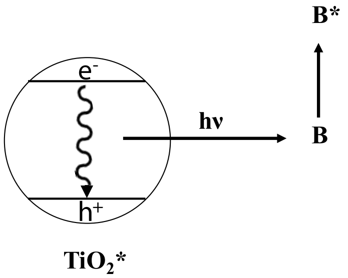

Figure 1. Trivial energy transfer mechanism.

$$B + h\nu \rightarrow B^* \tag{10}$$

This mechanism does not require electronic interaction or even contact between the irradiated semiconductor and the energy acceptor. The efficiency of this type of energy transfer does not depend on the distance between B and the surface of the semiconductor, but mainly on its concentration in the suspension. In fact, at higher B concentrations it increases the number of B molecules in the path of the emitted photons.

Other factors influencing the efficiency of the trivial mechanism are the charge recombination rate and the probability to emit photons rather than heat. Moreover, it is required that the emission spectrum of the semiconductor and the absorption spectrum of B overlap in order to avoid mismatch between the excited semiconductor and the acceptor.

Unlike the trivial mechanism, Förster and Dexter energy transfer are radiationless processes and depend on the distance of the acceptor from the semiconductor (even if with different dependence laws, see Eqs. 4-5).

No electron exchange between acceptor and donor occurs when Förster mechanism takes place (Figure 2). Indeed, the oscillating electric field locally produced by the separated charges behaves as a virtual photon which excites the acceptor through dipole-dipole interactions. Notably, the oscillating field can be generated both by charges localized in the valence and conduction bands upon band to band transitions, or within the conduction band by vibrational states transitions.

On the other hand, Dexter energy transfer mechanism occurs when simultaneously two electrons move in opposite directions (from donor to acceptor and viceversa) without net charge exchange (Figure 3).

It is generally accepted that in heterogeneous photocatalysis electronic interaction occurs through surface adsorption of a substrate, which generally gives rise to surface metal coordination compounds. Adsorption perturbates the electronic structure of both semiconductor and adsorbate at different extents.[28] This situation is

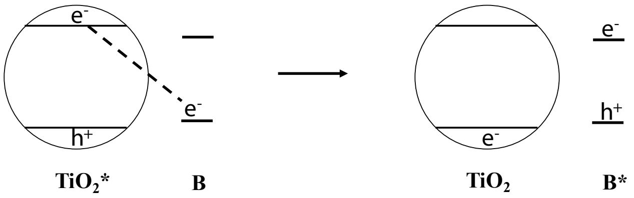

Figure 2. Förster energy transfer mechanism.

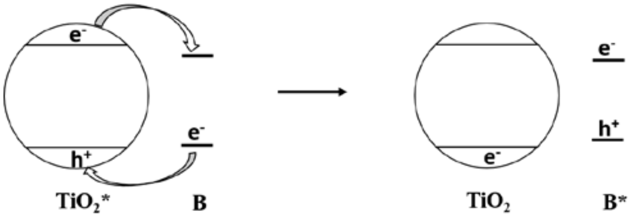

Figure 3. Dexter energy transfer mechanism.

similar to what occurs in Dexter processes at the initial stage of interaction but, as below detailed, generally it results in interfacial electron transfer.

Strong electronic coupling between adsorbate and semiconductors generates new energy levels.[29] Combination of the HOMO level of the adsorbate with conduction band surface states creates a surface hybrid HOMO-LUMO system between the adsorbate and the semiconductor which can extend deeply into the semiconductor due to its band structure. The resulting electronic system is generally characterized by novel ligand to metal electronic transitions, usually in the visible light region, which can be classified as optical electron transfer (OET). In this case, neither the semiconductor nor the adsorbate alone are able to absorb visible light, while the resulting charge transfer complex does. Various organic and some inorganic compounds present this behaviour when adsorbed onto a semiconductor such as aromatic 1,2 diols, some lignin components and SO_2. The extent of this electronic interaction is evident when considering the effects of the adsorption of these compounds onto colloidal semiconductor nanoparticles (ca. 3 nm sized). In fact, in this cases the electronic alteration of the band structure is extended to the whole particle and a significant red shift of the band gap is obtained rather than novel absorption bands. Notably, similar behaviour is reported also for other strongly interacting electronic systems such as solid solutions of semiconductors.[30] Weaker electronic coupling generally favours electron transfer from the adsorbate to the semiconductor or, in rare cases, viceversa. This mechanism, also known as photoinduced electron transfer (PET), usually takes place when chromophore species such as dyes are adsorbed on a semiconductor.[31] Visible light radiation absorption promotes the dye to its excited state which in turn injects an electron in the conduction band of the semiconductor. This weak electronic coupling determines high electron transfer efficiency and low charge recombination and, therefore, these systems are often used in dye sensitized solar cells. Notably, these considerations justify the necessity to avoid the use of dyes as model compounds when one needs to estimate the visible light photocatalytic efficiency of novel semiconductors. In fact, the dye degradation rate expresses the efficiency of electron injection from the excited dye to the conduction band of the semiconductor rather than the activity of the semiconductor.

It is generally accepted that the above reported electronic interactions favour optical or photoinduced electron transfer. On the other hand, as far as the energy transfer in photocatalysis is concerned, indirect observations suggest that energy transfer is prevailing when the surface of the semiconductor is grafted with species which block or substitute the surface hydroxyl groups, as in the examples reported in the next Section. Therefore, it seems that the direct contact between semiconductor and substrate favours electron transfer, while a mediated contact or a certain distance between them could favour energy transfer. For this reason, it seems plausible that some energy transfer processes observed by blocking the surface of the semiconductor could be of trivial or Förster nature.

Even if, up to now, the few examples of energy transfer driven photocatalytic reactions reported do not allow to further discriminate between them, it is possible to conclude that surface grafting can be proposed as a tool to switch between energy and electron transfer processes.

Hydroxyl groups mainly origin from dissociative adsorption of water at the surface of the semiconductor.[32] They determine the acidity and basicity of the surface, are responsible for the hydrophilicity (and superhydrophilicity) of the surface and influence the water dynamics and the competition between different substrates, greatly affecting the selectivity of photocatalytic reactions. In some cases, the hydroxylation density favours the photocatalytic activity even if not all of the surface hydroxyl groups are able to generate hydroxyl radicals. However, for the purpose of this paper, it is worth to stress the role of hydroxyl radicals in determining the electronic features of the semiconductor. First of all, protonation or deprotonation of hydroxyl groups changes the charge of the surface. Therefore, pH changes can shift the potentials of the valence and conduction band and influence the redox ability of the irradiated semiconductor. Moreover, hydroxyl groups can act as traps for the photogenerated charges which thus prolong their life time and facilitate interfacial electron transfer. Moreover, as mentioned above, they act as anchoring sites for organic species and mediate the electronic modifications induced by the interaction. As a consequence, blocking these sites may favour charge recombination thus reducing the probability of efficient charge transfer.[26]

3. EXAMPLES OF ENERGY TRANSFER DRIVEN PHOTOCATALYTIC REACTIONS

Some significant examples of energy transfer driven processes have been obtained in plasmonic photocatalytic composites used as sensors or as oxygen getters, but only rarely energy transfer driven processes have been invoked in classical heterogeneous photocatalysis for degradation or synthetic applications.

One of the first examples of energy transfer process in heterogeneous photocatalysis has been reported by Wang et al.[33] Authors hypothesized, without providing conclusive demonstration, that an array of vicinal TiO_2 nanoparticles could enable energy transfer through an antenna mechanism similar to the natural photosynthetic process of the same name (Figure 4).

An interesting case of photocatalytic mechanism which can be possibly interpreted as an energy transfer process is the hole induced oxidation of alcohols.[34] This reaction generally occurs through abstraction of a hydrogen atom from the α position, giving rise to α-hydroxyalkyl radicals (Eq. 11):

$$R{-}CH_2{-}OH + h^+ \rightarrow R{-}\dot{C}H{-}OH + H^+ \qquad (11)$$

These radicals are generally powerful reducing species which can then inject an electron into the conduction band of the semiconductor according to a photoelectrochemical process often referred to as "current doubling effect" which eventually produce the carbonyl compound.[35] This example is paradigmatic for at least two reasons. Firstly, by considering that the spatial charge separation of the photogenerated electrons and holes is only some Angstroms across the surface of the excited semiconductor, it is highly probable that the current doubling effect occurs in a concerted way rather than as a two-steps process. In this case it could be tentatively seen as a Dexter energy transfer. Secondly, the sole presence of the carbonyl product is not an evidence of an energy transfer mechanism, as the same product can be obtained also through other mechanisms. In fact, evidences of current doubling effects have been obtained by photocurrent measurement rather than by simple photocatalytic experiments. This example highlights the difficulties faced in trying to evidence energy transfer mechanisms in photocatalytic reactions.

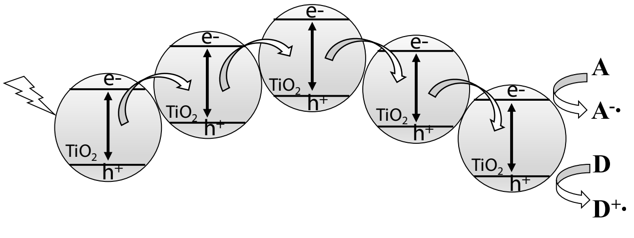

Figure 4. Photocatalytic antenna mechanism.

Direct or indirect detection of singlet oxygen in aqueous photocatalytic suspensions is an indirect demonstration of the existence of energy transfer triggered process in heterogeneous photocatalysis. Molecular oxygen exists in its ground state as a triplet. Two excited states of molecular oxygen can be obtained upon excitation. The energy of these two singlet states, denoted as $^1\Sigma_g^+$ and $^1\Delta_g$ lie 158 and 95 kJ·mol^{-1} above the energy of the ground state, respectively. The $^1\Delta_g$ state, commonly denoted as $^1O_2$, is the more stable of the two excited states and is enough long living to induce chemical transformation under mild conditions.

Formation of singlet oxygen in the presence of irradiated TiO_2 as the semiconductor has been explained by Nosaka et al.[36] in terms of double electron transfer in opposite direction. In fact, molecular oxygen can be first reduced by a photogenerated electron at the surface of TiO_2 to superoxide anion radical which in turn can be oxidized by a photogenerated hole giving rise to singlet oxygen. It is evident that the result of this mechanism is a neutral species (singlet oxygen) and no net charge exchange occurs. To the best of our knowledge, there are no clear evidences that this double electron transfer occurs in a consecutive or in a concerted way. In the second case, similarly to the current doubling effect mentioned above, the formation of singlet oxygen could resemble a Dexter type energy transfer mechanism.

Other authors hypothesized that trivial mechanism could be responsible for the formation of singlet oxygen, i.e. that the radiative emission occurring upon charge recombination in the semiconductor could afford triplet to singlet excitation of molecular oxygen.[37] However, Daimon et al. pointed out the energetic mismatch between the band gap of the considered semiconductor (TiO_2) and the energy difference between triplet and singlet oxygen states.[38] By taking into account this observation, recently Macyk et al.[39] proposed the formation of singlet oxygen in the presence of surface modified

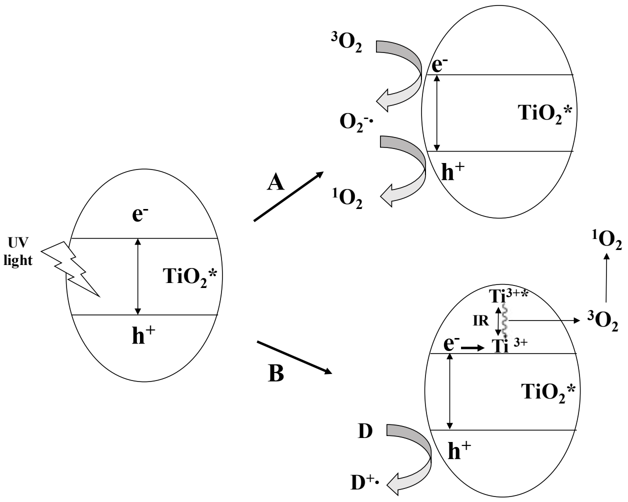

Figure 5. Mechanisms of singlet oxygen formation. A: Nosaka mechanism; B: Macyk mechanism. Notably, the TiO_2 surface has been functionalized in the experiments carried out by Macyk et al. [39]

TiO_2, through energy transfer from excited Ti^{3+} species to molecular oxygen. In this case the energetic differences between the states in the donor (semiconductor) and acceptor (molecular O_2) are compatible. The semiconductor quenching responsible for the transfer, in this case, is an intra-band transition (within the conduction band) rather than band to band recombination (Figure 5). Unfortunately, the nature of this energy transfer has not been highlighted.

Also in this case surface modifications performed by substituting hydroxyl with fluoride groups or by anchoring organosilanes, organic molecules or platinum complexes are reported to enhance the production of singlet oxygen. For instance, Janczyk et al.[37] observed efficient photocatalytic degradation of cyanuric acid only in the presence of surface modified TiO_2. In fact, cyanuric acid is one of the few compounds which cannot be photocatalytically degraded by bare TiO_2, due to its stability even in the presence of hydroxyl radicals, superoxide anions and peroxides, but it can be oxidized in the presence of singlet oxygen.

These reports elegantly demonstrate that (i) singlet oxygen can be produced in aqueous irradiated suspensions of TiO_2, and that (ii) modification of the surface of TiO_2 promotes the production of singlet oxygen.

A similar indirect demonstration of significant singlet oxygen formation in the presence of surface modified TiO_2 has been recently reported by Ciriminna et al. [40,41] In this case a synthetic approach has been used. The considered reaction is the epoxidation of limonene (see Figure 6).

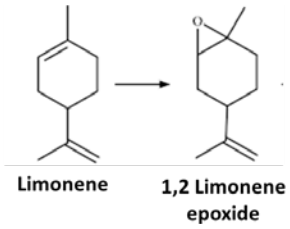

Figure 6. Limonene epoxidation.

This natural terpene is gaining increasing attention because it can be used as a raw material for the production of a promising biopolymer, i.e. polylimonene carbonate (PLC). PLC is biodegradable, presents high thermal resistance (transition temperature up to 180°C), high transparency, and exceptional gas permeation ability. These features make PLC a green alternative to the petrochemical derived polycarbonates with applications in the field of breathing glasses and food safe plastics. Moreover, the presence of an exocyclic C=C double bond, easy to functionalize, makes the properties of PLC extremely tunable for innovative applications such as sea water soluble polymers and antibacterial polymers. The bottle neck of the PLC production is its starting material, i.e. limonene epoxide (LE). LE is obtained industrially from limonene in low yields and harsh operative conditions (Prileshayew reaction). Recently, limonene epoxide has been obtained with high conversion and selectivity (up to 90%) in the presence of surface modified commercial TiO_2 (Evonik) under simulated solar light and in acetonitrile as the solvent. While OH radicals formed in the presence of bare TiO_2 mainly induced overoxidation of limonene, alkyl silane modification of TiO_2 favoured formation of singlet oxygen which selectively oxidizes limonene to 1,2 limonene epoxide.

Another example of energy transfer driven process is the photocatalytic isomerization of caffeic acid in aqueous TiO_2 suspensions and under nitrogen atmosphere[42] (Figure 7).

UV irradiation of aqueous solutions of *trans*-caffeic acid in the absence of the semiconductor induces photochemical formation of the *cis* isomer until a pho-

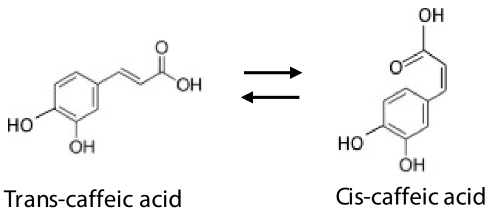

Figure 7. Isomerization of caffeic acid.

tostationary *cis/trans* ratio is achieved. In the presence of TiO_2 a higher *cis/trans* ratio has been observed. This finding suggests that photocatalysis contributes to isomerization along with the photochemical process. Various tests have been performed in order to highlight this result. Photocatalytic degradation of caffeic acid is suppressed being the reaction carried out under nitrogen atmosphere. This factor supports the hypothesis of energy transfer due to the high recombination probability in deoxygenated suspensions. Moreover, in the presence of 2-propanol as the hole scavenger, isomerization was totally inhibited and again surface modification of TiO_2 further enhanced the *cis/trans* ratio.

4. CONCLUSION AND PERSPECTIVES

Heterogeneous photocatalysis has been generally considered as the result of electron transfer reactions mainly occurring at the surface of the irradiated semiconductor. The possibility of addressing the product distribution of photocatalytic reactions and of obtaining selectively some reaction intermediates as high value added compounds, recently moved the attention of the scientific community towards photocatalytic syntheses rather than photocatalytic degradation. As a matter of fact, after ca. 50 years of scientific investigations on photocatalytic water purification, the gap between laboratory solutions and the needs of the water purification industry is evident. A change of direction is required in this field. It makes sense to use photocatalysis, possibly coupled with other advanced oxidation processes, to get rid of compounds harmful at low concentrations but only as a final treatment, after the application of technologies capable to efficiently treat high volumes of effluents. Robust and reusable photocatalysts should be used rather than elegant and complex composites and applicative and engineering issues must be faced rather than basic research. The situation is different when considering photocatalysis as a green alternative to traditional organic synthesis methods. In this case basic research is still needed to develop tools to control and address the selectivity of the process and to propose novel and sustainable synthetic solutions. From the few examples summarized hereby it is possible to conclude that when the substrate electronically interacts with the surface of the semiconductor, electron transfer is generally the prevailing process, even if Dexter-like double electron transfer processes cannot be excluded. On the other hand, trivial or Forster energy transfer processes likely occur at the surface of modified semiconductors where orbital overlapping is less probable. These preliminary results, however, require further efforts to understand the energy transfer processes occurring in irradiated photocatalytic systems. In our opinion this knowledge will induce the development of tools allowing to efficiently switch from electron to energy transfer reactions and will open novel possibilities especially in the field of the green photocatalytic synthesis of high value compounds.

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