

Photoinduced energy versus electron transfer processes at photoactive semiconductors

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Thinking of photoactivity of semiconducting materials usually photoinduced charge transfer processes are considered. They are responsible for photocurrent generation (photovoltaics) or photoinduced redox reactions (photocatalysis). Deactivation processes, like radiative or radiationless charge recombination, shall usually be diminished either in any type of photovoltaic devices or photocatalytic systems. In the latter application, however, also energy transfer processes, parallel to electron transfer, may play a beneficial role, especially when molecular oxygen is used as an energy acceptor. Generation of reactive singlet oxygen is usually considered in heterogeneous photosystems based on silicon or titanium dioxide. Since both materials may also be used for construction of various types of solar cells, a recognition of conditions suitable for $^1\text{O}_2$ generation seems to be important when designing photocatalytic systems as well as solar cells.

Charges photogenerated upon titanium dioxide excitation are capable of molecular oxygen reduction to superoxide and water oxidation to hydroxyl radicals. Superoxide radicals generated in these processes can undergo further reactions forming other reactive oxygen species (hydroperoxyl radicals, hydrogen peroxide etc.; Figure 1a).¹⁻³ A possibility of singlet oxygen generation at excited titanium dioxide particles is not as often considered as formation of radical-type ROS or hydrogen peroxide. The mismatch of band gap energy of titanium dioxide and singlet oxygen effectively lowers probability of a direct energy transfer process. Nevertheless formation of $^1\text{O}_2$ was reported in various TiO_2 -based systems.⁴⁻¹⁰ Beside a simple energy transfer the following mechanisms are considered as those responsible for singlet oxygen generation: (a) oxidation of superoxide radicals by holes⁶ and (b) recombination of two hydroperoxyl radicals leading to formation of $^1\text{O}_2$ and H_2O_2 (Figure 1b).^{7,8}

A direct energy transfer in the presence of TiO_2 may be favored in the case of modified materials, especially those sensitized with red or near-infrared light absorbing sensitizers (e.g. organic sensitizers, porphyrins, bacteriochlorins etc.). A possibility of direct energy transfer should also be considered when a relatively high population of electrons trapped in the conduction band is achieved. Formed titanium(III) centers absorb red and near-infrared light leading to generation of higher excited states characterized by a good energy match to the excited states of oxygen (Figure 2a). A possibility of this mechanism has been confirmed in experiments involving bichromatic light excitation (ultraviolet and red).

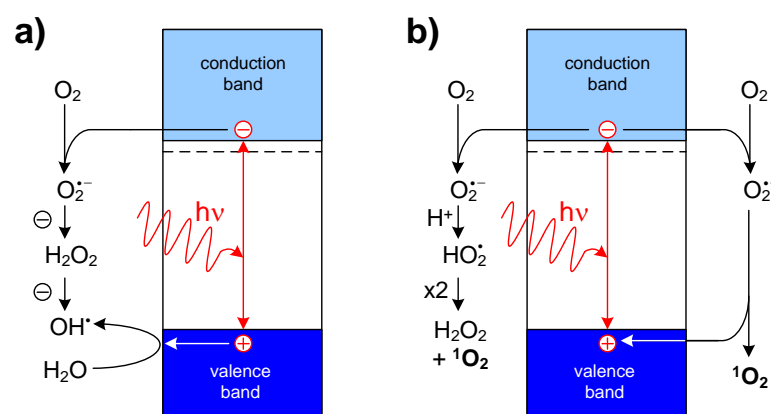


Fig. 1. Electron transfer processes leading to generation of reactive oxygen radicals (a) and singlet oxygen (b) at the surface of irradiated titanium dioxide.

The paths leading to ROS generation at TiO₂ may also depend on its crystal structure. Various efficiencies of hydroxyl radicals and superoxide generation were observed for anatase and rutile. In the case of aqueous solutions, a higher stability of O₂^{•-} was assured at the rutile surface than at anatase where further reduction of superoxide to hydrogen peroxide is privileged. Rutile shows a higher photoactivity than anatase in the reactions involving superoxide radicals. A good example is naphthalene¹¹ and anthracene¹² oxidation. Although the mechanism of this process may involve superoxide attack, the oxidation by singlet oxygen should also be considered.

Nanocrystalline and nanoporous silicon appeared one of the most efficient heterogeneous photosensitizers of oxygen.^{13,14} The control of particle size or porosity enables synthesis of materials characterized by band gap energies around 1.63 eV matching that of singlet oxygen in its ¹Σ state (Figure 2b). The energy transfer follows the Dexter mechanism and leads to formation of a short-living ¹Σ state which might relax to a more stable ¹Δ state (0.98 eV versus ³Σ ground state).

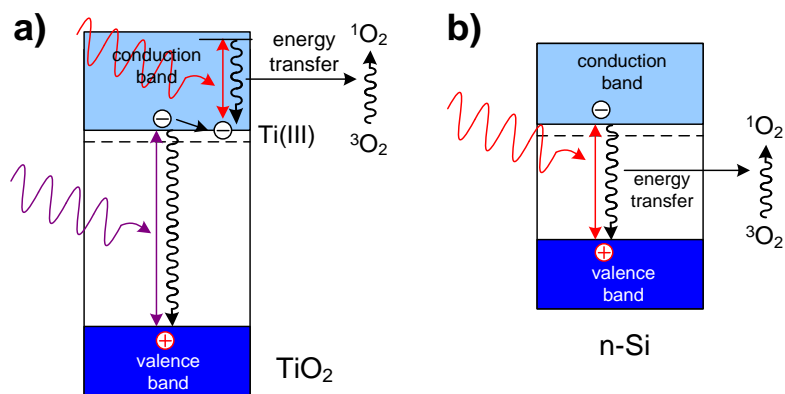


Fig. 2. Energy transfer processes leading to generation of singlet oxygen in the presence of titanium dioxide (a) and nanocrystalline silicon (b).

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