

What an electron-hole pair upon UV irradiation of TiO₂ can do besides the red-ox reactions

Cecilia B. Mendive^{1,2*}, David Hansmann³, Mariano Curti¹, Thomas Bredow³ and Detlef Bahnemann²

¹Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Dean Funes 3350, 7600 Mar del Plata, Argentina. Tel. 0054 223 475 6167

²Institut fuer Technische Chemie, Leibniz Universitaet Hannover, Callinstr. 3, D-30167 Hannover, Germany

³Institute for Physical and Theoretical Chemistry, Universitaet Bonn, Wegelerstr. 12, D-53115 Bonn, Germany

*corresponding author, E-mail: cbmendive@mdp.edu.ar

Photocatalytic processes on the surface of TiO₂ nanoparticles do not respond unanimously to the same mechanism. It depends on which kind of organic molecule is being photocatalytically degraded and the surface and bulk properties of the photocatalyst. Since these mechanisms involve the action of electrons and holes photogenerated upon the excitation of the semiconductor with the proper wavelength, they become the focus of many studies which intend to unravel the reasons for the different photocatalytic efficiencies found for different combinations of systems, i.e., different organic molecules and different TiO₂ nanoparticulate systems.

In this study we suggest that the electron-hole pairs can play an important role in photocatalysis beyond the red-ox reactions responsible for the degradation of the organic molecules at the surface of the photocatalyst.

We have performed infrared spectroscopic studies of a UVA irradiated layer of TiO₂ nanoparticles in contact with an aqueous solution free of any photocatalytic degradable compound. The surprising result was that we found that a volume of water is incorporated in the TiO₂ layer. We attributed such a phenomenon to a mechanism of deaggregation of some particles agglomerates resulting from the capacity of the system to use the energy released by recombination of an excess of photogenerated electrons and holes. In this mechanism, the bonds responsible for maintaining nanoparticles agglomerated are broken allowing the particles to separate. Thus, water molecules can fill the space in between the previously agglomerated particles.

In this new overall mechanism, photocatalysis extends beyond the oxidation and reduction reactions driven by holes and electrons, respectively, to the promotion of an enhancement of the adsorption capacity of the photocatalyst under UVA illumination by an increase of the exposed surface area. In this sense, the uselessness of the recombined electron-hole pairs is thus reverted to a partially useful thermal contribution to the efficiency of a photocatalytic system in water.