

## Paramagnetic Species in Nitrogen-doped TiO<sub>2</sub>: a Key to Understand Photocatalytic Activity in Visible Light?

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Photocatalytic oxidation constitutes one of the most promising methods for indoor and outdoor air purification. Mineralization of a number of organic pollutants can be achieved at ambient temperature and pressure, using the anatase phase of TiO<sub>2</sub> activated by UV irradiation<sup>1,2</sup>. Solar energy contains only about 5% UV light and much of the rest is visible light. In order to utilize solar energy efficiently in photocatalytic reactions, it is necessary to develop a visible light reactive photocatalyst having smaller band gaps than TiO<sub>2</sub> rutile and anatase.

In 1986 Sato<sup>3</sup> reported that calcinations of NH<sub>4</sub>Cl containing titanium hydroxide caused the photocatalytic sensitization of TiO<sub>2</sub> into the visible light region. The author proposed that the powder prepared according to the described method are actually NO<sub>x</sub>-doped TiO<sub>2</sub> and that the sensitization of these materials is due to the presence of NO<sub>x</sub> impurity.

Aim of our recent work was to synthesize and characterize new materials based on N-doped TiO<sub>2</sub>. Several N/TiO<sub>2</sub> materials were prepared via sol-gel technique using solutions containing various kind of nitrogen compounds. EPR was employed to verify the presence of paramagnetic entities formed during the synthesis. The presence of nitrogen (as paramagnetic N containing species) in the system has been, in fact, unambiguously demonstrated by CW-EPR<sup>4</sup> both in the X-band and in the Q-band mode. The EPR spectra have been recorded at room temperature and at 77K. Two different paramagnetic species are present, as confirmed by isotopic substitution of <sup>14</sup>N with <sup>15</sup>N, during the sol gel preparation. The former species is the nitric oxide molecular radical (NO) trapped in the porous system of the solid while the second one is an interstitial N atom in the oxide lattice which is responsible of a localized state in the oxide band gap as indicated by DFT calculations.

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<sup>1</sup> Peral J., Ollis D., *J.Catal*, **1992**, 136, 554.

<sup>2</sup> Coronado J.M., Maira A.J., Conesa J.C., Yeung K.L., Augugliaro V., Soria J., *Langmuir*, **2001**, 17, 5368.

<sup>3</sup> Sato S., *Chem. Phys. Lett.* **1986**, 123, 126.

<sup>4</sup> Livraghi, S, Votta A., Paganini, M.C., Giamello E., *Chem. Commun.* **2005**, 498.