Paramagnetic Species in Nitrogen-doped TiO$_2$: 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$_2$ activated by UV irradiation $^{1,2}$. 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$_2$ rutile and anatase.

In 1986 Sato $^3$ reported that calcinations of NH$_4$Cl containing titanium hydroxide caused the photocatalytic sensitization of TiO$_2$ into the visible light region. The author proposed that the powder prepared according to the described method are actually NO$_x$-doped TiO$_2$ and that the sensitization of these materials is due to the presence of NO$_x$ impurity.

Aim of our recent work was to synthesize and characterize new materials based on N-doped TiO$_2$. Several N/TiO$_2$ 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$^4$ 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 $^{14}$N with $^{15}$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.


