

# Oxygen vacancies and nonmetal dopant species in anatase TiO<sub>2</sub>: A lesson learned?

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Visible-light sensitization of TiO<sub>2</sub> is a holy grail of research on photocatalysis. With the aim of better exploiting solar radiation to activate the photocatalytic process, numerous strategies have been reported to extend TiO<sub>2</sub> light-response to the visible region, often with limited success. Among them, N-doping has been one of the most popular<sup>1</sup>. Although the benefits of N-doping in terms of visible light absorption are often outweighed by a stability loss and faster charge carrier recombination, the debate over these materials has spurred more fundamental questions about the nature of TiO<sub>2</sub> defects and the visible light absorption mechanism. These questions prompted us to develop a combined experimental and theoretical approach to overcome the limitations of individual techniques<sup>2</sup>. We investigated a broad range of N-doped sol-gel TiO<sub>2</sub> samples from several N-sources (NH<sub>3</sub>, urea, TEA) and nominal content. The materials structure and defectivity was studied by combining HR-XRD, EXAFS, EPR, DRS, PL spectroscopy, and DFT calculations of structural and electronic features. EXAFS and DFT results showed huge differences in the local environment of Ti centers as a function of the N-source type, mirroring a different interplay of N species location and O vacancies. Differential DRS spectra obtained before and after light irradiation<sup>3</sup>, supported by DFT electronic structure calculations and by PL spectra, provided further insight into the diverse structural defects in the three families of N-doped materials. Our results offered an interpretative basis for the different stability in time of samples' paramagnetic species and for their photocatalytic activity, as determined by UV and visible-light photocatalytic tests for the gas phase degradation of VOCs and of antibiotics in water.

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