Experimental and theoretical tools for studying TiO_2 defects: A methodological lesson from N-doping

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The debate over nonmetal doping of TiO_2, in particular N-doping, has extended for more than a decade. Although the benefits of these materials in terms of visible light absorption are often outweighed by a loss of stability and enhanced charge carrier recombination, the debate over N-doped TiO_2 has spurred other more fundamental questions about the nature of TiO_2 defects and the mechanism of visible light absorption [1]. These questions prompted us to develop a combined experimental and theoretical approach to overcome the limitations of individual techniques [2-4]. Knowing that conflicting literature results are often due to even slight differences in the preparation conditions, we investigated a broad range of N-doped TiO_2 samples of the sol-gel family, obtained by changing both the type of N-source (NH_3, urea, triethylamine) and its nominal amount. A detailed investigation of the materials structure and defectivity was carried out by combining high resolution X-ray diffraction (HRXRD), extended X-ray absorption fine structure (EXAFS), electron paramagnetic resonance (EPR), photoluminescence (PL) spectroscopy, UV-vis-NIR diffuse reflectance spectroscopy (DRS), and *ab initio* calculations (DFT) of structural and electronic features. EXAFS and DFT results showed huge differences in the local environment of Ti centers, and in particular in the distribution of axial distances, as a function of the type of N-source, mirroring a different interplay of N species location and O vacancies. Moreover, the effect of light irradiation (at several wavelengths) on the different regions of DRS spectra [5], supported by DFT electronic structure calculations and by PL spectra, provided further insight into the diverse occurrence of structural defects in the three families of N-doped materials. Such results offered an interpretative basis for the different stability in time of the paramagnetic and optical features of these sets of samples. UV and visible light photocatalytic tests for the gas phase degradation of VOCs (ethanol) and of emerging pollutants in water (antibiotics) complete the picture.

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