MS20-P6 XAS study of anatase TiO_2 doping with interstitial nitrogen and oxygen species

Marina Ilkaeva[1], Igor Krivtsov[1], Eduardo Salas-Colera[2], Ruben Garcia[1], Eva Diaz[1], Salvador Ordoñez[1]

1. University of Oviedo, Oviedo, Spain
2. ESRF, SpLine, Grenoble, France

email: ilkaevamarina@uniovi.es

Titanium dioxide is an inexpensive, non-toxic and efficient photocatalyst. Nowadays, the major quest in this field is to extend its activation to the visible-light range, thus taking an advantage of the energy of a broader part of the solar spectrum. One of the promising methods allowing activation of TiO_2 under visible-light is a non-metal doping. Besides the most common nitrogen-doping approach, some other intriguing doping methods exist. One of these is oxygen interstitial doping [1]. Here we report the XAS study of the nitrogen-doped anatase titania nanoparticles and the thermally-induced exchange of nitrogen- to oxygen-interstitials. The N-TiO_2 nanoparticles were prepared by gelling and calcining the aqueous ammonium peroxotitanate complex at 400, 500, 600 and 800 °C. The nitrogen doping occurs at temperature range of of 400 to 500 °C. According to XPS and EXAFS data the nitrogen atoms occupy the interstitial positions in the titania structure and present in the form of NO_x. The distance from the central Ti atom at which they are located is found to be between 2.34-2.45 Å (Fig. 1). The incorporation of the nitrogen dopants reduces the number of oxygens in the first coordination shell of Ti from 6 to 5. The heat treatment gradually eliminates the N-species and at temperatures equal or higher than 600 °C they are no longer detected. The oxygen vacancies in the first coordination shell, caused by the elimination of N-interstitials, causes the charge imbalance in the TiO_2 structure and tend to be filled with the atmospheric oxygen, which is firstly adsorbed on the surface and then gradually migrates towards the oxygen vacancies forming on its way O_2-interstitials. The incorporation of oxygen species results in the increase of a number of oxygen coordinating the titanium atom to 7, thus implying the formation of peroxo-bridges responsible for the absorption of visible-light irradiation and lowering the band gap of titania anatase to 3.05 eV. The test of the photocatalytic activity in the reaction of light-assisted degradation of a common pollutant p-cresol shows that the O-doped TiO_2 nanoparticles have high activity under UV-irradiation, while the N-doped are able to utilize a larger portion of the visible light.

References

[1] V. Etacheri, M.K. Seery, S.J. Hinder and S.C. Pillai, Adv. Funct. Mater., 2011, 21, 3744-3752.

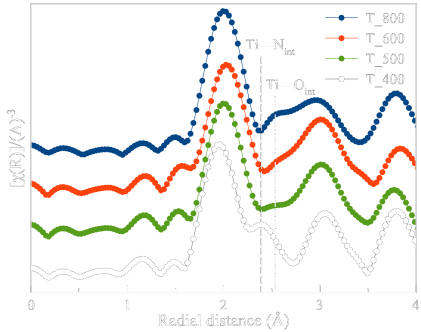

Figure 1. Extended region fitting using ARTEMIS in R-space

Keywords: titania, EXAFS, doping, photocatalysis