



Experiment title: Explaining the photocatalytic improvement of Ag-N codoped bulky nano-TiO₂ by in-situ XAFS and HRXRPD measurements

Experiment number:
MA-1781

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Report:

This work has been devoted to the investigation of the crystallographic structure and local distortions of the coordination geometry of Ag and Ti ions in both single-doped and co-doped TiO₂:Ag,N nanostructured photocatalysts.[1,2] To this end, high-resolution X-ray powder diffraction patterns and EXAFS spectra at the Ti and Ag K-edges were recorded on three series of powdered titania doped samples. The latter were synthesized by a sol-gel route at room temperature starting from titanium (IV) isopropoxide. Three different N sources have been considered, namely ammonia, triethylamine and urea, whereas the Ag precursor was AgNO₃. Various nominal N/Ti and Ag/Ti molar ratios ($0.05 \leq N/Ti \leq 0.5$, $0.01 \leq Ag/Ti \leq 0.05$) have been considered. In codoped samples, the N/Ti ratio has been kept fixed at 0.1, while the Ag/Ti ratio has been allowed to vary between 0.01 and 0.05. The synthesized xerogels were calcined at 400 °C under O₂ stream (9 nL h⁻¹).[3] A series of Ag-doped and Ag,N-codoped samples was also analyzed after a post-synthetic treatment with NaBH₄ in MeOH. Eventually, the effect of *ex-situ* visible light / UV irradiation on the Ag-doped powdered material was also investigated.

X-ray diffraction data were collected from 3° to 45° in 2θ at 2 °/min in Debye-Scherrer capillary geometry using Si-111 monochromatized X-rays with $\lambda = 0.50581(5)$ Å. A total of 4 or 5 acquisitions have been carried out for each doped sample, employing the 6-counting chains multi-detector system provided by SNBL-BM01B. The X-rays wavelength and the goniometer zero offset were calibrated using the NIST SRM 640b Si standard. The Rietveld method as implemented in the GSAS-EXPGUI program suite[4] was subsequently applied to provide quantitative estimates of the phase composition and lattice parameters as a function of the doping extent. EXAFS experiments have been performed in transmission geometry, with the active material having been carefully diluted, when necessary, in cellulose to avoid thickness effects. A Si-111 monochromated beam was employed to perform scans from 4.88 to 6.00 keV (Ti K edge) or from 25.3 to 26.5 keV (Ag K edge). The Horae suite of programs[5] was employed to interpret the spectral outcomes.

As expected, all the examined doped samples were biphasic, with a non-negligible minority of brookite mixed with the major anatase component. However, the more N dopant is present in the lattice, the lower is the brookite content. No other segregated phases were detected by the diffraction analysis. One of the most striking result we retrieved from this study was the systematic lengthening of the anatase *c* cell edge at increasing N dopant concentration within the N-doped materials (Fig. 1). From the comparison with solid-state quantum-mechanical outcomes at various theory levels and previously reported EXAFS results,[2] we

concluded[6] that at low N/Ti concentration nitrogen occupies predominantly substitutional sites in the anatase lattice. At the same time, translationally-correlated interstitial sites become also populated, triggering a significant lengthening of the anatase *c* cell edge.

Figure 2 below shows the normalized EXAFS spectra at the Ag K-edge for the series of Ag-doped and Ag,N-codoped TiO₂ samples. The coordination geometry of Ag atoms is very similar in the TiO₂:Ag and TiO₂:Ag,N series, no matter the concentration of the dopants (Fig. 2a,b). This likely indicates that Ag atoms are far from the bulk N ones, so that their coordination spheres do not directly influence each other. On the other hand, the Ag oxidization state influences the XAFS signal (Fig. 2c,d). Interestingly, the *ex-situ* chemical treatment of TiO₂:Ag,N with NaBH₄ (red curve in Fig. 2c) as well as irradiation with both visible and UV light (superimposed green and red curves in Fig. 2d) both produce modulations in the absorption coefficient that are comparable with those exploited by the reference metallic Ag foil (blue curve in Fig. 2d). On the contrary, the signal of the chemically reduced TiO₂:Ag sample (blue curve in Fig. 2c) appears to be somewhat intermediate among the fully oxidized TiO₂:Ag and the chemically reduced TiO₂:Ag,N ones (red and green curves in Fig. 2c). The fitting of the reported EXAFS spectra is currently in progress [7] and it is expected to provide more accurate and detailed information on the chemical state of Ag.

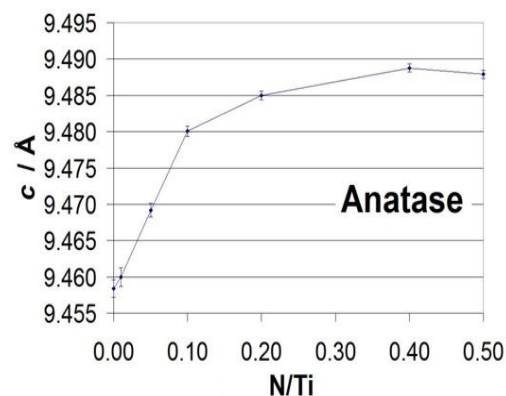


Fig. 1. Axis length of the *c* cell edge of the anatase phase for N-doped TiO₂ (precursor: triethylamine)

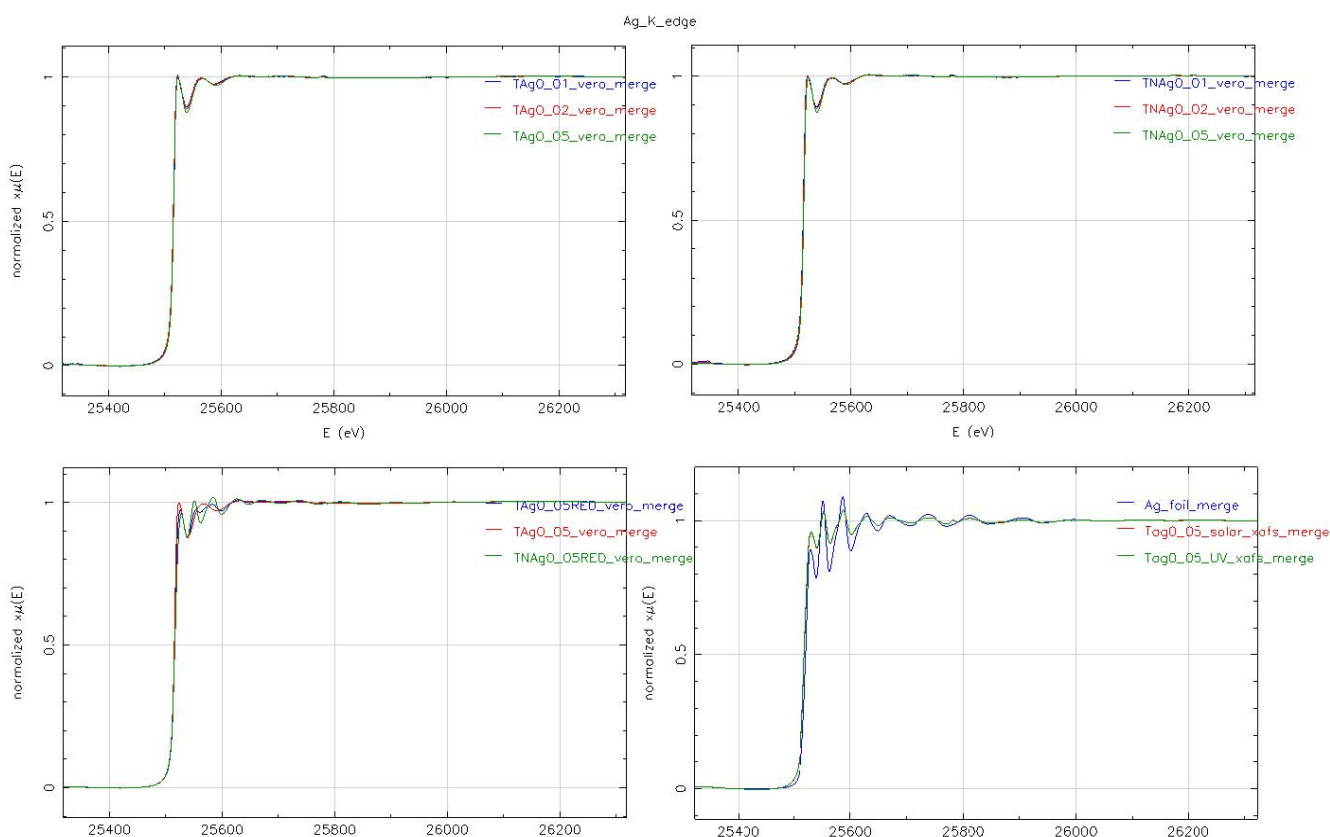


Fig. 2. Normalized Ag K-edge absorption spectra of relevant Ag(N)-doped TiO₂ nanostructured samples. The labels in the figure refer to the nature of the sample and are of the form T(N/Ag)_Y, where T stands for 'titania', (N/Ag) indicates the dopant specie and Y is the nominal Ag/Ti molar ratio. The N/Ti ratio, when N is present, is fixed to 0.1.

References

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