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| ESRF | **Experiment title:**<br>**Study of the relationship between structure and photocatalytic activity of $TiO_2$ doped with 3d metals and deposited Ag** | **Experiment number:**<br>**01-01-861** |
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| **Shifts:**<br>12 | **Local contact(s)**:<br>**Hermann Emerich** | *Received at ESRF:* |

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## Report:

During this beam time $TiO_2$ nanoparticles (NPs) doped with transition metals (Cr, Mn and Fe) and with Ag were characterized. K edges were measured for Ti, Cr, Mn, Fe and Ag (Ti: 4966 eV, Cr: 5989 eV, Mn: 6539 eV, Fe: 7112 eV, Ag: 25514 eV). Energy was calibrated with a metallic foil of the corresponding metal element. The measurements were performed in transmission mode in spite of the low dopants concentration in some of the samples (2 – 20 at%). All $TiO_2$-based samples were prepared by flame spray synthesis (FSS) and exhibited an average size of 25 nm and with ~ 2 nm sized Ag particles, as determined by TEM.

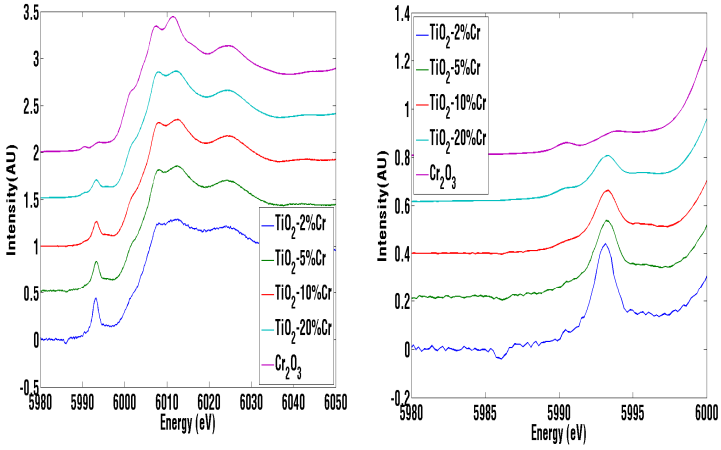


**Fig 1** – Left, Cr K edge of $Cr_2O_3$ and $TiO_2$:Cr with different dopant concentrations. Right: Zoom of pre-edge region.

The Cr K-edge XANES spectra of $TiO_2$:Cr with different dopant concentration exhibits the similar shape independently of the dopant concentration and with significant differences with respect to the spectrum of $Cr_2O_3$ (Fig 1). The same behavior was found in the Mn and Fe doped samples (Fig 2). The similar shape in the XANES spectra can be associated to similar environments of the dopants for all the range of doping. In the case of Cr doped samples, the increase of pre-peak intensity when decreasing the dopant concentration is interesting. The pre-peak intensity is associated with the loss of inversion center in the environment of the dopant [1,2]. The change in the pre-peak intensity with Cr concentration can be related to the lattice distortion induced by doping as previously reported [3].

The analysis of $E_0$ shift of dopant shows that with increased Fe concentration, $E_0$ shifts to lower energies, indicating a shift to lower oxidation state of the dopant. In the case of Mn, reverse behavior was observed while no trend was observed in the case of Cr.

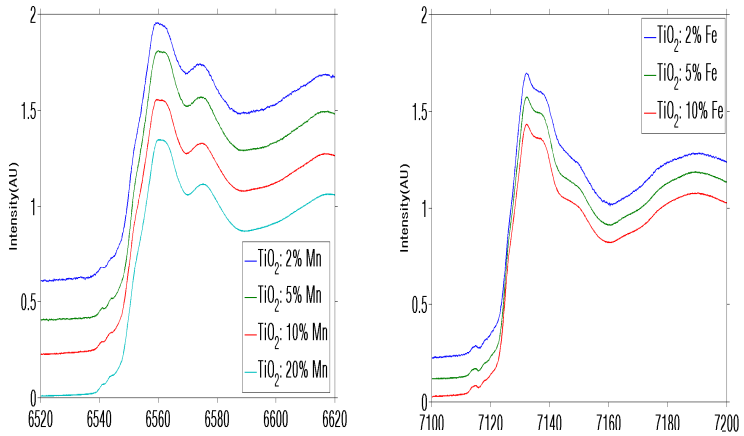


**Fig 2** – Left, Mn K edge of $TiO_2$:Mn samples with different dopant concentrations. Right: Idem Fe.

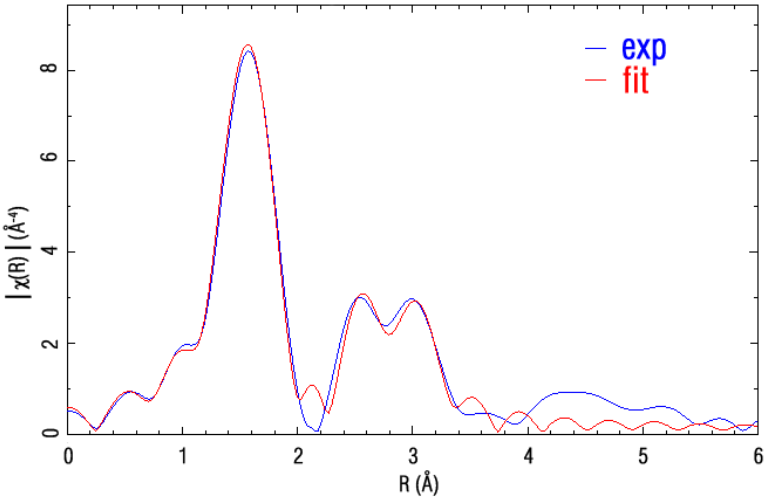


**Fig 3** – Fitting of $TiO_2$:Cr 20% in rutile environment.

The comparison between fresh and thermally treated (1h - 400°C to remove organic impurities) samples showed that Mn tends of slightly oxidize, while Ag tends to reduce. In the case of the Cr samples, the feature in the pre-edge tends to increase and the spectrum has slight changes in the shape, which can be associated with changes in the position of the dopant in the lattice or atomic rearrangements.

Samples prepared by FSS are composed of two $TiO_2$ polymorphs: anatase and rutile. To determine the location of the dopants in the lattice and in particular polymorph, fittings of EXAFS signal were performed. The best fittings were obtained for dopants which are located in rutile structure (Fig 3). Also, quantification of phase composition by XRD exhibited an increase of rutile with increasing dopant concentration. This indicates that the dopants stabilize the thermodynamically stable rutile phase [4].

Additionally, ZnO:Er and ZnO:Yb (Ln concentration ~3 at%) were measured at the Er and Yb K-edges (Er: 57486 eV and Yb: 61332 eV). The K-edge of lanthanides is useful to achieve longer k ranges due to the low absorption of the matrix at these energies. In this systems, the region of $k>10Å^{-1}$ is of special interest, because it makes possible to observe the correlation between heavy atoms [5,6]. In the case of the studied samples, a clear structure in the signal between 10 and 15 $Å^{-1}$ was observed indicating a correlation between lanthanides in the ZnO lattice.

Finally, given the facility of SNBL to perform diffraction measurements, $LaTiO_2N$ samples were measured to understand the relationship between structure and photocatalytic water splitting ability.

**References**


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