ESRF	**Experiment title:** Er-Yb-W tri-doping of Titania for Complete (UV-Vis-IR) use of Sunlight: a structural/electronic XAS study	**Experiment number**: **CH-4830**
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Names and affiliations of applicants (* indicates experimentalists):

Mario J. Muñoz-Batista,
Marcos Fernández-García,
Instituto de Catálisis y Petroleoquímica, CSIC, C/ Marie Curie 2, 28019, Madrid (Spain).

Report:

Titania is the universal photocatalyst. A main drawback of all titania based systems is however their limited performance upon excitation at wavelengths above the UV limit of ca. 380 nm. Doping of titania apperas as a common technology to solve this problem. Works on doped-titania mostly concern the use of visible light photons as an additional energy source (to UV photons) of the photocatalytic process. More recently, the use of near IR photons got attention of researchers in the photocatalytic field. Here we study the combination of previously tested and highly active photo-active materials concerning pure anatase powders doped with W (the visible light active cation and Er (the near IR active cation). Yb is used due to its known promoting effects of Er up-conjversion capabilities.

The evolution of Er-W and Er-Yb-W systems was followed by XAS. The report focuses on the Er-W system with a 10 % of W and a 2 at. % of Er (doping quantities maximizing photoactivity). To progress in the structural study of the Er-W system, we performed X-ray absorption experiments at the W and Er L_{III}-edges. The W L_{III}-edge results are presented in Figure 1. The XANES spectra of the single and codoped powders display a while line intensity (characteristic of the s → d transition) larger than a monoclinic WO_3 reference obtained using the same preparation procedure. This was previously observed in the single doped anatase-based material and indicates a +6 oxidation state of tungsten in the solid, as judged by the edge positions (equal within experiments error), but with electronic alteration with respect to the corresponding tungsten single oxide. No differences are encountered among our W-containing samples indicating their similar properties in respect to tungsten electronic properties. As the Fourier Transforms of the EXAFS spectra displayed in Figure 1 demonstrates, near identical spectra are obtained for our two tungsten-containing samples. This further corroborates the rather small (tungsten-related) differences between the single and codoped samples. The local structure of these two samples differs from the one of the WO_3 reference (the imaginary part of the Fourier transform indicates the different chemical nature of some neighboring atoms), particularly considering distances above the first W-O shell. In particular, the dashed lines at radial pseudo-distances near or above 2 Å in Figure 1B show marked differences in W-O-M (M being a cation) links with respect to the WO_3 reference.

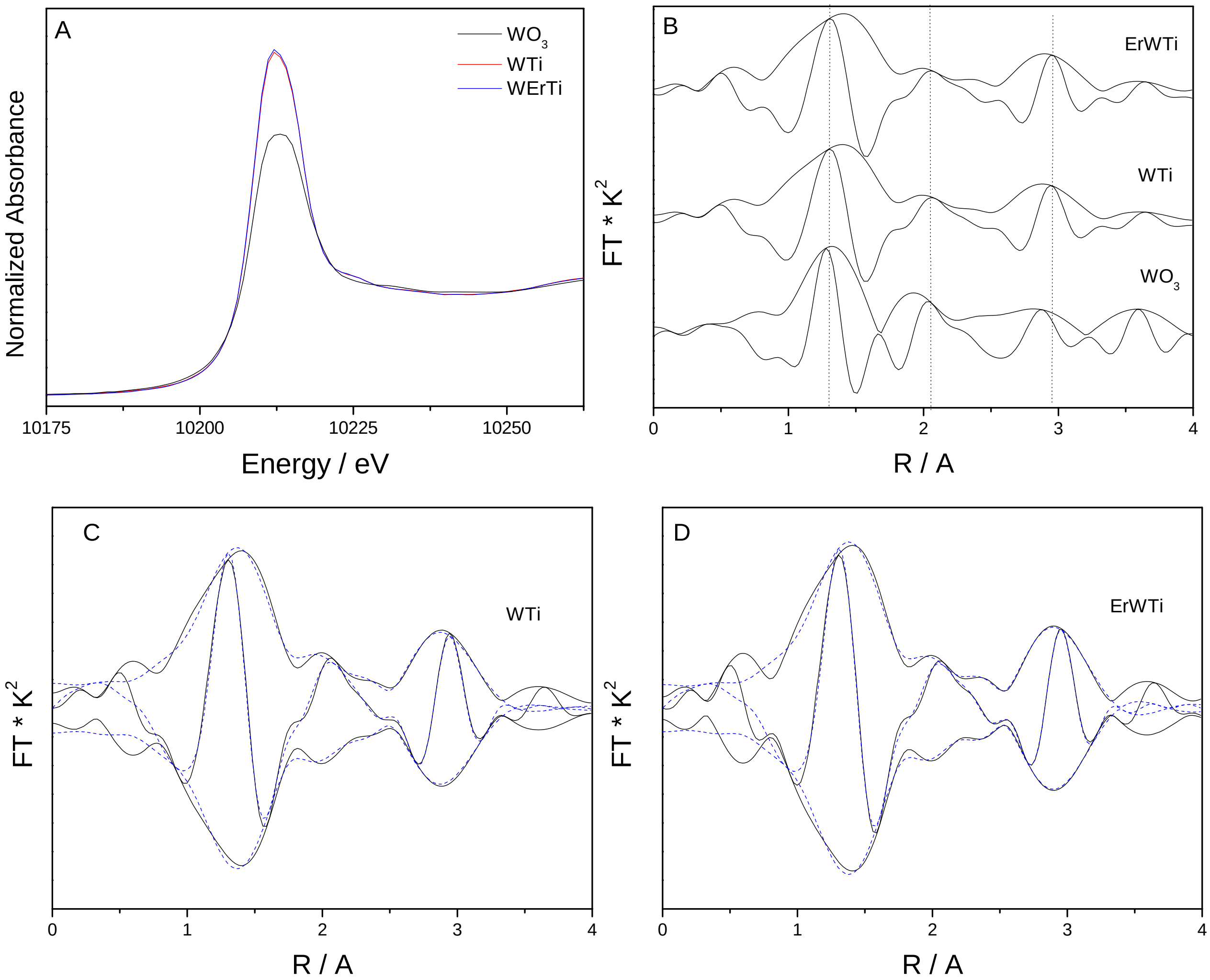

Fig.1. XAS W L_3-edge results for the WO_3 reference, and W-containing single and codoped samples; a) XANES spectra; b) Fourier Transform module and imaginary part of the EXAFS spectra; c and d) Fourier Transform module and imaginary part of the EXAFS signal (full lines) and modelling results (dashed lines).

Quantitative analysis of the W L_{III}-edge EXAFS spectra provides further insights. Fitting results are graphically displayed in Figure 1 (dashed lines in panels C and D). The agreement between experimental and modelling spectra is indicative of the goodness of the fitting results. According to the Nyquist theorem, we have a number of free parameters allowing the fitting of three shells. These three shells correspond to two W-O bonding distances of ca. 1.78 and 2.66-2.67 Å, and a third W-Ti at ca. 3.40 Å. The coordination numbers of the two W-O cells indicates the distortion of the octahedral local geometry of anatase in a 3+3 environment. Such environment is characteristic of tungsten oxides and would thus highlight the local order modification exerted by the cation into the anatase structure. The third distance demonstrates the formation of a W-Ti substitutionally disorder mixed oxide, where tungsten occupies Ti positions. Such substitution produces Ti vacancies as anatase would have a Ti-Ti second coordination shell number of 4. W expands the characteristic first cation-cation distance appearing in bare anatase at 3.05-3.10 Å, and reduces the coordination number in a quantity corresponding to a titanium cation vacancy for each 2 tungsten cations. The presence of a W and Ti occupying positions at the same cationic anatase sub-lattice is therefore demonstrated by XAS spectroscopies.

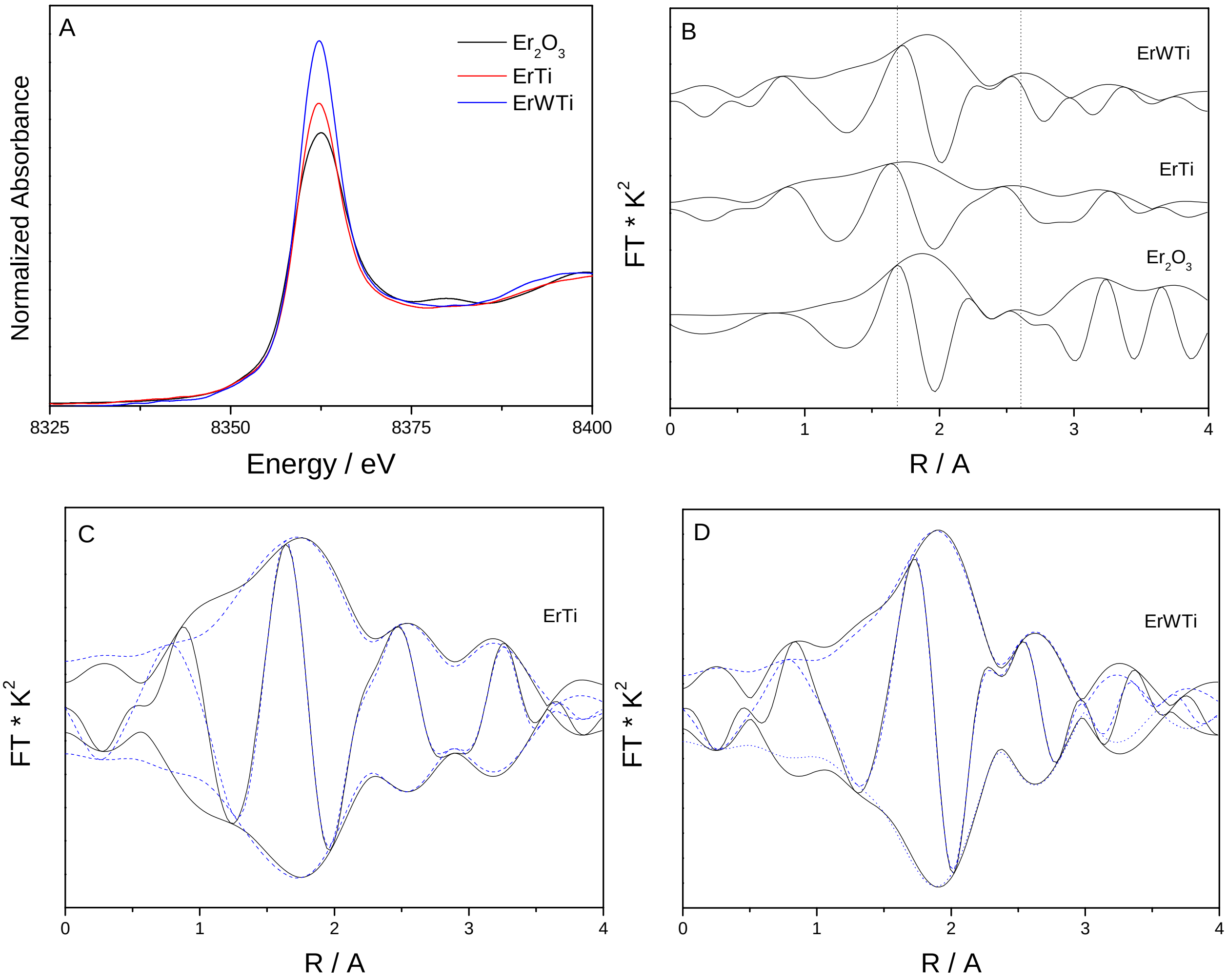

Fig.2. XAS Er L$_3$-edge results for the Er$_2$O$_3$ reference and Er-containing single and codoped samples; a) XANES spectra; b) Fourier Transform module and imaginary part of the EXAFS spectra; c and d) Fourier Transform module and imaginary part of the EXAFS signal (full lines) and modelling results (dashed lines).

Corresponding X-ray absorption experiments at the Er L$_{III}$-edge are shown in Figure 2. XANES spectra (panel A) do show differences between samples but also with respect to the Er$_2$O$_3$ reference. The same edge position of the tree XANES spectra the indicates a +3 oxidation state of Er, characteristic of the Er$_2$O$_3$ reference. As occurring in the W L$_{III}$-edge, our samples display larger white line intensity than the reference but in this case also showing differences among them. The codoped powder owns a more pronounced while line (dominated as mentioned by the p → d transition), indicative of a larger electronic modification in d electron count with respect to the single doped material and this in tum than the erbium oxide reference. The presence of erbium at the anatase structure alters this cation electronic structure with dependence of the chemical composition of the sample and particularly if tungsten is present or not. This is again inferred from the EXAFS Fourier Transform signals collected in Figure 2B. It is particularly evident the different environment of the three samples around and above ca. 2.5 Å, indicating drastic changes in local environment. This concerns the neighboring atoms nature (as demonstrated by the different behaviour of the imaginary part of the Fourier transform) and coordination numbers (module).

The quantitative Er L$_{III}$-edge EXAFS fitting results are graphically reported in Figure 2 (dashed lines in panels C and D). The results shed light into the local structure around Er cations due to the goodness of the fitting outcome. The number of free parameters in the erbium case allows the use of a maximum of three shells. In the single doped sample the fitting renders one Er-O at 2.18 Å and two Er-Ti shells at, respectively, 2.67 and 3.48 Å. The distance and corresponding coordination number (ca. 6.) of the Er-O shell are typical of the Er(III) oxidebut the next two coordination shells are strongly indicative that erbium is located at the anatase network in all cases (single and codoped samples). The erbium substitution generates, on the other hand, a strong distortion of the local environment in the anatase structure. This is due to the large difference in ionic radius between Ti (0.605 nm in octahedral coordination) and Er (0.89 nm), contrarily to tungsten (0.60 nm). In this single doped sample, the distances of the two Er-Ti shells would be the result of a mixture of local environments present in the single Er and Ti oxides, with a rather short second one. The Er-Ti coordination numbers are significantly lower than the (Ti-O-Ti) ones presented for a Ti position but the strong disorder precludes a definitive interpretation of such point. The short first Er-Ti distance would indicate that a limited number of Ti cations would occupy interstitial positions near Er (as a consequence of the charge neutrality defects occurring at anatase in presence of the doping cation).

The presence of tungsten in the anatase structure makes a strong influence in the erbium local environment for the codoped sample. A first point is the increase (with respect to the single doped material) of the Er-O coordination distance up to 2.29 Å, followed by the presence of tungsten at ca. 3.11 Å. Titanium cations may be likely present around or above the last distance mentioned, however the fit goodness (according to an F-test) does not increase enough to be statistically significant if a third shell is included. The presence of tungsten is thus part of the distortion displayed by the erbium local structure with respect to the single doped catalyst. It should be noted that erbium is not observed at the W local environment. This is primarily an effect of the different doping concentration; tungsten has a higher concentration than erbium by a factor of ca. 9. The corresponding W-Er shell would have thus a relatively low frequency and coordination number (the latter according to the Er-W one), being consequently not observed in the corresponding W L_{III}-edge due to the fact that X-ray absorption is a bulk-averaged technique. The XAS study of the two doping cations indicates that titanium, tungsten, and erbium are located at the anatase structure forming a substitutionally disordered mixed oxide.

Finally, we would like to acknowledge Dr D. Banerjee for supporting the experiments carried out at BM26A.