## Titanium ions dispersed into the ZrO<sub>2</sub> matrix. Spectroscopic properties and photo-induced electron transfer

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In ZT samples the identification of possible segregated TiO<sub>2</sub> phase represents a key factor for the understanding of the system. Unfortunately in this case, for this aim, XRD alone does not represent a suitable technique due to its low sensitivity (usually >5%). In Figure SI 1 spectroscopy features of ZT5 sample are compared with a mechanical mix (5%Mol.) of pure  $ZrO_2$  (tetragonal + monoclina) and pure TiO<sub>2</sub> (100% anatase). This mechanically mixed oxides sample will be labelled with the abbreviation MMO5.

From XRD (Fig. SI 1A) is clear that for low titanium loading the presence of  $TiO_2$  can be identified from the peak due to (101) planes only and for molar concentration lower than 5%  $TiO_2$  pattern is completely buried by the ZrO<sub>2</sub> pattern. This limitation however can be overcame by Raman spectroscopy. In Fig. SI 1B Raman spectrum of the same mechanical mix above described are reported and compared with that of pure ZrO<sub>2</sub>. From these second set of spectra is clearly evident how this technique is highly sensitive to  $TiO_2$  respect to  $ZrO_2$  and how this difference can be used to identify  $TiO_2$  in the case of extremely low concentration. In particular the first peak at lower Raman shift value can be used as a finger print of the  $TiO_2$  presence in ZT systems. Finally in Fig. SI 1C the DR-UV-Vis spectra of the MMO5 sample is compared with the ZT5 and Z samples. From this last comparison is evident how UV-Vis absorption modification observed in ZT systems is not due to the superimposition of the absorption features of the two pure oxides.

Figure SI 2 shows the typical EPR feature of pure  $ZrO_2$ . In this system two different signal can be observed depending on the oxidation state of the sample. On fully oxidized material the axial signal at  $g_{\perp}=1.98$  and  $g_{\prime\prime}=1.95$  can be observed. This signal is usually ascribed to  $Zr^{3+}$  centre<sup>[1]</sup> although this assignment is not commonly accepted. The same signal is assigned by other authors to  $Cr^{3+}$ 

impurity.<sup>[2]</sup> Whatever the real nature of the defect associated to this signal its represents a minor features of the system. In reduction condition the above described signal disappears and e new isotropic signal at g=2.003 appears. This second signal is surely due to trapped electrons which can easily react when the reduced solid is contacted with oxygen generating the  $O_2^{\bullet-}$  species.



Figure SI 1: Comparison of structural and UV-Vis absorption features of TZ5 sample whit those of a mechanical mixed oxide sample (MMO5).

A) XRD patterns comparison. Gray line,ZT5 sample and black line, MMO5 sample. , Tetragonal B Monoclina  $\downarrow$  TiO<sub>2</sub> (anatase) Inset show the TiO<sub>2</sub> feature in the MMO5 sample.

B) Raman spectra. a) MMO5, b) MMO5 multiply 5 times. c) Z sample. T and Z indicate  $TiO_2$  anatase and  $ZrO_2$  (monoclina + tetragonal) raman pattern.

C) DR-UV-Vis spectra. a) Z sample, b) MMO5 and c) ZT5 sample. Oval highlight the main differences in the UV light absorption of samples ZT5 and MMO5.



Figure SI 2: EPR feature of Z sample in different reduction states. a) after mild reduction. b) after deep reduction.

[1] Morterra, C.; Giamello, E.; Orio, L.; Volante, M. J. Phys. Chem. 1990, 94, 3111.

[2] Occhiuzzi, M. D.; Dragone, C. R. J. Phys. Chem. B 2002, 106, 12464.