Photochemistry of doped metal oxides. Is there some hope for applications in visible-light photocatalysis?

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Abstract: Typical metal oxides with relatively large band gap (zirconium dioxide, zirconium titanate, zinc oxide) are modified using cerium (or other rare earth elements) to influence their electronic structure. This cause the onset of new photochemical properties since the solids become photoactive under visible light. This means that irradiation with low energy photons allows the excitation of electrons in the conduction band, the formation of holes in the valence band and the onset of photocatalytic properties in these conditions.

Keywords: Photocatalytic oxides, doping, Electron Paramagnetic Resonance (EPR)

1. Introduction

The search for innovative materials in the area of heterogeneous photocatalysis is oriented to select systems having a suitable electronic structure capable of harvesting solar light and excellent potentials to perform the desired redox process. This is practically impossible to be found in a unique system. Solid materials with large band gap values correspond, in principle, to good reduction and oxidative potentials but unavoidably need high energy photons (UV light, scarcely present in solar irradiation at the earth surface) to perform the charge separation. On the other hand, semiconductors with smaller band gap value, compatible with visible light absorption, may have unsatisfactory potentials for both reduction and oxidation unless if they are coupled in a Z-scheme system. The latter, however, needs the presence of a redox shuttle to connect the two photocatalysts.

A possibility to overcome this drawback consists in modifying a semiconductor with relatively large band gap in order to make possible the absorption of visible light (band-gap engineering). In the present contribution the role of cerium in the modifications of various photocatalytic oxides will be illustrated. Two main kind of systems are observed. In the former case Ce(IV) ions enters in the lattice of the oxide in substitutional position forming a true solid solution (ZrO_2, $ZrTiO_4$) while in the second case Ce(IV) is not miscible with the principal oxide and biphasic systems are formed with cerium dioxide (TiO_2, ZnO).

Our research has followed a knowledge-based experimental approach (often in cooperation with a group of computational chemistry) investigating chemistry, photochemistry and spectroscopy of both pristine and modified (band engineered) solids aiming to understand the key-factors allowing the use of visible light in photocatalytic applications. Beside a characterization of the newly prepared systems using the experimental tools usually adopted in this field (XRD, Electron microscopy, UV-Vis spectroscopy) we employ a particular procedure based on EPR spectroscopy to preliminary check the photo-response of the solids. EPR can be used in dark, under irradiation and post irradiation. The technique is much suitable to monitor the charge separation processes and the stabilization of the photogenerated charge carriers and can thus be used as a preliminary screening of the various solids before photocatalytic tests.

2. Experimental

All samples were characterized via X-ray diffraction (XRD), N_2 adsorption to evaluate surface area (BET method), diffuse reflectance UV-Vis spectroscopy, transmission electron microscopy (TEM), and electron paramagnetic resonance (EPR).

3. Results and discussion

In the present abstract, for reasons of conciseness, only few results concerning the case of zirconium dioxide doped with Ce(IV) ions are shown. Figure 1 reports a comparison between the Diffuse Reflectance-UV-Vis spectra of pristine zirconium dioxide (a), pristine cerium dioxide (c) and of a 0.5% solid solution of Ce in zirconia (b).

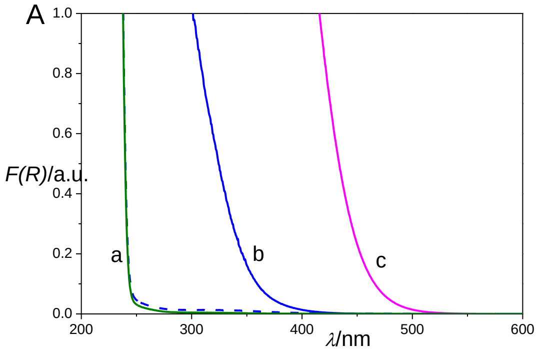

Figure 1. DR-UV-Vis spectra of ZrO_2 (a), Ce/ZrO_2 (0.5%) (b), CeO_2(c)

The Ce modified zirconia absorption, with 0.5% of ceria only, shows a red shift in comparison typical VB to CB transition of ZrO_2 and a weak tail in the visible. A solid produced by mechanical mixing of ZrO_2 and CeO_2 (with the same percentage of ceria, 0.5%) has an optical behavior practically coincident with that of bare ZrO_2 (dashed line Fig. 1). This point to an intimate interaction of Ce^{4+} and ZrO_2 conferring peculiar optical properties to the mixed solid which are reflected in the behavior under irradiation.

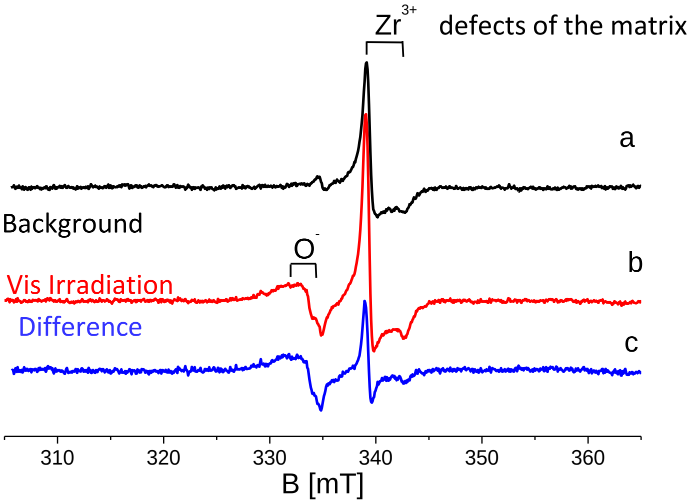

Fig. 2. EPR spectra recorded upon irradiation with visible light of Ce/ZrO_2 (0.5%)

This is shown in Fig. 2 where the EPR spectra recorded upon irradiation at $\lambda > 420$ nm (visible) show the formation of both trapped electrons by the zirconia matrix with formation of Zr^{3+} and trapped holes with formation of O- ions.

The photocatalytic results obtained with this (Ce-ZrO_2) and similar systems will be illustrated in the talk.

References

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