Journal of Energy Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

# Rare earth oxides in zirconium dioxide: How to turn a wide band gap metal oxide into a visible light active photocatalyst[☆]

Q1 Chiara Gionco[a], Maria C. Paganini[a], Elio Giamello[a,*], Olga Sacco[b], Vincenzo Vaiano[b], Diana Sannino[b]

[a] *Department of Chemistry, University of Torino,Via Giuria 7, 10125 Torino, Italy*
[b] *Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy*

ARTICLE INFO

*Article history:*
Received 30 May 2016
Revised 1 July 2016
Accepted 6 July 2016
Available online xxx

*Keywords:*
3rd generation photocatalysts
Zirconium dioxide
Rare earth ions
Dyes mineralization

ABSTRACT

In the present study, we investigated the effect of cerium and erbium doping in zirconium dioxide matrix. We synthesized doped samples using hydrothermal process. The amount of dopant used was 0.5%, 1% and 5% molar (rare earth oxide over zirconium dioxide). The samples have been studied via X Ray Diffraction measurements for the structural characterization. UV visible diffuse reflectance was used for the optical analysis, Branauer-Emmett-Teller (BET) model for the measurement of the surface area. Finally the samples have been analysed via electron paramagnetic resonance (EPR) for the electronic characterization. Then we tested the new synthetized materials to determine their photocatalytic activity in the reaction of degradation of methylene blue performed under irradiation by diodes (LEDs) emitting exclusively visible light.

## 1. Introduction

After the experiment of light induced water splitting by Honda and Fujishima in 1972, the concept of photocatalysis became familiar to the scientific community. Since then, the main routes of the experimental research in this field were essentially two. The first route seeks the advent of a new energetic system aiming to achieve an efficient photochemical production of hydrogen from water and the photoreduction of $CO_2$ (artificial photosynthesis). The second one concerns environmental chemistry as it deals with the remediation of pollutants in waters and in the atmosphere. In this second case, the oxidative capability of the photocatalyst is critical. For this reason titanium dioxide (which shows an optimal flat band potential for oxidation) has been the dominant photochemical system in this kind of environmental applications for many years. A further application with increasing importance concerns the role of titanium dioxide and other photocatalystsin determining alternative routes to traditional synthetic processes of organic chemistry both at laboratory and industrial level [1]. All the mentioned applications, however, employ UV light for irradiation [2,3]. The UV frequencies are in fact necessary to create the electron-hole photoinduced separation (excitation from valence band to conduction band, separated by about 3.2 eV) which is the starting act of the whole reactivity. However, after years of successful applications of $TiO_2$ photocatalysis for pollutants removal, the need of UV light to perform photocatalytic reactions started to be seen as a limit of this process. Also in view of the construction of larger scale photocatalytic plants the use of sunlight (quite poor in the UV component and rich in both visible and NIR light) started to become an unavoidable necessity.

Applications of visible light in photocatalytic reactions face an apparently irreconcilable contradiction. Using heterogeneous photocatalyst with lower band gap value, in fact, allows, on the one hand, the charge separation with lower energy photons (visible) but implies, on the other hand, to have less effective flat band potentials for Valence Band (VB) and Conduction Band (CB) therefore limiting (or even canceling) the photocatalytic activity.

To overcome this clear contradiction new generations of photocatalyst have been prepared and tested since the beginning of this century. The second generation of photocatalyst was essentially based on titanium dioxide modified with various dopants [4,5]. The most important member of this family, at least for historical reasons, is nitrogen doped $TiO_2$, proposed by Ashai in 2001 [6] and whose (moderate) effects under visible light have been rationalized later basing on the electronic structure of the system.

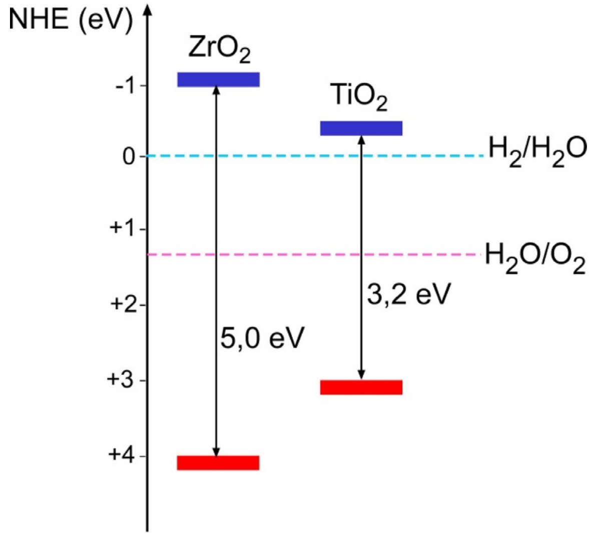
---

[☆] This work was supported by the CARIPLO Foundation with the Advanced Materials Grant 2013 "Development of second generation photocatalysts for energy and environment" and by the Local Funding of the University of Torino call_2014_L2_126.

[*] Corresponding author. Fax: +39 6707578.
*E-mail address:* elio.giamello@unito.it (E. Giamello).

http://dx.doi.org/10.1016/j.jechem.2016.07.006
2095-4956/© 2016 Published by Elsevier B.V. and Science Press.

Please cite this article as: C. Gionco et al., Rare earth oxides in zirconium dioxide: How to turn a wide band gap metal oxide into a visible light active photocatalyst, Journal of Energy Chemistry (2016), http://dx.doi.org/10.1016/j.jechem.2016.07.006



**Scheme 1.** Flat band potentials of $ZrO_2$ [9] and $TiO_2$ [12].

The third generation of photocatalysts tries to go beyond titanium dioxide and was initially a prediction proposed by Serpone and Emeline. This was based on the idea of a wide band gap semiconductor (hence with excellent flat band potentials) containing extra electronic levels at intermediate energy in the band gap [7,8] capable of allowing the transition of electrons from the VB to the CB with a double excitation. An example of such a behavior has been recently proposed by some of us reporting the properties of cerium doped zirconium dioxide. $ZrO_2$ has a band gap energy wider than that of $TiO_2$ (about 5 eV [9]) and better flat band potentials (in particular the reduction potential of the CB, see Scheme 1) than titania. Despite the band gap value, corresponding to high energy UV photons, we have shown in the case of Ce-doped $ZrO_2$, that visible light is capable to promote electrons in the CB creating holes in the valence band. This effect, that was monitored via Electron Paramagnetic Resonance spectroscopy following the fate of the photoexcited charge carriers, is certainly not huge in quantitative terms but remains conceptually significant in terms of proof of concepts [10]. Responsible of these properties, as also shown by theoretical modeling, are the $Ce^{4+}$ 4*f* empty levels that allow the described electron excitation. The sol–gel method adopted for the synthesis favors the intimate mixture of the components and the formation of isolated cerium centers in the lattice. Though uncommon, the presence of rare earth ions in photocatalytic systems is not totally new. In recent years, for instance, Zaleska and coworkers have reported the photocatalytic properties of titanium dioxide doped with various rare earth ions [11].

With the present work, we intended to test the real photocatalytic properties of this novel family of materials investigating two families of zirconium dioxide doped with Cerium and Erbium ions, respectively, at various quantitative levels. The two rare earth elements were selected in order to test ions rich of 4*f* electrons ($Er^{3+}$) or with 4*f* levels completely empty ($Ce^{4+}$). In the first part of the paper, a basic characterization of the structural, optical and photochemical properties of the prepared materials is reported. The second part is devoted to the investigation of their photocatalytic activity in the reaction of degradation of methylene blue performed under irradiation by diodes (LEDs) emitting exclusively visible light. This was done in order to verify the potentiality of the novel systems in photocatalytic reactions under low energy photons (i.e. in the absence of UV components) that is essential for future applications under true solar light.

## 2. Experimental

### *2.1. Synthesis of catalysts*

In this work samples of zirconium dioxide doped with rare earth (RE, RE=Ce, Er) ions were prepared. All reactants employed were purchased from Aldrich and were used without any further purification treatment.

The samples were prepared via a hydrothermal process starting from a 1.0 M aqueous solution containing the stoichiometric ratio of $ZrOCl_2{\cdot}8H_2O$ and $Ce(SO_4)_2$ or $Er(NO_3)_3{\cdot}5H_2O$. The pH was then adjusted to 11 using a 4.0 M NaOH aqueous solution, inducing the formation of a gel. The gel was then transferred into a 125 ml Teflon-lined stainless steel autoclave, 70% filled, which was heated in oven at 448 K overnight. The precipitates were then centrifuged and washed several times, then dried at 333 K. For comparison pure $ZrO_2$ was prepared with the same procedure.

For each dopant ($CeO_2$ or $Er_2O_3$), samples of different concentrations, namely 0.5%, 1% and 5% molar, were prepared. Samples will be labeled as Z for bare zirconia, CZ05 and EZ05 for zirconia doped with 0.5% of cerium and erbium respectively, CZ1 and EZ1 for zirconia doped with 1% of cerium and erbium respectively, and finally CZ5 and EZ5 for zirconia doped with 5% of cerium and erbium respectively.

### *2.2. Characterization of catalyst*

X-Ray Diffraction (XRD) patterns were recorded with a PANalytical PW3040/60 X'Pert PRO MPD using a copper $K\alpha$ radiation source (0.15418 nm) and a Bragg Brentano geometry. X'Pert High-Score software was used for data handling.

Diffuse Reflectance Spectroscopy (DRS) data were recorded using a Varian Cary 5000 spectrometer, coupled with an integration sphere for diffuse reflectance studies, using a Carywin-UV/scan software. A sample of PTFE with 100% reflectance was used as reference.

Electron Paramagnetic Resonance (EPR) spectra were recorded at room temperature and at liquid nitrogen temperature (77 K). They were run on a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation. The effect of light on EPR spectra was investigated using a 1600 W Xenon lamp (Oriel Instruments) equipped with a IR water filter. To simulate the solar spectrum a 400 nm cut-off filter has been used for selected experiments.

Surface area measurements were carried out on a Micromeritics ASAP 2020 using the Branauer-Emmett-Teller (BET) model on the $N_2$ adsorption measurement and 9 $p/p_0$ points. Prior to the adsorption run, all the samples were outgassed at 573 K for 3 h.

Photocatalytic experiments were carried out with a pyrex tubular photoreactor (Internal diameter = 2.5 cm) equipped with an air distributor device ($Q_{air} = 150$ ml/min (STP)), a magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution and a temperature controller [13]. The photoreactor was irradiated by a strip composed of 30 white light LEDs (nominal power: 6 W) with wavelength emission in the range 400–800 nm (with a maximum centered at about 475 nm) [14,15].

The LEDs strip was positioned around the reactor to assure uniform illumination of the reaction volume.

In a typical photocatalytic test, 3 g/l of photocatalyst was suspended in 100 ml solution. The system was kept in dark condition for 3 h to reach methylene blue (MB) adsorption equilibrium on the catalyst surface, and then the photocatalytic reaction was initiated by the LEDs lighting. Liquid samples were taken at regular time intervals during the test and centrifuged for 20 min at 4000 rpm for removing the photocatalyst particles. The centrifuged samples were analyzed to determine the change of MB

Please cite this article as: C. Gionco et al., Rare earth oxides in zirconium dioxide: How to turn a wide band gap metal oxide into a visible light active photocatalyst, Journal of Energy Chemistry (2016), http://dx.doi.org/10.1016/j.jechem.2016.07.006