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## Catalysis Communications

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

# Long-lived photoinduced charge-carriers in Er<sup>3+</sup> doped CaTiO<sub>3</sub> for



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photocatalytic H<sub>2</sub> production under UV irradiation

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#### ARTICLE INFO

Article history: Received 7 March 2016 Received in revised form 18 May 2016 Accepted 1 June 2016 Available online 02 June 2016

Keywords: Photocatalysis Hydrogen Erbium CaTiO<sub>3</sub> Charge-carriers

#### ABSTRACT

The incorporation of  $Er^{3+}$  ions in the CaTiO<sub>3</sub> structure provides an enhanced H<sub>2</sub> photoproduction due to the formation of long-lived charge-carriers in the semiconductor. Nitroblue tetrazolium reaction, photoluminescence and time resolved microwave conductivity techniques were used to investigate the generation of the superoxide species and the lifetime of the charge-carriers. The improved photoactivity has been explained in terms of the dopant agent, finding that phenomena such as a higher concentration of the superoxide radicals, a more efficient separation of the photogenerated charge-carriers, and a slower recombination process take place in the  $Er^{3+}$ doped CaTiO<sub>3</sub> compared to the undoped CaTiO<sub>3</sub>.

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### 1. Introduction

Global climate change has prompted the search for new technologies for the production of clean and renewable energy [1]. In this regard, hydrogen can be considered as an interesting and attractive fuel due to its zero carbon emission and renewable source [2]. Among the many reported methods for hydrogen generation, the photocatalytic water splitting process has been considered as one of the techniques with potential large-scale production [3]. In this sense, metal oxides with crystal structures such as pyrochlores ( $A_2B_2O_7$ ), spinels ( $AB_2O_4$ ) and perovskites ( $ABO_3$ ) are interesting and promising materials for photocatalysts [4–6].

CaTiO<sub>3</sub> is one of the most important perovskite-related materials and has received a lot of attention due its interesting catalytic, dielectric and photoelectric properties [7]. This semiconductor has suitable conduction band (CB) and valence band (VB) positions, *i.e.*, the CB potential negative to the redox potential of  $H^+/H_2$  and the VB potential positive to the redox potential of  $O_2/H_2O$ . Due to its similar band structure to TiO<sub>2</sub>, CaTiO<sub>3</sub> and its doped derivatives have shown to exhibit photocatalytic activity [8]. For instance, Shimura et al. have previously reported the

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preparation of  $Pt/CaTiO_3$  photocatalysts with a higher production rate of hydrogen in a flowing mixture of water vapour and methane [9]. Other studies report its use as photocatalyst in the degradation of dyes such as methyl orange, rhodamine B and methylene blue [10,11].

On the other hand, semiconductors usually exhibit low photocatalytic efficiencies probably because of their relatively low charge separation efficiencies and fast recombination of the photogenerated charge-carriers [12]. Therefore, several strategies have been developed in order to facilitate the separation of the charge-carriers. One of these strategies is the addition of dopants to assist the trapping of specific charge-carriers, thereby favoring their spatial separation. Among the dopants we can find to the  $\text{Er}^{3+}$  ion, which has been reported in other photocatalysts such as TiO<sub>2</sub> and BiVO<sub>4</sub> [13,14]. In this communication, we describe the preparation of an  $\text{Er}^{3+}$  doped CaTiO<sub>3</sub> photocatalyst with enhanced H<sub>2</sub> production under UV irradiation, where this improved photoactivity can be result of the formation of long-lived charge-carriers in the semiconductor.

#### 2. Experimental

#### 2.1. Preparation of the photocatalysts

First, TiO<sub>2</sub> powder was placed in a Teflon vessel, while the stoichiometric amount of CaCl<sub>2</sub> (Sigma Aldrich,  $\ge$  93%) was dissolved in 10 mL





Fig. 1. (a-b) TEM and SEM images of undoped CaTiO<sub>3</sub>; (c) SEM image of Er<sup>3+</sup>-doped CaTiO<sub>3</sub>.

of distilled water. Separately, aqueous solutions of NaOH 5 M (80 mL) and urea 2 M (10 mL) were prepared. Then, the three aqueous solutions were poured in the Teflon vessel containing the TiO<sub>2</sub>. The suspension was stirred and placed into a microwave reactor (Eyela MWO-1000 Wave Magic) and subsequently heated by microwave irradiation at 180 °C for 4 h, 400 rpm and a maximum variable microwave irradiation power of 150 W. The mixture was cooled to room temperature, neutralized with diluted HCl solution, filtered and washed with distilled water. Finally, the solid was dried at 70 °C for 12 h and calcined at 850 °C for 1 h. The synthesis of the  $Er^{3+}$ -CaTiO<sub>3</sub> photocatalyst was performed in the same way, where the  $ErCl_3$ °GH<sub>2</sub>O precursor (Sigma Aldrich, 99.9%) was dissolved in the NaOH aqueous solution. The nominal value of the dopant ion was 1% at. This erbium amount was chosen because it is the optimal value found in the photodegradation of methylene blue by the  $Er^{3+}$ -CaTiO<sub>3</sub> system [8].

#### 2.2. Materials characterization

X-ray diffraction (XRD) patterns were obtained using a D8 Bruker Advance diffractometer with Cu K $\alpha$  radiation. Diffuse reflectance spectroscopy was performed using a UV–vis spectrophotometer JASCO V-570 equipped with an integrating sphere. BET surface area was measured with a Bel-Japan Minisorp II Surface Area & Pore Size analyzer. The nitrogen adsorption-desorption isotherms were evaluated at -196 °C after a pretreatment at 150 °C for 2 h. The morphology of the samples was analyzed by field emission scanning electron microscopy using a FEI XL30 microscope equipped with a field emission gun. Also, transmission electron microscopy was performed through a Tecnai FEI 300 microscope operated at 300 kV. Erbium content was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis. The Er<sup>3+</sup> doped CaTiO<sub>3</sub> sample was dissolved in acid digestion (Hydrochloric acid, ACS reagent 37%) prior to the analysis with a Varian 700 ICP-OES Atomic emission spectrometer. Photoluminescence spectra (PL) were recorded with a Hitachi FL-4500 spectrofluorometer. The charge-carrier lifetimes under UV excitation of the photocatalysts were measured by Time Resolved Microwave Conductivity method (TRMC). A pulsed laser source with an optical parametric oscillator (OPO) EKSPLA, NT342B, tunable in the range between 220–2000 nm was used for TRMC measurements.

#### 2.3. Photocatalysts tests

The samples were tested by means of the photocatalytic hydrogen production using a homemade quartz inner-irradiation reactor connected to a closed glass gas system. In detail, 100 mg of the photocatalyst was dispersed in 200 mL of an isopropyl alcohol-water solution (1:10 v/v). A 0.5% wt. Pt as co-catalyst was photodeposited *in situ* on the surface of the photocatalyst on the initial stage of the reaction using H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (ACS reagent,  $\geq$  37.50% Pt basis) as precursor. Before test, the reaction medium was evacuated in order to remove air completely prior to irradiation. Then, the system was irradiated by means of a Hg pen-lamp (254 nm, 100 W) encapsulated in a quartz tube and placed inside the reactor. Hydrogen production was followed by gas chromatography (Varian CP-3800) using a thermal conductivity detector connected to a 5 A column molecular sieve. The temperature of the reaction was maintained at 25 °C.



**Fig. 2.** (a) Photocatalytic  $H_2$  production and (b) production of superoxide ions  $(O_2^-)$  by undoped and  $Er^{3+}$  doped CaTiO<sub>3</sub> photocatalysts.



Fig. 3. Photoluminiscence emission spectra ( $\lambda_{exc}=376$  nm) for undoped and  $Er^{3+}$  doped CaTiO\_3 photocatalysts.

The photocatalytic production of the superoxide ion  $(O_2^-)$  also was evaluated under the same UV irradiation conditions as the hydrogen production. The nitroblue tetrazolium (NBT) can be specifically reduced by the superoxide ion  $(O_2^-)$  in order to form the insoluble purple formazan (FZN), see Fig S1 [15]. The photocatalytic tests were made with an initial concentration of NBT  $5 \times 10^{-5}$  mol L<sup>-1</sup> and a 0.5 g L<sup>-1</sup> concentration of the photocatalyst. The production of the superoxide ion was quantitatively analyzed through the evolution of the absorption maximum at 259 nm of the nitroblue tetrazolium.

#### 3. Results and discussion

Undoped and erbium doped CaTiO<sub>3</sub> photocatalysts were identified as orthorhombic CaTiO<sub>3</sub> phase according the PDF 42–0423, see Fig. S2. From Rietveld analysis, a slight increase of the cell volume was observed for the erbium doped sample. This fact could indicate that the  $Er^{3+}$  addition can be carried out interstitially in the CaTiO<sub>3</sub> crystalline structure, as it was discussed in detail in a previous work [8]. As shown in Fig. S3, the calculated band gap value for pristine CaTiO<sub>3</sub> appears to be similar to those reported previously, being at about 3.56 eV [16]. On the other hand, the  $Er^{3+}$  doped photocatalyst exhibited a slightly lower value around 3.46 eV. The decrease of the optical band gap would be due to



Fig. 4. TRMC signal for undoped and  ${\rm Er^{3+}}$  doped  ${\rm CaTiO_3}$  photocatalysts after excitation at 320 nm.

the localized gap states induced by Ti<sup>3+</sup> and/or oxygen vacancies in the semiconductor [17]. Regarding the surface area, both samples show low values ( $\leq 1 \text{ m}^2/\text{g}$ ). The erbium content in the doped sample has been supported by chemical analysis using the ICP-OES technique, where the relative amount of erbium with respect to the titanium is in accordance with the nominal value. Also, the photocatalysts showed a well-defined prism-like morphology, similar to the previously reported by our research group, see Fig. 1 [18]. The presence of urea and NaOH in the preparation procedure provides the formation of CaTiO<sub>3</sub> with exposed (111) and (202) planes growing in the [121] direction.

Photocatalytic H<sub>2</sub> production for undoped and doped CaTiO<sub>3</sub> under UV light irradiation is illustrated in Fig. 2a. The obtained results showed that the  $\text{Er}^{3+}$  doped sample has a reaction rate of 5.72 mmol h<sup>-1</sup> g<sup>-1</sup> while pristine CaTiO<sub>3</sub> exhibits a reaction rate of 4.53 mmol h<sup>-1</sup> g<sup>-1</sup>. These values reveal that the addition of  $\text{Er}^{3+}$  ions provides an increase in the photocatalytic behavior of CaTiO<sub>3</sub>. In order to evaluate the transfer of the photogenerated electrons from the conduction band of the photocatalyst to the reaction medium, the photocatalytic production of superoxide ions (O<sub>2</sub><sup>-</sup>) has been examined under the same UV irradiation conditions, see Fig. 2b. As shown,  $\text{Er}^{3+}$  doped CaTiO<sub>3</sub> exhibits a high concentration along higher reaction time. Furthermore, undoped CaTiO<sub>3</sub> shows a lower rate under same conditions, which can be considered as clear evidence of the higher photocatalytic behavior of the  $\text{Er}^{3+}$  doped material.

Recently, an Er<sup>3+</sup> doped TiO<sub>2</sub> system has been reported with enhanced photocatalytic properties in the liquid-phase degradation of phenol, methylene blue and gas-phase photo-oxidation of toluene [13]. As well as our system, the improved photoactivity has been explained in terms of the dopant agent, where  $\mathrm{Er}^{3+}$  ions could also be reduced to  $Er^{2+}$  by trapping an electron under UV excitation, and thus the  $Er^{2+}$  species would react with the O<sub>2</sub> providing a spatial separation of the electron-hole pair (see Fig. S4). In this sense, Betenelli et al. argued that a small fraction of the trapping-detrapping process would be responsible for the lowering of the diffusion coefficient of the photogenerated electrons [19]. In order to confirm the above discussion, the photoluminescence spectra were carried out at room temperature. Photoluminescence analysis can be considered as a direct approach to understand the separation efficiency of the photogenerated charge carriers [20,21]. In this regard, the higher PL intensity represents a higher extent of an irradiative process associated with the electron-hole pair recombination [22]. Fig. 3 shows the PL spectra of the samples at an excitation wavelength near the absorption edge of the semiconductor  $(\lambda_{exc} = 376 \text{ nm})$ . Both samples exhibit two broad emission bands between 550–640 nm and 650–690 nm. As expected for  $Er^{3+}$  doped CaTiO<sub>3</sub>, the PL intensity decreases respect to the undoped sample. In addition, the doped sample shows well-defined peaks between 520-560 nm, which would correspond to the transitions of the  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  excited states to the  ${}^{4}I_{15/2}$  ground state of the lanthanide ion [8].

The understanding of the charge carrier dynamics in the early stages (femtosecond to picosecond time scales) is a crucial step to design photocatalysts with enhanced photocatalytic features. Thus, the charge-carrier lifetimes in our photocatalysts were determined by means of the Time Resolved Microwave Conductivity technique (TRMC) [23]. It is a contactless method based on the measurement of the change of the microwave power reflected by a sample induced by pulsed laser illumination. The relative change of the reflected microwave power is proportional to the conductivity of the sample. The TRMC signal allows following directly the decay of the number of electrons and of the holes after the laser pulse by recombination or trapping of the charge-carriers. Excess energy facilitates the migration of the charge-carriers to the surface providing a better response signal. Therefore, we deliberately chose to excite the samples at 320 nm (above bandgap excitation). Taking into account that trapped species have a small mobility that can be neglected, the TRMC signal gives a direct measurement of the lifetime of the free charge-carriers created in the

conduction band of the semiconductor [24]. From the corresponding TRMC data, it is noted that the undoped CaTiO<sub>3</sub> shows a higher maximum intensity I<sub>max</sub>, than the erbium doped sample, see Fig. 4 (inset graph). This phenomenon may indicate that the presence of  $Er^{3+}$  ions provides a fast capturing of the photogenerated electrons [25]. Furthermore, normalized data is displayed in the above Figure. The obtained data show that both samples have different decay profiles. The  $Er^{3+}$ doped sample displays a slower signal decay compared to the undoped sample. In this case, it would correspond to slower recombination phenomena, it means to longer charge-carrier lifetimes, reinforcing the assumption that the incorporation of erbium acts as an electron scavenging. In this manner, in the doped phase the charge-carriers have more time to migrate to the surface, increasing the photocatalytic performance [24].

#### 4. Conclusions

In summary, erbium-doped CaTiO<sub>3</sub> photocatalyst has been prepared by means of a microwave-assisted hydrothermal method. This doped material showed an excellent photocatalytic performance in the production of H<sub>2</sub> under UV irradiation compared with the pristine CaTiO<sub>3</sub>. The possible explanation about this improved photoactivity can be related with the long-lived charge-carriers in the doped semiconductor. The results from PL and TRMC provide a clearly evidence of the long life time of the charge-carriers in the Er<sup>3+</sup>- CaTiO<sub>3</sub> sample.

#### Acknowledgments

S. Obregón thanks CONACYT (México) for the concession of a Repatriation Grant (application No. 259649). Financial support from the CNRS, ECOS-Nord M11-P02 project (CNRS-CONACYT bilateral project) is highly acknowledged. Also, authors appreciate the grants 369647, 356872, 290752 and 216315 from CONACYT (México). M.G. Méndez-Medrano acknowledges Campus France for the Eiffel Excellence Scholarship.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2016.06.002.

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