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Long-lived photoinduced charge-carriers in Er^{3+} doped $CaTiO_3$ for photocatalytic H_2 production under UV irradiation

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ABSTRACT

The incorporation of Er^{3+} ions in the $CaTiO_3$ structure provides an enhanced H_2 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 $CaTiO_3$ compared to the undoped $CaTiO_3$.

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].

$CaTiO_3$ 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_2, $CaTiO_3$ and its doped derivatives have shown to exhibit photocatalytic activity [8]. For instance, Shimura et al. have previously reported the 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 Er^{3+} ion, which has been reported in other photocatalysts such as TiO_2 and $BiVO_4$ [13,14]. In this communication, we describe the preparation of an Er^{3+} doped $CaTiO_3$ photocatalyst with enhanced H_2 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_2 powder was placed in a Teflon vessel, while the stoichiometric amount of $CaCl_2$ (Sigma Aldrich, ≥93%) was dissolved in 10 mL

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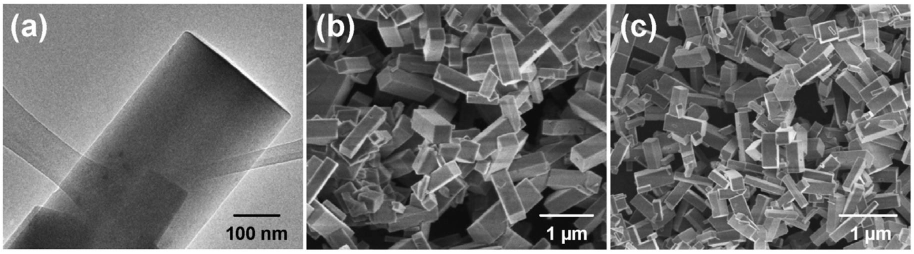

Fig. 1. (a–b) TEM and SEM images of undoped $CaTiO_3$; (c) SEM image of Er^{3+}-doped $CaTiO_3$.

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_2. 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+}-$CaTiO_3$ photocatalyst was performed in the same way, where the $ErCl_3{}^\circ 6H_2O$ 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+}-$CaTiO_3$ system [8].

2.2. Materials characterization

X-ray diffraction (XRD) patterns were obtained using a D8 Bruker Advance diffractometer with Cu Kα 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^{3+} doped $CaTiO_3$ 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 $H_2PtCl_6 \cdot 6H_2O$ (ACS reagent, ≥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.

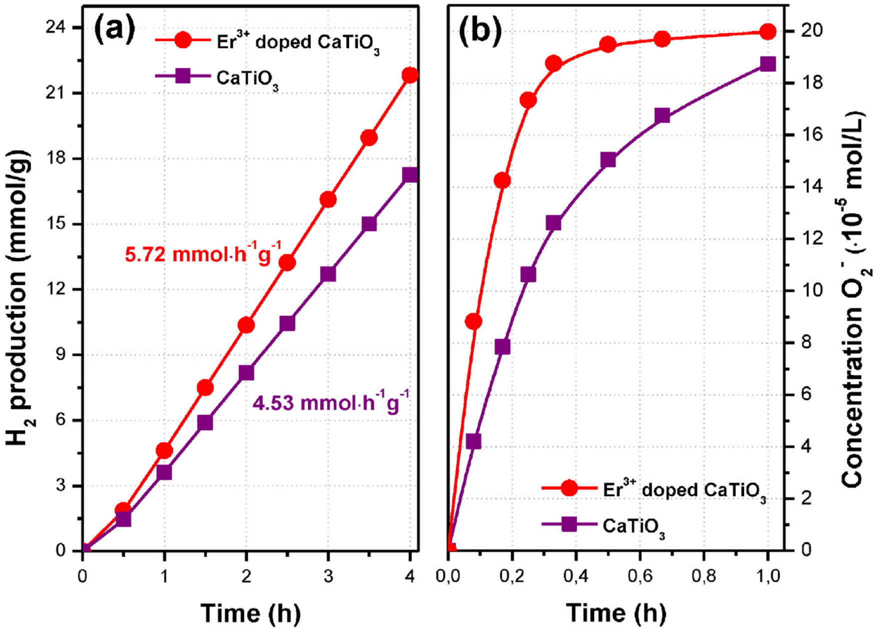

Fig. 2. (a) Photocatalytic H_2 production and (b) production of superoxide ions (O_2^-) by undoped and Er^{3+} doped $CaTiO_3$ photocatalysts.