Applied Catalysis B: Environmental 152–153 (2014) 328–334

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Excellent photocatalytic activity of Yb^{3+}, Er^{3+} co-doped $BiVO_4$ photocatalyst

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ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form 22 January 2014
Accepted 27 January 2014
Available online 2 February 2014

Keyword:
Erbium
Ytterbium
$BiVO_4$
Photocatalysis
Up-conversion
Methylene Blue
O_2 evolution

ABSTRACT

Ytterbium-Erbium co-doped $BiVO_4$ have been synthesized by means of a surfactant free hydrothermal method having good photoactivities under sun-like excitation for the degradation of *Methylene Blue* and O_2 evolution reactions. From the structural and morphological characterization it has been stated that the presence of Yb^{3+} and Er^{3+} induces the stabilization of the tetragonal phase probably due to its substitutional incorporation in the $BiVO_4$ lattice. The occurrence of the Yb^{3+},Er^{3+} co-doped monoclinic-tetragonal $BiVO_4$ heterostructure induces the higher photocatalytic activities. The best photocatalytic performance was attained for the sample with 1:4 Er^{3+}:Yb^{3+} ratio. The observed NIR photoactivity clearly denotes the occurrence of an up-conversion mechanism involved in the overall photocatalytic process.

1. Introduction

The recent research activity within heterogeneous photocatalysis is focused in the development of novel alternative materials to traditional TiO_2 capable to use of sunlight as the green energy source [1,2]. In this sense, bismuth vanadate (m-$BiVO_4$) has been found to be a promising candidate used as well as in water splitting and organic contaminants decomposition under visible-light irradiation [3,4]. From different studies reported it has been stated that the properties of $BiVO_4$ are strongly dependent on its morphology and microstructure [5,6]. In this sense, the best visible-light-driven photocatalytic performance was achieved for monoclinic $BiVO_4$. This is due to the effective hybridization of Bi *6s* with O *2p* to form the valence band leading to a narrower band gap (ca. 2.4 eV) with respect to the tetragonal $BiVO_4$ one (ca. 3.0 eV). This band configuration allows extending the absorption to the visible range.

A novel challenging approach to the visible light efficient utilization would consist on the assembly of the photocatalytic material with a luminescence material [7–10]. The mechanism involved within this complex configuration is based on increasing the number of incoming radiation photons absorbed by the photocatalyst provided by the luminescence emission. Thus, an up-converting luminescent material would absorb low energy radiation from visible or Near-IR (NIR) and emit higher energy radiation (i.e. in the visible and/or UV). Several examples of this cooperative photocatalytic-luminescence mechanism have been successfully reported [11–14]. We have also stated that Er^{3+}-doping on $BiVO_4$ clearly stabilizes the tetragonal structure, subsequently exalting the luminescence properties of this material [15]. A tentative supportive mechanism has been proposed. From those results, we proposed that the presence of Er^{3+} doping into TiO_2 as host matrix favors a double mechanism, under UV and NIR excitation.

In the present paper, we describe the substantial improvement obtained by Yb^{3+},Er^{3+} co-doping for *MB* degradation and O_2 evolution reactions. The combination of these two lanthanides ions with specific incidence over the structural, electronic and luminescence features of the photocatalyst clearly affects the final photocatalytic activity. The correlation between different structural and electronic techniques with the photoactivities under different irradiation conditions would provide a possible explanation about the role of this co-doping.

2. Experimental

2.1. Samples preparation

The $BiVO_4$ samples were prepared by a hydrothermal method. First, 5 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ (Sigma-Aldrich, ≥98.0%) were dissolved in 10 mL of glacial acetic acid at room temperature. Then, the stoichiometric amount of $Er(NO_3)_3$ and $Yb(NO_3)_3$ was also

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http://dx.doi.org/10.1016/j.apcatb.2014.01.054

dissolved in this bismuth solution. While the amount of erbium was fixed at 0.75 at%, ytterbium loading varies from 1:1 to 1:10 Er:Yb ratio. A second aqueous solution was prepared by dissolving the corresponding stoichiometric amount of NH_4VO_3 (Sigma-Aldrich, ≥99.0%) in 60 mL of hot distilled water. Afterwards, the ammonium metavanadate solution was added to the lanthanide-bismuth nitrate aqueous solution and the process was accompanied with a vigorous stirring. The pH of the obtained suspension was adjusted to 9.0 by adding concentrated NH_4OH (13 mol L^{-1}). The slurry was encased in a Teflon vessel and heated in oven at 140 °C for 20 h. The obtained precipitate was then cooled until room temperature, filtered and repeatedly washed and dried overnight at 120 °C. Afterwards, thus obtained samples were submitted to a further calcination treatment at 300 °C for 2 h.

2.2. Materials characterization

BET surface area and porosity measurements were carried out by N_2 adsorption at 77 K using a Micromeritics 2010 instrument.

X-ray diffraction (XRD) patterns were obtained using a Siemens D-501 diffractometer with Ni filter and graphite monochromator. The X-ray source was Cu Kα radiation (0.15406 nm). Rietveld analyses were performed by using XPert HighScore Plus software over selected samples. The diffraction patterns were recorded from 2θ 10° to 120° with step of 0.017° and 400 s per step.

Micro-Raman measurements were performed using a LabRAM Jobin Yvon spectrometer equipped with a microscope. Laser radiation ($\lambda = 532$ nm) was used as excitation source at 5 mW. All measurements were recorded under the same conditions (2 s of integration time and 30 accumulations) using a 100× magnification objective and a 125 mm pinhole.

The morphology of samples was followed by means of field emission-SEM (Hitachi S 4800). The samples were dispersed in ethanol using an ultrasonicator and dropped on a copper grid.

UV–vis spectra (Shimadzu, AV2101) were recorded in the diffuse reflectance mode (R) and transformed to a magnitude proportional to the extinction coefficient (K) through the Kubelka–Munk function, $F(R\infty)$. Samples were mixed with $BaSO_4$ that does not absorb in the UV–vis radiation range (white standard). Scans range was 240–800 nm.

The excitation and emission spectra of the catalysts were recorded at ambient temperature in a Horiba Jobin-Yvon Fluorolog3 spectrofluorometer operating in the front face mode operating with a 1.5 nm slit. The up-conversion optical measurements were performed for powdered pressed samples using a Jenoptik laser diode source at 980 nm. The resulting luminescence was dispersed by using an ARC Spectrapro 500-I monochromator and then detected with a photomultiplier tube.

2.2.1. Photocatalytic experimental details

Methylene Blue (*MB*) oxidation reactions were performed using a batch reactor (250 mL) using an arc lamp source (Oriel Instruments) equipped with an Hg-Xe lamp of 200 W. In the oxidation tests, an oxygen flow was employed as to produce a homogenous suspension of the catalyst in the solution. Before each experiment, the catalysts (1 g L^{-1}) were settled in suspension with the *MB* solution (150 mL) for 15 min. The evolution of the initial *MB* concentration (ca. 10 ppm) was followed through the evolution of the characteristic 664 nm band using a centrifuged aliquot ca. 2 mL of the suspension (microcentrifuge Minispin, Eppendorf). Reaction rates were calculated assuming a first order kinetic. In order to distinguish the different contributions of the different ranges of the lamp spectrum, visible and NIR photocatalytic experiments were performed. Thus for visible photocatalytic runs UV ($\lambda < 420$ nm) and IR ($\lambda < 800$ nm) cut-off filters were employed. Additionally, for NIR experiments, we use a 150 W IR lamp (Philips PAR38). The intensity of the incident UVA and visible light on the solution was measured with an HD2302 photometer (Delta OHM) using LP 471 UVA and LP 471 RAD sensors (spectral responses 315–400 nm and 400–1050 nm, respectively). The intensity of the lamp under different irradiation conditions is summarized in Table 1.

Table 1
Lamp irradiance (W/m^2) for different lamps used in the photocatalytic experiments.

Luxometer sensor	200 W Xe lamp		150 W IR lamp
	UV–vis–IR	Visible	
LP471 UVA (315–400 nm)	83	0.2	0.2
LP471 RAD (400–1050 nm)	542	170	1140

The photocatalytic activities of the samples were also evaluated for the oxygen evolution reaction from water in an $AgNO_3$ aqueous solution (0.02 M). The reaction media was continuously thermostated at 23–25 °C to prevent any significant evaporation of the solvent and discard any eventually temperature effect. The catalyst suspension (1 g L^{-1}) was firstly degassed with an N_2 stream (150 mL min^{-1}) for 30 min. After that the N_2 flow was settled at 15 mL min^{-1} and stabilized for 15 min. This nitrogen flow was used to displace the oxygen produced from the photoreactor headspace towards the GC measuring system. Then, the lamp (200 W Hg-Xe lamp, Oriel Instruments) was switched on and the effluent gases were analyzed to quantify O_2 production by gas chromatography (Agilent 490 micro GC) using a thermal conductivity detector connected to a Molsieve 5 A and Pora-PLOT Q columns.

3. Results and discussion

The structural information derived from the XRD patterns states that the initial monoclinic structure of $BiVO_4$ (*PDF* 75-1866) changes to a phase mixture when erbium is incorporated. Other phases such as $ErVO_4$ or $YbVO_4$ have not been detected. The stabilization of the tetragonal phase (*PDF* 14-0133) upon erbium doping was already reported in previous papers [15,16]. Moreover, the incorporation of different ytterbium amounts induces to an additional appearance of the tetragonal scheelite structure (Fig. 1a). From these results we can state that upon Yb^{3+},Er^{3+} doping a clear monoclinic to tetragonal transformation is taking place, being this later the predominant one as Er^{3+}:Yb^{3+} ratio is higher than 1:2 (Fig. 1b). At the same time, it is worthy to note that increasing the doping level a progressive decrease in the crystallite size is observed, which is in accordance with the tetragonal stabilization (Fig. 1c).

From Rietveld analysis it can be also pointed that the tetragonal cell is strongly affected by ytterbium incorporation (Table 2). This fact was already stated for Y^{3+} and Er^{3+} doping [15,17]. Thus, by following the evolution of the tetragonal cell parameters and volume, it can be noted that the tetragonal cell suffers a progressive contraction with increasing Yb^{3+} content. As a result, and taking into account the difference in ionic radii of bismuth and ytterbium (117 pm vs. 101 pm, respectively) [18], ytterbium incorporation would be achieved by considering the substitution of these doping ions in bismuth positions. On this basis, once the tetragonal phase is favored by lanthanides presence, both erbium and ytterbium ions would naturally occupy the Bi^{3+} positions.

The Raman spectra of Yb^{3+},Er^{3+} co-doped $BiVO_4$ also support the monoclinic to tetragonal phase transition as Yb^{3+} ratio increases (Fig. 2). Thus, it can be noticed the appearance of the ν_s(V–O) located at ca. 850 cm^{-1} corresponding to the tetragonal phase close to the band at 820 cm^{-1} assigned to the monoclinic one. Additionally, the disappearance of the $\delta(VO_4{}^{3-})$ doublet of the monoclinic phase is also an evidence of this phase transition. The occurrence of Er^{3+} ion favors the appearance of strong luminescence