Improved O₂ evolution from a water splitting reaction over Er³⁺ and Y³⁺ co-doped tetragonal BiVO₄

S. Obregón and G. Colón*

Erbium-yttrium co-doped BiVO₄ with a tetragonal structure is synthesized by means of a surfactant free hydrothermal method. The studied photocatalyst shows good photoactivity under sun-like excitation for the degradation of methylene blue (MB) and for O₂ evolution. From structural and morphological characterization, it has been stated that the presence of lanthanides induces the stabilization of the tetragonal phase. This is probably due to the substitutional occupation that occurs in the BiVO₄ lattice. The photocatalytic performance under visible-NIR radiation clearly evidences the occurrence of an up-conversion process involved in the overall photo-electronic mechanism. The tetragonal phase Er₀.0075,Y₀.03Bi₀.9625O₄ system gives the highest O₂ evolution rate (425 μmol g⁻¹ h⁻¹) under sun-like excitation, being 8 times higher than that attained for m-BiVO₄ (53 μmol g⁻¹ h⁻¹).

1. Introduction

Nowadays, the recent socioeconomic demands concerning energy and environmental pollution have led to the progress of new green technologies such as photocatalysis.¹,² Within this frame, in the last few years those working on heterogeneous photocatalysis have focused their attention toward the development of novel alternative materials to traditional TiO₂, which are capable of using sunlight as a green energy source.³,⁴ Since the discovery of photocatalytic water cleavage, plenty of effort has been put into developing new photocatalysts for overall water splitting, and some excellent results have been obtained.⁵,⁶ Nevertheless, the efficiencies achieved are still far from those required for practical applications. A typical approach to accomplishing overall water splitting is to design a two coupled photoreaction called a Z-scheme system.⁷,⁸ While H₂ production from aqueous solution containing sacrificial reagents has been demonstrated to be quite an efficient process, the O₂ production semi-reaction still remains a challenging redox process.⁹ Hence, the synthesis of a highly active photocatalyst for the O₂ evolution reaction is quite important for enhancing the efficiency of solar-hydrogen conversion. In this sense, it has been stated that BiVO₄ is one of the most active systems for this reaction.¹⁰,¹¹ This is due to its relatively low band gap (2.4 eV for monoclinic BiVO₄) and the adequate position of valence and conduction bands as compared to the redox potential for water oxidation. As is widely known, the photocatalytic properties of BiVO₄ are strongly dependent on its morphology and microstructure.¹²–¹⁴ Among the three main crystalline phases described (monoclinic scheelite, tetragonal zircon, and tetragonal scheelite), the monoclinic phase (m-BiVO₄) appears as the only one which shows a high photoactivity for the O₂ evolution reaction under visible-light irradiation.¹⁵–¹⁷ This is due to the particular structure of the valence band (which is formed by Bi 6s orbitals or a hybrid orbital of Bi 6s and O 2p) and the conduction band (formed by a V 3d orbital). This band configuration is responsible for its narrow band gap (ca. 2.4 eV) compared to 3.0 eV exhibited by the tetragonal phase.

A novel challenging approach, which would use solar light as efficiently as possible, consists of the assembly of a photocatalyst with a luminescent material.¹⁸–²¹ Within this configuration we have recently described the assembly of TiO₂ with Er³⁺ acting as the up-converting doping cation.²² From those results, we proposed that the presence of Er³⁺ doped into TiO₂ as a host matrix favors a double mechanism, under UV and vis-NIR excitation. We have also stated that Er³⁺-doping on BiVO₄ clearly stabilizes the tetragonal structure.²³ In this sense, a tentative cooperative mechanism has been proposed. Tetragonal phase stabilization has been also achieved by yttrium doping.²⁴ The occurrence of a heterostructured BiVO₄ formed by a tetragonal and monoclinic phase mixture has been demonstrated to have a clear beneficial effect on the final photoactivity of the system. Fan et al. reported that monoclinic/tetragonal heterostructured BiVO₄ in particular is expected to promote the separation of photo-induced electron–hole pairs.²⁵ These results clearly show that
the behaviour of photoinduced charges is markedly dependent on the BiVO₄ crystalline phases. Moreover, the presence of an interface in the monoclinic/tetragonal heterophase provides a spatial condition for charge transfer. This favours the separation of photoinduced electron–hole pairs, and changes the migration direction of the photoinduced carriers.

In the present paper, we describe the substantial improvements obtained by Er and Y co-doping for the O₂ evolution reaction. The combination of these two lanthanide ions with specific influences over the structural and electronic features of the photocatalyst clearly affects its final photocatalytic activity. The correlation between different structural and electronic techniques with the photoactivity under different irradiation conditions would provide a possible explanation of the role of this co-doping.

2. Experimental

2.1 Sample preparation

The BiVO₄ samples were prepared by a surfactant free hydrothermal method. First, 5 mmol of Bi(NO₃)₃·5H₂O (Sigma-Aldrich, ≥98.0%) and a stoichiometric amount of Er(NO₃)₃ (0.75 at%) were dissolved in 10 mL of glacial acetic acid at room temperature. A second aqueous solution was prepared by dissolving the corresponding stoichiometric amount of NH₄VO₃ (Sigma-Aldrich, ≥99.0%) or Y(NO₃)₃ (3.0 at%) in 60 mL of hot distilled water. Afterwards, the ammonium metavanadate solution was added to the erbium–bismuth nitrate aqueous solution and the process was accomplished by vigorous stirring. The pH of the obtained suspension was adjusted to 9.0 by adding concentrated NH₄OH (13 mol L⁻¹). The slurry was encased in a Teflon vessel and heated at 140 °C for 20 hours. The obtained precipitate was then cooled until it reached 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.

Tetragonal BiVO₄ (t-BiVO₄) has been also prepared as reference material. In this case we followed a similar procedure as for the m-BiVO₄, but using triethylamine as precipitating agent instead.

2.2 Materials characterization

BET surface area and porosity measurements were carried out by N₂ adsorption at 77 K using a Micromeritics 2010 instrument.

The chemical composition of the samples was studied by ICP analysis using a Horiba Jobin Yvon, Ultima 2.

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 using XPert HighScore Plus software for selected samples. The diffraction patterns were recorded with a 2θ of 10° to 120° with a step of 0.017° and 400 s per step. Crystallite sizes were obtained from Rietveld refinement.

The UV diffuse reflectance spectra were measured using an UV-vis spectrophotometer equipped with an integrating sphere (JASCO V-570). The reference sample used was a BaSO₄ coated standard pattern.

Micro-Raman measurements were performed using a LabRAM Jobin Yvon spectrometer equipped with a microscope. Laser radiation (λ = 532 and 780 nm) was used as the excitation source at 5 mW. All measurements were recorded under the same conditions (4 s of integration time and 10 accumulations) using a 100× magnification objective and a 125 mm pinhole.

2.3 Photocatalytic tests

MB oxidation reactions were performed using a batch reactor (150 mL) with a 200 W Xenon lamp. The intensity of the incident light on the solution measured with a HD2302 photometer (Delta OHM) was 90 W m⁻² and 500 W m⁻² for UV and vis-NIR spectral ranges, respectively. For this scope, an LP 471 UVA sensor with a spectral response of 315–400 nm and an LP 471 RAD sensor (spectral response 400–1050 nm) were used. The vis-NIR runs were performed using a cut-off filter (λ > 420 nm) which assured the complete withdrawal of UV incident photons. In the oxidation tests, an air flow was employed to produce a homogenous suspension of the photocatalyst in the solution. Before each experiment, the catalysts (1 g L⁻¹) were settled in suspension with the reagent mixture for 15 min. The blank experiment was performed without a catalyst, and no dye degradation was observed after 2 hours. The evolution of the initial MB (ca. 10 ppm) concentration was followed through the evolution of the characteristic 664 nm band, using a centrifuged aliquot of ca. 2 mL of the suspension (microcentrifuge Minispin, Eppendorf). The pH of the suspension was unchanged during the photo-degradation tests (pH ~ 6.5) for all BiVO₄ samples. Reaction rates were calculated assuming first order kinetics.

The photocatalytic activity of the samples was also evaluated for the photocatalytic oxygen evolution reaction from water in an AgNO₃ aqueous solution (0.02 M). The reaction media was continuously thermostated at 23°–25 °C to prevent any significant effect of temperature. The catalyst suspension (1 g L⁻¹) was firstly degassed with a N₂ stream (150 mL min⁻¹) for 30 min. After that, the N₂ flow was settled at 15 mL min⁻¹ and stabilised 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 analysed to quantify O₂ production by gas chromatography (Agilent 490 micro GC), using a thermal conductivity detector connected to Molsieve 5A and Poraplot Q columns.

3. Results and discussion

The XRD patterns shown in Fig. 1 depict the evolution of the crystalline phase upon the incorporation of different dopant ions. As can be observed, the original monoclinic structure...
(PDF 75-1866) exhibited by bare BiVO₄ is progressively lost as Er³⁺ and Y³⁺ are incorporated. The tetragonal phase (PDF 14-0133) stabilization is more pronounced when Y³⁺ is present. This marked stabilization is related to the higher doping level by yttrium in comparison to erbium. Finally, when both lanthanides are present only the tetragonal phase appears. For comparison we prepared a tetragonal reference sample, which exhibits a small fraction of the monoclinic phase.

The structural features of the studied samples are summarized in Table 1. In the case of single doping, a clear tetragonal stabilization is observed. By observing the monoclinic and tetragonal cell volumes, it becomes apparent that the incorporation of the dopant appears quite different. Thus, while the monoclinic unit cell volume exhibits a slight increase as the lanthanides are present only the tetragonal phase appears. For comparison we prepared a tetragonal reference sample, which exhibits a small fraction of the monoclinic phase.

![Image](48x540 to 284x735)

Fig. 1 XRD patterns for different BiVO₄ catalysts obtained by hydrothermal synthesis at 140 °C for 20 h.

Raman spectroscopy is an effective tool for the structural characterization of materials. In Fig. 2 we show the Raman spectra for the studied samples registered upon green laser excitation. The monoclinic BiVO₄ Raman spectrum is characterized by the presence of typical bands at 210, 324, 366, 640, 710 and 825 cm⁻¹.²⁷ These two latter bands are associated with stretching modes corresponding to the V–O bond, and provide valuable structural information.²⁸ For lanthanide doped samples, the monoclinic-to-tetragonal transition by the ν₃ (V–O) band shift from 820 cm⁻¹ to 850 cm⁻¹, and the disappearance of the δ (VO₄)²⁻ doublet of the monoclinic phase, can be seen (Fig. 2a). As has previously been reported, Raman spectra containing rare earth ions are strongly affected by the luminescence emission. Thus, Er³⁺-containing samples exhibit noticeable luminescence emission bands (Fig. 2b). It is worth noting that these luminescence bands appear highly intense for the co-doped BiVO₄ compared with Er³⁺-BiVO₄. This would indicate that the presence of yttrium improves upon the luminescent properties of erbium to a certain extent. This fact has been previously reported for Er³⁺-Y³⁺ co-doped TiO₂.²⁹ Thus, Ting et al. argued that the distorted local structure of the Er³⁺ ions due to the presence of the yttrium could increase the probability of a normally forbidden intra-4f transition, improving the photoluminescence process. In order to examine the structural evolution of the BiVO₄ samples without the interference of erbium luminescence emission, we performed Raman spectroscopy by red laser excitation (Fig. 3). From these spectra, the monoclinic-to-tetragonal transition due to lanthanide doping can be clearly seen. Thus the ν₃ (V–O) stretching mode at 825 cm⁻¹ for the monoclinic structure appears with a shoulder at a higher Raman shift when erbium or yttrium is incorporated. This evidently denotes the co-existence of both phases, as was suggested by the XRD results. Moreover, the co-doped BiVO₄ clearly shows a single band at 850 cm⁻¹ denoting the exclusive presence of a tetragonal phase. From the Raman shift position corresponding to the symmetric stretching mode, it is possible to attain information about the V–O bond length in the VO₄⁻ tetrahedron through the following expression:³⁰

### Table 1 Structural characterization of the BiVO₄ and Er³⁺,Y³⁺ doped catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Monoclinic a</th>
<th>Monoclinic b</th>
<th>Monoclinic c</th>
<th>Microstrain</th>
<th>Tetragonal a = b</th>
<th>Tetragonal c</th>
<th>Monoclinic cell volume (Å³)</th>
<th>Tetragonal cell volume (Å³)</th>
<th>Tetragonal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-BiVO₄</td>
<td>5.2015</td>
<td>5.1008</td>
<td>11.7198</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>310.95</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td>t-BiVO₄</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.005</td>
<td>7.3047</td>
<td>6.4613</td>
<td>—</td>
<td>—</td>
<td>344.6</td>
</tr>
<tr>
<td>Er³⁺-BiVO₄</td>
<td>5.2220</td>
<td>5.1031</td>
<td>11.7080</td>
<td>0.049</td>
<td>7.2969</td>
<td>6.4533</td>
<td>312.00</td>
<td>344.6</td>
<td>55</td>
</tr>
<tr>
<td>Y³⁺-BiVO₄</td>
<td>5.2062</td>
<td>5.1007</td>
<td>11.7200</td>
<td>0.206</td>
<td>7.2976</td>
<td>6.4540</td>
<td>311.23</td>
<td>343.9</td>
<td>68</td>
</tr>
<tr>
<td>Er³⁺,Y³⁺-BiVO₄</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.153</td>
<td>7.2955</td>
<td>6.4335</td>
<td>—</td>
<td>343.8</td>
<td>100</td>
</tr>
</tbody>
</table>
ν(cm⁻¹) = 21349e⁻¹.9176R(Å)

In Table 2 we present the calculated V–O bond distances (R) for bare BiVO₄ and the doped systems. By observing the calculated bond lengths it is worth noting that while the incorporation of erbium does not induce a significant distortion in the VO₄³⁻ tetrahedron in either the monoclinic or tetragonal structure, yttrium doping induces a slight decrease in both structures. This result is in accordance to the microstrain values for Er³⁺–BiVO₄ shown in Table 1, and could be correlated to the lower ionic radius of Er³⁺ compared to Y³⁺, as well as to the lower erbium doping level. The shorter bond length in yttrium doped systems would indicate a stronger packed tetragonal structure and would affect the lone pair distortion around the bismuth cation. It has been argued that structural distortion is directly proportional to the hole mobility.
In order to study the electronic states of the different systems studied, UV–vis DRS spectra were taken (Fig. 4). As can be seen from the figure, the absorption edges of the doped BiVO₄ samples varied in an order which matched the structural changes discussed above. It can be noticed that t-BiVO₄ shows a small absorption in the visible range. This small contribution denotes the presence of a residual m-BiVO₄ that was previously detected from the XRD results (see Table 1). Even the Er³⁺,Y³⁺–BiVO₄ sample presents a small shoulder in this region, in spite of Rietveld analysis and the Raman spectrum confirming that the monoclinic fraction present was negligible. Accordingly, the different phase compositions of BiVO₄ result in different band gaps (Table 3). As the monoclinic-to-tetragonal transition is taking place, the band gaps tend to shift from the visible region to the UV light region.

Other physicochemical properties such as the chemical composition and surface area of the studied systems are summarized in Table 3. The effectiveness of the doping is supported by chemical analysis using the ICP technique. The relative contents of erbium and yttrium with respect to bismuth are in accordance with the nominal values. Regarding the surface area values, it can be observed that the structural changes are clearly accompanied by a certain modification in the surface area values. As has been widely reported, tetragonal phase BiVO₄ exhibits relatively larger surface area values compared to the monoclinic phase.²³,²⁴

The morphology of BiVO₄ has been extensively reported to be dependent on the preparation route.³³ In our case, bare m-BiVO₄ shows a rod-like morphology (Fig. 5a) while t-BiVO₄ is composed of square-bar particles (Fig. 5b). As the erbium or yttrium ion is incorporated, the morphology of the sample clearly denotes the mixture of the two phases present (Fig. 5c and d).³³ For erbium doping the tetragonal particles present a clear evolution from a square-bar shape toward a thinner acicular morphology. Meanwhile, the monoclinic sample seems to evolve towards a well-defined prism-like morphology. As can be seen, the incorporation of yttrium induces quite a drastic change in morphology. The tetragonal acicular particles seem to decrease in size, showing a rod-like morphology.²⁴ Co-doped BiVO₄ follows the above mentioned evolution and only small rice-like particles appear (200–500 nm length and 100 nm width) (Fig. 5e and f).

In Fig. 6 we show the photocatalytic activity of the studied systems. The incorporation of either an erbium or yttrium ion into the BiVO₄ structure produces a clear improvement in the photodegradation of MB, with Er³⁺–BiVO₄ being slightly more active than Y³⁺–BiVO₄ (Fig. 6a). In both cases, the main crystalline phase was tetragonal, although for Er³⁺–BiVO₄ the monoclinic fraction is slightly higher. The simultaneous Er³⁺ and Y³⁺ doping improves the photocatalytic activity compared to single doped systems, despite the fact that a pure tetragonal phase is present. If we compare the calculated reaction

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Structural features found by Raman characterization for BiVO₄ and Er³⁺, Y³⁺ doped catalysts*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>Raman frequency (cm⁻¹)</td>
</tr>
<tr>
<td></td>
<td>Monoclinic</td>
</tr>
<tr>
<td>m-BiVO₄</td>
<td>824.99</td>
</tr>
<tr>
<td>t-BiVO₄</td>
<td>—</td>
</tr>
<tr>
<td>Er³⁺–BiVO₄</td>
<td>825.13</td>
</tr>
<tr>
<td>Y³⁺–BiVO₄</td>
<td>825.88</td>
</tr>
<tr>
<td>Er³⁺,Y³⁺–BiVO₄</td>
<td>—</td>
</tr>
</tbody>
</table>

* The positions of the most intense bands near 825 cm⁻¹ and 850 cm⁻¹ were determined by fitting to the Lorentzian peak function.
### Table 3  Surface, electronic and photocatalytic characterization for the BiVO₄ and Er³⁺,Y³⁺ doped catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET (m² g⁻¹)</th>
<th>Band gap (eV)</th>
<th>Ln³⁺ content</th>
<th>MB degradation reaction rate (10⁻⁴ s⁻¹)</th>
<th>O₂ evolution (μmol h⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Monoclinic</td>
<td>Tetragonal</td>
<td>Er³⁺/Bi³⁺</td>
<td>Y³⁺/Bi³⁺</td>
</tr>
<tr>
<td>m-BiVO₄</td>
<td>&lt;1</td>
<td>2.39</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>t-BiVO₄</td>
<td>5</td>
<td>2.86</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Er³⁺–BiVO₄</td>
<td>2</td>
<td>2.39</td>
<td>2.75</td>
<td>0.006</td>
<td>—</td>
</tr>
<tr>
<td>Y³⁺–BiVO₄</td>
<td>3</td>
<td>2.38</td>
<td>2.77</td>
<td>—</td>
<td>0.033</td>
</tr>
<tr>
<td>Er³⁺,Y³⁺–BiVO₄</td>
<td>5</td>
<td>—</td>
<td>2.83</td>
<td>0.006</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Fig. 5  FESEM images of the different BiVO₄ systems: a) bare m-BiVO₄; b) bare t-BiVO₄; c) Er³⁺–BiVO₄; d) Y³⁺–BiVO₄; e) Er³⁺,Y³⁺ co-doped BiVO₄; f) a TEM image of the Er³⁺ and Y³⁺ co-doped BiVO₄.
rates of this later sample with the corresponding rates for m-BiVO4 and t-BiVO4, a dramatic enhancement is displayed (Table 3). For the Er3+ and Y3+ co-doped sample the surface area value is slightly higher than for m-BiVO4. However, a comparison with t-BiVO4 clearly shows that the controlling parameter in the photoactivity is something other than the BET surface area.

In order to elucidate the specific role of erbium on the reaction mechanism, we performed the degradation reaction under vis-NIR irradiation (Fig. 6). As expected, m-BiVO4 shows the best photocatalytic performance while t-BiVO4 shows a negligible photoactivity. However, although all doped systems show a tetragonal-rich structure, their photoactivity under vis-NIR irradiation appears somewhat improved (Table 3). From this result it is clear that – besides the increase of surface area values due to the presence of a tetragonal phase in single doped BiVO4 compared to m-BiVO4 – the particular structural features of the systems (i.e. the monoclinic-tetragonal heterostructure) might be in principle the reason behind the photocatalytic activity enhancement. In this sense, as reported by Fan et al., the monoclinic–tetragonal heterostructured BiVO4 in particular is expected to promote the separation of photoinduced electron–hole pairs.22,23 These authors proposed that enhanced photoactivity would be achieved by the optimization of the electron–hole separation due to the heterostructure formation. On this basis, we could state that the conjunction of morphological and structural features clearly provides a better photocatalytic performance. Moreover, the presence of erbium would also particularly affect the photoelectronic mechanism under vis-NIR excitation, which could explain the better performance of Er3+-BiVO4 compared to Y3+-BiVO4.23 As we have previously reported, a cooperative luminescence effect is observed for Er-doped t-BiVO4, which would explain its vis-NIR photoactivity. In the case of co-doped BiVO4, which exhibits a pure tetragonal structure, the photocatalytic enhancement cannot be associated with the presence of a phase heterostructure. Furthermore, the reaction rate for this system is notably higher than for the single doped systems. Lower photoactivity reported for t-BiVO4 in the literature was explained by considering the wider band gap for this phase. Thus, in our case the increased photoluminescence observed in the Raman spectrum for Er3+,Y3+-BiVO4 compared to that for Er3+-BiVO4 upon illumination with 532 nm laser would suggest the participation of such a luminescence process in the overall mechanism. In summary, the notably enhanced photoactivity observed upon sun-like irradiation would be associated with a double cooperative mechanism. On one hand, yttrium incorporation would affect the conduction band position.31 The participation of the Y 4d orbital in the conduction band hybridization would shift it to a higher position compared to the conduction band for m-BiVO4. Thus, Y3+ would help to improve the photon efficiency, enhancing the UV-photoassisted process by increasing the electron–hole separation driving force. Secondly, the presence of erbium and the associated luminescence up-conversion process could improve the photoefficiency within the vis-NIR region by increasing the number of absorbed photons. A similar effect has already been observed for Er3+ doped TiO2, for which an up-conversion mechanism would be responsible in part for its better photocatalytic behaviour under vis-NIR irradiation.22,34

The durability of the Er,Y–BiVO4 system was evaluated through recycling the used catalyst (Fig. 7). For each cycle, the catalyst was collected by filtration and washed. As can be observed from consecutive degradation cycles, there was no apparent loss of photocatalytic activity across the four cycles performed. The diminution of photocatalytic activity was less than 2%. Therefore, it can be deduced that the Er,Y co-doped BiVO4 has good photostability and reusability which indicates its potential for industrial utilization.

Furthermore, Fig. 8 shows the photocatalytic water oxidation activity of different BiVO4 samples, from an aqueous solution containing AgNO3 as a sacrificial reagent under sunlight irradiation. Despite the fact that our m-BiVO4 does not initially show an excellent photocatalytic performance such
as that reported in ref. 10, O$_2$ evolution of our m-BiVO$_4$ is in the range of other reported bismuth vanadates. 35,36 Moreover, the O$_2$ evolution for different doped BiVO$_4$ catalysts plainly denotes a notably beneficial effect. In all cases, the O$_2$ evolution rates for these samples are markedly improved with respect to bare m- or t-BiVO$_4$ (Table 3). This trend is in accordance with the previous behaviour for the MB photocatalytic degradation reaction, as discussed above. Moreover, the photocatalytic performance shown by the Er$^{3+}$,Y$^{3+}$ co-doped BiVO$_4$ appears significantly enhanced compared to the single doped systems (425 μmol h$^{-1}$ g$^{-1}$ vs. ca. 300 μmol h$^{-1}$ g$^{-1}$). Thus, the calculated reaction rate for the co-doped system is 8 times higher than that for the m-BiVO$_4$ as reported in the present work. By observing the reaction rate for t-BiVO$_4$, this enhancement cannot be exclusively associated with the increase in surface area or a higher UV adsorption. The occurrence of both lanthanide ion dopants leads to a synergistic effect that could be explained by considering their different roles.

4. Conclusions

We have obtained a highly active Er$^{3+}$,Y$^{3+}$–BiVO$_4$ system which exhibits a tetragonal structure. Hydrothermal synthesis leads to homogeneous BiVO$_4$ rice-like nanoparticles ca. 200–400 nm in length. Chemical and structural analysis confirms the incorporation of lanthanide dopant ions into the BiVO$_4$ structure. The photocatalytic activity for methylene blue degradation and for O$_2$ evolution clearly evidences the beneficial effect of doping. Moreover, it is worth noting that the tetragonal phase co-doped BiVO$_4$ shows a significantly higher photoactivity than bare m-BiVO$_4$ and t-BiVO$_4$. From the photocatalytic experiments we tentatively propose a double mechanism which could explain the improved photocatalytic activity of the doped systems. On one hand, the presence of Er$^{3+}$ and Y$^{3+}$ improved the electronic charge separation process, enhancing the UV-photoassisted process. This mechanism is consistent with a classical doping conception, since we used BiVO$_4$ as the host material. Moreover, it can be seen that there is a small contribution of vis-NIR photons to the UV-active tetragonal co-doped BiVO$_4$ in the overall mechanism, probably due to an energy transfer process from the erbium ions. As a result, the Er$^{3+}$,Y$^{3+}$ co-doped BiVO$_4$ shows a notably improved photoactivity compared to the m-BiVO$_4$. By adjusting the band and photon absorption features, we propose a highly active material for O$_2$ evolution from a water splitting reaction.

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References