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## The bismuth oxyhalide family: thin film synthesis and periodic properties

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Bismuth oxyhalides (BiOX, where X = F, Cl, Br, I) are interesting materials due to their layered structure, which can be useful for different applications. In this work, we present the synthesis of the complete BiOX family in the thin film form. The tetragonal phase Bi<sub>2</sub>O<sub>3</sub> film deposited onto a glass substrate was transformed into BiOF, BiOCl or BiOBr by a simple immersion at ambient temperature in a halide (X = F, Cl, Br) containing solution. For these films, a residual phase from the oxide was present and for BiOF another phase (tentatively identified as Bi<sub>7</sub>O<sub>5</sub>F<sub>11</sub>) was present too. For the BiOI film synthesis, an iodine and bismuth containing solution was sprayed onto the glass substrate heated at 275 °C and a pure phase was obtained. Microstructural and morphological characterization was performed by X-ray diffraction and scanning electron microscopy, while the chemical environment was studied by X-ray photoelectron spectroscopy. Optical and photocatalytic properties were also obtained. The physical and chemical characteristics of the BiOX films follow a correlation with the atomic radius of the halogen atom incorporated into the corresponding lattice. All the BiOX films showed a photocatalytic response for the photodiscoloration of indigo carmine dye under simulated sunlight irradiation in an alkaline medium. The photocatalytic reactions occurred via 2 proton–electron transfer from the oxide or oxyhalide to the adsorbed IC dye, favoring its reduction to the corresponding leuco IC form.

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### 1. Introduction

Bismuth is an element which is becoming the protagonist in novel binary, ternary and quaternary compounds. Beyond its use as a lead replacing element in alloys due to its low toxicity, recent investigations have shown its importance in the emerging low-dimensional materials for topological insulators,<sup>1–3</sup> in perovskite structures for energy storage<sup>4</sup> and photovoltaics,<sup>5</sup> and for the design of other functional materials. Besides, bismuth is an abundant metal with a relatively low price, which is attractive for large scale applications.

Among the bismuth-based ternary compounds, bismuth oxyhalides (BiOX, X = F, Cl, Br, I) are a family which have recently attracted attention because of their layered growth that provide interesting potential applications in electronics,

and energy storage.<sup>6–8</sup> This family presents a tetragonal matlockite structure consisting of [Bi<sub>2</sub>O<sub>2</sub>] layers sandwiched between double halide [X] layers, to form [X–Bi–O–Bi–X] layers held by van der Waals interactions through the halogen atom along the [001] direction.<sup>6,9–12</sup> The arrangement of these layers provides a large space for the polarization of the atoms favoring the separation of photo-induced electron–hole pairs. Moreover, the high reactivity of specific facets, such as the {001} facet in BiOCl,<sup>13</sup> has been demonstrated, making them attractive for photocatalysis and photoelectrochemical applications.<sup>14</sup>

There are recent studies reporting the photocatalytic properties of BiOX powders, especially for X = Cl, Br and I.<sup>15–17</sup> There are also studies concerning the synthesis of bismuth oxyhalides as thin films where X = Cl, Br, I either by an aerosol assisted CVD method reported by Bhachu *et al.*<sup>9</sup> or by a sol–gel method reported by Shen *et al.*<sup>18</sup> In both cases, BiOX films showed photoactivity with BiOBr being the most active, but none of them included BiOF. BiOCl is the most studied bismuth oxyhalide, either in powder<sup>8,19,20</sup> or thin film form.<sup>21–24</sup> All reports show faceted laminar growth, which in some cases assembles to form flower-like structures. A diversity of methods have been used to individually obtain each halide of the family as thin films, such as MOCVD,<sup>24</sup> hydro-

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lysis<sup>23</sup> or electrochemical methods<sup>22</sup> for BiOCl, alcoholysis-coating methods for BiOBr,<sup>25</sup> or solvothermal synthesis for BiOI.<sup>26</sup> Unlike the synthesis of Bi<sub>2</sub>O<sub>3</sub>, in which the material's properties strongly depend on the growth technique, obtaining the oxyhalides seems relatively simple even at room temperature, especially with the use of wet methods. Previously, the transformation of a  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> film into pure BiOCl due to its contact with a HCl solution was reported.<sup>27</sup> This was a favorable reaction ( $\Delta E = -569.8 \text{ kJ mol}^{-1}$ ), considering the difference between the Gibbs energy of the products and the reactants. Due to its reactivity, the Cl<sup>-</sup> ion penetrated the Bi<sub>2</sub>O<sub>3</sub> lattice and substituted the O atom, changing the compound and its structure.

In this work, we report relatively simple methods to obtain the complete BiOX film family. The BiOF, BiOCl, and BiOBr thin films were chemically transformed from original spray deposited tetragonal Bi<sub>2</sub>O<sub>3</sub> by an immersion procedure of the films in the corresponding halogenated solution. The degree of transformation strongly depended on the nature of the solutions. For the BiOI films, a direct atomization method was used. After a complete characterization of the different films, we observed periodic behaviors of the structural, morphological and optical properties with respect to the atomic radius of each halogen. Their photocatalytic activity was tested by the photodiscoloration of an indigo carmine dye solution *via* the formation of leuco indigo carmine under simulated sunlight.

## 2. Experimental details

### 2.1 Synthesis of BiOF, BiOCl and BiOBr films

For the first three ternary compounds of the family, we started from a Bi<sub>2</sub>O<sub>3</sub> film that was obtained by the pneumatic spray pyrolysis method previously reported.<sup>27</sup> In summary, we used bismuth(III) acetate (Bi(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>, 98% from Sigma Aldrich) dissolved in acetic acid (25% of the total solution's volume) at 45 °C under constant stirring for one hour and then added 75% deionized water to obtain a completely transparent homogeneous solution. This solution was sprayed onto clean glass substrates at 450 °C with solution and gas flow rates of 7.7 mL min<sup>-1</sup> and 9.6 L min<sup>-1</sup>, respectively.

Each of the resultant Bi<sub>2</sub>O<sub>3</sub> films were immersed in a chemical bath of the corresponding solution (KBr, HCl and HF) at ambient temperature as indicated in Table 1. As the prepared solutions were corrosive, the films suffered surface

etching, and transformation of the oxide into the oxyhalide was achieved, as shown in the Results section.

### 2.2 Synthesis of BiOI films

The chemical bath method used for the previous samples was not adequate to obtain good quality BiOI films using either ammonium iodide or potassium iodide solutions for the bath. The chemical reactions with the NH<sub>4</sub>I solution produced cracking of the films and diminished its adhesion to the substrate. The films obtained in this way presented a mixture of phases (Bi<sub>2</sub>O<sub>3</sub>, BiOI and non-stoichiometric bismuth oxyiodide) that could not be transformed into pure BiOI. In order to avoid these drawbacks, we decided to deposit this material by spraying a precursor solution containing 0.02 M bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O, >98% Sigma Aldrich) and 0.04 M NH<sub>4</sub>I (% Sigma-Aldrich) dissolved in ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, 99%, Sigma Aldrich).<sup>28</sup> Precursor solutions were manually sprayed onto 275 °C substrates.

### 2.3 Characterization

X-ray diffraction (XRD) patterns were acquired with a Rigaku-Ultima IV system (Cu K $\alpha$  = 1.5406 Å, 40 kV, 44 mA) equipped with a thin film stage. For the identification of the diffraction peaks and the calculation of the lattice parameters, the software PDXL2® was used. Scanning electron microscopy (SEM) was performed on the films to analyze the surface morphology with a JEOL 7600F microscope. The thickness of the films was measured with a Veeco Dektak 150 profilometer. Optical properties were studied by diffuse reflectance UV-Vis spectroscopy (DRS) on a Shimadzu 2600 spectrophotometer using BaSO<sub>4</sub> as a reference. The spectra were converted from reflectance to absorbance by the Kubelka–Munk method to calculate the band gap energy ( $E_g$ ) of the films. X-ray photoelectron spectroscopy (XPS) was performed on the films with an ultra-high vacuum system scanning XPS microprobe PHI 5000 Versa Probe II of Physical Electronics. A monochromated Al K $\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) X-ray source was used at 25 W with 100  $\mu\text{m}$  beam diameter. The surface of each sample was etched for 3 min with 1 kVAr<sup>+</sup> at 55.56 nA mm<sup>-2</sup>. The XPS spectra were acquired at 45° from the surface in a constant pass energy mode (CAE) at  $E_0 = 117.40$  and 11.75 eV for survey and high-resolution spectra, respectively.

### 2.4 Photocatalytic tests

The photocatalytic response of the different BiOX materials was evaluated by the photodiscoloration reaction of an aqueous solution of the organic dye indigo carmine (IC) at a concentration of 5 mg L<sup>-1</sup> and pH ~ 11–12. The pH was adjusted by adding NaOH to reduce the adsorption of IC molecules on the photocatalyst surfaces. Prior to illumination, the samples were kept for 30 minutes in the dark with constant stirring; this time was enough to reach the adsorption–desorption equilibrium. The illumination source was a solar simulator Oriel 96000 (150 W, irradiance of 360 Wm<sup>-2</sup>). The photodiscoloration process was monitored by following the absorbance spectrum of the IC dye as a function of the

**Table 1** Conditions of the chemical baths

| Film material | Chemical bath solution                                  | Immersion time |
|---------------|---|----------------|
| BiOF          | HF (0.03 M) in deionized water                          | 15 min         |
| BiOCl         | HCl (0.15 M) in deionized water                         | 60 min         |
| BiOBr         | KBr (0.1 M) and acetic acid (0.03 M) in deionized water | 90 min         |

irradiation time. The discoloration percentage was calculated as:

$$\text{Discoloration \%} = \left(1 - \frac{A(t)}{A_0}\right) \times 100$$

where  $A(t)$  and  $A_0$  are the absorbance at an irradiation time  $t$  and the initial absorbance, respectively, of the typical band of the IC dye solution ( $\lambda = 610$  nm at pH  $\sim 11$ –12).

## 3. Results

### 3.1 Crystalline structure

Fig. 1 shows the diffraction patterns of the different oxyhalides, including the original  $\text{Bi}_2\text{O}_3$  film that corresponds to the tetragonal crystal structure –named  $\beta$  phase– according to the ICDD PDF no. 01-078-1793. It is worth mentioning that  $\text{Bi}_2\text{O}_3$  presents 6 polymorphs, but under the spray deposition conditions used, only the tetragonal  $\beta$ - $\text{Bi}_2\text{O}_3$  was obtained. When the  $\beta$ - $\text{Bi}_2\text{O}_3$  film was immersed in the HF aqueous solution,  $\text{Bi}_2\text{O}_3$  was transformed into the oxyfluoride, shown in Fig. 1 with peaks indexed from  $\text{BiOF}$  (PDF 01-073-1595), along with another phase, tentatively identified as  $\text{Bi}_7\text{O}_5\text{F}_{11}$  (PDF 050-0003) and some remaining  $\beta$ - $\text{Bi}_2\text{O}_3$ . For the film immersed in HCl, the peaks of  $\text{BiOCl}$  were detected and indexed to the ICDD file no. 01-082-0485; the peak at  $27.9^\circ$  corresponds to residual  $\beta$ - $\text{Bi}_2\text{O}_3$  (\*). For the bromide film, the pattern corresponds to file 01-073-2061 of  $\text{BiOBr}$ , but there is also the presence of the original  $\beta$ - $\text{Bi}_2\text{O}_3$  phase (\*). The sprayed iodide film resulted in the pure  $\text{BiOI}$  phase indexed to the file no. 01-073-2062. In this last case, the residual  $\beta$ - $\text{Bi}_2\text{O}_3$  phase was not detected as the  $\text{BiOI}$  film was formed directly. X-ray photoelectron spectroscopy (XPS) chemical shift data, dis-

cussed below, also confirm the formation of the bismuth oxyhalides.

$\text{Bi}_2\text{O}_3$  belongs to the space group  $P\bar{4}21c$ , and the complete oxyhalide family has a  $P4/nmm$  space group. It is interesting to note that the tetragonal structure remains, but the lattice parameters change, with the increasing atomic radius of the halogen, following the periodic table's trend, as shown schematically in Fig. 2. The obtained lattice parameters coincide with the calculated values reported by A. Ganose *et al.*<sup>12</sup> and Huang *et al.*<sup>29,30</sup> for  $\text{BiOX}$  and by Li *et al.*<sup>31</sup> for  $\beta$ - $\text{Bi}_2\text{O}_3$ , showing very small variations as shown in Table 2. The crystallite size was calculated using Scherrer's formula and the values are given in Table 2. In this case, the average crystal size is smaller for the oxyhalide where the halogen's atomic radius is larger.

### 3.2 XPS analysis

Chemical analysis of the films was performed using the XPS technique. Fig. 3a shows the high-resolution spectra of the halogen peaks corresponding to F 1s, Cl 2p, Br 3d and I 4d orbitals with their corresponding deconvolutions indicating the spin-orbit splitting from a single oxidation state. The binding energy of the halogens is in agreement with the reported values.<sup>32</sup> In addition, Fig. 3b shows the spectra of the Bi 4f orbitals in  $\beta$ - $\text{Bi}_2\text{O}_3$  and the  $\text{BiOX}$  films. The spectra show Bi in two oxidation states,  $\text{Bi}^{3+}$  and  $\text{Bi}^0$ ; two minor peaks centered at 159.79 and 157.90 eV are related to the  $\text{Bi}^0$  metallic state (chemical shift reported between Bi and  $\text{Bi}^{3+}$  is 2.0 eV (ref. 33)). This is probably a consequence of a slight reduction of  $\text{Bi}^{3+}$  occurring during the Ar cleaning.<sup>34</sup> The larger spin-orbit peaks that showed a shift to larger binding energies, as

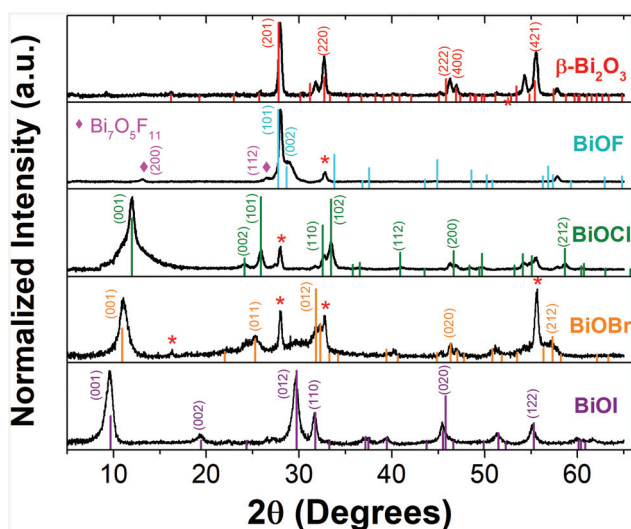


Fig. 1 XRD patterns of the  $\text{Bi}_2\text{O}_3$  film and the oxyhalide family. The vertical lines are the positions of the corresponding  $\text{BiOX}$  ICDD file, and the peaks marked with \* correspond to  $\beta$ - $\text{Bi}_2\text{O}_3$ . For the  $\text{BiOF}$  film, the peaks marked with ♦ correspond to the  $\text{Bi}_7\text{O}_5\text{F}_{11}$  phase.

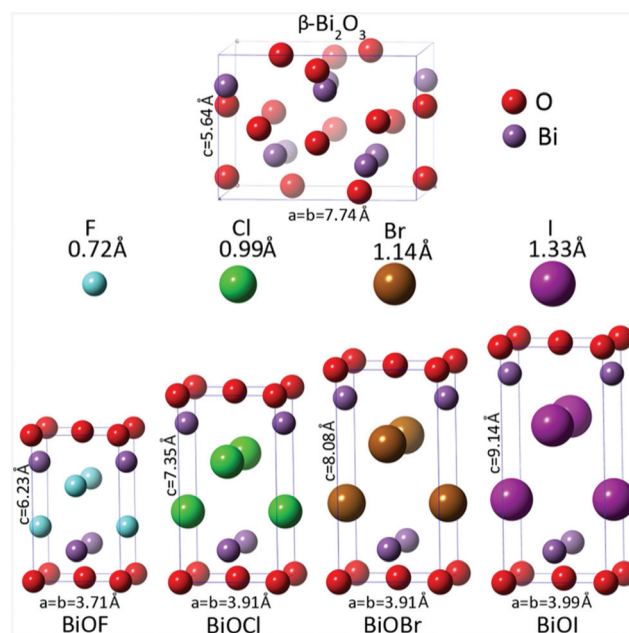


Fig. 2 Schematic representation of the unit cells of  $\text{Bi}_2\text{O}_3$  and  $\text{BiOX}$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).

Table 2 Lattice parameters and crystallite size of BiOX films

| Compound                                | Halogen's atomic radius (Å) | Lattice parameters (Å)   | Deviation from the values calculated by DFT | Crystallite size (nm) |
|---|-----------------------------|--------------------------|---|-----------------------|
| $\beta$ -Bi <sub>2</sub> O <sub>3</sub> | —                           | $a = b = 7.74, c = 5.64$ | $a: -0.25\%; c: 2.48\%^{31}$                | 22.2                  |
| BiOF                                    | 0.72                        | $a = b = 3.71, c = 6.23$ | $a: -0.27\%; c: 0.48\%^{12}$                | 22.5                  |
| BiOCl                                   | 0.99                        | $a = b = 3.91, c = 7.35$ | $a: +1.02\%; c: -0.95\%^{12}$               | 9.0                   |
| BiOBr                                   | 1.14                        | $a = b = 3.91, c = 8.08$ | $a: +0.25\%; c: -0.74\%^{12}$               | 9.7                   |
| BiOI                                    | 1.33                        | $a = b = 3.99, c = 9.14$ | $a: +0.25\%; c: -0.11\%^{12}$               | 9.5                   |

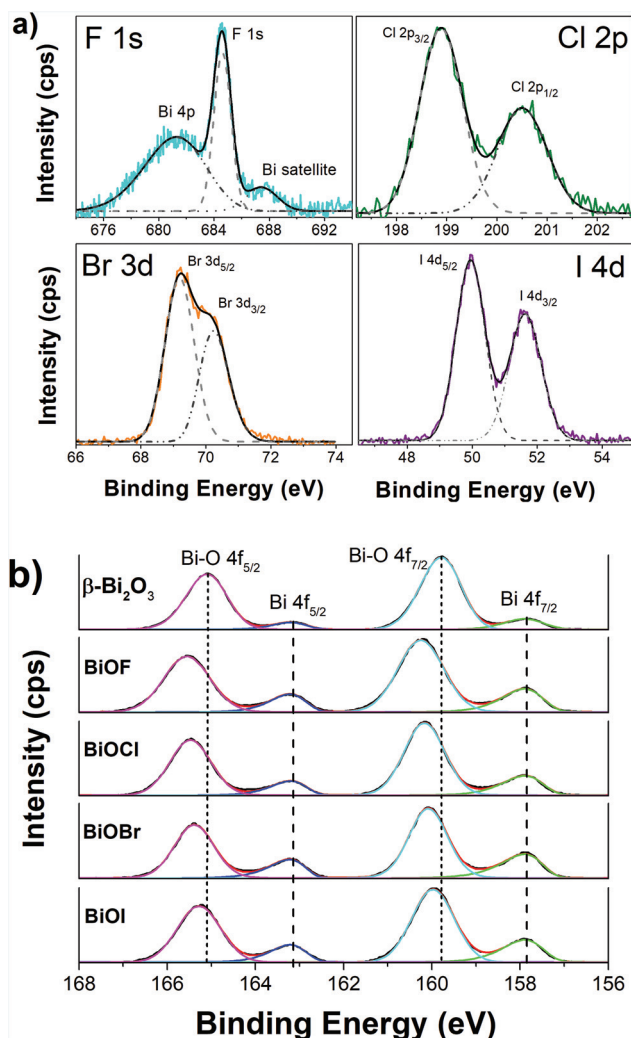


Fig. 3 (a) High resolution spectra of the halogen orbitals (F 1s, Cl 2p, Br 3d and I 4d). (b) Binding energy (eV) of the Bi 4f<sub>7/2</sub> orbital in  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and BiOX films.

the electronegativity of the halogen atom increases, correspond to the Bi–O for the  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> films and the Bi–O–X bonds. Fluorine is the most electronegative of the halogens (and of the elements) and its binding energy in the Bi 4f<sub>7/2</sub> orbital is 160.25 eV, which is the largest value among all in the family. Conversely, BiOI has the smallest value, 159.98 eV, as I is the least electronegative element of the halide family. In all oxyhalides, the signals of the Bi<sup>0</sup> metallic state were also observed in greater proportion than of the  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> film. In Table 3 are the binding energy values and the binding energy shift ( $\Delta$ BE) from the Bi 4f<sub>7/2</sub> orbital, which decreases while the atomic radius of the halogen increases (following the periodic table's trend).

### 3.3 Morphology

Fig. 4 shows the SEM images of the  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> film and the oxyhalides. The original sprayed pyrolyzed  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> film has a compact surface with irregular agglomerated grains on the top (Fig. 4a). After the chemical bath treatment, the BiOF film presents a more granulated surface in which these grains are better defined (Fig. 4b). The HCl chemical bath treatment of the Bi<sub>2</sub>O<sub>3</sub> film provoked a faceted structure, evidenced by thin plates with rounded ends (Fig. 4c). This trend continues for the chemical bath with KBr, giving a flake-like morphology of the BiOBr film (Fig. 4d). In this film, the nanoplates or nanoflakes are better defined, thinner and denser than in the BiOCl film. However, some irregular agglomerated grains corresponding to the  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> phase were also observed. Finally, for the sprayed BiOI film, very large thin plates appear randomly oriented, giving a highly porous and rough surface (Fig. 4e and f). Comparing the complete BiOX family, it is an evident evolution of the morphology towards a lamellar structure as the atomic radius of the halogen increases. This lamellar morphology is typically observed for BiOX films grown by different techniques, although some of them allow the formation of defined platelets easier.<sup>9</sup>

### 3.4 Optical properties

As a first approximation, we used DRS to evaluate the optical properties of the films, since they present an opaque aspect

Table 3 Binding energies, electronegativities and bandgap energies of the BiOX films

| Material                       | Bi 4f <sub>7/2</sub> (eV) | $\Delta$ BE (eV) | Electronegativity of the X atom | $E_g$ (eV) measured | $E_g$ (eV) reported              |
|--------------------------------|---------------------------|------------------|---------------------------------|---------------------|----------------------------------|
| Bi <sub>2</sub> O <sub>3</sub> | 159.79                    | 0                | —                               | 2.6                 | 2.4–2.8 <sup>35,36</sup>         |
| BiOF                           | 160.25                    | 0.46             | 3.98                            | 3.7                 | 3.64 <sup>37</sup>               |
| BiOCl                          | 160.17                    | 0.38             | 3.16                            | 3.6                 | 3.2–3.5 <sup>9,15–17</sup>       |
| BiOBr                          | 160.08                    | 0.29             | 2.96                            | 2.5                 | 2.6–2.8 <sup>9,15–17,25</sup>    |
| BiOI                           | 159.98                    | 0.19             | 2.66                            | 2.0                 | 1.7–1.9 <sup>9,15–17,38,39</sup> |



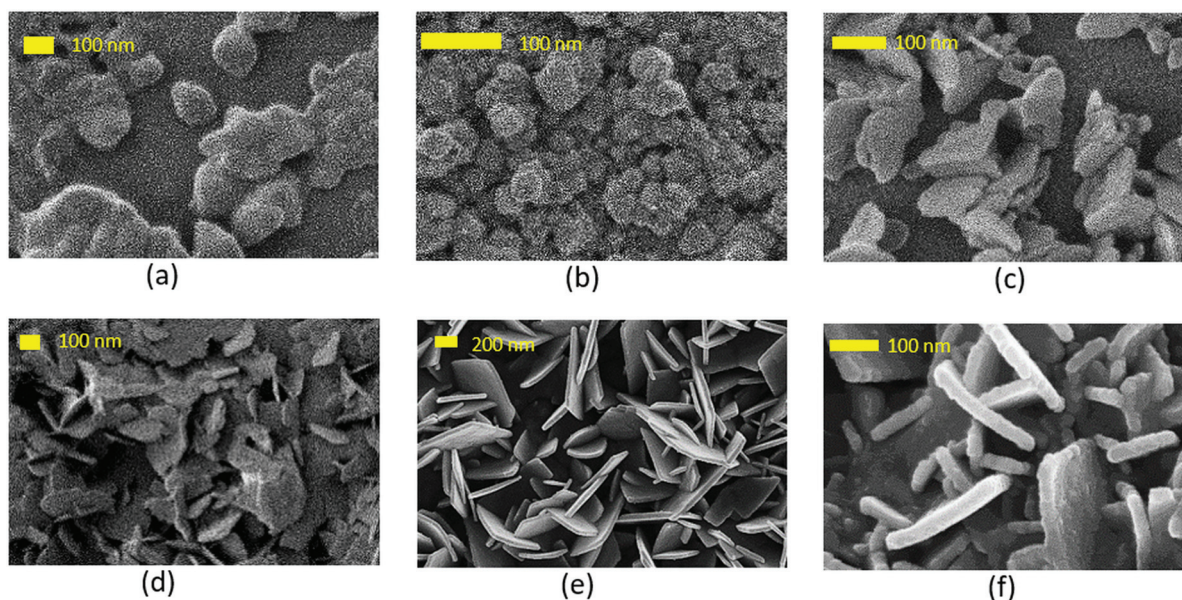


Fig. 4 SEM images of (a)  $\text{Bi}_2\text{O}_3$ , (b)  $\text{BiOF}$ , (c)  $\text{BiOCl}$ , (d)  $\text{BiOBr}$ , (e) and (f)  $\text{BiOI}$  films.

and their transmittance was very low (less than 10% for wavelengths shorter than 800 nm). The energy band gap ( $E_g$ ) was estimated by calculating the absorption coefficient through the Kubelka–Munk (K–M) function  $F(R_\infty)$ :

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \equiv F(R_\infty) \cong \alpha$$

where  $K$  and  $S$  are the Kubelka–Munk coefficients and  $R_\infty = R_{\text{sample}}/R_{\text{reference}}$  is the reflectance.  $E_g$  values were calculated inferring indirect transitions<sup>11</sup> considering that the materials are thin films and have a lot of surface defects; hence plots of  $(F(R_\infty) \cdot h\nu)^{1/2}$  vs.  $E$  were obtained and the  $E_g$  value was calculated by the extrapolation of the linear part to the horizontal axis, as shown in Fig. 5. The obtained  $E_g$  values appear in Table 3; again, this characteristic decrease following the periodic table's trend of the halogen group. Table 3 also lists the  $E_g$  values reported in previous studies, but most of them are for the materials in powder form.

### 3.5 Photocatalytic properties

The photocatalytic activity of  $\text{Bi}_2\text{O}_3$  and the  $\text{BiOX}$  family films was tested by following the photodiscoloration of IC dye at pH 12 under simulated sunlight (Fig. 6a and b). Under these conditions, the photolysis reached less than 12% discoloration. Fig. 6a shows the absorbance spectrum of IC dye solution during the adsorption process in the dark (dashed line) and its evolution as the time progresses until 180 min of reaction in contact with the original  $\text{Bi}_2\text{O}_3$  film under simulated sunlight. The peak located at 610 nm suffers a large decrease with time, disappearing almost completely. The decrease of this absorbance band is clearly observed and it is related to the discoloration of the IC dye solution. The analysis of the spectral changes in the UV range (240–270 nm) indicates that the

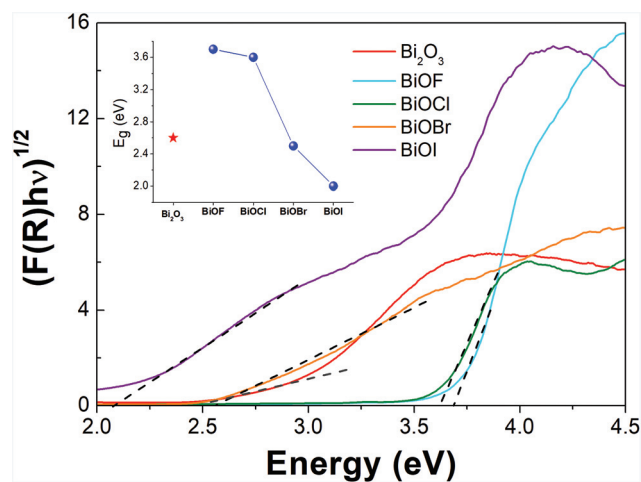


Fig. 5 DRS of  $\beta\text{-Bi}_2\text{O}_3$  and  $\text{BiOX}$  films, where the absorption edges are marked with dotted lines. The inset shows the change of  $E_g$  for the  $\text{BiOX}$  family films.

photodiscoloration pathway that took place during the photocatalytic reaction was the reduction of the IC into the leuco IC form. This reduction occurred *via* a 2 proton–electron transfer reaction in an alkaline medium with the subsequent hydrogenation.<sup>40,41</sup> Furthermore, the formation of leuco IC is confirmed by two isosbestic points (at 363 and 444 nm, clearly seen in Fig. 6a) according to the previously reported work.<sup>42</sup>

A similar absorbance time-evolution was observed for the  $\text{BiOX}$  films, so Fig. 6b shows the absorbance spectrum of the IC dye solution after 180 min of reaction in contact with each one of the formed oxyhalides ( $\text{BiOX}$  films) under simulated sunlight. In all cases, the band at 610 nm suffered a large decrease, especially for the  $\text{BiOCl}$  film, for which this peak

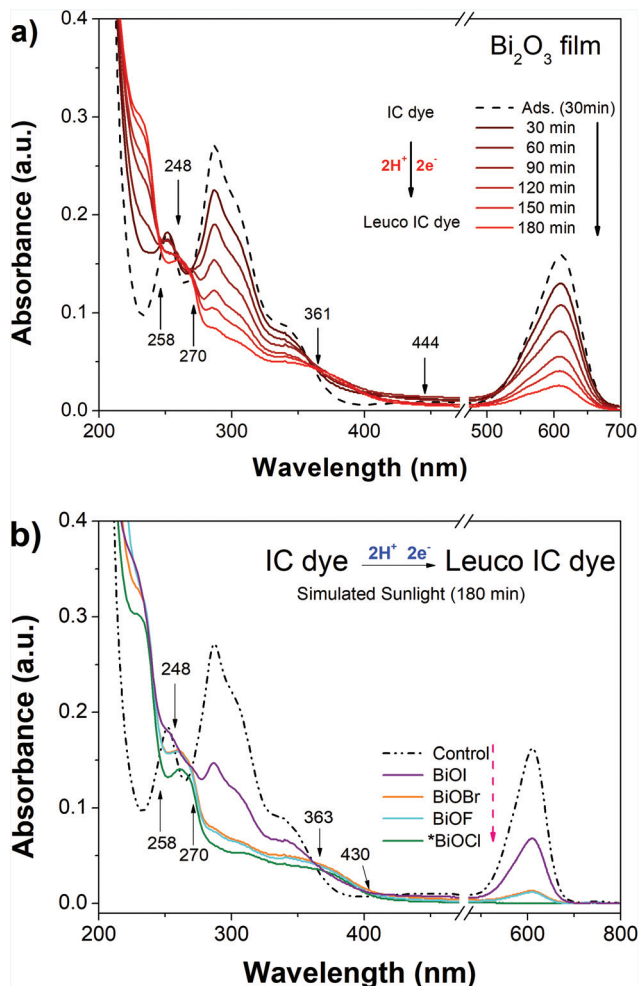


Fig. 6 Absorbance spectra of IC dye during simulated sunlight irradiation: (a) using the  $\beta$ - $\text{Bi}_2\text{O}_3$  film and (b) after 180 min of irradiation in the presence of BiOX films (except for BiOCl where the irradiation time is 90 min).

completely disappeared. The presence of five isosbestic points (258, 248, 270, 363 and 430 nm, Fig. 6b) indicates that the photodiscoloration process of IC dye was due to the transformation to its corresponding leuco IC form.

The percentage of discoloration achieved after 180 min for the  $\text{Bi}_2\text{O}_3$  and all the BiOX family films is presented in Fig. 7. The BiOCl film achieved  $\sim 97\%$  discoloration in only 90 min of sunlight irradiation, while the BiOI film exhibited the lowest response achieving  $\sim 58\%$  discoloration after 180 min. BiOF, BiOBr and  $\text{Bi}_2\text{O}_3$  presented also very good response with percentages between 84 and 92% in the same 180 min. It can be noted that the adsorption of the IC dye onto the films was negligible in all cases, suggesting that the discoloration process was achieved *via* the reduction reaction.

### 3.6 Calculated energy diagram

Based on the electronegativity of each atom, the energy diagram of  $\text{Bi}_2\text{O}_3$  and the BiOX family was calculated. Assuming a Nernstian behavior in aqueous solution for all the

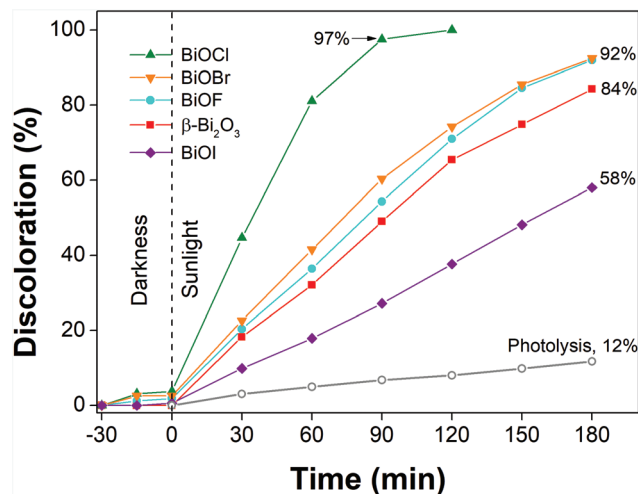
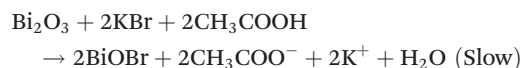


Fig. 7 Discoloration efficiency of IC dye at pH 12 by using  $\beta$ - $\text{Bi}_2\text{O}_3$  and the different BiOX films under simulated sunlight. Photolysis of the IC dye solution is also included.

materials, the band edge positions were plotted as a function of the pH solution *vs.* NHE (Fig. 8). Under the standard conditions (at pH = 0), the values of the conduction band of  $\text{Bi}_2\text{O}_3$  and BiOCl (Fig. 8a) are more negative ( $-0.03$  and  $-0.16$  V) than those of BiOF, BiOBr and BiOI (Fig. 8b) which are positive ( $>0.26$  V). However, according to the calculations, under the conditions of the photocatalytic reaction test (pH  $\sim 12$ ), the calculated value of the band-edge position for BiOF, BiOBr and BiOI may be displaced to more negative energies, reaching values of  $-0.44 \pm 0.01$  V, whereas for  $\text{Bi}_2\text{O}_3$  and BiOCl it is changed to  $-0.7$  and  $-0.87$  V, which results in a higher reducing power. On the other hand, the redox potential of the couple IC/leuco IC at the same pH  $\sim 12$  is  $-0.144$  V *vs.* NHE ( $-0.53$  V *vs.* Ag/AgCl)<sup>40,41</sup> and for the couple  $\text{O}_2/\text{O}_2^{*2-}$  it is  $-0.133$  V *vs.* NHE.<sup>43</sup>

## 4. Discussion

We have shown that it is possible to gradually transform the  $\beta$ - $\text{Bi}_2\text{O}_3$  structure to BiOX (X = F, Cl, Br) by immersion in a halogen containing solution at ambient temperature. Due to the electronegativity and the electronic configuration of the X halogen atoms (which have a  $p^5$  orbital avid for electrons), these X atoms penetrate into the tetragonal  $\text{Bi}_2\text{O}_3$  lattice by substituting the central oxygen layer. The chemical reactions for the transformation of bismuth oxide to the corresponding oxyhalide are expressed below:



for BiOF, BiOCl and BiOBr, respectively. The chemical nature of the immersion bath is an important factor for the duration

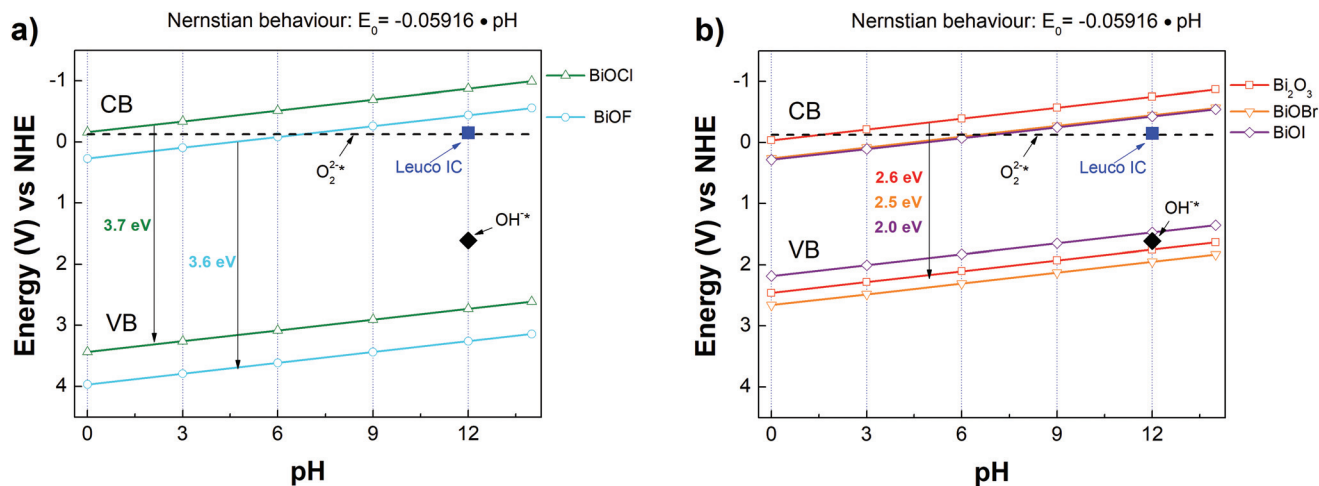


Fig. 8 (a and b) Energy diagram of the band-edge positions for the  $\text{Bi}_2\text{O}_3$  and  $\text{BiOX}$  family as a function of the solution pH. The redox potential of the couple IC/leuco IC and  $\text{O}_2/\text{O}_2^{\cdot 2-}$  is also included.

of the transformation process. When using HF solution, the immersion time was shorter than that for the other solutions even though the molar concentration of the solution was lower. Due to the fast transformation of  $\text{Bi}_2\text{O}_3$  into  $\text{BiOF}$ , it was difficult to precisely control the formation of a pure  $\text{BiOF}$  phase. For 15 min of immersion in HF solution, the XRD pattern shows a majority of  $\text{BiOF}$ , but also a  $\text{Bi}_7\text{O}_5\text{F}_{11}$  phase along with the original  $\beta\text{-Bi}_2\text{O}_3$ . For larger immersion times in HF, the etching of the film was strong enough to detach the film from the substrate, while for shorter immersion times the transformation was incipient and the presence of  $\text{Bi}_2\text{O}_3$  dominated. In the case of the  $\text{BiOCl}$  film, the transformation took a longer time (60 min of immersion), for which the film still had the presence of some residual  $\text{Bi}_2\text{O}_3$ , but a balance had to be made to avoid the detachment of the film from the substrate. When using the  $\text{KBr}$  in acetic acid solution, the transformation of  $\text{Bi}_2\text{O}_3$  into  $\text{BiOBr}$  was even slower (90 min of immersion), and due to that some remaining peaks of  $\beta\text{-Bi}_2\text{O}_3$  were also observed in the XRD pattern.

The  $\text{BiOI}$  sprayed film presented a pure phase that could not be achieved with the several chemical baths' conditions tested; hence, the spraying method is good to obtain this material, in accordance with the published studies<sup>9,28</sup> that also report good adhesion of the film to the substrate. The spray pyrolysis technique may have some advantages for growing  $\text{BiOX}$  films, as it is a one-step process and does not present the etching/detachment of the film, as it occurs during the chemical bath immersion of the  $\text{Bi}_2\text{O}_3$  film. One has just to be aware of the precursor solutions to be sprayed in order to obtain a good quality film.

Here we demonstrate the easiness to transform the bismuth oxide into the oxyhalide, but the conditions of the chemical baths can still be optimized in order to obtain pure phases. Even though the transformation for some samples was not complete, the presence of the oxyhalide was sufficient to show important changes in all their physicochemical properties.

Most of these properties follow a trend while going down along the halogen's group in the periodic table. As the halogen's atomic radius increases, the lattice parameters also increase; the morphology evolves from irregular grains to sharper and more defined laminar structures. The electronegativity decreases as  $\text{F} > \text{Cl} > \text{Br} > \text{I}$  and so does the binding energy in the  $\text{Bi } 4f_{7/2}$  orbital shifts and the energy bandgaps while going down in the group from 3.7 to 2.0 eV.  $\text{BiOF}$  and  $\text{BiOCl}$  absorb only UV-C light, whereas  $\text{BiOBr}$  and  $\text{BiOI}$  can absorb light from the visible region. Finally,  $\text{Bi}_2\text{O}_3$  and all the oxyhalides presented photocatalytic activity response for the photodiscoloration of IC dye in an alkaline medium ( $\text{pH} \sim 12$ ) under simulated sunlight. The photocatalytic reaction occurred *via* 2 proton–electron transfer reactions from the oxide or oxyhalide surface material to the adsorbed IC dye, reducing/hydrogenating to its corresponding leuco IC dye. The electron transfer process observed for all materials can be explained because in the alkaline medium ( $\text{pH} \sim 12$ ), they have enough negative potential ( $-0.4$  to  $-0.9$  V *vs.* NHE) to reduce the IC dye ( $-0.144$  V *vs.* NHE). Despite the fact that  $\text{BiOF}$  and  $\text{BiOCl}$  can only absorb UV-C light, they exhibited a high rate of electron transfer, whereas for  $\text{BiOI}$  which absorbs visible light, the low rate of electron transfer could be affected by the lamellar morphology, which leads to the change in the exposed surface area.

## 5. Conclusions

The thin film bismuth oxyhalide family  $\text{BiOX}$  was obtained by a chemical bath treatment of a sprayed pyrolyzed  $\text{Bi}_2\text{O}_3$  film in the case of  $\text{X} = \text{F}, \text{Cl}$  and  $\text{Br}$ , whereas the  $\text{BiOI}$  film was produced by a direct spraying of an iodine and bismuth containing solution. Immersion of the  $\beta\text{-Bi}_2\text{O}_3$  film in the corresponding halogenated solution causes a gradual transformation of the oxide into the oxyhalide, but the degree of transform-



ation strongly depends on the nature of the bath solution. The physical and chemical characteristics of these compounds follow the same trend as the halogen atoms in the periodic table: lattice parameters and lamellar morphology increase with the halogen's increasing atomic radius; binding energy shifts and the optical band gap decrease as the halogen's atomic radius increases. All the oxyhalides have the conduction band minimum at enough negative potential leading to a good photocatalytic response under simulated sunlight for the reduction of indigo carmine dye into leuco IC in the alkaline medium. BiOCl showed the highest photocatalytic performance even though it only absorbs UV-C light, this is due to its higher reductive power compared to the other oxyhalides.

## Conflicts of interest

There are no conflicts of interest to declare.

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