# Crystalline face engineering in diverse Bismuth Oxyhalides for enhanced amoxicillin removal from water

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**Significance and Relevance**

Water resources are in growing danger, because of persistent contamination, negative effects driven by climate changes and increasingly demand of water for livestock and agriculture: wastewater purification and reuse is then unavoidable. Advanced oxidation processes (AOPs), such as heterogeneous photocatalysis, have emerged as a promising solution, and the contemporary use of light irradiation and proper semiconductors (above all, $TiO_2$-based systems) has attracted a lot of interest: recently, research has been focused on different photocatalysts belonging to bismuth oxyhalides (BiOX, in which X represents Cl, Br o I), because of their intrinsic ability in promoting charge carrier separation and thereby enhancing photocatalytic activity.

*Preferred and 2nd choice for the topic:*
*1st choice - Photocatalysis and photoelectrocatalytic approaches, solar energy utilization;*
*2nd choice - Water treatment*
*Preferred presentation*: Oral only

**Introduction and Motivations**

In recent decades, the increasing presence of antibiotics in wastewater has become a critical issue: to address this concern, heterogeneous photocatalysis, have emerged as promising solutions[1]. In this context, bismuth-based materials, particularly bismuth oxyhalides (BiOX, where X = Cl, Br, or I), have gained attention due to their easy synthesis, high chemical stability, unique layered structure, and prolonged lifetime of electric charges after light irradiation[2]. The photocatalytic performance of BiOXs can be further optimized by tailoring their (micro)morphology, which significantly influence their surface reactivity and charge dynamics: as an example, in the present research the photocatalytic results obtained for Amoxicillin (AMX) degradation will be presented and discussed.

**Results and Discussion**

BiOXs are semiconducting materials with a distinctive tetragonal crystal structure in which $[Bi_2O_2]$ slabs are alternated with double slabs of halogen atoms, creating an internal static electric field perpendicular to the layers[3]. This unique configuration facilitates the transport of photo-induced electrons and holes within the crystal, promoting charge carrier separation and thereby enhancing photocatalytic activity. The photocatalytic performance of BiOXs can be further optimized by tailoring their exposed crystal facets: in fact, the growth of specific crystal facets can be tuned by carefully designing the synthesis process, manipulating factors such as (i) reaction temperature and time, (ii) solvent selection, (iii) use of capping agents, and (iv) choice of an appropriate halogen precursor. In this study, the preparation of BiOX photocatalysts, specifically BiOBr and BiOCl, obtained using potassium (K) and calcium (Ca) salts as halogen precursors was thoroughly investigated.

Many different experimental techniques were employed for the characterization of the various BiOX materials under investigation, coupled by a specific photocatalytic experiment devoted to the abatement by photodegradation of amoxicillin (AMX) under simulated sunlight.

Structural and morphological preliminary results indicated there is a peculiar impact of the halogen source on the BiOX crystal structure (as evidenced in Figure 1a), favoring the formation of the (110)

crystal facet when K-salts were used, even though the general ordered "flower-like" morphology, typical of BiOX systems is totally retained (see Figure b and c).

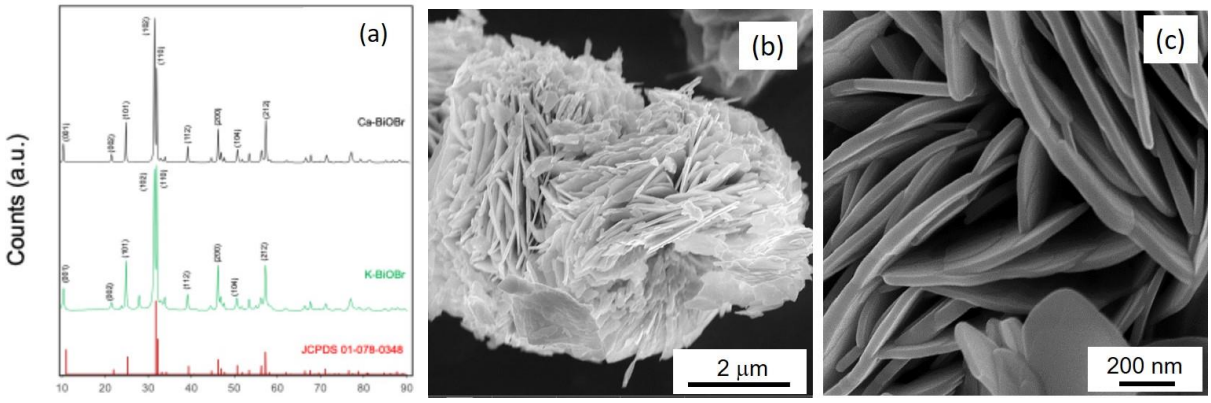
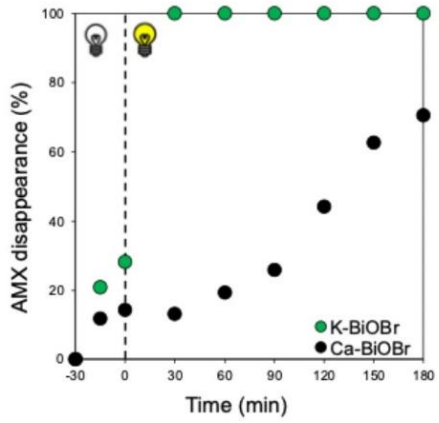



**Figure 1** Section (a): XRD diffractograms of BiOBr from K (green curve) and Ca salts (black curve); sections (b) and (c): FE-SEM images at different magnification of BiOBr from Ca salt.

To check for the successful employment of these systems in photodegradation reactions, when BiOBr from K-salts was used (Figure 2), complete AMX degradation was achieved within 30 minutes of irradiation, whereas BiOBr prepared from Ca-salts showed a slower degradation, reaching about 70% AMX degradation after 180 minutes of irradiation. A similar behavior was observed with BiOCl.




In conclusion, the tunability of BiOX crystal facets offers a powerful strategy to optimize their photocatalytic activity, enhancing their effectiveness in addressing antibiotic pollution in wastewater. By harnessing sunlight, these materials show great promise for sustainable water treatment applications.

**Figure 2** AMX (10 mg $L^{-1}$) photodegradation tests using BiOBr (0.25 g $L^{-1}$; different K – green dots - or Ca salts – black dots) under simulated sunlight (35 W $m^{-2}$).

**References**

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