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Regular Article

pH-dependent synthesis of iodine-deficient bismuth oxyiodide microstructures: Visible-light photocatalytic activity

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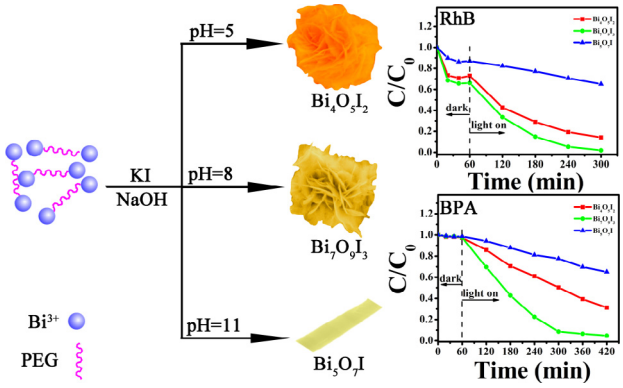
GRAPHICAL ABSTRACT

Iodine-deficient bismuth oxyiodides ($Bi_4O_5I_2$, $Bi_7O_9I_3$, Bi_5O_7I) were selectively synthesized through a pH-dependent aqueous procedure of 70 °C. Nanosheet constructed $Bi_7O_9I_3$ microflowers exhibited excellent visible-light photocatalytic activities on the degradation of RhB dye and colorless BPA.



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ABSTRACT

Bismuth oxyiodides have exhibited high potential for applications in visible-light photocatalytic environmental remediation and solar energy conversion. In this work, a series of iodine-deficient bismuth oxyiodides ($Bi_4O_5I_2$, $Bi_7O_9I_3$, Bi_5O_7I) can be simply prepared through a pH-dependent aqueous procedure with feeding Bi/I ratio of 2:1. The compositions of the Bi-based oxyiodides are closely related to acid-base circumstances, with $Bi_4O_5I_2$ formed in weakly acidic medium (pH = 5) and $Bi_7O_9I_3$, Bi_5O_7I in basic medium (pH = 8 and 11). Morphology differences of nanosheet-assembled $Bi_4O_5I_2$, $Bi_7O_9I_3$ architectures and rod-like Bi_5O_7I microstructures demonstrate different crystalline characters and construction of Bi-based oxyiodide crystals. UV–vis DRS results revealed good visible-light absorptions of $Bi_4O_5I_2$ and $Bi_7O_9I_3$ architectures and appropriate band structures for photocatalytic reactions, on comparison to Bi_5O_7I microrods. Low electrochemical impedance of $Bi_7O_9I_3$ microflowers with sheet-like units further facilitated the separation of e^-–h^+ carriers in the degradation process. Accordingly, among the bismuth oxyiodide samples, $Bi_7O_9I_3$ displayed prominent visible-light degradation performance for colorless bisphenol-A (BPA) due to the direct photoexcitation process.

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1. Introduction

Over the past decades, visible-light induced semiconductor photocatalysts have attracted considerable attention due to their potential applications in energy conversion and environmental decontamination [1,2]. Bismuth oxyhalides (BiOX, X = F, Cl, Br and I), as a class of novel ternary oxide photocatalysts, are intensively investigated for their unique layered structures characterized by $[Bi_2O_2]^{2+}$ slabs [3,4]. An internal static electric field between $[Bi_2O_2]^{2+}$ and halogen slabs is believed to facilitate the separation of photogenerated electrons-holes pairs, and thus enhance the photocatalytic performance [5].

Among these BiOX catalysts, BiOI attracted great interests owing to its the smallest band gap (~1.8 eV) and intensive absorption in visible-light region [6,7]. However, the practical applications of BiOI materials are still limited for its low position of conduction band, low conductivity and high recombination probability of photogenerated electron-hole pairs [8–10]. Many researchers are committed to find effective strategies to enhance the catalytic activities of BiOI crystals, such as heterologous hybridization [11], exposure of specific crystal faces [12,13], and morphological control [14]. These strategies concentrated on improving photocatalyst performances, intrinsic properties of BiOI (such as low conductivity, it is crucial for charge separation in photocatalysis) have not been tuned. Very recently, an iodine-deficient strategy was designed to evolve new photocatalysts through the atomic structure manipulation of BiOI [15–20]. The resultant I-deficient bismuth oxyiodides are homogenous in crystalline structure and possess some attractive properties including remarkably higher photoconductivity than its parent BiOI. Additionally, since the valence band (VB) top of bismuth oxyiodide is primarily composed of hybrid orbitals of I_{5p} and O_{2p}, and the conduction band (CB) bottom mainly consists of Bi_{6p} orbitals, the change of Bi:O:I ratio could tune the band structures of samples with varied reduction and oxidation potentials [17]. Ma group reported an alcohothermal route to synthesize $Bi_4O_5I_2$ and $Bi_7O_9I_3$ crystals at 130 °C for 12 h, in which $Bi_4O_5I_2$ degraded 90% of RhB within

Table 1
Synthetic conditions of I-deficient bismuth oxyiodide samples.

Samples	Feeding molar ratio of Bi/I	Molar ratio of OH^-/I^-	pH value	Crystalline Phase
S1	2:1	8:1	5.0	$Bi_4O_5I_2$
S2		9:1	8.0	$Bi_7O_9I_3$
S3		10:1	11.0	Bi_5O_7I

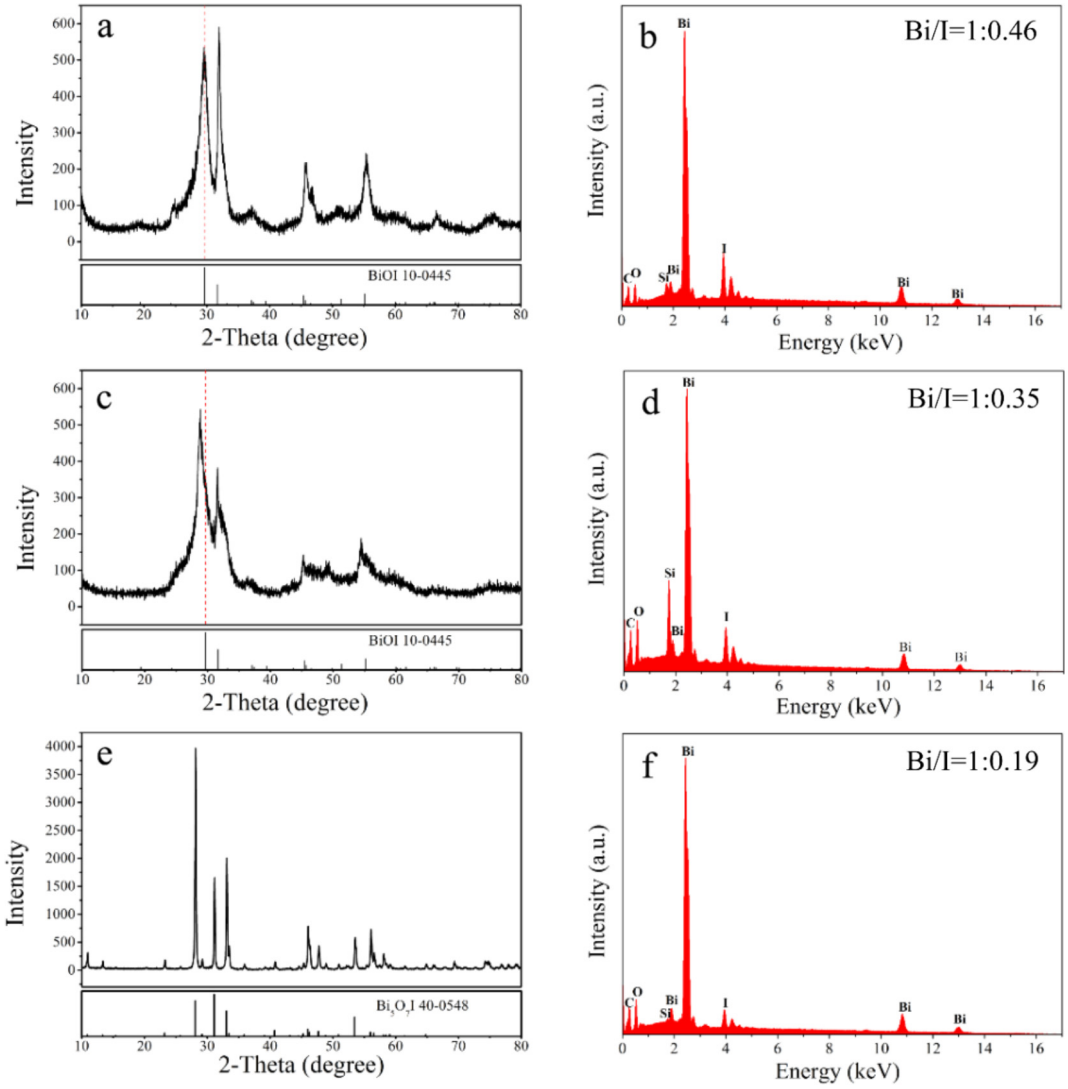

Fig. 1. XRD and EDX results of samples S1 (a, b), S2 (c, d) and S3 (e, f).