



# Low concentration nitric acid facilitate rapid electron–hole separation in vacancy-rich bismuth oxyiodide for photo-thermo-synergistic oxidation of formaldehyde



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## ABSTRACT

Searching for simple and effective methods for large-scale production of defective catalysts is of key importance, but remains a big challenge. Herein, we report a simple, scalable and effective method to produce defects in photocatalysts, which is significant for industrial application. Surprisingly, the defects on the photo-thermo-catalysts could not only available decrease the recombination of photoelectrons and holes, but also increase the production of reactive oxygen species, which demonstrated a superior improvement in photo-thermo-catalytic activity coupled with ultrastable stability. These findings feature the fundamental role of surface defects structure on producing more oxygen reactive species and may create advance avenues for the rational design of extremely efficient photo-thermo-catalysts via surface engineering.

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## 1. Introduction

Formaldehyde (HCHO) has been acknowledged as an indoor pollution, which may cause adverse effects on human health and are a main culprit for sick building syndrome [1]. Photocatalysis has been considered as a promising method to substantially solve this global environmental crisis [2–8]. Up to now, the photocatalytic activity is still far below the requirements of practical applications, which is restricted by the inactive charge-carrier separation in photocatalysts under the visible light irradiation [9–13]. Therefore, to enhance the photocatalytic efficiency of pollution degradation, the photoexcited electrons and holes should be consumed as far as possible during the photocatalytic process.

In principle, the photoelectrons are produced after the light irradiated the semiconductors. As some of them will recombine with the holes immediately, part of them will migrate to the surface of semiconductors and transfer the molecular oxygen to oxygen species, especially those physically adsorbed molecular oxygen on

the coordinative saturated oxide surface ( $O_2 + e^- \rightarrow O_2^{\bullet-}$ ) [14–16]. These reactive oxygen species could efficiently oxidize the substrate molecules located at the neighboring sites [17]. So, the question is: (i) will increasing reactive oxygen species production in photocatalysis promote the photocatalytic activity of degradation pollution? And (ii) If possible, how can we increase the reactive oxygen species? Most recently, we had demonstrated that oxygen vacancies could effectively separate the photoexcited electrons and holes and then improve the photocatalytic performance [18–20]. Naturally, we were curious whether photoexcited electrons could migrate to the catalysts surface to produce reactive oxygen species with the help of oxygen vacancies. If this method is feasible, we only need to generate more reactive oxygen species while simultaneously improving the photocatalytic activity. In addition, the photoelectrons will move quickly as the temperature increases. Therefore, increasing the temperature during the reaction will enhance the separation of photoelectrons and holes, which may improve the photocatalytic performance? For our proof-of-concept demonstration, {001} bismuth oxyhalide (BiOI) nanosheets, due to its special structure and suitable band gaps (Scheme S1) [21,22], were employed as a model photocatalyst. However, the methods to produce defective bismuth oxyhalides are restricted by the dangerousness, high costs and difficulty in scaling-up [18–20]. For

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examples, Ye et al. prepared oxygen defective BiOI by UV light irradiation with Ar blowing at high temperature [23]. Our previous work also demonstrated that BiOI with oxygen vacancies can be obtained via electroreduction, but this way was complicated [18]. A simple method was used to prepare oxygen defective BiOI nanosheets with NaBH<sub>4</sub> reducing reagents. The limitation of this way was that much hydrogen was produced in the reducing process, which was very dangerous for applications [20]. Thus, searching for simple and effective methods for large-scale production of defective catalysts is of key importance, but remains a big challenge.

Herein, for the first time, we demonstrated a simple and effective method to introduce oxygen vacancies into the {001} BiOI nanosheets via modifying with low concentrated nitric acid. Specifically, this method is highly suitable for industrial application due to the ease for large-scale production and cost-effectiveness. Enabled by the surface vacancies, more electrons transfer the molecular oxygen to reactive oxygen species, which facilitates charges separation. Meantime, the increase reactive oxygen species speed up the rate of reaction. Interestingly, our catalyst could not only be beneficial for the formaldehyde oxidation under visible light, but also exhibit significant improvement for thermal oxidation of formaldehyde. As a result, the efficiency of photo-thermo-catalytic degradation gas formaldehyde exhibits 6 folds superior enhancement compared to that of untreated BiOI nanosheets. More importantly, no obvious deactivation of the defective BiOI was observed after cyclic reaction. This work sheds light on the vital role of defects in increasing reactive oxygen species production in photocatalysis.

## 2. Experimental section

### 2.1. Preparation of BiOI and deficient BiOI nanosheets

The {001} BiOI nanosheets were prepared according to our previous literature [24]. Deficient BiOI nanosheets were prepared by using {001} BiOI nanosheets as the precursor. In a typical synthesis, 0.1 g {001} BiOI nanosheets was immersed into nitric acid with different quantities (5 mL, 8 mL, 10 mL) and then added 50 mL water, stirring for 30 min at room temperature. The synthesis of the deficient BiOI nanosheets can be seen in Video S1. Finally, the products were collected and washed with deionized water four times, drying at 60 °C overnight. The deficient BiOI were labeled as BiOI-5, BiOI-8 and BiOI-10, respectively.

### 2.2. Characterization

The crystal phase of all the samples were analyzed by Raman spectrometry (Reinshaw), powder X-ray diffraction (D8ADVANCE), FT-IR spectra (Nicolet Avatar 370 infrared spectrometer) and X-ray photoelectron spectroscopy (ESCALab250, Thermo VG). Scanning electron microscope (JSM-6330F) and transmission electron microscopy (JEM2010-HR, 200 kV) were used to ensure the morphologies of all the samples. The thick of photocatalysts was measured by SPM-9500J3 microscope. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method (ASAP 2020 V3.03H). Electron spin resonance (ESR) spectroscopy was used to examine unpaired electrons in materials at 77 K with a xenon lamp as the visible light source. DMPO (5,5'-dimethyl-1-pyrroline-*N*-oxide) was employed as a spin-trap reagent to trap the active species of hydroxyl (•OH) and superoxide radicals (•O<sub>2</sub><sup>-</sup>). 50 μL (1 g L<sup>-1</sup>) BiOI suspension and 50 μL of DMPO (25 g L<sup>-1</sup>) were mixed in different solvents in line with the targeted radical. Water and DMSO were used for hydroxyl (•OH) and superoxide radicals (•O<sub>2</sub><sup>-</sup>) trapping, respectively. The optical properties of all the

samples were recorded by the UV-vis spectrophotometer (UV-2450), using BaSO<sub>4</sub> as the reflectance standard. Photoluminescence spectra (360 nm excitation) and time-resolved PL spectra (255 nm excitation) were recorded by a FLS920 multifunction steady state and transient state fluorescence spectrometer. The electrochemical measurements of all the samples were performed with a standard three-electrode, which has been reported in our previous literature [24].

### 2.3. Photocatalytic activity tests

Photocatalytic performances of all samples were evaluated by the removal of HCHO (500 ppm). The catalysts (0.05 g) were put in the reactor, as shown in Scheme S2. Gaseous HCHO was generated by passing a purified air flow (N<sub>2</sub>/O<sub>2</sub> = 4100 mL min<sup>-1</sup>) over HCHO solution in an incubator kept at 0 °C. The reaction flask was put in a cooling water system to keep the reaction at room temperature. Prior to irradiation, the catalyst was magnetically stirred in the dark for 120 min to establish absorption-desorption equilibrium. A Xe lamp (300 W) was used as the visible light source with a UV light cutoff filter (420 nm). A gas chromatograph (Agilent 7890A) with a TCD detector and a Porapak-Q column was used to analyze the production of CO<sub>2</sub>. The HCHO conversion was calculated by the follows:

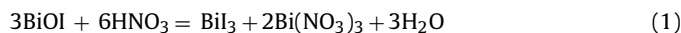
$$\text{HCHO conversion}(\%) = [\text{CO}_2]/[\text{HCHO}]_{\text{total}} \times 100$$

[CO<sub>2</sub>] and [HCHO]<sub>total</sub> in the formula are the CO<sub>2</sub> concentration in the products and the total HCHO concentration in the reactor, respectively. After the experiment, N<sub>2</sub> was bubbled into the photoreactor at a flow rate of 100 mL min<sup>-1</sup> to eliminate the HCHO in the photoreactor. Gaseous HCHO was generated again to evaluate the cycling photocatalytic performance.

## 3. Results and discussion

### 3.1. Synthesis and characterization of all the catalysts

The {001} BiOI nanosheets were prepared according to our previous literature [24]. The defective BiOI nanosheets were obtained by modifying the BiOI nanosheets with nitric acid at room temperature, which is a simple and effective method, as shown in Fig. 1a. The pristine BiOI nanosheets turn from red to black after injecting 2 mL HNO<sub>3</sub> solution, which was confirmed to be BiI<sub>3</sub> by X-ray diffraction patterns (XRD) and Raman spectroscopy (Eq. (1)) [25].



The XRD of BiI<sub>3</sub> is shown in Fig. 1b, which can be indexed to the rhombohedral BiI<sub>3</sub> (PDF no:48-1795). Likewise the Raman spectrum shown in Fig. 1c confirms the BiI<sub>3</sub> with corresponding peaks at 84, 114 and 154 cm<sup>-1</sup>, which are attributed to A<sub>g</sub>, E<sub>g</sub> and A<sub>g</sub> mode, respectively [25]. By adding water into the BiI<sub>3</sub> solution, the defect-rich BiOI was formed with the solution turning red immediately (Eq. (2)).



The whole process in the preparation of the defective BiOI can be seen in Video S1, and in this change process, some defects are produced (Fig. S1). More importantly, the concentrations of defects could also be controlled by the content of HNO<sub>3</sub> concentration, labeling as BiOI-5, BiOI-8 and BiOI-10, respectively.

In order to prove that this is a feasible method to construct defect-rich BiOI nanosheets, we apply this simple and scalable method to another pristine BiOI (d-BiOI) photocatalyst, which was prepared differently from {001} BiOI nanosheets [18]. It is worthy

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