



Facile synthesis of surface N-doped $\text{Bi}_2\text{O}_2\text{CO}_3$: Origin of visible light photocatalytic activity and in situ DRIFTS studies



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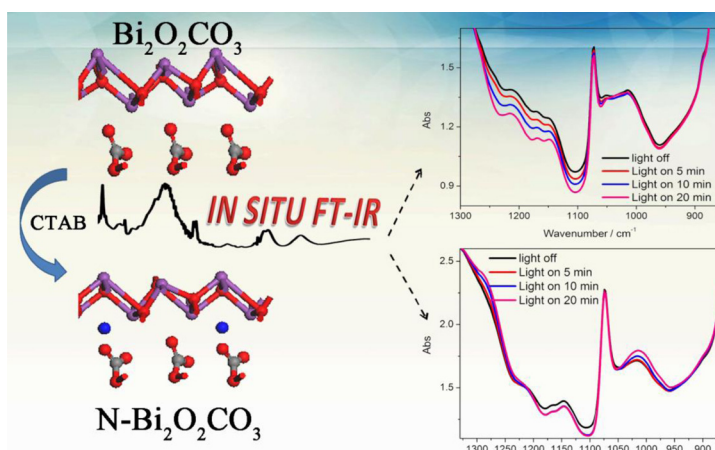
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HIGHLIGHTS

- Interstitially doping N in the $\text{Bi}_2\text{O}_2\text{CO}_3$ surface was achieved at room temperature.
- N-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ exhibited significantly enhanced visible light photocatalytic activity compared to the pristine $\text{Bi}_2\text{O}_2\text{CO}_3$.
- The formation of localized states from N–O bond could account for the visible light activity of $\text{Bi}_2\text{O}_2\text{CO}_3$.
- The photocatalytic NO oxidation process was monitored by in situ DRIFTS.

GRAPHICAL ABSTRACT

Surfactant (CTAB) can induce nitrogen interstitially doping in the $\text{Bi}_2\text{O}_2\text{CO}_3$ surface, leading to the formation of localized states from N–O bond, which probably account for the origin of the visible light activity. Moreover, the photocatalytic NO oxidation processes over $\text{Bi}_2\text{O}_2\text{CO}_3$ were successfully monitored for the first time by in situ DRIFTS.



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ABSTRACT

$\text{Bi}_2\text{O}_2\text{CO}_3$ nanosheets with exposed {001} facets were prepared by a facile room temperature chemical method. Due to the high oxygen atom density in {001} facets of $\text{Bi}_2\text{O}_2\text{CO}_3$, the addition of cetyltrimethylammonium bromide (CTAB) does not only influence the growth of crystalline $\text{Bi}_2\text{O}_2\text{CO}_3$, but also modifies the surface properties of $\text{Bi}_2\text{O}_2\text{CO}_3$ through the interaction between CTAB and $\text{Bi}_2\text{O}_2\text{CO}_3$. Nitrogen from CTAB as dopant interstitially incorporates in the $\text{Bi}_2\text{O}_2\text{CO}_3$ surface evidenced by both experimental and theoretical investigations. Hence, the formation of localized states from N–O bond improves the visible light absorption and charge separation efficiency, which leads to an enhancement of visible light photocatalytic activity toward to the degradation of Rhodamine B (RhB) and oxidation of NO. In addition, the photocatalytic NO oxidation over $\text{Bi}_2\text{O}_2\text{CO}_3$ nanosheets was successfully monitored for the first time using in situ diffuse

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reflectance infrared Fourier-transform spectroscopy (DRIFTS). Both bidentate and monodentate nitrates were identified on the surface of catalysts during the photocatalytic reaction process. The application of this strategy to another relevant bismuth based photocatalyst, BiOCl, demonstrated that surface interstitial N doping could also be achieved in this case. Therefore, our current route seems to be a general option to modify the surface properties of bismuth based photocatalysts.

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1. Introduction

The quest of efficient schemes for the use of solar energy is motivated by the depletion of fossil fuels reserves and the increasing demand of clean energy. Photocatalysis has been regarded as one of the ideal technologies for this purpose [1–5]. To take full advantage of solar energy, considerable efforts have been focused on the development of visible light driven photocatalysts [6]. Among the investigated catalysts, Bi(III)-based semiconductors, such as Bi₂WO₆ [7–9], Bi₆S₂O₁₅ [10,11], BiVO₄ [12–14] and Bi₂MoO₆ [15,16] have been intensively studied due to the hybridized valence band (VB) formed by the Bi 6s and 2p levels, which could not only narrow the band gap but also enhance the mobility of photogenerated holes in the VB [17].

Bi₂O₂CO₃, a typical “sillén” phase, with alternating Bi₂O₂²⁺ and CO₃²⁻ layers has been long used in medical and healthcare fields [18]. Recently, it was reported as a photocatalyst for the degradation of wastewater dyes and indoor air purification [19–23]. However, similar to TiO₂, Bi₂O₂CO₃ exhibits a wide band gap of ca. 3.4 eV, indicating that it can only be excited by UV light. Hence, many efforts have been conducted to overcome this bottleneck including doping [24,25], noble metal deposition [26–28] and the formation of heterojunction [22,29]. Among these strategies, doping with nonmetallic ions, especially with N, has been regarded as an effective approach [30]. For instance, bulk N doping in Bi₂O₂CO₃ has been achieved under hydrothermal treatment condition using dicyandiamide as nitrogen source [25]. Compared to bulk doping, surface doping is more favorable for photocatalytic reactions as the doped elements in bulk doping may become the recombination centers for the photogenerated carriers, thus reducing the photocatalytic activity [31]. However, the surface N doping in Bi₂O₂CO₃ has not been reported so far. On the other hand, the Bi₂O₂CO₃ dominated by {001} facets possesses high oxygen atom density with the low bonding energy of Bi–O, which could provide active sites to interact with other ions or molecules to achieve surface doping. Very recently, our work revealed that the strong interfacial interactions between Bi₂O₂CO₃ {001} facets and polyaniline (PANI) can promote oxygen vacancy formation at the interface [32]. Inspired by the easily formation of oxygen vacancy in {001} facets of Bi₂O₂CO₃, we believe that the N doping in Bi₂O₂CO₃ could be realized through the interaction between Bi₂O₂CO₃ and surfactants which can provide nitrogen at mild conditions [33–36].

Furthermore, despite manifold studies on the photocatalytic activity of Bi₂O₂CO₃, the monitoring of the intermediates during a photocatalytic reaction has rarely been considered. Such intermediate information could be obtained through ex situ analyses, but these indirect routes always bear the risk of isolating artifacts. For example, Dong et al. recently reported that the oxidation products can be changed from nitrate (NO₃⁻) to NO₂ as the irradiation time increases through ex situ IR investigations [37]. Nevertheless, the detail information of the intermediates cannot be obtained. Therefore, in situ monitoring of the reaction products can enhance our understanding on the photocatalytic reaction. For this purpose, in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) is the method of choice [38]. To the best of our knowledge,

there is no research monitoring the photocatalytic NO oxidation process over bismuth based photocatalysts by in situ DRIFTS.

Herein, we prepared 2D Bi₂O₂CO₃ nanosheets with exposed {001} facets through a facile room temperature chemical method. The addition of cetyltrimethylammonium bromide (CTAB) can decrease the thickness and size as well as enhancing the BET surface area. Importantly, the interaction between CTAB and Bi₂O₂CO₃ could promote N from CTAB doping in Bi₂O₂CO₃. The combination of DFT calculations and XPS experiments revealed that N interstitially doped in the surface of Bi₂O₂CO₃. The N 2p level could generate upon the VB of Bi₂O₂CO₃ and hybridize with the O 2p level, leading to the improvement of absorption for visible light as well as promoting charge separation. Therefore, surface N doped Bi₂O₂CO₃ nanosheets exhibited an enhanced visible light driven photocatalytic activity. Moreover, the photocatalytic NO oxidation processes over Bi₂O₂CO₃ nanosheets were successfully monitored by in situ DRIFTS. Considering the crystal structure similarity of BiOCl and Bi₂O₂CO₃, we further confirmed that the surface N doping induced by CTAB also occurred in BiOCl.

2. Experimental details

2.1. Synthesis

All the chemicals were analytical grade reagents and purchased from Chengdu Keshi Co., Ltd., which were used without any further purification. 2D Bi₂O₂CO₃ (BOC) nanosheets were prepared by a low temperature chemical method modified from a previously reported work [33]. In a typical procedure, 48.5 g Bi(NO₃)₃·5H₂O was dissolved in 100 mL of 1 M HNO₃ as solution A, while 84.5 g Na₂CO₃ was dissolved into 900 mL distilled water as solution B. Then, solution B was added into solution A by drops under stirring at 30 °C for 30 min. After that the final products were subsequently washed several times with isopropyl alcohol and distilled water and finally dried at 60 °C for 12 h. The CTAB modified BOC denoted as BOC–CTAB were prepared by the same procedure except adding 10 g CTAB in the solution B before mixing with solution A. Additionally, the hierarchical BOC microspheres prepared by hydrothermal method with BET surface area of 46 m²/g were denoted as BOC-ref for reference [26].

2.2. Characterizations

PXRD measurements were performed on a PANalytical X'pert diffractometer operated at 40 kV and 40 mA using Cu K α radiation. Hitachi S-4800 was used to conduct the SEM investigations. TEM images were obtained on a FEI Tecnai G2 20 microscope at 200 kV. Nitrogen adsorption–desorption isotherm were recorded on a nitrogen adsorption apparatus (AutoChem II 2920) and the samples were degassed at 100 °C for 6 h prior to measurements. XPS spectra were investigated on a Thermo ESCALAB 250Xi with Al K α emission at 1486.6 eV, and all of the binding energies were referenced to the C 1s at 284.8 eV. A Shimadzu 2600 UV–vis spectrophotometer was used to record the UV–vis absorption spectra. Raman spectroscopy was recorded on a Renishaw Ramascope 1000

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