



Efficient photocatalytic removal of nitric oxide with hydrothermal synthesized $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes



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ABSTRACT

In this study, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes were synthesized with a facile hydrothermal method using TiO_2 P25 (Degussa) and bismuth citrate ($\text{BiC}_5\text{H}_6\text{O}_7$) as precursors in concentrated NaOH and ammonia alkali solution. The samples were systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The as-prepared $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes exhibited superior activity for photocatalytic removal of gaseous nitric oxide (NO) over TiO_2 P25 (Degussa) under simulated solar-light irradiation, the NO removal rate can reach as high as ca. 200 ppb·min⁻¹ over the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes in a continuous reactor with an initial NO concentration of 400 ppb. The intrinsic hollow-nanotube structure of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ photocatalysts contributes to its superior activity under simulated solar light. This work provides a facile route to prepare $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes and suggests that the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes are ideal candidates for efficient removal of nitric oxide in indoor/outdoor air.

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1. Introduction

Nitric oxide (NO) released from combustion processes and vehicular emissions is a precursor of photochemical smog, which has serious implications on the indoor and outdoor air quality [1,2]. More and more attentions have been paid to air quality with increasing awareness of the public environment and health, especially in urban cities. Generally nitric oxide in industrial emission with high concentrations can be treated by conventional techniques including physical adsorption biofiltration, and thermal catalysis methods [3–7]. However, these methods suffer from the post disposal and regeneration problems and they cannot effectively remove nitric oxide at the parts per billion levels, which are typical concentrations in indoor and outdoor air environment.

Photocatalysis technology has gained considerable attention in view of solar energy conversion and wastewater cleaning, as well as indoor air pollutants purification even at low concentrations [8–12]. For instance, TiO_2 immobilized on different substrates [13], carbon doped TiO_2 [14], BiOBr–graphene composites [15],

Bi_3NbO_7 [16], and Bi_2O_3 [17] have been used to photocatalytically clean indoor air pollutants at parts per billion levels in a flow system. Despite these advances, the development of photocatalyst with high activity still needs to be greatly expanded to meet the ever-increasing demand.

Sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$), as a perovskite ferroelectric, has been widely used for the piezoelectric, ferroelectric and pyroelectric devices, and catalysis [18–22]. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ was generally synthesized by conventional solid-state method, but this method usually results in a high agglomeration powders as a result of the high-temperature treatment [19]. In comparison with solid-state techniques, the hydrothermal technique has superior advantages such as versatility, well controlled morphology, high purity and narrow particle size distribution of the prepared powders [23–26]. For instance, Dai reported that $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ powders could be hydrothermal prepared using TiCl_4 and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as raw materials and NaOH as mineralizer [27]. Recently, Wang's group synthesized a hierarchical $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ micro/nanostructure composed of nanosheets under hydrothermal conditions and found that $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ micro/nanostructure showed photocatalytic performance in the photodegradation of methyl orange [25]. However, synthesis of one-dimensional $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes has not been reported.

In the present work, we propose a facile hydrothermal approach for preparation of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes using TiO_2 P25

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(Degussa) and bismuth citrate ($\text{BiC}_5\text{H}_6\text{O}_7$) as precursors in concentrated NaOH and ammonia alkali solution. The as-prepared $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes exhibited superior activity on photocatalytic removal of gaseous nitrogen monoxide at part-per-billion level under solar-light irradiation. The study provides a facile route for preparation of one-dimensional $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes with efficient solar-light driven photocatalytic activity for removal of indoor and outdoor nitrogen monoxide.

2. Experimental section

2.1. Chemicals and synthesis

Bismuth citrate ($\text{BiC}_5\text{H}_6\text{O}_7$) (Sigma–Aldrich) and TiO_2 P25 (Degussa, Germany) were used as the precursors. NaOH was analytical grade without any purification. Deionized water was used in all experiments. In a typical synthesis, 0.2 g TiO_2 P25 was added into 9 mL of 20 M NaOH to obtain the suspension A, then 0.2 g of $\text{BiC}_5\text{H}_6\text{O}_7$ was dissolved in 9 mL of concentrated ammonia solution to form a transparent solution B at room temperature. Subsequently, the bismuth citrate ammonia solution B was added into the suspension A and stirred for about half an hour. Finally, the mixed suspension was poured into a 22-mL Teflon vessel autoclave. The autoclave was allowed to be heated at 220 °C for 18 h under autogenously pressure, and then air cooled to room temperature. The resulting precipitates were collected and washed with ethanol and deionized water thoroughly and vacuum dried at 50 °C. For comparison, the counterpart $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ powders were hydrothermally prepared according to the published literature [26].

2.2. Characterizations

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Scanning electron microscopy images were performed on a LEO 1450VP scanning electron microscope. Transmission electron microscopy (TEM) study was carried out on a Philips CM-120 electron microscope. The samples for TEM were prepared by dispersing the final powders in ethanol; the dispersion was then dropped on carbon–copper grids. X-ray photoemission spectroscopy (XPS) was recorded on a PHI 5600 multi-technique system with a monochromatic Al K α source (Physical Electronics) operated at 150 W (15 kV, 10 mA). The nitrogen adsorption and desorption isotherm at 77 K was measured using a Micromeritics ASAP2010 system after the sample was vacuum-dried at 473 K overnight. A Varian Cary 100 Scan UV–visible system equipped with a Labsphere diffuse reflectance accessory was used to obtain the reflectance spectra of the catalysts over a range of 200–800 nm. The Labsphere USRS-99-010 was employed as a reflectance standard. The spectra were converted from reflection to absorbance by the Kubelka–Munk method. The photoluminescence measurements were conducted at room temperature using a Ni:yttrium–aluminum–garnet laser (325 nm) as the excitation source and photomultiplier detector (PTi, MODEL 810/814).

2.3. Photocatalytic nitric oxide removal experiments

The photocatalytic experiments for the removal of gaseous nitric oxide were performed at ambient temperature in a continuous flow reactor. The volume of the rectangular reactor which was made of stainless steel and covered with Saint-Glass was 4.5 L ($10 \text{ cm} \times 30 \text{ cm} \times 15 \text{ cm}$ (H $\times$ L $\times$ W)). One sample dish containing 0.1 g of the sample was placed in the middle of the reactor. A 300 W commercial tungsten halogen lamp (General Electric) was used as the simulated solar-light source. The lamp was vertically placed outside the reactor above the sample dish and a glass filter was placed to remove light below 420 nm. Four mini-fans were fixed around the lamp to avoid the temperature rise of the flow system. The NO gas was acquired from a compressed gas cylinder at a concentration of 48 ppm NO (N_2 balance, BOC gas) with traceable National Institute of Standards and Technology (NIST) standard. The initial concentration of NO was diluted to about 400 ppb by the air stream supplied by a zero air generator (Thermo Environmental Inc. model 111). The desired humidity level of the NO flow was controlled at 70% (2100 ppmv) by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 4 L min^{-1} by a mass flow controller. After the adsorption–desorption equilibrium among water vapor, gases, and photocatalysts was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc. model 42c), which monitors NO, NO_2 , and NO_x (NO_x represents $\text{NO} + \text{NO}_2$) with a sampling rate of 0.7 L min^{-1} . For comparison, the gaseous NO removal was also performed with the prepared $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes under dark, without the catalyst under light irradiation, and using the counterpart $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ powder hydrothermally prepared according to the literature [26]. The reaction of NO with air was ignorable according to the results of control experiments in dark or under solar light in the absence of photocatalyst.

3. Results and discussion

3.1. Characterizations

Fig. 1 shows the XRD patterns of the powders synthesized in a concentrated NaOH and ammonia solution at 220 °C for 18 h. Here NaOH is used not only as sodium source but also offers the alkalinity that is needed for powders crystallization and mineralization. As seen from Fig. 1, the diffraction peaks of the prepared samples could be indexed to monoclinic sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, JCPDS card No. 46-1) with lattice constants of $a = 3.55 \text{ \AA}$, $b = 6.67 \text{ \AA}$, $c = 5.52 \text{ \AA}$, where the diffraction peaks at 2θ values of 22.73° , 32.42° , 39.96° , 46.72° , 58.10° , and 50.50° were ascribed to the reflection of (110), (102), (210), (220), (321), and (242) planes of the monoclinic $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, respectively. The broadening of the diffraction peaks is ascribed to the nanocrystalline nature of the samples. No other diffraction peaks are found, indicating that pure monoclinic sodium bismuth titanate could be synthesized with the hydrothermal method by using sodium hydroxide, bismuth citrate, and TiO_2 powder as the sodium, bismuth and titanium sources, respectively.

The morphology of the resulting samples was firstly investigated by SEM (Fig. 2a and b). It can be observed that the sample consists of aggregated porous 3D microspheres, meanwhile, the microspheres are built by a plenty of 1D nano-whiskers. No other morphologies can be detected, indicating a high yield of these 3D microspheres. Transition electron microscopy (TEM) was used to further investigate the morphology of the samples (Fig. 2c and d). It is obvious that each nano-whiskers is with nearly uniform diameters of around 30 nm and lengths of around several hundred nanometers. Additionally, a strong contrast between the inner and outside parts of the nano-whiskers was observed, suggesting the hollow nanotube structures of the synthesized samples (Fig. 2c). The TEM image with high magnification further shows that the samples consist of nanotube structures as inner parts are much lighter than the outside parts (Fig. 2d). The aggregation and/or assembly of the nanotubes may produce abundant hierarchical pores on nanoscale (Fig. 2a).

X-ray photoelectron spectroscopy (XPS) was further used to elucidate the detailed surface chemical compositions and their electronic states of the as-prepared $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ nanotubes (Fig. 3). As shown from the survey spectra in Fig. 3a, element Bi, Na, Ti, C, and O coexisted in the samples, where the carbon peaks are attributed to the residual carbon from the sample and

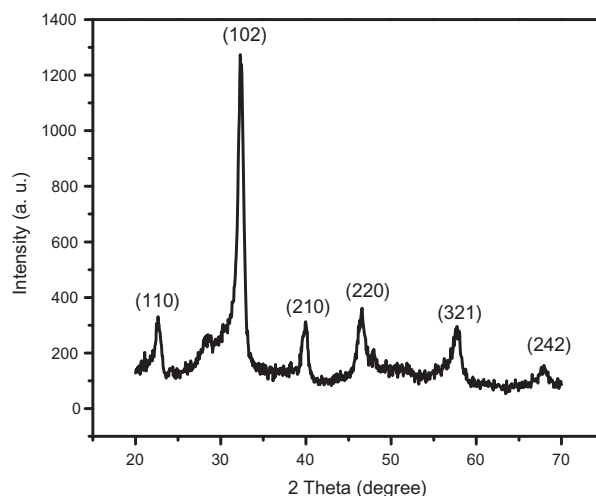


Fig. 1. XRD patterns of the as-prepared samples.

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