



# Fabrication of nitrogen-doped TiO<sub>2</sub> monolith with well-defined macroporous and bicrystalline framework and its photocatalytic performance under visible light

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## Abstract

In this study, hierarchically porous bicrystalline nitrogen-doped titania (N-doped TiO<sub>2</sub>) monolithic material was fabricated by a simple two-step approach: (i) preparation of TiO<sub>2</sub> porous monolith by a sol–gel process of titanium alkoxide in a mild condition utilizing a chelating agent and mineral salt and (ii) annealing of TiO<sub>2</sub> porous monolith obtained under a modest flow of ammonia gas at 700 °C for 2 h. The phase composition, crystal structure, morphology, pore structure, and porous properties of the final product were studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), mercury porosimetry, and nitrogen physisorption measurement, respectively. The resultant N-doped TiO<sub>2</sub> porous monolith possesses a bicrystalline (anatase and rutile) framework with a well-defined macroporosity. The results from X-ray photoelectron spectroscopy (XPS) confirm the formation of O–Ti–N bonds in the N-doped TiO<sub>2</sub> porous monolith. The photocatalytic activity of N-doped TiO<sub>2</sub> porous monolith was evaluated by the photodegradation of Rhodamine B over the samples under visible light. Nearly 50% of Rhodamine B in aqueous solution was efficiently degraded by N-doped TiO<sub>2</sub> porous monolith with the mixed-phase of anatase and rutile under visible light within 120 min.

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## 1. Introduction

In recent years, much attention has been paid to the development of bimodal porous metal oxide materials, including titania that has been proven to be an excellent material for environmental remediation and energy conversion.<sup>1–3</sup> In order to improve

photocatalytic activity, undoped and doped mesoporous titania with either anions or cations was synthesized by various synthesis methods.<sup>4–7</sup> Particularly, a partial inclusion of macropores in mesoporous materials was demonstrated to show enhanced photocatalytic activity compared to single-sized mesoporous materials because of the increase in mass transport through the material and the maintenance of a higher specific surface area on the level of fine pore systems.<sup>8–11</sup>

Titanium dioxide exhibits three polymorphs: rutile, anatase, and brookite. While rutile is the stable phase, both anatase and brookite are metastable. Mixed-phase of anatase and rutile TiO<sub>2</sub> has been shown to exhibit enhanced photocatalytic activity compared to single counterparts. It is considered as a

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result of improved charge carrier separation, possibly through the trapping of electrons in rutile and the consequent reduction in electron–hole recombination. So far, mixed-phase of anatase and rutile TiO<sub>2</sub> has been synthesized by applying different methods, such as flame pyrolysis,<sup>12</sup> solvothermal,<sup>13</sup> hydrothermal,<sup>14</sup> chemical vapor deposition,<sup>15</sup> physical vapor deposition,<sup>16</sup> calcination,<sup>17</sup> ultrasound irradiation,<sup>18</sup> sol–gel,<sup>19</sup> nitrogen doping,<sup>20</sup> etc.

The enhancement of photocatalytic activity of meso-macroporous titania is associated with the increase in photo-absorption efficiency and efficient diffusion of molecules caused by the macropores.<sup>3</sup> In fact, the macroporous channels could serve as light-transfer paths for the distribution of photon energy onto the large surface of inner photoactive mesoporous frameworks. In addition, a substitutional doping in the meso-macroporous titania could additionally improve photocatalytic activity under visible light. Shao et al.<sup>21</sup> prepared N-doped titania with hierarchical meso-macroporous structure as an active visible light-responsive photocatalyst by nitridation of template-free-synthesized meso-macroporous titania by employing urea as a nitrogen source. Their following report has demonstrated the preparation of nitrogen and phosphorus co-doped titania with hierarchical meso-macroporous structure by a simple two-step process: (i) the direct phosphation of meso-macroporous titania with phosphoric acid during the hydrolysis of titanium butoxide and (ii) further nitridation of phosphated meso-macroporous titania using urea.<sup>22</sup>

Recently, we have developed a facile method for preparing highly homogeneous TiO<sub>2</sub> monoliths by decreasing high reactivity of titanium alkoxide by utilizing a chelating agent and mineral salts under a mild condition.<sup>23</sup> In addition, we have also developed the pathway for the fabrication of hierarchically porous TiO<sub>2</sub> monoliths by a sol–gel reaction accompanied by a phase separation.<sup>24</sup>

In this work, we demonstrate the facile preparation of N-doped titania monolithic materials with well-defined macroporous structure and bicrystalline framework by a simple two-step process: (i) preparation of TiO<sub>2</sub> porous monolith by a sol–gel process of titanium alkoxide in a mild condition utilizing a chelating agent and mineral salt and (ii) annealing of TiO<sub>2</sub> porous monolith obtained under a modest flow of ammonia gas at 700 °C for 2 h.

The resultant meso-macroporous pure and N-doped TiO<sub>2</sub> monoliths are systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), UV–vis spectroscopy (UV–vis), Hg-porosimetry, and N<sub>2</sub> adsorption–desorption analysis. The photocatalytic activity is evaluated by the photodegradation of Rhodamine B over the samples under visible light.

## 2. Experimental

### 2.1. Synthesis

The preformed TiO<sub>2</sub> monolith was synthesized according to the experimental procedure reported previously elsewhere.<sup>24</sup> Briefly, given amounts of Ti(OPr)<sub>4</sub>, PrOH, and EtAcAc were first

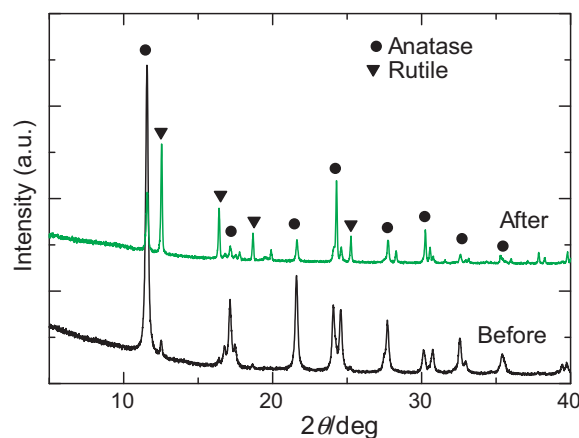


Fig. 1. XRD patterns of TiO<sub>2</sub> porous monoliths before and after nitrogen doping.

mixed together, and PEG was introduced into that mixed yellow solution and heated at 60 °C to dissolve. The solution was then cooled down to 40 °C, and 1 M NH<sub>4</sub>Cl aqueous solution was slowly added to the solution under vigorous stirring. After being stirred for 3 min, the obtained homogeneous solution was aged at 40 °C for 24 h. In order to obtain a crack-free TiO<sub>2</sub> monolith, the obtained wet gels were sequentially immersed in the EtOH/H<sub>2</sub>O solutions with different ratios of EtOH and H<sub>2</sub>O at 60 °C in the following order: 1st step – ethanol (EtOH) → 2nd step – EtOH:H<sub>2</sub>O = 9:1 → 3rd step – EtOH:H<sub>2</sub>O = 8:2 → 4th step – EtOH:H<sub>2</sub>O = 7:3 → 5th step – EtOH:H<sub>2</sub>O = 1:1 → 6th step – EtOH:H<sub>2</sub>O = 3:7. A time period for each immersion step was 8 h. The as-synthesized wet gels contain EtAcAc which coordinates to Ti atoms, and TiO<sub>2</sub> networks consequently become weak. The dried gels can break down easily into the pieces after calcination. Therefore, the removal of EtAcAc requires an extended aging of the gels in water. In the EtOH/H<sub>2</sub>O solution, EtAcAc was hydrolyzed to acetoacetic acid. The generated acetoacetic acid was then immediately decarbonized with acetone and CO<sub>2</sub>. The EtOH/H<sub>2</sub>O ratio has to be gradually reduced so that the hydrolysis of EtAcAc is allowed to take place slowly. Note that the gels were cracked when immersed directly in H<sub>2</sub>O. The samples were finally immersed in H<sub>2</sub>O at 60 °C for 24 h. The obtained gels were dried at 40 °C, and the resultant xerogels were calcined at 600 °C for 2 h. The N-doped TiO<sub>2</sub> porous monolith was produced by ammonolysis of pure TiO<sub>2</sub> porous monolith at 700 °C for 2 h under a modest flow of ammonia gas.<sup>25</sup>

### 2.2. Characterization

The phase compositions and crystal structures of N-doped TiO<sub>2</sub> porous monolithic samples were determined by X-ray diffraction (XRD) using a D8 Advance diffractometer (Bruker, USA) with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at a scanning speed of 2° min<sup>-1</sup> in the 2 $\theta$  range of 5–40°. The microstructures of the fractured surfaces of the samples were examined by using an XL30 FEG scanning electron microscope (Philips, The Netherlands), with an acceleration voltage of 15 kV. Before the SEM observation, the samples were sputtered with a thin gold layer to avoid charging. A Poremaster 60-GT mercury

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