



# The role of annealing temperature in enhancing the photocatalytic activity of nitrogen-doped hexaniobate



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## ABSTRACT

By controlling the annealing temperature, we obtained the optimum crystalline structure for nitrogen-doped hexaniobate ( $K_4Nb_6O_{17}$ ) for efficient decomposition of rhodamine B via visible-light photocatalysis. The annealing temperature for hexaniobate was closely related to the crystallinity and charge recombination rate. The rate of charge recombination could be controlled by varying the annealing temperature. The optimum photocatalytic activity of hexaniobate with or without nitrogen doping could be obtained at an annealing temperature at 400 °C. The long lifetime of photogenerated carriers was evident from measurements of hydroxyl radical concentrations resulting from catalysis by nitrogen-doped hexaniobate. The results indicate that improvements in photocatalytic activity of the annealed materials were mainly attributed to the decrease in recombination rate and to the high rate of separation of photogenerated carriers.

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## 1. Introduction

In the past decades, semiconductor photocatalysis has been intensively studied because of its potential applications in many fields such as environmental remediation [1–4], solar energy conversion [5,6], and hydrogen generation [7].

One class of the most promising materials for photocatalytic applications is Nb-based semiconductors, which feature a two-dimensional layered structure with corner- and/or edge-shared  $MO_6$  ( $M=Nb$ ) octahedral units. Each layer sheet is negatively charged, and alkali-metal cations that compensate the negative charge of the layers are located between the sheets [8–12] (Fig. 1). Nb-based

materials exhibit photocatalytic activity under UV light that is higher than that of titanium(IV) oxide ( $TiO_2$ ) [13].

Their photocatalytic activity depends mainly on the recombination rate of photogenerated charge-carriers and on the rate of solar energy utilization [4,14–16]. The high rate of charge-carrier recombination leads to a discrepancy between the relatively large penetration depth of photons and the short mean free paths of charge carriers [17,18], which allows separated carriers to recombine before they participate in photocatalytic reactions. Various approaches, including physical and chemical methods such as phase and morphology transformation [19–23] or material crystallization [24–29], have been found to have a significant impact on charge-carrier separation and transport and, therefore, to efficiently resolve these issues. Many approaches have been employed to improve solar energy utilization. For example, nitrogen-doping has been widely adopted to enhance visible-light response of wide-band-gap materials [30]. Substitutional doping of N with annealing pretreatment has

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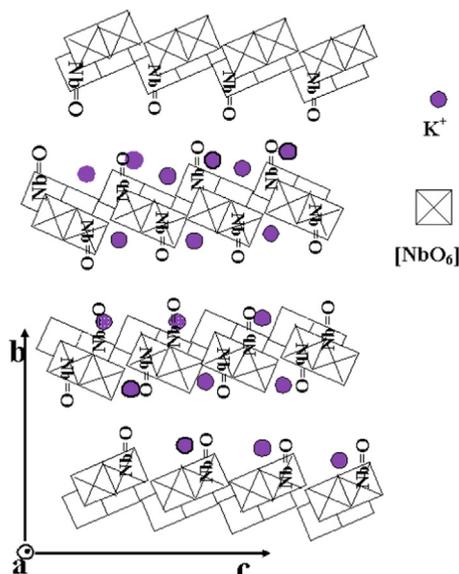


Fig. 1. The structure graph of layered  $K_4Nb_6O_{17}$ .

been proven to be an effective and controllable method for reducing the band gap [31]. Most of such studies have found that nitrogen doping by annealing pretreatment enhances photocatalytic activity under visible light [32,33]. However, few have reported a correlation between photocatalytic activity and annealing temperature, crystallinity, and charge recombination rate, which significantly affects all properties of such materials.

In the present study, we demonstrated that the recombination problem could be addressed by changing the material from a crystalline to amorphous) through annealing. The recombination rate of photogenerated charge carriers was significantly decreased by the annealing treatment. Meanwhile, good photocatalytic activity of treated samples with or without nitrogen doping could be obtained by annealing them at 400 °C. Thus, the temperature for efficient charge separation was 400 °C. The lifetime of photogenerated carriers in nitrogen-doped amorphous niobate was longer than that of carriers in crystal niobate.

## 2. Experimental

### 2.1. Synthesis of $K_4Nb_6O_{17}$

The  $K_4Nb_6O_{17}$  sample was prepared according to a method described elsewhere [13]. A mixture of 0.4 g of  $Nb_2O_5$  powder in 40 mL of 3 M KOH solution was pretreated in a Teflon coated autoclave at 180 °C for 10 h. A clear solution was obtained. Urea (3 g) and deionized water (27 mL) were then added to 13.5 mL of the clear solution in a Teflon-coated autoclave. The autoclave was placed in an oven and heated at 220 °C for 24 h. The resulting precipitate was separated by centrifugation, washed several times with deionized water, and then dried at 70 °C overnight. The resulting sample was  $K_4Nb_6O_{17}$  (JCPDS 53–0780).

### 2.2. Synthesis of nitrogen-doped hexaniobate

Nitrogen-doped hexaniobate was synthesized by following a method similar to that employed for other nitrogen-doped materials ( $HNb_3O_8$ ,  $HTiNbO_5$ ) [32,33]. A mixture of dried  $K_4Nb_6O_{17}$  sample and urea with a mass ratio of 1:2 was finely milled and then heated in a crucible at 400 °C for 2 h. The resulting yellow product was crushed, washed thoroughly with water several times, and then dried at 70 °C overnight. The resulting sample was labeled as  $K_4Nb_6O_{17}(N)$ -400. Other samples were similarly defined based on the temperature, and other conditions were employed during sample preparation. For example,  $P_{25}(N)$ -400 represents a sample of commercial titanium dioxide ( $P_{25}$ ) doped with nitrogen and annealed at 400 °C for 2 h.  $K_4Nb_6O_{17}$ -400,  $K_4Nb_6O_{17}$ -300, and  $K_4Nb_6O_{17}$ -500 represent  $K_4Nb_6O_{17}$  that was annealed at 400, 300, and 500 °C, respectively, for 2 h.

### 2.3. Evaluation of photocatalytic properties

A suspension containing 50 mg of photocatalyst and rhodamine B (RhB) aqueous solution ( $1 \times 10^{-5}$  M, 100 mL) was stirred for 40 min in the dark until adsorption–desorption equilibrium was established. Subsequently the suspension was irradiated by using a 300 W Xe lamp equipped with a cutoff filter ( $\lambda > 420$  nm). The concentration of RhB during catalytic reaction was monitored from its UV–visible (UV–vis) absorption spectra.

### 2.4. Measurement of hydroxyl radical concentration

The concentration of hydroxyl radicals were assessed by following a previously described protocol [34]. A suspension of 10 mg of  $K_4Nb_6O_{17}(N)$ -400 or  $K_4Nb_6O_{17}$  and 3 mM terephthalic acid (TA) in 80 mL of 0.01 M NaOH solution was irradiated by using a Xe lamp (300 W) equipped with a cutoff filter ( $\lambda > 420$  nm). A 5 mL sample of the irradiated suspension was collected every 30 min and then centrifuged. The resulting supernatant was analyzed by fluorescence (FL) spectroscopy.

### 2.5. Sample characterization

X-ray diffraction (XRD) patterns should be recorded using a D8 advance X-ray diffractometer (Bruker, Germany) (40 kV, 40 mA), with nickel-filtered Cu  $K\alpha$  radiation ( $\alpha = 1.54056 \text{ \AA}$ ). UV–vis diffuse reflectance spectra were obtained on a Shimadzu 3100 UV–vis–near-infrared spectrometer. Fluorescence (FL) and photoluminescence (PL) spectra were recorded on Hitachi (F-7000) instrument. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5700 ESCA System with Al  $K\alpha$  radiation source (1486.7 eV).

## 3. Results and discussion

### 3.1. XRD analysis

Figs. 2 and 3 show the XRD patterns of  $K_4Nb_6O_{17}$ ,  $K_4Nb_6O_{17}$ -300,  $K_4Nb_6O_{17}$ -500,  $K_4Nb_6O_{17}$ -400, and  $K_4Nb_6O_{17}(N)$ -400.

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