

# Synthesis and Characterization of N-doped TiO<sub>2</sub> Nanowires with Visible Light Response

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**Abstract** Unique N-doped TiO<sub>2</sub> nanowires with one-dimensional nanostructure were synthesized in presence of NH<sub>3</sub> gas at different temperature with titanate nanowires as precursor. Structure and morphology of the obtained samples were investigated by TEM, HRTEM, SEM, XRD, XPS, and UV–Vis. The results revealed that a clear visible-light response could be induced by N-doping. Nanowire structure was maintained after N-hybridization of TiO<sub>2</sub> framework even at 600 °C, while distance between two contiguous layers shrunked a little. The incorporated nitrogen atoms are located in position of oxygen in TiO<sub>2</sub> lattice to form O–Ti–N structure according to XPS result. An excellent photocatalytic activity of nitrogen-doped TiO<sub>2</sub> nanowires for degradation of methyl orange was achieved.

**Keywords** Nitrogen-doped · TiO<sub>2</sub> nanowires · Visible light · Photocatalysis

## 1 Introduction

Since Fujishima and Honda [1] discovered the phenomenon of photocatalytic splitting of water on a TiO<sub>2</sub> electrode under ultraviolet (UV) light [2], TiO<sub>2</sub> has been widely studied in areas ranging from photovoltaics and photocatalysis [3–5]. To enhance photoelectric properties and photocatalytic activity of TiO<sub>2</sub> under UV light and induce

TiO<sub>2</sub> with visible light response, preparation of low dimensional TiO<sub>2</sub> [6–8], porous TiO<sub>2</sub> [9, 10], and modification of TiO<sub>2</sub> host with metal ions and nonmetal ions [11, 12] have been widely researched.

One dimensional materials have shown huge potential in photocatalysis, sensors, photochemistry and energy sources, and has been focused by scientists [13]. Titanate nanowires prepared by hydrothermal method used TiO<sub>2</sub> powder as precursor show low density and layered structure, and have attracted attention as a prospective lithium electrode, sensor material, and photocatalyst [14–16]. However the traditional synthesis procedures of titanate nanowires through hydrothermal method need rigorous condition [17, 18], such as high temperature and high alkali concentration (240 °C, NaOH 15 mol/L) [19, 20]. If titanate nanowires are synthesized in revolving autoclave, more mild condition could be enough [21] (130 °C, NaOH 10 mol/L). It is indicated that flow conditions in rotating autoclave may be favorable for the oriented attachment mechanism [21].

Among all of TiO<sub>2</sub> modification methods, non-metal impregnation shows obvious advantages in inducing visible light response of TiO<sub>2</sub> and enhancing visible light activity [12]. Recently, people found that N-doping can enhance photocatalytic activity of TiO<sub>2</sub> in visible region, which shows great potential in photocatalytic field. There have already been numerous reports about various on synthetic procedures, such as reactive sputtering [22, 23], hydrolysis [24], chemical vapor deposition [25], thermal treatment [12] and so on. In most of chemical doping routes, treating TiO<sub>2</sub> in NH<sub>3</sub> or N<sub>2</sub> flow at high temperature was found not only to be an essential method for promoting reaction, but also more effective and facile than others [12].

In this paper, we tried a new route to get N-doped TiO<sub>2</sub> nanowire through nitridation of titanate nanowire. It was

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found to be a simple and facile way to obtain N-doped TiO<sub>2</sub> nanowire with excellent degradation of methyl orange under visible light. Using titanate nanowire as precursor, which was then nitridated at suitable temperature in NH<sub>3</sub> flow, we could combine transformation of titanate to TiO<sub>2</sub> and N-doping into one simple process. At the same time, as a comparison, commercial photocatalyst Degussa P25 TiO<sub>2</sub> was also treated under the same condition and obtained P25-600N. The results indicated that N-TiO<sub>2</sub> nanowires synthesized in the way showed a considerably enhanced activity of visible-light-induced photodecomposition of methyl orange.

## 2 Experimental Section

As starting materials, titanate nanowire was synthesized through commercially titania as reported in Ref. [21] in which Degussa P25 was mixed with a NaOH (10 M) aqueous solution in a Teflon vessel at 130 °C at autoclave for 36 h. After having been washed with deionized water and 0.1 M HCl aqueous solution, H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> · xH<sub>2</sub>O in form of nanowire was formed. Nitridation of titanate nanowires was carried out in a tubular quartz reactor by flowing ammonia at 300–600 °C with a heating rate of 5 °C min<sup>-1</sup> for 5 h, then cooled to room temperature and following dried in vacuum at 150 °C, 0.076 Mpa. The N-doped TiO<sub>2</sub> nanowires obtained at different temperature (300, 400, 500, 600, 700 °C, none nitrided) were labeled as NW-300N, NW-400N, NW-500N, NW-600N, NW-700N, and NW-0N as well. The sample P25 TiO<sub>2</sub> was nitrided at 600 °C for 5 h, marketed as P25-600N.

Structure of the as-synthesized samples and nitridated samples was determined by a powder XRD (Rigaku D/max-2500) diffractometer with Cu K $\alpha$  radiation (40 kV and 100 mA). UV-Visible spectroscopy (UV-Vis) absorbance spectra were recorded in air against MgO in the region of 190–800 nm on a JASCO V-570 UV-Vis spectrophotometer. Particle morphology was observed on a Tecnai G220S-TWIN TEM at an accelerate voltage of 200 kV. Nitrogen species in products was determined by a PHI 5300 ESCA X-ray photoelectron spectroscopy (XPS). XPS measurement was acquired by monochromatic Mg K $\alpha$  excitation, and all the bonding energies were calibrated to C1s peak at 284.6 eV of surface adventitious carbon. N content was determined by Elementar Vario El.

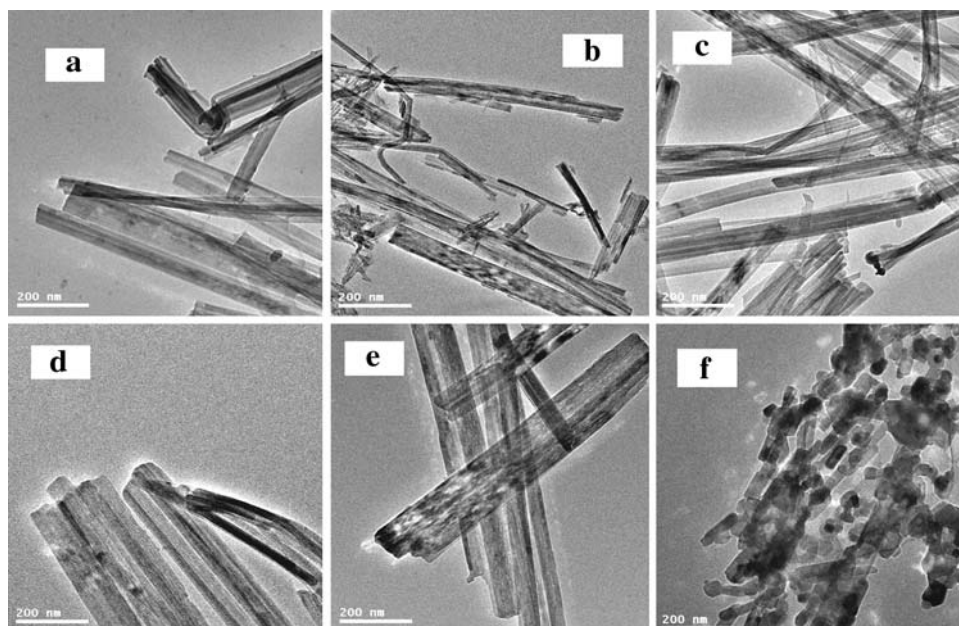
Photocatalytic performances of the as-synthesized samples were investigated by degradation of methyl orange under a 125 W super-high-pressure Hg lamps (main  $\lambda = 420$  nm). Under illumination of visible-light, 200 mL 40 mg/L methyl orange aqueous solution with 0.1 g catalyst powders was decanted into a photoreactor. Recycled cooling water kept the temperature of photoreactor constant at 25 °C. Concentration of methyl orange was monitored by colorimeter with a Shimadzu, UV-240 spectrometer, at  $\lambda = 505$  nm.

## 3 Results and Discussion

### 3.1 Physicochemical Properties of N-TiO<sub>2</sub> Nanowires

Microstructure of samples are firstly investigated by TEM, Fig. 1 shows TEM images of titanate nanowires nitridated

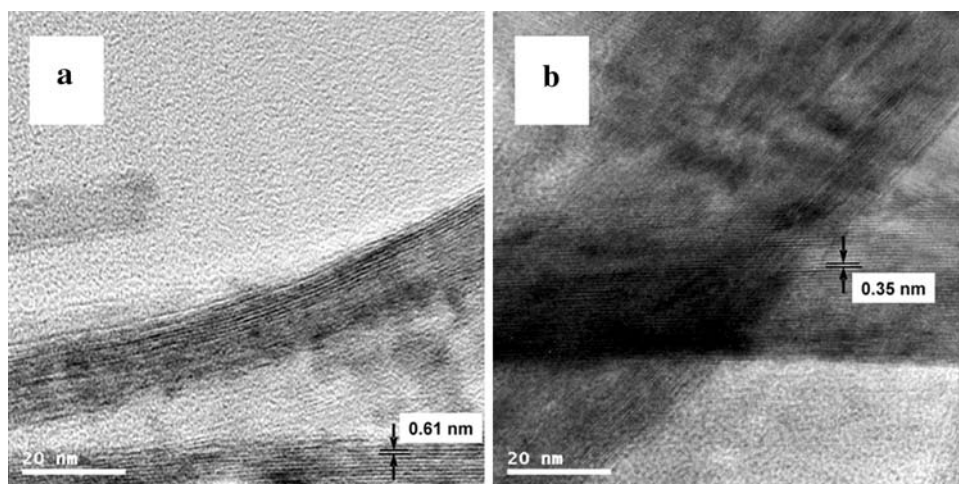
**Fig. 1** TEM images of nitrogen-doped TiO<sub>2</sub> nanowires: **a** NW-0N, **b** NW-300N, **c** NW-400N, **d** NW-500N, **e** NW-600N, **f** NW-700N



at different temperature. It can be seen from Fig. 1a that the as-synthesized titanate nanowires were uniform and solid, and diameter of nanowire is in the range of 100–200 nm. It is indicated from Fig. 1 that nanowire structure could be kept well even after 600 °C NH<sub>3</sub> flow treatment. But, when the temperature elevated to 700 °C, the nanowire structure could not continually be maintained anymore, and some nanowires fractured, so that amount of nanorods were observed.

Figure 2 shows HRTEM images of titanate nanowire and N-doped TiO<sub>2</sub> nanowire. Clear lattice stripes in Fig. 2 showed that both of the nanowires before and after nitridation both have high crystallinity with fewer defects.

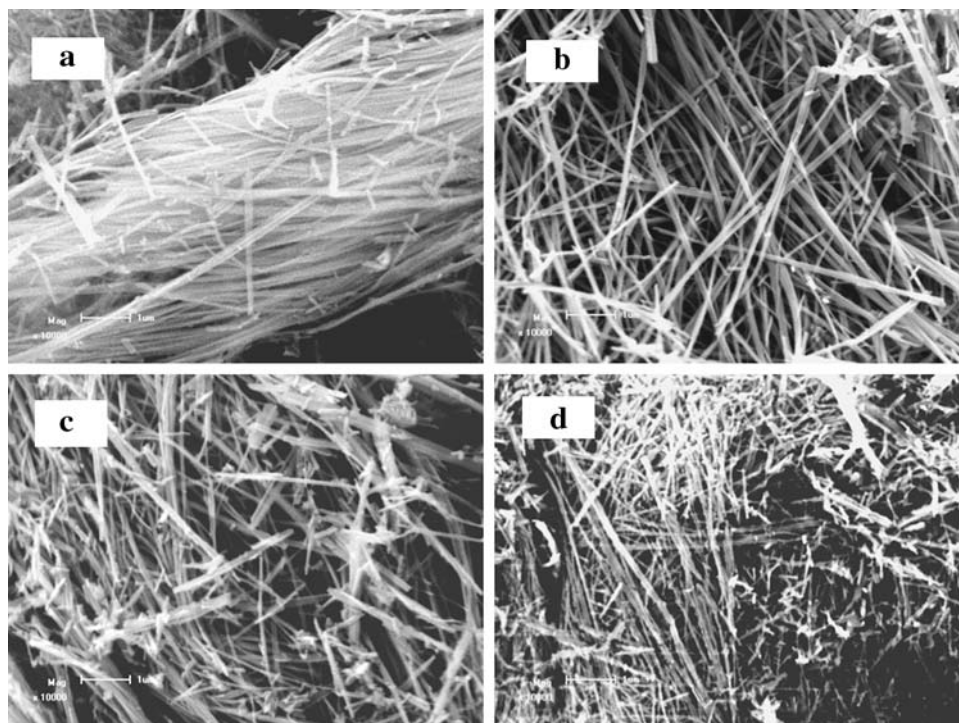
**Fig. 2** HRTEM images of nitrogen-doped TiO<sub>2</sub> nanowires: **a** NW-0N, **b** NW-600N

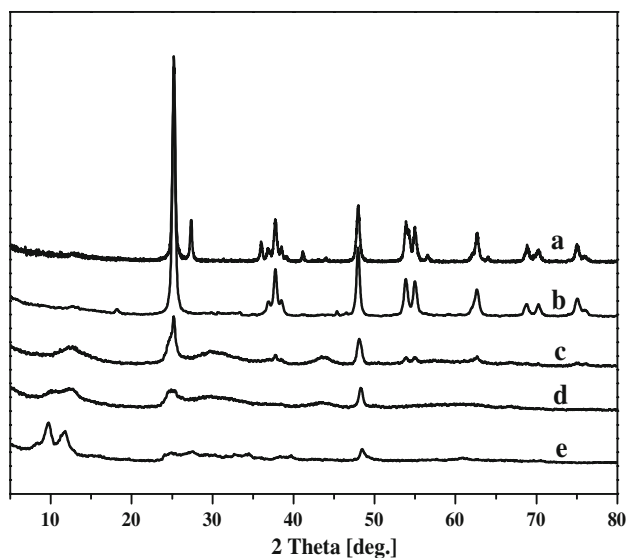


In Fig. 2a corresponding HRTEM image of the titanate nanowire shows lattice planes, and plane intervals of 0.61 nm agrees with  $d_{101}$  spacing in XRD of titanate nanowire [26]. For the sample after nitridation, plane intervals in Fig. 2b changed to 0.35 nm, which corresponds to distance between two (101) planes of anatase TiO<sub>2</sub> [27]. From difference of HRTEM of the two samples could conclude that the titanate nanowires turned into TiO<sub>2</sub> nanowires after nitridation.

Figure 3 shows SEM images of N-doped TiO<sub>2</sub> nanowires before and after nitridation at different temperature. Numerous wire-like products can be obviously observed and nanowires post-heated at 400–600 °C for 5 h maintain

**Fig. 3** SEM images of nitrogen-doped TiO<sub>2</sub> nanowires: **a** NW-0N, **b** NW-400N, **c** NW-500N, **d** NW-600N





**Fig. 4** XRD patterns of N-TiO<sub>2</sub> nanowires: (a) P25-600N, (b) NW-600N, (c) NW-500N, (d) NW-400N, (e) NW-0N

nanowire morphology. Otherwise, the as-synthesized nanowires shows high aspect ratios with a diameters around 100–200 nm.

The Crystallinity of samples was determined by X-ray diffraction technique and the XRD patterns of P25-600 N and as-synthesized nanowires are shown in Fig. 4. As confirmed by XRD in Fig. 4e, the as-synthesized titanate nanowires were well crystallized at mild temperature 130 °C with characteristic diffraction peaks of H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> · xH<sub>2</sub>O [28], and no diffraction peaks of starting TiO<sub>2</sub> power (Degussa P-25) and other impurities, (such as NaOH and NaCl), are observed. According to Fig. 4b, e, during the nitridation process the titanate phase gradually disappeared with elevated temperature. Only diffraction peaks assigned to anatase TiO<sub>2</sub> existed, when temperature reached to 600 °C (Fig. 4b). Meanwhile, no TiN peak was found in all XRD patterns. Combined with TEM images and SEM images, after nitridation at 600 °C pure anatase TiO<sub>2</sub> was obtained and titanate nanowires turned into anatase TiO<sub>2</sub> nanowires completely. Structural changes of titanate to TiO<sub>2</sub> may be according to following equation [29]  $\text{H}_2\text{Ti}_3\text{O}_7 \rightarrow 3\text{TiO}_2 + \text{H}_2\text{O}$ . It is obviously that protons replaced sodium ions and facilitated the acid catalyzed condensation of OH groups during heat treatment and lead to formation of TiO<sub>2</sub> [29], and we hope that the transformation process could be benefit to N doping and induce high visible light response.

Table 1 shows BET surfaces and N contents of samples. According to elemental analysis, N content of as-doped samples was amounted to 1.4 wt% for NW-600N, and 0.8 wt% for P25-600 N, respectively. The differences in N-doping amount should be attributed to precursor properties, since nitridation conditions such as NH<sub>3</sub> flow rate,

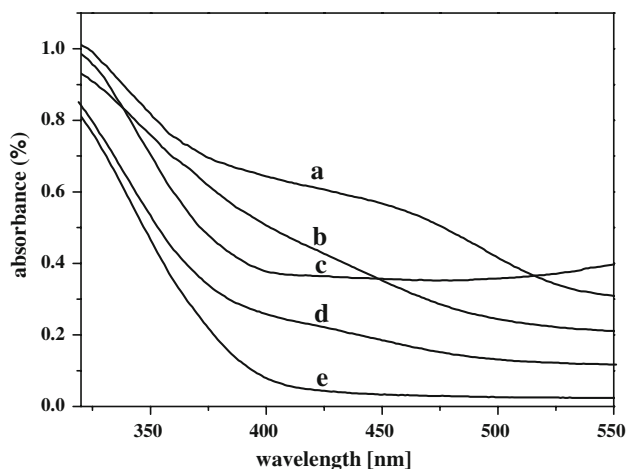
**Table 1** BET surfaces and the N content of the samples

	BET surfaces (m <sup>2</sup> g <sup>-1</sup> )	N content (%)
NW-0N	123.5	0
NW-600N	84	1.4
P25-600N	28	0.8

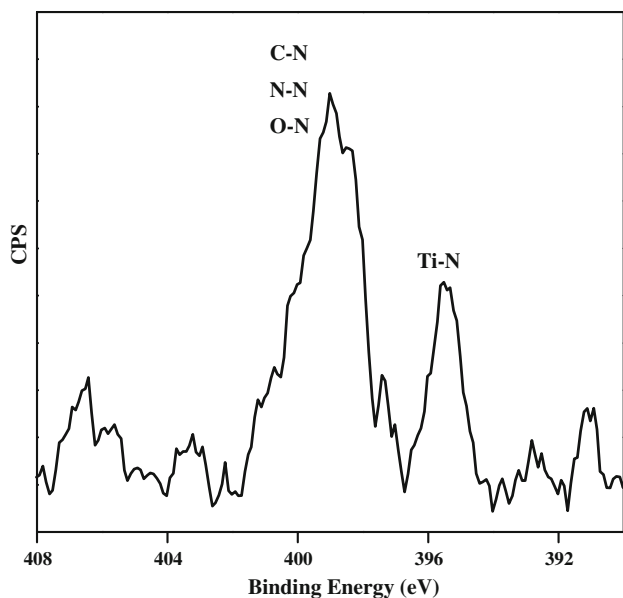
temperature and time on stream were same for both samples. BET surface of N-doped TiO<sub>2</sub> nanowires reached 84 m<sup>2</sup>/g, which is much larger than that of P25-600N (28 m<sup>2</sup>/g).

Figure 5 shows UV-Vis spectra of N-TiO<sub>2</sub> nanowires. No absorption peak was observed in visible light region in curve of Fig. 5e. However, the adsorption edge shifted to visible region and showed obvious absorption peak, whatever it is obtained from the N-doped TiO<sub>2</sub> nanowires or from P25-600N, which proved the O atoms in TiO<sub>2</sub> have been partly substituted by N atoms. Furthermore, the absorption edge was red shifted gradually as N content increased (the color of samples turned from white to brilliant yellow). A large difference of absorption intensity was found between NW-600N and P25-600N, even though they were treated at the same condition. The most possible reason for that is N content of NW-600N is much higher than that of P25-600N, and which confirms that transformation of titanate to TiO<sub>2</sub> benefits the doping of N atoms.

Figure 6 shows N1s XPS spectra NW-600N. As N1s peak generally existed at 396–404 eV [12, 30, 31], peaks at 396–397 eV should be attributed to substitutional N atoms, and other peaks >399 eV could be assigned to interstitial N [32]. In the results, presence of O–Ti–N bond was confirmed by N1s peak around 396 eV, it is accepted that small amount of nitrogen atoms is located at position of oxygen sites of the N doped TiO<sub>2</sub> nanowires. Interstitial N around 400 eV [32] could be also observed, which is



**Fig. 5** UV-vis spectra of N-TiO<sub>2</sub> nanowires: (a) NW-600N, (b) NW-500N, (c) P25-600N, (d) NW-400N, (e) NW-0N

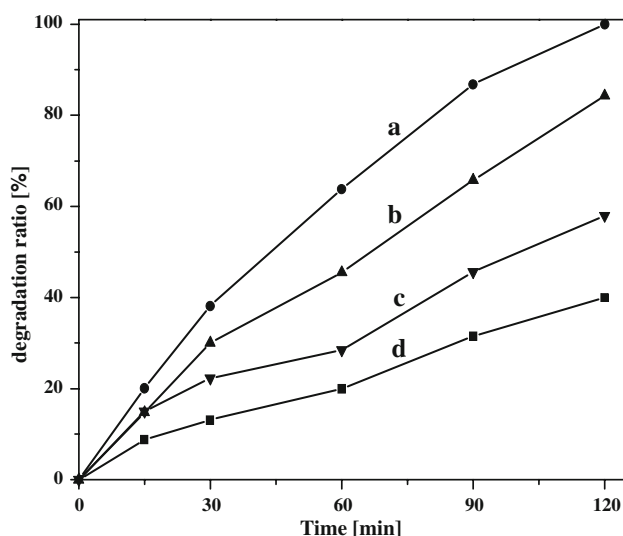


**Fig. 6** N1s XPS spectra of the NW-600N

attributed to the N atoms existing in lattice space of TiO<sub>2</sub> nanowires.

### 3.2 Photocatalytic Activity

Methyl orange degradation on N-doped TiO<sub>2</sub> nanowires is presented in Fig. 7. Among all of the samples, NW-600N showed the highest activity of 100% after 2 h reaction, while P25-600N has only 38% degradation ratio. It may be, on one hand, based on lower N content and BET surfaces. On the other hand, morphology and particle size distribution of the catalyst could also critically effect



**Fig. 7** Methyl orange degradation ratio of the TiO<sub>2</sub> nanowires: (a) NW-600N, (b) NW-500N, (c) NW-400N, (d) P25-600N

photoactivity of TiO<sub>2</sub> [33]. It is very clear that photoactivity varied with increasing of nitrogen content in TiO<sub>2</sub> nanowires lattice and the nanowire morphology is beneficial to photocatalytic activity according to the reaction results.

## 4 Conclusions

A facile route to obtain N-doped TiO<sub>2</sub> nanowires with high visible light activity by heating in NH<sub>3</sub> flow at different temperatures using titanate nanowires as precursor was shown in this paper. Characterizations of physicochemical properties proved that a simple nitridation at suitable temperature could result in an incorporation of N atoms into titanate nanowires and re-arranged to visible-responed TiO<sub>2</sub> nanowires easily. The transformation of titanate to TiO<sub>2</sub> favored N doping than nitridation process of normal TiO<sub>2</sub> and resulted in a higher N-content. The doped N atoms existed in both O–Ti–N state and interstitial N state which then induced a visible light response. On the as-synthesized samples, a superior photocatalytic degradation performance under visible light irradiation was achieved in comparison with N-doped P25 TiO<sub>2</sub>. The optimal conversion of 100% for methyl orange has been achieved at NW-600N under stirring at room temperature.

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