



# Photocatalytic activity of nitrogen doped TiO<sub>2</sub> nanotubes prepared by anodic oxidation: The effect of applied voltage, anodization time and amount of nitrogen dopant



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## ABSTRACT

Nitrogen doped TiO<sub>2</sub> nanotube arrays were prepared by anodizing Ti foils in an organic electrolyte containing specified amounts of urea as nitrogen precursor. The photocatalytic activity of the samples was evaluated by analyzing the degradation kinetics of phenol in water. The influence of tubes' length, tubes' surface morphology and amount of nitrogen in the TiO<sub>2</sub> lattice on hydroxyl radical formation efficiency, photocatalytic activity and stability in four cycles was investigated. It was found that the photocatalytic activity as well as the charge carrier recombination rate depends on nitrogen concentration and the process parameters. 3.5 μm-long nanotubes containing 0.34 at.% of nitrogen seems to be favorable in phenol degradation and OH radicals generation under visible light. Comparison of XPS and photocatalytic activity test results shows decrease in phenol degradation efficiency with increasing amount of carbon contaminants on photocatalysts' surface.

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## 1. Introduction

TiO<sub>2</sub> nanostructures, especially highly ordered nanotube arrays prepared by the anodization of titanium, have been widely used for recent years as photocatalysts due to their special features including unique structure, high specific surface area, better adsorption ability (comparing to powder photocatalysts) and unidirectional charge transfer [1–3]. TiO<sub>2</sub> nanotubes could be potentially used for photocatalytic degradation of pollutants in water [3,4] and gas [5] phases, inactivation of microorganisms [6], hydrogen production [7–9] and photoconversion of CO<sub>2</sub> [10]. However, major disadvantages of using TiO<sub>2</sub> nanotubes, which have not been fully overcome, are their relatively large band gap (3–3.2 eV) and high recombination rate of photogenerated electron–hole pairs [1,11]. These two

major factors lead to low quantum yield of photocatalytic process and necessity to use of UV irradiation, which disables to apply them on an industrial scale. Many different strategies were proposed to solve these problems, such as transition metal cations doping [12,13], nonmetals doping [14–16], dye sensitization [17] and surface modification with noble metals and with low band gap semiconductors [18–20].

The incorporation of nonmetal atoms into the TiO<sub>2</sub> structure is still one of the most popular and effective method to enhance its photocatalytic performance. Among various investigated nonmetals, nitrogen attracts great attention since nitrogen atoms can be introduced into the TiO<sub>2</sub> lattice inducing a new N2p energy level above the valence band, thereby narrowing the band gap of TiO<sub>2</sub> and finally leading to a shift in the optical response towards visible range [21]. Furthermore, under UV irradiation, nitrogen atoms act as an efficient electron trap preventing electron–hole recombination [22]. It should be also noted that additional benefits from nitrogen doping of TiO<sub>2</sub> result from the fact that nitrogen have

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small ionization energy and atomic size comparable with oxygen, is stable and able to form metastable centers [23].

Nitrogen doped TiO<sub>2</sub> nanotubes could be prepared via various routes including ion implantation method [24,25], chemical bath deposition [26–30], ammonia annealing at low [31] and high temperatures [32,33], anodization of titanium in the electrolyte containing nitrogen precursor [34,35], and others [15,36–38]. Generally, all of these approaches can be classified into two categories: one and two-step synthesis processes. In the typical two-step route, amorphous TiO<sub>2</sub> nanotubes are obtained in the first step followed by nitrogen incorporation into the TiO<sub>2</sub> nanotubes in the second step, using immersing in hot ammonia solutions [29], annealing TiO<sub>2</sub> nanotubes with ammonia at high temperatures [26], by hydrothermal treatment of TiO<sub>2</sub> nanotubes [15] and by chemical vapor deposition [39]. Some of these methods, such as ion implantation, can cause strong structural alterations [40]. However, in view of industrial applications, two-step approach is cost intensive and operationally difficult [34]. In the one-step approach, nitrogen doped TiO<sub>2</sub> nanotube formation is mostly carried out using ethylene glycol-based electrolytes containing a small amount of nitrogen precursor, such as urea [34] and NH<sub>4</sub>NO<sub>3</sub>/NH<sub>4</sub>OH [38] or by anodization of TiN alloy [36]. Recently, this method has been more and more popular as a straightforward, cost effective preparation process to produce nitrogen modified TiO<sub>2</sub> nanotubes of high purity at relatively low temperature. Antony et al. [34] prepared nitrogen doped TiO<sub>2</sub> nanotubes by anodization of Ti foil in the electrolyte composed of NH<sub>4</sub>F, water, ethylene glycol and urea. The effect of nitrogen concentration on the optical band gap was investigated. They showed that nitrogen atoms are incorporated into TiO<sub>2</sub> structure in two forms: substitutional and interstitial. They also showed that band gap value of nitrogen doped TiO<sub>2</sub> nanotubes depends on the amount of nitrogen precursor. Kim et al. [36] obtained nitrogen doped TiO<sub>2</sub> nanotubes by anodization of TiN alloy in the glycerol-based electrolyte. Photocurrent experiment showed that nitrogen doped sample have lower and higher photoresponse under the influence of UV and visible light irradiation compared to undoped one, respectively. Shankar et al. [38] prepared nitrogen doped TiO<sub>2</sub> nanotubes by one-step approach in the electrolyte containing HF, NH<sub>4</sub>NO<sub>3</sub> and ammonium hydroxide. Nitrogen doped samples exhibited enhanced optical absorption in the wavelength range of 400–510 nm.

Generally it could be concluded that photocatalytic activity of powder TiO<sub>2</sub> under the UV and visible light irradiation is strongly dependent on the amount of nitrogen incorporated into the bulk phase of TiO<sub>2</sub> [21], while the photoactivity of undoped TiO<sub>2</sub> nanotubes under UV irradiation mainly depends on the tubes' parameters (length and wall thickness) [1,5]. On the other hand, in most reports photocatalytic activity of nitrogen modified TiO<sub>2</sub> nanotubes were measured using dyes as model substances on photodegradation tests [28,30,37]. Dyes are not recommended to be used as model compounds due to their absorption properties (dye sensitization), large photoabsorption coefficient and complicated mechanism of degradation [41].

In view of this, we have recently obtained nitrogen doped TiO<sub>2</sub> nanotubes prepared via one-step electrochemical method under various conditions of anodization process (U=20–50 V and t=30–120 min). For the first time, the morphology of nitrogen doped TiO<sub>2</sub> nanotubes, as well as the chemical character and nitrogen content were related to the efficiency of electron-hole recombination process, efficiency of phenol degradation and hydroxyl radicals formation under both UV and Vis irradiation. Additionally, the influence of carbon-like surface contaminants on the photocatalytic activity of nitrogen doped TiO<sub>2</sub> nanotubes was studied. A possible mechanism of pollutants degradation on the surface of nitrogen doped TiO<sub>2</sub> nanotubes under visible light was proposed as well.

## 2. Experimental

### 2.1. Preparation of nitrogen doped TiO<sub>2</sub> nanotubes

Prior to anodization, the Ti foils were ultrasonically cleaned in acetone, isopropanol, methanol and deionized water (each solvent 10 min) and dried in air stream. The anodization was carried out using a two-electrode system with Ti foil as anode and platinum mesh as cathode. The distance between the electrodes was kept constant at 2 cm. Ag/AgCl reference electrode was used only for controlling the process and obtaining information about actual potential of Ti working electrode. All anodizations were carried out at room temperature. The anodization took place in the electrolyte composed of ethylene glycol (EG) with 2 vol% water, containing 0.09 M NH<sub>4</sub>F and different weight percentage of urea, used as nitrogen precursor. Ti foil was anodized for 30–120 min at the applied voltage from the range of 20–50 V using programmable DC power supply (MANSON SDP 2603). Finally, the obtained samples were rinsed with deionized water, sonicated in water (5 min), dried in air (80 °C for 24 h) and calcined at 450 °C (heating rate 2 °C/min) for 1 h.

### 2.2. Characterization of nitrogen doped TiO<sub>2</sub> nanotubes

The morphology of obtained undoped and nitrogen doped TiO<sub>2</sub> nanotubes was determined by using scanning electron microscopy (SEM, FEI Quanta 250 FEG). Crystal structure of prepared samples was determined from X-Ray diffraction patterns (XRD) measured in the range of  $2\theta = 20\text{--}80$ , using X-ray diffractometer (Xpert PRO-MPD, Philips) with copper K $\alpha$  radiation ( $\lambda = 1.5404 \text{ \AA}$ ). The XRD estimation of the crystallite size was based on the Scherrer formula. All XPS spectra were recorded on PHI 5000 VersaProbe™ (ULVAC-PHI) spectrometer with monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ). X-ray beam was focused to diameter 100  $\mu\text{m}$ , measured area was defined as a 250  $\mu\text{m}$  square. Both the survey and high-resolution (HR) XPS spectra were collected with the hemispherical analyzer at the pass energy of 117.4 and 23.5 eV and the energy step size of 0.4 and 0.1 eV, respectively. The UV–vis reflectance and absorbance spectra of undoped and nitrogen doped TiO<sub>2</sub> nanotubes were recorded on Shimadzu UV–Vis Spectrophotometer (UV 2600) equipped with an integrating sphere. The baseline was determined using barium sulphate as a reference. The spectra were registered in a range of 300–800 nm, with a scanning speed of 250 nm/min at the room temperature. Bandgap energy values were obtained as the intercept of the tangent of the Kubelka-Munk function transformation plot ( $F_{KM}^{0.5} E_f^{0.5}$ ) vs. photon energy. The photoluminescence (PL) measurements were carried out at room temperature using LS-50B Luminescence Spectrophotometer equipped with Xenon discharge lamp as an excitation source and a R928 photomultiplier as detector. The excitation radiation (360 nm) was directed on the sample's surface at an angle of 90°.

### 2.3. Measurement of photocatalytic activity

Photocatalytic activity of undoped and nitrogen doped TiO<sub>2</sub> nanotubes was determined in two model processes: cleaning of water from phenol and •OH radicals generation efficiency (using terephthalic acid). Phenol was selected as a model pollutant because it is a nonvolatile and common contaminant present in industrial wastewaters [42]. Terephthalic acid reacts with hydroxyl radicals to form highly fluorescent product: 2-hydroxyterephthalic acid. The photocatalytic activity tests were carried out in a photoreactor made of quartz with the working volume of about 15 mL. The phenol and terephthalic acid concentration was 0.21 mM and 0.5 mM, respectively. The samples with the surface area of 4 cm<sup>2</sup> were immersed in phenol or terephthalic acid solution for 30 min

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