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<td>Lai, Yue-Kun; Huang, Jianying; Zhang, Hui-Fang; Subramaniam, Vishnu-Priya; Tang, Yuxin; Gong, Dangguo; Sundar, Latha; Sun, Lan; Chen, Zhong; Lin, Changjian</td>
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Nitrogen-doped TiO$_2$ nanotube array films with enhanced photocatalytic activity under various light sources

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Abstract

Highly ordered nitrogen-doped titanium dioxide (N-doped TiO$_2$) nanotube array films with enhanced photocatalytic activity were fabricated by electrochemical anodization, followed by a wet immersion and annealing post-treatment. The morphology, structure and composition of the N-doped TiO$_2$ nanotube array films were investigated by FESEM, XPS, UV-vis and XRD. The effect of annealing temperature on the morphology, structures, photoelectrochemical property and photo-absorption of the N-doped TiO$_2$ nanotube array films was investigated. Liquid chromatography and mass spectrometry were applied to the analysis of the intermediates coming from the photocatalytic degradation of MO. The experimental results showed that there were four primary intermediates existing in the photocatalytic reaction. Compared with the pure TiO$_2$ nanotube array film, the N-doped TiO$_2$ nanotubes exhibited higher photocatalytic activity in degradating methyl orange into non-toxic inorganic products under both UV and simulated sunlight irradiation.

Keywords: TiO$_2$ nanotube array; Nitrogen-doping; Visible light activity; Methyl orange; Intermediate

1. Introduction

Since the discovery of water photolysis on TiO$_2$ electrode by Fujishima and Honda [1] in 1972, TiO$_2$ became one of the most widely researched materials for use in solar cells [2,3], pollutant degradation [4–6], photolysis of water [7,8], gas sensor [9,10] and bio-applications [11,12] due to its unique and favorable physiochemical properties. However, the anatase TiO$_2$ material cannot efficiently utilize visible light ($\lambda > 380$ nm) of the solar energy because of its comparably large band gap. To overcome this
problem, considerable efforts have been taken to narrow the band gap. Doping with different types of transition metal cations [13–15], surface modification with noble metal [16–19], as well as doping with nonmetal anions [20–41] have been explored in an effort to increase the visible light absorption or suppress the recombination of photogenerated carries.

Asahi et al. reported a visible light active TiO$_2$$_x$N$_x$ film by sputtering the TiO$_2$ target in a N$_2$/Ar gas mixture, which attracted a great attention of N-doped TiO$_2$ as a visible light photocatalyst [20]. The common approaches to form N-doped TiO$_2$ photocatalyst include sputtering of TiO$_2$ targets in N$_2$ mixture gas [31,32], annealing TiO$_2$ or Ti-compounds under ammonia gas [33–37], ion implantation and thermal treatment [38,39], and hydrolysis of N-containing solutions [40,41].

Although N-doped TiO$_2$ has been widely fabricated and studied for the photocatalysis under visible light irradiation, most of the work uses either powders or thin compact films. In the present work, we investigate the N-doped TiO$_2$ nanotube array film prepared by treating TiO$_2$ nanotube array film with ammonia solution. This method avoided the use of hazardous ammonia gas, or laborious ion implantation process. Moreover, to our knowledge, there are so far few reports about the effect of N-doping and annealing temperature on the photocatalytic performance of TiO$_2$ photocatalyst under different light sources. In the current work, high-pressure mercury lamp and tungsten–halogen lamp light sources have been used. Photocatalytic activity of doped and undoped TiO$_2$ nanotube films was investigated.

2. Experimental

2.1. Preparation of N-doped TiO$_2$ nanotube arrays

Highly ordered TiO$_2$ nanotube arrays with a tube length about 350 nm were grown from Ti sheets (>99.6% purity) via electrochemical anodization in 0.5% HF electrolyte with Pt counter electrode under 20 V for 20 min as previously described in the literature [42,43]. The as-prepared samples were immersed in 1 M NH$_3$·H$_2$O solution for 10 h and annealed in a muffle furnace under ambient atmosphere for 2 h to obtain N-doped TiO$_2$ nanotube array electrode with crystalline phase.

2.2. Characterization of N-doped TiO$_2$ nanotube arrays

The morphologies of the prepared samples were observed using a field emission scanning electron microscope (FESEM, LEO-1530) and their crystalline phase was identified using an X-ray diffractometer (Philips, Panalytical X’pert, Cu Kα radiation). The surface chemical composition of samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantum 2000) with Al Kα radiation source. All the binding energies were referenced to the C1s peak at 284.8 eV of surface adventitious carbon. The absorption properties of the samples were recorded using a diffuse reflectance UV-vis spectrometer (Varian, Cary 5000) with wavelength range of 300–650 nm.
2.3. Photoelectrochemical and photocatalytic measurements

Photoelectrochemical measurements were carried out in 0.1 M Na$_2$SO$_4$ solution using an LHX 150 Xe lamp, a SBP 300 grating spectrometer, and an electrochemical cell with a quartz window. The generated photocurrent signal was collected by a lock-in amplifier (5210, EG and G, PAR Co., USA) with a light chopper at zero bias with a step of 5 nm in the range of 300–600 nm. The reproducibility was checked by repeating the measurement at least three times and the average value is taken as the reported photocurrent. Electrochemical impedance spectroscopy (EIS) spectra were measured by applying an AC voltage of 10 mV amplitude within the frequency range of $10^5$–$10^{-2}$ Hz in 0.1 molL$^{-1}$ Na$_2$SO$_4$ solution.

For the photocatalytic degradation experiments, methyl orange (MO) was chosen as a target compound. The detail processes are similar with the ones previously described in the literature [44,45]. The initial concentration of the dye was 20 mg/L and the pH value of the MO solution (pH = 3.0) was adjusted with H$_2$SO$_4$. The quartz glass reactor was equipped with a water jacket to control the temperature. The photo-irradiation was performed with a 200W high-pressure mercury lamp emitting at a wavelength of 365 nm as the UV light source and 500W tungsten–halogen lamp was used to produce the simulated sunlight. Before the photocatalytic degradation, the photocatalyst (1.0cm × 1.5cm) was soaked in 30 mL MO solution for 30 min to establish the adsorption/desorption equilibrium. The solution periodically taken from the reactor was analyzed with a UV-vis spectrophotometer (Shimadzu UV-2100, Japan). The analytical wavelength selected for optical absorbance measurement was 508 nm. The blank test was also carried out by irradiating MO homogeneous solution without TiO$_2$ photocatalyst for checking the self-photolysis of MO.

Samples were taken from the reaction vessels and filtered through a 0.2 μm cellulose membrane filter. HPLC analysis was carried out using Agilent 1200 series HPLC with UV DAD detector. RP-C18 column (Agilent Zorbax XDB C-18, 250mm × 4.6 mm; 5mm particles) was used to separate the degradation products present in the reaction mixture. Acetonitrile/Ammonium acetate (10mM, pH=6.6) were used as a mobile phase with 24/76 (v/v) and 0.8 ml min$^{-1}$ as a flow rate. The products were detected by UV-vis diode array detector. MALDI-TOF mass spectra were recorded on a Shimadzu Biotech Axima ToF$^2$ MS instrument equipped with the delayed extraction option. Ionisation (negative) was achieved using a N$_2$ laser source (337 nm). The mass spectrometer was operated in a reflectron negative mode, and for this operation mode the instrument was calibrated using small-cal-mix samples. The analyses were done without aid of any matrix.

3. Results and discussion

3.1. Characterization of N-doped TiO$_2$ nanotube array films

Fig. 1 shows top-view SEM images of the as-prepared TiO$_2$ nanotube array annealed at 450°C (Fig. 1(a)) and the N-doped TiO$_2$ nanotube array (Fig. 1(b)–(d)) annealed at 450, 600 and 700°C for 2 h. Both N-doped and pure TiO$_2$ film annealed at 450 °C show
similar morphology to the as-prepared sample. This indicates low temperatures have no great effect on surface morphology and architecture of the TiO\(_2\) nanotube array. The nanotube arrays have an average tube diameter around 80 nm and a wall thickness of about 15 nm. When annealed at 600 °C, the diameter of the N-doped TiO\(_2\) nanotube slightly decreases and the wall thickness increases, indicating the obvious anatase crystal growth and rutile phase transition of TiO\(_2\) nanotube. When annealing temperature increased to 700 °C, some part of the nanotube array architecture collapsed, this is ascribed to high temperature and phase transition heat lead to the rapid grain growth within the thin tube wall and in the underlying titanium foil [46–48].

It is well known that surface morphology change is close related to crystal growth and phase transformation. Therefore, XRD was investigated to analyze the effect phase transformation on the change of surface morphology and TiO\(_2\) nanotube structures. Fig. 2 shows the XRD patterns for the pure titania nanotube film and N-doped titania nanotube films under various annealing temperatures. The as-grown TiO\(_2\) thin film (curve a) exhibits an amorphous structure except for the existence of typical diffraction peaks of metallic titanium [49,50]. Hence, the annealing process is necessary to transfer the amorphous TiO\(_2\) film into a well-crystallized anatase phase. For samples annealed at 300 °C for 2 h (curve c), two weak diffraction peaks appeared at 25.4° and 48.1°, in well accordance with the (1 0 1) and (2 0 0) peaks of anatase titania, indicating the initial formation of tiny crystalline anatase phase, whereas no evidence of the existence of rutile phase is observed. Further increasing the annealing temperature, the strength of these two anatase peaks also increases. Moreover, the pure TiO\(_2\) nanotube samples have more obvious rutile peaks (curve b) than that of N-TiO\(_2\) sample (curve d) under 450 °C heat treatment. This indicates that the incorporation N-dopants into the TiO\(_2\) lattice via O–Ti–N bonding can suppress the anatase-rutile phase transition to enhance the thermal stability of anatase owing to the strong crystal distortion force [51,52]. In addition, the presence of porous nanotube structures and the N-doping might inhibit the migration and the arrangement of Ti and O atoms to form rutile during high temperature calcinations [48,53]. When annealed at 500 °C (curve e), a small peak appeared at 27.61°, indicating the starting transition of anatase phase to more stable rutile phase. As the temperature rose (curves f and g), the diffraction peak of rutile phase became stronger and the diffraction peaks of anatase phase nearly disappeared at 700 °C.

The high resolution spectrum of XPS was used to identify the nitrogen elements present on the TiO\(_2\) nanotube arrays. Fig. 3 shows the high resolution XPS N 1s core level spectra of ammonia treated TiO\(_2\) nanotube array film before and after annealing. It is cleared that only a strong N species peak at around 402.0 ± 0.2 eV can be observed before heat treatment (dotted line). The intensity became weak after annealing, indicating the N-state is just molecularly chemisorbed on surface of TiO\(_2\) in the soaking process. However, a new and strong peak appeared at 395.9 ± 0.2 eV can be assigned to N\(^3\)–substituting for O\(^2\)– at anion site [54]. This indicates that the heat treatment has led to the change from absorbed state to the substituting state in TiO\(_2\).

The UV-vis diffuse reflection spectra of pure TiO\(_2\) nanotube array film and N-doped TiO\(_2\) nanotube array films by the different annealing temperature are displayed in Fig. 4. It is apparent that the absorbance of all the N-doped TiO\(_2\) nanotube array films are stronger than that of the pure TiO\(_2\) nanotube array film at wavelengths greater than 400
nm. Moreover, the absorption edges of the N-doped TiO$_2$ nanotube array films show a slight red-shift. This red-shift of the absorption edge is related to the N-doping in the intrinsic band gap of TiO$_2$ and the interaction between N 2p and O 2p orbit. The broad absorption peaks were identified to be the sub-band gap states of the TiO$_2$ nanotube array due to its special nanotube structures [55,56]. The doped TiO$_2$ nanotube array firstly increases the UV-vis absorption below 450 °C. It shows that the calcined N-doped TiO$_2$ nanotube array achieved the great absorbance at 450 °C. The absorbance decreases with the further increasing annealing temperature from 450 to 700 °C. The reason may be due to the phase transformation from the anatase to rutile which combined with the rapid growth of crystallites and decrease of the surface area of the TiO$_2$ nanotube array.

3.2. Photoelectrochemical property

Fig. 5 shows the photocurrent versus wavelength plots for the different annealing temperature of N-doped TiO$_2$ nanotube array films. The photocurrent first increased significantly with the annealing temperature of the N-doped nanotube array film, and a maximum was observed for the sample annealed at 450 °C. This is due to the phase change from amorphous to anatase according to the XRD results. The increasing anatase phase ratio of the N-doped TiO$_2$ nanotube array films may enhance the separation and transferring efficient of the photo-generated carriers, resulting in an increase in photogenerated current [57,58]. Further increasing the annealing temperature leads to a decline of photocurrent intensity, and a shift of photocurrent peak to higher wavelength. When annealed at temperatures higher than 450 °C, the anatase phase started to change to the more stable rutile phase with a lower band gap. This transition process is accompanied by thicker nanotube wall or even the destruction of the uniform nanotube array structures. These situations would deteriorate the separation and transferring of photogenerated carries. For instance, comparing the photocurrent of sample annealed by 450 °C (curve d) and 600 °C (curve f), a difference of about six times was observed.

The inset figure shows the corresponding $(I_{ph} \times h\nu)^{1/2}$ versus $h\nu$ plots of the pure TiO$_2$ and N-doped TiO$_2$ samples which were used for the determination of the indirect band gap energy of the TiO$_2$ films. Clearly, the band gap energy of the 450°C annealed N-doped TiO$_2$ nanotube array sample is approximately 3.07 ± 0.05 eV, which is lower than that of the pure TiO$_2$ nanotube array sample (3.16 ± 0.05 eV) and the typical value reported for anatase phase [59,60]. This is also in accordance with the above UV-vis absorption result.

Fig. 6 gives the typical Nyquist plots of EIS spectra for TiO$_2$ nanotube array electrodes with or without UV light irradiation. The impedance arc radius of electrodes in the dark were much bigger than that under UV light irradiation, which indicated that there were few electrons across the TiO$_2$-electrolyte interfaces in dark. While under the UV light illumination, the arc radius of the N-doped TiO$_2$ nanotube array electrode is smaller than that of the un-doped electrode. This demonstrated that the N-doped nanotube array electrode displayed greater separation efficiency of photogenerated electron–hole pairs and faster charge transfer than that of the pure
TiO$_2$ nanotube film at the solid–liquid interface. Therefore, heat treatment of TiO$_2$ nanotube soaked with high concentrated ammonia is a promising way to improve the efficiency of photocatalyst.

3.3. Comparison of photocatalytic activity

Fig. 7 demonstrates the kinetic behaviors of the MO photodegradation by the TiO$_2$ nanotube array catalyst calcined at different temperatures for 2 h under the high-pressure mercury lamp illumination. The MO photodegradation clearly obeyed the first-order reaction kinetics. The photolysis experiments, in the absence of TiO$_2$ photocatalyst, revealed that the self-degradation of MO was almost negligible under UV illumination. Table 1 shows the effect of annealing temperature of the TiO$_2$ nanotube array photocatalysts on the first-order rate constant $k$ of photocatalytic degradation under different light sources. The apparent rate constant of photocatalytic degradation with the presence of TiO$_2$ nanotube photocatalyst was significantly higher than that of MO self-photofading under both light sources, indicating the TiO$_2$ play an important role in the photocatalytic process. From the plot of absorption vs. wavelength under different light source irradiation (Fig. 8), it can be seen that a rapid decrease in the absorbance peak at 508 nm reflects the degradation of MO on the N-doped TiO$_2$ nanotube array photocatalyst. The color removal of MO pollutant was almost completely in 15 min under high-pressure mercury light irradiation (Fig. 8(a)), and more than 80% under tungsten–halogen lamp illumination after 60 min (Fig. 8(b)). Under the high-pressure mercury lamp illumination, the photocatalytic degradation rate of MO initially increased with increasing of the annealing temperature of N-doped TiO$_2$ nanotube array film between 300 and 450°C (0.071–0.169 min$^{-1}$), and then decreased. The optimized efficiency was obtained for the one annealed at 450 °C. This is attributed to the higher content in the crystalline anatase phase for the samples calcined at 450°C than those at 300 and 600°C. According to the XRD results, the phase transformation from amorphous TiO$_2$ to anatase was not incomplete at 300 °C. At 600 °C, some of anatase phase was transformed to the more stable but photocatalytically less active rutile phase. Moreover, the rapid TiO$_2$ crystallite growth by sintering resulted in a thickening of tube walls, and decrease in surface area.

The photocatalytic process under tungsten–halogen lamp illumination has a similar trend in the reaction rate constant with that of high-pressure mercury lamp, except for the 450°C heat treatment of pure TiO$_2$ nanotube sample. The apparent rate constant $k$ increases from 0.0241 to 0.0270 min$^{-1}$ as the annealing temperature increases from 300 and 450 °C, and then decreases to 0.0200 min$^{-1}$ at 500 °C, indicating that the N-doped TiO$_2$ nanotube array films do have a good visible light photocatalytic activity. Although the larger percentage of anatase and has a better UV light photocatalytic activity (0.0967min$^{-1}$), the visible light photocatalytic activity of 450°C annealing pure TiO$_2$ sample (~0.0178 min$^{-1}$) is lower than that of N-doped TiO$_2$ nanotube array films calcined under 300°C (0.0241 min$^{-1}$) by using tungsten–halogen lamp. This is ascribed to the fact that visible light can more effectively excite the valence band electrons in the N-doped TiO$_2$ sample than pure TiO$_2$ sample.
Therefore, the main contribution from visible light absorption has beneficial effect for the enhancement of photocatalytic activity.

Beside the excellent photocatalytic degradation performance, the N-doped TiO\textsubscript{2} nanotube arrays also show good stability of photocatalytic activity during the acidic liquid solution of MO. As shown in Fig. 9(a), the N-doped TiO\textsubscript{2} nanotube array structures kept without collapse and showed no apparent change in surface morphology after 10 cycles of repeat use in the photocatalytic process. In addition, the MO removal rate had only a slightly reduction within 8\% under different light sources (Fig. 9(b)). However, the photocatalyst can recover its original activity as it was re-annealed at 450°C for 2 h. This may be due to the absorption of some intermediates not being fully removed during the photocatalytic experiment. These results indicated that the N-doped TiO\textsubscript{2} nanotube array film can remain active for long-term service without much degradation of its activity.

3.4. Preliminary discussion on degradation intermediates of methyl orange

The determination of intermediates and/or the photodegradation mechanism of azo dyes have been reported using GC/MS or HPLC/MS techniques [61–65]. However, there are few studies on the intermediates and photodegradation pathway of the quinonoid MO (pH 3.0). Fig. 10(a) reports the chromatogram of the solution before and after photocatalytic degradation for different times. The intensity changes indicate the transversion of the degradation products. Before UV light irradiation, it can be seen that there exists only one peak corresponding to the MO with a negative ion at \( m/z = 304 \) and appeared at the retention time of 22.5 min in HPLC spectrum. After 10 min of UV light irradiation, the main absorption peak of MO decreased a lot and four additional fragment peaks corresponding to new main intermediate by-production initially appeared at \( m/z = 320 \) at 28.5 min, \( m/z = 306 \) at 10.3 min, \( m/z = 290 \) at 8.6 min and \( m/z = 276 \) at 7.9 min. Increasing the UV irradiation time, intermediate peaks gradually decreased except the peak at \( m/z = 306 \) at 10.3 min first increased but was still with low intensity at 20 min. At last, the peaks of methyl orange and intermediate products all almost disappear in HPLC after the 30 min UV irradiation, indicating that the photocatalytic degradation in the presence of anatase TiO\textsubscript{2} nanotube array can effectively mineralize many organic pollutants.

In the case of simulated solar light irradiation (Fig. 10(b)), the MO and intermediate peaks are eventually disappeared after 1 h photocatalytic reaction with the N-doped TiO\textsubscript{2} nanotube array catalyst. However, MO and main intermediate peaks were still observed with pure TiO\textsubscript{2} nanotube array catalyst under identical experimental conditions. Hence, under the artificial solar light, the MO dye showed a clearer trend to be degraded into low molecular weight byproducts by the photocatalyst with N-doping.

Fig. 11(a) shows the MALDI-TOF mass spectrometry profile recorded for MO solution after UV irradiation for different times. MO exhibited a clear MS signal corresponding to a negative ion of \( m/z = 304 \). After 10 min UV irradiation, it is found that four new peaks (\( m/z = 320, 306, 290 \) and 276) are clear observed, indicating MO quickly changed to other chromophore groups. The compound of \( m/z = 320 \) is attributed
to the monohydroxylated product of MO. The compound of m/z = 306 is the oxidation in the aromatic ring and loses one methyl group from nitrogen atom of amino group. The peak of m/z = 290 and 276 can be attributed to the loss of one or two methyl groups from MO (see Fig. 12).

Further increasing the irradiation time, these chromophore groups can decompose to lower molecular weight by-production by the attack of oxidative species (·OH and ·O₂⁻) through two primary processes of dealkylation and hydroxylation. The compound of m/z = 320 yields the intermediate by-products corresponding to [M–H–SO₂]⁻ at m/z = 256 and [M–H–N₂C₆H₃(OH)N(CH₃)₂]⁻ at m/z = 156. The compound of m/z = 306 yields the intermediate by-products corresponding to [M–H–SO₂]⁻ at m/z = 242 and [M–H–N₂C₆H₃(OH)NHCH₃]⁻ at m/z = 156. The compound of m/z = 290 yields the intermediate by-products corresponding to [M–H–SO₂]⁻ at m/z = 226, [M–H–CH₃]⁻ at m/z = 275 and [M–H–N₂C₆H₄NHCH₃]⁻ at m/z = 156. The compound of m/z = 276 yields the intermediate by-products corresponding to [M–H–SO₂]⁻ at m/z = 212, and [M–H–N₂C₆H₄NH₂]⁻ at m/z = 156.

Finally, the photogenerated oxidative species forming over TiO₂ nanotube array catalyst surface further decompose these intermediates to the final carbon dioxide and some non-toxic inorganic products (SO₄²⁻, NO₃⁻ and NH₄⁺) as shown in following equation:

\[ \cdot \text{OH}/\cdot \text{O}_2^- + \text{MO} \rightarrow \text{intermediates} \rightarrow \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+ \]

The MS results (Fig. 11(b)) of MO solution by TiO₂ nanotube array catalyst with or without N-doping under tungsten–halogen lamp irradiation for 3 h showed that the N-doped photocatalyst exhibits better visible light activity than pure TiO₂ nanotube array to mineralize parent pollutant into non-toxic inorganic molecular.

On the basis of the preceding experimental results, we propose the four main intermediates were found during the initial photocatalytic degradation process of quinonoid MO followed by decomposing into smaller molecular weight by-products and finally mineralized. The possible degradation pathway of quinonoid MO is shown in Fig. 12. In addition, there were other fragment ions engendered in the degradation process which were not showed here. Those peaks were at m/z = 171 and 143. N-doped TiO₂ nanotube array catalyst shows enhanced photocatalytic activity than pure TiO₂ nanotube array catalyst to mineralize MO into non-toxic inorganic products under both high-pressure mercury lamp and tungsten–halogen lamp irradiation.

4. Conclusions

A simple method was developed for the fabrication of highly visible light active and stable nanocrystalline N-doped TiO₂ photocatalysts by ambient heat treatment of the TiO₂ nanotube array film pre-soaked in ammonia solution. The effect of annealing temperature on the photocatalytic activity of pure TiO₂ nanotube array films and N-doped TiO₂ nanotube array films under UV or visible light sources were investigated. It was found that photo-catalytic activity of N-doped TiO₂ array strongly depended on
the calcination temperature and the light source used for the degradation experiment. The N-doped TiO$_2$ array films calcined at 450°C have the highest photocatalytic activity to degrade MO pollutant under visible (0.027 min$^{-1}$) or UV light (0.169 min$^{-1}$) sources. With combined advantages of large absorption area of the nanotube structures and the extended light absorption of N-doping, N-doped TiO$_2$ nanotube arrays shows good potential for sustainably photocatalytic degradation of environmental hazardous substances.

Acknowledgments

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References


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Fig. 1 SEM top-view images of (a) TiO$_2$ nanotube array annealed at 450 °C, N-doped TiO$_2$ nanotube arrays annealed at various temperatures (b) 450 °C, (c) 600 °C, and (d) 700 °C.

Fig.2 XRD patterns of the pure TiO$_2$ nanotube array film and N-doped TiO$_2$ nanotube array films annealed at temperatures ranging from 300 to 700 °C. Pure TiO$_2$ nanotube samples: (a) before annealing, (b) 450 °C; N-doped TiO$_2$ nanotube samples: (c) 300 °C, (d) 450 °C, (e) 500 °C, (f) 600 °C, and (g) 700 °C. A, R, and T represent anatase, rutile and titanium, respectively.

Fig. 3 The high-resolution spectra of N1s region of the before (dotted line) and after 450 °C annealing for 2 h (solid line).

Fig. 4 UV-vis absorption spectra of TiO$_2$ nanotube arrays under different annealing temperatures.

Fig. 5 Photocurrent spectra of as-prepared pure TiO$_2$ nanotube array film without annealing (a), pure TiO$_2$ nanotube array annealed at 450 °C (b) and N-doped TiO$_2$ nanotube array films annealed at different temperatures. (c) 300 °C; (d) 450 °C; (e) 500 °C; (f) 600 °C. The inset shows the $(I_{ph} \times hv)^{1/2}$ versus $hv$ plots of the 450 °C annealed pure and N-doped TiO$_2$ nanotube array film.

Fig. 6 Nyquist plots of the 450 °C annealed TiO$_2$ nanotube array electrodes in dark and under UV light illumination.

Fig. 7 Comparison of photocatalytic degradation rates of MO for pure TiO$_2$ and N-doped TiO$_2$ nanotube array films with different annealing temperatures under high-pressure mercury lamp illumination (a) and tungsten–halogen lamp illumination (b).

Fig. 8 UV-visible spectra of MO at different time intervals under high-pressure mercury lamp illumination (a), under tungsten–halogen lamp illumination (b).

Fig. 9 Recycling test of the N-doped TiO$_2$ nanotube arrays film on the MO removal rate under different light sources. The inset shows the SEM image of the N-doped TiO$_2$ nanotube arrays after ten repeated cycles test.

Fig. 10 HPLC profiles of methyl orange dye at different times during photocatalytic reaction under UV(a) or simulated solar lights (b) by the TiO$_2$ nanotube array photocatalyst with or without N-doping.

Fig. 11 MALDI-TOF mass spectrometry profiles of methyl orange and its oxidative intermediates corresponding to the solutions after being degraded under UV for different times (a) or simulated solar lights for 3
h (b) at pH 3.0.

Fig. 12 Proposed degradation products and mechanism during the photodegradation process of MO.
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</tr>
</tbody>
</table>
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 9
Fig. 10

UV light

0 min

10 min

20 min

30 min

Visible light

Blank

Non-doping

N-doping
Fig. 11
Fig. 12