Solvothermal synthesis of N-doped TiO$_2$ nanotubes for visible-light-responsive photocatalysis†

Zheng Jiang,*[ab] Fan Yang,[b] Nianjun Luo,[a] Bryan T. T. Chu,[a] Deyin Sun,[b] Huahong Shi,[a] Tiancun Xiao[a] and Peter P. Edwards*[a]

Visible-light-responsive tubular N-doped TiO$_2$ nanocrystallites were synthesized *via* an environment-conscious solvothermal treatment of protonated titanate nanotubes in an NH$_4$Cl/ethanol/water solution.

Nano-structured TiO$_2$ materials have recently been studied extensively due to their high surface areas and finite length scales, allowing highly efficient electron-hole charge separation and reduced recombination. Such materials hold great promise as highly efficient photocatalysts and solar cells.[1] Titanium dioxide nanotubes (hereafter TDNTs) have attracted particular attention owing to their interesting one-dimensional hollow structure, large surface areas and potential applications in photocatalysis,[2] gas storage[3] and photovoltaic cells.[4–7] However, the practical application of TDNTs is significantly hindered by its intrinsic electronic band gap of some 3.3–3.87 eV,[8] which ensures that these materials can only be excited by UV light, and this comprises less than 5% of the solar spectrum. In order to harvest solar energy efficiently, enhancing the visible-light response of TDNTs by doping with either metal or nonmetal is highly desirable. Unfortunately, to date, limited methods have been reported for preparation of TDNTs with visible-light-response.[4,6,9–16]

Motivated by the recent progress in narrowing the electronic band gap of TiO$_2$ by anion doping,[17] N-doped TiO$_2$ nanotubes (N-TDNTs) have been explored for visible-light-driven photocatalysis.[9–11,13,14] Mainly, the preparation of N-TDNTs includes synthesis of TDNTs or protonated titanate nanotubes (H-TNTs, *e.g.* H$_2$TiO$_3$, H$_2$Ti$_2$O$_5$, *etc.*) and then nitriding of these materials to form N-TDNTs. For the chemical synthesis of TDNTs, three general approaches have been developed, they are template,[18,19] electrochemical[20] and hydrothermal[21] routes; however, the as-prepared TDNTs are predominately amorphous TiO$_2$ that show low photocatalytic activity and such materials are also prone to collapse during the annealing process.[22] Consequently, additional crystallization is always

required for those TDNTs since their photocatlytic performance is closely related to crystallinity.[2,18,20] Although bulk materials of N-doped TiO$_2$ have been extensively investigated for visible-light photocatalysis,[9–11,13,14,17] the feasible nitridization of TDNTs for syntheses of N-TDNTs is still a critical challenge. The most widespread nitriding route centres on ammonolysis of TDNTs in flowing ammonia gas at high temperature, but this process drastically damages the TDNTs due to sintering and collapse.[10] An ammonia wet-impregnation method was also reported for synthesis of N-TDNTs; unfortunately, high temperature crystallization of this N-TDNT is unavoidable.[9] In the nitriding methods mentioned above, the use of gaseous ammonia is also an environmental concern. Ion implantation can be used to synthesize N-TDNTs at low temperature, but this route involves costly equipment which counteracts its environmental benefits.[14] A high temperature solvothermal synthesis had been adopted to synthesize N-doped TiO$_2$ nanocrystallites; however, a toxic N-source HMT (hexamethylenetetramine) was involved.[23] Therefore, it is particularly worthwhile to develop a facile, environment-conscious method for the synthesis of N-doped TiO$_2$ nanotubes but obviously not at the expense of destroying the attractive tubular morphology.

We report here a relatively simple low-temperature synthesis of N-doped anatase nanotubes *via* ethanol–water solvothermal treatment of a H-TNT suspension with NH$_4$Cl at 120 °C. This method is environmentally friendly and energy efficient, avoiding the use of ammonia and high-temperature nitriding. The as-prepared N-TDNTs not only retain a tubular morphology up to 600 °C, but also have high visible-light activities. H-TNTs were synthesized *via* an alkaline hydrothermal process at 150 °C for 48 h.[19] The as-recovered H-TNTs were then well dispersed in an ethanol–water solution (1 : 1 volume ratio) containing 20 wt% NH$_4$Cl prior to heating in an autoclave at 120 °C for 5 h. After cooling to room temperature, the resulting white precipitates were filtrated and washed with deionized water and ethanol, alternatively. The obtained materials were dried at 80 °C overnight prior to annealing at 450 and 600 °C. The as-prepared H-TNT nanotube with the solvothermal treatment of H-TDNT at 120 °C is here denoted as N-TDNT-120. The protonated titanate nanotube and N-doped TiO$_2$ nanotubes are denoted as H-TNT and N-TDNT-X, respectively, where X refers to the annealing temperatures.

The morphology and size of the as-prepared N-TDNT materials were characterized by SEM and TEM analysis. In Fig. 1(a) and (b), we show the TEM images of as-recovered and calcined N-doped TiO$_2$ nanotubes. The as-recovered

[a] *Inorganic Chemistry Laboratory, University of Oxford, UK OX1 3QR. E-mail: peter.edwards@chem.ox.ac.uk; Fax: +44 1865 272656; Tel: +44 1865 272680*
[b] *State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, 100080 Beijing, China. E-mail: zhjiang76@hotmail.com*
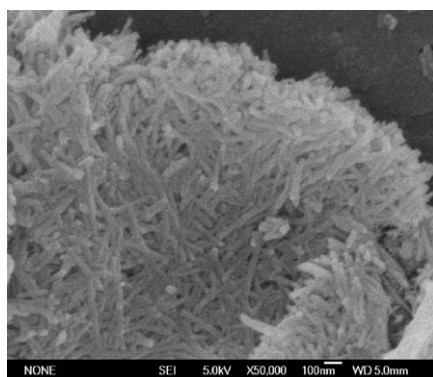
† Electronic supplementary information (ESI) available: 1. Synthesis of protonated titanate nanotubes; 2. photocatalytic reaction tests. 3. Possible formation mechanism of N-TDNTs using ammonia salts as N-sources. 4. Fig. S1: XRD-patterns of N-TDNTs synthesized through solvothermal route with different nitrogen sources. See DOI: 10.1039/b815430a
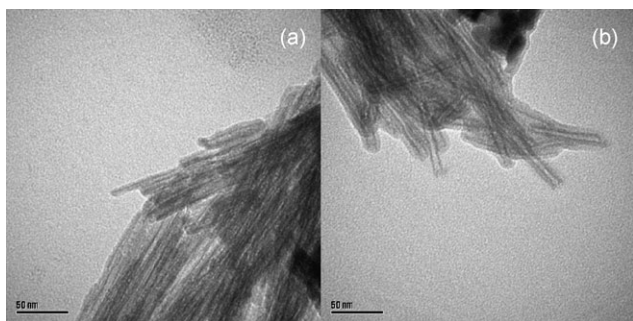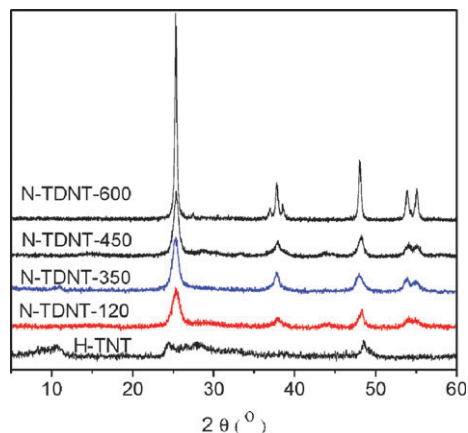
Fig. 1 TEM images of N-doped TiO_2 nanotubes (a) N-TDNT-120; (b) N-TDNT-450 (scale bar: 50 nm).

Fig. 3 XRD patterns of H-TNT and N-TDNT.

materials from the solvothermal treatment clearly inherit the tubular structures of the protonic titanate nanotubes. They are open-end nanotubes with a high aspect ratio: remarkably, several micrometers in length, but only 10–13 nm in diameter (measured inner and outer diameters of the N-TDNTs are 5–8 and 10–13 nm, respectively). As can be seen in the corresponding SEM micrograph (Fig. 2), the as-prepared N-doped materials were mainly composed of interwoven nanotube bundles. The interwoven bundles give rise to difficulties in precisely determining the length and diameter of individual nanotubes. The SEM images of the sample calcined at 450 °C are very similar (not shown), suggesting the morphology remains intact after heating. Indeed, no distinguishing changes of the tubular morphology are observed from the TEM images for these N-TDNTs even after calcinations at 450 °C (Fig. 1(b)), indicating the materials are quite thermally stable. In fact, further annealing at 600 °C does not induce any drastic damage of the tubular structure of N-TONT. In contrast, for amorphous TDNTs,[22] their tubular structures begin to disappear when the thermal crystallization temperature exceeds 350 °C.

The structures of N-TDNT are totally different from the H-TDNT precursors as reflected in the XRD patterns of the H-TDNT and N-TDNT materials (Fig. 3). Interestingly, although the temperature of the solvothermal treatment is as low as 120 °C, a well-crystallized anatase phase (JCPDS 71-1168) is observed in the as-prepared N-TDNT-120 sample, suggesting that the solvothermal method is effective for preparing TiO_2 nano-crystals. A trace of titanate phase (44-0131) is also observed in the XRD pattern. Further annealing

N-TDNT-120 nanotubes to a temperature of 450 °C significantly enhances the crystallinity of the anatase phase. In that the crystal structure is thermally stable relative to amorphous TiO_2 structures, as expected, the crystallized N-TDNT-120 is more structure stable than the amorphous TiO_2 counterparts and resistant to collapse of tubular structures in calcinations at higher temperatures; this finding is also confirmed by TEM (Fig. 1(b)).

In Fig. 4(a), we show the UV-Vis diffuse reflection spectra of the protonic titanate and N-TDNT nanotubes. There are no significant differences between protonic titanates and N-TDNT-120, indicating the nitrogen atom has not fully incorporated into the matrix of TDNT. Considering the

Fig. 2 SEM image of N-TDNT-120 nanotubes (scale bar: 100 nm).
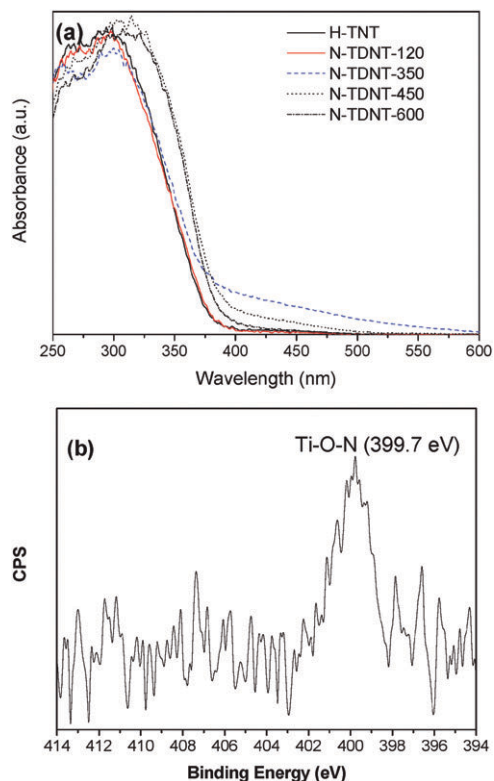
Fig. 4 UV-Vis diffuse reflection spectra of N-TONTs calcined at different temperatures (a), and N 1s XPS of N-TDNT-450 (b).
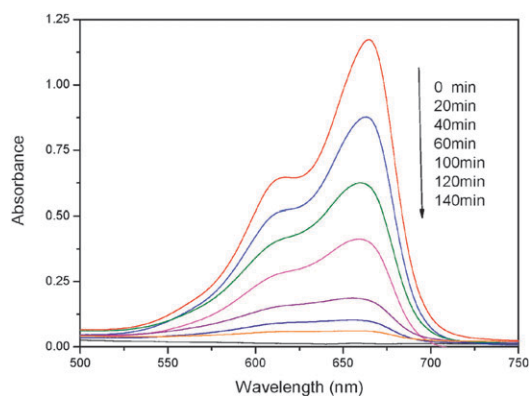
Fig. 5 Photodegradation of Methylene Blue over N-TDNT-450 under visible light irradiation.

rolling mechanism of forming TDNT,[16] there would be three kinds of ammonia species existing in the NTDBT-120: contained in the space of anatase nanotube walls, surface adsorbed ammonia as well as as-formed ammonia titanates. After annealing at 350 °C or above, however, the UV-Vis absorbance edges of N-TDNT-X (X > 350) significantly shift to the visible-light region, which also implies that the nitrogen has indeed doped into the TiO$_2$ matrix.[24] The N 1s XPS spectrum shown in Fig. 4(b) evidenced the N-doping in the N-TDNT-450. The binding energy at 399.7 eV signifies that the nitrogen is in the Ti–O–N site in the N-TDNT matrix.[25] So far, the assignment of the N-dopant in TiO$_{2-x}$N$_x$ is under debate in the literatures, but most researchers agree that N-doped into TiO$_2$ induces photocatalytic activity under visible light illumination, a situation previously not found in TiO$_2$ itself.[25] In Fig. 5, we show the photodegradation of Methylene Blue in aqueous solution, the solution (10 ppm) is completely decolorized under solar-light simulator irradiation in 140 min with a 1.0 g/L N-TDNT-450 suspension.

In order to understand the formation mechanism of N-TDNT in the present work, we have replaced NH$_4$Cl by aqueous NH$_3$, (NH$_4$)$_2$CO$_3$, urea and NH$_4$NO$_3$ in the solvothermal processes. However, for these additions, only titanate phases can be detected by XRD for the as-recovered nanotubes (see ESI†). The titanate phase converts to anatase after annealing over 350 °C regardless of the salts used. This suggests that chloride ion (Cl$^-$) appears to play a particular key role for formation of crystallized TDNT or the transition from titanate to TiO$_2$ at low temperature. It was reported that TiO$_2$ nanocrystals were ready to form by hydrothermal treatment of titanium hydrogel with the existence of Cl$^-$ in the solution.[26,27] In the present work, Cl$^-$ probably results in formation of TiO$_2$ anatase nanotubes, while NH$_3$ absorbed on the walls of the nanotubes and partially formed ammonia titanates, then visible-light-responsive N-TDNTs are formed upon annealing them. It appears that the N-TDNTs are uniform in composition because the walls of TDNTs are extremely thin.

In summary, an environmental friendly solvothermal methodology has been developed to synthesize N-doped TiO$_2$ tubular nanocrystals at modest temperatures. The obtained N-TDNTs are thermally stable and robust for photodegradation of Methylene Blue under visible light irradiation. The possible synthesis mechanism has also been tentatively proposed.

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