Simple fabrication of thermally stable apertured N-doped TiO$_2$ microtubes as a highly efficient photocatalyst under visible light irradiation

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Abstract

Apertured N-doped TiO$_2$ microtubes have been fabricated by simple hydrolysis of titania tetrachloride using ammonia without any external templates. The morphology and microstructure characteristics of apertured N-doped TiO$_2$ microtubes were characterized by means of the specific surface area (BET), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transformed infrared (FT-IR), UV–visible diffuse reflectance spectra (DRS) and X-ray powder diffraction (XRD). The unique morphology of microtubes and mesoporous microstructure were maintained after a heat treatment at 723 K for 3 h, exhibiting significantly thermal stability. The catalysts exhibited high ultraviolet and visible light photocatalytic activity in degrading phenol and methyl orange.

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1. Introduction

Semiconductor photocatalysis is an efficient method for the chemical utilization of solar energy. TiO$_2$, among various photocatalysts, is most frequently employed owing to its cheapness, nontoxicity, and structural stability [1–5]. However, the widespread technological use of TiO$_2$ is impaired by its wide band gap (ca. 3.2 eV for crystalline anatase phase) which requires the use of UV light during the reaction, thus limiting the possibility of employing solar light in TiO$_2$ photocatalysis.

Sato et al. reported in 1986 that modification of TiO$_2$ with the N dopant is a powerful way to extend the adsorption light from UV to visible area, since substitution of the lattice oxygen with nitrogen might narrow the band gap by mixing the N$_{1s}$ and O$_{1s}$ states [6]. Up to now, most N-TiO$_2$ samples were prepared by treating TiO$_2$ under NH$_3$ atmosphere at very high temperature. Besides the energy waste, the treatment at such high temperature usually resulted in the low surface area due to the undesirable sintering of nanocrystallites [7,8]. Hence, the seeking of new facile approaches to the synthesis of N-TiO$_2$ caught hold of increasingly interesting.

It is also known that hierarchically ordered mesoporous TiO$_2$ materials may be promising candidates in the field of photocatalysis owing to their large surface area and convenient mass transfer in mesopores in degrading large pollution molecules. However, these TiO$_2$ materials are traditionally prepared by using surfactant templating in which supramolecular aggregates are considered to direct inorganic deposition across a range of length scales.
The organic templates must then be removed by thermal treatment, resulting in high energy consumption, environmental pollution and most important the agglomeration and collapse of pore structure in many cases [11–13]. So most reported mesoporous titania have a low thermal stability. To the best of our knowledge, no hierarchically ordered mesoporous N-TiO$_2$ material with highly thermal stability has been reported yet without any templates under mild conditions.

In the present work, we use a simple template-free approach to the synthesis of N-TiO$_2$ photocatalysts with visible light response via a low-temperature precipitation treatment of TiCl$_4$ by ammonia with the presence of glacial acetic acid. The reaction condition is much milder than that of conventional methods. In addition, it is more interesting to find that the N-TiO$_2$ sample shows a unique apertured microtube structure which has never been reported yet.

2. Experimental

Titanium tetrachloride (TiCl$_4$, analytical reagent grade) was used as titanium precursor of the preparation of the apertured N-TiO$_2$ microtubes. Commercially available reagents were obtained from Aldrich and used without further purification. In a typical procedure, 25 mL of dilute aqueous solution of TiCl$_4$ (3.0 mol L$^{-1}$) was carefully added into 150 mL deionized water with gentle stirring in ice-water bath to avoid a drastic hydrolysis of TiCl$_4$ in water at room temperature. Then the solution was heated to 323 K. After that, 4.5 mL of glacial acetic acid and a 35 wt.% solution of ammonia was added dropwise with vigorous stirring until pH 8, then the mixed solution was quickly cooled down to ambient temperature (about 298 K) by rinsed with running water. After aging in the mother liquor for a few days, the resultant slurry was suction-filtered and washed with distilled water until pH 7 and then washed carefully with absolute ethanol for three times. The N-TiO$_2$ microtube samples were finally obtained after the as-prepared filter residue being vacuum-dried at 353 K for 12 h, followed by calcination at 723 K in flowing nitrogen atmosphere.

3. Results and discussion

The SEM image displayed in Fig. 1a shows that the unique morphology of the apertured N-TiO$_2$ microtubes can be preserved well after calcination. The average diameter of each microtube is about 10 $\mu$m with the shell thickness about 1 $\mu$m. An expanded view in inset (a) gives the array of vortices exhibited regularly on the shell of the microtubes, and the average diameter of each hole is about 1 $\mu$m with the interval of ca. 4 $\mu$m. TEM analyses were performed to examine the nanocrystallites that make up the microtubes. Fig. 1b presents the nanocrystalline nature of anatase TiO$_2$. It is found that the size of anatase nanocrystallites is approximately 10 nm. High resolution TEM (top inset of Fig. 1b), confirmed that the sample were comprised of connected crystalline titania nanoparticles (the ovals in the figure), with a lattice spacing consistent with the anatase phase (0.352 nm), giving evidence the polycrystalline nature of N-TiO$_2$ sample which fit well with the XRD patterns. Besides, we can directly examine the average crystallite size of TiO$_2$ nanoparticles which is consistent well with that calculated from the XRD data (see Fig. 2), calculate the average pore diameter and compare with the result...
from N_2 adsorption characterization (see Fig. 4). The selected-area electron diffraction (SAED) characteristics (middle inset of Fig. 1b) further confirmed that the titania nanoparticles showed crystalline anatase phase. Such high anatase crystallinity in the mesoporous TiO_2 was highly desirable in photocatalysis [14].

The formation of hierarchical porous shapes was usually explained by facet selectivity of the templates during the crystallite growth of the synthesis, while no template is used in our present work for the synthesis and the formation of apertured titania microtubes happens during the processing. There might be another mechanism for the formation of TiO_2 microtubes. In order to examine the processing parameters that control the morphology and structural properties of the TiO_2 microtubes, factors affecting the hydrolysis process including the amount of acetic acid additive, TiCl_4, reaction temperature, aging temperature and time were investigated. By varying these parameters, we found that the preparation parameters were of vital importance in the final formation of titania. It was found that a higher precipitating temperature and aging at ambient temperature may favor the formation of TiO_2 microtubes with well-developed mesoporosity. The use of acetic acid as a dispersing agent was of crucial importance in the preparation of titania with apertured microtube morphology. The essential role of acetic acid in promoting the formation of mesoporous TiO_2 microtubes might be understood by taking into account the behavior as a ligand and the modification of the polymeric structure at a molecular level, which promoted the emergence of polymeric structures [15].

It is known that acetic acid is a rather weak electrolyte with a low degree of dissociation, so here it is a good buffer, which can keep a stable pH range in this reaction system. The suitable pH value could effectively control the hydrolysis rate of TiCl_4 in the initial reaction stage. There are lone pair electrons on nitrogen atoms of ammonia, which provides the possibility that TiCl_4 can combine with the ammonia to form a complex. During the hydrolysis process, the titania nanoparticles begin to form and tend to aggregate each other. The presence of glacial acetic acid can kinetically control the growth rate of titania nanoparticles and their assembly into microtubes [16]. In addition, the assemble process become slower and halt while the concentration of Ti source decreases, so the microtubes were not finally formed and some vantages were remained in the wall. To confirm this mechanism of the formation of the apertured TiO_2 microtubes, various concentration of TiCl_4 was tested and we found more TiCl_4 would lead to TiO_2 microtubes without vantages and less TiCl_4 would result in twist-like helix microbelts.
The well crystallization and high stability of titania microtubes can be explained by the XPS spectra (Fig. 3). There are two kinds of N species in N-doped TiO\textsubscript{2} materials, the N bonded with Ti and molecularly chemisorbed NH\textsubscript{3}. After a thermal treatment at 723 K for 3 h, almost all of the chemisorbed NH\textsubscript{3} can be eliminated [17]. According to the XPS result, the nitrogen percent in the N-TiO\textsubscript{2} remains 2.9% after calcination, which can prove the formation of N–Ti–O bond [8,18]. The formation of these bonds can inhibit the integratation of titania particles and enhance the crystallization degree of anatase phase during calcination process. Moreover this unique apertured microtube N-TiO\textsubscript{2} prepared by ammonia treatment exhibited an outstanding thermal stability to at least 773 K, whereas the ordinary mesoporous titania samples completely collapse at a calcination temperature at 623 K [19].

The porosity of the titania materials has been investigated using nitrogen adsorption–desorption isotherms. Fig. 4 gives the nitrogen adsorption–desorption isotherm of the as-prepared sample, it exhibits a type IV isotherm with an inflection of nitrogen adsorbed volume at $P/P_0 = 0.45$ (type H2 hysteresis loop), being representative of well-developed mesoporosity in the titania samples. A typical value for the specific surface area using the BET method is 419 m\textsuperscript{2} g\textsuperscript{-1}, much higher than the reported TiO\textsubscript{2} obtained by conventional method [20]. The inset in
Fig. 4 shows the pore size distribution (PSD) plots estimated using the BJH (Barrett–Joyner–Halenda) equation from the desorption branch of the isotherm. The PSD measurements show that the titania sample had pronounced mesoporosity of a very narrow pore size distribution with an average pore diameter at ca. 4.3 nm. The mesopores of N-doped TiO₂ microtubes was located in the interparticle of nanocrystallites. According to the XRD data, the size of TiO₂ nanocrystallites estimated by Scherrer equation were about 10 nm, also we can find the size of nanocrystallites was nearly the same from the TEM image. These nanocrystallites were accumulated and suggested to form mesopores between each other. The average accumulative pore diameter was ca. 4.3 nm, which was shown in the HRTEM figure (top inset of Fig. 1b). These results illustrate that the doping with nitrogen does not change the textural properties of TiO₂ significantly. The nitrogen species are embedded in the TiO₂ network of the mesoporous pore walls, and the pore channels remain open. Such open mesoporous architecture, large surface area and 3D-connected pore system, play an important role in catalyst design for its ability to improve the molecular transport of reactants and products [21] (see Table 1).

The UV–visible DRS spectra of the mesoporous N-TiO₂ samples are shown in Fig. 5. The optical band edge of the mesoporous N-TiO₂ exhibits a remarkable red-shift with respect to that of pure TiO₂ (P25). This can be assigned to the substitution of crystal lattice O to N species, which is consistent with the XPS results. The enhanced ability to absorb visible light makes this mesoporous N-TiO₂ an effective photocatalyst for solar-driven applications.

FT-IR spectrum of N-TiO₂ samples was shown in Fig. 6. The FT-IR characterization can further confirm the substitution of crystal lattice O to N species and the formation of N–Ti–O bond. The absorption peaks at 3400, 2930 and 2850 cm⁻¹ were assigned to the OH species [22]. The absorption peak at 1630 cm⁻¹ belongs to the Ti–O structure, 1380 cm⁻¹ corresponding to the surface adsorbed NH₃ molecules [23]. The peaks at 1450, 1230, and 1090 cm⁻¹ could be attributed to the nitrogen atoms embedded in the TiO₂ network [19,24]. These results clearly demonstrated that the hydrolysis of TiCl₄ in ammonia solution under this reaction conditions resulted in not only the chemisorption of NH₃ molecules on the TiO₂ surface but also the nitrilation of the TiO₂ lattice. The nitrilation occurred by replacing the oxygen atom in the TiO₂ with the nitrogen atom in the NH₃ molecule, resulting in the formation of the O–Ti–N and the N–Ti–N as well the OH species. The Raman characterization was also performed and besides the three main peak attributed to anatase TiO₂, a weak peak at 570 cm⁻¹ belonged to TiOₓN₂–ₓ was also found, which can further confirm the existence of N–Ti–O bond [18].

### Table 1

<table>
<thead>
<tr>
<th>Calcination temperature (K)</th>
<th>Sₘₑₐₓ (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Average pore diameter (nm)</th>
<th>Anatase (%)</th>
<th>Rutile (%)</th>
<th>Anatase (nm)</th>
<th>Rutile (nm)</th>
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<td>As-synthesized</td>
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<td>0.56</td>
<td>4.3</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td>–</td>
<td>–</td>
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<tr>
<td>623</td>
<td>166</td>
<td>0.44</td>
<td>7.4</td>
<td>100</td>
<td>0</td>
<td>7.0</td>
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<tr>
<td>723</td>
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<td>0.34</td>
<td>9.0</td>
<td>100</td>
<td>0</td>
<td>9.9</td>
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<tr>
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<td>0.16</td>
<td>9.0</td>
<td>92</td>
<td>8</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>P25</td>
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<td>16</td>
<td>77</td>
<td>23</td>
<td>21</td>
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</table>

Fig. 5. UV–visible diffuse reflectance spectra of (a) Degussa P25 and (b) 723 K calcined N-TiO₂.

Fig. 6. FT-IR spectra of the as-prepared mesoporous apertured N-doped TiO₂ microtubes.
To evaluate and compare the photocatalytic activity of the mesoporous N-TiO₂ microtubes, the reactions of phenol and methyl orange degradation were performed as photoreaction probes under UV and visible irradiation, respectively. Results of the photocatalytic evaluation are summarized in Figs. 7 and 8. The commercial catalyst Degussa P25 is a little more effective than N-TiO₂ microtubes under 254 nm irradiation, however, the latter demonstrates a comparatively higher reaction rate under 365 nm irradiation. This was because the differences of absorbing capacity of UV light, while under 254 nm UV irradiation, the absorbance of P25 is a little more than N-TiO₂ samples (see Fig. 5), meaning that P25 can absorb more UV radiation than N-TiO₂. While under 365 nm UV irradiation, the absorbance of N-TiO₂ is far more than that of P25 owing to its significant red shift. This is the main reason why these two catalysts show opposite performance under various wavelength of light in UV range. In the visible light region (>420 nm), the N-TiO₂ microtubes keep relativity high performance while P25 has nearly no activity at all. The expanded photoactivity under visible light is due to the nitrogen doping according to the common accepted opinions. The excellent photocatalytic activity of the N-TiO₂ samples could be attributed to the well-crystalline anatase phase which facilitates the transfer of photo-induced holes from bulk to surface for degradation of organic compounds and also effectively inhibits the recombination between the photo-induced holes and electrons which may enhance the quantum yield [25]. The photocatalytic performance is also related to the mesoporous microstructure of the N-TiO₂ samples with large BET surface areas and a 3D-connected pore system which can help to concentrate the reactant molecules for the photoreactions and the photos might be scattered in between the nanosized TiO₂ particles [26].

4. Conclusions

In summary, we have demonstrated a facile and template-free method for the fabrications of apertured N-TiO₂ microtubes with remarkably thermal stability. The new photocatalysts show high visible light photocatalytic activity on the degradation of phenol and methyl orange owing to their large specific surface area, surface permeability
and well anatase crystallization. The doped nitrogen species play a key role in expanding the photoactivity to visible light region and improving the anatase crystallization and thermal stability. Further work for the examination of the formation mechanism of these apertured N-TiO$_2$ samples is being under way.

Acknowledgements

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