Article

Efficient Visible-Light Photocatalysis of TiO$_2$-δ Nanobelts Utilizing Self-Induced Defects and Carbon Doping

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Abstract: Efficient visible-light photocatalysis was realized by exploring self-induced defect states, including the abundant surface states of TiO$_2$-δ nanobelts synthesized through metal–organic chemical vapor deposition (MOCVD). The TiO$_2$-δ nanobelts exhibited two strong defect-induced absorption peaks at 2.91 and 1.92 eV, overlapping with the conduction band states so that photoexcited carriers can contribute effectively for the photocatalysis reaction. To further enhance visible-light photocatalytic activity, carbon atoms, the by-product of the MOCVD reaction, were self-doped at the judiciously determined growth conditions. The resulting visible-light photocatalysis suggests that the large surface area and consequent high concentration of the surface states of the TiO$_2$-δ nanobelts can be effectively utilized in a wide range of photocatalysis applications.

Keywords: TiO$_2$; photocatalysis; nanobelts; chemical vapor deposition

1. Introduction

Efficient photocatalytic activity of TiO$_2$ has attracted extensive interest for various photochemistry applications, such as in the elimination of pollutants [1–3] and the splitting of water for hydrogen fuel [4,5], as well as for their applications in solar-cell electrodes [6,7]. Recently, much attention has been focused on the use of low-dimensional TiO$_2$ nanostructures, such as nanotubes [7], nanowires [8], and nanobelts [9,10], with high specific surface areas to further enhance their reactivity. Particularly, TiO$_2$ nanobelts have been extensively studied in various applications such as photocatalysis, solar cells, gas sensors, and biosensors due to their unique morphology, fast charge transport in the axial direction, short travel distance from inside to surface, and strong surface reactivity [9,10]. However, the wide band gap energy (∼3.0–3.2 eV) of TiO$_2$ limits its excellent photocatalytic reactivity to UV light. For practical applications, special attention has to be paid to the development of 2D TiO$_2$ nanostructures that can yield high reactivity under visible light. Visible-light photocatalysis possesses a tremendous advantage given that the main part (∼43%) of the solar spectrum and even room lighting can be utilized. Toward this end, considerable efforts have been exerted to extend the reactivity of TiO$_2$ to a visible-light regime via the doping of a number of cationic metals [2,11] or anionic non-metals such as nitrogen [3] and carbon [5,12]. Among them, carbon doping is considered one of the most effective dopants for visible-light photocatalytic reaction [5,12–16]. However, simple self-doped approaches have been limited to thin films [13,14], nanoparticles [15], and nanotubes [16]. Little information is available on realizing visible-light photocatalysis in 2D TiO$_2$ nanostructures. Moreover, meaningful visible-light photocatalysis has not so far been reported by utilizing surface defect states, which are abundant especially for 2D TiO$_2$ nanostructures with high specific surface areas. It is known that coordinatively unsaturated Ti sites, such as Ti$^{3+}$, on the surface are photocatalytically active [17]. As such, they can be hydroxylated in organic medium or ambient at room temperature [18,19].

In this study, we explored self-induced defect states, such as the abundant surface states of TiO$_2$-δ nanobelts synthesized by metal–organic chemical vapor deposition.
(MOCVD), for visible-light photocatalysis. In addition, we utilized carbon, which was the by-product of the MOCVD reaction, as a dopant to further enhance visible-light photocatalysis. The synthesis of TiO$_2$-δ nanobelts was carried out without using an oxidant, and the synthesis temperature was judiciously determined at 510 °C, which was slightly lower than the complete decomposition temperature (>527 °C) [20] of the Ti precursor. In this manner, the significant amount of carbon could reside in the grown TiO$_2$-δ. This approach of utilizing self-induced defects and carbon doping is very simple and effective to realize efficient visible-light photocatalysis of TiO$_2$ nanostructures.

2. Materials and Methods

TiO$_2$-δ nanobelts were grown on bare Si(001) and glass substrates for 10 min by MOCVD. The growth process was carried out without the use of any metal catalysts at a high density. The (C$_{11}$H$_{19}$O$_2$)$_2$(C$_3$H$_7$O)$_2$Ti (Kosundo) was used as a Ti precursor and bubbled at 210 °C with an Ar gas flow of 150 SCCM (SCCM denotes standard cubic centimeters per minute). The growth temperature, pressure, and total Ar flow were fixed at 510 °C, 10 Torr, and 300 SCCM, respectively. For the annealed TiO$_2$ nanobelt sample, as-grown TiO$_2$-δ nanobelts were rapid-thermal annealed at 600 °C under an O$_2$ gas flow of 200 SCCM for 10 min. After loading as-grown TiO$_2$-δ nanobelt samples in the RTA chamber, the sample temperature was increased at the rate of 100 °C/min to 600 °C. In addition, as a counterpart of the nanobelt samples, the TiO$_2$ thin film was grown under the exactly same conditions as the TiO$_2$-δ nanobelt sample, except for an O$_2$ gas supply of 50 SCCM.

The samples were characterized by using scanning electron microscopy (SEM, JEOL JSM-7000F, Zhaodao City, Japan), an X-ray diffractometer (XRD, Rigaku D/Max-RC, Cu K$_\alpha$ radiation, and a Ni filter, Tokyo, Japan), transmission electron microscopy (TEM, JEOL 2100F), X-ray photoelectron spectroscopy (XPS, ESCALAB 200R, Waltham, MA, USA), and UV–VIS spectroscopy (Shimadzu UV-2450, Tokyo, Japan). Photocatalytic activity was studied by measuring the decomposition of methylene blue (MB) in an aqueous solution using UV–VIS spectroscopy. The initial concentration of MB solution was 10$^{-5}$ mol·L$^{-1}$. The TiO$_2$ samples were dipped in the MB solution in a Petri dish and illuminated with visible and UV lights. The white light (100 mW·cm$^{-2}$) of a common room lighting bulb and the UV light of 365 nm (10 mW·cm$^{-2}$) were used as visible light and UV irradiation sources, respectively.

3. Results

Figure 1 shows typical SEM images of TiO$_2$-δ nanobelts grown on a bare Si (001) wafer for 10 min. The nanobelts appear as thin rectangular belts at a high density. The nanobelts have a length of ~5–8 µm, while the width and thickness are ~300–500 nm and ~20–50 nm, respectively. We have previously demonstrated the synthesis of such TiO$_2$-δ nanobelts and nanosheets governed by a vapor–solid (V–S) growth mechanism [21,22]. It should be emphasized that the various TiO$_2$-δ nanobelts and nanosheets, which we synthesized via the approach presented here, demonstrated efficient visible-light photocatalysis characteristics.

In this work, we focused on the fundamental issue to reveal the origin of the observed visible-light photocatalysis of the TiO$_2$-δ nanobelts as shown in Figure 1 (referred to here as TiO$_2$-δ nanobelts). To gain insight on such an origin, the TiO$_2$-δ nanobelts were rapid-thermal annealed at 600 °C under an O$_2$ environment for 10 min (hereby referred to as annealed TiO$_2$ nanobelts). The annealed TiO$_2$ nanobelt sample was an insulator with a very low resistivity value that was ~1000 times larger than that of the TiO$_2$-δ nanobelt sample due to the significant decrease in oxygen vacancies. Note that the TiO$_2$-δ nanobelts were grown without using an oxidant. As a result, the grown TiO$_2$-δ was significantly reduced, with a thickness of ~0.1 µm was studied as a counterpart of the nanobelt samples.
has defect stoichiometry yielding Ti$^{3+}$ defect sites, which are photocatalytically active [17].

The chemical states and carbon doping of the TiO$_2$-$\delta$ nanobelts, the annealed TiO$_2$ nanobelts, and the TiO$_2$ thin film were studied using XPS. As seen in Figure 3a, the Ti 2$p_{3/2}$ peak of the TiO$_2$-$\delta$ nanobelts has a small shoulder at a lower binding energy side and can be deconvoluted into two Gaussian components peaked at 458.7 and 456.7 eV (referred to as peak one and two, respectively). Peak one and two can be assigned to Ti$^{4+}$ (normal state) and Ti$^{3+}$, respectively. The peak separation (2.0 eV) of peak one and two is in agreement with the reported value (~1.8–1.9 eV) of Ti$^{4+}$ and Ti$^{3+}$ states [19,23]. The area ratio of peak two to one is ~0.18, indicating that a significant amount of Ti$^{3+}$ states exists. The ratio of peak two to one was not noticeably changed in the annealed TiO$_2$ nanobelts. As seen in Figure 3b, the O 1$s$ peak of the TiO$_2$-$\delta$ nanobelts can be resolved into two peaks as well. Peak one (530.2 eV) and peak two (531.9 eV) correspond to the oxygen bonded to Ti (Ti–O) and the oxygen from hydroxyl species (OH$^-$), respectively [19,23]. The hydroxyl species can result from the existence of Ti$^{3+}$ states, which are photocatalytically active and can be

![Figure 1. SEM images of the TiO$_2$-$\delta$ nanobelts grown on a bare Si (001) wafer.](image1)

![Figure 2. (a) The XRD pattern of the TiO$_2$-$\delta$ nanobelt sample. (b) A typical high-resolution TEM lattice image of the TiO$_2$-$\delta$ nanobelts and its SAD pattern (inset).](image2)
hydroxylated in organic medium or ambient at room temperature [17–19]. Figure 3c shows that carbon (C) significantly resides on the as-grown surface of the TiO$_2$-$\delta$ nanobelts. As seen in the inset of Figure 3c, peak one at 284.5 eV corresponds to non-functionalized C–C bond [24]. Peak two at 286.1 eV can be attributed to the elemental carbon atoms bonded to Ti (substitutional carbon doping) and to carbon atoms linked to a single oxygen atom (C–OH) [12,24]. Peak three at 288.0 eV corresponds to carbonate species [12,24]. After surface etching (~10 Å) by Ar$^+$ ion sputtering, the overall peak intensity is remarkably decreased, and peak three which arose from carbonate species is diminished. However, it is clearly seen that peak one and two still exist significantly inside the TiO$_2$-$\delta$ nanobelts. As seen in Figure 4, the annealed TiO$_2$ nanobelts exhibited a C 1$s$ spectrum similar to the TiO$_2$-$\delta$ nanobelts, suggesting that a significant amount of carbon still remained in the TiO$_2$ nanobelts after annealing. In addition, the Ti 2$p_{3/2}$ and O 1$s$ peaks of the annealed TiO$_2$ nanobelts were almost the same as those of the TiO$_2$-$\delta$ nanobelts (Figure S1 in Supporting Information). Compared with the nanobelt samples, the TiO$_2$ thin film showed a very weak shoulder peak at 288.0 eV (Figure 4). After surface etching (~10 Å), the carbon peak of the TiO$_2$ thin film almost disappeared (Figure S2).

Figure 3. (a) The XPS spectrum of the Ti 2$p$ core level of the TiO$_2$-$\delta$ nanobelts. (b) The O 1$s$ spectrum resolved into two peaks at 530.2 (peak 1) and 531.9 eV (peak 2). (c) The C 1$s$ spectrum of the as-grown and the etched surface (~10 Å). The inset shows three deconvoluted peaks of the C 1$s$ spectrum of the as-grown surface: Peak 1 at 284.5 eV, peak 2 at 286.1 eV, and peak 3 at 288.0 eV correspond to non-functionalized C–C bond, the elemental carbon atoms bonded to Ti and to a single oxygen atom, and carbonate species, respectively.
similar absorption peaks at 2.70 and 1.75 eV. These peaks of the annealed TiO$_2$ nanobelts satisfy the energies by carbon substitutional doping are too deep in the gap to overlap with the intragap states placed at ~0–1 eV below the conduction band edge [25,26]. The possibility of carbon contribution cannot be completely ruled out, but calculations [3] show that the intra-gap states are placed at ~0–1 eV below the conduction band edge [25,26].

The red-shifted energies correspond to the absorption-threshold shift from point B to point C (0.17 eV) after annealing. This behavior can be explained by a shift of the valence band edge as seen in the inset of Figure 5. It was reported that the narrowed bandgap energy (~0.14 eV) of carbon-doped TiO$_2$ powders was attributed to the shifting of the valence band edge [12]. It should be emphasized that the defect-state bands, which peaks at 2.91 eV of the TiO$_2$-δ nanobelts and 2.70 eV of the annealed TiO$_2$ nanobelts, satisfy the important requirements of visible-light photocatalysis. The energy states in the gap can create photoexcited carriers by visible-light absorption. Moreover, the defect-state bands overlap sufficiently with the conduction band states of TiO$_2$ so that photoexcited carriers can transfer to reactive sites at the surface for photocatalysis. The high specific surface area and very thin thickness (~20–50 nm) of the nanobelts can be a great advantage for efficient carrier transfer to surface without recombination. Meanwhile, the TiO$_2$ thin film shows a larger absorption threshold energy of 3.53 eV (point A), which is most probably related to the onset of direct optical transitions. The larger energy may be a result of anatase structure and less carbon content. We note that although the TiO$_2$ thin film has very broad absorption over the visible-light regime, the band did not overlap with the band states of TiO$_2$.

**Figure 4.** The XPS C 1s spectra of the TiO$_2$-δ nanobelts, the annealed TiO$_2$ nanobelts, and the TiO$_2$ thin film (as-grown surface).

Figure 5 shows the optical absorption spectra of the TiO$_2$-δ nanobelts, the annealed TiO$_2$ nanobelts, and the TiO$_2$ thin film. The TiO$_2$-δ nanobelts show an optical absorption threshold at 3.20 eV (point B), whereas the annealed TiO$_2$ nanobelts show another absorption threshold at 3.03 eV (point C) along with that at ~3.20 eV. The second absorption threshold (point C) is the result of an enhanced substitutional carbon doping by annealing. In relation, Khan et al. [5] reported that rutile thin film showed two absorption thresholds due to carbon doping by natural gas flame pyrolysis. We also note that the TiO$_2$-δ nanobelts show two strong broad absorption peaks centered at 2.91 and 1.92 eV. There is a greater likelihood that these absorption peaks can be attributed to bands of surface states and interstitial Ti$^{3+}$ ions [25,26]. Other workers reported that surface states were shallow intragap states placed at ~0–1 eV below the conduction band edge [25,26].

Unlike reduced anatase TiO$_2$-δ [27], these absorption peaks cannot be due to oxygen vacancies either because the annealed TiO$_2$ nanobelts also show similar absorption peaks at 2.70 and 1.75 eV. These peaks of the annealed TiO$_2$ nanobelts are red-shifted by 0.21 and 0.17 eV, respectively, with respect to those of the TiO$_2$-δ nanobelts. The red-shifted energies correspond to the absorption-threshold shift from point B to point C (0.17 eV) after annealing. This behavior can be explained by a shift of the valence band edge as seen in the inset of Figure 5.
Photocatalytic activity was evaluated by measuring the decomposition of methylene blue in an aqueous solution. As seen in Figure 6a, the TiO$_2$-$\delta$ nanobelts decompose methylene blue effectively through photocatalytic reaction under visible-light irradiation, whereas the TiO$_2$ thin film does not show any photocatalytic activity. Visible-light photocatalysis is further enhanced for the annealed TiO$_2$ nanobelt sample, indicating that the observed visible-light photocatalysis cannot be due to oxygen vacancies. Under UV irradiation, the TiO$_2$-$\delta$ nanobelts also show much stronger photocatalytic activity than the TiO$_2$ thin film (Figure 6b) because of its much larger specific surface area. Moreover, the annealed TiO$_2$ nanobelts show a little bit better photocatalytic activity than the TiO$_2$-$\delta$ nanobelts because of the improved structural quality via annealing.

4. Conclusions

In conclusion, we demonstrated the efficient photocatalysis of TiO$_2$-$\delta$ nanobelts synthesized by MOCVD in both visible and UV light radiation. Visible-light photocatalysis was realized by utilizing self-induced defect states, including the abundant surface states.
of nanobelts and self-doped carbon atoms. The carbon atoms, the by-product of MOCVD, could be self-doped in the TiO$_2$-δ nanobelts by determining the growth conditions judiciously. The approach we used was simple and very efficient for visible-light photocatalysis, and the TiO$_2$-δ nanobelts can be effectively utilized in a wide range of photocatalysis applications, such as the elimination of pollutants and the electrodes of solar cells.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/nano11061377/s1, Figure S1: XPS Ti 2p and O 1s spectra of the annealed TiO$_2$ nanobelts title, Figure S2: XPS C 1s spectra of the TiO$_2$-δ nanobelts, the annealed TiO$_2$ nanobelts, and the TiO$_2$ thin film after surface etching (~10 Å).

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**Data Availability Statement:** Data are available in the main text.

**Conflicts of Interest:** The authors declare no conflict of interest.

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