Improved Solar-Driven Photocatalytic Performance of Highly Crystalline Hydrogenated TiO$_2$ Nanofibers with Core-Shell Structure

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Hydrogenated titanium dioxide has attracted intensive research interests in pollutant removal applications due to its high photocatalytic activity. Herein, we demonstrate hydrogenated TiO$_2$ nanofibers (H:TiO$_2$ NFs) with a core-shell structure prepared by the hydrothermal synthesis and subsequent heat treatment in hydrogen flow. H:TiO$_2$ NFs has excellent solar light absorption and photogenerated charge formation behavior as confirmed by optical absorbance, photo-Kelvin force probe microscopy and photoinduced charge carrier dynamics analyses. Photodegradation of various organic dyes such as methyl orange, rhodamine 6G and brilliant green is shown to take place with significantly higher rates on our novel catalyst than on pristine TiO$_2$ nanofibers and commercial nanoparticle based photocatalytic materials, which is attributed to surface defects (oxygen vacancy and Ti$^{3+}$ interstitial defect) on the hydrogen treated surface. We propose three properties/mechanisms responsible for the enhanced photocatalytic activity, which are: (1) improved absorbance allowing for increased exciton generation, (2) highly crystalline anatase TiO$_2$ that promotes fast charge transport rate, and (3) decreased charge recombination caused by the nanoscopic Schottky junctions at the interface of pristine core and hydrogenated shell thus promoting long-life surface charges. The developed H:TiO$_2$ NFs can be helpful for future high performance photocatalysts in environmental applications.
black TiO$_2$ nanoparticles by treating pristine TiO$_2$ nanoparticles (crystal-white) under 20 bar pure H$_2$ atmosphere at 200°C for 5 days. The authors also demonstrated an approach to enhance solar absorption by introducing disorder in the surface layers of nanoscale TiO$_2$ through hydrogenation. The role of hydrogen in producing lattice disorder was presented in anatase TiO$_2$ nanoparticles, and the highly localized nature of the mid-gap states results in spatial separation of exciton in hydrogenated TiO$_2$ surface. It accounts for its high photocatalytic efficiency as verified by density functional theory. Moreover, hydrogenated TiO$_2$ nanoparticles exhibit the characteristics of low bandgap, which matches well with visible light absorption. Wang et al. reported the hydrogen treatment as a simple and effective strategy to improve the performance of photovoltaic water splitting using one dimensional hydrogenated TiO$_2$ material. In practical applications, one dimensional material titanate materials are typically better than the corresponding nanoparticles. In addition, Liu et al. reported a facile synthesis of hydrogenated TiO$_2$ nanobelts. It shows an outstanding UV and visible photocatalytic decomposing of methyl orange and water splitting for hydrogen production. An elongated one dimensional material is easier to achieve a percolated electrical network than with zero-dimensional materials. Bundling of one dimensional material contributes to mechanical strength in tangled networks and thus results in macroscopic films. Furthermore, the hydrothermal synthesis has opened up new possibilities for large scale production of TiO$_2$ nanofibers by simply thermal treatment of the obtained titane nanofibers in air.

It is noted that hydrogenated TiO$_2$ may worsen the photocatalytic activity under simulated solar light as compared to the pristine material. High pressure hydrogenation can be counterproductive to improve the photocatalytic activity of TiO$_2$ due to the formation of bulk vacancy defects. However, we suggest that the suitable staggered band alignments between highly-crystalline TiO$_2$ and disordered TiO$_2$ have the enhanced photocatalytic activity in hydrogenated TiO$_2$, as it provides a driving force for the separation of photoexcited electron and hole. Hence, the hydrogenated process and its parameters play important role in whether the photocatalytic properties of the material improve or degrade.

In the present work, we demonstrate hydrogenated TiO$_2$ nanofibers (H:TiO$_2$ NFs) having highly crystalline one dimensional anatase TiO$_2$ core and highly defective surface with oxygen vacancies and Ti$_{3+}$ interstitial defects obtained by hydrothermal synthesis and subsequent heat treatment in H$_2$ of partial pressure in N$_2$ gas flow. An optimal calcination condition is proposed to fine tune the photocatalytic activities. The photo-induced charge carrier distribution and carrier dynamics are systematically investigated to understand the role of surface defects. Photo-induced decoloration of various organic dyes under solar light irradiation confirms the correlation between hydrogenation conditions and the photocatalytic activities.

**Results and Discussion**

The hydrogen sodium titanate nanofibers were calcined at various temperatures in the mixture of H$_2$/N$_2$ for 12 hrs to find the optimal calcination process that produces the most active photocatalyst. The crystal structure of various H:TiO$_2$-X NFs was characterized by synchrotron X-ray diffraction (Fig. 1). (Note, the number in the name of the samples after H:TiO$_2$ denotes the calcination temperature.) The results show that H:TiO$_2$ NFs calcined below 600°C comprises a major anatase TiO$_2$ phase along with a minor transition phase of monoclinic β-TiO$_2$. The reflection intensity at 2θ = 16.8° increases with ascending calcination temperature. The higher calcination temperature improves the ordering of the anatase TiO$_2$ lattice. When the applied calcination temperature is above 650°C, the crystal structure transforms to pure anatase TiO$_2$ phase. All diffraction peaks can be perfectly indexed as the body-centred tetragonal structure of anatase TiO$_2$, with unit cell parameters $a = 4.55$ Å and $c = 9.52$ Å [COD ID:720675]. The reflection intensity at 2θ = 16.8° decreases at calcination temperatures above 700°C indicating the formation of rutile TiO$_2$ phase from anatase. Also, we synthesized a series of pristine TiO$_2$ NFs calcined at various temperatures under the air flow for 12 hrs in comparison with H:TiO$_2$ NFs (Fig. 1b). Their mean crystalline domain sizes calculated by Debye-Scherrer equation are 41.6 nm and 51.0 nm, respectively. It says that H:TiO$_2$: NFs has larger crystallite size.

The microstructures of pristine TiO$_2$-650 NFs and H:TiO$_2$:650 NFs are examined by scanning electron microscopy and field emission transmission electron microscopy (Fig. 2). Insets of Fig. 2(a) and (c) show both pristine TiO$_2$ NFs and H:TiO$_2$ NFs have the length up to several micrometres and diameter of ~100–200 nm. High-magnification lattice images of pristine TiO$_2$ NFs and H:TiO$_2$:150 NFs are shown in Fig. 2(b) and (d), respectively. The (101) crystal plane of pristine TiO$_2$ NFs and H:TiO$_2$: NFs can be observed in the corresponding fast Fourier transformed pattern as displayed in the insets of Fig. 2(b) and (d). The $d$ spacing of (101) crystal plane for H:TiO$_2$:650 NFs (3.46 Å) is smaller than that for pristine TiO$_2$:650 NFs (3.52 Å). The result suggests that hydrogenated process alters the surface lattices on H:TiO$_2$: NFs at high calcination temperature. The fine control of the microstructure can warrant extra effort from a materials science point of view.

The chemical compositions of pristine TiO$_2$: NFs and H:TiO$_2$: NFs were analysed by X-ray photoelectron spectroscopy (XPS) as shown in Table 1. Ti 2p orbital and O 1s orbital from pristine TiO$_2$: NFs and H:TiO$_2$: NFs are shown in Fig. S1 of supplementary information. The XPS results suggest that the crystal surface has oxygen vacancy defects and Ti$_{3+}$ interstitial defects. The resolved Ti 2p orbital evidences the presence of Ti$_{3+}$ signals at around 457 eV (Fig. S1(a) and (c) of supplementary information), whereas the resolved O 1s orbital show the existence of O-H bond at around 531.0 eV as shown in Fig. S1(b) and (d) of supplementary information. The oxygen concentration in H:TiO$_2$: NFs series is always lower than in pristine TiO$_2$: NFs synthesized at the corresponding calcination temperature caused by the lack of oxygen surrounding during calcination carried out under H$_2$/N$_2$ mixed gas atmosphere. Brunauer-Emmett-Teller (BET) surface area, Barrett-Joyner-Halenda (BJH) cumulative volume of pores and BJH average pore width of pristine TiO$_2$:650 NFs and H:TiO$_2$:650 NFs were measured by Accelerated Surface Area and Porosimetry System. The detail experimental results is listed in Table 2. The absorption and desorption isotherms and the pore diameter distribution curves of pristine TiO$_2$:650 NFs and H:TiO$_2$:650 NFs can be found in Fig. S2 of supplementary information. After hydrogenated process, the specific surface area and total pore volume of H:TiO$_2$:650 NFs are larger than pristine TiO$_2$:650 NFs. The reason could be due to...
the surface defect formation of H:TiO$_2$-650 NFs for nitrogen gas adsorption/desorption, such as oxygen vacancy defects and Ti$^{3+}$ interstitial defects. As a result, the average pore diameter of H:TiO$_2$-650 NFs should be decreased after the hydrogenated process due to the formation of small surface defects.

Camera images and corresponding absorbance spectrum of pristine TiO$_2$ NFs and H:TiO$_2$ NFs are shown in the Fig. 3. H:TiO$_2$ NFs is having a greyish color with respect to the white pristine TiO$_2$ NFs. As compared to pristine TiO$_2$ NFs, the absorbance spectrum of H:TiO$_2$ NFs is enhanced in the visible region. The bandgaps of pristine TiO$_2$ NFs and H:TiO$_2$ NFs can be estimated to be approximately 3.17 and 3.14 eV respectively. The enhanced visible absorption behavior could be due to the surface defects, including the oxygen vacancy and the Ti$^{3+}$ interstitial defects. When the Ti$^{3+}$ interstitial defects which reduces Ti$^{4+}$ into Ti$^{3+}$ is on the surface, it introduces mid-gap state into TiO$_2$ crystal for enhanced optical absorption$^{33,48}$. Computer simulation is used to examine the absorption behavior caused by the oxygen vacancy. All simulations are based on CASTEP (Cambridge Serial Total Energy Package) module in Materials Studio developed by Accelrys Software Inc. Structures of pristine TiO$_2$ and H:TiO$_2$ with the oxygen vacancy used in this study are made of (3 $\times$ 3 $\times$ 1) anatase TiO$_2$ supercell (Fig. S3

Figure 1. Synchrotron X-ray diffraction of (a) various H:TiO$_2$-X NFs and the standard powder of anatase TiO$_2$ and (b) pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs. (c) Magnified peak around 16.8°.
of supplementary information). The theoretical calculations presented in Fig. S4 of supplementary information verify the enhanced absorption of H:TiO₂ NFs.

Tip-enhanced Raman spectroscopy (TERS) gives the information about the surface vibrational modes of the synthesized TiO₂. Both pristine TiO₂ NFs and H:TiO₂ NFs were measured by two-laser TERS system to observe the phase transformation in certain depth profile. The information provided by 532 nm excitation probes more efficiently the outside surface structure, while the 633 nm scatters from the entire volume of the nanowires. As
observed, Fig. 4 depicts the inside/outside surface structure of both pristine TiO2 NFs and H:TiO2 NFs. It is transformed to anatase phase when the calcination temperature was settled at 650 °C. For the anatase TiO2 phase, the major Raman bands are located at 144, 200, 398, 515, 517 and 640 cm$^{-1}$, with superimposed Raman bands at 515 and 517 cm$^{-1}$. The individual Raman bands are attributed to the six Raman-active modes of anatase TiO2 phase with the symmetries of Eg, Eg, B1g, A1g, B1g, and Eg (Fig. 4(a)). The outside surface structure of H:TiO2 NFs is similar to anatase phase, however, oxygen vacancy defect and the Ti3$^{+}$ interstitial defects (partial TiO2 transformed to Ti2O3) are included. It can be inferred that the formation of Ti3$^{+}$ interstitial defects in anatase results in the red shift of Eg phonons (144 and 200 cm$^{-1}$) caused by the multi-phonon B1g of the Ti2O3. The third Eg phonon at 640 cm$^{-1}$ is blue shift affected by the A1g phonon in Ti2O3. It is also noted that the mixed phase of anatase TiO2, oxygen vacancy defect and the Ti 3$^{+}$ interstitial defects in the outside surface of H:TiO2 NFs has broaden peaks with respect to pristine TiO2 NFs as shown in Fig. 4(b). TEM microstructure analysis and the TERS reveals that H:TiO2 NFs contains a highly crystalline anatase TiO2 core and a hydrogenated TiO2 shell.

The photo-assisted Kelvin probe force microscopy (photo-KPFM) is a useful technique to predict the photocatalytic capability of materials in the development of high performance photocatalysts. Here, it was applied to elucidate the carrier distribution on pristine TiO2 NFs and H:TiO2 NFs. Topographic images and surface potential mappings of pristine TiO2 NFs and H:TiO2 NFs in Fig. 5. Figure 5(a-1) and (b-1) show the topographic images of pristine TiO2 NFs and H:TiO2 NFs without any ultraviolet light illumination. The average surface potentials of pristine TiO2 NFs and H:TiO2 NFs are $-49.4$ mV and $-53.4$ mV as shown in Fig. 5(a-2) and (b-2), i.e. their surface potential are pretty close. However, the average surface potentials of pristine TiO2 NFs and H:TiO2 NFs are negative shifted to $-118.7$ mV and $-150.1$ mV under ultraviolet light irradiation (i.e., UV-B light with a $\lambda_{\text{max}}$ of 312 nm), respectively. The electron-hole pairs are generated under UV-B irradiation. It results in the splitting of $E_f$ into quasi-Fermi energy, $E_{\text{fn}}$ and $E_{\text{fp}}$, for electrons and holes. $E_{\text{fn}}$ is usually considered in TiO2 because of its characteristic as an n-type semiconductor with electrons being the majority carriers. A considerable drop of surface potential was observed in the case of H:TiO2 NFs ($-96.7$ mV), presenting the larger shift of $E_{\text{fn}}$ relative to $E_f$ than that of pristine TiO2 NFs ($-69.3$ mV). The photo-KPFM results show that the H:TiO2 NFs has larger photo surface potential shift than pristine TiO2 NFs. The accumulated electrons in H:TiO2 NFs hence caused the decreased surface potential and shifted $E_{\text{fn}}$ closer to the TiO2 conduction band. It means that the electron-hole...
pairs can be generated under UV-B light leading to an upward shift of Fermi energy from $E_f$ to $E_{fn}$ and the resulting detected negative shift of surface potential. We assume that the electrons of the H:TiO$_2$ NFs excited by pulse laser will be transferred to the H:TiO$_2$ NFs surface.

Figure 6(a) shows the PL spectra of pristine TiO$_2$ NFs and H:TiO$_2$ NFs excited by 375 nm picosecond pulsed laser. Intense PL at the position approximately 500 nm from the pristine TiO$_2$ NFs is surprising at first glance. Even though pristine TiO$_2$ NFs has defect density in the structure so as to give strong PL response around 500 nm, we expected that the H:TiO$_2$ NFs would provide higher carrier transport based on the results of the TERS and photo-KPFM in highly crystalline of anatase TiO$_2$. In order to address the behaviour of intrinsic PL, the results of micro time-resolved photoluminescence ($\mu$-TRPL) was obtained by keeping the wavelength at 425 nm for understanding the carrier transport (Fig. 6(b)). The transient PL decay plots were fitted by bi-exponential kinetics function:

$$F(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right)$$  \hspace{1cm} (1)

where $A_1$ and $A_2$ are the corresponding amplitudes. $\tau_1$ and $\tau_2$ are fast decay time and slow decay time. The average lifetime was calculated using the following equation:

$$\tau_{avg} = \frac{\sum_i A_i \tau_i}{\sum_i A_i}$$  \hspace{1cm} (2)

The transient PL decay fitting curve of pristine TiO$_2$ NFs and H:TiO$_2$ NFs depicts that the hydrogenated process could influence the charge transport efficiency. Table 3 is the summary of the measured fast decay time ($\tau_1$), slow decay time ($\tau_2$), and PL average lifetime ($\tau_{avg}$) for pristine TiO$_2$ NFs and H:TiO$_2$ NFs. For the pristine TiO$_2$ NFs, the fast decay lifetime is 0.50 ns, the slow decay lifetime is 1.45 ns and their corresponding amplitudes are 54.4% and 45.6% respectively. Surprisingly, the fast decay lifetime of H:TiO$_2$ NFs significantly decreases to 0.34 ns
and the amplitudes increases to 94.3%. It suggests the improvement of the efficiency of electron transfer to surface and reduces the electron-hole recombination. It is reasonable to know that the average lifetime of the pristine TiO\textsubscript{2} NFs is 0.93 ns and that of the H:TiO\textsubscript{2} NFs is 0.40 ns. For the inner structure of the H:TiO\textsubscript{2} NFs, the highly crystalline anatase TiO\textsubscript{2} phase could deliver electrons effectively (Fig. 1(c)). It is believed that the outside surface structure of the H:TiO\textsubscript{2} NFs has large amount of surface defects (including the oxygen vacancy and Ti\textsuperscript{3+} interstitial defect). The hetero-phase junction delivers electron to the surface defect on the outside structure of H:TiO\textsubscript{2} NFs. The excited electron irradiated by ultraviolet light is located in the surface defects, and it is easily trapped in the mid-state of conduction band which consists with the large negative surface potential at photo-KPFM studies.

The photodegradation of several organic dyes, including methyl orange, rhodamine 6G and brilliant green, under simulated solar light irradiation were performed by AEROXIDE\textsuperscript{®} TiO\textsubscript{2} P25, pristine TiO\textsubscript{2} NFs and H:TiO\textsubscript{2} NFs. The absorption spectra of methyl orange, rhodamine 6G and brilliant green, as a function of irradiation time were recorded in Fig. 7. The $\lambda_{max}$ in the measured absorbance spectrum is used to calculate the various organic dye concentration using a calibration curve. The $\lambda_{max}$ of methyl orange, rhodamine 6G and brilliant green are 464.0, 527.5 and 624.5 nm. The colour of suspension changed from the initial colour to colourless and showed good agreement with first-order kinetics i.e. $ln(C/C_0) = -kt$; where $C$ is the concentration of the dye at time $t$, $C_0$ is the initial concentration, and $k$ is the apparent reaction rate constant\textsuperscript{58}. For the catalyzed photodegradation of various organic dyes, the H:TiO\textsubscript{2} NFs is superior to pristine TiO\textsubscript{2} NFs and the commercial AEROXIDE\textsuperscript{®} TiO\textsubscript{2} P25\textsuperscript{60,61}. Based on our results thus three mechanisms may be assumed for the high photocatalytic activity of H:TiO\textsubscript{2} NFs: (1) highly crystalline anatase TiO\textsubscript{2} exhibit the high charge transport rate (Fig. 1), (2) the hydrogenated process promotes the visible absorption behaviour to increase exciton generation (Fig. 3), and (3) surface charge can photo-induce the electron to decrease charge recombination (Fig. 6). The photocatalytic degradation mechanism of organic dye over H:TiO\textsubscript{2} NFs is described in equations (3)–(9)\textsuperscript{81}.

$$\text{TiO}_2 + h\nu \rightarrow h^+ + e^- \quad (3)$$

$$O_2 + e^- \rightarrow O_2^- \quad (4)$$

$$O_2^- + H^+ \rightarrow HO_2^- \quad (5)$$

$$H_2O + h^+ \leftrightarrow OH^- + H^+ \quad (6)$$

$$OH^- + h^+ \leftrightarrow OH \quad (7)$$

$$O{H^-} + \text{organic dye} \rightarrow \text{oxidation products} \quad (8)$$

$$H{O_2}^- + \text{organic dye} \rightarrow \text{oxidation products} \quad (9)$$

First, when TiO\textsubscript{2} is irradiated by a light that energy is greater or equal to its bandgap, the photon will excite the valence electron ($e^-$) to the conduction band and electron-hole pair will be generated. After that, the electron reacts with the oxygen ($O_2$) to form superoxide ions ($O_2^-$). The superoxide ions possess a significant reducing ability, hence it will react with proton ($H^+$) and reduce to hydroperoxyl radical ($HO_2^- \bullet$). Whenever the organic molecules adsorbed on the photocatalyst surface, the hole ($h^+$) would react with the hydroxide ions ($OH^- \bullet$) or water molecules to form hydroxyl radicals ($OH \bullet$) and $H^+$. Most of these free radicals behaves excellent oxidation ability, among which $OH \bullet$ and $HO_2^- \bullet$ have the strongest oxidation potential. They will quickly adsorb any organics on the surface of TiO\textsubscript{2} and undergo oxidation-reduction reactions leading to the production of low molecular weight intermediates. It finally oxidizes these intermediates into environmentally harmless products such as water or carbohydrate. Many studies have focused on the factors that affect the $OH \bullet$ formation such as irradiation time, pH and phase structures. Under acidic environment, low pH will promote the formation of $OH \bullet$ because of the lower redox potential for hole at valance-band. Also, the phase structures of TiO\textsubscript{2} affects the formation rate of $OH \bullet$ significantly. Amorphous TiO\textsubscript{2} possesses lots of defect that induces the recombination of electron-hole pairs and suppress the $OH \bullet$ formation. Thus, the proper crystalline phase structure design facilitates the photocatalytic phenomenon\textsuperscript{62,63}. The high-performance photocatalyst should maintain the activities after repeated irradiations. To further evaluate the stability and reusability of the pristine TiO\textsubscript{2} NFs and H:TiO\textsubscript{2} NFs, the recycled photocatalytic activities were measured by executing repeated degradation reaction of methyl orange over pristine TiO\textsubscript{2} NFs and H:TiO\textsubscript{2} NFs for five recycling runs under UV-B light irradiation. The photostability testing of pristine TiO\textsubscript{2} NFs and H:TiO\textsubscript{2} NFs were shown in Fig. S5 of supplementary information. H:TiO\textsubscript{2} NFs exhibits the higher stability behavior than pristine TiO\textsubscript{2} NFs under UV-B irradiation. After two recycling runs, the photostability

| Sample            | $A_1$ (%) | $\tau_1$ (ns) | $A_2$ (%) | $\tau_2$ (ns) | $\tau_{avg}$ (ns) |
|-------------------|----------|---------------|----------|---------------|------------------|
| Pristine TiO\textsubscript{2} NFs | 54.4     | 0.50          | 45.6     | 1.45          | 0.93             |
| H:TiO\textsubscript{2} NFs      | 94.3     | 0.34          | 5.7      | 1.32          | 0.40             |

Table 3. Summary of the measured fast decay time ($\tau_1$), slow decay time ($\tau_2$), and PL average lifetime ($\tau_{avg}$) for pristine TiO\textsubscript{2} NFs and H:TiO\textsubscript{2} NFs.
testing for H:TiO$_2$-650 NFs shows no obvious decay. Hence, H:TiO$_2$ NFs is more chemically stable than pristine TiO$_2$ NFs, and it cannot be easily photocorroded under UV light irradiation.

When H:TiO$_2$ NFs absorbs solar light with energy larger than its bandgap, excitons are generated. The electrons generated in H:TiO$_2$ NFs are effectively transferred to the surface defect, and it can capture the photogenerated electrons effectively thus reducing the rate of electron-hole recombination. In order to confirm the position of valence band and conduction band, the pristine TiO$_2$ NFs and H:TiO$_2$ NFs were measured by Ultraviolet Photoelectron Spectroscopy (UPS). The UPS spectra of pristine TiO$_2$ NFs and H:TiO$_2$ NFs are shown in Fig. S6(a) of the supplementary information. Work function (WF) is derived from subtracting the cut-off binding energy with the photon energy (21.22 eV). The WF of pristine TiO$_2$ NFs and H:TiO$_2$ NFs are 5.33 and 5.91 eV, respectively$^{64}$. The expanded valence spectra of pristine TiO$_2$ NFs and H:TiO$_2$ NFs are shown in Fig. S6(b) of the supplementary information. The valence band maximum (VBM) of pristine TiO$_2$ NFs and H:TiO$_2$ NFs are found to be located at about 2.59 and 2.22 eV below the Fermi level ($E_F$). Hence, the VBM position of the pristine TiO$_2$ NFs and H:TiO$_2$ NFs are $-7.92$ and $-8.13$ eV, respectively$^{64}$. The schematic diagram of the band alignment between the surface defect and anatase TiO$_2$ are shown in Fig. 8(a). The holes generated in H:TiO$_2$ NFs could stay on the area without surface defects due to the VBM of H:TiO$_2$ NFs is lower than that of pristine TiO$_2$ NFs. If the holes are not directly recombined with electrons in H:TiO$_2$ NFs, they are able to be further transferred to react with the organic dyes. During the charge separation and migration processes, some of the excited charges may recombine. If the electrons generated in H:TiO$_2$ NFs are effectively transferred to the oxygen vacancy and Ti$^{3+}$ interstitial defects, it captures the photogenerated electrons effectively and to reduce the rate of electron-hole recombination. In addition, the electronic structure and optical properties were also calculated to confirm the result with UPS study by the first-principles calculations based on density functional theory. The density of states of pristine TiO$_2$ and H:TiO$_2$ is also calculated, and the detail data of structure is shown in Fig. S7 of the supplementary information. Each electronic structure was analyzed in order to obtain the origin of the band discontinuity. In comparison of density of state, the conduction band and valence band of both the pristine TiO$_2$ and H:TiO$_2$ is attributed to the Ti $3d$ and O $2p$ orbital, respectively. The results show that a mid-state of H:TiO$_2$ can be considered as an extension of conduction band. As a consequence, the mid-state of H:TiO$_2$ could narrow the band gap and lead to the excited electrons richly transported from conduction band to new mid-state (Fig. S7 of the supplementary information). Figure 8(b) illustrates the outside material of H:TiO$_2$ NFs is consisted of the surface defects, including the oxygen vacancy and Ti$^{3+}$ interstitial, and highly crystalline anatase TiO$_2$. The photocatalytic activity depends on the...
amount of working electrons and holes on the surface of the photocatalyst. The H:TiO2 NFs with a core-shell structure prepared by the hydrothermal synthesis and subsequent heat treatment at low H2 partial pressure in the N2 gas flow can be helpful for searching the high-performance visible-light-active photocatalyst in the field of degradation of pollutants with solar light.

Conclusion
In summary, H:TiO2 NFs was prepared by a safe and easy process, and its characteristics were studied to understand the correlation between the hydrogenated process and the solar-light-assisted photocatalytic performance. The high absorption in solar light is due to the oxygen vacancy and Ti3+ interstitial defects on the surface of the H:TiO2 NFs. The photo-KPFM analysis and μ-TRPL confirms the lower recombination rate and higher charge transport in H:TiO2 NFs compared with pristine TiO2 NFs. For the photodegradation of various organic dyes, including methyl orange, rhodamine 6G and brilliant green, H:TiO2 NFs gave the fastest decoloration phenomenon under solar light irradiation than TiO2 P25 and pristine TiO2 NFs. Our study indicates that the significant photodegradation activity is obtained by adding the surface defect (the oxygen vacancy and Ti3+ interstitial defect) into TiO2 NFs surface. Three mechanisms were elucidated: (1) enhancement in absorbance to increase exciton generation, (2) highly crystalline anatase TiO2 to increase the charge transport rate, and (3) decreased charge recombination to increase surface charge. The result illustrates a soft controlling of the hetero-phase junction and highly crystalline anatase TiO2. It may strongly change the ability of the materials in photodegradation of pollutants.

Methods
Preparation of H:TiO2 NFs. For the preparation of H:TiO2 NFs, we suspend 2.50 g TiO2 anatase powder (Aldrich, 98%) in 62.5 mL of 10.0 M NaOH aqueous solution, followed by a treatment in a Teflon-lined autoclave at 150 °C for 24 hrs, applying revolving around its short axis. Then, sodium titanate NFs was then washed in 0.10 M HCl to exchange sodium ions for protons. The neutralized product was washed with deionized water and finally filtered and dried in the air at 70 °C to obtain the hydrogen sodium titanate NFs. The hydrogen sodium titanate NFs were calcined at in 15% H2 (in N2 buffer) flow for 12 hrs to obtain the various H:TiO2-xxx NFs.

Characterization of TiO2 NFs. The crystal structure of pristine TiO2-650 NFs and H:TiO2-650 NFs were determined by synchrotron X-ray spectroscopy (λ=1.025 Å) on beam line 13A1 of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. Spherical- aberration corrected field emission transmission electron microscope (JEOL, JEM-ARM200FTH, Japan) was used to observe the microstructures of pristine TiO2-650 NFs and H:TiO2-650 NFs. In addition, UV-vis absorption spectra of various synthesized TiO2 samples were measured by absorption spectrophotometer (Jasco Analytical Instruments, V-650, Japan) in the 200–800 nm wavelength range. XPS (X-ray photoelectron spectroscopy) spectra were recorded with a PHI 5000 Versa Probe system (ULVAC-PHI, Chigasaki) using a micro focused (100 μm, 25 W) Al X-ray beam. BET surface area, BJH cumulative volume of pores and BJH average pore width of pristine TiO2-650 NFs and H:TiO2-650 NFs were measured by Accelerated Surface Area and Porosimetry System (ASAP 2020, Micromeritics). The system of micro time-resolved photoluminescence (μ-TRPL) with one lasers as Picosecond diode laser driver with 375 nm Laser head (with integrated collimator and TE cooler for temperature stabilization) was integrated by UniNanoTech Co., Ltd. Andor iDus CCD with 1024 × 128 pixels was used to take the PL signal and the Pico

![Figure 8.](image-url)
Absorption spectrum of the retained organic dye and its derivatives in the supernatant was recorded by absorption near room temperature. The distance between each lamp and reactor was about 15.0 cm. Before the actual photodegradation testing, 20.0 mg of pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs were sonicated for 10 min in 150 mL of 10.0 ppm organic dye aqueous solution, respectively. The temperature of the stirred dispersion was kept near room temperature. The surface potential maps of samples were taken with and without illumination at room temperature. The surface potential difference is then denoted as the photo surface potential shift. The surface potential was obtained in the dark or under UV-B illumination. The height variation and contact potential by electrostatic force between the conductive tip and the surface of the samples are measured simultaneously. A line is scanned using AFM in tapping mode to acquire the topographic information of the material, then the same line is rescaned with the tip lifted to a height of 20 nm. During the second scan, $V_{DC}$ is applied at the tip to nullify the electrostatic oscillations, position by position, and the contact potential difference is observed and measured. The surface potential distributions of pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs were mapped in the dark or under the illumination of a UV-B lamp (Sankyo Denki, G8T5E, 8 W). In addition, the function of the cross-section analysis was used to get detailed information on the topographic height and the surface potential across the selected line. The surface potential was obtained in the dark or under UV-B illumination. The surface potential difference is then denoted as the photo surface potential shift.

**Photodegradation of organic dyes under solar simulator.** AEROXIDE® TiO$_2$ P25, pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs were tested in the photodegradation of organic dyes, including methyl orange (C$_{12}$H$_{14}$N$_2$NaO$_6$S, Acros Organics, pure), rhodamine 6G (C$_{31}$H$_{38}$N$_2$ClIN$_2$O$_6$, Acros Organics, pure), and brilliant green (C$_{35}$H$_{28}$N$_2$O$_6$S, Acros Organics, pure) under solar light irradiation. AM 1.5G solar simulator (Yamashita Denso, YSS-180S) was used as the irradiation source for the photodegradation of various organic dyes. The intensity of the simulated sunlight was calibrated to be 100 mW/cm$^2$ by a silicon photodiode. In this experiment, 20.0 mg of AEROXIDE® TiO$_2$ P25, pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs were sonicated for 10 min in 150 mL of 10.0 ppm organic dye aqueous solution, respectively. The temperature of the stirred dispersion was kept near room temperature. The distance between each lamp and reactor was about 15.0 cm. Before the actual photodegradation experiments, the suspensions were left to relax for 30 min in order to minimize the error of the dye concentration measurements caused by initial surface adsorption. After centrifuging for 15 min at 5000 rpm, the absorption spectrum of the retained organic dye and its derivatives in the supernatant was recorded by absorption spectrophotometer (JASCIO Analytical Instruments, V-630, Japan) in the 300–900 nm wavelength range.

**Photostability Testing for pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs.** A photostability testing on the pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs was carried out according to the literature$^{11}$. In this measurement of photostability testing, 20.0 mg of pristine TiO$_2$-650 NFs and H:TiO$_2$-650 NFs were sonicated for 10 min in 300 mL of 10.0 ppm methyl orange aqueous solution, respectively. The temperature of the stirred dispersion was kept near room temperature. The temperature of the stirred dispersion was kept near room temperature. The distance between the 4 pieces of UV-B lamp (Sankyo Denki, GST5E, 8 W) and reactor was about 10.0 cm. After the reaction of first run testing under UV-B light irradiation, the suspensions were centrifuged to obtain the photocatalyst, which was washed with ethanol and deionized water carefully and then dried at 105 $^\circ$C for 24 hr. The fresh 10.0 ppm methyl orange aqueous solution was mixed with the used photocatalyst to perform the 2nd run photoactivity testing. Similarly, the recycled 3rd, 4th and 5th tests were also performed.

**Computational simulation.** Computational simulation used in this paper is based on density functional theory with a GGA-PBE (Generalized Gradient Approximation Perdew-Burke-Ernzerhof) functional implemented in CASTEP which uses a plane wave basis set to expand the electron wave function. As for the pseudopotential, two setups are adopted depending on the characteristic we are simulating. This is because that pseudopotential will have better accuracy in predicting the properties they suit. In the simulations of absorption spectrum and density of states (DOS), TiO$_2$ is modelled by a (3 × 3 × 1) supercell with/without oxygen vacancy (Fig. S2 of supplementary information). In this case, a norm-conserving pseudopotential is used due to its accuracy in predicting optical properties, and the calculations are conducted with an energy cutoff of 450.0 eV and a k-point set of 1 × 1 × 2.

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**Author Contributions**

M.-C.W., T.-F.L. and K.-M.L. wrote the manuscript. C.-H.C. carried out the TERS and TRPL analyses. W.-K.H., P.-Y.W. and S.-H.C. prepared TiO2-based nanofibers and measured the photocatalytic activity. C.-F.L. and J.-J.S. carried out the XPS analysis and UPS analysis. T.-H.L. conduct the computational simulation and acquisition of data. Y.-H.C. carried out the photostability testing. K.-C.H. is responsible for the measurement of KPFM. K.-H.H. and J.-F.H. made the substantial contributions to conception and design. W.-F.S. and K.K. give final approval of the version to be submitted and any revised version.

**Additional Information**

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