This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
COMMUNICATION

Black and Yellow Anatase Titania Formed by (H,N)-doping: Strong Visible-light Absorption and Enhanced Visible-light photocatalysis

Shunhang Wei, Rong Wu, Jikang Jian, Fengjuan Chen and Yanfei Sun

Received in XXX, XXX Xth XXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXX 20XX
DOI: 10.1039/b000000x

We produce black and yellow anatase TiO$_2$ doped with hydrogen and nitrogen elements annealing in N$_2$/Ar/air atmosphere. More interestingly, one kind of black TiO$_2$ has excellent performance for degradation of methylene blue under visible-light irradiation but photodegradation of the other one is quite limited.

Titanium dioxide (TiO$_2$) has emerged as the most widely investigated photocatalyst for using in solar-driven clean energy.$^1$ The photocatalytic process is carried out through the activation of a semiconductor material with UV or visible light illumination.$^2$ Thus high effective light absorption is essential to maximize photocatalytic performance. However, conventional white TiO$_2$ has poor visible absorption because of a wide band gap (3.2 eV for anatase).$^3$ Also, the rapid electron-hole recombination of TiO$_2$ often results in poor photocatalytic activity. Many methods to prepare TiO$_2$-based photocatalysts that enable efficient utilization of visible light have been developed. A frequently used method is doping TiO$_2$ with metals or nonmetals such as Ag, Mo, N, C.$^7$ Nevertheless, the above two major issues affecting the efficiency of light absorption and photocatalysis have not been well resolved. Recently, hydrogenation has been used to produce black TiO$_2$ to improve visible light absorption and photocatalytic activity, which has attracted extensive attention.$^5$ Indeed, Chen et al.$^6$ have shown that black TiO$_2$ produced by hydrogenation can have a narrow band gap of 1.54 eV, which improves visible and infrared optical absorption. However, the visible-light photocatalytic activity of this sample was not very high.$^9$ To date, four methods have mainly been used to produce black TiO$_2$, including (1) high H$_2$-pressure process,$^8$ (2) annealing in hydrogen atmosphere,$^9$ (3) aluminum reduction$^{14}$ and (4) solution evaporation process.$^{15}$ Method (1) is dangerous because it is difficult to control a hydrogenation process conducted at high pressure (20 bar) using pure hydrogen. Through methods (2) and (3) possess well photocatalysis performance under visible-light illumination, the appearance of hydrogen also makes these experimental processes unsafe. Method (4) is a safer option, which synthesizes black anatase titania without hydrogenation, and provide a new path for the preparation of black TiO$_2$. However, the existing approach is troublesome to handle. The major reasons are that TiCl$_4$ as experimental material is easy volatile so that need operational process making under ice water bath and produce corrosive gas when it meet water. Therefore, a safer and more simple synthesis method is required to produce black titania with excellent photocatalytic activity.

Herein, a new facile synthetic method to produce black TiO$_2$ is developed by chemical synthetic approach. In this method, tetrabutyl titanate is used as a titanium precursor and the equipments used before calcined are very simple: a heat-preservation device and magnetic stirrer. The synthesized black TiO$_2$ sample exhibits excellent visible-light absorption, which highly increases photocatalytic activity. In this process, yellow TiO$_2$ with good performance can also be produced using different heating environment.

The X-ray diffraction (XRD) patterns of the TiO$_2$ samples annealed under different gases are presented in Fig. 1a: black TiO$_2$ heated in Ar atmosphere (B(Ar)), black TiO$_2$ heated in N$_2$ atmosphere (B(N$_2$)), yellow TiO$_2$ heated in air (Y(air)). The patterns are all consistent with anatase TiO$_2$. The intense XRD diffraction peaks indicate that the yellow and black TiO$_2$ samples are highly crystalline. The structural characteristics of the three samples were further investigated by Raman spectroscopy, as shown in Figure 1b. Anatase TiO$_2$ has six Raman-active modes at 144, 197, 399, 515, 519 (superimposed with the 515 cm$^{-1}$ band), and 639 cm$^{-1}$, respectively.$^1$ Therefore, the Raman spectra unambiguously indicate that all of these samples are typical anatase TiO$_2$. Compared with yellow TiO$_2$, the most intense peak at 144 cm$^{-1}$ of the two black TiO$_2$ samples exhibits a blue shift, which is ascribed to the crystal domain size and nonstoichiometry.$^{14}$
tetravalent Ti on the outermost surface of the black anatase TiO₂. The related binding energies are 457.6 and 458.5 eV for the sample annealed in Ar, respectively, and 458.4 and 458.7 eV for that annealed in N₂, respectively (see Fig.1S for more details in the ESI†). The proportion of trivalent to tetravalent Ti in B(Ar) is calculated to be 1:24.85 from the peak areas for the outermost surface, while that for B(N₂) is 1:18.20. Therefore, B(Ar) and B(N₂) are assumed to possess stoichiometries of TiO₂.985 and TiO₂.974 for the outermost surface, respectively. The presence of Ti⁴⁺ in the samples is further supported by electron paramagnetic resonance (EPR). A strong EPR signal observed at g-value of ~2.002 is assigned to surface Ti⁴⁺ (Fig.2S in the ESI†). Given that the signal area is correlated with the amount of Ti⁴⁺, it indicates that the largest amount of Ti⁴⁺ and oxygen vacancies exist in B(N₂) samples. In contrast, Ti³⁺ is not present in the yellow TiO₂ (Fig.2a and Fig.2S). In other words, there are fewer oxygen vacancies in the yellow TiO₂ sample than in the black ones. To the outermost surface, oxygen deficiency ratios of 0.02 and 0.05 exceed 0.01 too much, which result in anatase TiO₂ undergoing phase transformation. However, the results of XRD (Fig.1a) and Raman spectroscopy (Fig.1b) demonstrated that the samples are typical anatase TiO₂. A similar inconsistency was also reported by Myung et al. Based on above results, such apparent contradiction can be ascribed to the introduction of N and H during high-temperature annealing. Forms of being of N and H in samples are reflected by the N 1s XPS spectrum (Fig.3S). The peaks of Y(air) at 396 eV is the absence of NH₃ or NH₄⁺ rather than its absence. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is employed to further demonstrate our assumption. The results show that NH₃⁺ (m=17) and NH₄⁺ (m=18) do exist in two black samples (Fig.3S in the ESI†). Based on this result, besides very little amounts of them exist in B(N₂), the absent FTIR peak of NH₃⁺ in B(N₂) shows the amounts of NH₃⁺ less than NH₄⁺. It is consistent with the deduction that ammonium decomposition more entirely. None carbon-related fragments are detected, such as C⁺ (m=12), C₂⁺ (m=24) and C₂H⁺ (m=25) (Fig.4S in the ESI†). Therefore, the ToF-SIMS date demonstrate two black TiO₂ are carbon-free samples.

Fig. 2 XPS obtained for (a) Y(air), (b) B(Ar), and (c) B(N₂). (d) FTIR spectra of the three TiO₂ samples.

FTIR spectra of the black and yellow anatase TiO₂ samples are illustrated in Fig. 2d. The peaks at around 3400 and 1620 cm⁻¹ are attributed to stretching and bending vibrations of hydroxyl groups, respectively. The peak at around 2000 cm⁻¹ is attributed to stretching and bending vibrations of NH₃. An additional peak at 1390 cm⁻¹ is found for black anatase TiO₂ that can be assigned to the bending vibration of NH₂. Interestingly, the peak at around 2000 cm⁻¹ is not present in the FTIR spectrum of B(N₂). This is mainly because the furnace used to calcine B(N₂) possessed better gas tightness than that used to calcine the other samples, so ammonium was decomposed more entirely during heat treatment. The FTIR spectra are consistent with the presence of N and H in the samples. At the same time, the results of FTIR demonstrate the peak of B(Ar) centered at 401.4 eV is ascribed to the coexistence of NH₃⁺ and NH₄⁺ rather than one of them and the absence of the peak at around 401 eV in B(N₂) is attributed to very little amount of NH₃⁺ or NH₄⁺ rather than its absence. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is employed to further demonstrate our assumption. The results show that NH₃⁺ (m=17) and NH₄⁺ (m=18) do exist in two black samples (Fig.3S in the ESI†). Based on this result, besides very little amounts of them exist in B(N₂), the absent FTIR peak of NH₃⁺ in B(N₂) shows the amounts of NH₃⁺ less than NH₄⁺. It is consistent with the deduction that ammonium decomposition more entirely. None carbon-related fragments are detected, such as C⁺ (m=12), C₂⁺ (m=24) and C₂H⁺ (m=25) (Fig.4S in the ESI†). Therefore, the ToF-SIMS date demonstrate two black TiO₂ are carbon-free samples.

Comparing Fig. 2a with b and c, we note the absence of trivalentTi in the yellow anatase TiO₂. However, the FTIR spectrum of Y(air) shows that N and H are also doped in yellow anatase TiO₂. It is assumed that during heat treatment, the oxygen present in air makes it difficult for ammonium to enter TiO₂, the following decomposition can not go on entirely and finally make the formation of NH₃. The presence of oxygen decreasing the amounts of N and H doped into TiO₂ makes the reduction of tetravalent Ti unsuccessful. This assumption is consistent with the above deduction that good gas tightness with less oxygen present during heat treatment improves doping with N and H and entirely decomposition of ammonium.
to examine the microstructure of the black anatase TiO$_2$ samples, as shown in Fig. 3b and d. These images indicate that the distance in the crystal lattices are ~0.33 and ~0.325 nm, consistent with (101) lattice planes. The surface of two black samples also show the absence of carbon layers. The sample heated in Ar atmosphere is very black before milling with an agate mortar. After milling, a small amount of the sample appears dark green. This phenomenon is attributed to the diameter of the nanocrystals being decreased by milling, which changes the refractive index of the sample.

Annealing in air, Ar or N$_2$ controlled whether yellow or black TiO$_2$ was obtained. The different colors indicate that these samples possess different light-absorption properties. Fig. 4a shows UV-vis spectra of the black and yellow anatase TiO$_2$ samples. The black samples absorb visible light much more strongly than the yellow sample, and black TiO$_2$ (N$_2$) absorbs visible light better than black TiO$_2$ (Ar). In addition, the yellow samples absorb visible light better than P25 (a mixture of anatase and rutile) which is nearly no absorbance in visible light.

The band-gap energies of the samples were calculated from their absorbance spectra by assuming a direct transition in the anatase TiO$_2$ crystal from $(A h)_2$ versus $h v$, where $A$ is absorbance, $h$ is Planck’s constant, and $v$ is the frequency of light. The band-gap energies of the samples are presented in Fig. 4b. The band gap energy of the yellow sample is 2.5 eV, which is considerably smaller than that of typical TiO$_2$ (3.2 eV). The difference is assumed to be associated with the small number of doped H and N atoms. The band-gap energies of B(Ar) and B(N$_2$) are 2.0 and 1.5 eV, respectively. Apparently, the presence of Ti$^{3+}$ and doped elements N and H narrow the band gap of black TiO$_2$.

The photoluminescence emission spectroscopy (PL) emission spectroscopy has been widely used to determine the effectiveness of charge carrier trapping, migration and transfer of charge carriers, and understand the fate of electron/hole pairs in semiconductors because PL emission results from the recombination of free carriers. Fig. 4c shows the PL spectra of the yellow TiO$_2$ and black TiO$_2$ samples in the wavelength range of 350–600 nm following excitation at 300 nm. The first peak at 400 nm (3.2 eV) is attributed to the emission from the band-gap transition. The second peak at 420 nm is ascribed to band-edge free excitons, while the other two peaks at 482 and 493 nm are attributed to bound excitons. The main PL emission peaks of three samples appear at 451 and 469 nm, which are attributed to surface oxygen vacancies and defects of TiO$_2$ samples. The intensive peak at 469 nm reaching the summit demonstrate the formation of oxygen defects in all the three samples. Some other peaks observed in the PL spectra may result from surface defects present in the samples.

The photoluminescence emission peaks of three samples appear at 451 and 469 nm, which are attributed to surface oxygen vacancies and defects of TiO$_2$ samples. The intensive peak at 469 nm reaching the summit demonstrate the formation of oxygen defects in all the three samples. Some other peaks observed in the PL spectra may result from surface defects present in the samples.

The intensity of the PL spectra show a significant decrease due to the presence of Ti$^{3+}$ and vast oxygen vacancies. The reduction of PL intensity indicates that B(N$_2$) and B(Ar) have a relatively low recombination rate result in excellent photocatalytic activity. The high spectral response range and low photogenerated carrier recombination rate result in excellent photocatalytic activity. The introduction of Ti$^{3+}$, numbers of oxygen vacancies and surface defects layer make both B(N$_2$) and B(Ar) with these properties. And the different performance between B(N$_2$) and Y(air) also demonstrate the result. It is unexpected that B(Ar) contains such species but has quite limited photocatalytic activity. According to our knowledge, such discovery on anatase titania has not been reported before, so we decided to investigate the reason behind it.

![Fig. 4](image-url) (a) Spectral absorbance of the yellow TiO$_2$ (Y(air)) and the black TiO$_2$ calcined in Ar (B(Ar)) and N$_2$ (B(N$_2$)). (b) Band-gap energies of three samples (c) PL emission spectra of samples (d) Visible-light photocatalytic degradation of methylene blue (MB) by various samples

![Fig. 5](image-url) Schematic diagrams of the band structures of black TiO$_2$ samples

The difference of the electronic structure of black TiO$_2$ crystals are clearly seen upon comparing the UV-visible absorption spectra of B(N$_2$) and B(Ar). As shown in Fig. 4a, an absorption valley at 386 nm (3.2 eV) indicates an unchanged intrinsic bandgap. However, owing to the appearance of vast oxygen vacancy, oxygen vacancy band (Vo) making the transition of electron from valance band more easy is induced, which is the reason that the bandgap of them is narrowed to about 1.5 eV and 2.0 eV, respectively. Interestingly, an additional visible light absorption band with an edge extending to around 600 nm (2.0 eV) is observed for B(Ar) but not B(N$_2$). In order to further understand this phenomenon in our black titania samples, the
The mechanism of band structures of B(Ar) and B(N\textsubscript{3}) in our experiment is schematically illustrated in Fig. 5. The substitutional nonmetallic doping of N and H, especially the p states of N, contribute to the band-gap narrowing by mixing with O 2p states, making the formation of new valence band (V\textsubscript{n}). The formation of a visible-light absorption band is ascribed to V\textsubscript{n}, which lies below conduction band minimum. Based on the data of XPS, FTIR, and ToF-SIMS, it is deduced that the presence of more amount of NH\textsubscript{3\textsuperscript{+}} leads to this phenomenon.

Theoretical work suggested that the high enough concentration of Ti\textsuperscript{3+} can induce a continuous vacancy band of electronic states just below the conduction band edge of TiO\textsubscript{2}, while a low Ti\textsuperscript{3+} doping concentration only creates localized oxygen vacancy states that actually reduce the electron mobility and exhibit a negligible visible photoactivity.\textsuperscript{28,29,30} Hence, V\textsubscript{n} in B(N\textsubscript{3}) exist just below the conduction band due to high concentration of Ti\textsuperscript{3+}, which also supported by the absence of other visible-light absorption bands.

The reason that B(Ar) shows poor photocatalytic activity can be deduced that the presence of more amount of NH\textsubscript{3\textsuperscript{+}} impedes the vacancy-induced band of electronic states closing to conduction band and the formation of lots of Ti\textsuperscript{3+} so that the location of oxygen vacancy-induced band (V\textsubscript{o}) lies below the H\textsubscript{2}O redox potential.\textsuperscript{28,31} In addition, NH\textsubscript{3\textsuperscript{+}} is also present in Y, but Y\textsubscript{3} performs better than B(Ar). It can be assumed that the amount of NH\textsubscript{3\textsuperscript{+}} in B(Ar) is greater than in Y. Less existence of NH\textsubscript{3\textsuperscript{+}} results in better photocatalytic degradation performance. Therefore, our results indicate that the excellent photocatalytic performance of B(N\textsubscript{3}) can be attributed to two factors: (1) the presence of Ti\textsuperscript{3+}, which increases the number of oxygen vacancies, leading to the formation of an oxygen vacancy-induced band; (2) the presence of less NH\textsubscript{3\textsuperscript{+}}, which benefits to the oxygen vacancy-induced band closing to conduction bands.

Conclusions

In summary, the present work demonstrates a new chemical approach to prepare black anatase TiO\textsubscript{2} and yellow anatase TiO\textsubscript{2} nanoparticles by doping with N and H. The introduction of trivalent Ti and numerous oxygen vacancies strongly enhances visible-light absorption and the photocatalytic performance of the catalysts under visible light. The band-gap energy of the samples is also decreased substantially. By comparing the performance of three samples, we found that the appearance of more amount of NH\textsubscript{3\textsuperscript{+}} can be attributed to superior gas tightness during annealing and limits photocatalytic activity because it causes V\textsubscript{o} to lie below the H\textsubscript{2}/H\textsubscript{2}O redox potential. We developed a simple, safe method to prepare black anatase titanium with excellent absorption and photocatalytic performance. This method may provide a new way to improve TiO\textsubscript{2} photocatalysis for water cleaning applications.

Notes and references

This work was financially supported by the National Natural Science Foundation of China (No.11164026).

Key Laboratory of Solid-state Physics and Devices, School of Physical Science and Technology, Xinjiang University, Urumqi 830046, China. Email: wurongxjj@xj.cn

\textsuperscript{†} Electronic Supplementary Information (ESI) available: Experimental details / EPR / XPS / ToF-SIMS. See DOI: 10.1039/c000000x/

---