Photocatalysis

DOI: 10.1002/anie.201206375

A Highly Efficient Photocatalyst—Hydrogenated Black TiO_2 for the Photocatalytic Splitting of Water

*Yun Hang Hu**

hydrogen · hydrogenation · photocatalysts · TiO_2 ·
water splitting

Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes, which ushered in a new era in heterogeneous photocatalysis in 1972.[1] This prompted worldwide research efforts on TiO_2-based photocatalysis for energy conversion and storage.[2–5] However, TiO_2 has a large band gap energy (3.0 eV for rutile and 3.2 eV for anatase) and thus it does not absorb visible light; consequently, its photoconversion efficiency is less than 2.2 % under air mass (AM) 1.5 global solar illumination.[6] This efficiency is much lower than the acceptable solar-to-hydrogen efficiency (10 %) for benchmark applications.[7] Two strategies have been explored to extend the working spectrum of TiO_2-based materials to the visible-light region (about 45 % of the total solar energy): 1) modifying the valence band by introducing nonmetal ions (such as C, N, and S) into TiO_2 to form acceptor states above the valence band[8–13] and 2) forming donor states below the conduction band of TiO_2 by incorporating metal ions into TiO_2.[14] Very recently, the hydrogenation of TiO_2 was shown to boost the photo-absorption of TiO_2 and its photocatalytic activity for the splitting of water to H_2.[15–17]

To enhance the visible- and infrared-light absorption of TiO_2, Mao and his co-workers devised a novel approach to generate disordered nanophase TiO_2 and simultaneously incorporate a dopant through the hydrogenation of TiO_2 nanocrystals.[15] They prepared nanophase TiO_2 by heating a precursor solution (consisting of titanium tetraisopropoxide, ethanol, hydrochloric acid, deionized water, and an organic template, Pluronic F127) at 40 °C for 24 h, followed by evaporation and drying at 110 °C for 24 h and final calcination at 500 °C for 6 h. The obtained TiO_2 nanoparticles were highly crystalline with anatase structure and an average crystal size of approximately 8 nm. Hydrogenation of the TiO_2 sample at 20 bar and about 200 °C for 5 days generated two phases: crystalline TiO_2 quantum dots (or nanocrystals) as the core and a highly disordered surface layer (ca. 1 nm thick) with hydrogen dopants. As a result, the optical absorption of such hydrogenated TiO_2 nanocrystals shifts from the ultraviolet (UV) to near infrared, accompanied by a dramatic color change from white to black (Figure 1). The optical gap of the hydrogenated black TiO_2 nanocrystals is about 1.0 eV, which is much lower than that (3.30 eV) of the untreated TiO_2 sample. Furthermore, the hydrogenated black TiO_2 exhibited excellent activity and stability for the photocatalytic production of hydrogen from water. Under simulated sun illumination (about 1 Sun power), 0.02 g black TiO_2 nanocrystals with 0.6 wt % Pt produced 0.2 mmol of H_2 per hour (i.e. 10 mmol h^{-1} per g cat.) from water with methanol as the sacrificial reagent. This hydrogen production rate is about two orders of magnitude larger than that of most semiconductor photocatalysts.[2,18] The energy conversion efficiency, which is the ratio of the energy of the produced hydrogen to the energy of the incident sunlight, reached 24 %. Throughout 15 testing cycles in 15 days, the high H_2 yield remained unchanged without catalyst regeneration, indicating an excellent stability for the black TiO_2. Under the same experimental conditions, no H_2 was produced from the unmodified white TiO_2 nanocrystals loaded with Pt.

Li et al. revealed the significant effect of hydrogen treatment on the photocatalytic properties of rutile TiO_2 nanowire arrays (diameters of 100–200 nm), which were prepared on a fluorine-doped tin oxide (FTO) glass substrate.[16] They found that the color of the hydrogen-treated rutile TiO_2 nanowire films changed from white (untreated sample) to yellowish green (350 °C) and finally to black (450 °C or above). Under simulated sunlight illumination (100 mW cm^{-2}), the photo-current densities of the hydrogenated TiO_2 nanowire samples are at least two times higher than that of pristine TiO_2 nanowires. Furthermore, the photocurrent density increases with increasing hydrogen-annealing temperature up to 350 °C. The measured photocurrents for the photoanode constructed from the hydrogenated TiO_2 nanowire films for each cycle of gas production (H_2 and O_2) are nearly the same, indicating excellent stability. Huang et al. also evaluated the effect of hydrogen treatment on the photocatalytic activity of anatase TiO_2 nanowires.[17] They showed that the hydrogen production rate (2.15 mmol h^{-1} per g cat.) over hydrogenated TiO_2 nanowires is 3.2 and 3.8 times higher than those over air-treated TiO_2 and commercial TiO_2 (P25), respectively. In addition, Li et al. observed similar effects of hydrogen treatment on the photoproperties and photocatalysis of TiO_2 anatase nanotubes.[16]

The enhancement in the visible-light absorption of hydrogenated black TiO_2 was attributed to two factors: 1) surface disorder[15] and 2) the formation of oxygen vacancies.[16] Mao

---

[*] Prof. Y. H. Hu
Department of Materials Science and Engineering
Michigan Technological University
Houghton, MI 49931 (USA)
E-mail: yunhangh@mtu.edu

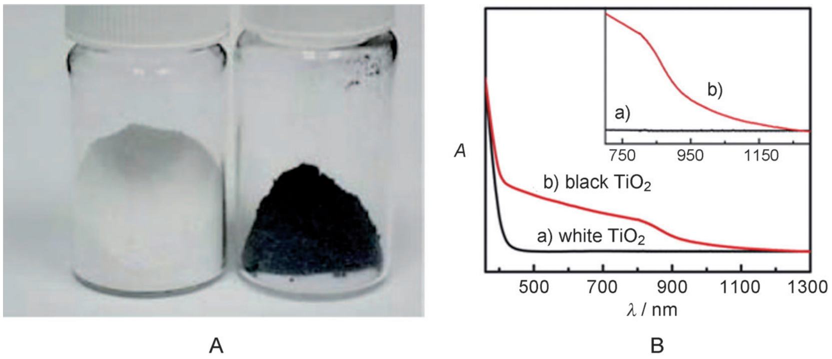

Figure 1. A) Unmodified white and hydrogenated black TiO$_2$ nanocrystals and B) spectral absorbance of the white and black TiO$_2$ nanocrystals [reproduced from Ref. [15] with permission from the American Association for the Advancement of Science].

et al. showed that the surface disorder of anatase TiO$_2$ nanoparticles following hydrogen treatment shifted the valence band position by 2.18 eV.[15] As a result, the energy gap between the valence band and the conduction band was dramatically narrowed to the point that it was small enough for visible- and infrared-light absorption. However, Li et al. found that rutile TiO$_2$ nanowires with and without hydrogen treatment possess the same valence band.[16] Therefore, they attributed the absorption of visible and infrared light to the formation of oxygen vacancies in hydrogenated rutile TiO$_2$. The energy levels of the oxygen vacancies are about 0.75 and 1.18 eV below the conduction band of plates of hydrogen-reduced rutile TiO$_2$ single crystals.[19] The visible- and near-infrared-light absorptions are associated with the transitions from the TiO$_2$ valence band to the oxygen vacancy levels or from the oxygen vacancies to the TiO$_2$ conduction band.[19–21]

Interestingly, it was found that the dramatic improvement in visible-light absorbance of hydrogenated black TiO$_2$ is not a main contributor to its enhanced photoactivity.[15–17] As shown by Mao and his co-workers, when full solar radiation was filtered so that only visible and infrared light was allowed to reach hydrogenated TiO$_2$ with Pt, the rate of H$_2$ production dropped from 10 to 0.1 mmol h^{-1} per g cat.[15] A similar result was obtained by Huang et al.[17] Namely, with only visible light, the rate of photocatalytic H$_2$ production over hydrogenated TiO$_2$ nanowires decreased from 2.15 to 0.12 mmol h^{-1} per g cat.[17] These results are consistent with IPCE measurements (incident-photon-to-current-conversion efficiency) reported by Li et al.[16] For hydrogenated TiO$_2$ nanowires, IPCE values are higher than 95 % in the wavelength range from 300 to 370 nm, indicating that the UV light is effectively used for water splitting.[16] In contrast, the IPCE value decreases from roughly 95 % at 370 nm to about 1 % at 420 nm. This further confirms that the enhanced photocatalytic activity of the hydrogenated TiO$_2$ is mainly due to the improved IPCE in the UV region. Furthermore, electrochemical impedance measurements revealed that hydrogen treatment of TiO$_2$ nanowires increased their donor densities.[16] The oxygen vacancies were demonstrated to be electron donors in TiO$_2$[22] and considered to contribute to the enhanced donor density in hydrogenated TiO$_2$.[16] The increased donor density can improve charge transport in TiO$_2$ and shift the Fermi level of TiO$_2$ toward the conduction band.[19] Such a shift of the Fermi level can facilitate the charge separation at the semiconductor/electrolyte interface. Therefore, the enhanced charge separation and transportation were believed to be major reasons for the observed IPCE enhancement in the UV region.[16] However, when the concentration of the oxygen vacancies is too high, the defects can also act as charge-recombination centers and thus cause a negative effect on the photocatalytic performances.

In summary, the remarkable enhancement in the visible-light absorption and the photocatalysis of TiO$_2$ after hydrogen treatment is truly a breakthrough in the photocatalytic splitting. This would increase the reality of H$_2$ production with solar energy. However, hydrogenated black TiO$_2$ does not fully exploit visible light for the photocatalytic process, because its enhanced photocatalysis is mainly due to the IPCE increase in the UV region. Therefore, it would be an interesting and important research direction to boost the photocatalytic activity of the hydrogenated black TiO$_2$ in the visible-light region. Very recently, Mullins et al. reported a synergistic effect after co-treatment of TiO$_2$ nanowire arrays with H$_2$ and NH$_3$, which remarkably improved the water photo-oxidation performance under visible-light illumination.[23] This could be a novel approach for further improving in photocatalytic properties of TiO$_2$.

Received: August 8, 2012

[1] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38.
[2] X. Chen, S. S. Mao, *Chem. Rev.* **2007**, *107*, 2891–2959.
[3] A. L. Linsebigler, G. Lu, J. T. Yates, Jr., *Chem. Rev.* **1995**, *95*, 735–758.
[4] A. J. Bard, *Science* **1980**, *207*, 139–144.
[5] K. Kalyanasundaram, M. Grätzel, E. Pelizzetti, *Coord. Chem. Rev.* **1986**, *69*, 57–128.
[6] A. B. Murphy, P. R. F. Barnes, L. K. Randeniya, I. C. Plumb, I. E. Grey, M. D. Horne, J. A. Glasscock, *Int. J. Hydrogen Energy* **2006**, *31*, 1999–2017.
[7] A. J. Bard, M. A. Fox, *Acc. Chem. Res.* **1995**, *28*, 141–145.
[8] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, *293*, 269–271.
[9] S. U. M. Khan, M. Al-Shahry, W. B. Ingler, Jr., *Science* **2002**, *297*, 2243–2245.
[10] X. Chen, C. Burda, *J. Am. Chem. Soc.* **2008**, *130*, 5018–5019.

[11] J. H. Park, S. Kim, A. J. Bard, *Nano Lett.* **2006**, *6*, 24 – 28.

[12] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, *Appl. Phys. Lett.* **2002**, *81*, 454 – 456.

[13] S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, C. B. Mullins, *Nano Lett.* **2012**, *12*, 26 – 32.

[14] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69 – 96.

[15] X. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science* **2011**, *331*, 746 – 750.

[16] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R. C. Fitzmorris, C. Wang, J. Z. Zhang, Y. Li, *Nano Lett.* **2011**, *11*, 3026 – 3033.

[17] Z. Zheng, B. Huang, J. Lu, Z. Wang, X. Qin, X. Zhang, Y. Dai, M. Whangbo, *Chem. Commun.* **2012**, *48*, 5733 – 5735.

[18] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253 – 278.

[19] D. C. Cronemeyer, *Phys. Rev.* **1959**, *113*, 1222 – 1226.

[20] W. T. Kim, C. D. Kim, Q. W. Choi, *Phys. Rev. B* **1984**, *30*, 3625 – 3628.

[21] A. Naldon, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. Cappelli, C. L. Bianchi, R. Psar, V. D. Santo *J. Am. Chem. Soc.* **2012**, *134*, 7600 – 7633.

[22] A. Janotti, J. B. Varley, P. Rinke, N. Umezawa, G. Kresse, C. G. Van de Walle, *Phys. Rev. B* **2010**, *81*, 085212.

[23] S. Hoang, S. P. Berglund, N. T. Hahn, A. J. Bard, C. B. Mullins, *J. Am. Chem. Soc.* **2012**, *134*, 3659 – 3662.