

Photocatalytic activity of mesoporous titanium dioxide nanoparticles under visible light irradiation

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ABSTRACT

Hydrogen production capability of mesoporous C and N-doped TiO₂ was tested under visible light. Since the visible light contained small amount of UV light, the test was performed without/with a filter which cut UV light with wavelength of 420 nm or less. It was found that the main contribution of hydrogen production for C and N-doped TiO₂ fired at 500°C and 600°C was probably coming from UV light present in visible light. C and N-doped TiO₂ fired at 400°C absorbed both UV light and visible light when studied by UV-visDRS. This sample produced almost the same amount of hydrogen under visible light without/with filter, although the amount of hydrogen was small.

Keywords: photocatalysis, titanium dioxide, mesoporous, hydrogen, visible light

1 INTRODUCTION

Titanium dioxide (TiO₂) is the most extensively investigated photocatalyst [1, 2] because it is inexpensive, chemically stable, and non-toxic [3]. However, because of its large band gap energy (3.2 eV), it can only utilize the UV region of the solar spectrum. Therefore, considerable efforts have been made to extend the photoresponse of TiO₂-based systems further into the visible-light region by using dopants [4, 5]. Anionic dopants such as carbon, sulfur, and nitrogen may be possible for extending the photocatalytic activity of TiO₂ into the visible-light region because the related impurity states are expected to be close to the valence band maximum [6, 7].

Photocatalytic activity of TiO₂ takes place on the surface of the oxide. One way to increase the efficiency of photocatalysis is to increase the surface area of the oxide. Mesoporous materials with 3D porous structures provide highly porous hosts that offer easy and direct access to guest species, thereby facilitating inclusion or diffusion through the pore channels without blocking the pores. We have developed a method for synthesizing highly crystalline mesoporous TiO₂ co-doped with carbon/nitrogen [8]. In this method, mesoporous silicon oxide was first prepared. Silicon in this oxide was replaced by Ti to form mesoporous TiO₂. The oxide had very large surface area

and good crystallinity. This material was expected to be effective for decomposing organic compounds. When the oxide was placed in methanol solution and two different UV light was exposed to the oxide [9], it was found that UV light with short wave length was more effective in producing hydrogen than UV light with longer wave length. In addition, mesoporous TiO₂ was tested using different source of light [10]. Sunlight produced the most hydrogen. UV light produced the second most hydrogen. The visible light produced less hydrogen than other light.

Visible light source could include some contribution from UV light. Therefore, the present study seeks to determine whether mesoporous C/N-doped TiO₂ could be used to produce hydrogen gas by visible light with almost no contribution from UV region.

2 EXPERIMENTAL

In order to make mesoporous silica (tetragonal KIT-6) we followed the procedure developed by Kim *et al.* [11]. In the next step, Si in KIT-6 was replaced by Ti to form mesoporous TiO₂. In a typical synthesis of mesoporous C and N-doped TiO₂, KIT-6 was added to ethylenediamine (99%, Wako Pure Chemical, Japan) and carbon tetra chloride (99.8%, Wako Pure Chemical, Japan). They were mixed thoroughly. To this mixture, titanium tetra isopropoxide (97%, Sigma-Aldrich, U. S. A.) dissolved in 1-propanol (99.5%, Wako Pure Chemical, Japan) was added and the resultant mixture was heated in an oil bath at 90°C for 5h. Then, the obtained solid mixture was dried at 150°C and ground into a fine powder. The C and N-doped TiO₂ composite was then heat-treated in the presence of nitrogen flow at 400°C, 500°C and 600°C to obtain well crystallized, highly ordered mesoporous C and N-doped TiO₂: N-doped TiO₂ (400), N-doped TiO₂ (500), and N-doped TiO₂ (600). The presence of C and N was confirmed elsewhere [8].

The powder x-ray diffraction (XRD) pattern of N-doped TiO₂ was collected using a Rigaku diffractometer with Cu K α ($\lambda=0.154$ nm) radiation. The samples were also studied by diffuse reflectance spectroscopy in UV and visible light region (UV-Vis DRS).

3 RESULTS AND DISCUSSION

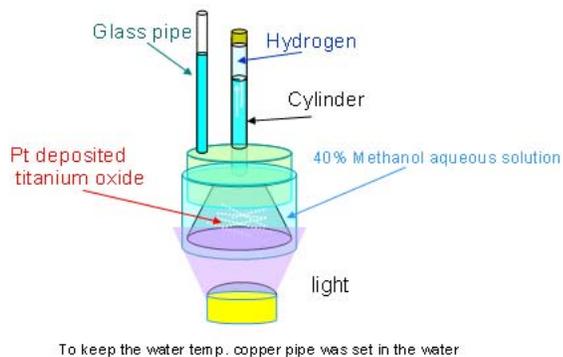


Figure 1. Hydrogen production apparatus.

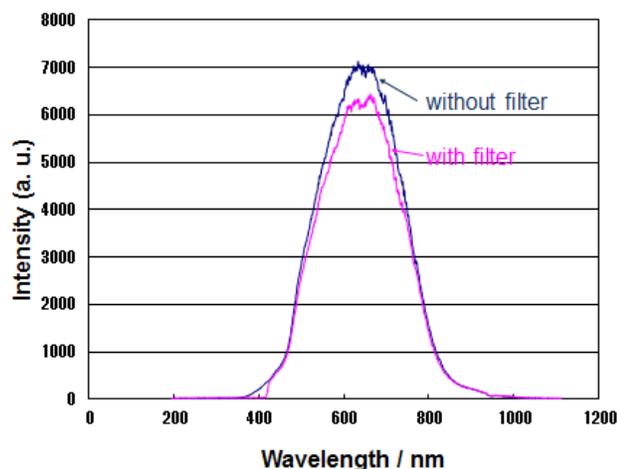


Figure 2. Spectra of visible light used in this study.

Pt was deposited on the surface of N-doped TiO₂ by using the procedure reported by Ikuma and Bessho [12]. Concentration of Pt was 0.003 mol of Pt per 1 mol of TiO₂. Pt-deposited, N-doped TiO₂ was placed in hydrogen production apparatus shown in Figure 1. In this apparatus 40% methanol aqueous solution was used [12]. The spectra of visible light used in this study are shown in Figure 2. The visible light has its maximum intensity at 610 nm. When a filter was used, UV light in the range of 420 nm or less was cut. Consequently, the visible light with filter has almost no contribution from UV light in the range of 420 nm or less in wavelength. The decrease of maximum intensity at 610 nm, when the filter was used, is seen. However, this is very small and will not affect the results of hydrogen production very much. The concentration of hydrogen produced was determined by gas chromatography.

The results of XRD of N-doped TiO₂ are shown in Figure 3. It shows that N-doped TiO₂ (400) and (500) were anatase TiO₂ and were well crystallized. N-doped TiO₂ (600) was also well crystallized but contained some rutile TiO₂ in addition to anatase TiO₂. Similar sample which was prepared by firing at 600°C in oxygen atmosphere contained only anatase TiO₂. Obviously the presence of nitrogen within TiO₂ or in the atmosphere promoted the transformation of anatase TiO₂ to rutile TiO₂.

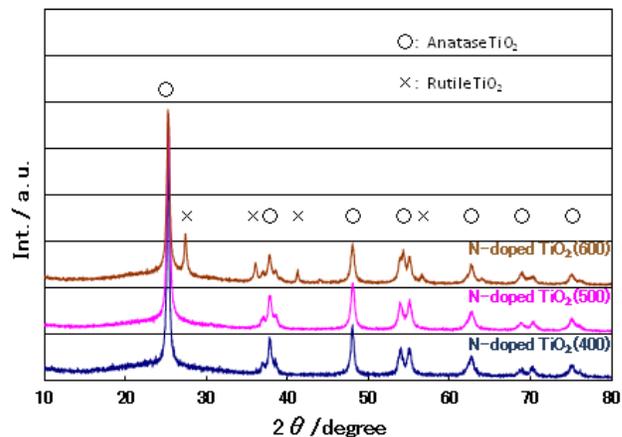


Figure 3. X-ray diffraction pattern of N-doped TiO₂ (400), (500), and (600).

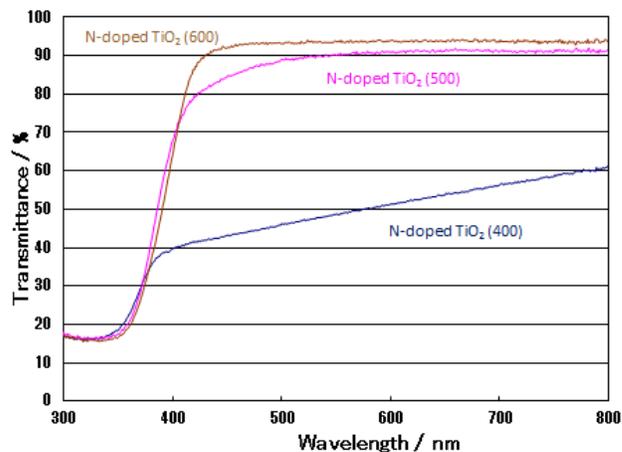


Figure 4. UV-visDRS of N-doped TiO₂ (400), (500), and (600).

The results of UV-visDRS measurement are shown in Figure 4. All samples showed strong absorption in UV light region. N-doped TiO₂ (600) showed almost no

absorption in visible light region. N-doped TiO₂ (500) exhibited a slight absorption in 400-550 nm region. On the other hand, N-doped TiO₂ (400) showed much higher absorption in visible light region.

The results of hydrogen production with Pt-deposited N-doped TiO₂ under visible light without/with filter are shown in Figures 5 and 6, respectively. Amount of hydrogen shown in the figure is the total amount of hydrogen produced between previous data point and the relevant point. Each data point does not represent the accumulated volume of hydrogen during the entire irradiation time, but is the amount of hydrogen produced during the period of 20 to 40 h. For N-doped TiO₂ (500) without filter (Figure 5), hydrogen production at 40 h is the highest. N-doped TiO₂ (600) shows less hydrogen production at 40 h. N-doped TiO₂ (400) produces very small amount of H₂ at 40 h. When filter was used, almost no UV light in the range of 420 nm or less in wavelength was present (Figure 2). The results of hydrogen production (Figure 6) are different from Figure 5. First, amount of hydrogen was very small in all three samples in Figure 6. For N-doped TiO₂ (600) hydrogen production at 40h is about 1/1000 of the same sample at visible light without filter. For N-doped TiO₂ (500), it is about 1/400 of the same sample without filter. For N-doped TiO₂ (400) it decreased only by 1/1.6 as compared to the same sample without filter.

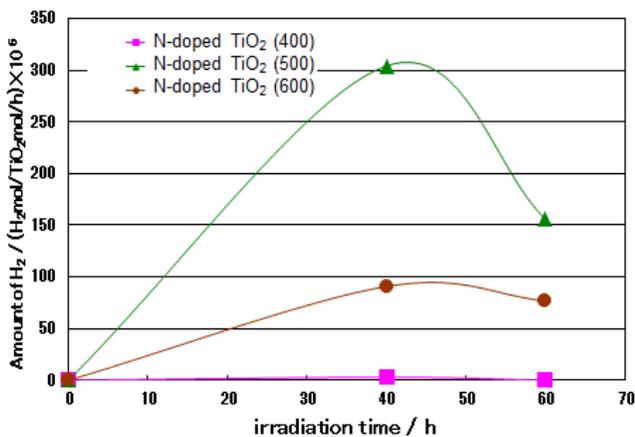


Figure 5. Amount of hydrogen produced by irradiation of visible light without filter.

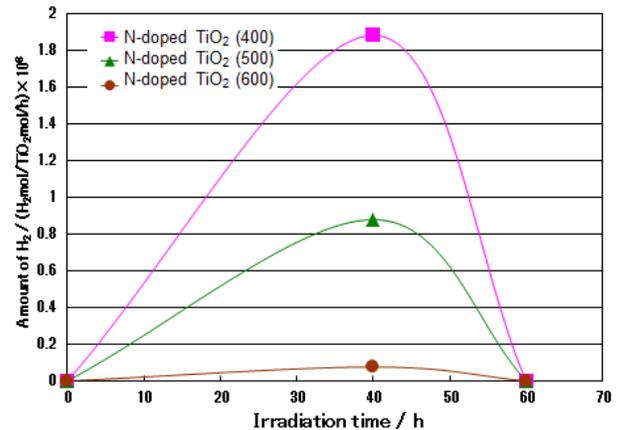


Figure 6. Amount of hydrogen produced by irradiation of visible light with filter.

Considering the fact that N-doped TiO₂ (600) mainly absorb the light in the range of 400 nm or less (Figure 4), production of hydrogen in N-doped TiO₂ (600) must be done by light in UV region; there must be almost no contribution from visible light in this case. In this material, the existence of rutile TiO₂ did not work favourably for the hydrogen production. This is contrary to the performance of Degussa P-25 which contains about 20 % rutile TiO₂ in addition to anatase TiO₂ and is photocatalytically very active.

Since N-doped TiO₂ (500) mainly absorb the light in the range of 400 nm or less, the hydrogen production by this material must be done by light in UV region. However, it produced slightly more hydrogen by visible light even when filter was used (Figure 6). This may be the reflection of the difference in the results of UV-visDRS of N-doped TiO₂ (500) and (600) shown in Figure 4.

The hydrogen production of N-doped TiO₂ (400) shown in both Figure 5 and 6 is almost the same. This implies that main contribution of N-doped TiO₂ (400) was from visible light region. The smaller amount of hydrogen production of N-doped TiO₂ (400) by visible light without filter compared to N-doped TiO₂ (500) and (600) is due to the fact that UV light which is the main contribution for N-doped TiO₂ (500) and (600) has higher energy than visible light which is the main contribution for N-doped TiO₂ (400).

4 CONCLUSIONS

Mesoporous C and N-doped TiO₂ (N-doped TiO₂ (400), (500), and (600)) were exposed to visible light without/with filter. The filter cuts the UV light with the wavelength of 420 nm or less. It was found that the main contribution of hydrogen production for N-doped TiO₂ (500) and 600) is probably coming from UV light present in visible light.

Although N-doped TiO₂ (600) contained small amount of rutile in addition to anatase TiO₂, it did not produce as much hydrogen as N-doped TiO₂ (500). This is contrary to the performance of Degussa P-25.

N-doped TiO₂ (400) did produce small amount of hydrogen under both visible light with and without filter, because the main contribution for this material is from visible light region.

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REFERENCES

- [1] A. Fujishima and K. Honda, *Nature*, 238, 37-38 (1972).
- [2] A. Fujishima, X. Xiang, D. A. Tryk, *Sur. Sci. Rep.* 63, 515-582 (2008).
- [3] J. Nowotny, T. Bak, M. K. Nowotny, L. R. Sheppard, *Int. J. Hydrogen Energy*, 32, 2609-2629 (2007).
- [4] J. -M. Hermann, J. Disdier, P. Pichat, *Chem. Phys. Lett.*, 108, 618-622 (1984).
- [5] M. Anpo, Y. Ichihashi, M. Takeuchi, H. Yamashita, *Res. Chem. Intermed.*, 24, 143-149 (1998).
- [6] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science*, 293, 269-271 (2001).
- [7] S. U. M. Khan, M. Al-Shahry, W. B. Ingler, Jr., *Science*, 297, 2243-2245 (2002).
- [8] S. Anandan, Y. Ikuma, K. Kakinuma, K. Niwa, *NANO*, 3 [5] 367-372 (2008).
- [9] K. Niwa, K. Tamura, S. Anandan, Y. Ikuma, *Adv. Appl. Ceram.*, 111 [1-2], 34-38 (2012).
- [10] K. Niwa, R. Kuramoto, S. Anandan, Y. Ikuma, *Proceedings of IUMRS-ICA 2011* (Taiwan), No. 578 in USB memory (2011).
- [11] T.-W. Kim, F. Kleitz, B. Paul, R. Ryoo, *J. Am. Chem. Soc.*, 127, 7601-7610 (2005).
- [12] Y. Ikuma and H. Bessho, *Int. J. Hydrogen Energy*, 32, 2689-2692 (2007).